

INVESTIGATION INTO FABRICATION AND CHARACTERIZATION OF VERTICALLY ALIGNED HEXAGONALLY PATTERNED CARBON NANOPILLARS AND THEIR APPLICATIONS

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**Investigation into fabrication and characterization of vertically aligned
hexagonally patterned carbon nanopillars and their applications**

by

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Submitted

in fulfilment of the requirements of the degree of the Doctor of Philosophy

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Dedicated to my teachers

CERTIFICATE

This is to certify that the thesis entitled “ **Investigation into fabrication and characterization of vertically aligned hexagonally patterned carbon nanopillars and their applications** ” being submitted by **Mr. Sahil Kumar Yadav** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy** in the Department of Mechanical Engineering is a bonafide research work carried out by him under our supervision and guidance. To the best of our knowledge, the thesis has reached the requisite standard. The research reports and the results presented in this thesis have not been submitted in parts or in full to any other University or Institute for the award of any degree or diploma.

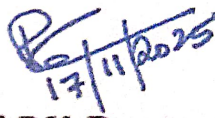

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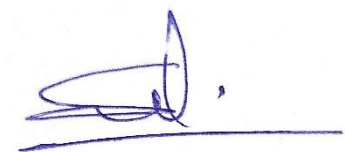
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ABSTRACT

The precise control over surface morphology and material composition at the nanoscale enables novel functionalities that are unattainable in conventional materials. Large area nanopillar fabrication on a polystyrene surface has been explored as a self-cleaning functional surface. Nanopillars are first fabricated with a reusable AAO mould with an ordered pore size of 75 nm. Hexagonally ordered domain nanopores were made with different anodization parameters, further improved by pore widening. A single-step approach of hot embossing is used to make different aspect ratio nanopillars of polystyrene. Hot embossing process parameters, such as embossing pressure, temperature, and holding time, are optimized for contact angle as a response parameter. The moth-eye type textured nanopillars have the maximum water contact angle. The water contact angle obtained increased from 63.1° to 153° for for moth-eye type nanopillars. Moreover, vertically aligned and hexagonally patterned carbon nanopillars (CNPs) were fabricated by the growth of carbon atoms through anodized aluminium oxide, followed by mechanical polishing and chemical etching. This nano-template was investigated to understand the effects of varying the carbon deposition time for 0.5 h and 4 h at flow rates of 20 sccm and 100 sccm. Hot embossing process parameters, such as embossing pressure and temperature, are optimized to fabricate nanoholes on a large area of a polystyrene sheet. The best results for replicated nanoholes were achieved at an embossing pressure of 3 MPa and slightly above the glass transition temperature. Additionally, the tunable antireflective behavior of nanoholes across varying operational wavelengths has been analyzed using the Finite-Difference Time-Domain (FDTD) simulation technique. Experimental findings reveal that hot embossed nanohole architectures can achieve minimum reflectance values of 5%, within the 400–700 nm wavelength range. A non-conventional alternative to nano-indentation was demonstrated for carbon nanopillars supported in AAO pores by utilizing an atomic force microscopy tip as a nano indenter by applying a load in the nanometer range. The CNPs pillars'

Young's modulus was calculated to be 15 GPa by using the Hertz equation in the elastic regime. In addition, large area, vertically aligned one-dimensional (1D), hexagonally patterned materials have been found to efficiently explore the surface enhanced Raman spectroscopy (SERS). Here, we have a facile substrate for SERS performance as vertically grown carbon nanopillars inside the porous hexagonally patterned anodic aluminium oxide was developed. This facile SERS substrate was prepared by depositing Au to form SERS-active hot spots. This CNP-Au hybrid substrate for 30 nm Au deposition shows the uniform sub-10 nm gap between subsequent nanopillars. Rhodamine (R6G) dye was investigated for its very low concentration up to 10^{-9} M due to its genotoxic and carcinogenic effects on human life. The electric field enhancement was validated with a 3D FDTD Lumerical simulation for CNP-Au-30 nm substrate for a 10 nm gap. Additionally, a new approach has been developed in this study to engineer efficient electrodes for high-performance supercapacitors based on zinc oxide (ZnO) nanosheets (NSs) grown on carbon nanopillars synthesized within an anodic aluminium oxide template. A three-electrode system incorporating a KOH/PVA gel electrolyte was employed to assess the electrochemical properties. The CV curves of the AAO/CNP electrode showed a near-rectangular form, indicative of ideal electric double-layer capacitor performance with a maximum current density of $370 \mu\text{A}/\text{cm}^2$, showing fast ion diffusion and efficient charge storage. In contrast, the AAO/CNP@ZnO electrode revealed a nearly symmetric triangular profile with a specific capacitance of $3.1 \text{ mF}/\text{cm}^2$ at a current density of $0.5 \text{ mA}/\text{cm}^2$ in galvanostatic charge–discharge tests. These findings indicate that the AAO/CNP@ZnO hybrid electrode is a viable solution for high-performance next-generation supercapacitor applications.

KEY WORDS: Anodized aluminum oxide, Carbon nanopillars, Chemical vapor deposition, Hot embossing, Nanotexturing, contact angle, Raman spectroscopy, Anti-reflectivity, supercapacitor.

सार

नैनोस्केल पर सतह की आकृति विज्ञान और सामग्री संरचना पर सटीक नियंत्रण, नई कार्यक्षमताओं को सक्षम बनाता है जो पारंपरिक सामग्रियों में अप्राप्य हैं। एक पॉलीस्टीरिन सतह पर बड़े क्षेत्र के नैनोपिलर निर्माण को एक स्व-सफाई कार्यात्मक सतह के रूप में खोजा गया है। नैनोपिलर को पहले 75 nm के क्रमबद्ध छिद्र आकार के साथ एक पुनः प्रयोज्य AAO साँचे के साथ बनाया जाता है। षट्कोणीय रूप से क्रमबद्ध डोमेन नैनोपोर को विभिन्न एनोडीकरण मापदंडों के साथ बनाया गया था, जो छिद्र चौड़े होने से और बेहतर हुए। हॉट एम्बॉसिंग के एकल-चरणीय दृष्टिकोण का उपयोग पॉलीस्टीरिन के विभिन्न पहलू अनुपात नैनोपिलर बनाने के लिए किया जाता है। गर्म उभरे हुए प्रक्रिया पैरामीटर, जैसे उभरे हुए दबाव, तापमान और पकड़ने का समय, प्रतिक्रिया पैरामीटर के रूप में संपर्क कोण के लिए अनुकूलित हैं। मॉथ-आई प्रकार के बनावट वाले नैनोपिलर में अधिकतम जल संपर्क कोण होता है। मॉथ-आई टाइप नैनोपिलर के लिए प्राप्त जल संपर्क कोण 63.1° से 153° तक बढ़ गया। इसके अलावा, ऊर्ध्वाधर रूप से संरेखित और षट्कोणीय पैटर्न वाले कार्बन नैनोपिलर (सीएनपी) को एनोडाइज्ड एल्यूमीनियम ऑक्साइड के माध्यम से कार्बन परमाणुओं के विकास द्वारा गढ़ा गया था, जिसके बाद यांत्रिक पॉलिशिंग और रासायनिक इचिंग की गई थी। 20 एस. सी. सी. एम. और 100 एस. सी. सी. एम. की प्रवाह दर पर 0.5 घंटे और 4 घंटे के लिए कार्बन निक्षेपण समय को बदलने के प्रभावों को समझने के लिए इस नैनो-टेम्पलेट की जांच की गई थी। गर्म एम्बॉसिंग प्रक्रिया पैरामीटर, जैसे एम्बॉसिंग दबाव और तापमान, एक पॉलीस्टीरिन शीट के एक बड़े क्षेत्र पर नैनोहोल बनाने के लिए अनुकूलित किए जाते हैं। प्रतिकृति नैनोहोल के लिए सबसे अच्छे परिणाम 3 एमपीए के उभरे हुए दबाव पर और कांच संक्रमण तापमान से थोड़ा ऊपर प्राप्त किए गए थे। इसके अतिरिक्त, फाइनाइट-डिफरेंस टाइम-डोमेन (एफ. डी. टी. डी.) सिमुलेशन तकनीक का उपयोग करके विभिन्न परिचालन तरंग दैर्ध्य में नैनोहोल के ट्यूनेबल एंटीरिफ्लेक्टिव व्यवहार का विश्लेषण किया गया है। प्रयोगात्मक निष्कर्षों से पता चलता है कि गर्म उभरे हुए नैनोहोल आर्किटेक्चर 400-700 एनएम तरंग दैर्ध्य सीमा के भीतर 5% के

न्यूनतम परावर्तन मूल्य प्राप्त कर सकते हैं। नैनो-इंडेंटेशन के एक गैर-पारंपरिक विकल्प को नैनोमीटर रेंज में एक भार लागू करके नैनो इंडेंटर के रूप में एक परमाणु बल माइक्रोस्कोपी टिप का उपयोग करके AAO छिद्रों में समर्थित कार्बन नैनोपिलर के लिए प्रदर्शित किया गया था। सीएनपी स्तंभों के यंग के मापांक की गणना लोचदार क्षेत्र में हर्ट्ज समीकरण का उपयोग करके 15 जीपीए की गई थी। इसके अलावा, बड़े क्षेत्र, ऊर्ध्वाधर रूप से संरेखित एक-आयामी (1डी) षट्कोणीय पैटर्न सतह संवर्धित रमन स्पेक्ट्रोस्कोपी (SERS) का कुशलतापूर्वक पता लगाने के लिए पाये गए। हमारे पास SERS प्रदर्शन के लिए एक आसान सब्सट्रेट है क्योंकि छिद्रपूर्ण षट्कोणीय पैटर्न वाले एनोडिक एल्यूमीनियम ऑक्साइड के अंदर ऊर्ध्वाधर रूप से उगाए गए कार्बन नैनोपिलर विकसित किए गए थे। यह आसान एसईआरएस सब्सट्रेट एसईआरएस-सक्रिय हॉट स्पॉट बनाने के लिए, स्वर्ण जमा करके तैयार किया गया था। 30 nm Au निक्षेपण के लिए यह CNP-Au संकर सब्सट्रेट बाद के नैनोपिल्लरों के बीच एक समान उप-10 nm अंतर को दर्शाता है। मानव जीवन पर जीनोटॉक्सिक और कार्सिनोजेनिक प्रभावों के कारण रोडामाइन (R6G) डाई की जांच 10^{-9} M तक की बहुत कम सांद्रता के लिए की गई थी। विद्युत क्षेत्र वृद्धि को 10 एनएम अंतराल के लिए सीएनपी-एयू-30 एनएम सब्सट्रेट के लिए 3D एफडीटीडी संख्यात्मक अनुकरण के साथ मान्य किया गया था। इसके अतिरिक्त, इस अध्ययन में एक एनोडिक एल्यूमीनियम ऑक्साइड टेम्पलेट के भीतर संश्लेषित कार्बन नैनोपिलर पर उगाए गए जिंक ऑक्साइड (ZnO) नैनोशीट (NSs) पर आधारित उच्च-प्रदर्शन वाले सुपरकैपेसिटर के लिए कुशल इलेक्ट्रोड इंजीनियर करने के लिए एक नई विधि विकसित की गया है। विद्युत रासायनिक गुणों का आकलन करने के लिए एक के. ओ. एच./पी. वी. ए. जेल इलेक्ट्रोलाइट को शामिल करते हुए एक तीन-इलेक्ट्रोड प्रणाली का उपयोग किया गया था। एएओ/सीएनपी इलेक्ट्रोड के सीवी वक्रों ने एक निकट-आयताकार रूप दिखाया, जो $370 \mu\text{A}/\text{cm}^2$ के अधिकतम वर्तमान घनत्व के साथ आदर्श विद्युत दोहरी परत संधारित्र प्रदर्शन का संकेत देता है जोकि तेज आयन प्रसार और कुशल चार्ज भंडारण को दर्शाता है। इसके विपरीत, AAO/CNP@ZnO इलेक्ट्रोड ने गैल्वेनोस्टैटिक चार्ज-डिस्चार्ज परीक्षणों में $0.5 \text{ mA}/\text{cm}^2$ के वर्तमान घनत्व

पर 3.1 mF/cm^2 के विशिष्ट कैपेसिटेंस के साथ लगभग सममित त्रिकोणीय प्रोफ़ाइल का खुलासा किया। इन निष्कर्षों से संकेत मिलता है कि AAO/CNP@ZnO हाइब्रिड इलेक्ट्रोड उच्च-प्रदर्शन अगली पीढ़ी के सुपरकैपेसिटर अनुप्रयोगों के लिए एक व्यवहार्य समाधान है।

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ABBREVIATIONS

AAO	Anodized aluminium oxide
AFM	Atomic force microscopy
Al	Aluminium
AR	Anti-reflective
CNP _s	Carbon nanopillars
CNT _s	Carbon nanotubes
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
EBL	Electron beam lithography
EDLC _s	Electric double-layer capacitors
EF	Enhancement factor
EIS	Electrochemical impedance spectroscopy
FDTD	Finite-Difference Time-Domain
FESEM	Field emission scanning electron microscopy
FIB	Focused ion beam
GCD	Galvanostatic charge–discharge
HE	Hot embossing
LSPR	Localized surface plasmon resonance
NM _s	Nanomaterials
NP _s	Nanopillars
NS _s	Nanostructures
PVD	Physical vapor deposition
R6G	Rodamine6G
SERS	Surface-enhanced Raman spectroscopy
TEM	Transmission electron microscopy
UV-NIL	Ultraviolet nanoimprint lithography
VA-CNT _s	Vertically aligned carbon nanotubes
ZnO	Zinc oxide

Chapter 1

Introduction

1.1 Definition of Nanoscience and Nanotechnology

The term ‘nano’ originated from the Greek prefix, meaning ‘dwarf’ or extremely small, and depicts a length scale of a billionth of a meter (10^{-9}m). Nanoscience and nanotechnology are two different terms that represent a rapidly growing field, which involves materials, structures, and devices whose novel behavior and characteristics arise from atomic arrangement at the nanoscale, typically between 1 and 100 nanometers. Nanoscience is the study of material and molecular structure at the nanometer level, typically from 1 to 100 nm, while nanotechnology refers to the implementation of this knowledge in practical applications such as devices, etc. For comparison, the thickness of a human hair is 60,000 nm, while the diameter of the DNA double helix measures just 1 nanometer. Nanoscience has its philosophical background in ancient Greece, particularly in the 5th century B.C., when scientists or thinkers pondered whether matter could be divided endlessly into smaller pieces, indivisible and indestructible particles, which are now identified as atoms. Nanotechnology is considered one of the most transformative technologies of the 21st century, involving applying principles of nanoscience to real-world uses by organising, measuring, studying, manipulating, and producing materials at the nanometer scale. In 1959, the American physicist and Nobel Prize winner Richard Feynman proposed the idea of nanotechnology and posed the question “why can’t we write the complete 24-volume Encyclopaedia Britannica on the tip of a pin?” and described a future where machines could contract smaller machines and reach down to the molecular level.

1.2 History of Nanotechnology

In the 4th century AD, nanoparticles and nanostructures were unknowingly utilized by the Romans and demonstrated one of the most remarkable examples in the ancient world. The

Lycurgus Cup, housed in the British Museum, stands as a most outstanding example of advanced craftsmanship in the ancient glass industry. This Dichroic glass refers to a type of glass that exhibits different colours depending on lighting conditions, green appearance under reflected light, and shifting to red-purple when light transmits through it, as illustrated in Figure 1.1(a). In 1990, scientists used transmission electron microscopy (TEM) to investigate the dichroic effect of the Lycurgus cup and observed that the colour-changing behaviour was caused due to the presence of particles ranging in size from 50 to 100 nanometres. Further X-ray analysis revealed that the nanoparticles were composed of a silver-gold alloy, with a ratio of 7:3 (Ag: Au), and contained around 10% copper (Cu) distributed within the glass matrix. A similar phenomenon was observed in late medieval church glass windows, where luminous red and yellow colours were due to the incorporation of different sizes of Ag, Au NPs in the glass. Figure 1.1 (b) provides the evolution and progression in nanotechnology made possible through the blessed contribution of nanoscience.

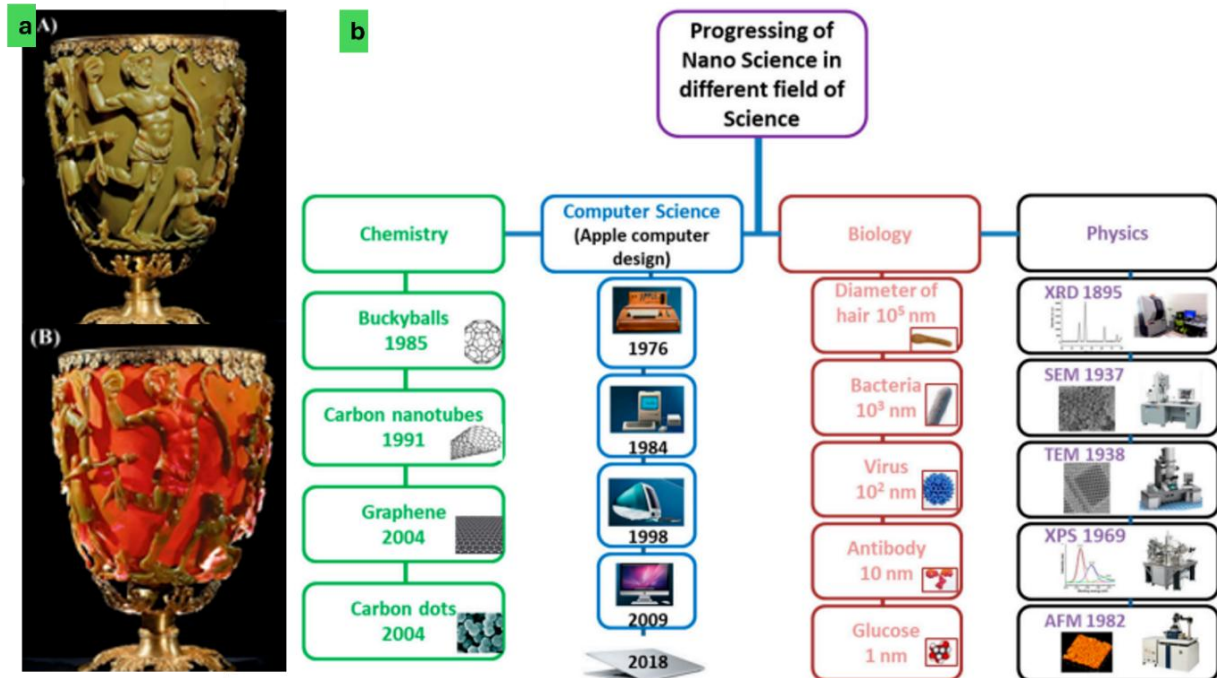


Figure 1.1 (a) The Lycurgus cup, the green appears in reflected light (A) and red-purple in transmitted light mode (B) [1,2] (b) Progresses in Nanotechnology [3].

1.3 Modern Era of Nanotechnology

Although nanometers have been consistently used from the ancient period, recognition in society was gained from the late 20th century when researchers made billions of transistors on a silicon chip by scaling it down to 10 nm. This achievement marked the true beginning of the modern nanotechnology era, showcasing how miniaturization could drastically improve device performance. Since then, nanotechnology has expanded into diverse fields, from advanced materials to healthcare, shaping today's technological landscape.

1.4 Nanomaterial vs bulk material

When the size of a material drops below 100 nanometers, quantum confinement effects begin to strongly influence its thermal, electrical, and optical behaviour. At this scale, a high proportion of the atoms are located on the surface of the nanoparticle. The fraction percentage of total atoms to surface atoms in an NP (surface to volume ratio) is inversely related to the diameter of the NP. Therefore, NPS have enhanced chemical reactivity, different melting points, different electronic properties, etc. Table 1.1 shows the comparative difference between bulk material and nanoparticles [4].

Table 1.1 Nanomaterial and bulk material characteristics.

Nanomaterial	Bulk material
Large surface area	Small surface area.
Chemically more reactive	Chemically less reactive.
Faster in performance	Slower in performance
Lighter material.	Heavier material.
Cheaper than bulk.	Expensive.
More energy efficient.	Not energy efficient
Different properties at a small scale.	Properties remain same

1.5 Classification and applications of nanomaterials

NMs can be grouped according to their dimensions, shape, physical state, and chemical composition. Based on their dimensionality, NMs can be divided further into 4 classes (0D,1D,

2D,3D). Further, it can be categorized on the basis of its morphology (pillar, flat, and spherical) and chemical composition, which are described in Figure 1.2.

1. Metal NMs - gold, iron, silver, copper, and other metallic NPs.
2. Metal oxide NMs- TiO_2 , Fe_2O_3 , Al_2O_3 , ZnO , and SiO_2 .
3. Bimetallic NMs - Fe-Cu , Ag-Au , Ag-Cu , Au-Pd@SiO_2 (composed of two metals).
4. Carbon-based NMs -fullerene (0D), CNT(1D), graphene sheets(2D), nanodiamonds (3D).
5. Ceramic NMs- porous hydroxyapatite, $\text{Al}_2\text{O}_3\text{-ZrO}_2$
6. Metal–organic frameworks consisting of inorganic metal ions and organic ligands (Fe-BTC)
7. Polymer NMs – Chitosan, polystyrene

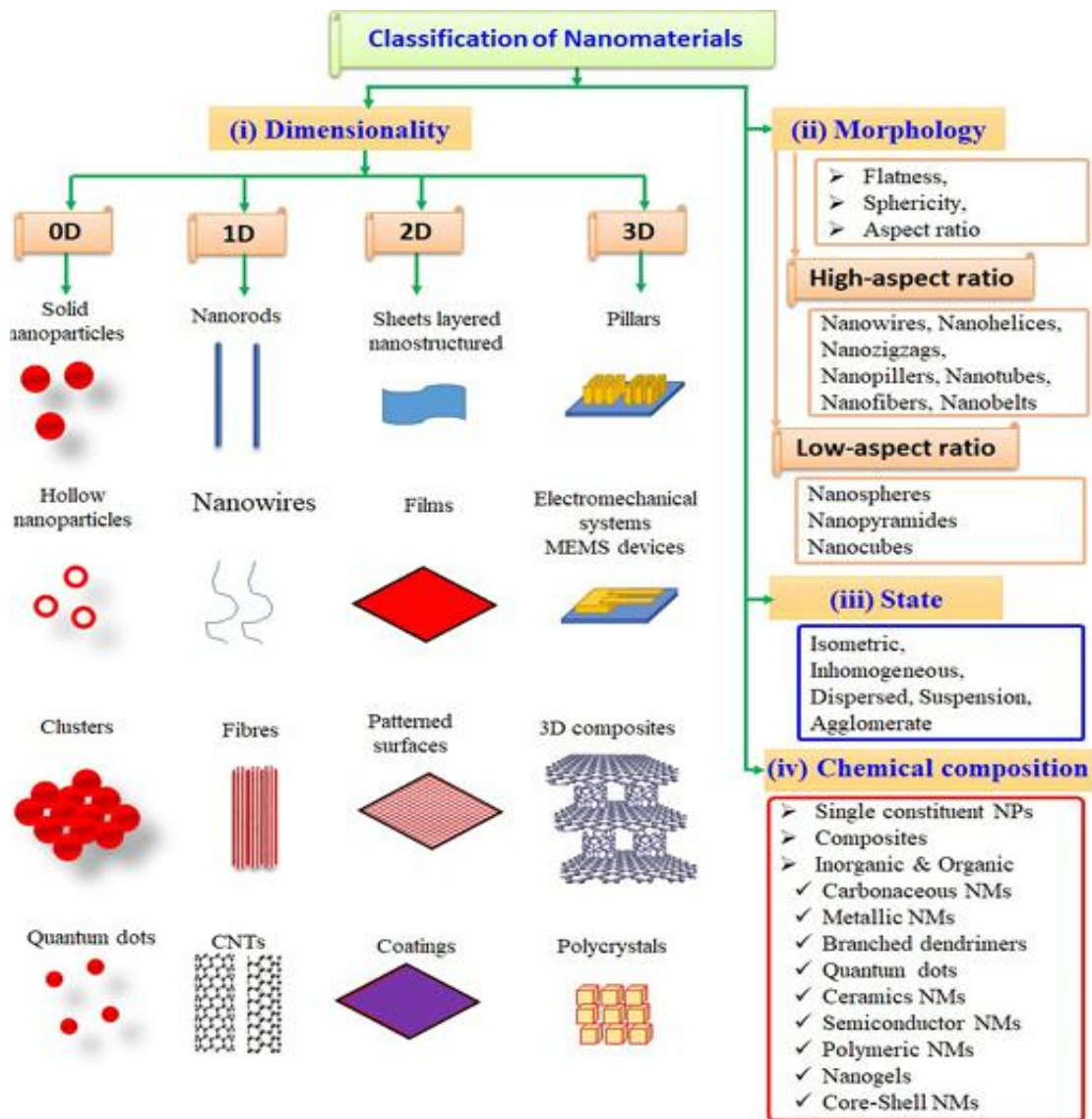


Figure 1.2 Schematic illustration of nanomaterials classification [5].

However, following the classification, NMs' dimensions, composition, and functionality become imperative for the adoption of fabricating a nanostructured (NS) system. All-dimensional nanostructures offer a basic framework of how nanoscale materials are efficiently organized and integrated into larger functional architectures. So, this transition from nanoparticles to a patterned array of nanostructures is not only a scale-up quantity leap but also a quality approach towards achieving uniformity, spatial control, and device-based applicability. Depending on the targeted applications, these NSs need to be oriented with deliberate control over shape and size, high precision, and positioned on selective sites. These various NSs can be synthesized by various approaches, including the top-down and bottom-up approaches. In the top-down approach, the bulk particle is trimmed down to the desired NPs. Some examples are electron beam lithography (EBL), ion beam milling, ball milling, and laser ablation. In the bottom-up approach, NPs are first obtained at the atomic size and then integrated into clusters, which form desired NPs. This approach considers physical vapour deposition (PVD), chemical vapour deposition (CVD), the sol-gel method, hydrothermal, and the self-assembly process [6–8]. Each process has its own trade-off in resolution, scalability, and cost associated in terms of compatibility with substrate, environment, and application. The ability to make such NSs over a macroscopic area is a cornerstone in various applications such as electronics, sensing, photonics, energy harvesting, and many more. This patterned NSs allow us to offer precise tuning over fundamental properties, including electric conductivity, optical response, and surface chemistry. Despite the improvements in the top-down nanofabrication process, numerous inherent restrictions have increasingly controlled their applicability in large-scale, cost-effective, and adaptable nanostructure manufacturing. For instance, EBL can produce high-resolution sub-10 nm, but an inherent series of intermediate processes leads to long processing time and low throughput. This makes it impractical for such applications that require wafer-scale patterning and demand a high production rate. In addition to that, EBL

systems are highly expensive to operate and maintain, and the resist handling steps are involved, which are delicate to environmental conditions, which can introduce inconsistency in feature geometry [9]. Similarly, FIB milling is ideal for prototyping or localized modifications at the nanometer scale [10]. On the other hand, it is too slow and equipment-intensive for scalable production; moreover, it poses high risks of sample damage owing to high-energy ion bombardment, which can change the material's physical and chemical properties at the nanoscale. However, NIL was developed to address some throughput limitations of EBL but relies completely on the quality and durability of the mould utilized for imprinting. Any imperfections or deformations in the mould are replicated across all imprinted surfaces, leading to a multiplication of defects in macroscale area patterning [11]. Conventionally, top-down approaches, moulds are naturally made up of rigid materials such as silicon or quartz wafers using complex lithographic and etching techniques, including EBL, UV-lithography, and reactive ion etching (RIE). Even though these materials offer excellent precision and dimensional accuracy, they come with key limitations, such as the fabrication process requiring cleanroom environments, expensive equipment, and significant processing time. Moreover, these processes provide limited flexibility in terms of pattern variability and surface functionality, which makes them less appropriate for fast prototyping and large-area applications. In addition to that, such moulds are usually not compatible with flexible substrates or free-form surfaces, limiting their adoption in evolving fields like flexible electronics and wearable sensors. The material rigidity and brittleness, especially for Si, quartz, and sapphire, pose challenges in repeated imprinting cycles, resulting in durability concerns over time. These restrictions highlight the need for alternative methods that are not only scalable but also capable of producing robust, high-fidelity, and low-cost moulds from a wider variety of materials. This requirement has led to increasing interest in bottom-up fabrication strategies, especially those that rely on self-organizing processes to fabricate nanoscale order without the need for costly,

precision-driven top-down tools. Among the various bottom-up systems explored for nanostructure, templating growth is a more versatile and facile approach to make periodic structures without area restrictions. For example, block copolymers can separate into self-organized nanoscale size domains, with a range of morphologies including lamellae, spheres, and cylinders as a function of their applied processing conditions and chemical compositions. Nevertheless, their susceptibility to thermal instability, poor long-range ordering, and complicated annealing step restricts their effective use in mould fabrication. Likewise, porous silicon, formed through electrochemical etching, enables controlled pore architecture, yet low mechanical strength and limited chemical resistance remain significant drawbacks. Colloidal crystal templates, formed through self-assembly monolayer or 3D periodic structure of micro/nanospheres, can generate a hexagonally or FCC-packed structure due to capillary forces and particle-particle interactions [12]. However, due to a lack of architectural uniformity over a large area, the multi-step associated process is often used. Conversely, mesoporous silica powder offers a high surface area and excellent chemical flexibility is mainly suited for chemical templating rather than mechanical imprinting owing to its mechanically fragile framework. In comparison, anodized aluminium oxide (AAO) is an exceptionally versatile and robust self-assembled template.

1.6 Anodized alumina oxide

Anodized aluminium oxide (AAO) or porous anodic aluminium oxide (PAA) is a high-density of ordered pore structure of diameter in the range of 20-500 nm with a length scale of the micrometre range. In mild acidic electrolytes (like oxalic, sulfuric, or phosphoric acid), AAO develops a porous structure due to controlled dissolution of alumina at the pore base. In contrast, neutral solutions promote uniform oxide growth without significant dissolution, leading to a compact, also called nonporous AAO layer. The pore formation and growth mechanism is explained in four stages.

Stage 1

In this stage, an exponential decline in current density is observed due to the rapid development of thick oxide growth. This insulating behaviour causes an increase in electric resistance, leading to a reduction in overall current density.

Stage 2

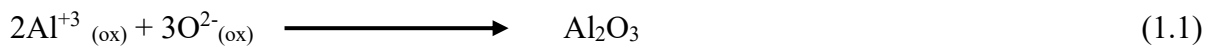
The rising trend in current density at this point signifies the early stage of pore formation, which progresses until a local peak is attained. The current density attains the local maxima when the oxide barrier layer begins to break down, allowing the formation of a disordered pore nucleation to commence. Two predominant models explain pore nucleation during anodization: the field-assisted model and the stress-induced mechanism. The field-assisted model, proposed by O'Sullivan and Wood, attributes pore formation to electric field-driven processes[13]. In this model, local defects in the barrier oxide layer cause imperfection growth, leading to pore initiation at its thinner areas due to concentrated current flow. The second model, Shimizu and Thompson's stress-driven model, attributes tensile stress generated at the metal/oxide interface due to volumetric expansion [14]. This stress leads to cracking in the oxide layer, resulting in localized current concentration and uneven oxide formation.

Stages 3 and 4

As anodization prolongs, a steady-state regime is eventually established, characterized by a significant reduction in pore density and the gradual alignment of irregular pores into well-defined, parallel to each other oriented pores perpendicular to the surface. At this stage, the thickness of the barrier layer (t_b) remains constant, and the porous film continues to grow in thickness due to a dynamic balance between two competing processes, the formation of aluminium oxide and its concurrent dissolution, as mechanisms described by reactions 1.1 and 1.2, respectively.

Oxygen-containing ions such as O^{2-} and OH^- migrate into the metal–oxide interface, allowing the continuous formation of the oxide layer (reaction 7 in Figure 1.3). Meanwhile, Al^{3+} ions eject through the barrier and form a water-soluble compound with electrolyte anions, as noted in reaction (5) in Figure 1.3. Additionally, the adsorption of these electrolyte anions along the pore walls results in the formation of an anion-contaminated alumina layer in close contact with the electrolyte. Over the time, all associated electrochemical reactions reach a dynamic steady state, in which the rates of oxide formation and dissolution are in equilibrium. A conceptual illustration of this steady-state growth, along with the relevant reactions, is provided in Figure 1.3.

Deposition of oxide



Dissolution of oxide

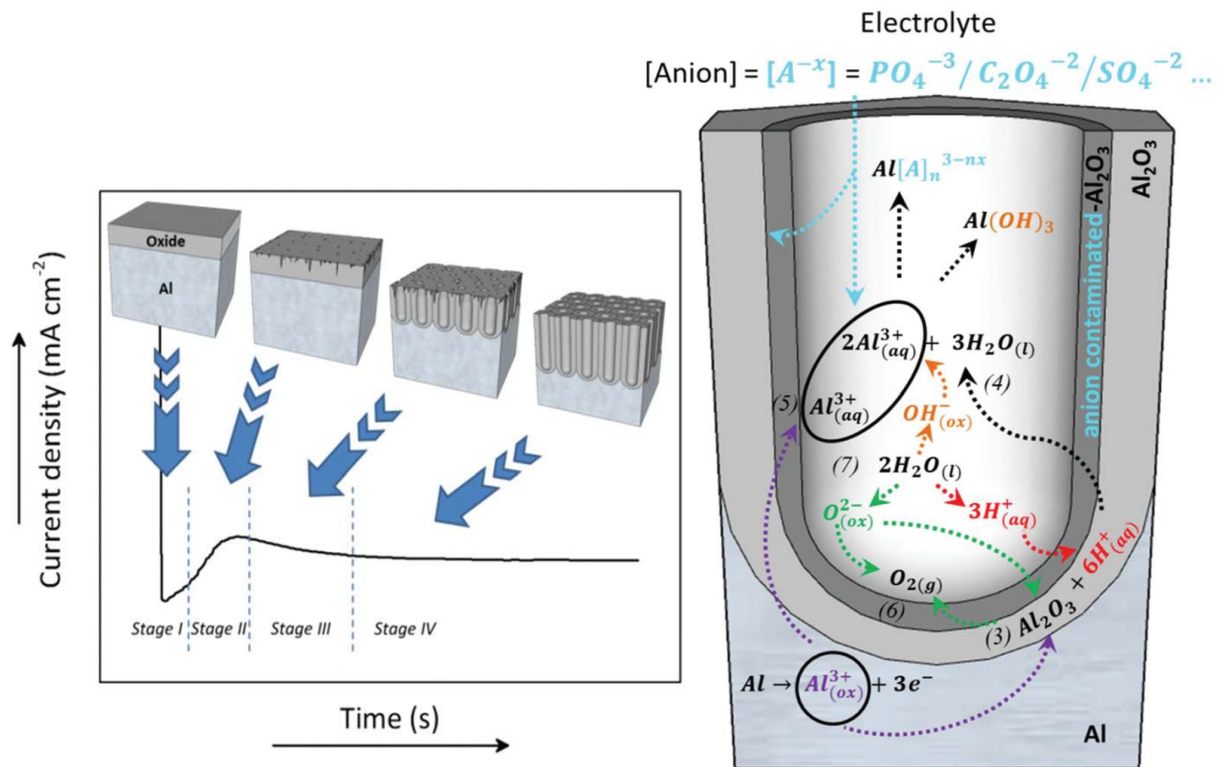


Figure 1.3 Pore formation and pore growth mechanism [15].

1.7 Mild anodization

The term "mild anodization" refers to a regime where the applied voltage is maintained below the threshold limit at which the oxide layer begins to degrade. Crossing this voltage limit often leads to structural issues in the oxide film, including thermal damage and crack formation. The phenomenon of self-organization within anodic alumina's nanoporous architecture was initially investigated by Masuda et al. using a two-stage anodization approach in 0.3 M oxalic acid. As illustrated in Figure 1.4, the initial anodization was carried out at 40 V and 0 °C electrolyte temperature for a duration of 24 h, which led to the formation of a well-aligned pore arrangement at the metal/oxide interface. The resultant porous alumina layer was then chemically removed using a mixture of 6 wt.% H_3PO_4 and 1.8 wt.% H_2CrO_4 , exhibited a distinct hexagonal texture of the aluminium surface. The second anodization, performed under identical conditions, facilitated the formation of a more uniform and organized pore structure.

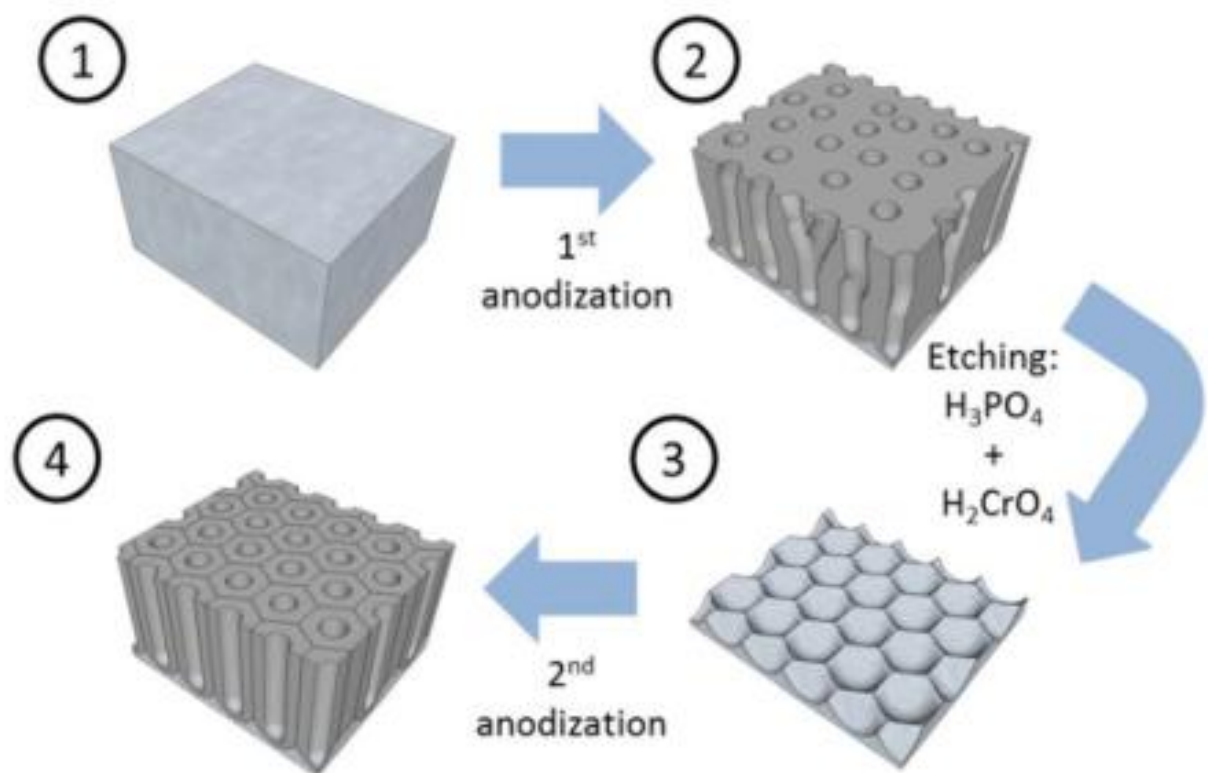


Figure 1.4 Two-step anodization process [16].

Further investigations identified that optimal self-ordering could also be attained at 25 V and 195V as optimal voltages in 0.3 M H₂SO₄ and H₃PO₄, respectively, producing average interpore distances of 65 nm and 500 nm at 0°C [17,18].

1.8 Synthesis of carbon nanomaterials within AAO templates

Carbon offers several allotropes due to its ability to undergo sp , sp^2 , and sp^3 hybridization. This exceptional ability to form various types of covalent bonds allows carbon to construct a wide array of structures, each with unique physical and chemical characteristics, suitable for various technological applications. As shown in Figure 1.5, these carbon allotropes span from 0D to 3D frameworks, each exhibiting distinct properties. Notably, graphite and diamond serve as prime examples where graphite is a soft, lubricative, and conductive material, whereas diamond is extremely hard and an electrical insulator. As discussed, porous anodic alumina templates support a versatile framework for the controlled arrangement and confinement of carbon nanotubes within nanoscale channels, allowing for precise structural tuning.

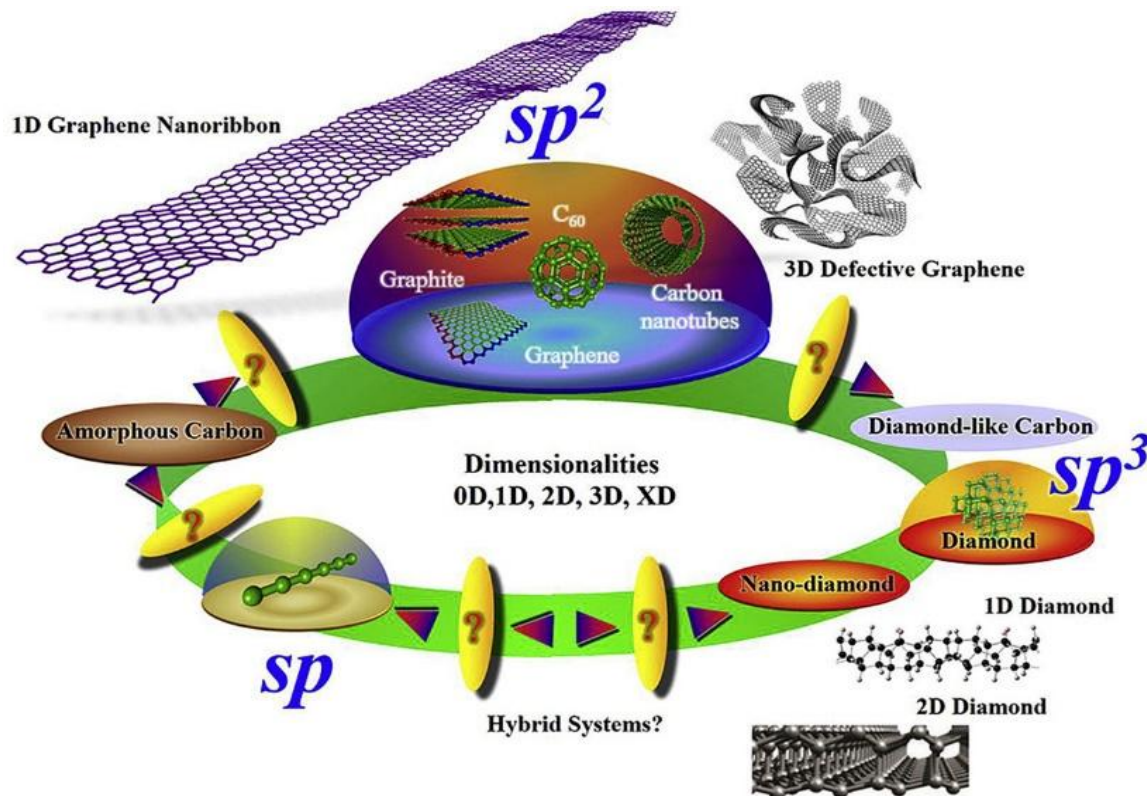


Figure 1.5 Carbon nanomaterial allotropes in different shapes and dimensions [19].

1.8.1 Carbon Nanotubes (CNTs)

A single-walled carbon nanotube (SWCNT) can be envisioned as a single graphene sheet rolled into a cylindrical shape with sp^2 -hybridized carbon atoms. Based on the number of graphene layers, carbon nanotubes are classified into single-walled, double-walled, or multi-walled (MWCNTs) types. SWCNTs typically have diameters of a few nanometers, while MWCNTs exhibit outer diameters ranging between 2 nm and 100 nm, based on the number of concentric tubular layers. The CNTs can vary significantly in length, from a few nanometers to several centimeters, resulting in extremely high aspect ratios that can exceed the order of 1,000,000 times. This unique geometry, combined with their exceptional mechanical strength, electrical conductivity, thermal resistance, and chemical stability, allows them to be utilized as an ideal material for a broad spectrum of technological applications. A key factor that influences these remarkable properties is the atomic arrangement of the graphene sheet from which the nanotube is derived. This rolling configuration, known as the chirality, defined by the chiral vector describing how the graphene sheet is rolled, plays a crucial role. Armchair-type CNTs exhibit metallic behaviour and high conductivity, whereas zigzag and chiral CNTs may be either semiconducting or metallic depending on their chiral indices. This tunable conductivity based on chirality makes them essential in nano-device engineering. The chiral vector representation, along with armchair and zigzag configurations of CNTs, is illustrated in Figure 1.6(a–c).

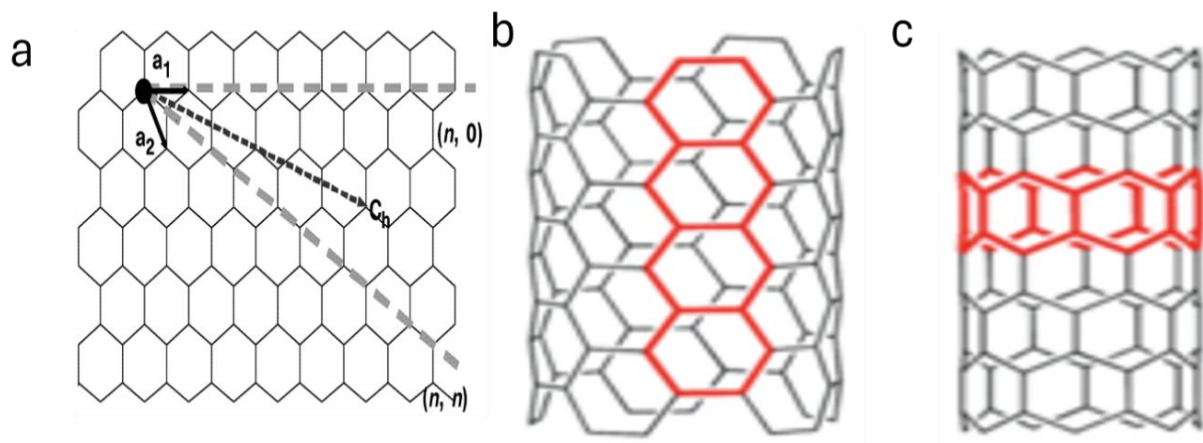


Figure 1.6 (a) Chiral representation, (b) armchair, (c) zigzag CNTs [20].

In recent times, a variety of methods have been developed for the synthesis of carbon nanotubes, including arc discharge, laser ablation, and CVD. Among these, the arc discharge method stands out as one of the most cost-effective and straightforward techniques for producing substantial quantities of MWCNTs. Nevertheless, compared to CVD, arc discharge and laser-based methods offer limited control over nanotube characteristics such as patterning, chirality, and diameter uniformity. The catalytic chemical vapor deposition has emerged as the most reliable and efficient technique for synthesizing well-aligned and structurally uniform vertically aligned carbon nanotubes (VA-CNTs). Two primary growth models have been proposed for the formation of CNTs on catalytic nanoparticles: tip growth and base growth, as shown in Figure 1.7(a). In the first model, CNT growth occurs when the interaction between the metal catalyst and the substrate is relatively weak. This weak adhesion results in the catalyst forming an acute angle with the substrate surface. Hydrocarbon molecules decompose on the surface of the catalyst particles, and carbon atoms diffuse downward through the metal, leading to CNTs emerging from the base of the catalyst. The continuous formation of hexagonal carbon rings is sustained as long as the top of the nanoparticle remains exposed. In contrast, the second model depicts strong adhesion between the metal catalyst and the substrate, causing carbon to diffuse upward from the base of the nanoparticle and exit from the top, resulting in a different CNT growth direction. Figure 1.7(b) shows the SEM image of a patterned CNT pillar array.

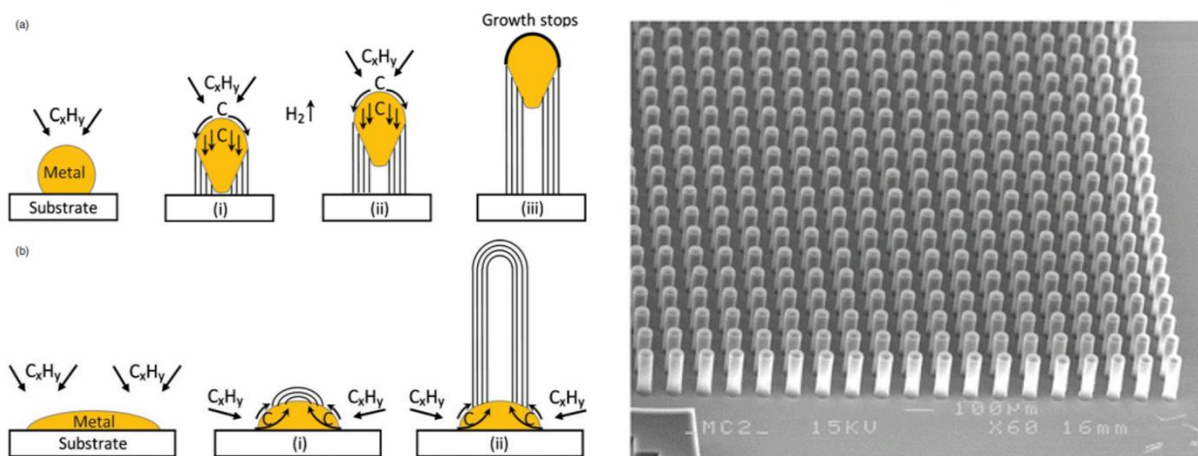


Figure 1.7 (a, b) CNT growth mechanism, tip growth and base growth, SEM image of patterned CNT pillars [21,22].

1.8.2 Synthesis of CNTs by the AAO Template Method

In catalytic CVD using porous anodic alumina templates, hydrocarbon gases undergo thermal decomposition, leading to the deposition of carbon along the internal pore walls. A significant benefit of this technique is that the dimensions of the resulting CNTs are strictly determined by the length and diameter of the pores. CNT growth inside AAO templates generally proceeds through five sequential stages: (i) pyrolytic breakdown of the carbon source, (ii) dissociation of carbon in the deposition area, (iii) infiltration of carbon into the template, (iv) nucleation over the catalyst or along the inner walls, and (v) MWCNT growth. Moreover, this process is not limited to CNT growth but is also useful for AAO-graphene and AAO-nanodiamond growth [23]. Figure 1.8(a, b) depicts the schematic of CVD and AAO. The AAO/CNTs composites can be employed in a wide range of advanced applications owing to their unique combination of high surface area, aligned nanostructure, and excellent electrical conductivity. These include surface-enhanced Raman scattering (SERS) for sensitive molecular detection, supercapacitors for high-performance energy storage, field emitters due to their efficient electron emission properties, and biosensors where their conductive and biocompatible architecture enhances detection sensitivity. Their high mechanical properties and closed-capped tubes morphology, also called carbon nano pillars (CNPs), make them suitable as a mould for hot embossing lithography.

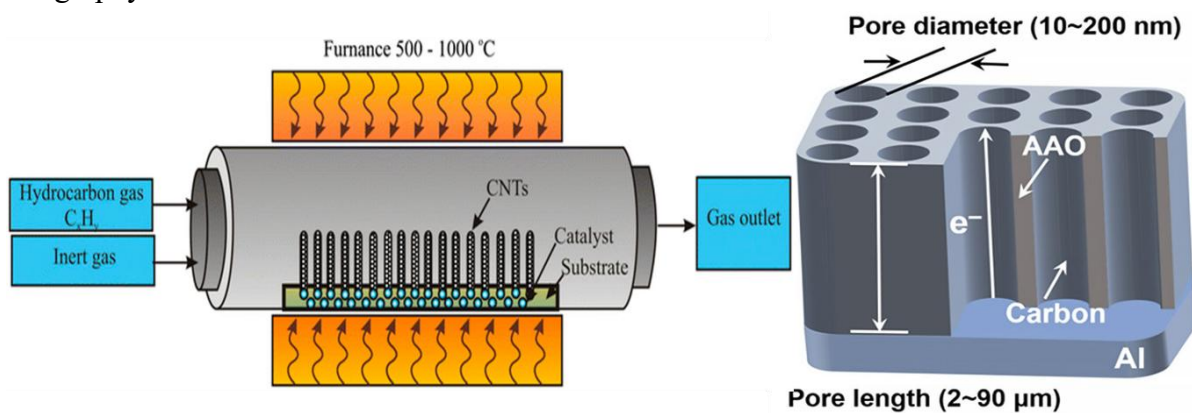


Figure 1.8 Thermal CVD schematic for CNTs growth, and schematic of AAO-assisted template growth [24].

1.9 Nano hot embossing lithography

In recent decades, technological progress has driven a shift toward more compact and miniaturized products, demanding components with functional elements spanning from the macro to the micron-size, and nanoscale. This necessity has accelerated the evolution of micro and nano-replication technologies, leading to a surge in research activity. The prominent replication methods include injection moulding (IM), hot embossing (HE), and UV-based imprint lithography. With the growing interest in micro and nanotechnology, there is a necessity for scalable, cost-effective methods for producing miniature polymer replicas. Among these moulding techniques, nano hot embossing (nano-HE), or HE, is frequently employed as a standard technique for polymer replicating nanostructures. This process involves transferring features from a nano-patterned master, commonly referred to as a mould insert, onto a thermoplastic polymer. Its effectiveness and high throughput are a compelling alternative to other nanofabrication processes with delicate structures and high aspect ratio features. The versatility of HE makes it applicable across various domains. It is widely employed in the fabrication of optical nanostructures, including nanolens arrays, antireflective layers, and light-guiding plates. The technique is also suitable for producing biomedical tools, such as drug delivery systems and molecular separation devices for DNA and RNA. HE can be configured in different modes such as plate-to-plate (P2P), roll-to-roll (R2R), and plate-to-roll (P2R). The P2P configuration is generally considered the conventional approach, offering precise control over pressure and temperature, while R2R is better suited for large-area, continuous, and scalable fabrication. The hot embossing process follows various sequential steps. Initially, the polymer substrate is heated to a temperature slightly above its softening point, which is defined as the glass transition temperature (T_g). This temperature is essential to make the polymer viscous for processing, and is strongly influenced by the polymer's molecular weight, chemical structure, and monomer ordering. Viscosity, or the material's resistance to deformation, also

influences process control. Once the desired thermal conditions are achieved, the mould is pressed onto the softened polymer, applying either a specific force or displacement. The pressure is maintained for a set duration to ensure full feature replication, as illustrated in Figure 1.9. After embossing, the system is cooled to solidify the polymer and preserve the imprinted features. Once the temperature drops below the viscoelastic point, the mould is carefully separated from the substrate, ensuring a clean transfer of the nanostructures. Proper cooling minimizes thermal stress, while controlled demoulding helps avoid cracks or deformation. This step is crucial for maintaining the fidelity and reusability of both the mould and the embossed surface.

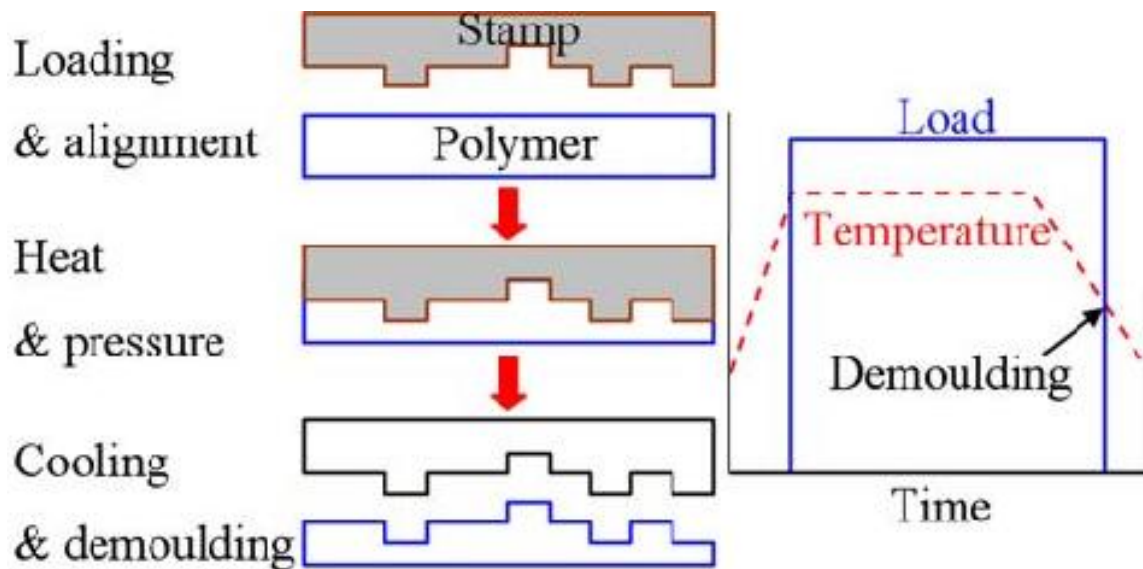


Figure 1.9 Hot embossing process [25].

1.10 Application of AAO and AAO/CNPs nanostructures

1.10.1 Large area nanofabrication

Inspired by natural systems such as the lotus leaf, cicada wings, which exhibit remarkable water repellence owing to their hierarchical micro/nano surface structure, biomimetic approaches have driven the development of artificial superhydrophobic, antireflective surfaces. These engineered textures, when replicated using hydrophobic or oleophobic materials, significantly enhance liquid repellent properties compared to smooth films of the same material, which is

explained by two different wetting regime models, Wenzel and Cassie-Baxter models, as given in equations 1.3 and 1.4. The scalability and uniformity of AAO make it a promising candidate for producing robust, self-cleaning, anti-fogging, and anti-biofouling polymeric surfaces with lotus-leaf-inspired functionality. Additionally, biomimetic surface engineering has advanced significantly through inspiration from nature, where structures such as moth eyes, butterfly wings, and cicada wings exhibit unique functionalities like antireflection. The growth of CNPs inside the AAO template behaves like vertical pillars named as vertically aligned carbon nano pillars (VA-CNPs), where their closed or capped ends lead to the development of nanohole structures. By utilizing the AAO and AAO/CNPs composite moulds in HE, such antireflective nanohole/nanopillar patterns can be reliably replicated onto polymer substrates over large areas with high precision. The moth-eye effect arises from a gradual refractive index transition between air and the substrate, which minimizes Fresnel reflections (R). According to the effective medium theory, given in equations 1.5 and 1.6, the subwavelength nanopatterns act as a graded medium, enabling broadband and angle-independent antireflective behaviour. The combination of highly ordered AAO templates and vertically aligned CNPs offers a robust and tunable mould platform, enabling the creation of complex, hierarchical textures that mimic biological surfaces while imparting optical and wetting functionalities suitable for solar, optical, and biomedical applications. The schematic image of a lotus leaf demonstrating superhydrophilicity and the moth-eye structure exhibiting antireflective properties are shown in Figure 1.10(a, b).

$$\cos \theta_c = r \cos \theta \quad \text{Wenzel model} \quad (1.3)$$

$$\cos \theta_c = -1 + f(1 + \cos \theta) \quad \text{Cassie -Baxter model} \quad (1.4)$$

Where θ_c is water contact angle of the textured surface, and f is the fraction of the pattern area.

$$n_{eff}^2 = f n_{air}^2 + (1 - f) n_p^2 \quad (1.5)$$

$$R = \left| \frac{(n_{eff} - 1)}{(n_{eff} + 1)} \right|^2 \quad (1.6)$$

Where n is the refractive index, f is the fraction of the pattern, and R is the Fresnel reflection.

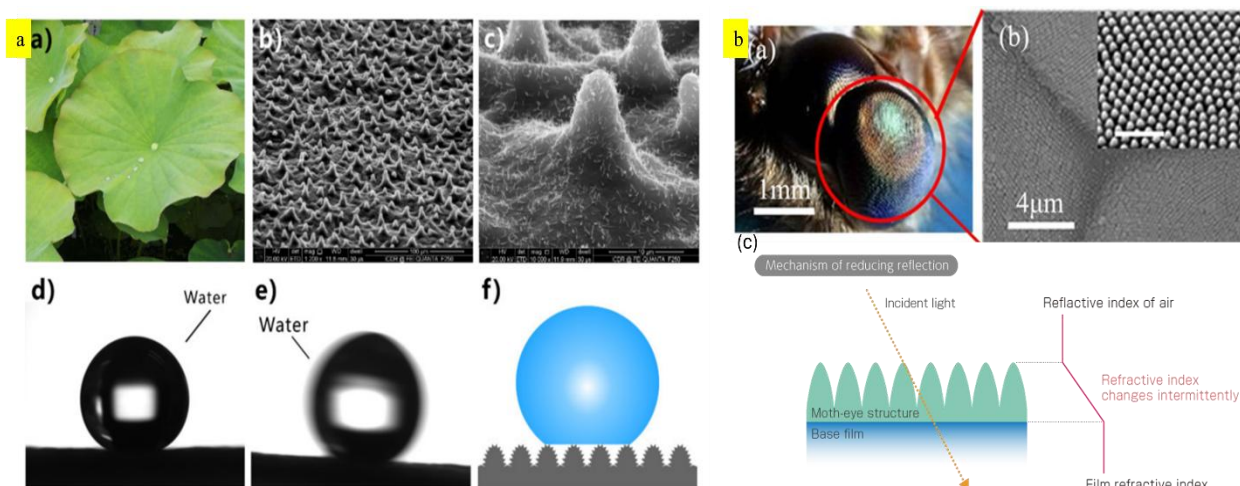


Figure 1.10 (a) SEM image of a lotus leaf as a superhydrophobic surface (b) moth-eye structure as an antireflective surface [26,27].

1.10.2 Surface-enhanced Raman spectroscopy

The recent advancement of nanotechnology has revealed unprecedented opportunities in the development of highly sensitive optical sensors and spectroscopic tools. One such powerful technique is Surface-Enhanced Raman Scattering (SERS), which exploits the interaction of light with nanostructured materials to amplify weak Raman signals of analyte molecules. Owing to its powerful signal boosting properties, SERS facilitates ultra-sensitive detection, thus considered a transformative approach in molecular-level detection of chemical and biological species. Depending on the wavelength of light, the type of interacting medium, and the surrounding conditions, light can be absorbed, transmitted, or scattered when incident on any material. Understanding the basic principles of plasmonics is essential to fully comprehend the mechanisms that drive SERS. Plasmonic, a specialized field within photonics, investigates the phenomena of surface plasmons generated by the light-induced oscillation of electrons at metal and dielectric junctions. These electron oscillations can be broadly classified into two categories: surface plasmon polaritons (SPPs), which propagate along the metal-dielectric interface, and localized surface plasmons (LSPs), which are confined to nanostructured metallic domains such as nanoparticles. Among these, LSPs are particularly important for

SERS applications because they are capable of generating intense localized electromagnetic (EM) fields. When metallic nanoparticles, especially those composed of noble metals like Au and Ag, are exposed to incident light, their conduction electrons resonate at specific frequencies, depending on the size, shape, and dielectric environment of the particles. Gold nanostructures exhibit high polarizability due to their free electron density, inter-band transition, inert nature, and ability to sustain coherent electron motion, which enhances their optical response under resonance conditions. The occurrence of resonance causes a strong intensification of the electromagnetic field in certain localized zones near the nanoparticle surfaces, known as hot spots. The field enhancement mechanism is quantitatively described by considering the total electric field (E_{total}) as the sum of the incident field (E_{inc}) and the field scattered by the nanostructure (E_{scat}).

$$E_{\text{total}} = E_{\text{inc}} + E_{\text{scat}}.$$

The enhancement factor (EF) for the Raman signal is approximated by $EF \approx \left| \frac{E_{\text{total}}}{E_0} \right|^4$. Here, E_0 is the amplitude of the incident field. This fourth-power dependence results because both the excitation and scattered Raman photons experience the local field enhancement. Hence, the stronger and more localized the EM field, the more efficient the Raman signal enhancement. Such a significant enhancement has enabled SERS to detect molecular concentrations as low as single-molecule levels. Consequently, the method has been successfully applied in diverse areas such as environmental monitoring, biomedical diagnostics, food safety, and homeland security. The versatility of SERS arises not only from its sensitivity but also from the wide range of nanostructured substrates that can be engineered to support localized surface plasmon resonance (LSPR). At this stage, substrate engineering becomes pivotal. The SERS measurement mainly comprises three crucial variables for signal enhancement: incident light, analyte molecule, and plasmonic nanoparticle/nanostructure (i.e., gold, silver, copper) [28,29]. The most often method for doing SERS analysis is to mix analyte with colloidal silver

nanoparticles (AgNPs) or gold nanoparticles (AuNPs) solution, followed by analysis utilizing Raman spectroscopy, however, the colloidal base sample has some limitations: (1) poor sensitivity to certain analyte (2) low spectral repeatability due to weak affinity to specific analyte (3) complex pretreatment steps limitations (e.g. extraction, purification) [30]. Therefore, many studies consider creating a more uniform substrate using techniques such as UV-lithography, soft lithography, EBL, NIL, and pulsed laser deposition (PLD), which requires a clean room facility, is very time-consuming, and is not economically sound for large-area patterns [31,32]. In order to generate strong and reproducible hot spots, ordered nanostructures are necessary. AAO membranes provide a reliable and cost-effective template for creating such ordered architectures. These characteristics make AAO a preferred choice for scalable nanofabrication. However, to further enhance the plasmonic performance and surface area, integration with carbon nanomaterials, especially VA-CNPs, has proven beneficial. The synergy between AAO and CNPs creates a hybrid framework that is particularly well-suited for functionalization with plasmonic material such as Au. By depositing a thin layer of gold onto this AAO/CNPs hybrid structure via sputtering, one can generate nanoscale gaps and junctions where strong plasmonic coupling occurs. The morphology of the deposited gold/silver layer can be controlled by sputtering parameters such as deposition time, power, and angle, which play a decisive role in determining the density and distribution of hot spots. Sputtering is a physical vapor deposition technique that enables uniform and conformal coating of metal films over complex nanostructured surfaces. In the context of AAO/CNPs hybrids, sputtering facilitates the formation of a discontinuous or semi-continuous gold layer over the CNP tips and walls. These nanoscale metallic domains act as efficient plasmonic antennas, thereby significantly enhancing the SERS response. Furthermore, the vertical orientation of CNPs within AAO not only facilitates effective light coupling and analyte adsorption but also promotes thermal stability and reusability, which are key attributes for real-world applications.

The versatility of this platform extends beyond SERS with appropriate functionalization. AAO/CNP@Au structures could also be explored for photothermal therapy, photocatalysis, and energy harvesting applications. Figure 1.11(a) presents the schematic of localized surface plasmon resonance in metallic nanoparticles, (b) shows the SERS electromagnetic enhancement in near and far fields, whereas (c) depicts the finite-difference time-domain (FDTD) simulation of Au nanoparticles that how size of AuNP scattered light, and (d) shows the schematic of electric field enhancement variation on shape and gap in an Au dimer.

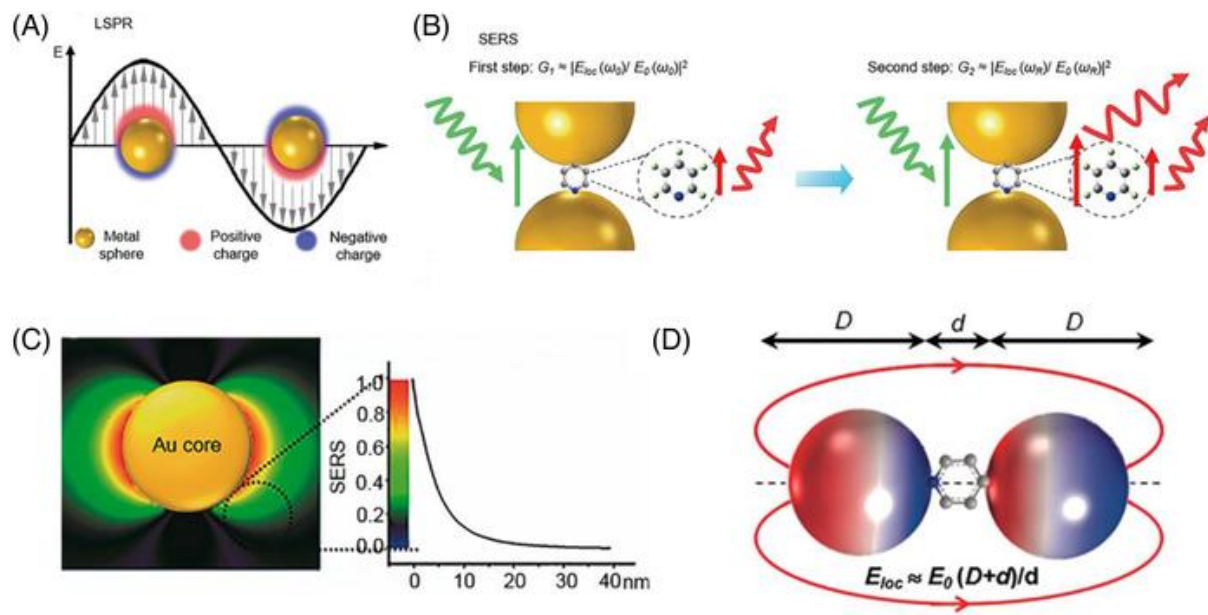


Figure 1.11 (a) Schematic of LSPR by metallic nanoparticles, (b) SERS electromagnetic enhancement in near field and far field, (c) finite difference -time domain of Au NPs, (d) schematic of electric field distribution of Au dimer [33].

For a spherical particle of radius, $a \ll \lambda$

- $\alpha = 4\pi r^3 \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m}$ where α is polarizability, ϵ_p, ϵ_m are dielectric constant of the particle and the medium
- for LSPR $Re(\epsilon_p) = -2\epsilon_m$, α is very high

- $\sigma_{scat} = \frac{K^4}{6\pi} \alpha^2$ and $\sigma_{abs} = k \text{Im}(\alpha)$ (1.7)

Where σ_{scat} and σ_{abs} are the scattering cross-section and absorption cross-section, respectively [34].

Qualitative estimation of Raman signal enhancement or enhancement factor (EF) can be calculated with the given formula [35]

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{Raman}}{N_{SERS}} \quad (1.8)$$

Where EF is the enhancement factor, I_{SERS} and I_{Raman} are the SERS and Raman intensities for the respective Raman peak, N_{Raman} is the number of analyte molecules contributing to the Raman intensity, whereas N_{SERS} is the number of analyte molecules contributing to the SERS intensity.

1.10.3 Current collector in energy storage device

Supercapacitors, also known as electrochemical capacitors, store energy via electrostatic charge accumulation at the electrode/electrolyte interface and are known for their high-power density, rapid charge/discharge rates, and long cycle life. Supercapacitors are widely used in renewable energy systems for smoothing power fluctuations, in electric vehicles for regenerative braking and quick acceleration, and in portable electronics as backup power sources. Incorporation of nanomaterials in supercapacitors significantly boosts their performance by offering a much larger surface area for charge storage, which enhances capacitance. The nanoscale size helps shorten the ion diffusion distance, enabling quicker charge and discharge cycles. Materials like carbon nanotubes, graphene, and metal oxides also provide superior electrical conductivity, ensuring efficient electron movement. Moreover, porous nanostructures allow better electrolyte access to active sites, improving overall utilization. By adjusting the morphology of nanomaterials, it becomes possible to achieve higher energy density while maintaining high power density, making them ideal for advanced

energy storage systems. Figure 1.12 illustrates the schematic of SC's electrode, where the specific surface area was improved by the incorporation of NMs.

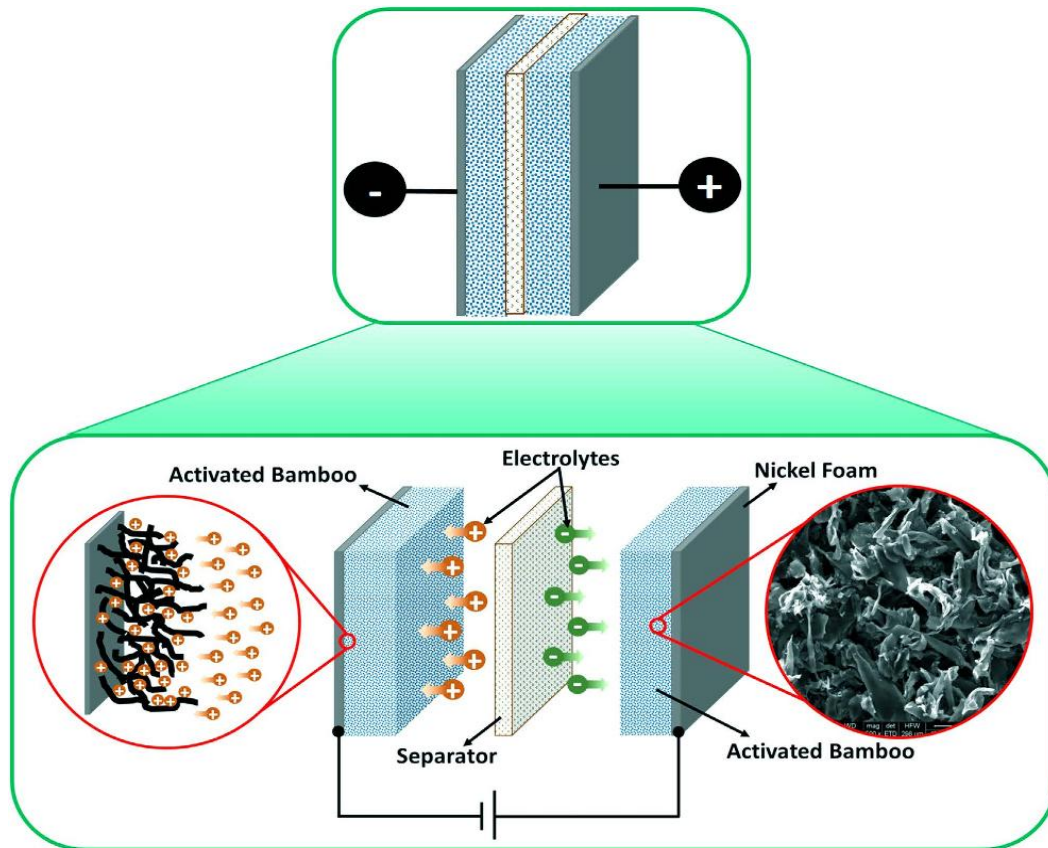


Figure 1.12 Schematic of supercapacitor electrodes [36].

The unique morphology of the AAO/CNPs composite structure, beyond its role in optical applications like SERS, has also shown great promise in the realm of energy storage, particularly in the development of high-performance supercapacitors. In this context, the current collector plays a pivotal role in determining the efficiency of charge transport and overall electrochemical performance. CNPs, due to their exceptional electrical conductivity, large specific surface area, and chemical inertness, are considered ideal materials for use as active components or conductive networks in supercapacitor electrodes. When VA-CNPs are grown within the ordered nanopores of an AAO template, the resulting hybrid material offers a well-aligned, high-surface-area scaffold that supports rapid electron transport and efficient ion diffusion. This vertically integrated architecture ensures direct contact between the CNPs

and the current collector, minimizing resistance and maximizing active material utilization. The AAO template, in this case, provides a mechanically stable and thermally robust framework that guides the uniform growth of CNPs. Its nanoscale pore geometry can be finely tuned by adjusting anodization parameters, enabling precise control over the spacing, diameter, and length of the embedded CNPs. This ordered arrangement not only enhances the mechanical adhesion of the composite film to the substrate but also promotes efficient electrolyte infiltration, which is essential for achieving high areal and volumetric capacitance. Furthermore, the AAO/CNPs architecture is particularly well-suited for hybrid supercapacitors that incorporate pseudocapacitive materials. By depositing metal oxides such as MnO_2 , RuO_2 , or $\text{Ni}(\text{OH})_2$, or conductive polymers like polyaniline (PANI) or polypyrrole (PPy) onto the CNT surface, one can enhance the energy storage capacity via fast Faradaic redox reactions [37]. The integration of nanostructured semiconducting materials, such as zinc oxide (ZnO), has emerged as a highly effective strategy. ZnO nanosheets, when grown over AAO/CNPs frameworks, offer additional electrochemical and surface advantages due to their high electron mobility, wide bandgap (~3.2 eV), and large specific surface area [38,39]. These two-dimensional nanosheets provide extensive active sites for redox reactions in supercapacitor applications, while also improving charge transport pathways and ion diffusion dynamics. The synergistic combination of vertically aligned CNPs, the ordered AAO scaffold, and the surface-enriched ZnO layer results in a multifunctional hybrid architecture, well-suited for high-capacity energy storage. The specific capacitance (C) and power density (P) can be calculated by following the equations [40]

$$C = \frac{\int_{v_1}^{v_2} i dv}{A v \Delta V}, \text{ whereas } P = \frac{C v^2}{2 t} \quad (1.9)$$

where $\int i dv$ is the area under the i-v curve in the CV plot, v_1 and v_2 are the switching voltage window, A is the electrode area, v is the sweep/scan voltage, and ΔV is the voltage window.

Chapter 2

Literature Review

Over the past decade, significant progress in nanofabrication techniques have propelled the rapid advancement of nanotechnology. Continuous innovation in fabrication approaches has facilitated the incorporation of engineered nanostructures into multifunctional devices, expanding their potential in diverse technological domains. The large-scale and commercial implementation of nanofabrication technologies has opened outstanding opportunities for engineered surfaces with tailored functionalities. The different micro/nanoscale dimensional architecture (0D, 1D, 2D, 3D) of structures offers a special and significant type of functionality, including examples of optical instruments that can sense and interact with electromagnetic waves, energy storage devices with huge areal energy density owing to large specific surface area, and biomedical equipment. Such complex nanoscale structures are difficult to achieve through microsystem technologies. As a result, in order to create 3D nanoscale features on relevant materials, different techniques such as selective patterning and material removal from bulk and guided construction of nanoscale entities are sometimes considered as top-down and bottom-up approaches, respectively.

2.1 Top-down nanofabrication

In top-down nanofabrication, various lithographic techniques have been employed to pattern two-dimensional nanoscale structures. Conventional lithography typically relies on the use of a protective mask, where the unmasked regions of the material can be selectively removed through chemical etching or mechanical/physical etching using UV-rays, X-rays, or electron beam.

2.1.1 Optical lithography, e-beam lithography, and FIB nanofabrication

Lithography has been the most widely adopted technique in the microelectronics industry since 1970. Conventional photolithography is a straightforward technique capable of achieving

feature resolutions of approximately 1 μm when using light with a wavelength around 350 nm. In order to attain higher resolution, variants of photolithography employ projection systems, where the photomask is positioned at the focal plane, allowing the pattern to be accurately transferred onto a photoresist-coated substrate [41]. Moreover, to overcome the diffraction limit of light by using e-beam helps to create low-dimensional nano features ~ 10 nm. Although significant progress has been made in EBL instrumentation, advancements in resist materials are progressing more slowly. A low-molecular-weight, single-source precursor resist based on cadmium(II) ethylxanthate complexed with pyridine, has been able to produce 4 nm resolution, which is approaching the physical resolution limit of electron probe size ~ 3.8 nm [42]. However, EBL is still constrained by its low throughput, high fabrication cost, and the limited performance of available resist materials, which collectively hinder its scalability for large-area nanofabrication and commercial applications. Moreover, FIB technology has become a powerful and essential tool enabling the direct 3D patterning and machining of nanostructures on any solid sample, irrespective of hardness and shape. A focused Ga^+ ion beam, operated at currents up to maximum current of 65 nA and an acceleration voltage of 30 kV, was employed for the formation of a single-crystal boron-doped diamond (BDD) tip on a silicon cantilever for AFM study [43].

2.2 Bottom–up nanofabrication methods

The primary objective of bottom-up nanofabrication is to develop a functional system involving assembling atoms or molecules into complex-shaped nanostructures.

2.2.1 Atomic layer deposition

Atomic layer epitaxy (ALE) or ALD, originally developed by Sultola and Antson, has become a key technique to fabricate precise and controlled thin films of ~ 1 nm. The main advantage is to create core-shell complex morphologies such as Cds@ZnO , PS@TiO_2 for light absorption in a 40 nm GaAs-on-Si, and photoelectrochemical H_2 evolution, respectively [44,45].

Moreover, controlled 1D templated nanopillars of ZnO, TiO₂, and Al₂O₃, etc, can be synthesized by the atom layer assembly method; however, ALD's high equipment cost, availability for limited precursors, and slow deposition rate limit its large-scale industrial application [46].

2.2.2 Self-assembly nanofabrication

This bottom-up technique is useful for building homogeneous nanostructures across a wide area, utilizing affordable electrochemical processes. Anodization of aluminium is a controllable process with a well-organized, uniform pore structure. The AAO mould can serve as a reusable, mechanically robust template capable of large-area pattern replication. Moreover, AAO can be used for high-temperature nanomaterials synthesis, where conventional templates/membranes, such as nafion or etched polycarbonate, have limitations [47].

2.2.3 Vapor phase deposition of nanomaterials

Vapour phase deposition is broadly grouped into CVD and PVD based on the underlying deposition process. In CVD, gaseous precursors break down and chemically react under external activation by thermal energy, plasma, leading to the formation of stable solid nanomaterials. Among the various methods to grow carbon allotropes, CVD is still favoured, primarily choice and control of the catalyst, carbon feedstock, and operating conditions. CVD has been extensively used to grow various carbon nanostructures, including SWCNTs, MWCNTs, diamonds, and lately graphene, on various substrates. This enables better dimensional control, reduced amorphous carbon formation, and higher efficiency in carbon conversion into a graphitic structure. CVD is particularly suitable for growing hard carbon allotropes with high structural integrity over large, wafer-scale areas [48]. However, other bottom-up fabrication methods like sol-gel processing and molecular self-assembly are generally confined to polymeric materials or suffer from weak substrate adhesion, making them unsuitable for creating robust mechanical moulds.

2.3 Hybrid nanofabrication

Nanoimprinting lithography is a highly suitable top-down lithography process for high-throughput advanced nanofabrication processes. However, thermal nanoimprint lithography (T-NIL), also known as the hot embossing process, has the advantage of employing flexible thermoplastic materials by eliminating chemicals and solvents. A pre-fabricated mould development with a bottom-up approach makes this hybrid process more versatile to transfer patterns with a higher resolution over a large area. However, most research studies are limited to electrodeposited Ni stamp, silicon stamp developed by EBL, or replica stamp of PDMS, SU8 elastomers [49]. In order to make a hydrophobic polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) film, a water contact angle of $\sim 150^\circ\text{C}$, a PDMS negative replica of a nickel-based master was used to create micropillar arrays [50]. Gold metalized, C-shaped nanostructures were developed by UV-NIL, to detect thiabendazole (TBZ) water pesticides. High accuracy replicated NIL-based gold decoration demonstrated TBZ detection down to 10^{-7} M by integrating microfluidic sensors based on SERS [51]. Over a 2 nm iron catalyst, an array of 100 nm grating was successfully patterned with NIL, in order to grow next-generation 3D CNTs [52]. High-aspect ratio nanostructures ($\text{HAR} > 8$) with a lower than 60 nm diameter of TiO_2 meta-atoms were efficiently transferred using NIL with an ALD-deposited TiO_2 master mould/PDMS replica recipe. The resulting TiO_2 -based inorganic patterns exhibited a refractive index of approximately $n = 1.9$. As a proof of concept, metalenses with numerical apertures (NAs) up to 0.2 were realized, achieving focusing efficiencies exceeding 50% [53]. Imitating nature and comprehending its workings has gained recent interest in developing functional surfaces. However, this UV-NIL variant is generally limited to photocurable resist materials, restricting its applicability to certain polymer types. In contrast, T-NIL or HE techniques can be employed for a wide range of thermoplastic polymers, thereby greatly extending the versatility and material compatibility of the process. Thus, the HE process

requires a mechanically robust and thermally stable mould to withstand the applied pressure and temperature during imprinting. Therefore, AAO template-based moulds emerge as an excellent choice, offering high stiffness, thermal stability, and nanoscale precision for reliable hot embossing applications.

2.4 Anodization

Over the years, research has moved beyond its conventional use in corrosion resistance and decorative treatments, extending toward advanced fields such as photonics, energy storage, sensing technologies, and catalysis. A key advantage lies in the precise tunability of pore dimensions, distribution, and overall morphology, which can be systematically controlled through parameters including electrolyte composition, applied voltage, current density, and processing temperature, thereby establishing anodization as a versatile platform for engineering functional nanomaterials. Although a wide range of metals can undergo anodization, the resulting oxide morphology is strongly influenced by the volumetric expansion of the oxide layer and the stresses generated at the metal–oxide interface. These parameters govern pore initiation and growth, leading to significant variations in structural features across different metals. Metals such as Al, Ti, Ta, Nb, V, Hf, and W are commonly referred to as noble metals, as their surfaces spontaneously develop a thin native oxide layer, typically only a few nanometers thick, upon exposure to oxygen-rich environments. This naturally formed oxide film acts as a passivation barrier, significantly reducing the surface reactivity and thereby limiting further oxidation. For instance, AAO exhibits a highly ordered and uniform pore arrangement, which differs considerably from the less-regular morphologies typically obtained in Fe, Cu, and Mg, due to their distinct oxide growth dynamics. Self-organized nanotubular magnesium oxyfluoride architectures on magnesium-based alloy (WE43) through anodization in a non-aqueous 0.2M HF ethylene glycol electrolyte at 70V, as depicted in the FESEM image of Figure 2.1(a) [54]. In order to extend these anodization strategies, researchers have also

applied similar methods to copper, enabling the formation of diverse nanostructured surfaces by performing the anodization. CuO has been reported to grow in the form of nanowires, and nanosheet-like architectures in KOH aqueous solution [55]. The Sn foil (98.8%) was also examined for a similar study, which was subjected to anodization in 1M NaOH at 2 V. Tin oxide (SnO₂) was obtained of a 1.5µm thick porous layer of 20nm pore diameter with a disordered morphology, as shown in Figure 2.1(c) [56]. A 0.25 mm thick iron foil was anodized in an ethylene glycol-based solution containing 0.2 M NH₄F at 50V. The porous ferrous oxide layers of 40 nm were developed, showing an optical band gap of 2.1ev, morphology of the porous film is shown in Figure 2.1(d) [57]. Moreover, p-type semiconducting nickel oxide (NiO) was formed on silicon wafers and transparent conductive oxide (TCO)-coated glass substrates, by depositing Ni film by sputtering followed by anodization in an electrolyte comprised of 97 vol% diethylene glycol (DEG), 0.15 M KOH, and 0.1 M NH₄F [58]. In this series, Ti anodization also showed the remarkable nanotechnology application, such as photoelectrochemical water splitting and supercapacitor applications, owing to its tubular morphology as shown in Figure 2.1 (e) [59]. The lattice type of a metal, and the volumetric expansion ratio ($\frac{V_{ox}}{V_m}$) or Pilling–Bedworth ratio (PBR) of metal oxide to metal strongly influences the pore arrangement that develops after anodization, as summarized in Table 2.1. When the Pilling–Bedworth ratio (PBR) is less than 1, the oxide film experiences tensile stress, making it prone to cracking. For $1 < \text{PBR} < 2$, the oxide layer forms a uniform and protective coating on the metal surface. However, when PBR exceeds 2, the oxide becomes highly compressive and tends to flake or crumble, as seen with iron oxide on iron [60]. Metals with a simple face-centered cubic (FCC) lattice generally produce well-organized nanopore arrays. In contrast, metals with a hexagonal close-packed (HCP) structure tend to generate ordered nanotube arrays. For body-centered cubic (BCC) metals, however, achieving a uniform porous structure is more challenging, and highly ordered films are not easily obtained [61,62].

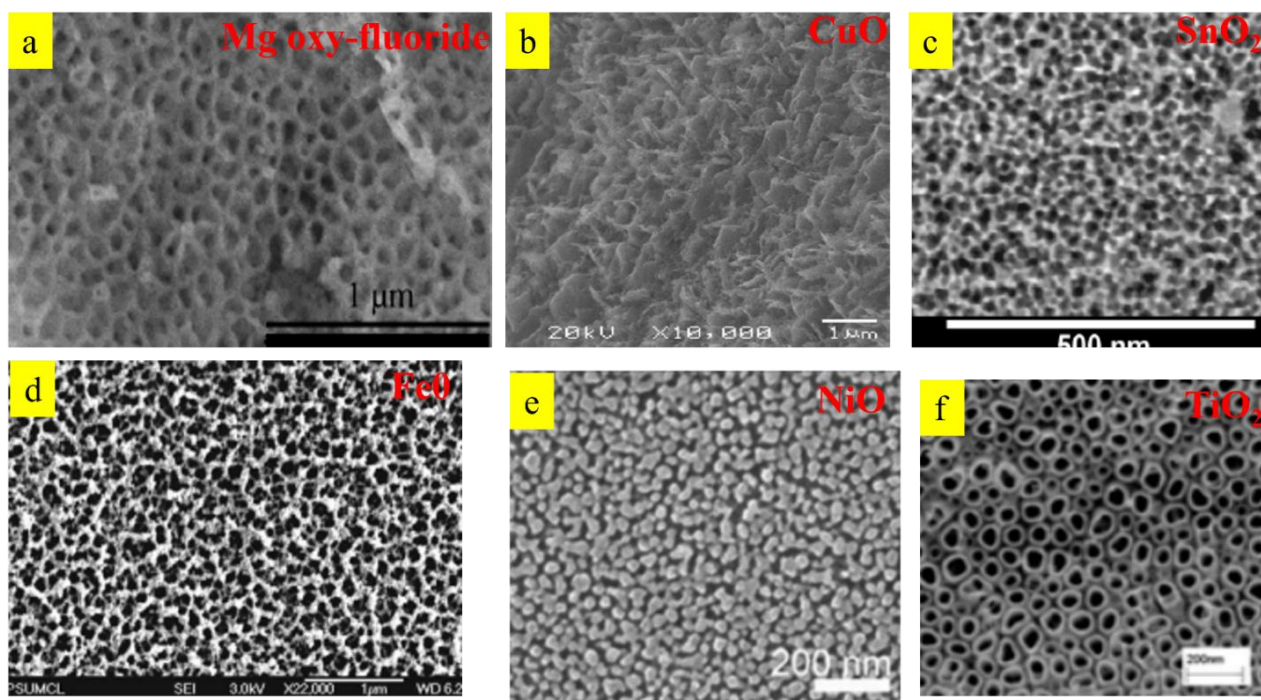


Figure 2.1 Anodization of various metals, (a) MgO, (b) CuO, (c) SnO₂, (d) FeO, (e) NiO, (f) TiO₂, reproduced from ref. [54–59].

Table 2.1: Morphology of porous structures during anodization.

Crystle structure	Method oxides	Pore morphology	Regularity	Reference
Al (FCC)	Al ₂ O ₃	Nanopores	Ordered	[63–65]
Ti, Zr, Hf (HCP)	TiO ₂ , ZrO ₂ , HfO ₂	Nanotubes	Ordered	[59,66–68]
Fe, W	Fe ₂ O ₃ , WO ₂	Nanotube/pores	Disordered	[69]

2.5 Anodization of aluminium

Among valve metals, aluminum has been the most extensively studied for anodization due to its ability to form self-organized AAO under appropriate electrochemical conditions. Early investigations established that the morphology of AAO is highly dependent on anodization voltage, electrolyte type, and processing time, enabling the creation of well-ordered nanoporous arrays. Subsequent research demonstrated that pore diameter, interpore distance,

and oxide thickness can be systematically tuned, making AAO a versatile template for nanofabrication.

2.5.1 Effect of the type of electrolyte and concentration

Electrolyte composition plays a crucial role in dictating the pore size and ordering of anodic alumina structures. Commonly, sulfuric, oxalic, and phosphoric acids are employed, each leading to characteristic pore dimensions under similar anodization conditions. For instance, anodization in sulfuric acid generally produces fine pores in the range of 10–30 nm, oxalic acid gives rise to medium-sized pores between 30–80 nm, while phosphoric acid favors the formation of much larger pores exceeding 100 nm [17,18,70]. Such variations are primarily attributed to the different dissolution kinetics of alumina in these electrolytes and their specific interaction with the applied voltage. Among all electrolyte combinations, oxalic acid, a non-toxic organic acid, produces hexagonally ordered self-aligned intermediate-sized pores. AAO has been fabricated by pulse anodization in oxalic acid concentration variations (0.3–0.9 M) at electrolyte temperature of 25 °C and showed a slight increase in pore diameter (42.8–46.5 nm), whereas after widening, the pore size decreased from 85 to 80.0 nm with increasing concentration. The reduced etching rate at higher concentrations was attributed to greater incorporation of anions in the AAO walls. Here, a higher oxalic acid concentration elevated the anodizing current, leading to a rise in local temperature, resulting in the enlargement of pore diameter, which can therefore be associated with the enhanced dissolution rate under these conditions [71].

2.5.2 Effect of electrolyte temperature

Electrolyte temperature at the electrode–electrolyte interface is a critical factor, alongside parameters such as pH, applied voltage, and electrolyte concentration. It directly influences the reaction kinetics of ion diffusion, thereby affecting oxide growth, layer dissolution, and pore propagation through the aluminum thickness. Recent studies have further shown that anodizing

can induce a temperature rise of nearly 10°C due to Joule heating at the interface, which plays a significant role in determining surface morphology, pore ordering, and the overall growth mechanism. The anodization of pure aluminum for direct current and pulsed current conditions was investigated. Pulsed current-based AAO still has fine morphology and ordering at 15°C, whereas AAO formed by DCA degraded at 15°C as a result of temperature-enhanced dissolution due to a sudden rise in anodizing current under direct current, which can be attributed to defects in the high-purity aluminum foil, such as grain boundaries or dislocations, that promote excessive Joule heating. Ultimately, an imbalance between the alumina formation and dissolution rates leads to electrical breakdown within the barrier layer [72]. It was studied the different ion transportation mechanisms for different voltage ranges (0-120V), and temperature ranges (0 to 50°C) for a 0.3 M oxalic acid electrolyte. There are three different regimes: (1) kinetic regime, also called mild anodization, till 50 V, (2) mixed regime between 50-100 V, where ion transports through migration at the solid/electrolyte interface, and diffusion of ions, (3) diffusion-controlled regime for the voltage range 100 to 150 V, also called hard anodization. It was reported that the apparent activation energy for aluminium anodization is considerably higher in the kinetic regime at low current densities (0.49 ± 0.01 eV) compared to that observed under high-voltage diffusion-controlled conditions (0.19 ± 0.02 eV). Consequently, raising the electrolyte temperature shifts the boundaries between kinetic and diffusion regimes toward lower applied voltages. It has also been observed that for thicker oxides at elevated temperatures, the growing contribution of diffusion currents causes a transition from kinetically controlled anodization to a mixed regime, which ultimately disrupts the long-range hexagonal pore ordering. Therefore, subroom temperature (0-15°C) gives more pore ordering as compared to 50°C [73]. Conventionally, well-ordered AAO templates are prepared through a two-step self-organized anodization of aluminum at very low temperatures (1–3°C). In contrast, this studies demonstrate that anodization in 0.3 M oxalic acid at 30–65 V

and moderately higher electrolyte temperatures (20–30°C) can significantly accelerate porous oxide growth, achieving rates nearly an order of magnitude greater than those at low temperatures. Despite this faster growth, the most regular hexagonal pore arrangement is still obtained near 40 V. Furthermore, extending the duration of the first anodization step enhances the degree of ordering in the hexagonal/triangular pore lattice observed after the second anodization. From an industrial perspective, such elevated-temperature anodization presents a cost-effective alternative, as it eliminates the need for cooling systems and significantly reduces fabrication time due to the accelerated oxide growth rate [74]. The current density J follows the exponential dependence on temperature, $J \propto e^{-\frac{E_a}{RT}}$, E_a represents the ionic activation energy, and T is temperature. An increase in temperature enhances ionic conductivity, which in turn results in higher current density. Under optimized anodizing conditions, the activation energy is reported as approximately 0.41 eV for 1 M H_2SO_4 at 20 V and 0.34 eV for 0.4 M oxalic acid at 40 V [75].

2.5.3 Influence of anodization voltage

Controlling the anodization voltage plays a crucial role in determining the pore geometry of AAO. An increase in anodization voltage leads to an approximately exponential rise in both pore diameter and interpore distance. Moreover, varying the anodization voltage or duration allows precise control over the oxide film thickness. The thickness of the AAO film was observed to increase approximately linearly with rising anodization voltage in the range of 20–60 V for 4 wt.% chromic acid electrolyte conditions. Extending the anodization duration leads to a higher rate of film growth. Specifically, the thickness growth rates were reported to be about 1.32 $\mu\text{m}/\text{V}^{-1}$ for 4 h anodization, 1.74 $\mu\text{m}/\text{V}$ for 6 h, and 2.23 $\mu\text{m}/\text{V}$ for 10 h. However, the proportionality between these growth rates and their corresponding anodization durations does not follow a simple linear trend, suggesting that the influence of anodization time on film thickness involves a more complex kinetic relationship rather than a direct time–thickness

dependence [76]. Furthermore, the AAO film at 100 V exhibited a rapid growth rate of approximately 1.9 $\mu\text{m}/\text{min}$, which is significantly larger than that achieved under conventional mild or hard anodization conditions and nearly 18 times greater than the rate obtained at 40 V, without any observable burning effects. The enhanced electric field at elevated voltages allows the AAO growth rate to exceed conventional limits, leading to significantly faster oxide formation. Nevertheless, the growth rates observed at 80 V and 100 V show only a minor variation, suggesting that beyond a certain threshold voltage, the increase in growth rate tends to saturate. Moreover, it was investigated that the anodization voltage rises from 40 V to 100 V, the porosity of the AAO layer decreases from approximately 10.2% to 6.7%, which is consistent with the observed expansion in interpore distance at higher voltages [77].

Furthermore, for pure aluminum anodization, the pore diameter of AAO increases consistently with rising anodization voltage, reflecting the strong dependence of oxide morphology on the applied electric field. At low voltages of 20 V, well-defined nanopores of 22–35 nm are formed, which gradually widen with increasing potential. Beyond 50 V, the enhanced field accelerates ionic migration, intensifying oxide growth and field-assisted dissolution. Simultaneously, increased Joule heating and stress accumulation at higher voltages promote localized wall thinning and partial breakdown, yielding larger pores up to 110–125 nm at 65 V. This behavior indicates that the interplay among electric field strength, ion transport, and mechanical stress governs the voltage-dependent evolution of pore size in AAO [78]. Low-purity aluminum (<99%) foils result in poor uniformity of AAO pore distribution due to the presence of surface impurities and alloying elements that disturb the local electric field during anodization. These inhomogeneities promote irregular pit formation on the Al surface, disrupting the self-ordered pore initiation process, however, it can be further improved with pulse DC optimization. Therefore, high purity (>99.99%) is important in order to obtain ordered pores [79].

2.6 Morphological variations in porous structures induced by anodization

A significant progress in aluminium anodization involves developing advanced fabrication techniques that enable the tailoring of novel pore geometries. Among these, notable innovations are branched pore networks where single pores bifurcate or merge, and nanopores with controlled diameters, accomplished by alternating anodization conditions between mild and hard regimes. To further improve the pore ordering and geometry, various pre-patterning techniques have been introduced. These include direct indentation methods such as FIB, AFM-assisted patterning, as well as interference lithography, RIE, and hybrid lithographic approaches involving polymer resists, PMMA, or AAO masks, followed by wet chemical etching. Such methods not only improve the pore ordering but also allow non-hexagonal arrangements, enabling configurations with square or triangular lattice geometries.

2.6.1 Branched nanoporous structures

Under steady-state anodization, a decrease in applied voltage is governed by the equal-area model, which maintains that the total cross-sectional area of the pore stays unchanged. If a single pore branches into n smaller ones, the diameter of each resulting pore becomes smaller based on the formula $d_2/d_1 = \frac{1}{\sqrt{n}}$ to preserve this area, where d_1 is the original pore size and d_2 is the size of each new branch. Specifically, generating n Y-shaped branches from a single pore involves systematically reducing the anodization voltage by a factor of $\frac{1}{\sqrt{n}}$ from the original voltage V_1 . Figure 2.2(a) illustrates the branched nanoporous in the barrier layer.

2.6.2 Nanopores with modulated diameters

Various approaches can be employed to modulate the pore diameter during nanopore fabrication. These include modifying the electrolyte by incorporating agents such as ethylene glycol to enhance its viscosity, applying a combination of constant voltage anodization with cyclic chemical etching, or employing hard anodization under high voltage conditions. By

periodically switching the voltage between mild and hard anodization conditions, a technique known as pulsed anodization, a modulated diameter can be achieved, as presented in Figure 2.2(b).

2.6.3 Pre-patterned structures on the alumina surface

It is the spatial arrangement of the pre-patterns, not their individual shapes, that determines the emergence of various pore geometries, such as square, triangular, hexagonal, or diamond-like patterns. FIB-induced patterns on aluminium serve as pore nucleation sites, directing both the development and layout of the pore structure, as illustrated in Figure 2.2(c).

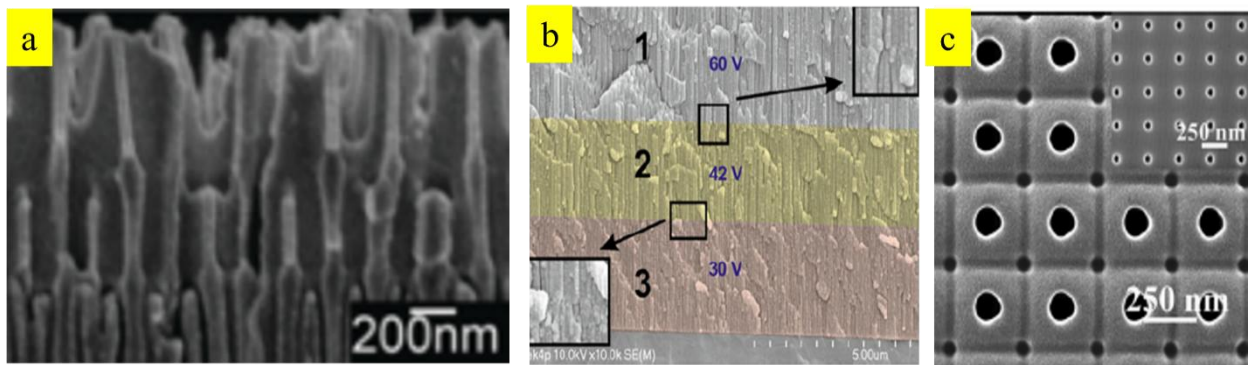


Figure 2.2 FESEM image of (a) branched pores, (b) modulated diameter, (c) pre-patterned by FIB to get a square lattice, Reproduced from ref.[15]

2.7 AAO-based 1D nanostructures

Over the past two decades, porous AAO has been extensively employed as a template, stencil mask, or scaffold for fabricating functional nanostructures and nanodevices. Various techniques, such as ECD, ALD, CVD, PVD, sol–gel deposition, surface functionalization, and RIE, have been applied using AAO templates. These methods have enabled the creation of diverse nanostructures, including CNTs, metallic, semiconducting, and polymeric nanowires or nanotubes, as well as ordered nanodot and nanohole arrays. AAO film served as a template in order to fabricate low-temperature 100°C TiO₂ nanorods in ALD. With deposition of Ag NPs leads to slowing down the electron-hole pair recombination and enhances the photodecomposition activity of methylene orange [80]. Similarly, AAO was explored for

tunable magnetism in highly ordered Fe_2O_3 nanotubes by controlled oxidation state in ALD [81]. Moreover, high-temperature synthesis process in CVD, Diamond nanopillars, and CNTs were grown successfully in vertical alignment [23]. However, electrochemically deposited nanopillars of Cu, Ni, or Au are also extensively explored with AAO for different applications of sensing and optoelectronics. Figure 2.3 gives a brief illustration of AAO-based 1D nanomaterials by utilizing it in various processes of nanofabrication [60].

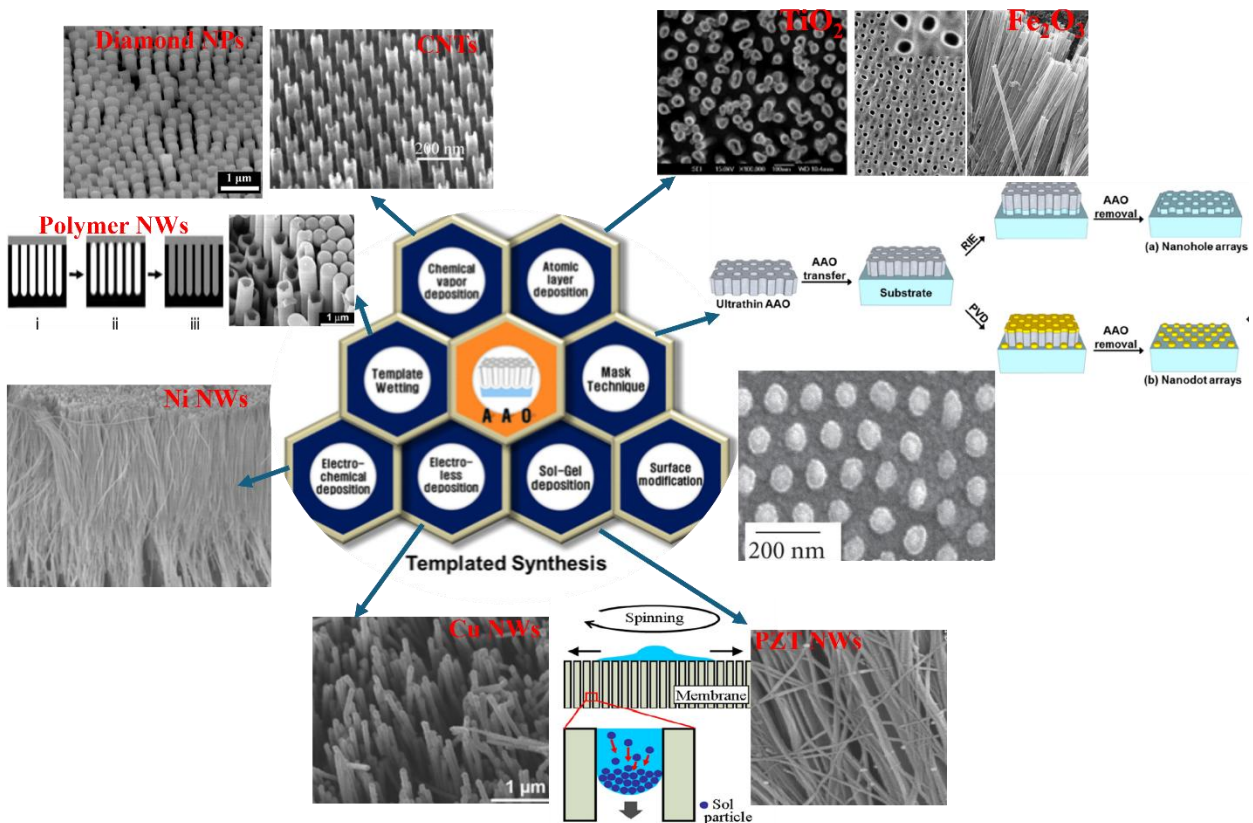


Figure 2.3 Different materials' 1D nanostructures, including TiO_2 , Fe_2O_3 , polymer, Ni, and Cu, fabricated in AAO template by using different nanofabrication processes. Reproduced from ref [60].

2.8 Carbon nanopillars growth

AAO can be employed as an effective scaffold for CNPs growth inside the pore, owing to uniform, ordered, controlled nanoscale dimensions. Commonly synthesized in CVD processes such as plasma-enhanced CVD(PECVD) or thermal CVD (TCVD) by purging of hydrocarbon precursor under high temperature conditions.

2.8.1 Various morphologies of CNPs /CNTs grown in TCVD

CNTs can be grown on various substrates using catalyst deposition; however, such deposition results in randomly entangled CNTs or a lithographically patterned array that lacks nanoscopic precision. In contrast, nanofeatured template-assisted enables the fabrication of vertical pillar-shaped morphologies that can be utilized as a nanomould. Generally, CNTs are most prominently used to enhance the mechanical and electrical properties by growing over different porous scaffolds. In Figure 2.4(a) electrical conductivity of ZnO was enhanced with CVD-grown entangled CNTs. Entangled CNTs do not exhibit directional and uniform properties; therefore, among all alignments, vertical configuration is more advantageous due to their inherent capacity to grow in self-supported alignment and stability for high aspect ratio nanofeatures [82]. Figure 2.4(b) illustrates the FESEM image in which thick deposited VA-CNTs demonstrated to absorb 70-80% of terahertz radiation in the wavelength range of 40-200 μm . In order to fabricate ordered nanoscopic CNTs alignment, more efforts have been devoted towards various lithography processes, as in Figure 2.4(d) shows the hexagonal VA-CNTs micropillars grown on 10 nm Al_2O_3 and 1 nm of Fe catalyst patterned using nanosphere lithography. However, still achieving nanoscopic alignment is not possible with conventional lithography processes. Therefore, AAO templated alignment with a controlled deposition is still a challenge without overgrown carbon residue. Figure 2.4(c) shows the recent contributions towards the fabrication of multi-layered assemblies of CNTs decorated with gold nanoparticles Au NPs on AAO, where immobilized Au decorated CNTs were coated over the AAO surface to improve the catalyst performance in the reduction of p-nitrophenol (p-NP) to p-aminophenol (p-AP). This improved catalytic performance is attributed to the synergy between inhibiting their agglomeration, while AAO provides a stable framework. Moreover, CVD-grown, open-ended, AAO/CNPs membrane was used for high-efficiency gene transfection of cells. The cap was opened with the help of ion milling, followed by NaOH

etching. This novel approach has been established for delivering genes and biomolecules into large populations of mammalian cells using arrays of vertically aligned hollow carbon nanotube membranes, as shown in Figure 2.4(e) [83].

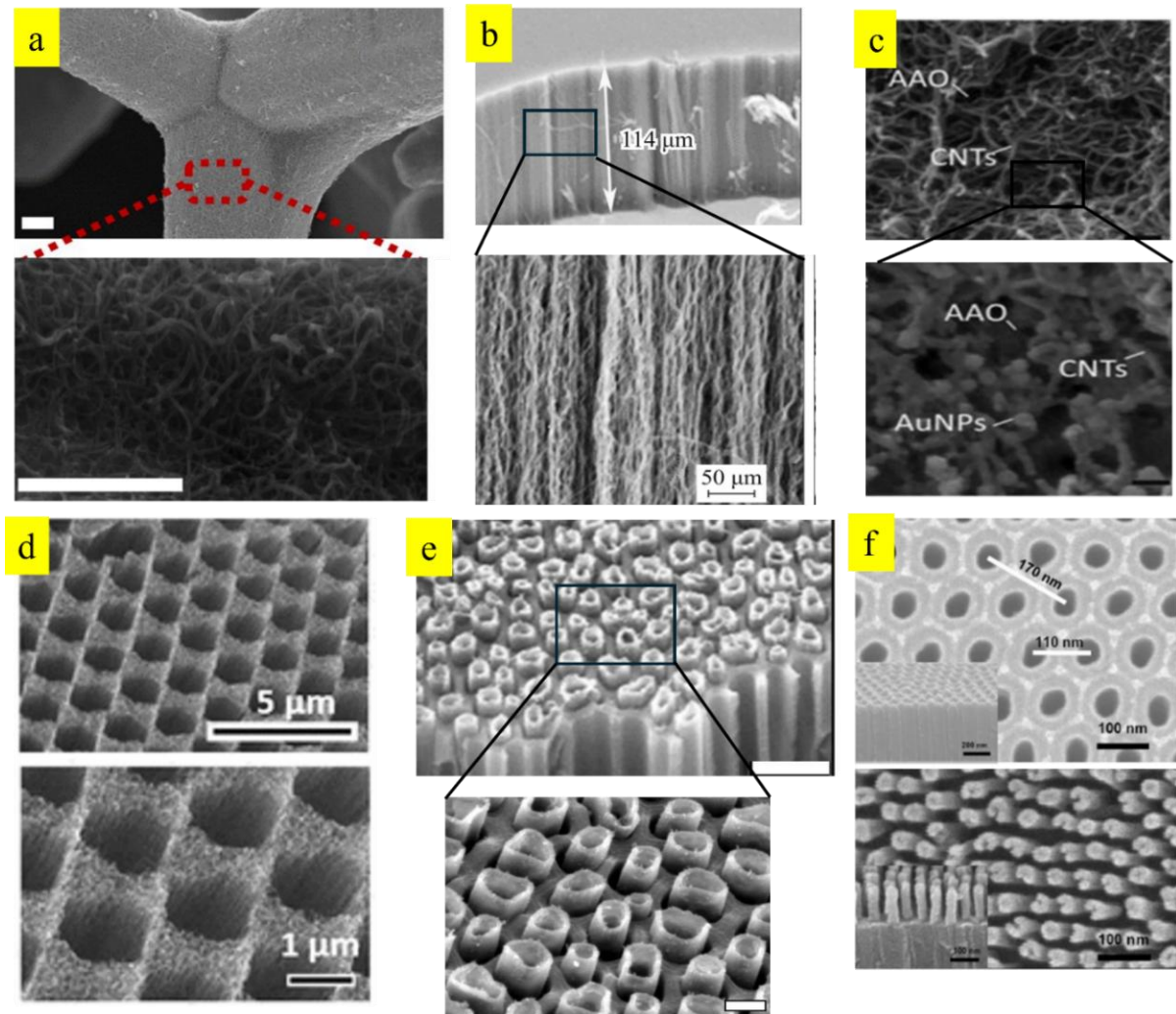


Figure 2.4 (a-d) FESEM image of a randomly grown to single CNT vertical alignment.

Reproduced from ref [83–88]

2.9 Hot embossing for functional surfaces fabrication

In order to overcome the limitations of the conventional nanofabrication method, HE fulfills the need for a simple, cost-effective, and scalable approach to replicate nanoscale and biomimetic structures over a large area with high precision. Over the years, numerous studies have been conducted on HE to engineer functional polymer surfaces with tailored micro and

nanoscale features, aiming to replicate various nature-inspired structures. A wet-etched EBL-made Si/SiO₂ master mould was used for nanogroove structures on an acrylic film by the micro-embossing process. AFM scan confirms the average groove width of 200 nm and height of 85 nm [89]. In order to create a moth-eye structure of polycarbonate by using nickel-cobalt alloy, a master mould of Ni-Co electroformed inside AAO, and transferred the pattern by heating to 190°C for 25min and 300kg pressure. The average surface reflectance decreased from 10.85% to a minimum of 3.5%, and increased contact angle from 91.46 to 138.69° [90]. Moreover, the stainless steel template surfaces were ablated with laser pulses generated by an amplified Ti: Sapphire laser with a pulse duration of 140 fs and a maximum power of about 2 W. For flat polylactic acid (PLA) water contact angle was 60 to the textured surface is 160°, with water contact angle hysteresis (CAH) below 10°.obtained. Microtextured PDMS surfaces were successfully replicated from Si master moulds using Cu metal-assisted chemical etching to improve solar cell efficiency by reducing the total reflectance of light by 8% [91]. The flow behavior and filling accuracy of SU-8 photoresist can be achieved up to 98% with optimum hot embossing parameters [92]. A silicon substrate was used to create a double-sided micro pyramid mesh array, which reduced the overall reflectance by 2% in the 300–1000 nm wavelength range [93]. Hierarchical features of a natural lotus leaf were precisely replicated onto UV-curable waterborne polyurethane acrylate (UV-WPUA) films. A PDMS negative mould, prepared via replica moulding, was used to imprint the UV-WPUA resin under 172 nm Xe₂* excimer and mercury lamp exposure. The resulting UV-WPUA surfaces exhibited superhydrophobic behaviour with strong water adhesion and a contact angle of approximately 160.8° [94]. A few studies were carried out using the AAO/carbon nanostructure (CNSs) mould, which was used to transfer metal nanodots of gold and platinum on silicon to investigate the plasmon resonance [95] and catalytic reaction [96], by utilizing NIL with precision control. However, in order to create nanoholes by individual CNT, two attempts were made in UV-

curable NIL. First, CNTs were vertically aligned by a standard catalyst lift-off process, where 1nm Fe catalyst was patterned using EBL, and transferred over the resist polymer, but still, a high throughput was a challenge [97]. In the second study, a single CNT was aligned in the AAO template, which served as a NIL mould, but explored for photoresist for electronics applications [88].

2.10 SERS performance of different sensors

Numerous studies in a variety of disciplines, including biology, optics, and electronics, reveal that plasmonic-based photonic technology will offer novel performance with enhanced device efficiency [98]. Noble metallic nanostructures have acquired a lot of attention in recent years due to their distinct optical properties and enormous promise for highly efficient nanoscale optoelectronics devices in the domains of nanophotonic, photothermic, photovoltaics, photocatalysis, and biosensing. Particularly, it has been extensively shown that metallic nanostructures with strongly enhanced local electric fields include label-free, extremely sensitive, and non-destructive biosensors. However, the majority of plasmonic layers employed metal nanoparticles with tens of nanometers in size, typically creating dimensional plasmonics. Such alignment has limited EM enhancement due to the plasmonic effect only in plasmonic probes. This confined enhancement can be improved with a three-dimensional plasmonic nanostructure [99,100]. Fleischmann, Hendra, and Mcquillan first discovered a variant of Raman spectroscopy, SERS, which can increase the scattering cross-section and hence contribute to an overall improved Raman signal [101]. The SERS measurement mainly comprises three crucial variables for signal enhancement: incident light, analyte molecule, and plasmonic nanoparticle/nanostructure (i.e, gold, silver, copper) [28,29]. SERS analysis is generally carried out by way of mixing analyte with colloidal silver nanoparticle (AgNP) or gold nanoparticle (AuNP) solution, followed by analysis utilizing Raman spectroscopy, however, the colloidal base sample has the following limitations :(1) poor sensitivity to certain

analyte (2) low spectral repeatability due to weak affinity to specific analyte (3) complex pretreatment steps limitations (e.g. extraction, purification) [30]. Therefore, many studies consider on creating a more uniform substrate using techniques such as UV-lithography, soft lithography, Electron beam lithography (EBL), nanoimprint lithography, and pulsed laser deposition (PLD). A SERS substrate was prepared by generating ordered nanoscale patterning on a nanoscale by deep UV-lithography, followed by surface coating with a silver and gold hybrid for glucose sensing.[102]. Moreover, low-cost associated pillars such as ZnO, over Si, can be fabricated by a pulsed DC magnetron as a ZnO seed layer sputtering. ZnO nanopillars were grown in a hydrothermal process subjected to a solution of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine (HMT), followed by Au decoration by sputtering or thermal evaporation process [103]. This study confirms that the controlled deposition of sputtered Au makes a capped hot-spot junction to enhance plasmonic properties, which leads to the detection of pentaerythritol tetranitrate (PETN), which is commonly used in industrial explosives. Template-assisted nanopillars, including gold and silver, were extensively studied for SERS measurement. Initially, funnel-pore AAO templates were produced by further oxidizing conical-pore AAO structures obtained through multistep anodization and etching. Subsequently, Au nanotubes and Ag nanoparticles were deposited via physical sputtering using these templates as sacrificial moulds. The fabricated Ag-NPs@Au-NT exhibited a SERS enhancement factor of 1.8×10^7 , along with a consistent response to rhodamine 6G at a concentration of 10^{-11} M [104]. Single-layer graphene (SLG) is the thinnest 2D rolled sheet in CNTs and is gaining interest in plasmonic applications. A SLG onto a three-dimensional Au@Ag core-shell nanostructure, which significantly enhances light-matter interactions. The underlying nanostructure induces ripple formation in the graphene sheet, effectively modulating its light absorption properties [105]. Moreover, graphene oxide-Au-based mixed hybrids were explored for a detection limit of 10^{-7} M with a possibility of chemical

enhancement [106]. Carbon nanotubes have recently gained interest in obtaining high throughput, to decorate 3D tunable plasmonic nanostructures due to their facile fabrication process without a high equipment cost associated. A VA-CNTS forest grown over a Si/Fe combination provides a substrate to decorate sputtered Ag NPs, which can sense the highly sensitive carcinogenic dye with a high fluorescence spectrum count [107].

2.11 Supercapacitor performance of different electrodes

Unlike batteries, which store energy as faradaic redox reactions, supercapacitors store energy either electrostatically through charge separation at the electrode-electrolyte interface (in electric double-layer capacitors, EDLCs) or rapid surface redox reactions (in pseudo capacitors). Among the various materials studied for supercapacitor electrodes, transition metal oxides have drawn particular interest owing to their rich redox chemistry, abundance, and moderate cost. Very recently, it was reported that ZnO (an n-type semiconductor with a bandgap ~ 3.3 eV)-based composite electrode materials can provide good electrochemical reversibility, high specific capacitance, high power density, high energy density, and good cycling stability, which makes them promising materials for advanced supercapacitors [108]. The nitrogen-doped, activated CNT-based symmetric supercapacitors demonstrated stable performance within a broad potential range (0–3.5 V) and achieved a specific capacitance of 98 F/g at 1 A/g. A study reports a hybrid energy storage device incorporating graphene as the first electrode, owing to its large surface area, and zinc oxide electrodes the second electrode. ZnO nanocrystals were used due to its defective structure, combining the high-power density of a supercapacitor with the enhanced energy density of a battery, resulting in a high specific capacitance value ($C = 448 \text{ F g}^{-1}$). Influence of synthesized ZnO nanorods by ultrasonic technique on multi-walled CNTs (5:0 wt.%, 10:1 wt.%, 10:3 wt.%, and 10:5 wt.%) and attained a specific capacitance value of 115.7 F/g for 3 wt.% CNTs, which exhibit the lower resistance to ion transportation due to the synergistic effect of both components [109]. The hierarchical

graphene-ZnO nanocomposite (G-ZnO) composites, achieving superior electrochemical performance of 122 F/g as compared to graphene oxide (2.13 F/g) and rGO (102.5 F/g) at 5 mV/s scan rate, 6 M KOH electrolyte solution, and long-term stability along with 98.25% of its initial capacitance after 1500 cycles [110]. Furthermore, the integration of vertically aligned CNPs grown inside AAO templates enables precise control over nanotube alignment, length, and diameter, which is beneficial for ensuring uniform current distribution and ion transport [111]. However, a limited number of studies were done on AAO-grown carbon nanotubes for supercapacitor performance to make a transparent, flexible supercapacitor CNT-carbon nanocups (CNC) electrodes, showing the specific capacitance of 1 mF/cm² at a scan rate of 1 mV/s in 1 M LiPF₆ electrolyte [112]. In another study, the AAO membrane was developed and bonded with Si during CNTs grown in CVD. This Si/AAO@CNTs electrode was examined for the electrochemical performance of a 0.44 mF/cm² specific capacitance value for novel system-on-a-chip applications, including sensing and energy storage. Moreover, AAO/CNTs were used as a current collector to investigate the electrochemical performance of asymmetric V-MnO₂ and MoO₃/Polypyrrole (PPy) nanocomposite. This nanocomposite exhibited better capacitance than that of AAO/CNTs and observed the enhanced capacitance as compared to AAO/CNTs [37].

2.12 Research gaps

Based on an extensive review of the existing literature, it is evident that significant progress has been made in fabricating nanostructures using advanced lithographic techniques such as nanoimprint lithography, electron beam lithography, Reactive ion etching, and UV lithography. However, comparatively attention given to surface texturing of thermoplastic polymers through hot embossing is less. Hot embossing is a simple, cost-effective, and scalable method that holds great potential for large-area nanostructure replication. In particular, the potential of AAO/CNP hybrid structures as durable and reusable moulds for hot embossing has not been thoroughly

explored, despite their excellent mechanical strength and nanoscale ordering. Moreover, templated carbon nanostructured surfaces remain largely underutilized for their exceptional multifunctional properties, such as plasmonic metal decoration for ultrasensitive molecular detection and metal oxide nanomaterial growth for advanced energy storage applications.

Based on the thorough literature survey, the following objectives are formulated.

2.13 Objectives

1. To fabricate an AAO mould using mask/maskless-anodization of aluminium.
2. To fabricate vertically aligned nanopillars CNPs mould using the AAO mould.
3. To fabricate an array of micro/nanostructures on a large area by using an indigenously fabricated hot embossing setup.
4. To characterize structured polymer and mould surfaces for their morphological and mechanical properties.
5. To evaluate the nanostructured surfaces for their wetting, anti-reflectivity, SERS applications, and energy storage applications.

Chapter 3

Materials and Methodology

3.1 Introduction

This chapter outlines the experimental procedures employed for the fabrication and application of nanostructured surfaces derived from anodic aluminium oxide and carbon nanopillar composites. The methodology followed a multi-step process, beginning with the synthesis of well-ordered AAO templates through a two-step anodization process. These templates serve as a foundation for direct CNP growth, forming vertically aligned CNPs within the AAO matrix using chemical vapor deposition. The resulting AAO and AAO/CNP frameworks can be subsequently employed as master moulds for transferring nanoscale features onto polymer surfaces, specifically polystyrene, using thermal embossing. This nanoimprinting replication process has facilitated the transfer of nanoscale surface topographies with high fidelity. The embossed surfaces can be subsequently analyzed to evaluate their multifunctional behaviour, such as superhydrophilicity and anti-reflectivity. The AAO/CNPs structures can be thoroughly investigated for their SERS activity and supercapacitor performance. Gold thin film can be sputter-deposited onto selected regions to induce plasmonic activity for enhanced optical performance. ZnO nanostructures can be deposited onto the AAO/CNP framework to enhance its electrochemical characteristics for energy storage applications. A schematic diagram illustrating the complete research study is shown in Figure 3.1. Each fabrication step can be carefully optimized to maintain nanoscale features and support multifunctional performance in the final structure. The selected characterization tool offers both morphological and functional insights, validating the effectiveness of the overall fabrication workflow. This comprehensive approach integrates nanostructure fabrication, pattern transfer, and application-driven testing to realize a versatile platform for advanced surface engineering and device development. The methodology adopted in this work is explained in the following section.

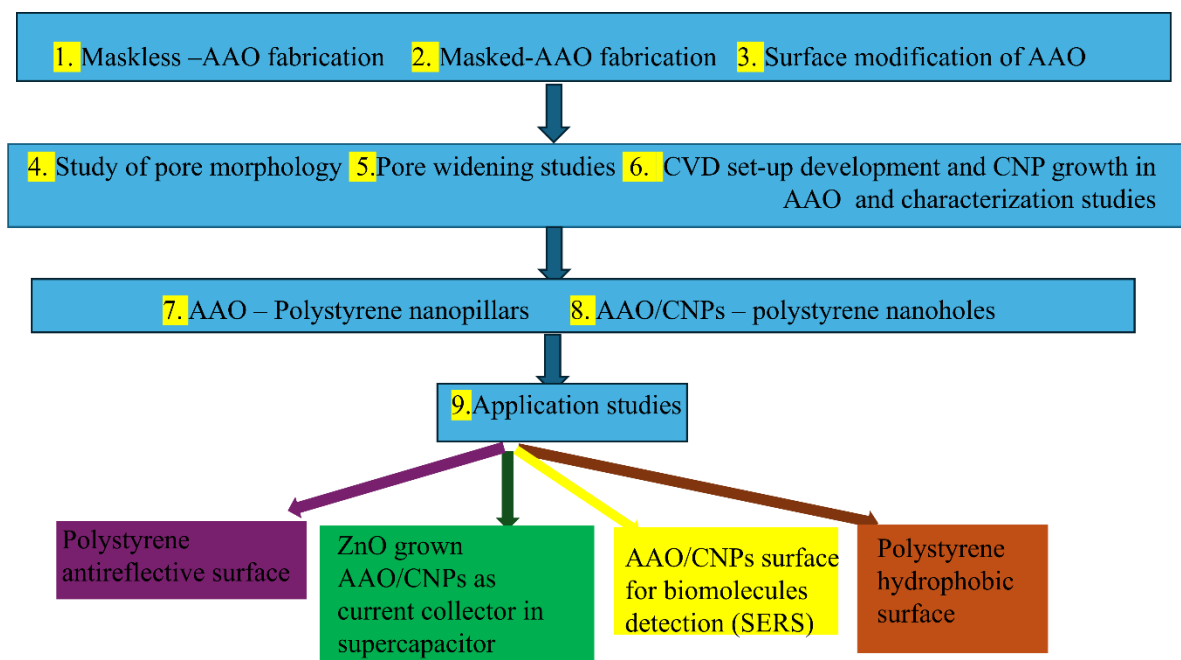


Figure 3.1 Schematic representation of the experimental workflow for AAO/CNT-based nanostructure fabrication and functional applications.

3.2 Fabrication of AAO template

The formation of uniform nanoporous structures was achieved by preparing AAO templates using two distinct anodization approaches. The first method involved a maskless two-step anodization process, which relies on self-organization to form uniform pore arrays across large areas. The second method incorporated photolithography to define masked regions, enabling selective anodization only in exposed areas. Each method employed conventional electrolytic parameters along with chemical etching to precisely tailor pore size and spatial distribution.

3.2.1 Maskless anodization of aluminium

A high-purity aluminium foil (99.99%, Thermo Fisher), measuring 3 cm × 1 cm and a thickness of 0.25 mm, was accurately cut for the anodization process. The sample underwent sequential ultrasonic cleaning in acetone, isopropyl alcohol (IPA), and deionized (DI) water for 5 min each to remove surface contaminants. The native oxide layer was eliminated by immersing the aluminium foil in 1 M NaOH solution for 2 min, followed by a 10 min ultrasonic rinse in

deionized water. This oxide removal procedure was repeated twice to ensure a completely clean surface. The electropolishing was carried out using a custom-built electrochemical system with a 4:1 ethanol to perchloric acid solution. A voltage of 10 V and a temperature of 5°C were maintained for 2 min during the process to accomplish a polished, reflective finish. Following electropolishing, the aluminium foil was ultrasonically cleaned for 10 min to eliminate any remaining acidic residues. A customized anodization setup was constructed using an annular glass-beaker configuration fabricated using a glass-blowing process, where a 3 L outer beaker served as a cooling bath surrounding the 500 mL inner anodization chamber. A mercury thermometer of range (0-100°C) and resolution of 1° was positioned between the electrodes to accurately monitor electrolyte temperature. The setup was placed on a magnetic stirrer to maintain consistent thermal distribution and prevent localized heating at the anode. The aluminium sample served as the anode, while a larger aluminium strip (5 cm × 2 cm × 0.5 mm) acted as the cathode. Once the electrolyte temperature stabilized at 10°C, a 45 V potential was applied in a 0.3 M oxalic acid solution. The first anodization was performed for 3 h across all experiments under identical conditions. After anodization, the sample was rinsed with DI water, and the porous alumina layer was dissolved using a mixture of 1.8 wt.% chromic acid and 6 wt.% phosphoric acid at 60°C for 1 h. The completion of oxide elimination was verified by checking electrical continuity with a multimeter. The sample was again cleaned ultrasonically to remove residual etchants. The second anodization was carried out for 2 h, during which the electrolyte temperature was systematically varied to identify optimal conditions for ordered pore growth. Subsequently, the anodization time was also adjusted based on the results. In order to widen the pores, the AAO was treated in 5 wt.% phosphoric acid at room temperature for various durations. Final samples, exhibiting uniform nanoporous alumina textures, were rinsed with DI water to eliminate any remaining acid residues.

3.2.2 Process parameters for AAO mould fabrication

During AAO mould fabrication, the second anodization step was optimized by systematically varying electrolyte temperature across different experimental sets, while maintaining all other parameters constant. In the first set of four experiments, the anodization time was fixed at 2 h, and the electrolyte temperature was changed as detailed in Table 3.1. In the second series, anodization duration was altered to study its influence on AAO pore formation, while maintaining a constant electrolyte temperature of 10°C. The experimental details for this set of experiments are provided in Table 3.2. After anodization, pore widening was performed by exposing the AAO pores in a 5 wt.% phosphoric acid solution for five different time intervals. This process is essential because the initially formed porous alumina exhibited non-uniform and slightly asymmetric pore opening structures. The phosphoric acid etching not only enlarged the pores but also helped in removing residual aluminium oxide. In order to evaluate the thickness of the anodic alumina layer, both the underlying aluminium and the barrier oxide layer were eliminated separately. This was accomplished in two steps: first, the aluminium substrate was dissolved using a 1 M CuCl_2 solution, and then the remaining barrier layer was removed by immersing the sample in 5 wt.% phosphoric acid for 1 h. Figure 3.2 is the schematic representation of the experimental setup used for AAO fabrication, whereas Figure 3.3 is an illustration depicting the stepwise process involved in AAO template fabrication.

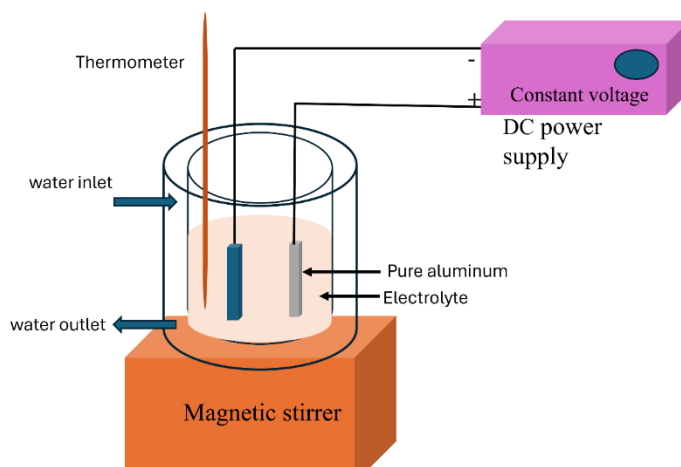


Figure 3.2 Schematic illustration of AAO fabrication setup.

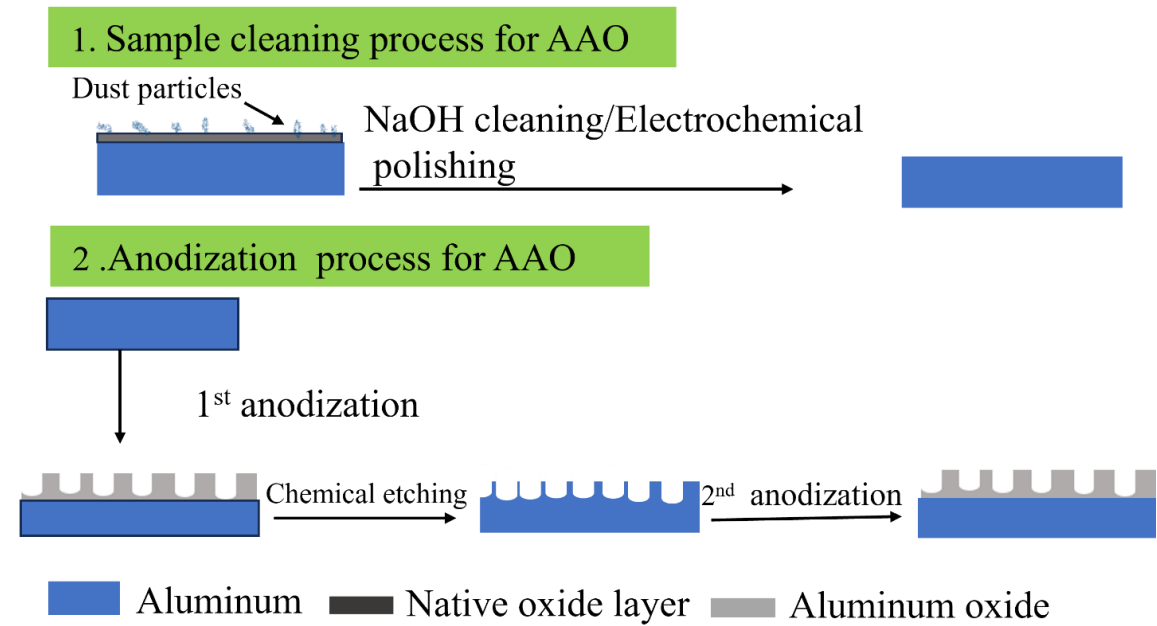


Figure 3.3 Schematic of the AAO fabrication process.

Table 3.1 Anodization parameters for different electrolyte temperatures.

Exp No.	Anodization time (h) 1 st	Anodization time (h) 2 nd	Voltage (V)	Temperature(°C)	Electrolyte
1	3	2	45	5,10,15,20	0.3 M oxalic acid
2	3	2			
3	3	2			
4	3	2			

Table 3.2 Anodization parameters for different anodization durations.

Exp No.	Anodization time (h) 1 st	Anodization time (h) 2 nd	Voltage (V)	Temperature(°C)	Electrolyte
1	3	2	45	10°C	0.3 M oxalic acid
2	3	3			
3	3	4			
4	3	5			

3.3 Masked Anodization of aluminium

A lithography-based masking process was utilized to enable controlled anodization in specific regions of the aluminium surface. This top-down strategy facilitated the formation of nanoporous structures only in designated areas, allowing precise alignment with pre-patterned microscale features. High-purity aluminium foil (99.99%, Thermo Fisher) with dimensions of 3 cm × 1 cm and a thickness of 0.25 mm was precisely cut to use as the substrate for the two-

step anodization process. The aluminium strip was first subjected to ultrasonic cleaning in acetone, isopropyl alcohol, and deionized (DI) water to remove any surface contaminants. Subsequently, the aluminium foil was immersed in a 1 M NaOH solution for 2 min to eliminate the naturally formed native oxide layer. The sample was then cleaned again in DI water using a bath ultrasonicator for 10 min, and this oxide-removal cycle was repeated twice to ensure a completely cleaned surface. Following the cleaning process, a 1.3 μm -thick layer of S1813 photoresist was deposited on the aluminium surface using spin coating. The spin-coating process involved two steps: an initial spreading step at 500 rpm for 10 sec, followed by a high-speed coating step at 3000 rpm for 30 sec. The coated sample was then soft baked on a hot plate at 110°C for 1 min to evaporate the solvent and improve resist adhesion. A prefabricated photomask with circular microfeatures, created through laser direct writing, was used for UV exposure. The photoresist-coated surface was exposed to ultraviolet light with an energy of 450 mJ/cm^2 , allowing selective cross-linking of the photoresist. The exposed pattern was developed using MF-319 developer for 30 sec, then rinsed in DI water for 1 min to reveal the circular openings in the resist layer. This patterned aluminium, now containing microscale openings in the resist, was subjected to anodization using the same parameters optimized during the maskless AAO process. A schematic illustrating the masked anodization procedure is shown in Figure 3.4(a, b).

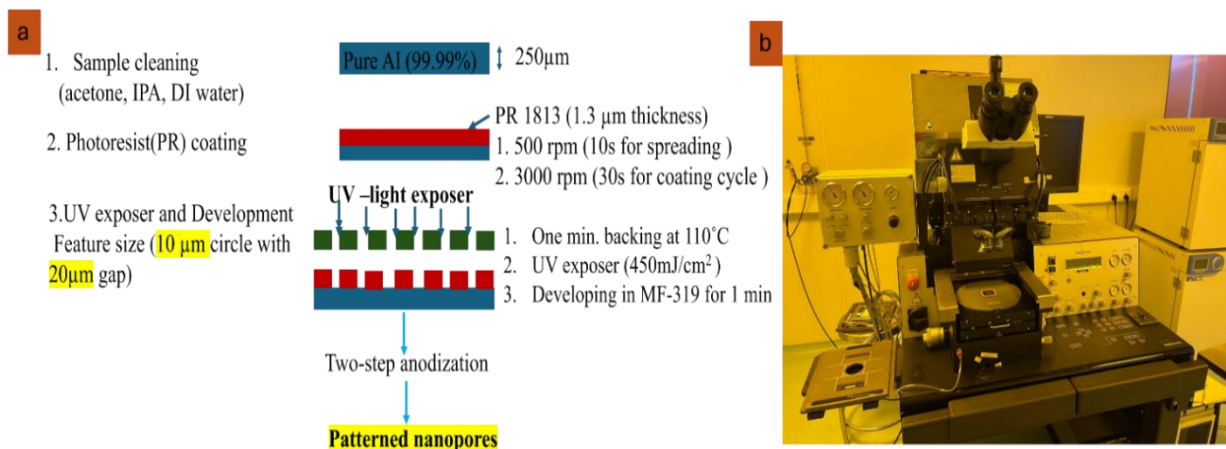


Figure 3.4 (a) Schematic of standard UV-lithography process for masked-anodization of aluminium, (b) UV-lithography setup photograph.

3.4 Growth of CNPs inside AAO

CNPs are widely studied for their unique electrical, thermal, and mechanical properties, and their controlled synthesis often requires a structured template. Anodic aluminium oxide, with its uniform and vertically aligned pores, provides an ideal platform for guiding CNP growth. Its chemical resistance and thermal stability make it suitable for high-temperature CVD processes. Prior to nickel electrodeposition at the base of AAO nanopores, a barrier layer thinning (BLT) process was carried out to minimize the insulation of oxide thickness at the pore bottoms. As-grown barrier layer can act as a major restriction to ionic mobility, adversely affecting the uniformity of metal deposition. In order to address this, a stepwise voltage reduction technique was employed at the end of the anodization process, gradually decreasing the applied voltage at a rate of 2 V/min. This regulated voltage reduction facilitated the development of thinner oxide zones and finer secondary pores, thereby enhancing accessibility for later deposition steps. Nickel was deposited galvanostatically at the pore bases of the AAO structure, functioning as the catalytic layer essential for CNP synthesis. The deposition was carried out by applying a constant voltage of 2 V for a duration of 1 min, ensuring uniform distribution of the nickel catalyst within the confined nanopores, as supported by previously reported methods. The electrolyte used for nickel electrodeposition comprised an aqueous solution containing 300 g/L of nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), 45 g/L of nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), and 45 g/L of boric acid (H_3BO_3). To stabilize the pH of the electrolyte and improve deposition efficiency, two drops of sulfuric acid were added to the solution. This adjustment maintained the pH within the optimal range of 3 to 4, which is critical for achieving consistent and adherent nickel deposition inside the pores. The pH of the electrolyte was precisely measured using a calibrated standard pH meter to ensure reproducibility and chemical stability during the process. Stabilizing the pH is essential for promoting consistent nickel deposition and reducing unwanted hydrogen gas formation that

might compromise nanoscale uniformity. This controlled electrodeposition of nickel forms the catalytic base for aligned carbon nanopillars. The CNPs were grown by utilizing an in-house developed thermal chemical vapor deposition system. In order to optimize the process parameters of CVD, some preliminary experiments were performed for the Fe-deposited silicon wafer. After the electrodeposition of the nickel catalyst layer, carbon nanostructure in the form of pillars were synthesized. The AAO template, fabricated on an aluminium substrate, was carefully placed approximately 100 mm downstream within a horizontal quartz tube, where optimal deposition conditions had been previously established for this setup. The CNP growth process was carried out at 625°C, with the system heated uniformly at a ramp rate of 10°C/min. To ensure a controlled and safe environment, a gas mixture comprising 70% nitrogen and 30% hydrogen was introduced at a total flow rate of 200 sccm. This mixture served both as a carrier and a reducing agent to activate the nickel catalyst and remove oxygen residues from the reaction zone. This mixed gas reduces the risks associated with using pure hydrogen, thereby enhancing safety. Once the target temperature of 625°C was achieved, acetylene (C_2H_2) gas was introduced at two different flow rates of 20 sccm and 100 sccm for controlled durations of 30 min and 4 h, respectively, as outlined in Table 3.3. These variations helped examine the influence of growth time and precursor concentration on the morphology of the resulting carbon nanopillars. Upon completion of the growth phase, the furnace was switched off, and the sample was gently shifted further downstream within the tube to facilitate gradual cooling under an inert gas environment. Figure 3.5 illustrates the schematic of the flow curve of gas and temperature during the AAO/CNPs growth. To remove the excess amorphous carbon that had deposited on the AAO surface during growth, post-treatment methods such as mechanical polishing and ion milling were employed independently. Finally, the embedded carbon nanostructures were exposed by selectively dissolving the alumina template using a 0.5 M NaOH solution for varying durations of 2, 5, 8, and 10 min.

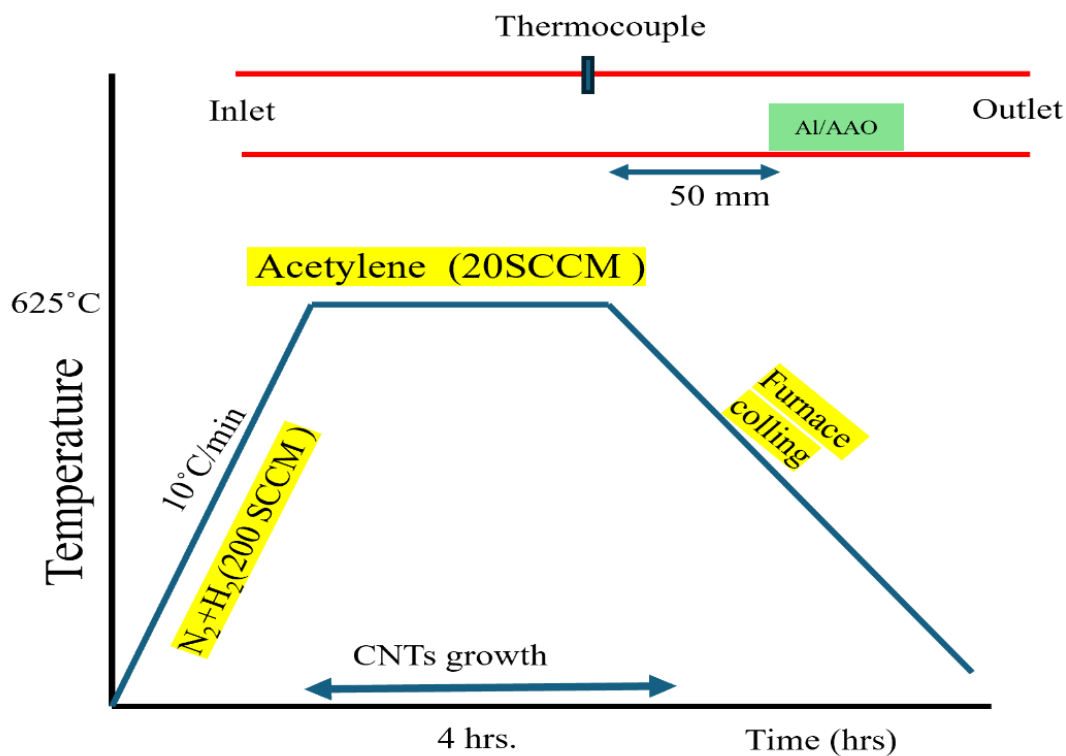


Figure 3.5 Flow graph for the complete recipe of CNPs growth inside AAO.

Table 3.3 Process parameter for gas purging.

Flow rate (SCCM)	Duration of growth (h)	Type of precursor gas
20	0.5, 4	Acetylene
100	0.5	

The excessive amorphous carbon layer formed on the AAO surface during CNP growth was eliminated through two separate post-treatment methods: mechanical polishing and ion milling. Each technique was applied independently to ensure effective removal of surface carbon, enabling clear exposure of the underlying nanostructures without damaging the AAO template. Ion milling was performed at 600 V and 30 mA for durations of 10 and 60 min to remove the surface carbon layer without damaging the underlying structures. This was followed by chemical etching in 0.5 M NaOH solution for 5 min to reveal the carbon nanostructures embedded within the AAO template. In the mechanical polishing approach, the sample was polished using a rotating wheel set at 120 RPM for a duration of 2 min. An alumina suspended

slurry was used in conjunction with a polishing pad to gently abrade the surface and remove the overgrown carbon layer. All process parameters are tabulated in Table 3.4 for both processes.

Table 3.4 Operating parameters for carbon removal.

Type of process	Process parameters
Mechanical polishing	Polishing wheel speed (120 rpm) Duration of polishing (2 min) Alumina slurry over a polishing pad 0.5M NaOH etching
Ion milling	Voltage 600V Current 30mA Duration 10 min and 60 min 0.5M NaOH etching

3.5 Fabrication of a replica polymer by using a hot embossing setup

3.5.1 Preparation of polystyrene sheet

A polystyrene sheet was prepared by dissolving 2 g of styrene with 10 mL of benzene, functioning as the solvent medium for the solution. Magnetic stirring was performed for 15 min to facilitate the thorough dissolution and homogeneous dispersion of the polystyrene in the benzene. Following the mixing, the solution was gently heated on a hot plate maintained at 50°C for 5 min. This mild heating step improved the solubility and contributed to achieving a homogeneous, free of entrapped air bubbles polymer-solvent mixture. Once a uniform solution was obtained, it was carefully poured into a clean 2-inch diameter petri dish. The pouring process was carried out slowly to ensure an even spread and to maintain consistent thickness. The solution was allowed to settle naturally within the dish, forming a uniform film with an approximate thickness of 500µm. The petri dish containing the polystyrene solution was then placed undisturbed in a clean and dust-free environment at room temperature. The solidification process was allowed to proceed over a period of 24 h to ensure slow and uniform

solvent evaporation, resulting in the formation of a flat, air bubble-free polystyrene sheet. The resulting film was suitable for subsequent hot embossing or nanostructuring applications.

3.5.2 Surface modification of AAO template

Prior to hot embossing, the AAO mould surface was chemically treated to enhance demoulding efficiency and reduce the risk of polymer sticking during the imprinting process. This was achieved through a vapor-phase silanization technique using trichloro (1H,1H,2H,2H-perfluorooctyl) silane, a fluorinated silane compound known for its excellent anti-sticking and low surface energy characteristics. In this procedure, approximately 10 drops of the silane agent were placed inside a sealed glass desiccator along with the AAO sample. The system was then subjected to a controlled thermal treatment at 120°C for 15 min. The elevated temperature promoted the vaporization of the silane and its subsequent condensation onto the AAO surface, where it reacted with surface hydroxyl groups to form a self-assembled monolayer. This monolayer significantly reduced the surface energy of the AAO, making it highly hydrophobic and enhancing the demoulding efficiency during the embossing process. Figure 3.6(a) shows the schematic representation of vapor phase surface modification.

3.5.3 Hot embossing setup

Hot embossing was employed to transfer the nanopatterns from the AAO or AAO/CNPs template onto the polystyrene substrate under controlled operating parameters. The plate-to-plate configuration ensures faithful replication of surface nanofeatures while maintaining large-area uniformity. For the hot embossing experiment, a 500 μm -thick polystyrene sheet with a 2-inch diameter was first cut into square sections of 1 cm $\times$ 1 cm. These PS samples were ultrasonically cleaned in deionized water for several min to remove surface contaminants and dust particles, ensuring a clean interface during pattern transfer. The prepared polymer samples were thermally preheated close to their glass transition temperature to soften them, ensuring effective deformation when pressure was applied. The preheating was performed using a

copper–chromium (Cu–Cr) heater capable of fine temperature control with a resolution of 0.1°C . The embossing temperature was monitored using a thermocouple, which was positioned close to the sample to ensure accurate measurement and control during the process. The hot embossing setup was integrated with a stepper motor and controller to precisely drive the X–Y stage. In order to prevent adhesion between the polymer and the heater during the process, an alumina ceramic plate was placed between the two, serving as an inert thermal interface. Figure 3.6(b, c) illustrates the schematic and photographs of the hot embossing system, where all the accessories are labelled properly.

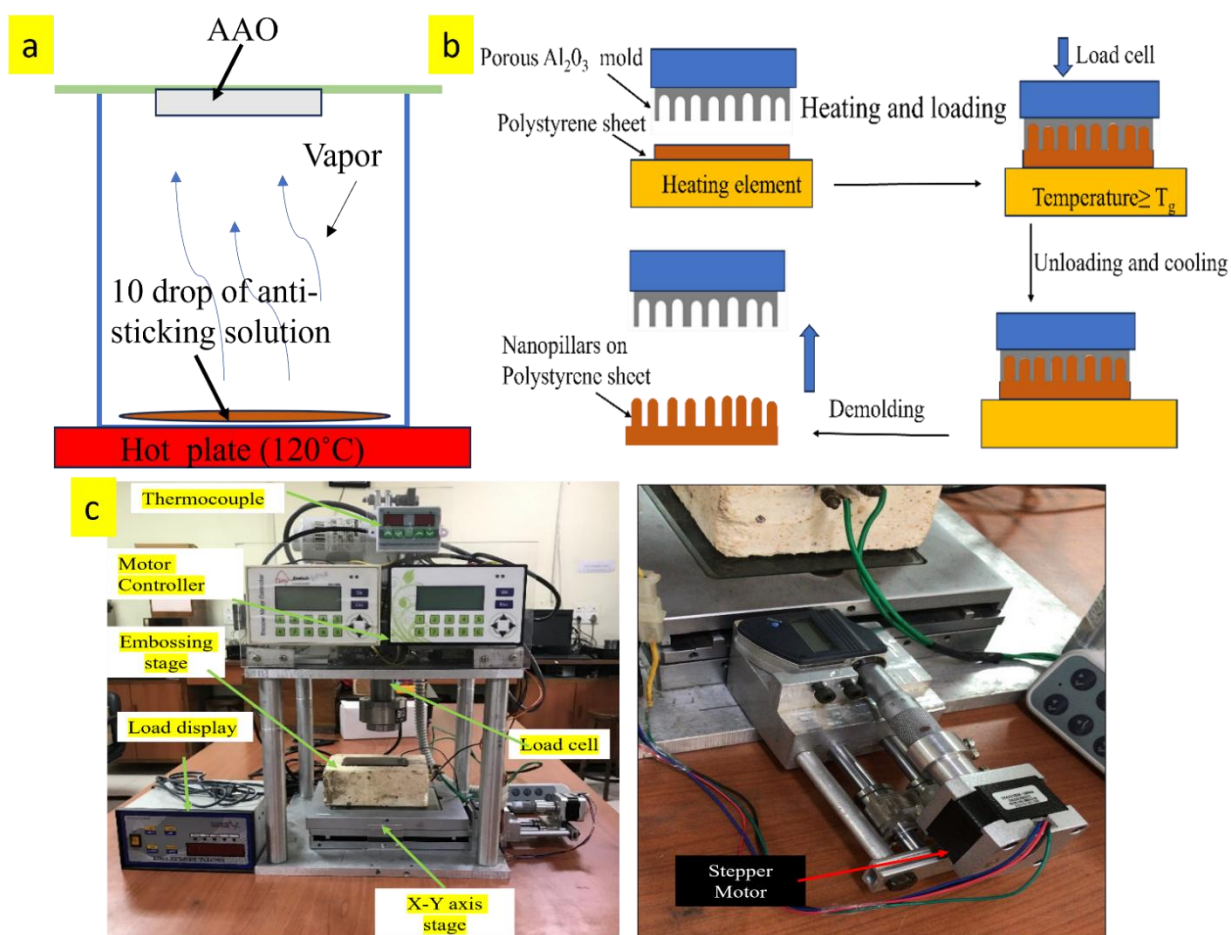


Figure 3.6 (a) Schematic of vapor phase surface modification, (b) Schematic illustration of hot embossing setup, (c) photograph of embossing setup.

Each PS sample was preheated at 100°C for 5 min to achieve uniform softening across the surface. Following this, the surface-functionalized anodic aluminium oxide mould was carefully aligned and pressed onto the softened polymer using a vertical load cell with a

maximum capacity of 1000 N. The embossing pressure was applied while maintaining a stable temperature, ensuring that the nanostructures on the AAO mould were accurately transferred into the PS sheet. After embossing, the system was allowed to cool naturally to room temperature under ambient conditions. Once the polymer became solidified, the mould was gently separated, and the replicated film was detached without causing structural damage. To remove any residual material or moisture, the patterned PS film was rinsed and subsequently dried at 40°C. This process yielded high-fidelity negative replicas of the AAO nanopatterns. In order to fabricate nanopillar patterns, a bare AAO template was used as the mould, while for generating nanohole structures, a composite AAO/CNPs mould was employed, allowing high-aspect-ratio replication into the polymer.

3.5.4 Selection and Design of Process Parameters in hot embossing for nanopillar replication

The key parameters that govern the quality and reliability of hot embossed nanostructures include the heating temperature (to induce polymer softening), applied embossing pressure, and the holding time for which pressure is held during mould contact. These variables significantly influence the flow behaviour of the polymer and its ability to replicate the underlying nanostructure. Table 3.5 outlines the different levels and corresponding values of each selected process parameter. Initially, the polystyrene samples were heated to their glass transition temperature of approximately 100°C and held for 5 min to ensure sufficient softening and viscous behaviour suitable for moulding. After this, a 1 cm² square-shaped AAO mould was applied to the softened PS surface. The embossing experiments were performed across three distinct temperature values, three pressure levels, and three holding times to evaluate the effect of each factor on the replication process. To systematically analyze the influence of these parameters, a statistically guided experimental approach was adopted; the Taguchi method utilizing an L9 orthogonal array was employed to design the experiments efficiently. This

method allowed for the evaluation of multiple parameters with a reduced number of experiments while preserving analytical accuracy. The full matrix of nine experiments, including all combinations of embossing pressure, temperature, and holding time, is presented in Table 3.6. The embossing pressures were selected based on the theoretical requirement for effective mould filling. This includes both the resistance to wetting and the viscous resistance of the polymer flow into the nanopores. The minimum required pressure was estimated using the Hagen–Poiseuille equation for pressure-driven flow in cylindrical pores

$$P_{\text{emb}} = \frac{4\eta L^2}{tr^2} + \frac{2\gamma \cos\theta}{r} \quad (3.1)$$

where η represents the PS viscosity at T_g , L is the filling depth, t is embossing time, r is pore radius, γ is the surface tension (30–35 mN/m), and θ is the contact angle ($\sim 100^\circ$). Based on this relation, a minimum pressure threshold of ~ 1 MPa was determined for successful imprinting.

Table 3.5 Operating parameters of hot embossing.

Parameters	Symbol	Level 1	Level 2	Level 3
Embossing pressure (MPa)	A	1	5	10
Temperature ($^\circ\text{C}$)	B	100	110	120
Holding time (min)	C	1	2	3

Table 3.6 Experimental design for hot embossing.

Experiment No.	Symbol	Embossing pressure (MPa)	Temperature ($^\circ\text{C}$)	Holding time (min)
1	A1B1C1	1	100	1
2	A1B2C2	1	110	2
3	A1B3C3	1	120	3
4	A2B1C2	5	100	2
5	A2B2C3	5	110	3
6	A2B3C1	5	120	1
7	A3B1C3	10	100	3
8	A3B2C1	10	110	1
9	A3B3C2	10	120	2

Table 3.7 Experimental design for hot embossing.

Parameters	Symbol	Level 1	Level 2	Level 3
Embossing pressure (MPa)	A	1	3	5
Temperature (°C)	B	90	100	110

3.5.5 Process Parameters in hot embossing for nanoholes replication

Before the embossing process, the surface of the nanopillar-structured AAO/CNPs mould was treated with a self-assembled monolayer (SAM) using fluorinated silane, specifically trichloro (1H,1H,2H,2H-perfluorooctyl) silane. This surface modification significantly reduced the surface energy of the mould, minimizing adhesion between the polymer and the nanostructures. Initially, the polystyrene sheet was heated to its glass transition temperature of 100°C over a period of 5 min to induce a viscous state suitable for embossing. A 1 cm² square-shaped AAO/CNPs mould was then pressed onto the softened polymer. For embossing with the AAO/CNPs mould, the holding time of 2 min was kept constant while varying three levels of embossing pressure and three temperature values, as listed in Table 3.7. A total of nine experiments were designed using the Taguchi L9 orthogonal array. The softened polystyrene was embossed using the AAO/CNPs mould under the selected conditions. After maintaining the fixed holding time, the system was allowed to cool naturally. Viscous demoulding was then performed to gently separate the polymer from the mould without damaging the replicated features.

3.6 AAO/CNPs as SERS substrate

The SERS activity of the fabricated AAO/CNP@Au substrates was investigated to evaluate their plasmonic performance and Raman signal enhancement capability. Well-ordered hexagonally arranged nanoporous AAO templates were fabricated using a two-step anodization process. High-purity (99.999%) aluminium foil was first electropolished and anodized in 0.3 M

oxalic acid at 45 V and 10°C. After removing the initial disordered alumina layer using a mixture of phosphoric and chromic acids, a second anodization under identical conditions was carried out for 2 h to form uniform pores. The membrane was then chemically etched in 5 wt.% phosphoric acid at 30°C to widen the pores to the desired diameter. Barrier layer thinning was performed by stepwise voltage reduction (2 V/min) before depositing a nickel catalyst at the pore bottoms using an aqueous solution containing $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and boric acid. The carbon nanopillars were synthesized using CVD at 620 °C using a 70:30 $\text{N}_2\text{:H}_2$ gas mixture, followed by acetylene introduction of a 20 sccm flow rate for 4 h. Post-growth, samples were mechanically polished and chemically etched in 0.5 M NaOH to expose the nanostructures. To enable plasmonic activity suitable for SERS applications, gold nanoparticles were deposited onto the surface of the AAO/CNP nanostructures using a DC sputter coater technique. The sputtering was carried out at a current of 20 mA under an argon atmosphere with a working pressure of 5×10^{-2} mbar. Deposition times of 1, 3, 5, and 7 min were selected to tune the surface coverage and interparticle spacing. This variation directly influenced the formation of nanogaps between adjacent particles and features, which are critical for generating localized surface plasmon resonance (LSPR). These nanogaps act as hot spots, significantly enhancing the electromagnetic field intensity at the surface, thereby boosting the Raman signal of adsorbed molecules and improving overall SERS sensitivity and reliability. Rhodamine 6G, a well-known Raman-active dye, was selected as the probe molecule to evaluate the SERS performance of the AAO/CNP@Au substrates. The R6G dye poses health risks because it can cause skin, eye, and respiratory irritation and may be absorbed or inhaled in ways that harm the central nervous system and reproductive health. A concentration of 10^{-4} to 10^{-10} M aqueous solution of R6G was prepared and drop-cast onto the gold decorated samples to allow adsorption onto the plasmonic nanostructures. The interaction between R6G molecules and

gold nanogaps facilitated strong electromagnetic coupling, allowing sensitive detection of characteristic Raman signals. The schematic of AAO/CNPs@Au is ascribed in Figure 3.7.

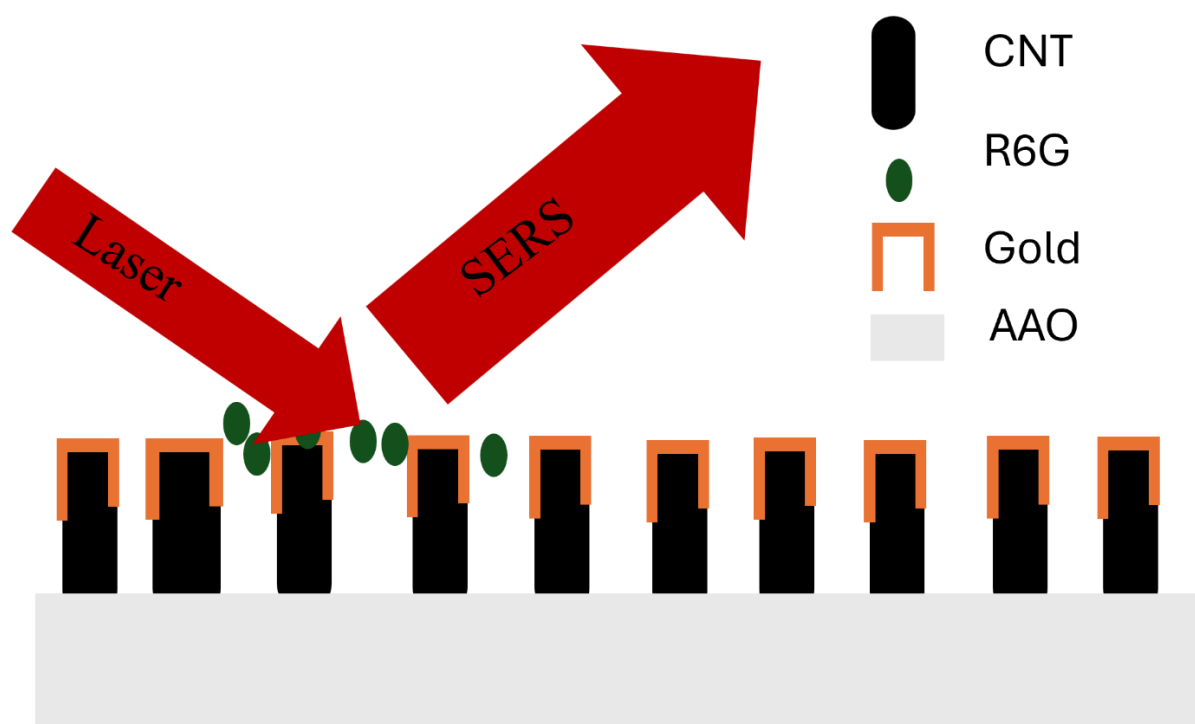


Figure 3.7 Schematic of AAO/CNP@Au as SERS.

3.7 AAO/CNPs as a current collector in a supercapacitor

The vertically aligned carbon nanostructures embedded in anodic aluminium oxide templates were used as a robust and conductive framework for supercapacitor current collectors. The AAO/CNP hybrid structure provides high surface area, vertical alignment, and good mechanical stability, making it an ideal platform for subsequent deposition of active materials like metal oxides. The AAO/CNP hybrid structure was fabricated by growing carbon nanopillars inside the pores of a two-step anodized AAO template. After pore widening and barrier layer thinning, a nickel catalyst was electrodeposited at the bottom of the pores under galvanostatic conditions (2 V for 1 min). CNP growth was carried out in a custom-built thermal CVD system at 620 °C. A mixed carrier gas of N₂ and H₂ (70:30) was used at a flow rate of 200 sccm to create a reducing environment, followed by the introduction of acetylene gas of

20 sccm for 4 h to grow vertically aligned carbon nanopillars. After the growth process, the samples underwent surface treatment involving mechanical polishing followed by chemical etching in 0.5 M NaOH solution. To enhance the electrochemical performance of the AAO/CNP structure for supercapacitor applications, three-dimensional ZnO nanosheets (3D-ZnO NSs) were synthesized over the exposed carbon nanopillar surface using a hydrothermal growth method. The precursor solution was prepared by dissolving 12.5 mM zinc nitrate hexahydrate and 25 mM hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, 99% purity) in deionized (DI) water. This solution was stirred continuously for one h to ensure homogeneity. The AAO/CNP hybrid substrate was then vertically immersed in a 20 mL teflon-lined stainless-steel autoclave containing the prepared solution. The hydrothermal reaction was conducted at 120 °C for two separate durations of 30 min and 1 h to assess the growth morphology and density of ZnO nanosheets. In post-synthesis, the samples were thoroughly rinsed with DI water to remove loosely bound residues and dried under ambient conditions. The resulting ZnO-decorated CNPs formed a vertically aligned, hierarchical nanostructure expected to improve specific surface area and charge storage capability. To assemble the supercapacitor device, a gel-type electrolyte was prepared using polyvinyl alcohol (PVA) and potassium hydroxide (KOH). Specifically, 5 g of KOH pellets were dissolved in 150 mL of DI water, followed by the addition of 10 g of PVA. The mixture was continuously stirred and heated at 90 °C for 4 h until a viscous, honey-coloured gel was formed. This gel electrolyte was cast into a petri dish and left to solidify overnight at room temperature. For testing, aluminium served as the current collector, and electrical contacts were made on the Al side of the structure. Two configurations were evaluated: sample 1 (AAO/CNP) and sample 2 (AAO/CNP@ZnO), both integrated with the gel electrolyte. Their comparative schematics are illustrated in Figure 3.8 (a, b, c).

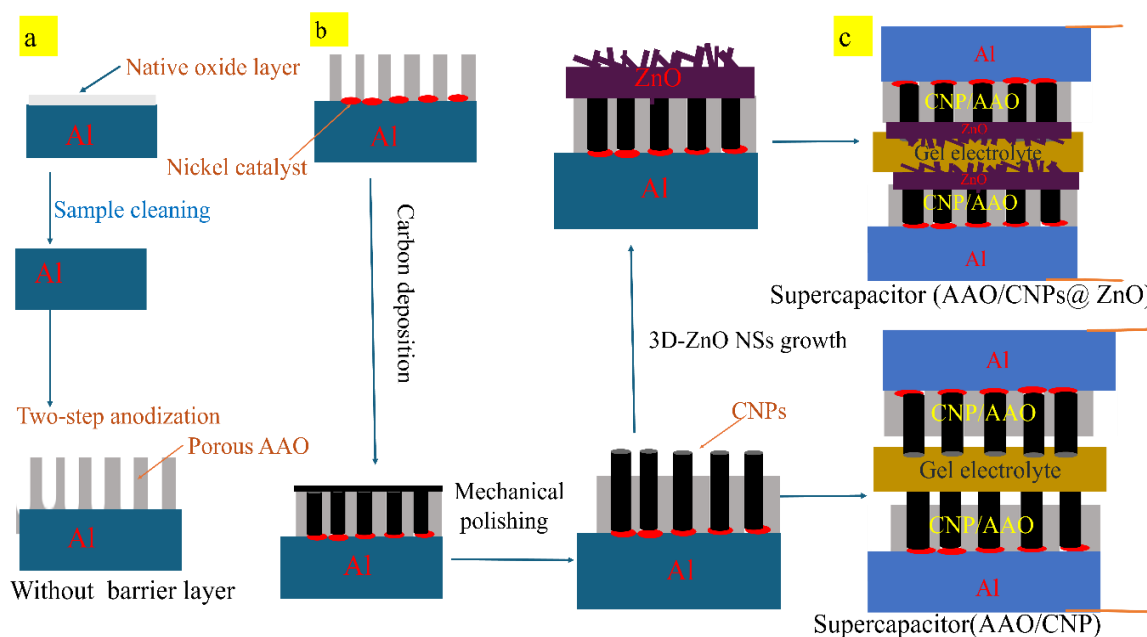


Figure 3.8 Schematic of (a) AAO fabrication, (b) catalyst deposition and CNPs growth, (c) AAO/CNPs and AAO /CNPs@ZnO supercapacitor.

3.8 Characterization

To investigate the structural, morphological, optical, and electrochemical properties of the fabricated nanostructures, a wide range of characterization techniques was employed.

3.8.1 Morphological Characterization

The surface morphology and nanostructural arrangement of the AAO templates, carbon nanopillars, and ZnO nanosheets were examined using field emission scanning electron microscopy (FESEM). FESEM imaging was performed using a TESCAN and ZEISS EVO 18 system operated at an accelerating voltage of 5–10 kV. High-resolution SEM images provided detailed insights into pore arrangement, nanopillar height, and the uniformity of ZnO growth over the AAO/CNPs framework. For detailed internal structure analysis, high-resolution transmission electron microscopy (HRTEM) was carried out using a JEOL JEM-2100 microscope operated at 200 kV. The samples were carefully transferred onto carbon-coated copper grids for TEM analysis. This technique helped confirm the wall thickness and internal hollow structure of CNPs. Additionally, Atomic Force Microscopy (AFM) was employed in tapping and contact mode (Bruker system) to evaluate the surface topography and roughness

of the embossed polymer replicas and AAO/CNPs surfaces. The scan area was typically $1 \times 1 \mu\text{m}^2$, and the root mean square (RMS) roughness values were extracted to quantify surface uniformity.

3.8.2 Thermal Characterization

Differential scanning calorimetry (DSC) was used to calculate the glass transition temperature (T_g) of the polystyrene sheet. An aluminium reference material was used with an initial weight of 6 mg to observe changes in specific heat at a heating rate of $5^\circ\text{C}/\text{min}$.

3.8.3 Optical Characterization

Optical characterization of the prepared SERS-active substrates was performed using UV–Vis spectrophotometry and Raman spectroscopy. The optical absorption properties were studied with a UV–Vis–NIR spectrophotometer in the wavelength range of 300–800 nm. This helped to observe the characteristic plasmonic resonance of gold nanoparticles and the vibrational modes of ZnO. The shift in absorption spectra confirmed the successful deposition and interaction between Au, CNPs, and ZnO nanostructures.

Raman spectroscopy was carried out using a Raman microscope (Renishaw) with a 532 nm laser excitation source at a power of 1 mW. The Raman measurements were conducted in the range of $300\text{--}1800 \text{ cm}^{-1}$ with an acquisition time of 10 s. Characteristic D and G bands of CNPs, along with ZnO and R6G peaks, were identified to confirm nanostructure quality and evaluate SERS performance.

3.9 FDTD Simulation

Finite-Difference Time-Domain (FDTD) simulations were performed to investigate two key optical phenomena: electric field enhancement for SERS in plasmonic nanostructures, and the antireflective behaviour of nanohole arrays. These simulations provide a quantitative understanding of electromagnetic field distribution, resonance behaviour, and optical response of nanostructured surfaces. The simulations were carried out using commercially available

Lumerical FDTD software, which solves Maxwell's curl equations in the time domain over a spatially discretized mesh.

3.9.1 Simulation Domain Setup

The simulation domain was configured based on the physical dimensions of the nanostructures, particularly, anti-reflectivity of polystyrene nanoholes and gold decorated plasmonic AAO/CNPs substrate. A 3D model of the unit cell of the nanohole array of diameter 80 nm, whereas periodic spacing and etched depth are considered 100nm each. Similarly, the diameter of gold is 90 nm, and the spacing is 10 nm, and simulations were conducted with and without gold coating to observe the comparative field enhancement. Gold described using experimental permittivity data fitted with Drude–Lorentz model parameters. Alumina is treated as a lossless dielectric with a constant refractive index ($n = 1.65$), whereas air has a refractive index of 1.0, transparent and non-absorbing.

3.9.2 Boundary Conditions

To minimize reflections and to accurately simulate an open system, Perfectly Matched Layers (PML) were applied along the z-axis, in the propagation direction of the incident wave. These absorbing boundary conditions prevent non-physical reflections from simulation boundaries, thus mimicking an infinite domain. In the lateral directions (x and y), periodic boundary conditions were employed depending on the structure and field polarization. These settings assume that the physical structure extends infinitely in the lateral directions and maintains periodicity.

3.9.3 Source Configuration: Plane Wave Excitation

A broadband Total-Field Scattered-Field (TFSF) source or a simple plane wave source was used to excite the structure from the top (air side). The incident wave was linearly polarized, with its electric field vector aligned to the x-axis, while propagation occurred along the negative z-direction (toward the substrate). The source covered a wavelength range of 400–900 nm,

allowing a comprehensive sweep through visible and near-infrared regimes for nanoholes. In SERS simulations, particular attention was given to $\lambda = 514$ nm wavelength, which corresponds to common Raman excitation sources.

3.9.4 Monitors and output parameters

Different types of monitors were set up in the simulation region to extract optical characteristics

- **Field Monitor:** 2D and 3D electric field monitors were placed at cross-sections to capture local electric field intensities ($|E|^2$). In plasmonic simulations, regions between adjacent gold particles or sharp corners showed maximum enhancement, which is captured by field monitoring.
- **Frequency-domain Power Monitor:** This is used to calculate reflection, transmission, and absorption spectra. These values were utilized to evaluate anti-reflectivity based on reflectance dips at target wavelengths.

3.10 Electrochemical characterization

Electrochemical performance of the supercapacitor electrodes was studied using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and galvanostatic charge–discharge (GCD) tests. All measurements were performed in a three-electrode configuration using an Admiral instrument workstation.

EIS was conducted over a frequency range of 0.01 Hz to 100 kHz with an AC amplitude of 10 mV to evaluate internal resistance, charge transfer kinetics, and diffusion behaviour. CV measurements were carried out at scan rates of 10, 20, 50, 100, and 500 mV/s in the voltage window of 0–1 V to determine the capacitive behaviour and reversibility of the electrodes. GCD measurements were performed at various current densities (0.075, 0.1, 0.2, and 0.5 mA/cm²) to calculate specific capacitance, energy density, and cycling stability. The nearly triangular shape of the GCD curves indicated ideal capacitive behaviour and good electrochemical reversibility.

Chapter 4

CVD furnace development and parameter optimization

4.1 Fabrication of a single-zone CVD furnace

A customized thermal chemical vapor deposition system was developed in-house to enable the controlled growth of carbon nanopillars within anodic aluminium oxide templates. The system was specifically designed to provide precise control over growth parameters such as gas flow rate, temperature, pressure, and reaction time, all of which play a crucial role in determining the structure, alignment, and quality of the synthesized carbon nanomaterials. This tailored setup offers a cost-effective and flexible alternative to commercially available systems and allows modifications based on specific experimental requirements. The core of the system consists of a horizontal tubular furnace equipped with a high-temperature resistant quartz tube, which serves as the reaction chamber. The furnace is coupled with a programmable PID (Proportional–Integral–Derivative) temperature controller that enables accurate ramping and stable thermal conditions across a wide temperature range up to 1100°C with a temperature control accuracy of $\pm 1^\circ\text{C}$. The heating element used in the CVD furnace is made of kanthal wire, known for its high-temperature resistance and stability. It is embedded within the furnace walls and insulated with high-grade ceramic fibre double-wall air insulation, ensuring uniform heat distribution, energy efficiency, and minimal thermal loss during prolonged operation. The quartz tube used in the CVD system has a total length of 700 mm, with an outer diameter (OD) of 75 mm. The effective hot zone length, where the samples are positioned for deposition, spans 300 mm at the center, providing a uniform thermal environment essential for consistent CNP growth within the AAO templates. The Chromel–Alumel thermocouples, commonly known as type K sensors, are employed in the CVD system for accurate temperature monitoring. These sensors offer a wide temperature range, fast response, and high stability, making them ideal for maintaining precise thermal control. The PID controller allows programmable ramp rates

ranging from 0.1°C/min to 10°C/min. The gas delivery is managed through high-purity gas cylinders connected to individual mass flow controllers (MFCs) or calibrated rotameters, allowing precise regulation of flow rates for each gas. The standard gases used include nitrogen (N₂) as an inert carrier, hydrogen (H₂) as a reducing agent, and a hydrocarbon gas such as acetylene (C₂H₂) as the carbon source. To enhance safety during the CVD process, a mixed gas composition of nitrogen (N₂) and hydrogen (H₂) was used instead of pure hydrogen. This mixture reduces the flammability risk while maintaining a reducing environment necessary for catalyst activation and controlled CNP growth within the AAO template. The modular architecture of the in-house CVD system allows easy disassembly for maintenance and cleaning, and its transparent setup facilitates real-time monitoring of the process. This setup has proven to be a reliable tool for conducting template-assisted nanofabrication experiments in a controlled and customizable environment. All design specifications are listed in Table 4.1. A schematic of the in-house developed thermal CVD is shown in Figure 4.1, and actual photographs of the setup are depicted in Figure 4.2.

Table 4.1 Design parameters for thermal CVD furnace.

Maximum working temperature	1100°C
Temperature control accuracy	±1°C
Heating element	Kanthal-AI wire with double-walled air insulation
Tube material	Quartz (Hot zone= 300mm, Total length = 700mm, outer diameter= 70mm)
Temperature controller	Programmable PID controller (0.1°C/min to 10°C/min)
Sensors	Chromel–Alumel (K-type thermocouple)

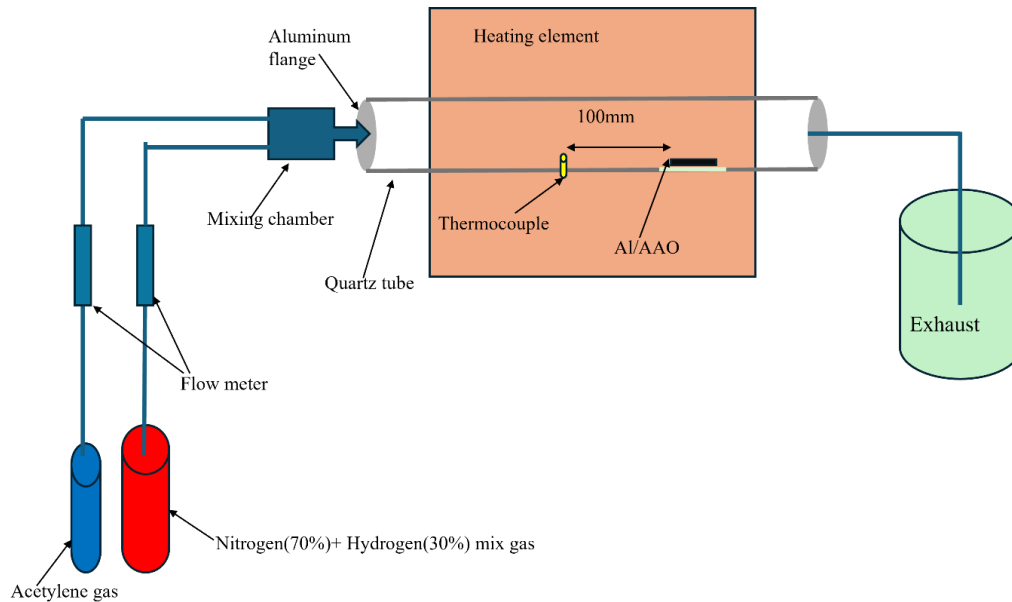


Figure 4.1 Schematic of the in-house developed thermal CVD.

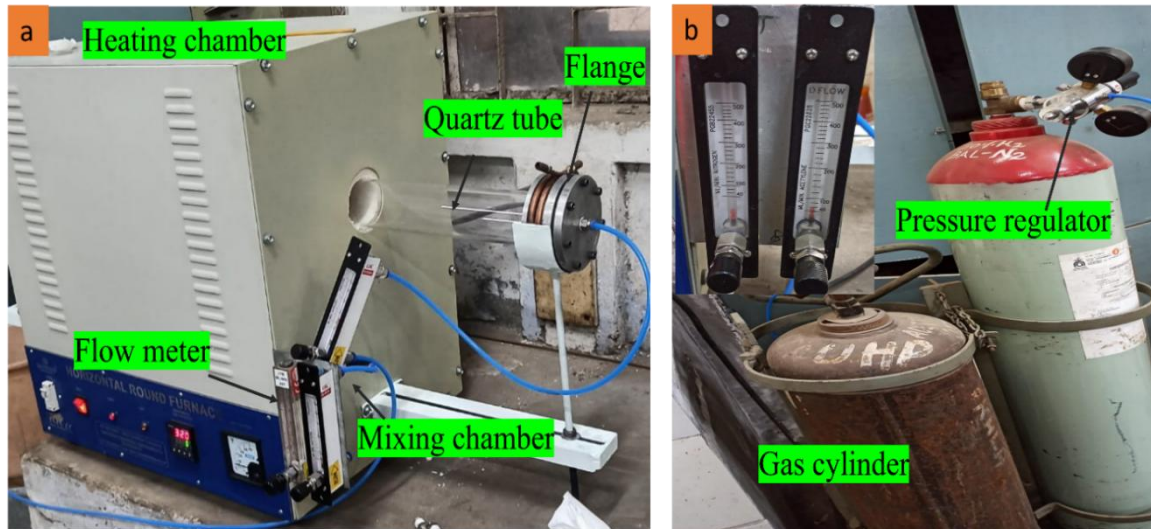


Figure 4.2 (a, b) Photographs of the thermal CVD setup and gas assembly.

4.2 CNTs growth on Si substrate

Before initiating the fabrication of carbon nanopillars inside AAO templates, preliminary experiments were carried out on flat silicon substrates to optimize the CVD growth parameters. The silicon wafer served as a convenient platform to test the furnace conditions, such as temperature profile, sample positioning, gas composition, and catalyst thickness. In addition to that, the catalyst patterning was done using UV lithography to enable site-specific and well-controlled CNT growth. A 2-inch, n-type silicon wafer (100) was cleaned with acetone, IPA,

and DI water sequentially for 5 min each in an ultrasonic bath and gently dried in hot air. A 300 nm SiO₂ native oxide layer was grown by thermal oxidation furnace in the tubular furnace by purging oxygen at a temperature of 1000°C. After SiO₂ growth, the wafer was cleaned in piranha solution for 5 min. Moreover, a 10 nm thin Al₂O₃ film was deposited in atomic layer deposition over the SiO₂ film to prevent diffusion/migration of the catalyst. A 1.3 μm thick layer of photoresist S1813 was spin-coated on a cleaned Al₂O₃ surface, initially in a spreading cycle at 500 rpm for 10 sec, then at 3000 rpm for 30 sec in the coating cycle. After that, the wafer was baked for 1 min at 110°C on a hot plate. The different types of prefabricated features with different dimensions on the mask plate were used to expose the wafer with UV-light of 450mJ/cm². A circular array of different dimensions was developed in the MF-318 developer for 30 sec and rinsed in DI water for 1 min. The iron catalyst was deposited by a sputtering process. The thickness was first optimized with trial deposition at the rate of 2.5nm/min, at a power of 25W while maintaining a base pressure of 1×10⁻⁷ torr, working pressure of 1.1×10⁻³ torr, and argon gas flow rate of 12 sccm. The iron catalyst thin film was deposited for three different times of 30 sec (1.25 nm), 2 min (5 nm), and 4 min (10 nm). The resist lift-off process was used to pattern the catalyst. The sample was ultrasonicated twice in fresh acetone for 5 min, which dissolved the photoresist and resulted in the catalyst pattern on exposed areas of the lithography process [52]. After that, the wafer piece was transferred to a beaker with IPA and soaked for 5 min. The catalyst was deposited on a 2-inch silicon wafer manually scribed with a diamond cutter and cleaved into a piece of dimension 5mm×5mm. A bare piece of silicon wafer with dimensions 20 mm×50 mm was used as a boat to support and load the patterned catalyst sample into the horizontal tubular furnace. This boat is only for smooth sample loading/unloading and does not support the growth process. The catalyst-coated sample was placed on a boat and loaded 200 mm downstream of the furnace thermocouple with a clean stainless-steel rod. The quartz tube, connected with an aluminium flange at both sides to seal

the tube without any disturbance in the position of the boat or patterned sample. A mixed carrier gas, nitrogen (70%) and hydrogen (30%), was flushed initially at 500 sccm at room temperature for 10 min. The temperature ramped up to 850°C in 2 h while keeping the mixed gas flow rate constant of 300 sccm. After reaching the desired temperature, the sample was held for 30 min with the same flow rate. This holding step causes the thin film to chemically reduce from iron oxide to iron and dewet into spherical nanoparticles. After 30 min of holding, a gas as precursor was purged at a flow rate of 100 sccm for 5 min for CNTs growth. The height of CNTs can be controlled with growth time. The sample was cooled down by manually sliding the quartz tube downstream near the furnace insulation. The furnace was cooled down to room temperature with a 200 sccm flow rate prior to sample retrieval. The schematic in Figure 4.3 describes briefly the UV-lithographic process and the complete CNT growth process.

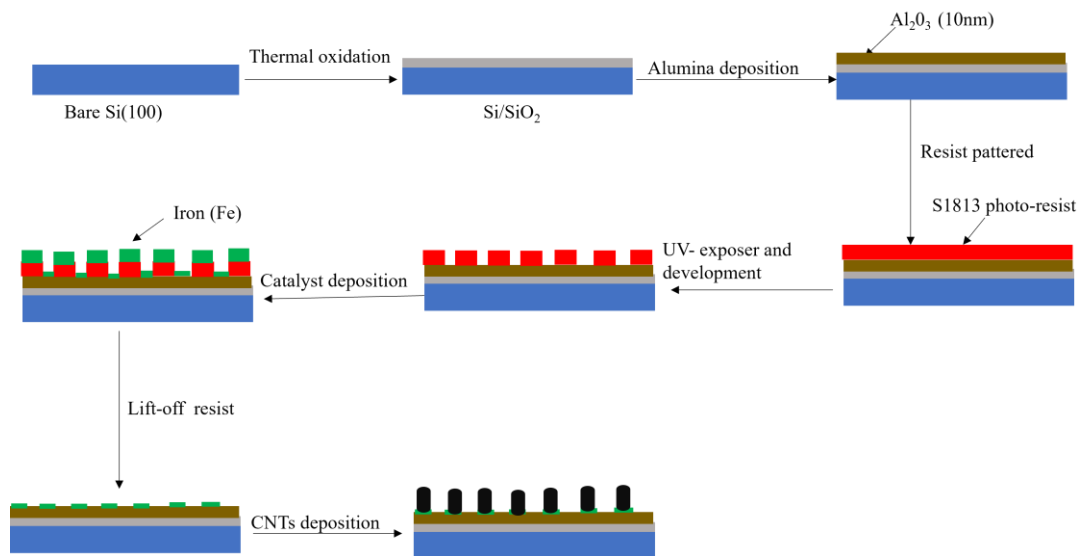


Figure 4.3 Process of patterned CNTs deposition in CVD.

4.3 Influence of substrate position in the quartz tube

In order to study the effect of sample positioning inside the quartz tube, the catalyst-coated silicon substrates (2 min Fe deposition) were positioned at three different locations inside the quartz tube: the center, the forward stream side (FSS, 100 mm away from the center towards the gas inlet), and the downstream side (DSS, near the gas outlet) Separate experiments were conducted for each case, ensuring the tube was properly cleaned and baked prior to every run.

The carrier gas (N_2/H_2) was maintained at 500 sccm, while acetylene was supplied at 100 sccm for CNT growth. The furnace was heated at a rate of $10^\circ C/min$, held at $850^\circ C$ for 30 min, and deposition was carried out for 10 min under these conditions. Among the three positions, the DSS location exhibited the most prominent vertically aligned CNT growth, characterized by thin-walled tubular structures, as shown in the FESEM image of Figure 4.4. Figure 4.4(a) shows the cross-section of thick-walled VA-CNTs for FSS, whereas quality and crystallinity have improved for the center position and DSS. However, for the same growth time, it was observed longer for FSS. This improved growth quality at the downstream position can be attributed to the longer residence time of the precursor gases along the flow path, allowing more effective decomposition and catalyst–carbon interaction [113].

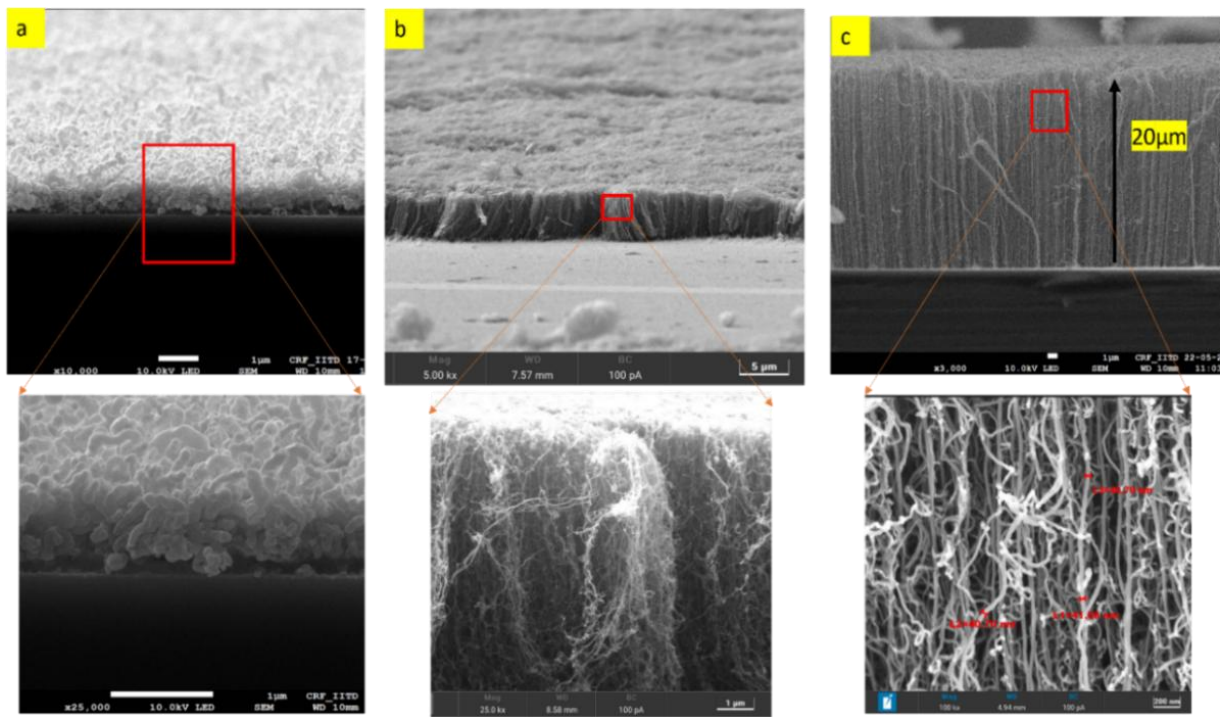


Figure 4.4 FESEM image of VA-CNTs, (a) BSS, (b) center sample, (c) DSS.

4.4 Iron catalyst thickness influence on CNTs growth

In order to investigate the catalyst thickness effect, three different Fe thicknesses (1.25 nm, 5 nm, and 10 nm) were deposited on a substrate stack consisting of 10 nm Al_2O_3 , 300 nm SiO_2 ,

and a 250 μm Si wafer. The samples were annealed, followed by growth and furnace cooling. During annealing, the iron oxide layer transformed into metallic Fe nanoparticles as the thin film underwent reduction while being held at 850°C for 30 min in hydrogen hydrogen-reducing environment [114]. The catalyst films with deposition times of 30 sec, 2 min, and 4 min were examined after annealing. Thin polycrystalline Fe film typically experiences solid-state dewetting, which begins with void nucleation along grain boundaries, followed by void enlargement and their subsequent coalescence, ultimately leading to the formation of discrete Fe islands [115]. Figure 4.5 (a-c) shows the nanoparticle distribution for catalyst deposition times of 30 sec, 2 min, and 4 min, respectively. The resulting surfaces were examined by FESEM, as shown in Figure 4.5(a), the 1.25 nm Fe film transformed into sparsely distributed nanoparticles, predominantly around 30 nm in size, with a few larger particles (~ 60 nm) also present. In the case of a 5 nm film, the catalyst dewetted into 80 nm particles with relatively uniform spacing. A further increase in thickness to 10 nm resulted in larger nanoparticles (~ 130 nm), often appearing as clustered aggregates. The thickness of the catalyst layer significantly influences both the diameter and density of the NPs. Although CNT formation occurs through the catalytic decomposition of hydrocarbon gases, growth does not proceed directly on a continuous thin Fe film. Instead, the catalyst film must fragment into nanosized islands within a reducing atmosphere during the annealing step. Figure 4.5(a-c) confirms that increasing the catalyst thickness leads to the formation of larger nanoparticles with reduced particle density. Conversely, a thinner catalyst layer results in smaller, more densely distributed nanoparticles due to the presence of additional grain boundary defects and nucleation sites [116]. Figure 4.5(d) shows the smooth deposition of Al_2O_3 interlayer to reduce diffusion of Fe NPs towards SiO_2 , whereas (e, f) gives the validation of the substrate used, interlayers, and Fe catalyst in the EDX spectrum.

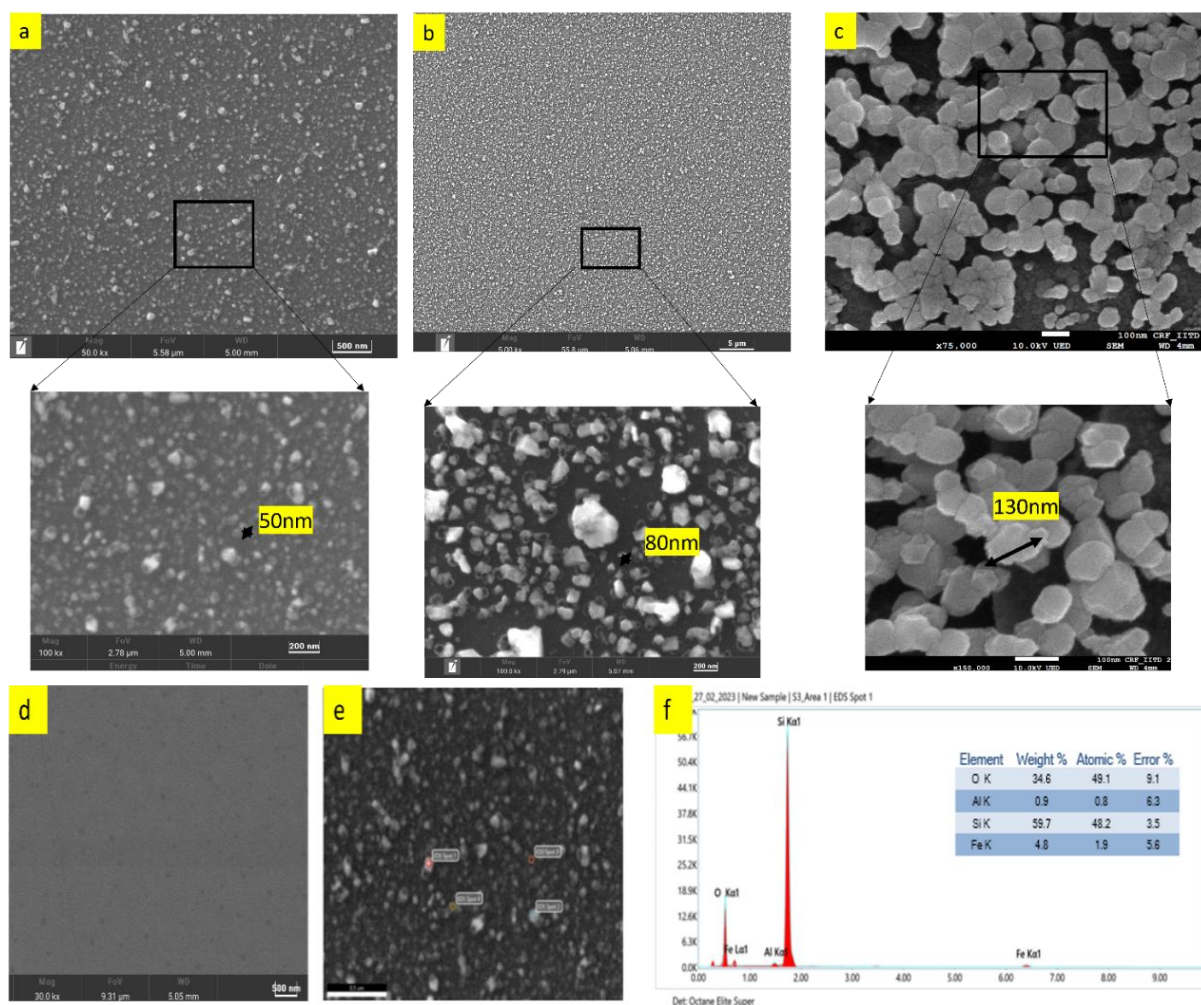


Figure 4.5 FESEM image of dewetted iron nanoparticles at 850°C, (a) 30 sec deposition time, (b) 2 min deposition time, (c) 4 min, (d) Al₂O₃ deposited surface, (e & f) EDX mapping of iron catalyst.

Subsequent CNT growth experiments were carried out at 850°C in the DSS position. A separate experiments were performed for all three samples in order to observe growth perfectly. After the growth, all three samples were examined through FESEM. Among these, the catalyst corresponding to the 2-min Fe deposition (5 nm thickness) produced more vertically aligned CNTs for the same growth duration. However, due to the increased size of the catalysis particle, a thicker tube with more graphene sheets resulted in less growth for the same duration.

Figure 4.6(a–c) shows the cross-sectional view of nanotubes grown over Si for different Fe catalyst thicknesses of 1.25 nm, 5 nm, and 10 nm. The diameter for 1.25 nm thickness was obtained an average of 40nm, whereas it increased to 50 nm for 5 nm, and 100 nm for 10 nm thickness.

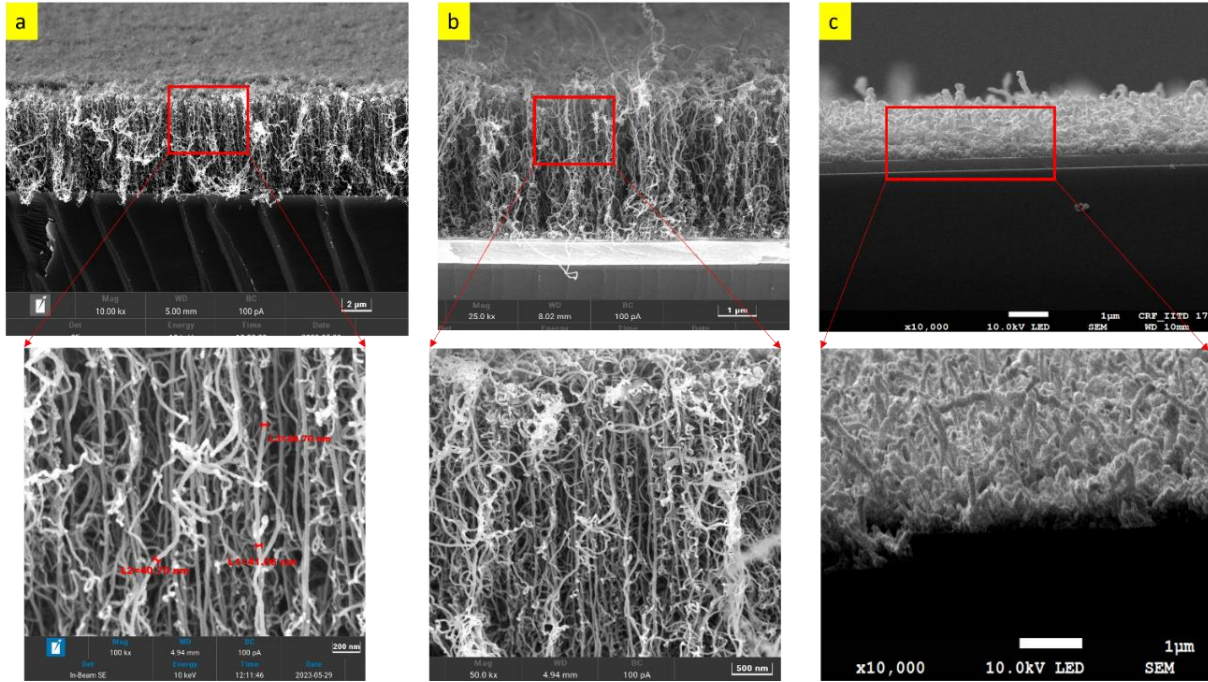


Figure 4.6 FESEM image of VA-CNTs for (a) 30 sec deposition of iron catalyst, (b) 2 min deposition (c) 4 min deposition.

The catalyst film deposited for 2 min was selected for further study to evaluate the effect of deposition time on the thickness of vertically aligned CNTs, as it has provided a uniform and dense nanoparticle distribution. CNT growth was carried out for four different durations: 5, 10, 15, and 20 min. For the initial duration, the growth rate was less, which further increased rapidly for 10 min due to sufficient hydrocarbon molecules present. For a 5-min growth, the VA-CNTs reached a height of approximately 12 μm with an average diameter of 45, whereas for 10 min, 15 min, 20 min, a height of VA-CNTs was observed 25, 120, 150 μm , respectively. In general, longer growth durations produced taller VA-CNT arrays, with minimum sub-branched grown CVD, demonstrating the time-dependent nature of the catalytic CVD process [117]. Figure 4.7(a-d) shows the cross-sectional FESEM to measure the VA-CNTs forest

thickness. The average diameter of CNTs obtained in the range of 45-50 nm, which was not affected by growth duration.

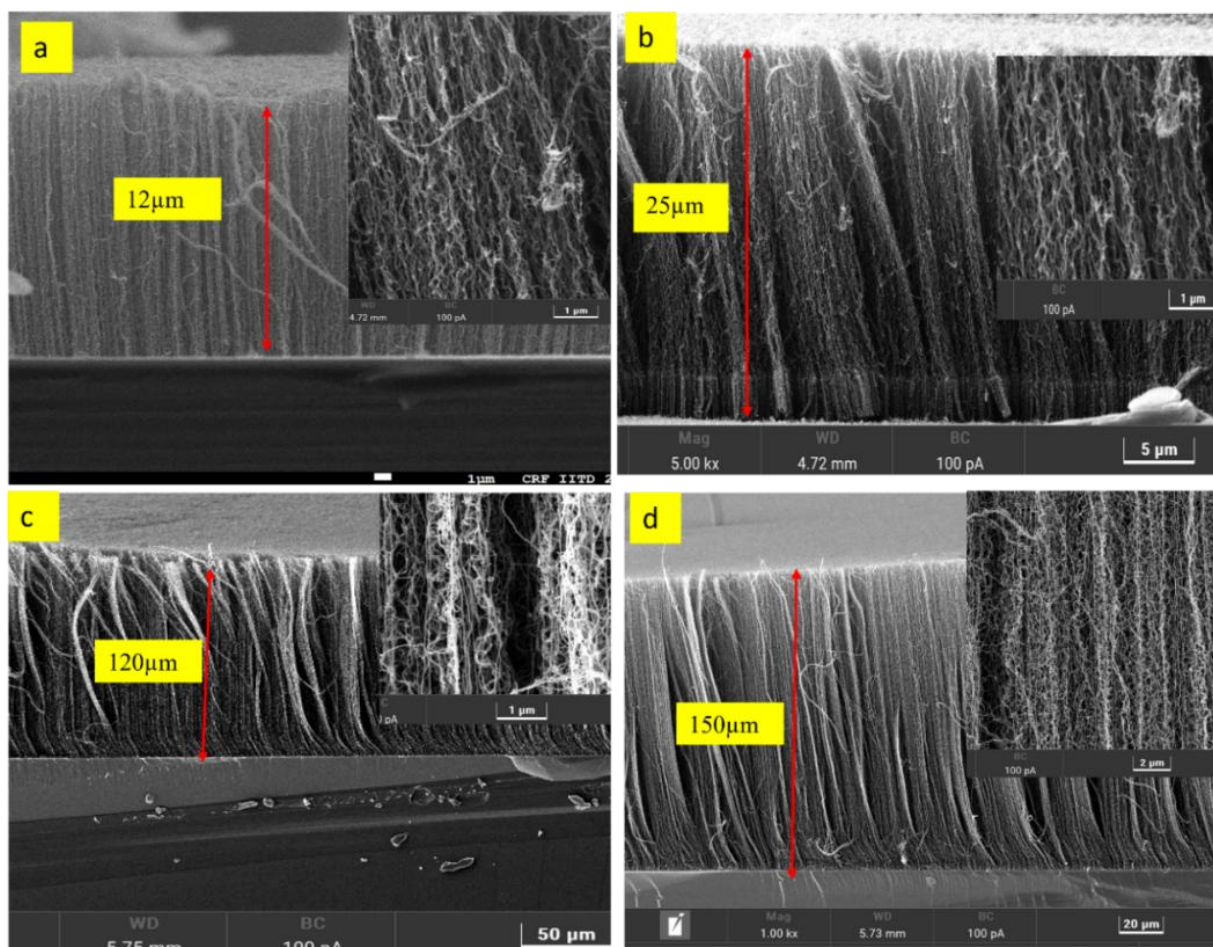


Figure 4.7 FESEM image of VA-CNTs, (a) 5 min growth, (b) 10 min growth, (c) 15 min, (d) 20 min.

4.5 Patterned CNTs array

After optimizing the parameters for VA-CNT growth, patterned catalyst samples were employed to achieve selective CNT arrays. The operating conditions, such as temperature, carrier gas flow rate, and catalyst thickness, were maintained the same as those used for uniform growth across the Si wafer. Specifically, the CVD growth was performed at 850°C with a 300 sccm carrier gas flow and a 5 nm Fe catalyst layer on lithographically patterned substrates. It was observed that smaller features, such as the 20 μm circles, yielded CNT pillars

with relatively reduced height compared to larger 100 μm features, indicating that pillar height is strongly dependent on growth time and feature size. Figure 4.8(a) shows the laser-written photomask, whereas (c) presents optical micrographs of the patterned S1813 photoresist with circular openings. In contrast, Figure 4.8(b, d) shows FESEM images of the corresponding patterned CNT structures.

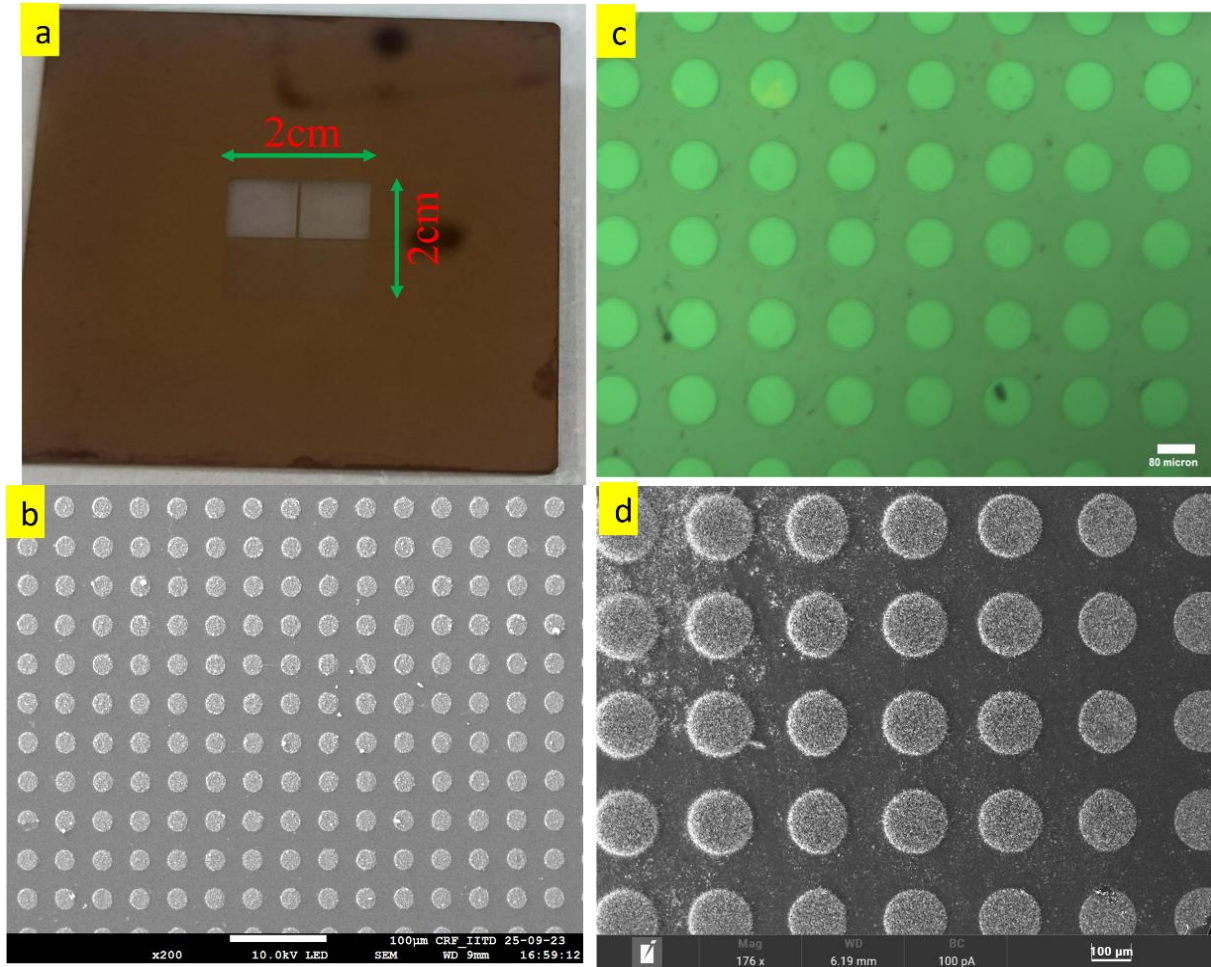


Figure 4.8 (a) Chrome-plated photomask, (c) optical image of mask plate having feature of a 100 μm diameter circle, (b, d) FESEM image of CNTs pillars 20 and 100 μm diameter.

Summary

This chapter considers the following key outcomes

- This in-house developed thermal CVD can grow CNTs with all possible alignments.
- A 5 nm Fe catalyst is required to support a good quantity of VA-CNTs forest growth.
- In a duration of 20 min, 150 μm tall CNTs (aspect ratio~3000) can be obtained.
- A 20 μm circular-patterned CNT array can be fabricated over a larger silicon wafer.

Chapter 5

Fabrication and Characterization of AAO and AAO Integrated CNPs Structures

This chapter outlines the synthesis and characterization of anodic aluminium oxide (AAO) nanostructures and their modification with carbon nanopillars (CNPs), aiming to develop a hybrid platform for multifunctional applications. AAO is a well-established nanostructured material known for its highly ordered, tunable pore architecture, chemical stability, and ease of fabrication through electrochemical anodization. To enhance the functionality of AAO, vertically aligned CNPs were grown within the nanopores using a chemical vapor deposition technique. The hybrid AAO/CNP structures were thoroughly characterized using field emission scanning electron microscopy (FESEM), Atomic force microscopy (AFM), and Raman spectroscopy to evaluate their morphology, elemental composition, and graphitic nature. The results presented in this chapter provide fundamental insights into the structural evolution and material quality of these nanocomposites, laying a strong foundation for application-focused studies in subsequent chapters.

5.1 Surface morphology of AAO fabrication

5.1.1 Temperature effect on pore size and pore regularity of anodized aluminium

The temperature of the electrolyte at the electrode-electrolyte interface is one of the important parameters, like pH, supplied voltage, and concentration of electrolyte solution. It controls the reaction kinetics of the ion species diffusion, which further affects the deposition of oxide, dissolution of the oxide layer, and pore propagation along the aluminium thickness. Moreover, in a recent report, it was observed that during anodizing, a temperature increase of approximately 10°C due to joule heating at the tool-electrolyte interface, which is pertinent to observing the effect of temperature on surface morphology, pore regularity, and a reasonable mechanism [118]. The studies on pore ordering have been established with the empirical

formula $R=Bt^n$ where t is the time of anodization and B is the temperature-dependent constant. At constant voltage, a lower temperature value has more pore ordering and decreases with further temperature increase, which is validated by Fast Fourier Transformation (FFT) [119]. The influence of 0.3M oxalic acid electrolyte for pore regularity and pore widening is carried out for various temperatures at a constant power supply of 45 V, and constant anodization time of 2 h, which is shown in FESEM image of Figure 5.1(a) 5°C, (b) 10°C, (c) 15°C, (d) 20°C, respectively.

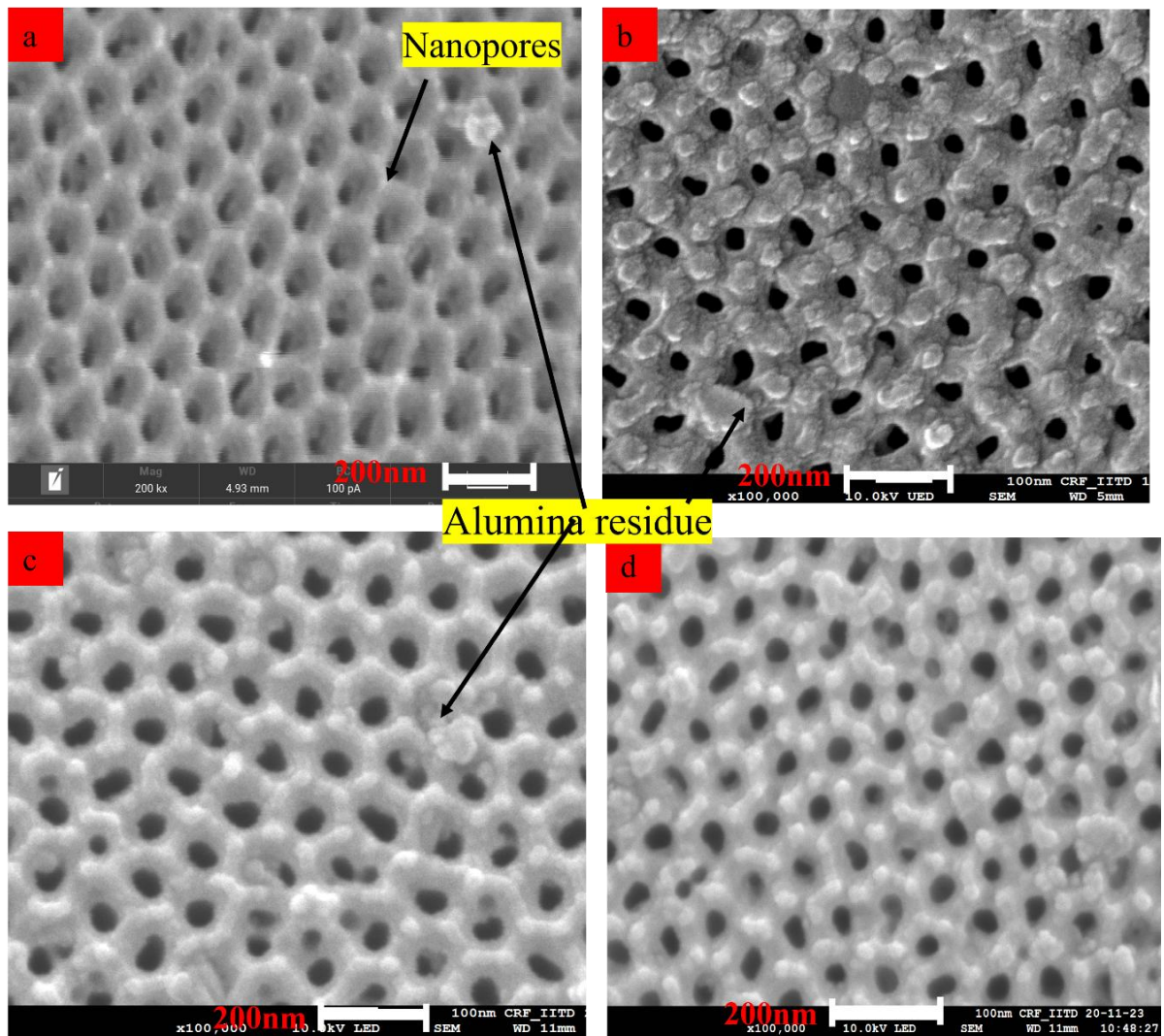


Figure 5.1 FESEM image of as-grown AAO for temperature (a) 5°C, (b) 10°C, (c) 15°C, (d) 20°C.

Figure 5.2(a-d) shows the pore distribution of AAO calculated by software Image J, irrespective of electrolyte temperature (a) 5°C, (b) 10°C, (c) 15°C, and (d) 20°C. The temperature changed

from 5°C to 10°C, the variation in pore diameter is very less, which is 41±2 nm at 5°C, and 43±3 nm at 10°C. It is due to lower ionic species diffusion and more self-pore ordering. At 15°C, pore diameter increases drastically as a sudden increase in mobility of ionic species, which form the tiny holes at the top edge of the pore with an average pore diameter of 46±3 nm, whereas at 20°C, an average pore diameter of 48±6 nm was accomplished. This could be due to the exponential dependence of temperature on the rate of dissolution and deposition. The current density (j) is directly proportional to the rate of reaction (k), which further depends on the temperature of the electrolyte [16].

$$j = zF.k \quad (5.1)$$

$$j = zF A e^{\frac{-E_a}{RT}} \quad (5.2)$$

where A is a constant, z is valency, F is the Faraday constant, E_a is the activation energy, R is the universal gas constant, and T is electrolyte temperature.

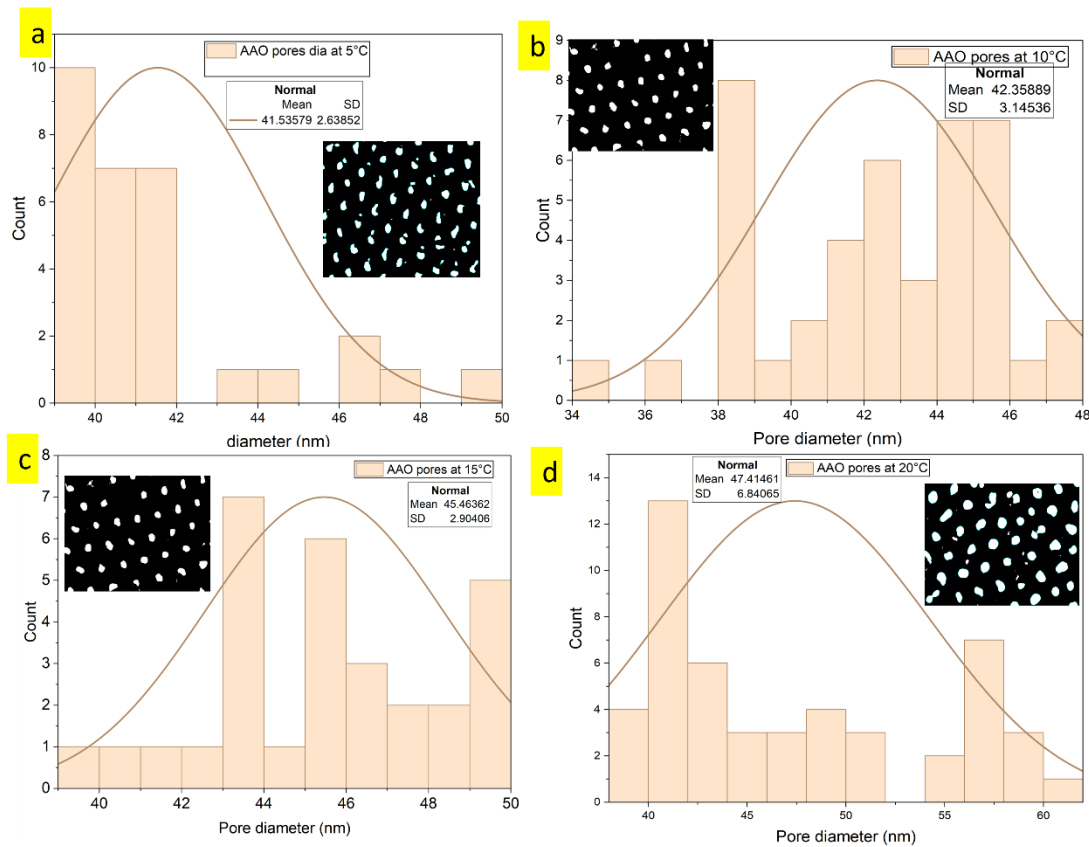


Figure 5.2 Pore size distribution by ImageJ for temperature (a) 5°C, (b) 10°C, (c) 15°C, (d) 20°C.

At higher temperatures, the higher ionic current density induces high mechanical stress, which leads to either the formation of alumina residue over the interpore gaps or the separation tiny pores in between ordered pores. Moreover, the atomic density of aluminium in aluminium oxide is 1.7 times higher than that of metallic aluminium, which is a possible origin of forces between the pores; therefore, some mechanical stresses are associated with volumetric expansion, while oxide formation at the metal oxide interface [120]. Since the oxide formation is uniform throughout the bottom of the pores, the material can only expand in the vertical direction, so the pore walls would be pushed upward. At lower temperatures, due to equilibrium deposition and dissolution pore wall upshifting is more uniform and makes the hexagonal packing in order to minimize strain energy. According to the 10% porosity rule, it is observed that the volume expansion factor is $\epsilon \sim 1.2$ while increasing the electrolyte temperature, volume expansion factor increases ($1.3 < \epsilon < 2$), which disturbs the pore ordering. Moreover, at higher temperatures, the mechanical stress induced is increased, which leads to fast oxide dissolution, resulting in an increase in the pore diameter. Figure 5.3(a-d) inset shows the FFT-generated image depicts six bright spots observed around the center point, indicating that the highly ordered hexagonal pattern is present at a lower sub-room temperature. However, an increasing temperature of 20°C exhibits the diffuse ring, which reduces the hexagonal regularity. The pore ordering ratio (POR) was calculated by $\frac{\sqrt{N}}{S^{3/2}} \frac{H}{W_{1/2}}$, where N is the number of pores, S is the analyzed surface area, H is the FFT intensity height, $W_{1/2}$ is the width at half height. In order to calculate POR, the FFT intensity vs FFT radius curve was plotted by using the ImageJ FFT module, as shown in Figure 5.3(a-d). Figure 5.3(e) ascribes the maximum pore ordering at the lowest temperature of 5°C. However there was a marginal difference was observed for 5 and 10°C, therefore electrolyte temperature was fixed to 10°C for further experiments. At 20°C, it decreased significantly as the temperature profile depends exponentially.

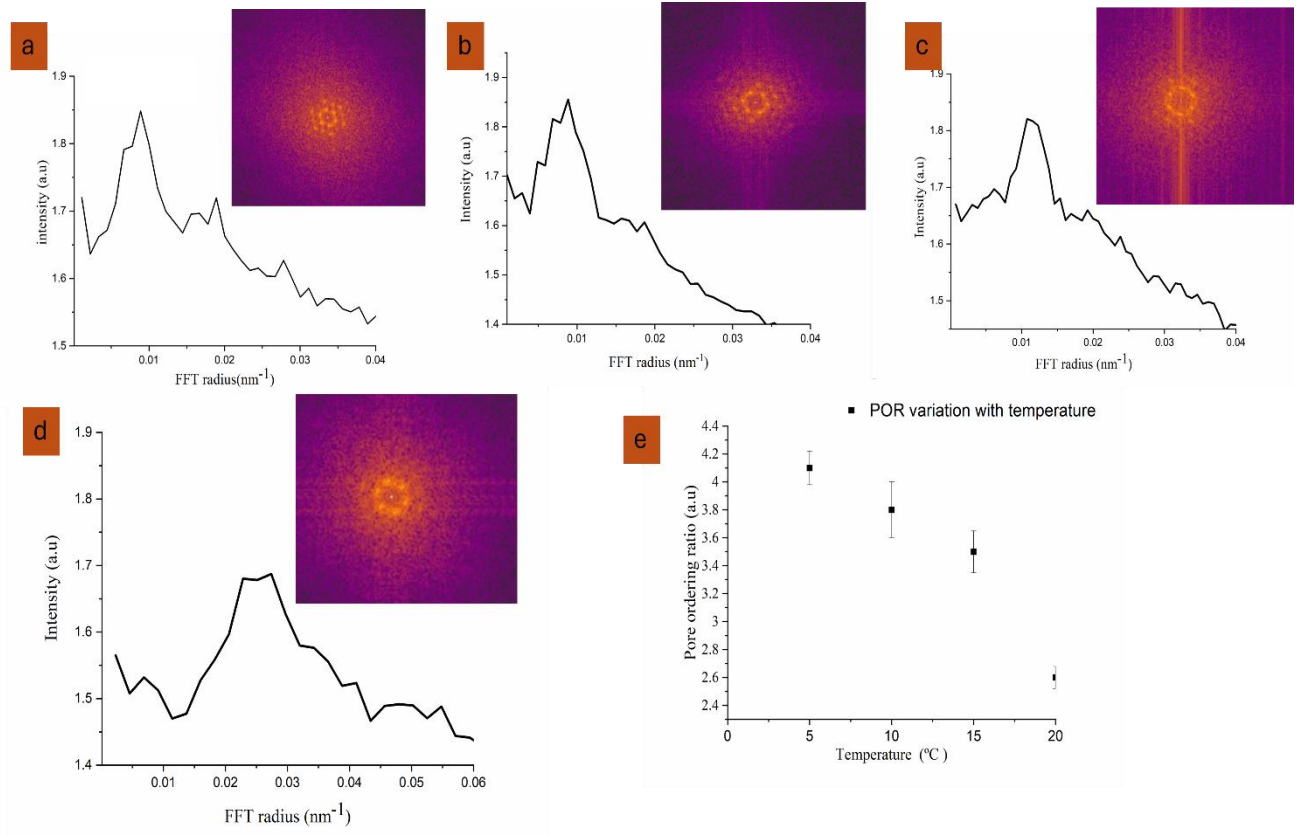


Figure 5.3 2D-FFT image for self-ordered hexagonal system at temperature (a) 5°C, (b) 10°C, (c) 15°C, (d) 20°C, (e) POR vs temperature for n=3.

At higher temperatures, pore walls start to dissolve and increase the pore diameter as well as porosity. For the self-ordered 10% porosity rule, porosity (p) is given by $p = \frac{\pi}{2\sqrt{3}} \left(\frac{d_p}{d_{int}} \right)^2$, where d_p is pore diameter and d_{int} is inter-pore distance [121]. Figure 5.4(a) shows the graphical presentation of pore diameter and inter-pore distance distribution with electrolyte temperature. From Figure 5.4(b), at 10°C, porosity comes out to approximately $10 \pm 0.5\%$, which is further used as a fixed perimeter to make the AAO mould. The current density behaviour was recorded for the first few seconds during the second anodization while keeping the DC voltage constant. The current density at the beginning is high due to the absence of oxide layer formation, but rapidly decreases in a few seconds due to the thinning of the oxide layer. With increasing electrolyte temperature, there is an increase in current density in a steady state, as depicted in

Figure 5.4(c). For electrolyte temperature 10°C current value was measured initially at 10 mA, but as soon as nano porosity starts to form, it increases to 12 mA, which becomes stable for a longer time.

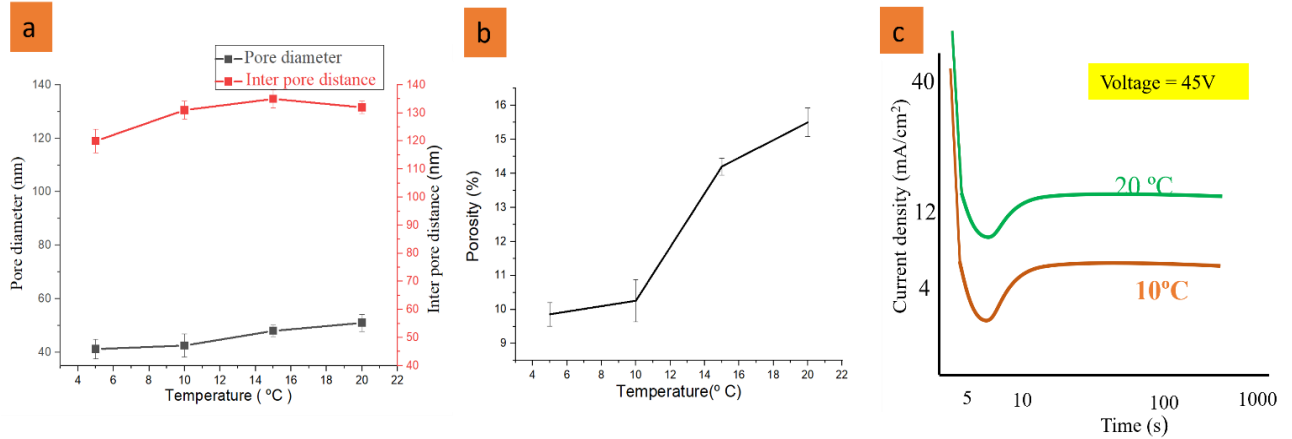


Figure 5.4 (a) Pore size, inter-pore distance, porosity variation for different temperatures, (b) Porosity variation with temperature for three independent standard samples(n=3), (c) Current density vs time plot.

5.1.2 Effect of etching time on pore widening

Pore widening is an effective method to finely tune the diameter of pores for different applications, such as optical tuning, wettability control, and required polymer pillar imprinting. Etching in 5wt.% H_3PO_4 is subjected to different durations. As the time of etching increases, pores start to enlarge, whereas the pore wall thickness reduces. due to hydrated alumina deposition along the pore walls of crystalline alumina. The pore parameters, such as pore height, pore diameter, interpore distance, and shape of pore opening, are depicted in Figure 5.5(a, b). As illustrated in Figure 5.6(a), as-grown AAO has alumina residue near to pore opening, which can be cleaned by the etching process. With increasing the duration of etching for 30 min, 45 min, it starts removing the excess residue and penetrates through the pores, as a result pores get widened.

As etching is done for a longer duration of 60 min, shown in Figure 5.7 (a, b), it starts to dissolve the opening of the hole more compared to the inside of the hole due to excess etchant available at the pore opening, and it forms a funnel-shaped opening which is more slanted at one side. Further increasing to 90 min, the ordered pore of 78 ± 3 nm was accomplished with a porosity of 52 %, which is finally selected as the AAO mould to perform a hot embossing experiment on a polystyrene sheet. Therefore, 90 min duration of etching was performed on all AAO moulds while keeping all process parameters constant, such as anodization temperature of 10°C , and anodization voltage of 45 V.

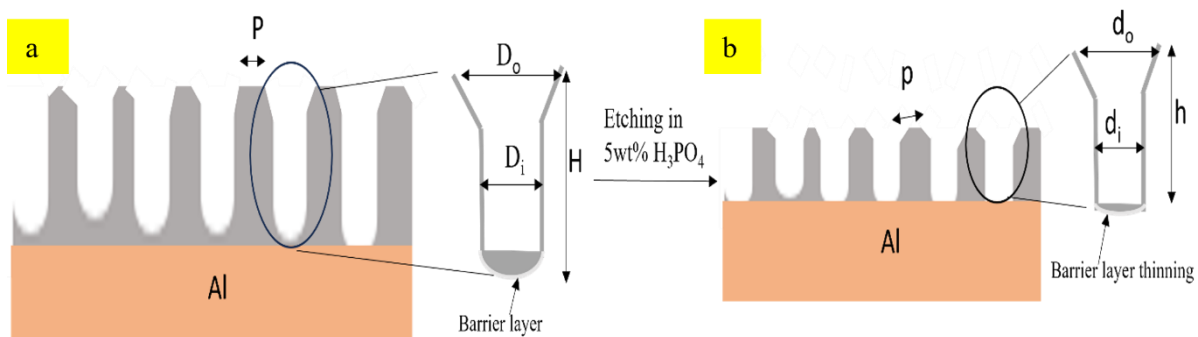
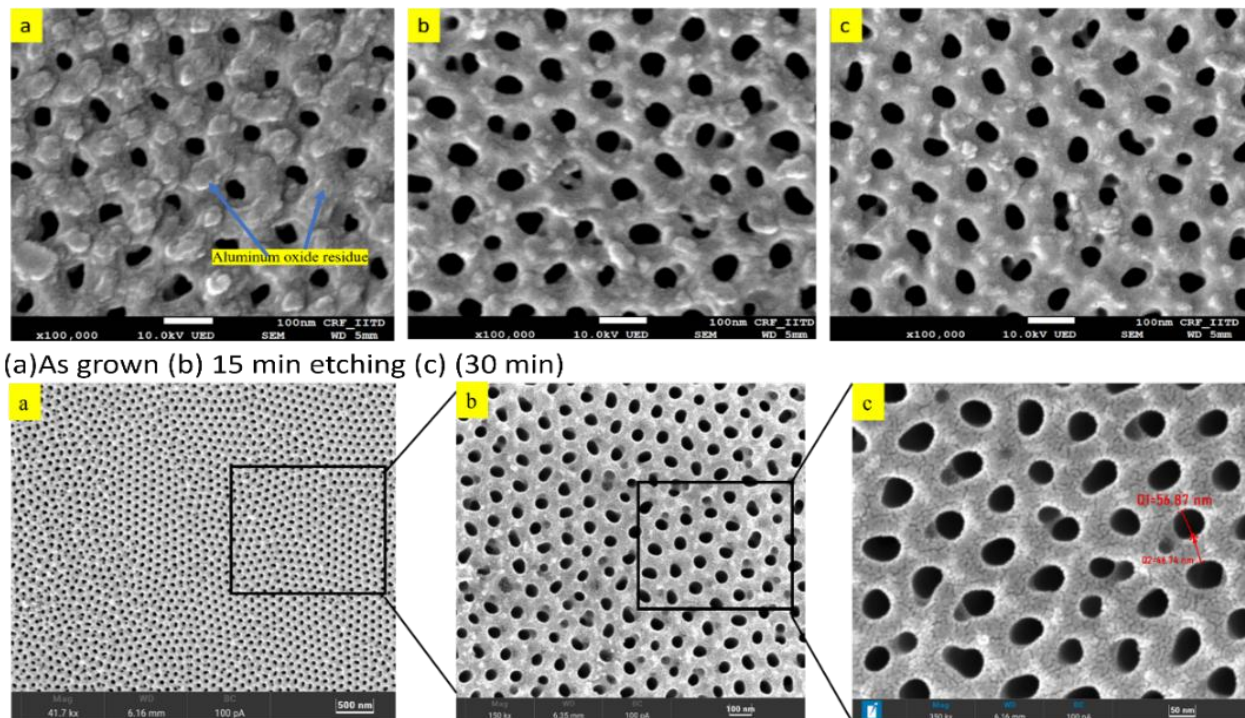


Figure 5.5 (a) Schematic of pore parameters for AAO membrane, (b) influence of pore parameters on etching time.



45 min. etching (a) 40kx (b) 150kx (c) 350kx

Figure 5.6 FESEM image after 5wt.% etching for as-grown, 15, 30, 45 min.

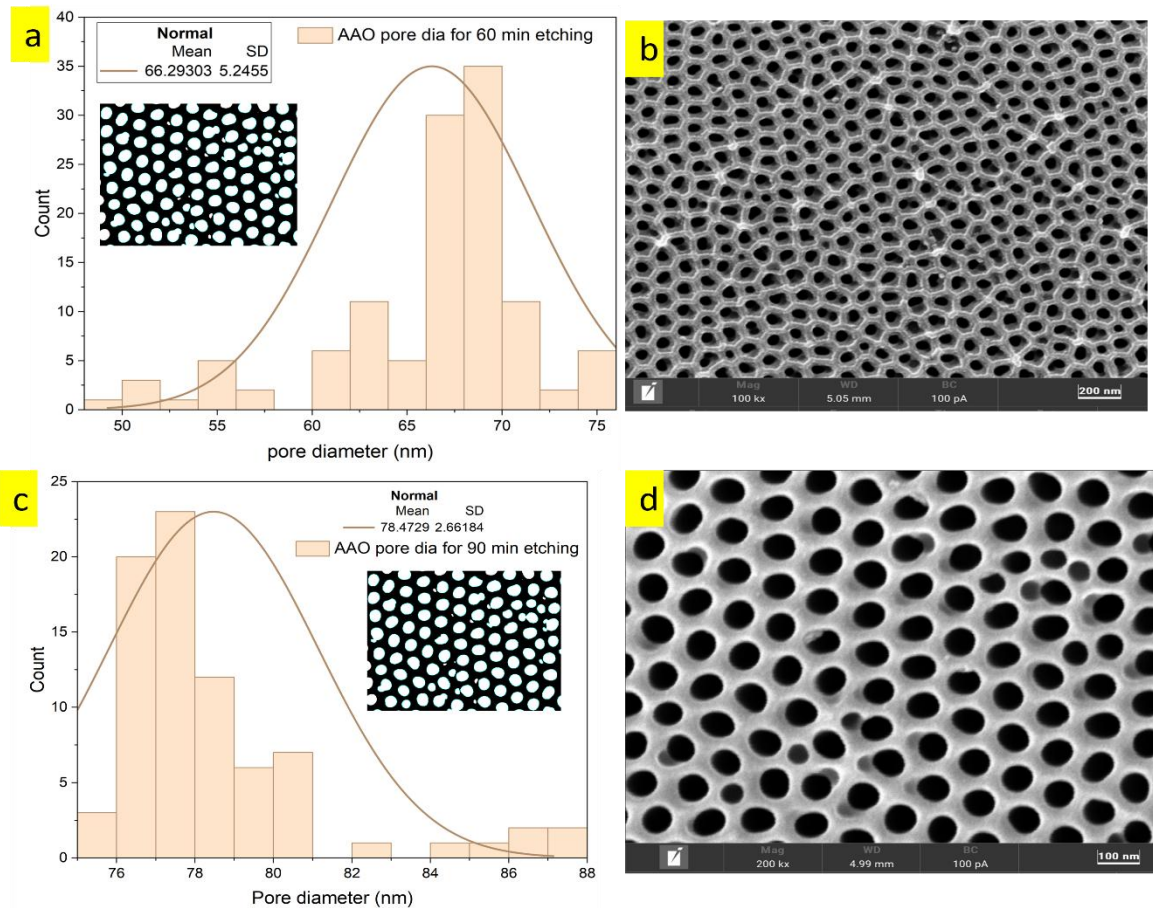


Figure 5.7 (a) Pore diameter distribution for 60 min etching, (b) FESEM image of AAO after 60 min etching, (c) pore size distribution for 90 min, (d) FESEM image of AAO for 90 min etching.

5.1.3 Thickness variation of AAO membrane with anodization time

The thickness of the membrane is observed to be increased with increased duration of second anodization; however, the diameter of pores remains constant with increasing time. Pore size depends on the duration of the first anodization. As the time of first anodization increases, nano-pores start to collapse into each other and make a honeycomb texture which can be observed after chemical etching in chromic acid and phosphoric acid at 60°C. The thickness of the oxide membrane was controlled with a duration of second anodization. For 2 h anodization duration, the obtained membrane thickness is 10 μm , found sufficient to make a mould for hot embossing process, whereas for 5 h duration, $\sim 26 \mu\text{m}$ thickness was produced. FESEM image of the AAO membrane for different durations of second anodization of 2 h, 3 h, 4 h, and 5 h while keeping the constant electrolyte temperature at 10°C, which is shown in Figure 5.8(a-d).

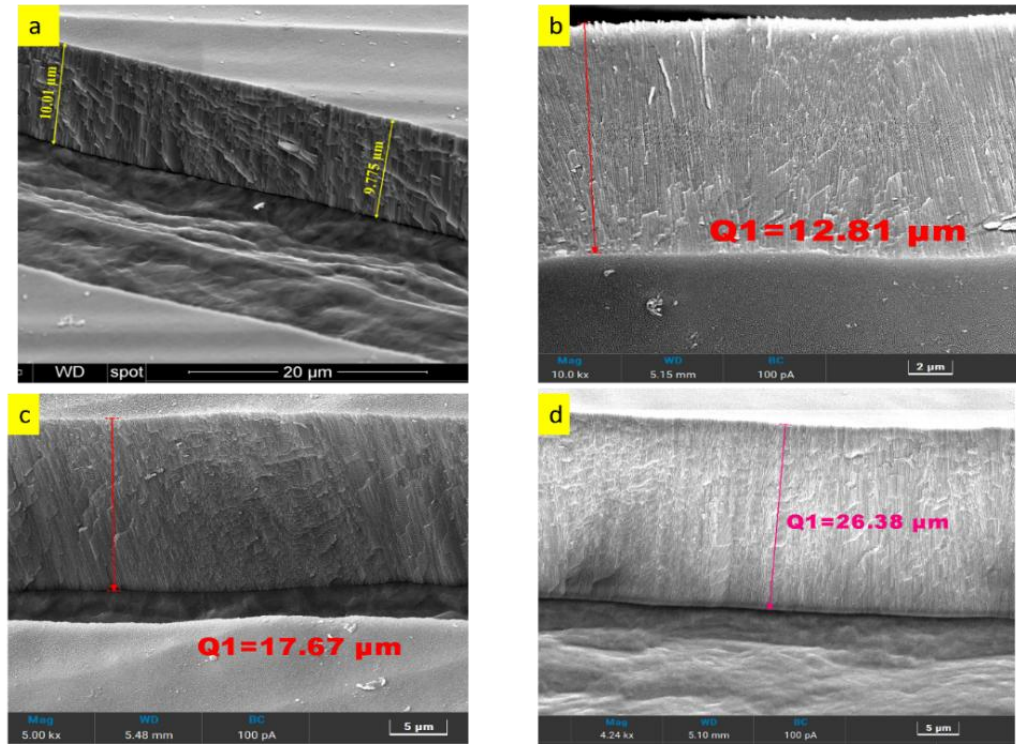


Figure 5.8 Thickness of AAO membrane (a) 2 h, (b) 3 h, (c) 4 h, (d) 5 h growth.

Moreover, Figure 5.9 (a) shows the AAO thickness variation with anodization time, whereas (b) is the growth rate for different electrolyte temperature values of 5°C, 10°C, 15°C, and 20°C. The thickness of membrane Q_1 was achieved at values $10 \pm 1 \mu\text{m}$, $12.8 \mu\text{m}$, $17.67 \mu\text{m}$, and $26.38 \mu\text{m}$ for 2, 3, 4, 5 h of anodization time, respectively. The growth rate, r (nm/s), was calculated by dividing the film thickness by the second anodization time, as shown in Figure 5.9(b).

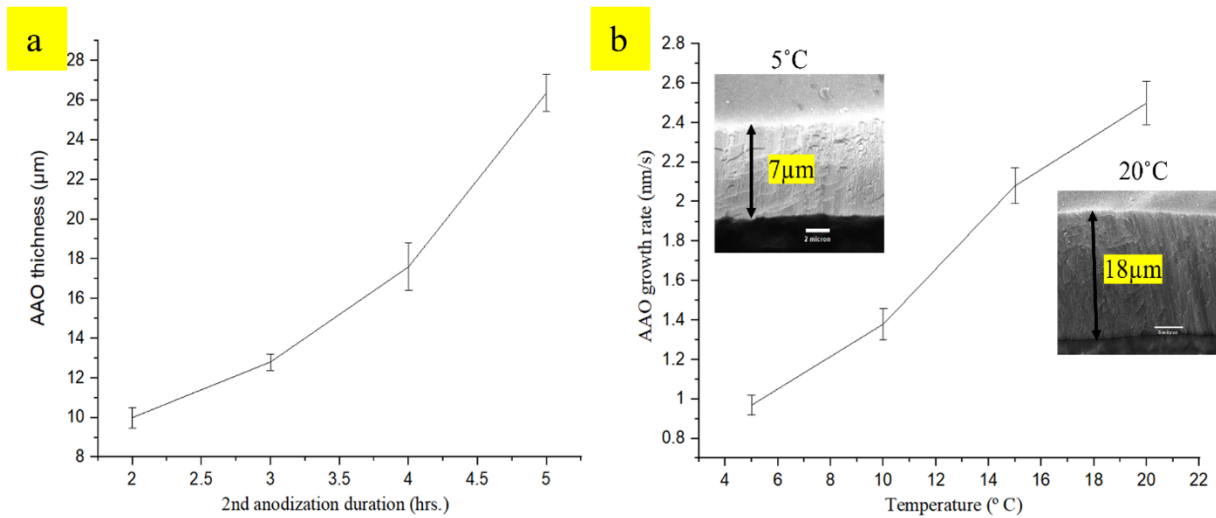


Figure 5.9 (a) Variation of AAO growth thickness with time, (b) growth rate of AAO at different electrolyte temperatures for $n=3$.

The barrier oxide layer was removed by first removing of aluminium base in 0.1M CuCl_2 followed by 0.5wt.% phosphoric acid chemical etching for 90 min at room temperature by delicately removing brown colour copper residue. Figure 5.10(a-c) shows the etched morphology of the thin oxide barrier layer with time. The vertically parallel aligned pores are depicted in Figure 5.10(b). As the grown oxide layer was 50 nm, however, it started to etch out with time, and 90 min of etching removes the complete layer with a pore opening of 95 nm diameter, and pore widening starts for the next 15 min, which is illustrated in Figures 5.10(d). This honeycomb-type patterned hexagonal pore is a suitable geometry to use this surface as a mould for hot embossing.

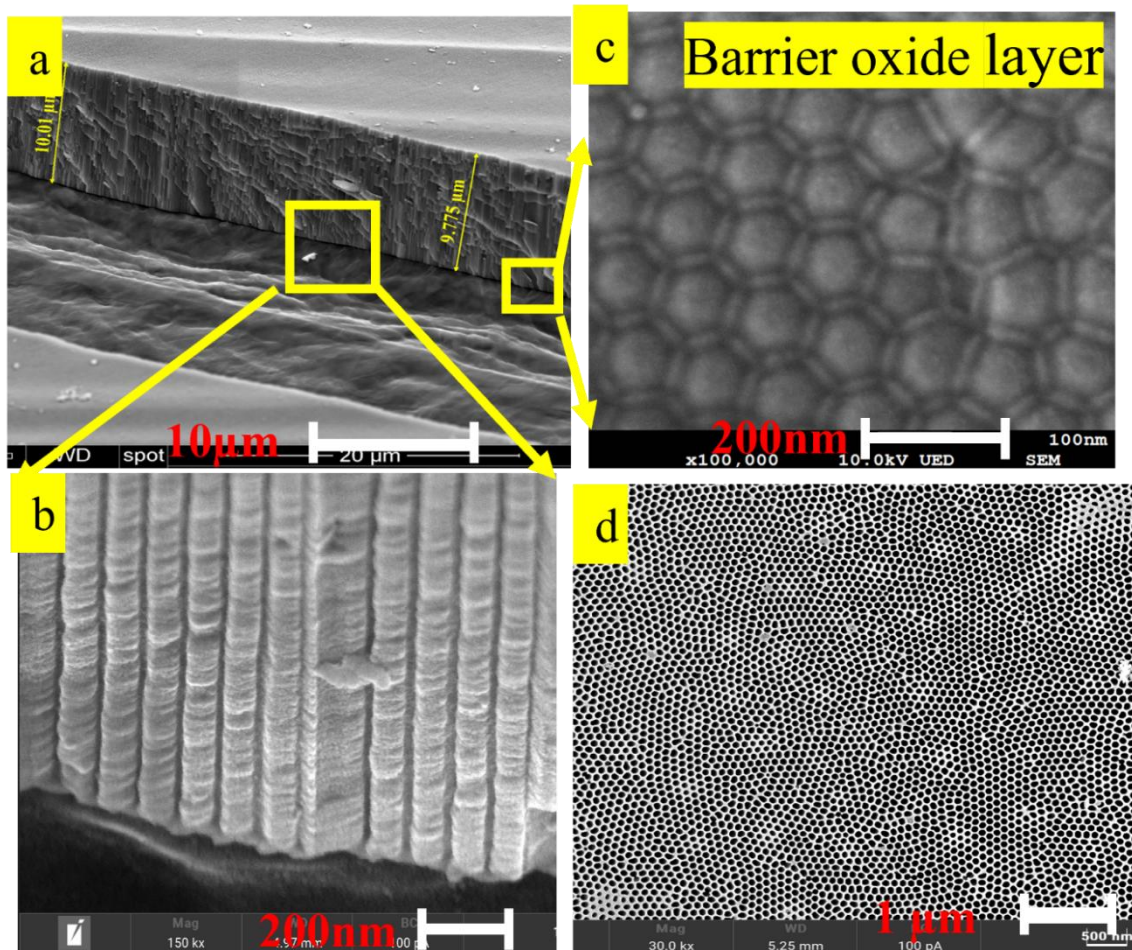


Figure 5.10 (a) -section of AAO membrane (b) AAO nanochannels, (c) oxide barrier layer at the bottom, (d, e) top view of bottom pores after 90 min etching.

5.2 Anodization of masked Aluminium

At the beginning of the AAO fabrication process, a thin layer of S1813 positive photoresist was uniformly applied. This step was aimed at enabling area-selective anodization by using the resist as a protective mask. Ultraviolet (UV) irradiation at a wavelength of 365 nm was employed to initiate photochemical transformations within the photoresist. During exposure, the active compounds in S1813, particularly the diazonaphthoquinone (DNQ) groups, underwent decomposition, making the exposed regions more reactive to the subsequent developing process. A development step lasting 1 min followed, during which the exposed regions were cleanly dissolved, revealing sharply defined openings in the resist layer. These openings selectively exposed the underlying aluminium surface, allowing for spatial control during the anodization process. As a result, the UV-treated sections of the photoresist became soluble in the developer solution, allowing for clean and well-defined removal of the targeted areas. This procedure effectively created precise openings in the resist, exposing the underlying aluminium in a controlled manner and defining the regions intended for anodization. The effect of electrolyte stirring during the anodization process was found to be a critical factor influencing both the structural integrity of the S1813 photoresist and the quality of the resulting anodic aluminium oxide layer. When the resist remained partially intact under high stirring, localized bubbling or vortex formation near the electrode surface caused visible surface defects in the anodized regions. These observations suggest that careful optimization of stirring is not only important for photoresist protection but also for achieving smooth, defect-free oxide growth. An anodization temperature of 10°C was selected to achieve uniform pore formation while minimizing excessive current density and thermal effects. Lower temperatures are known to enhance the self-ordering of AAO by slowing down oxide dissolution and promoting more controlled film growth. However, sub-zero conditions can introduce mechanical challenges, especially for photoresist layers like S1813, which may become brittle and prone to cracking

or delamination due to thermal stress. Despite this, operating at 10°C helped suppress the rapid rise in current density typically observed at higher temperatures, which often results in irregular pore structures and increased defect rates. This controlled, low-temperature approach provided a more stable anodization environment, preserving both pore regularity and photoresist integrity. Figure 5.11(a) shows the photograph of the photomask, which was made over the chrome-plated soda glass with 4 regions of 1 cm × 1 cm with different features and sizes. Figure 5.11(b) shows the SEM image of resist pattern opening, whereas (c, d) show the FESEM image of Al nucleations and anodized pores after 2nd anodization, respectively. Such hierarchical texture enhances the multifunctional properties of the surface.

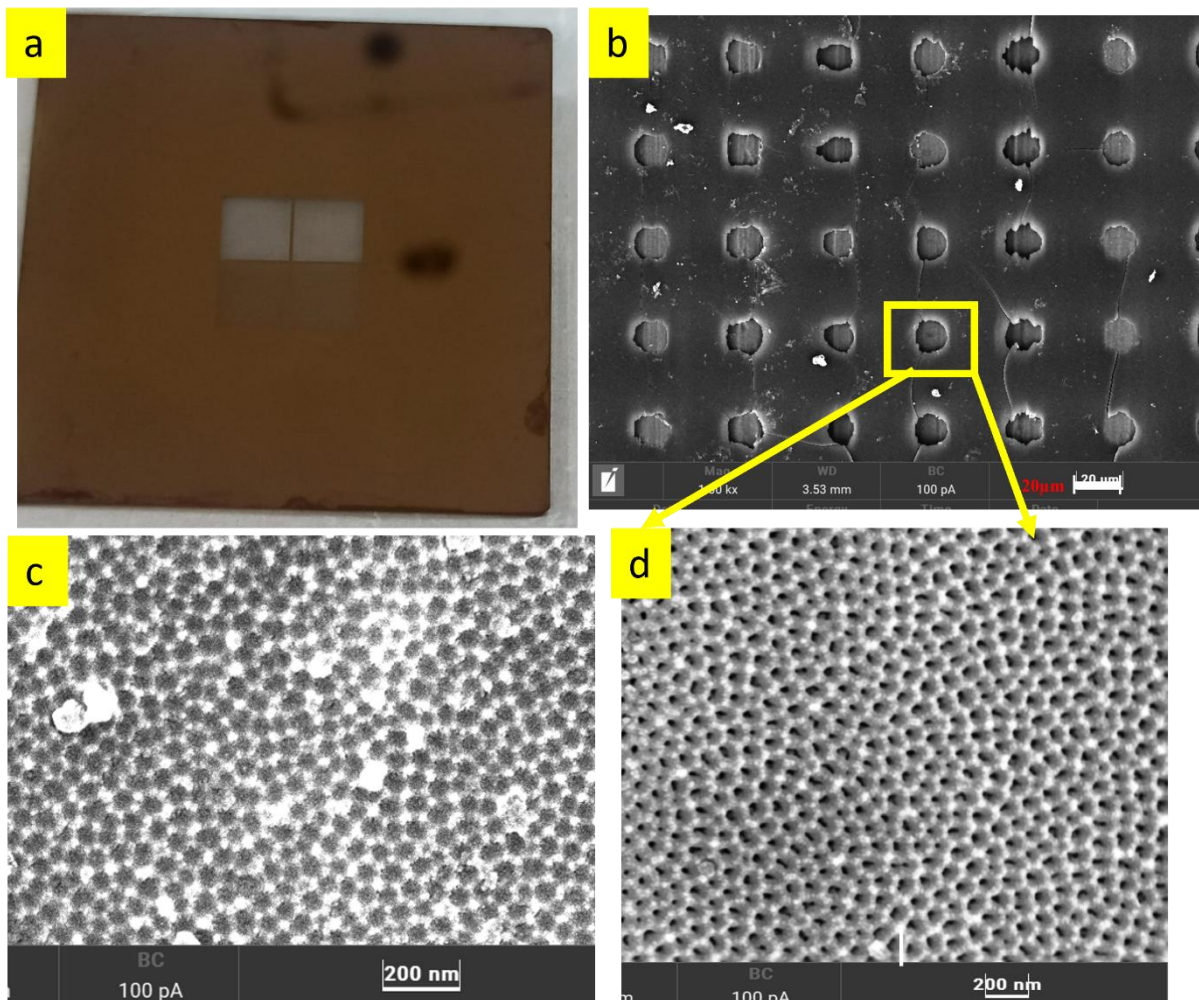


Figure 5.11(a) photomask, (b) FESEM image of photoresist patterned on Aluminium, (c) aluminium texture after 1st anodization, (d) FESEM image of AAO pores after 2nd anodization.

5.3 Surface morphology of AAO-assisted CNPs growth

The AAO served as an effective template and catalyst support, enabling vertical confinement and guided growth of CNPs within its highly ordered pores. The growth was performed under a controlled atmosphere using a hydrocarbon precursor gas, acetylene, in the presence of a Ni metal catalyst. Post-synthesis, the hybrid structure was analyzed using FESEM to confirm the presence and alignment of CNPs within the AAO framework. In order to facilitate effective electrodeposition within the AAO structure, the insulating barrier layer located at the bottom of the nanopores needed to be thinned. This was accomplished by implementing a gradual voltage reduction protocol directly after completing the second anodization step. The anodization voltage was systematically lowered in incremental steps, which led to a gradual reduction in the electric field across the oxide layer. This controlled approach enabled uniform thinning of the barrier layer at the pore bottoms, while preserving the structural integrity of the AAO framework. As a result, the oxide base became progressively thinner, allowing for improved electrical connectivity with the aluminium substrate beneath. The formation of branched pores at the base of the AAO structure during stepwise voltage reduction can also be rationalized using the constant area principle, which governs the self-organized growth of porous alumina. According to this concept, the total interfacial area available for oxide formation and dissolution remains nearly constant throughout the anodization process. As the voltage is gradually reduced, the system adjusts to a new equilibrium where the interpore distance and barrier layer thickness decrease proportionally. However, instead of enlarging individual pores or allowing uniform dissolution at the base, the system often compensates by increasing the number of pores, leading to bifurcation or branching of existing pores to preserve the total electrochemical interface area. FESEM images of cross-sections in Figure 5.12(a, b) showed a noticeable tapering of the pore bottoms, confirming the effectiveness of the voltage ramp-down approach.

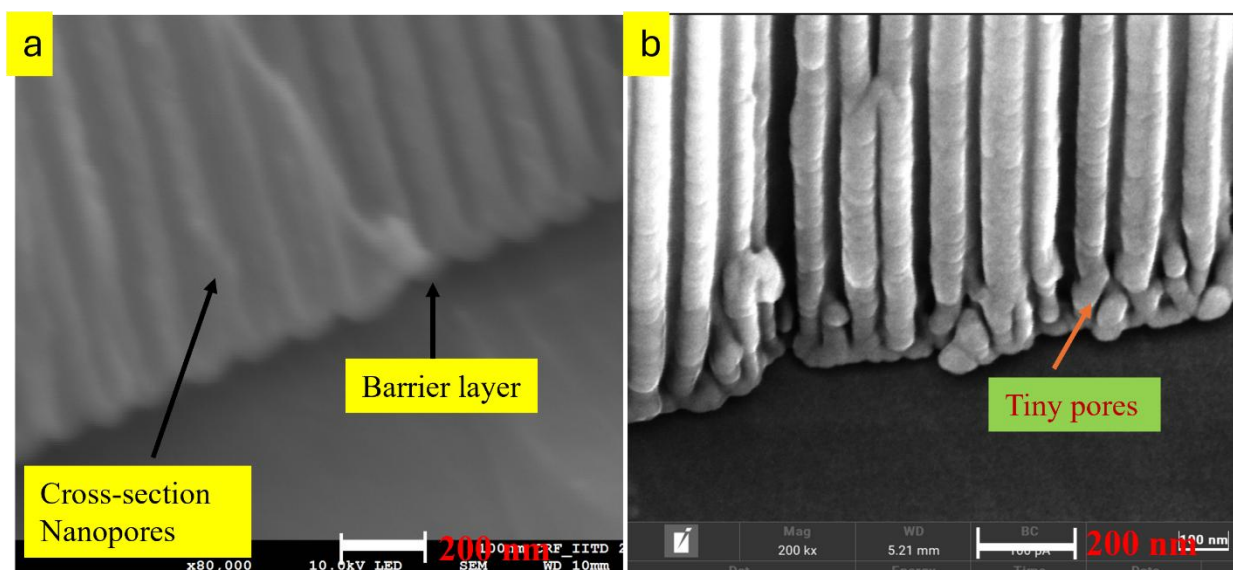


Figure 5.12 FESEM image of (a) the bottom of the AAO layer after a sudden stop, (b) AAO cross-section for a stepwise voltage reduction during anodization.

5.3.1 Nickel catalyst electrodeposition

To facilitate the growth of carbon nanopillars within the AAO template, a nickel catalyst layer was electrodeposited at the base of the pores. Nickel was selected due to its well-established electrodeposition and catalytic activity for CNT synthesis. As a transition metal with a high carbon solubility and diffusivity, Ni serves as a nucleation site for carbon atoms, enabling the decomposition of hydrocarbon gases and promoting the formation of graphitic structures [122,123]. Nickel electrodeposition was performed at a constant DC potential of 2.1 V for varying durations of 1, 5, and 15 min to investigate the influence of deposition time on catalyst distribution within the AAO template, as shown in Figure 5.13(a, b). The process was initiated with a steady current of 0.01 A, ensuring uniform nucleation at the base of the pores. For 1 min deposition, a sufficient amount of Ni nanoparticles was observed in bottom of AAO pores, whereas for 5 min AAO pores started to fill with Ni nanopillars. As the deposition progressed for 10-15 min, a gradual rise in current density was observed, reaching nearly 100 mA after 15 min. This increase is attributed to the ongoing reduction of Ni^{2+} ions and the accumulation of metallic nickel, which enhances the conductivity of the system. For the larger deposition time, a noticeable metallic film began to appear on the surface of the AAO, indicating that the pores

were likely saturated with nickel, and excess metal had started to deposit on the template surface. This surface layer suggests a transition from pore-confined deposition to bulk overgrowth, which may interfere with selective CNP nucleation if not carefully controlled. The time-dependent evolution of current response and surface morphology thus provides valuable insights into the optimization of catalyst loading for effective and localized CNP growth within the AAO nanopores. Therefore, with one min of Ni deposition sample CNPs growth was processed. Figure 5.13(c), EDX spectrum confirms the presence of the FESEM image of Ni deposition in the bottom of the pores.

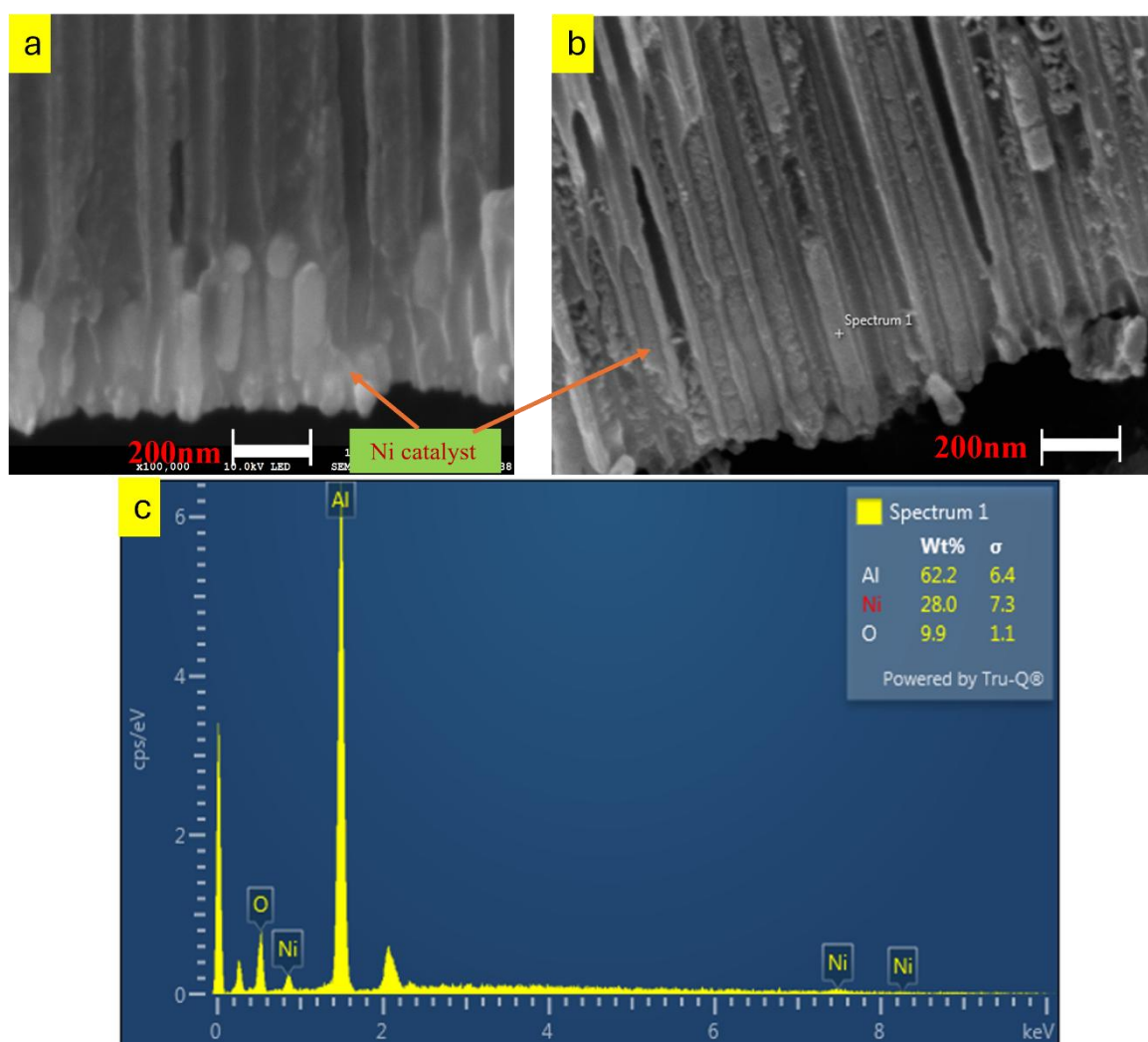


Figure 5.13 (a, b) FESEM image of Ni deposition in the bottom of pores for 1 min and 5 min, respectively, (c) EDX mapping at the bottom of AAO.

5.3.2 Carbon nanopillar growth

Carbon nanopillars growth within the AAO template was significantly influenced by the combination of acetylene flow rate and deposition time during the CVD process. Two sets of flow rate and growth time conditions were investigated to evaluate their effect on carbon infiltration and pillar formation. It was observed that a lower acetylene flow rate of 20 sccm at 625°C, when combined with a longer deposition duration of 4 h, resulted in successful CNPs growth spanning the entire depth of the AAO pores, from the base to the surface. This condition promoted steady and controlled carbon diffusion into the confined geometry of the nanopores, enabling the formation of aligned CNPs without disrupting the template structure. However, a lower deposition rate does not give the complete formation of tubes. Additionally, the carrier gas at 200 sccm helped to dilute the acetylene concentration, preventing carbon oversaturation and minimizing the formation of undesired amorphous carbon. In contrast, a higher acetylene flow rate of 100 sccm led to an entirely different growth behaviour. Under this condition, carbon infiltration into the pores was significantly limited, and the deposited carbon started to accumulate at the top surface of the AAO membrane. This resulted in the formation of a thick amorphous carbon layer over the surface, which acted as a barrier and inhibited further carbon penetration into the pores. The excessive precursor supply likely caused premature decomposition of acetylene before it could effectively reach the catalyst particles inside the nanopores, leading to poor CNP yield. These observations highlight the critical importance of optimizing the carbon precursor flow rate and exposure duration in CVD-based template growth. Proper tuning of these parameters ensures uniform CNP vertically aligned nanostructures within porous AAO. Figure 5.14(a) shows the AAO top surface post CNPs growth, (b, c) shows the cross-sectional FESEM of AAO/CNPs at top and middle, whereas (d) is the bottom side of AAO/CNPs, which indicates the complete growth of CNPs.

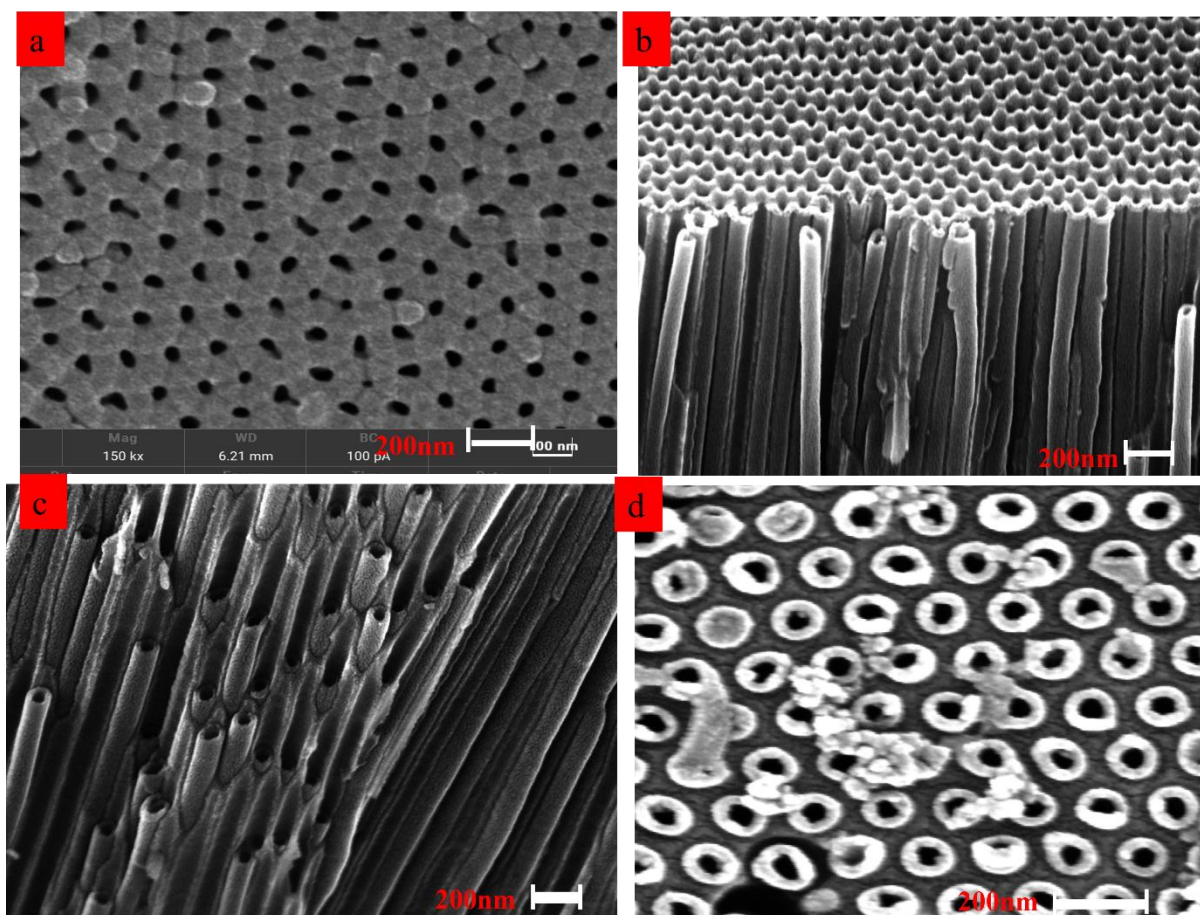


Figure 5.14 (a) FESEM image (a) top view of AAO surface after growth, (b) cross-section view of CNPs, (c) CNPs in the middle of AAO pores, (d) bottom side of AAO/CNPs.

5.3.3 Chemical etching of AAO

To prepare the CNP-filled AAO templates for mould applications and nanostructure fabrication, two different techniques were employed to expose the embedded carbon nanopillars at the surface: (1) ion milling followed by chemical etching, and (2) mechanical polishing followed by chemical etching. Both techniques aimed to remove the overgrown amorphous carbon on the top of the anodic aluminium oxide membrane while preserving the integrity and vertical alignment of the CNPs within the pores. Ion milling was conducted at 600 V and 30 mA for durations of 10 and 60 min, using an argon plasma beam to physically sputter the top surface of the AAO layer. This process selectively removed the upper alumina without chemically disturbing the CNPs. A 10 min exposure partially thinned the alumina surface, while extended milling for 60 min significantly reduced the oxide thickness by

approximately 30–40 nm, as shown in Figure 5.15(a–c). However, prolonged ion bombardment began to erode the tips and edges of the CNPs as well, as evidenced after subsequent NaOH etching (0.5 M, 5 min). This indicates that while ion milling effectively exposes CNPs, careful optimization is required to prevent unwanted nanotube damage during extended exposure to high-energy plasma.

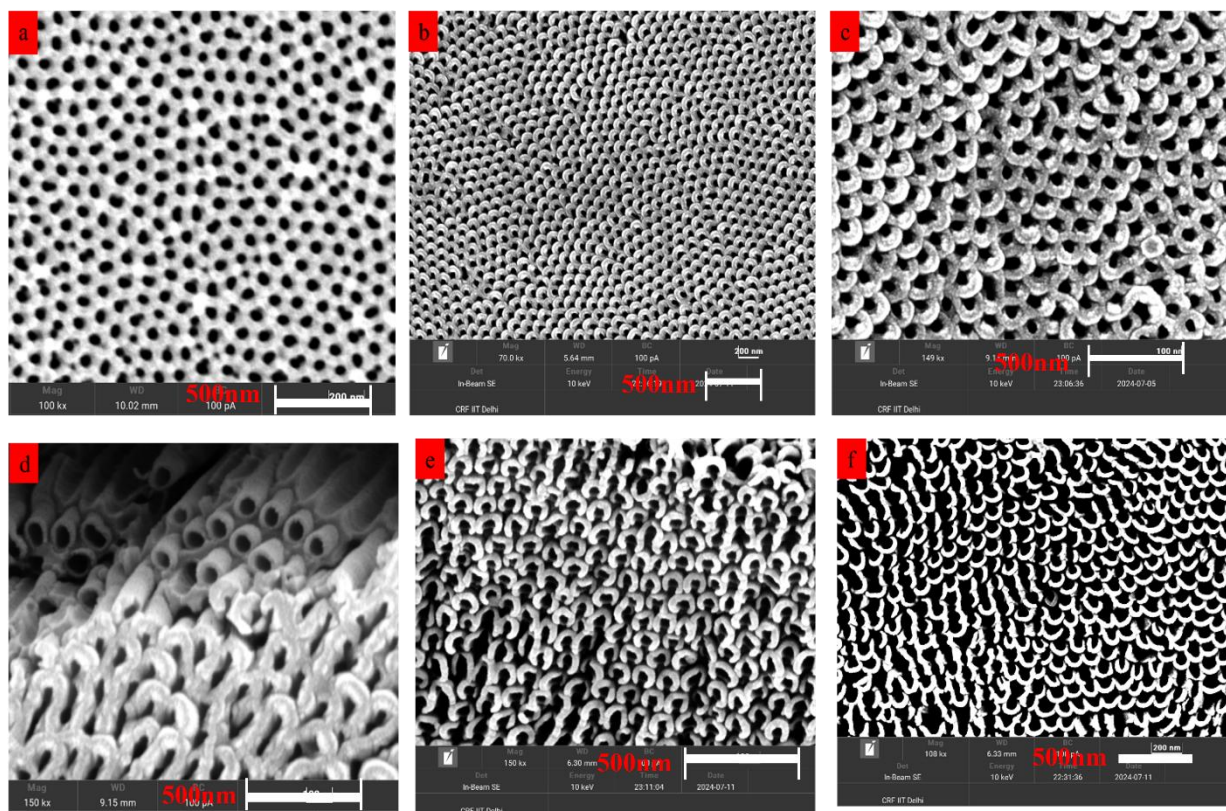


Figure 5.15 FESEM image of (a) as-grown top AAO/CNP surface, (b) 10 min Ar ion milled, (c, d) 60 min Ar ion milled top and tilt view, (e) NaOH etching of (b), (f) NaOH etching of (c).

Mechanical polishing followed by chemical etching was adopted as an alternative method to expose the embedded CNPs within the AAO matrix. This approach proved particularly effective in removing excess amorphous carbon that accumulated on the AAO surface during CVD growth. Using a soft polishing pad and hard alumina abrasive slurry, the sample was polished at a speed of 125 rpm for 2 min, allowing gradual material removal without damaging the underlying nanotubes. The mechanical action preferentially removed the overgrown carbon layer due to its relatively weaker adhesion and lower mechanical strength compared to the

oxide matrix. Moreover, the flat polishing motion ensured uniform thinning of the AAO surface, which helped bring the CNPs' tips closer to the surface for subsequent etching. This technique was found to be affordable, gentler than ion milling, and offered better control in eliminating surface residues, especially when amorphous carbon masked pore openings. FESEM imaging confirmed improved surface cleanliness and clear CNP exposure post-treatment. In order to evaluate the structural integrity of vertically aligned CNPs after the AAO removal, chemical etching was performed for varying durations: 2, 5, 8, and 10 min using 0.5 M NaOH. FESEM analysis in Figure 5.16(a-d) revealed that short etching times (2–5 min) successfully removed a portion of the alumina while maintaining the upright orientation and alignment of the CNPs, while longer duration led to agglomeration of CNP tips.

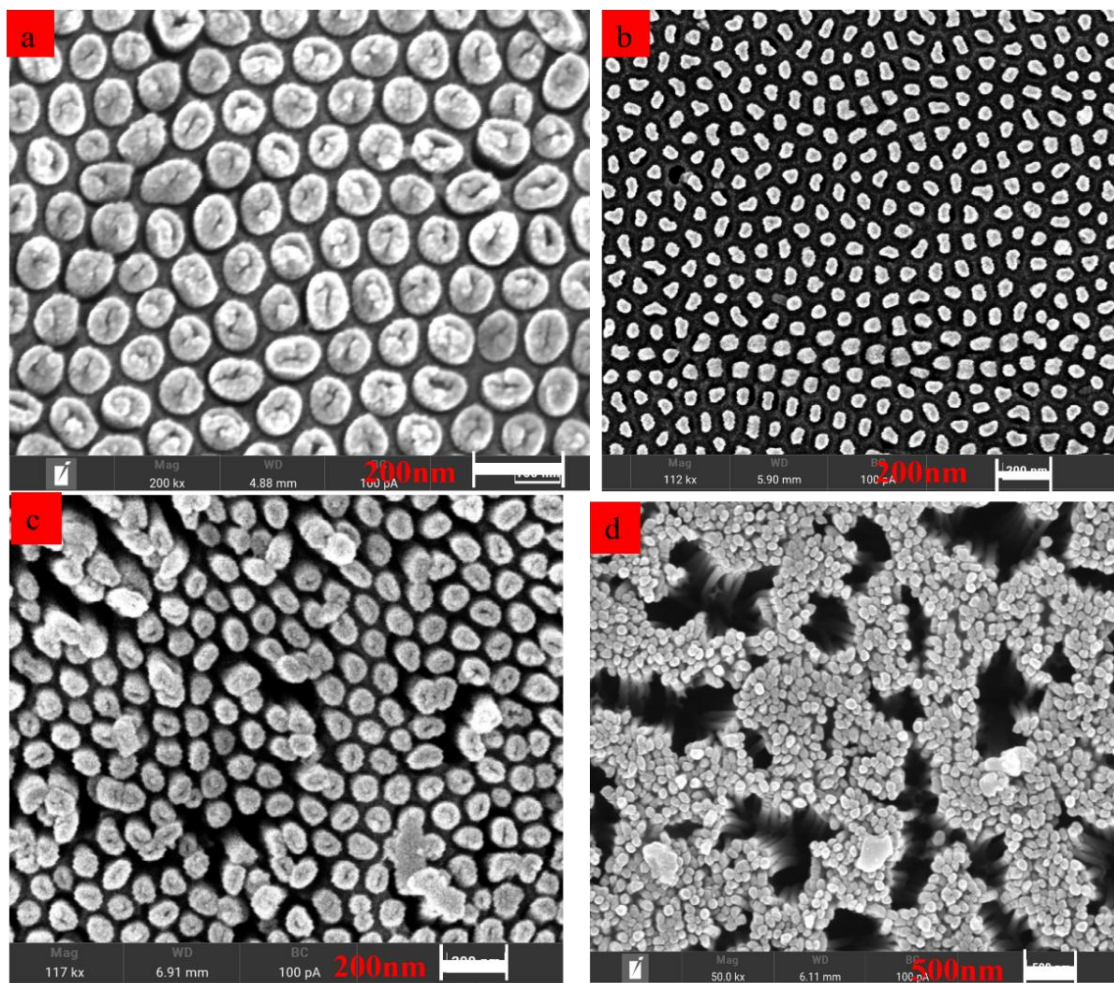


Figure 5.16 FESEM image of mechanically polished carbon nanopillars after 0.5M NaOH etching (a) 2 min, (b) 5 min, (c) 8 min, (d) 10 min.

However, as the etching duration increased beyond 8 min, a noticeable loss of vertical integrity was observed. The CNPs began to exhibit signs of bending, collapsing, or aggregation, particularly in regions where neighbouring tubes lacked adequate spacing or support. This behaviour is attributed to the gradual loss of the supporting oxide matrix, which typically stabilizes the individual nanotubes. With extended etching, surface tension forces during drying, and the absence of structural confinement, led to mechanical instability. Therefore, optimizing the etching time is critical to achieving sufficient AAO removal while preserving the vertical alignment necessary for mould-based applications. The EDX elemental mapping of the AAO/CNPs sample revealed a strong carbon signal uniformly distributed across the examined area, confirming successful exposure of CNPs after partial etching. In addition to carbon, distinct aluminium and oxygen peaks were also observed, indicating the partial presence of the alumina matrix in Figure 5.17. This suggests that the etching process did not completely remove the oxide layer but selectively exposed the CNPs while retaining structural support in some regions. The coexistence of carbon with residual alumina provides further evidence of CNPs embedded within the porous AAO and validates that the controlled etching.

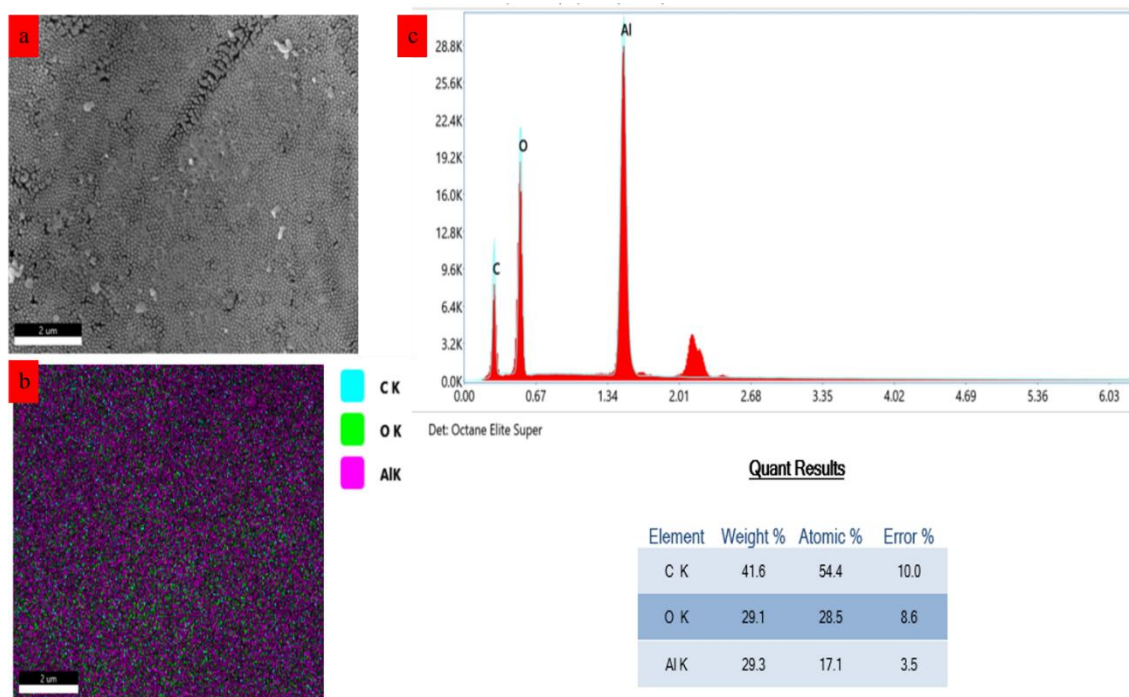


Figure 5.17 (a, b, c) EDX area mapping of CNPs inside AAO.

5.4 Structural characterization of CNPs

In order to evaluate the morphology and uniformity of carbon nanostructures grown within the AAO matrix, a combination of Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), and Raman spectroscopy was conducted. AFM was used to assess the surface topography after partial AAO etching. As illustrated in Figure 5.18(a, b), the AFM scans revealed a densely packed array of vertically oriented nanostructures. The inter-pillar spacing was found to be around 25 nm, closely matching the diameter of the AFM tip (~ 20 nm), which posed certain challenges in accurately measuring the height of the structures within the narrower regions. Despite this, an average vertical height of approximately 150 ± 20 nm was recorded following a 5 min etching in 0.5 M NaOH, suggesting partial AAO removal and exposure of the carbon nanostructures from the top surface. The consistent spacing and height observed over a large area indicate a high degree of uniformity in the CNP growth throughout the AAO template.

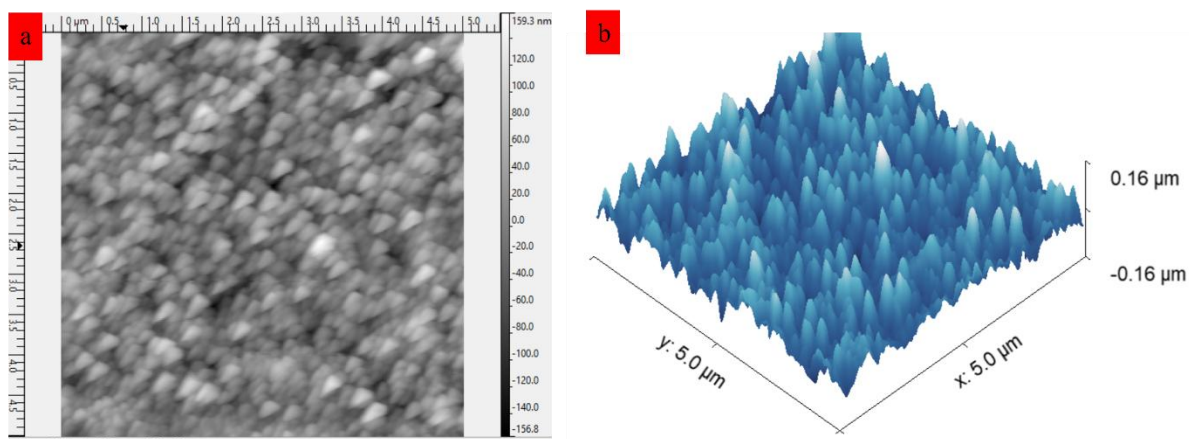


Figure 5.18 (a, b) AFM 3D topography of CNPs.

To further explore the internal structure and wall characteristics of these nanostructures, TEM analysis was conducted on isolated CNPs. The AAO/CNP composite was first subjected to a sequential chemical etching process to release the embedded structures. Initially, the underlying aluminium substrate was dissolved using 0.5 M CuCl_2 , followed by an extended etching step in 1 M NaOH for 30 min to fully remove the remaining AAO. The released nanostructures were

then dispersed in ethanol via ultrasonication to ensure adequate separation. A droplet of the dispersion was deposited onto a carbon-coated copper grid, allowing for individual nanotubes to be observed under TEM. As shown in Figure 5.19(a, b), the TEM micrographs confirmed the tubular morphology of the nanostructures. The outer diameter of the individual carbon nanotubes was consistently measured at $\sim 76 \pm 3$ nm, while the wall thickness was found to be around 15 nm. The hollow core, along with clearly distinguishable concentric walls, confirms the multi-walled nature of the nanotubes and supports the hypothesis that carbon deposition occurred along the pore walls rather than entirely filling them.

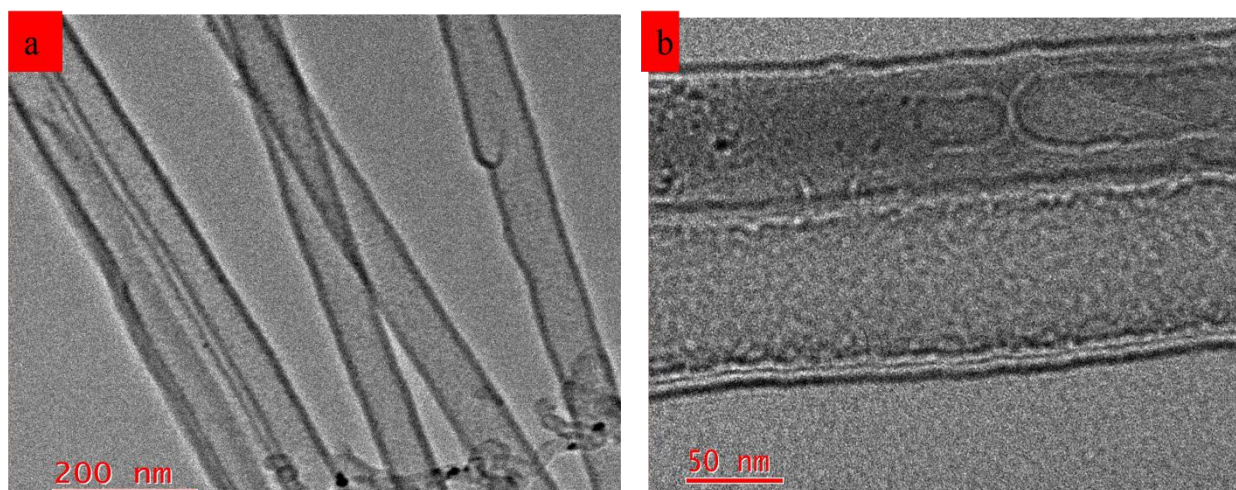


Figure 5.19 (a, b) TEM image of CNP.

The chemical structure and degree of crystallinity of the carbon material were further validated through Raman spectroscopy. Two prominent peaks were identified: one at ~ 1350 cm^{-1} , corresponding to the D-band, and another at ~ 1590 cm^{-1} , representing the G-band [124]. The D-band arises due to defects and disorder in the carbon structure, associated with the breathing modes of sp^2 carbon atoms in rings, particularly near the edges or imperfections. In contrast, the G-band originates from the E_{2g} phonon stretching mode of graphitic carbon, indicative of ordered sp^2 -bonded carbon domains [125]. The ratio of the G-band to D-band intensity ($I_G/I_D \sim 1.3$) suggests a moderately high degree of graphitization, implying that the deposited carbon is of good structural quality with relatively low defect density, an essential parameter for

mechanical robustness and electrical properties in device applications. Figure 5.20 shows the Raman spectrum of the CNP-exposed sample.

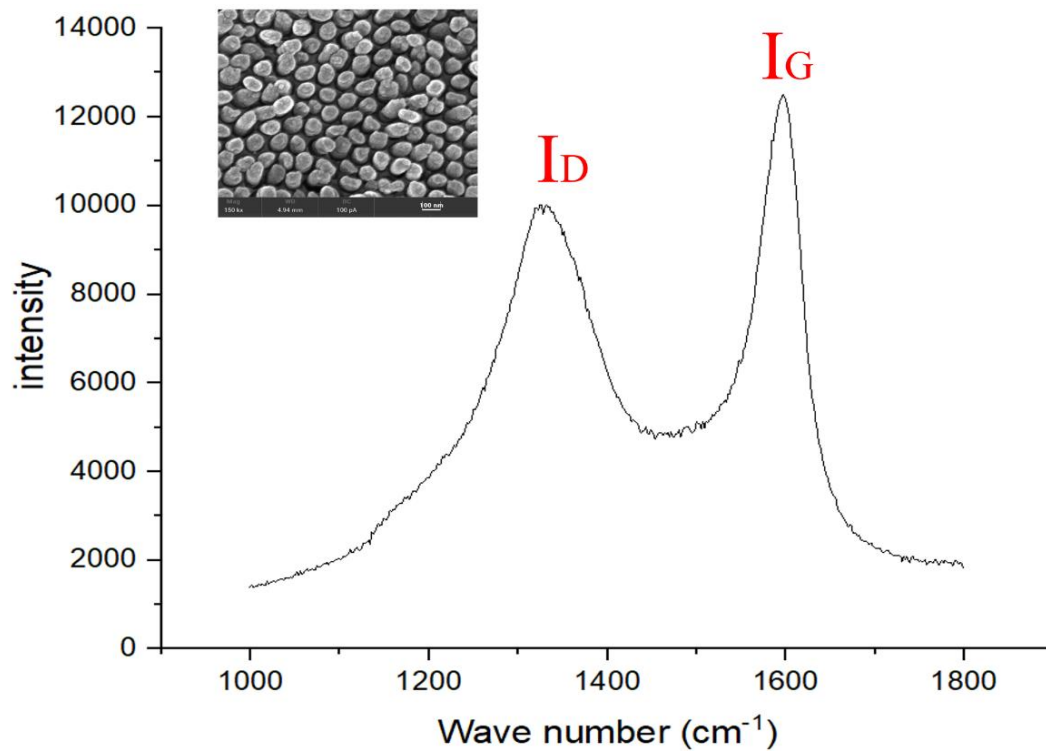


Figure 5.20 Raman spectra of CNPs.

Interestingly, despite being grown inside confined pores, the carbon nanostructures did not appear to have open tubular ends at the surface after etching. This structural feature is particularly advantageous for hot embossing applications, where a mechanically stable, closed-end pillar structure enhances pattern transfer fidelity and minimizes material deformation during the imprinting process. Collectively, the AFM, TEM, and Raman analyses confirm the successful formation of vertically aligned, tubular carbon nanostructures with controlled dimensions and good crystallinity inside the AAO matrix. The uniform inter-pillar spacing, consistent tube geometry, and low structural defect ratio highlight the reliability of the synthesis process and support the potential of these AAO-templated CNPs in applications ranging from nanoimprint lithography to electrochemical systems. The characterization techniques not only validate the growth mechanism but also provide a comprehensive understanding of the morphology and structural integrity of the fabricated nanostructures.

5.5 Summary

In this chapter, the research and development of the AAO and AAO/CNPs hybrid nanostructure were systematically presented. Initially, AAO was optimized with anodization parameters, such as temperature, duration, in order to obtain a highly ordered pores morphology. Additionally, the AAO membrane was developed separately. Subsequently, the AAO template served as a scaffold for CNPs growth using the CVD system. The growth parameters, including catalyst deposition duration, gas composition, and gas flow rate, and growth duration were optimized to obtain vertically aligned CNPs within the nanopores of AAO. This chapter is having following key findings

- Hexagonally ordered nanopores can be obtained at 10°C, 45V for 0.3 M oxalic acid electrolyte.
- 2 h of anodization yields a membrane thickness of 10 μm with an average pore size of 75 nm after 90 min pore widening process.
- Barrier layer thinning is needed to deposit the catalyst in the bottom of nanopores, a 2.1 V for 1 min Ni deposition is sufficient to support CNPs growth.
- A 20 sccm acetylene flow, with 200 sccm of carrier gas for 4 h duration at 625°C is optimum to infiltrate carbon inside AAO and growth of carbon nanopillars.
- Mechanical polishing with moderate speed of 125 rpm, in alumina suspension is a suitable alternative to ion milling, in order to expose CNPs from AAO moulds.
- Five min wet etching in 0.5 M NaOH gives a height of 150 nm CNPs without observing any bending or agglomeration of CNP tips.

Chapter 6

Fabrication and Analysis of AAO and AAO/CNP mould-based nanostructures using hot embossing

Hot embossing (HE) is a versatile and cost-effective nanoimprinting technique widely employed for the replication of micro and nanostructures onto thermoplastic substrates. It relies on the mechanical deformation of polymers under controlled temperature and pressure conditions, allowing the high-fidelity transfer of nanoscale features from a rigid mould. In this chapter, AAO and AAO-assisted vertically aligned carbon nanopillars were explored as nanoimprint moulds for patterning polymer films. The rigid and highly ordered porous structure of AAO makes it suitable for replicating well-defined nanopillar arrays, while the incorporation of CNPs adds height tunability and functional surface features, potentially enhancing the performance of the replicated structures in various applications. This chapter also presents the detailed results and discussion related to the hot embossing process, including replication, optimization of embossing parameters, and characterization of imprinted patterns. The fidelity and reproducibility of pattern transfer using both AAO and AAO/CNP moulds were examined, along with a comparison of structural integrity and dimensional accuracy. This investigation not only demonstrates the suitability of these nanostructured moulds for thermal nanoimprinting but also highlights the potential for scalable fabrication of functional surfaces for advanced applications.

6.1 Glass transition temperature of polystyrene

Differential scanning calorimetry (DSC) was employed to determine the glass transition temperature (T_g) of polystyrene, which provides the critical insight of polymer chain mobility. Glass transition temperature is an essential parameter for thermal nanoimprinting and hot embossing applications. The self-prepared solvent-based PS sheet of 500 μ m was used. The

experiment was conducted using an aluminium pan as the reference material, with an initial PS sample weight of approximately 6 mg. It allows the detection of thermal transitions such as T_g , melting point, and crystallization. In Figure 6.1, a distinct endothermic shift in the heat flow curve was observed at 100°C, where material enters a progressively softening viscoelastic regime rather than undergoing an abrupt transition. This relaxation temperature window governs the balance between sufficient flowability and structural integrity of the polymer. This drop in the baseline indicates a decrease in the heat capacity of the polymer, corresponding to the glass transition temperature of PS. At T_g , the polymer transitions from a rigid, glassy state to a soft, rubbery state, which significantly affects its flow behaviour during embossing. The sharpness and position of the transition confirm the amorphous nature of PS and its suitability for thermal processing.

6.2 Surface Modification of AAO

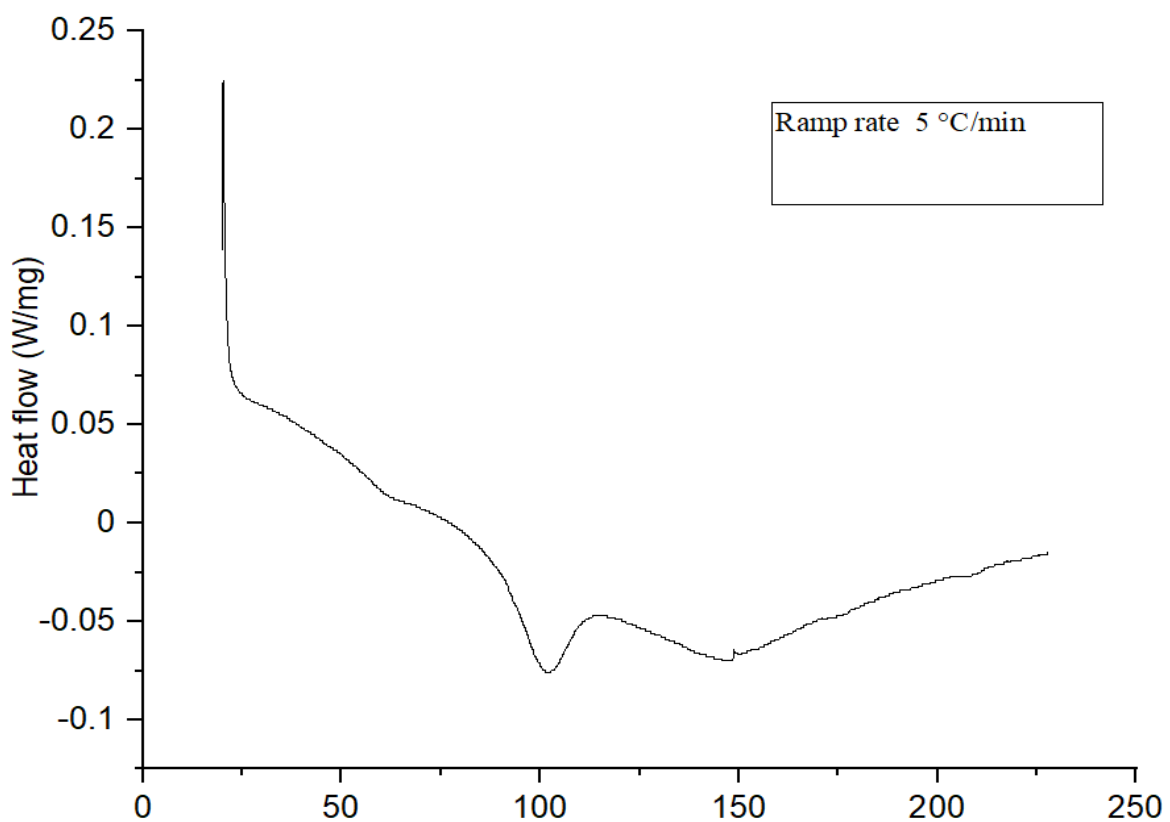


Figure 6.1 DSC curve of polystyrene sheet.

Prior to hot embossing, a surface modification step was essential to ensure defect-free demoulding and preserve the fidelity of transferred nanopatterns. Both bare AAO and CNP-filled AAO moulds underwent fluorinated silanization using trichloro(1H,1H,2H,2H-perfluorooctyl) silane (FOTS) to impart anti-adhesive properties. The as-fabricated AAO surface contains abundant hydroxyl (-OH) groups, which serve as reactive sites for silane molecules. When treated with FOTS in a vapor-phase environment, covalent Si-O-Al bonds are formed between the silane head group and the hydroxylated alumina surface, anchoring the fluorinated tail outward. This results in a hydrophobic, low surface energy layer that significantly reduces adhesion with polymer substrates during embossing. It is well experimented that contact angle measurements post-treatment confirmed the hydrophobicity of the surface, increasing from $\sim 35^\circ$ (untreated AAO) to $>100^\circ$, indicating successful grafting of fluorosilane [126]. This anti-stiction layer played a critical role in clean polymer release without damaging either the nanostructures or the mould.

A time-dependent study was conducted to evaluate the extent of silane penetration and coverage within the nanopores to ensure uniform coverage across the entire AAO mould surface [127]. Four different exposure durations of 5, 10, 20, and 30 min were used while maintaining the treatment at 120°C . At shorter exposure times (5–10 min), the anti-adhesive layer formed predominantly on the top surface of the AAO, leaving the pore openings relatively clear. However, with increased exposure time (20–30 min), partial filling of the pores was observed, indicating diffusion of the silane molecules into the nanochannels. At 30 min, all pores appeared to be completely filled, potentially obstructing the mould's pattern transfer efficiency. Hence, 5 min treated AAO surface was utilized for embossing applications. The FESEM image in Figure 6.2(a-e) was employed to visualize the surface morphology of post-silanization.

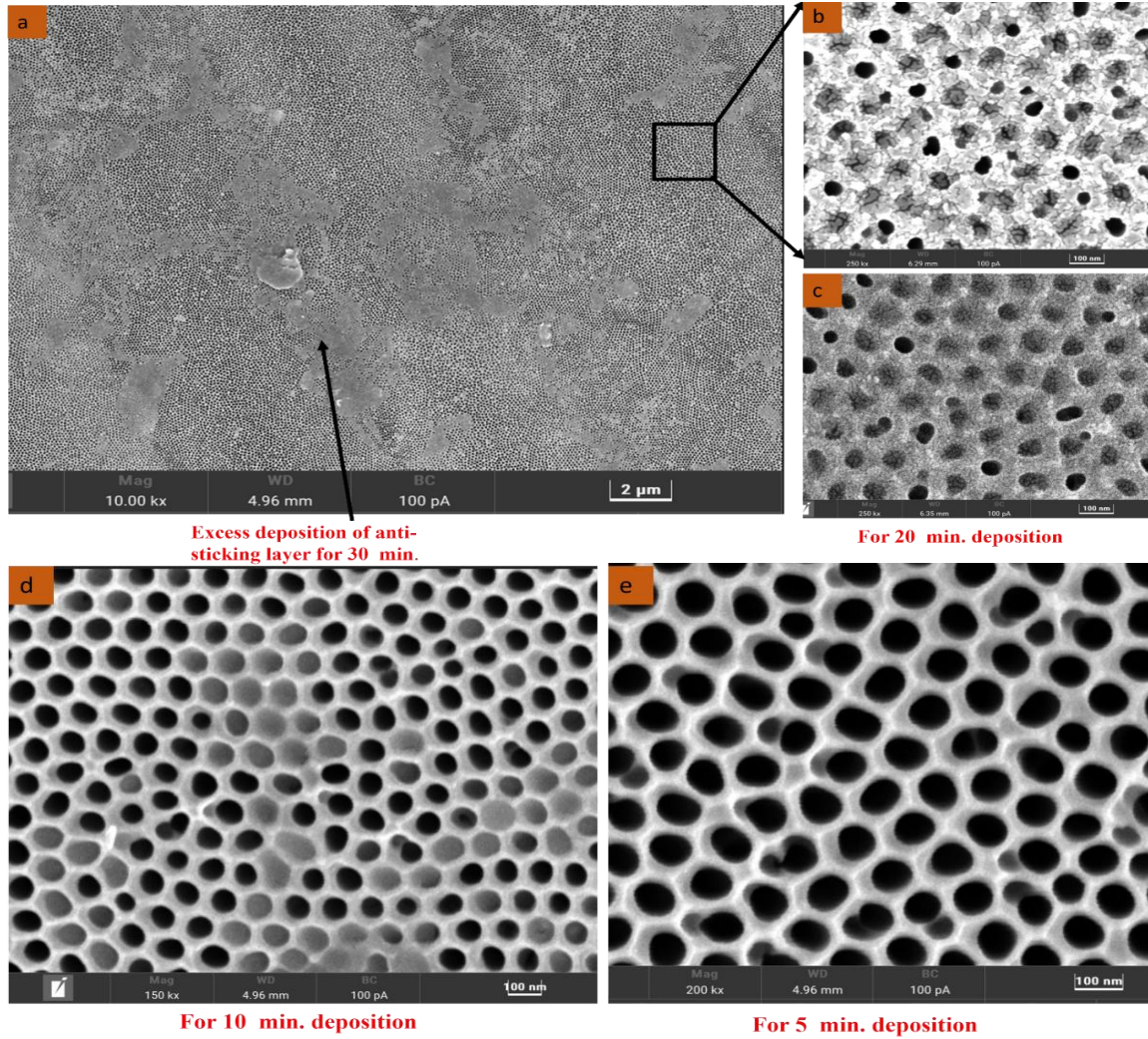


Figure 6.2 FESEM image of AAO after surface modification with silane (a, b) 30 min deposition, (c) 20 min, (d) 10 min, (e) 5 min (b, c, d, e scales are 100 nm).

6.3 Surface morphology of polystyrene nanopillar fabrication using hot embossing

The replication of polymeric nanopillar arrays was successfully achieved using an ideally optimized ordered anodic aluminium oxide template with an average pore diameter of 78 nm and an interpore distance of 125 nm. Based on the limitations observed during preliminary embossing trials, an L9 orthogonal array design of experiments was employed to systematically investigate the influence of embossing parameters on the morphology of PS nanopillars. This design enabled the study of three critical factors, embossing pressure, temperature, and

embossing time, at three levels each, reducing the total number of required experiments while maximizing parameter coverage. Three different levels of embossing pressure are (1/5/10 MPa), temperatures (110°C/110°C/120°C), and holding time (1/2/3 min). The embossing pressure values in the L9 experimental design were strategically selected based on theoretical considerations derived from the Hagen–Poiseuille and capillary flow equations. These models provide insight into the behaviour of viscous polymer flow within confined nanoscale geometries such as the cylindrical pores of the AAO template. According to the Hagen–Poiseuille equation, the volumetric flow rate Q of a polymer into a pore is directly proportional to the applied pressure difference ΔP and the fourth power of the pore radius r , and inversely proportional to the polymer viscosity η and pore length L .

$$Q = 8\eta L \pi r^4 \Delta P \quad (6.1)$$

$$\Delta P = \frac{4\eta L^2}{\pi r^2} \quad (6.2)$$

This relationship highlights how even small pressure increases can dramatically improve polymer infiltration, especially in high-aspect-ratio nanostructures. In parallel, the capillary equation also plays a role, where capillary pressure P_c is inversely proportional to the pore radius and governed by surface tension effects. Therefore, the required embossing pressure is the sum of capillary resistance and viscous resistance, given by equation 6.4 [128].

$$P_c = \frac{2\gamma \cos\theta}{r} \quad (6.3)$$

$$P_{\text{emb}} = \frac{4\eta L^2}{\pi r^2} + \frac{2\gamma \cos\theta}{r} \quad (6.4)$$

Here, γ is the surface tension and θ is the contact angle. In nanoconfined geometries like AAO, capillary forces alone may be insufficient for complete filling, thus requiring externally applied pressures exceeding the capillary threshold. After considering the optimum contact angle of

polystyrene on the AAO surface, the minimum embossing pressure required for successful nanopore infiltration was estimated to be approximately 1 MPa. This value was derived by combining insights from capillary pressure analysis and the wettability behaviour of PS. Thus, applying an external pressure equal to or greater than this capillary pressure is essential. Based on these parameters, 1 MPa was determined as the minimum effective pressure required to initiate pore filling without causing excessive deformation or thermal degradation. This pressure serves as a baseline in the embossing process, ensuring at least partial feature replication (such as nanolens formation), while higher pressures (5 MPa and 10 MPa) are used to achieve deeper filling and high-aspect-ratio (HAR) structures. The goal was to identify optimal conditions for achieving high-aspect-ratio, vertically aligned nanopillars with minimal deformation. The highly uniform and symmetric moth-eye-type high-aspect-ratio PS nanopillars were obtained under an optimized hot embossing pressure of 5MPa. The imprinting behaviour of PS was systematically studied to understand the effect of process conditions on the fidelity and morphology of the resulting nanostructures. Using the L9 matrix, it was found that pressure continued to play a dominant role in polymer penetration. However, temperature also showed a significant influence, as embossing temperature increased from 100°C to 120°C, the viscosity of polystyrene decreased, improving its mouldability and enhancing nanopore filling. At lower temperatures, the radial shear force generated by the mould–polymer interface was insufficient, resulting in underfilled or collapsed structures. In the first set of experiments, the embossing pressure was varied for 1 MPa, 5 MPa, and 10 MPa at a constant glass transition temperature of 100°C. At 1 MPa, the aspect ratio (AR), defined as the height-to-width ratio of the nanopillar, was approximately 1, which indicates minimal polymer penetration into the nanopores, resulting in shallow dome-like features resembling a nanolens array. Increasing the pressure to 5 MPa led to improved polymer infiltration and the formation of well-ordered, symmetric, and vertically aligned nanopillars resembling a moth-eye pattern, known for their

uniform spacing and moderate aspect ratios. At the highest pressure of 10 MPa, the polymer filled the nanopores almost completely, producing high-aspect-ratio nanopillars with significantly increased height, though slight deflection was observed due to mechanical instability. Increasing the embossing pressure to 5 MPa and 10 MPa significantly enhanced polymer infiltration, resulting in nanopillars with ARs of ~ 4 and ~ 20 , respectively, as shown in Figure 6.3(a–c). These results highlight how embossing pressure governs the fidelity of nanostructure transfer, low pressure favours surface patterning, moderate pressure promotes uniform nanorod replication, and high pressure enables deep pore filling.

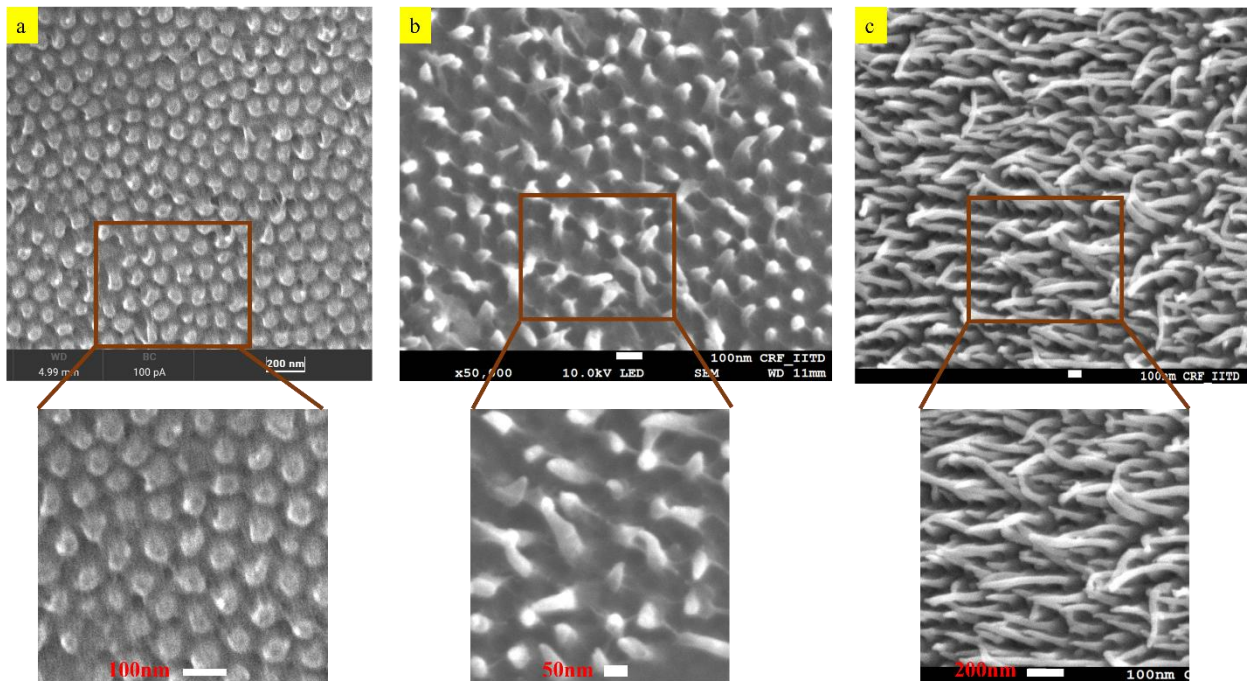


Figure 6.3 FESEM image for different experiment runs (a) 1 MPa, 100°C, 1 min holding time, (b) 5 MPa, 100°C, 3 min, (c) 10 MPa, 100°C, 2 min holding time.

The remaining six experiments in the L9 design, conducted at elevated temperatures of 110°C and 120°C, further validated the influence of thermal softening on nanostructure formation, as shown in the FESEM image of Figure 6.4(a–e). As the embossing temperature increased, the viscosity of polystyrene decreased, significantly improving its flow behaviour within the nanopores [129]. This enhanced mouldability facilitated better infiltration, especially at moderate pressures, resulting in the successful replication of vertically aligned moth-eye-type

nanopillar arrays. At 110°C and 5MPa, partial improvement in pillar height was observed, indicating the onset of sufficient polymer softening. However, at 120°C, the replication quality improved substantially across multiple pressure–time combinations, producing uniform and defect-free moth-eye structures in Figure 6.4(c, d). For 10MPa, 110°C, and 120°C tilted nanopillar was accomplished with connected tips as depicted in Figure 6.4(e, f).

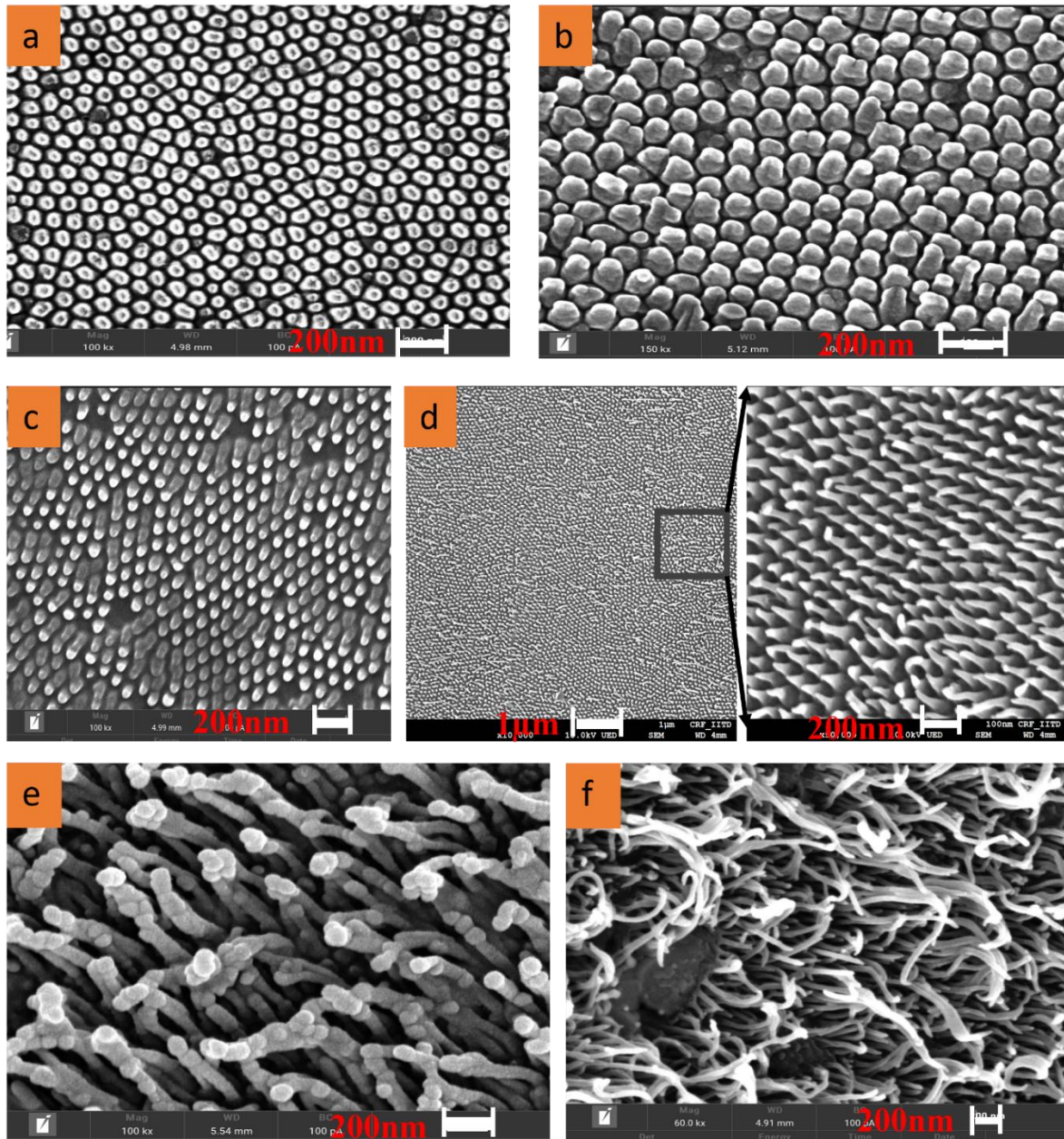


Figure 6.4 FESEM image of PS nanopillars for different embossing process parameters (a) 1MPa embossing pressure, 110°C holding temperature, 2 min, (b) 1MPa, 120°C, 3 min holding time (c) 5MPa, 110°C, 2 min holding time, (d) 5MPa, 120°C, 1 min holding time, (e) 10MPa, 110°C, 3 min holding time, (f) 10MPa, 120°C, 1 min holding time.

These findings emphasize the importance of temperature in fine-tuning the embossing conditions, where an optimal balance between thermal energy and applied stress is necessary to fabricate high-fidelity nanostructures. The minimum temperature value was selected by calculating T_g , and a maximum of above 120°C gives improper demoulding in the preliminary experiment. Thus, the L9 design confirmed that raising the embossing temperature to 110–120°C significantly benefits the formation of moth-eye nanopillar arrays by lowering polymer viscosity and enabling more efficient pore filling.

Moreover, atomic force microscopy in tapping mode was used to analyze the shape of the polystyrene nanopillars. A sharp AFM tip with a 10 nm curvature radius and a spring constant of 10 N/mm was employed for 3D imaging of polystyrene NPs. As illustrated in Figure 6.5(a, b), the nanopillars exhibit a distinct conical or funnel-like geometry, with the tip diameter noticeably smaller than the base. This shape results from the gradual widening of the AAO pore structure during chemical etching, which leads to anisotropic replication. The AFM analysis confirms the successful transfer of this tapered morphology into the PS nanopillars.

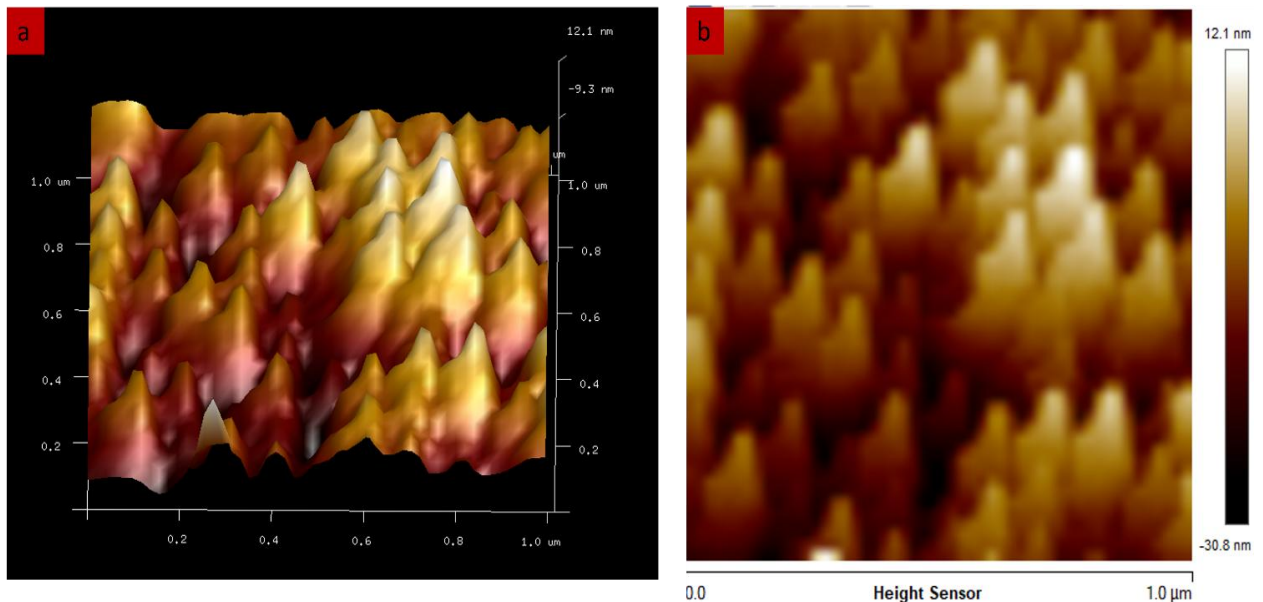


Figure 6.5 AFM image of PS nanopillars for moth-eye texture (a) 3-D view (b) 2-D view.

6.4 Replica of CNPs on polystyrene for nanohole fabrication

Nanoscale hole arrays were imprinted onto polystyrene sheets across nine experimental combinations using a hot embossing setup. The same L9 approach was used as for nanopillars with two factors and three levels. The levels for embossing pressure (1/3/5 MPa), temperature range (90°/100°/110°C) are considered to perform 9 experiments. The mould comprised AAO integrated with carbon nanopillars, prepared under optimized mechanical polishing conditions, followed by chemical etching in 0.5 M NaOH for 5 min. Silane-treated AAO/CNPs for 5 min were used as an embossing mould with a pillar height of 150 nm. It was observed that insufficient preheating time prevented the softening of the polymer, while exceeding 5 min led to polymer swelling and deformation. Therefore, a duration of 5 min was used to ensure uniform heat distribution throughout the sheet volume. The holding time during embossing was standardized at 2 min after the mould cavity was filled, as variations in this parameter showed negligible influence during preliminary tests. Embossing pressure and temperature parameters were finalized based on initial trials. It was noted that temperatures above a certain limit caused the polystyrene to adhere strongly to the mould during demoulding, leading to the upper temperature limit being set at 110°C. The applied embossing pressures were deliberately chosen to be higher than the yield strength of PS at its glass transition temperature to ensure effective pattern transfer. To minimize shrinkage and facilitate easy demoulding, a viscous separation approach was adopted [130]. A sudden application of embossing load was preferred over gradual loading, considering that sufficient preheating made the polymer sufficiently soft, enabling successful pattern transfer within a short holding time of 2 min. The FESEM images shown in Figure 6.6(a) demonstrate that at a low pressure of 1 MPa and 90°C, the nanopillars did not fully penetrate the polymer due to inadequate pressure. However, increasing the temperature to 110°C, as shown in Figure 6.6(b), led to the formation of partially regular hexagonal pores (marked with circles), although uniformity was compromised due to

insufficient pressure. As the pressure was raised to 3 MPa, the nanopillars began penetrating the softened polymer more effectively, and a hexagonal nanohole pattern above T_g was observed in Figure 6.6(d). However, increasing the pressure further to 5 MPa led to a deterioration in the quality of the replicated texture and the appearance of broken pillars, as visible in Figure 6.6(f). These defects likely arose from carbon pillars grown in irregular or defective pores, which either lacked full pore coverage or had tapered structures that reduced their mechanical stability.

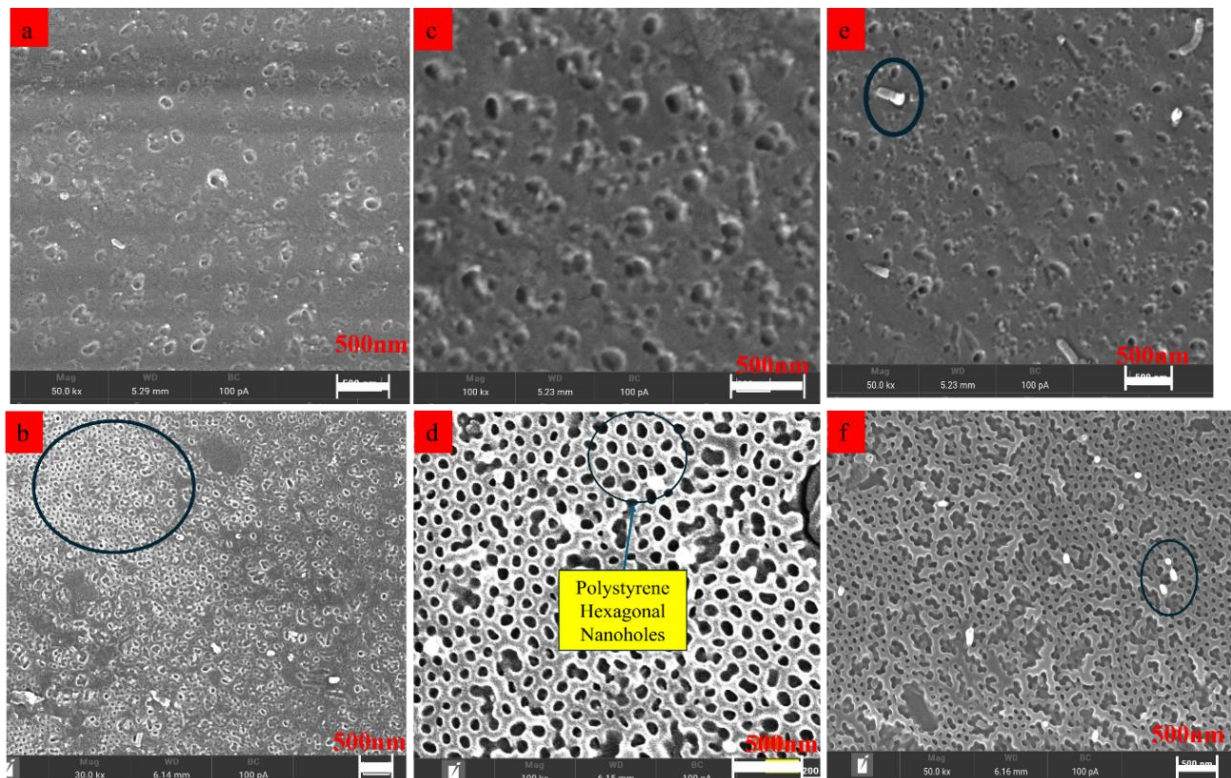


Figure 6.6 FESEM image of nanoholes in polystyrene (a) 1 MPa embossing load, 90°C temperature, (b) 1 MPa embossing pressure, 110°C temperature, (c) 3 MPa embossing pressure, 90°C temperature, (d) 3 MPa embossing pressure, 110°C temperature, (e) 5MPa embossing pressure, 100°C temperature, (f) 5MPa embossing pressure, 110°C temperature.

Moreover, the roughness of nanoholes in polystyrene was calculated, which is average value of ~ 7 nm with a 50 nm hole depth. Figure 6.7(a-d) shows the 3D AFM image for nanoholes generated by WSxM for a proper visualization of holes arrangements, whereas Gwyddion software was utilized to calculate all roughness parameters and texture profile of holes. In order to evaluate the structural reliability and potential for reuse of the AAO/CNP mould in hot

embossing applications, a detailed mechanical characterization of the embedded carbon nanopillars was carried out using AFM with force modulation mode.

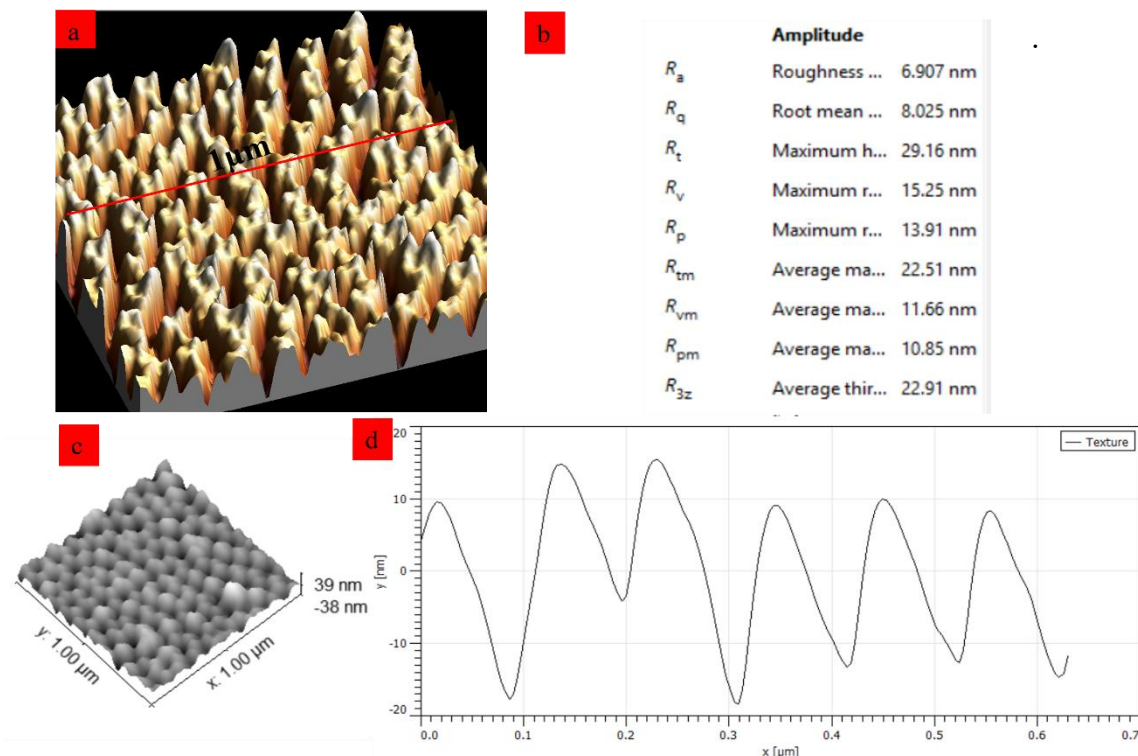


Figure 6.7 (a) AFM image of WSxM-generated 3D image, (b, c, d) roughness values and profile of nanoholes texture measured in Gwyddion software.

6.5 Mechanical properties of the AAO/CNPs mould for reusability

In order to evaluate the structural reliability and potential for reuse of the AAO/CNPs mould in hot embossing applications, a detailed mechanical characterization of the embedded carbon nanopillars was carried out using atomic force microscopy in force modulation mode, as illustrated in the schematic of Figure 6.8(a, b). This approach enabled the analysis of individual nanopillars by applying a controlled force with a precision AFM tip. When the tip made contact with the top surface of the CNPs, the instrument recorded force versus piezoelectric displacement data. These raw measurements were then mathematically converted into force versus indentation depth curves, which provided a basis for assessing the deformation

behaviour of the nanopillars under applied loads. Figure 6.8(d) depicts the AFM contact mode image of nanopillars, where 5 different indentations were made for each CNPs.

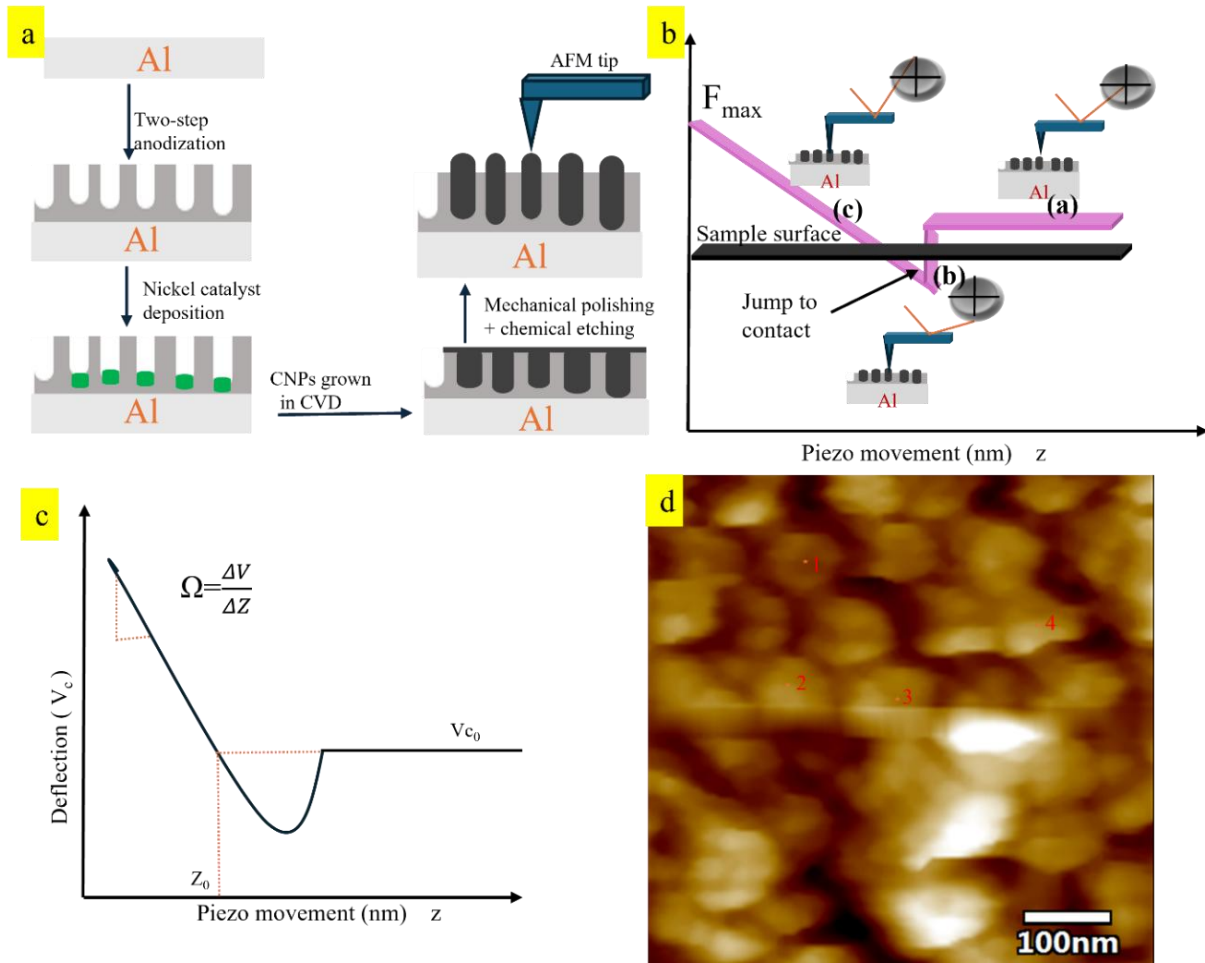


Figure 6.8 (a) Schematic of AAO /CNPs mould (b) AFM schematic of probe nanopillar interaction (c) graphical representation of cantilever deflection – piezo movement (d) contact mode AFM image AAO/CNPs.

Once drawing the F-d plot, Hertz contact theory is applied owing to their hard and stiff properties. The AFM tip of silicon ($E_1 = 120$ GPa, $\nu_1 = 0.22$), and CNP's effective elastic modulus can be calculated by using the Hertz model in the elastic region by following the relations in equations 6.5 and 6.6, whereas ν_1 and ν_2 are Poisson's ratios of the AFM tip and CNP, respectively. The slope of the $F-d^{3/2}$ curve gives an effective elastic modulus [131,132].

$$F = \left(\frac{4E_{eff}}{3}\sqrt{R}\right)d^{3/2} \quad (6.5)$$

$$\frac{1}{E_{\text{eff}}} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \quad (6.6)$$

$$\text{Hardness } H = \frac{F}{\pi r d} \quad \text{and stiffness is given by } K = \frac{dF}{dd} = 2E_{\text{eff}} R^{1/2} \sqrt{d}$$

From this model, the elastic modulus of the nanopillars was determined from the slope of the plot of Figure 6.9(a, b), which is 15 GPa, suggesting that the CNPs exhibit a high degree of stiffness and resistance to elastic deformation. Alongside this, the hardness was estimated to be about 2.5 GPa, which reflects the material's resistance to localized plastic deformation or permanent indentation. Additionally, the stiffness of the pillars was found to be approximately 119 N/m for an indentation depth of 2 nm, indicating their ability to resist displacement under an applied load. These mechanical properties strongly support the hypothesis that the carbon nanopillars embedded within the anodic aluminium oxide framework possess sufficient strength and rigidity to withstand the thermal and mechanical stresses encountered during repeated embossing processes.

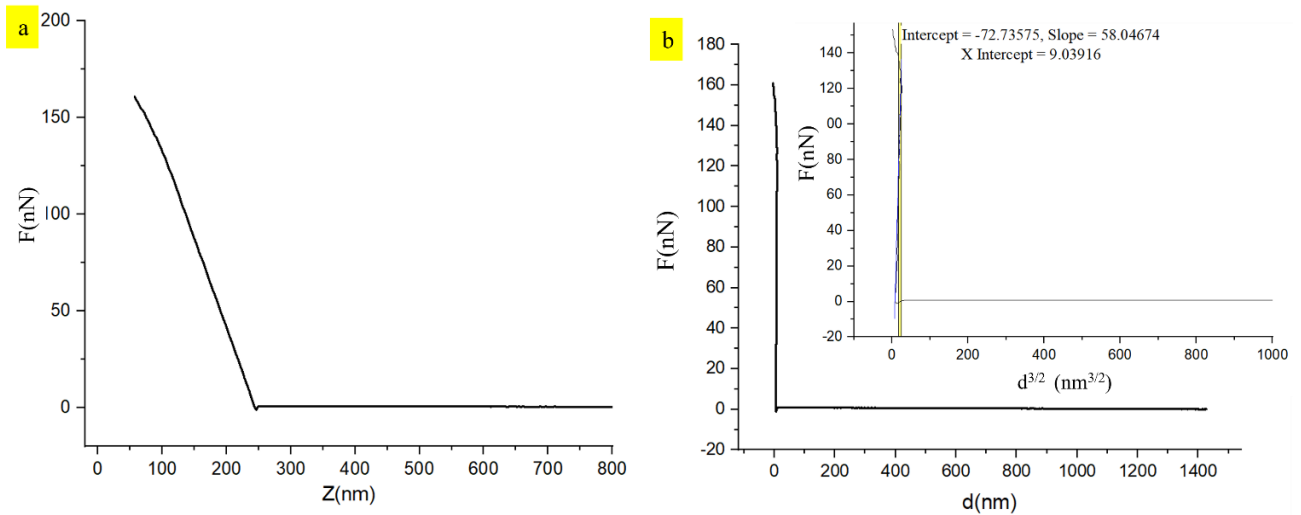


Figure 6.9 (a) F vs Z piezo movement plot (b) F vs. d plot mode AFM of CNPs.

Notably, the measured elastic modulus of the CNPs far exceeds the yield strength of polystyrene of 50 MPa. However, at the viscoelastic point, which is the critical point where the polymer softens and becomes mouldable. At its glass transition temperature, this value is almost negligible as compared to the CNPs' calculated value listed in Table 6.1. This substantial

difference in mechanical strength ensures that the mould features retain their shape and dimensional integrity even when subjected to the elevated temperatures and compressive loads necessary for nanopatterning thermoplastic surfaces like polystyrene. Moreover, the high stiffness and hardness values imply that the CNPs are not only resistant to wear but also unlikely to experience structural failure, such as buckling or breaking, during the embossing cycles. This durability is particularly important for applications involving multiple replication cycles, where the fidelity of the mould pattern must be preserved to ensure consistent nanostructure formation on the polymer surface. The AFM-based nanoindentation analysis thus provides crucial evidence of the robustness and reusability of the AAO/CNP mould, making it a promising candidate for high-throughput fabrication of nanoscale features using thermoplastic materials.

Table 6.1 AFM-based CNPs mechanical properties

Mechanical properties	Formula	Values	Comparison with existing Values
Young's modulus (E)	Slope (C) = $58 \times 3.16 \times 10^4 \text{ N/m}^{3/2}$ (unit conversion) $E_{\text{CNP}} = 15 \text{ GPa}$	15 GPa	$E = 2.7 \times 10^4 (R)^{-1.6} \text{ MPa}$, where R is $\frac{I_D}{I_G}$ of MWCNTs ~42 GPa [133] E = 5-50 GPa for CVD-grown MWCNTs [134]
Depth of penetration (d)	$F = C \times d^{3/2}$	2 nm	
Hardness (H) and stiffness (K)	$H = \frac{F}{\pi r d}$ and $K = 2E_{\text{eff}} R^{1/2} \sqrt{d}$	2.55 GPa and 120 N/m	

6.6 Summary

The following chapter shows the robustness and reusability of AAO and AAO/CNPs mould for the imprinting of nanofeatures in polystyrene counterparts. This chapter have the following key findings.

- The glass transition temperature of polystyrene can be calculated through the DSC technique, which is 100°C.
- In order to perform easy demoulding, vapor phase treatment of AAO mould is adequate for 5 min duration without any pore filling.
- The replication of a large area of polystyrene nanostructures were performed in a hot embossing process with an AAO mould of 75 nm diameter. At 1 MPa, a nanolens array was replicated uniformly, while high pressures of 5 MPa, 10 MPa enabled the transfer of moth-eye structure and high aspect ratio NPs.
- The AAO/CNPs mould employed at 3 MPa pressure and 110°C temperature proved effective for nanohole texturing on the polystyrene surface.

Chapter 7

Application of AAO/CNPs and polystyrene nanostructured surfaces

In this chapter, research and development efforts are directed towards demonstrating the multifunctional applications of AAO/CNPs and hot embossed polystyrene nanostructures. These nanostructured surfaces exhibit unique optical, wetting, and electrochemical properties that make them suitable for advanced technological applications. By tuning the morphology and surface characteristics of PS nanostructures, it can simultaneously offer self-cleaning and antireflective behaviour, while enhancing surface-enhanced Raman scattering (SERS) performance, and improving charge storage capability in supercapacitors by AAO/CNPs nanostructures. Such multifunctionality arises from the synergistic combination of ordered nanostructures, high aspect ratio features, and conductive or plasmonic modifications. The following sections present a detailed discussion of each application, highlighting the design rationale, experimental results, and device performance outcomes.

7.1 Fabrication of a hydrophobic/self-cleaning surface

Water droplet contact angle (WDCA) measurements were carried out using a drop shape analyzer (Model: KRUSS ADVANCE 1.6.2.0, sessile drop method) on both plain and nanopillar textured polystyrene surfaces. A droplet volume of 3 μL was dispensed at a temperature of 20°C. The wettability characteristics of the surface are strongly influenced by the geometry and scale of the underlying nanostructures. Surface texturing enhances roughness, resulting in an increase in the water droplet contact angle from $\sim 60^\circ$ to the hydrophobic or even superhydrophobic regime [135]. The wettability characteristics of both textured and untextured polystyrene surfaces are analyzed with respect to hot embossing parameters, namely embossing pressure, temperature, and holding time. The experimentally measured contact angles corresponding to different process parameter variations were further compared and validated

against theoretical values. The theoretical estimation of the contact angle is expressed by Equation 7.1 [136]. Furthermore, Figure 7.1 (a-c) illustrates the wetting states corresponding to the Wenzel and Cassie–Baxter models, while (d) depicts the schematic of cylindrical nanopillars, where a denotes the nanopillar diameter and d represents the spacing between nanopillars. Under Wenzel’s wetting regime, the apparent contact angle is represented as θ_w^* , whereas in the Cassie–Baxter state it is denoted as θ_{CB}^* .

$$\cos \theta_c = -1 + \frac{\pi a^2}{4(a+d)^2} (1 + \cos \theta) \quad (7.1)$$

For embossing pressure of 5 MPa, pillar diameter $a = 45\text{nm}$, $d = 65\text{nm}$ and $\theta = 63.1^\circ$

$$\cos \theta_c = -1 + \frac{\pi 45^2}{4(45+65)^2} (1 + \cos 63.1)$$

$$\theta_c = 143^\circ$$

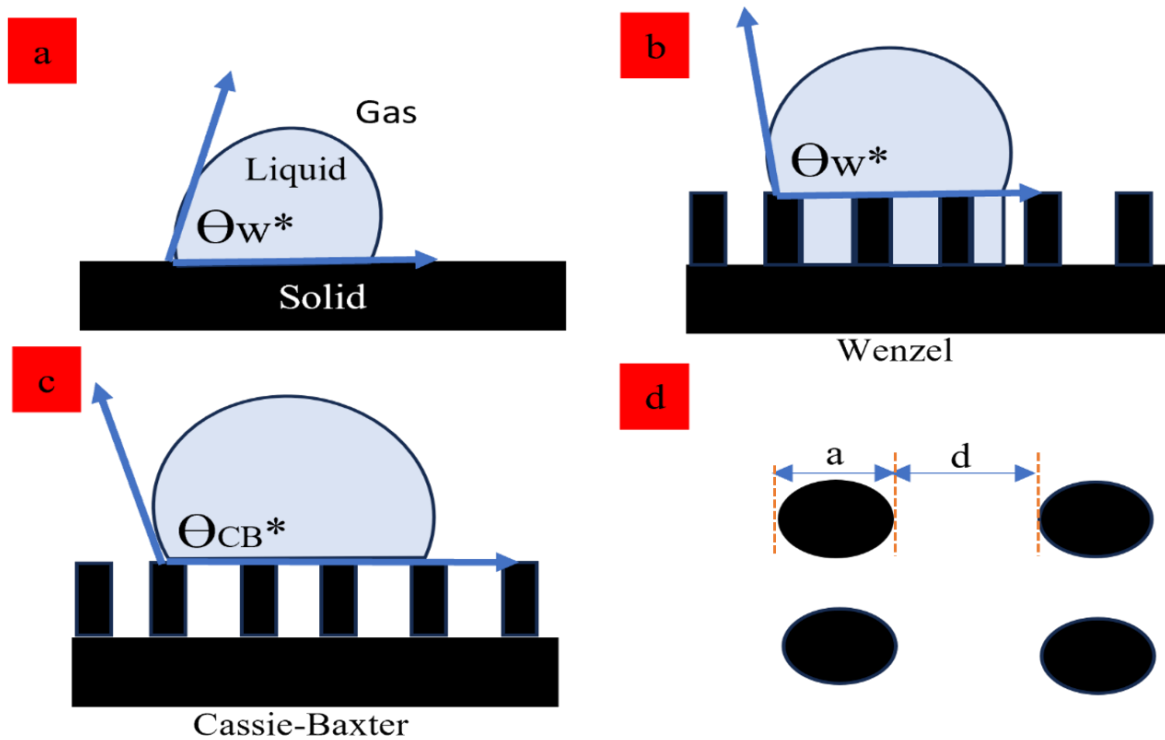


Figure 7.1 (a-d) Schematic of Wenzel and Cassie-Baxter wetting model.

Here, θ represents the intrinsic contact angle on a plain polystyrene surface, while θ_c corresponds to the contact angle predicted by the Cassie–Baxter wetting state. By substituting the measured values of pillar diameter and spacing into equation 7.1, theoretical contact angles

were obtained. The average pillar diameter and inter-pillar spacing were determined using AFM. Table 7.1 presents the experimental and theoretical CA values for different NP morphologies. These calculated values were then compared with experimental results. At a lower embossing pressure of 1 MPa, the AAO mould produced shallow impressions where the polymer cannot penetrate the pores, resulting in smaller pillar gaps, denoted with a nanolens array. Increasing the embossing pressure to 5 MPa led to the development of conical or moth-eye shaped features, which reduced pillar diameter and increased the spacing between pillars, thereby enhancing the contact angle. At 10 MPa, however, the pillars exhibited a higher aspect ratio, called HAR NPs, causing tip bending that widened the pillar diameter and narrowed the spacing due to the fixed interpore distance of the AAO template. For instance, at 1 MPa, the predicted value was 108°, whereas the average of 103°, 110°, and 116° gave a theoretical estimate of 109°. The maximum observed deviation between theoretical and experimental measurements was within 5°, particularly at 10 MPa embossing pressure.

Table 7.1 Water contact angle for plain and textured polystyrene sheet.

Experiment symbol	Experimental contact angle(°)	Pillar diameter (a) (nm)	Distance between pillars (d) (nm)	Theoretical contact angle (°)(from eq 7. 1)	Aspect ratio (l/a)
Plain sheet	63.1				
A1B1C1	103±1.2	80	25	108	Nanolens (1-2)
A1B3C2	110±1.72				
A1B2C3	116±1.34				
A2B1C2	135± 3.2	45	65	143	Moth-eye (4-6)
A2B2C3	142± 2.4				
A2B3C1	153± 1.03				
A3B1C3	125 ± 1.38	65	50	130	HAR(15-20)
A3B2C1	133±3.07				
A3B3C2	120± 2.09				

The Taguchi L9 orthogonal array experimental design was employed to optimize embossing parameters for maximizing the contact angle, considering embossing pressure, temperature, and holding time as input factors. The embossing parameters (A, B, C) and levels (1, 2, 3) are tabulated in the previous section 3.5.4. The experimentally obtained contact angles under these

parameter conditions are shown in Figure 7.2(a-d) for a plain sheet, nanolens array, moth-eye pattern, and high-aspect-ratio nanopillars, respectively.

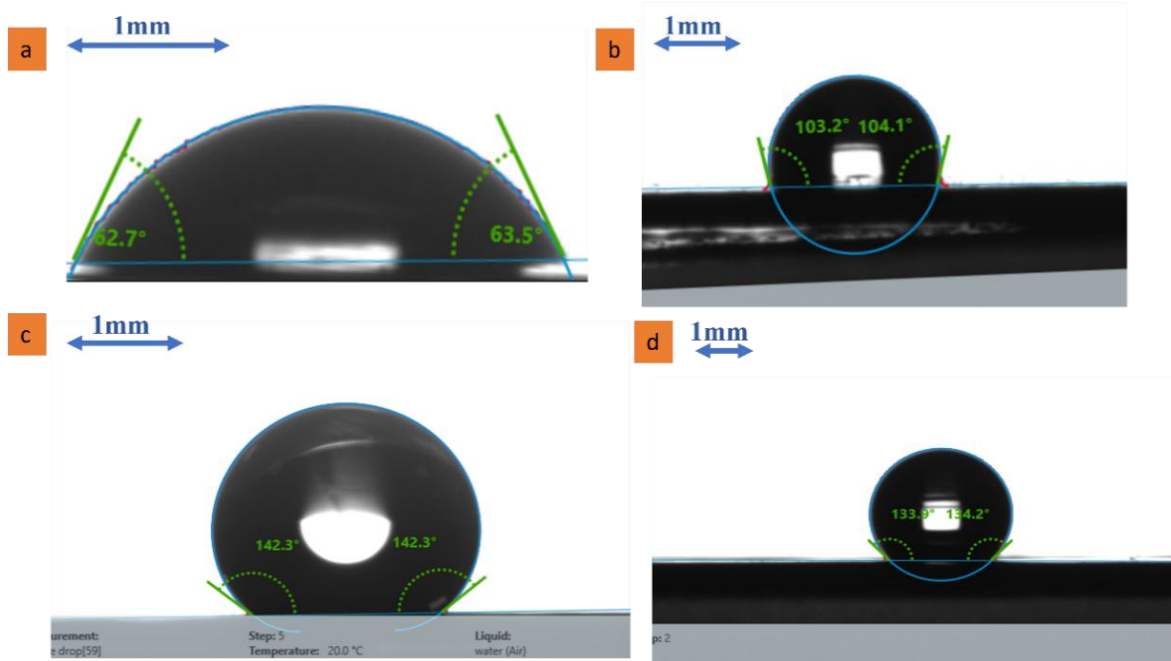


Figure 7.2 Contact angle for (a) Plain polystyrene sheet, (b, c, d) is for nanopillar textured at nanolens (1 MPa), moth-eye (5 MPa), and HAR (10 MPa), respectively.

From the optimization results, an embossing pressure of 5 MPa, temperature of 120°C, and holding time of 1 min were identified as the most suitable conditions to maximize the mean effect plot of contact angle. However, embossing pressure is the main dominating parameter, most influencing the flow behaviour, and requires a minimum value to apply. In contrast, the holding time is the least influencing parameter as described in Equation 3.1, where viscous resistance pressure is proportional to $\frac{l^2}{tr^2}$. Since the radius of the pore is constant, and minimum pressure value was calculated for 2 min for effective imprinting. When increasing the holding time, the aspect ratio improves, thereby leading to contact angle enhancement. However, while reducing the holding time to 1 min, immediately applying pressure, the polymer flows faster due to the accumulated preheat temperature, causing faster cavity filling. Moreover, under such immediate pressure applications, the polymer undergoes sufficient deformation, and once the

mould cavity starts to fill, the pressure value slightly relaxes. When holding time extends from 1 to 2 min, accumulated heat starts to transfer towards the AAO moulds and becomes more balanced. However, prolonged heating beyond 2 min may increase the heat accumulation again and favour the polymer mouldability for deeper penetration. Similarly, while increasing embossing pressure, the pillar aspect ratio increases. When it exceeds 5 MPa, high aspect ratio tilted NPs structures are obtained, as previously discussed in FESEM image (Figure 6.4). In this condition, inter-pillar spacing (d) is reduced, and the average value of the contact angle decreases. In addition, temperature also plays a crucial role in enhancing the contact angle. When it exceeds 120°C, the polymer becomes excessively soft and adhesive, resulting in poor demoulding and surface defects. Using the optimized parameters, a maximum contact angle of 153° was achieved for the moth-eye nanopillar textured surface. ANOVA was performed on the hot embossing Taguchi experiments, as represented the significance or contribution of all parameters with cross interactions and square terms in Table 7.2. The inclusion of the quadratic term of P^2 , significantly reduces the residue error, indicating the presence of curvature in the response and confirming that the effect of pressure on the output is nonlinear rather than purely linear. Accordingly, statistical analysis using the L9 orthogonal array has been carried out for the S/N ratio plots (larger-is-better) and the main effect plot for means. The corresponding variation of factor levels with contact angle is presented in Figure 7.3(a, b). Since the objective was to maximize the contact angle of the replicated nanopillar structures, the “larger-is-better” S/N criterion was adopted. The S/N and mean plots clearly indicate that embossing pressure has the most pronounced influence on the contact angle, followed by temperature, while holding time shows comparatively minimal effect. Moreover, the regression equation is calculated for all cross variations of process parameters in equation 7.2.

Regression equation

$$CA = -49.1 + 36.64 P + 1.388 T - 4.46 t - 1.320 P^2 - 0.1828 P \cdot T - 0.095 P \cdot t \quad (7.2)$$

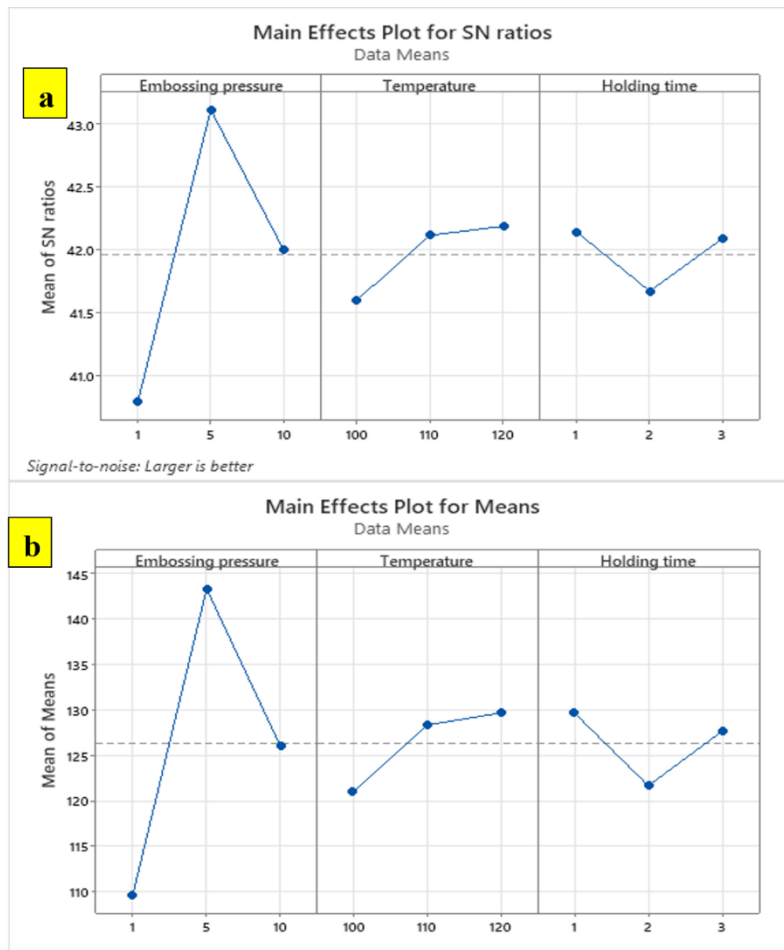


Figure 7.3 (a) main effect plot for S/N ratio (larger is better), (b) main effect plot for means, the variation of contact angle with embossing pressure, temperature, and holding time.

Table 7.2 ANOVA performance of Taguchi L9 experiments.

Source	DF	Seq SS	Seq MS	F-Value	P-Value	Contribution (%)	Significance
Regression	6	2002.87	333.81	20.15	0.048	98	Significant
Pressure (P)	1	311.68	311.68	18.82	0.049	15.2	Significant
Temperature (T)	1	112.67	112.67	6.80	0.121	5.5	Not significant
Time (t)	1	6.00	6.00	0.36	0.608	0.2	Not significant
P*P	1	1388.99	1388.99	83.86	0.012	68	Significant
P*T	1	183.11	183.11	11.05	0.080	8.9	Least significant
P*t	1	0.43	0.43	0.03	0.886		Not significant
Error	2	33.13	16.56			1.6	Not significant
Total	8	2036.00				100	

The theoretical contact angle was calculated using average structural parameters such as pillar diameter and spacing, independent of individual embossing pressures. Additionally, the Wenzel wetting state cannot explain the experimental findings, as its roughness factor ($r > 1$), the ratio of the actual area of a rough surface to the geometric projected area on the horizontal plane, would inherently make the surface more hydrophilic, which is inconsistent with the hydrophobic behaviour observed in this study [137]. Moreover, the contact angle of nanoholes nanohole-textured sample was examined, and it was observed reduced from 62 to 44°. This hydrophilic regime follows the Wenzel model, where the roughness factor is ~ 1.45 calculated for a hexagonally patterned nanohole. Figure 7.4(a, b) shows the CA for the nanopillar exhibiting superhydrophobic and nanoholes shows the hydrophilic wetting behaviours from 62° of plain polystyrene sheet.

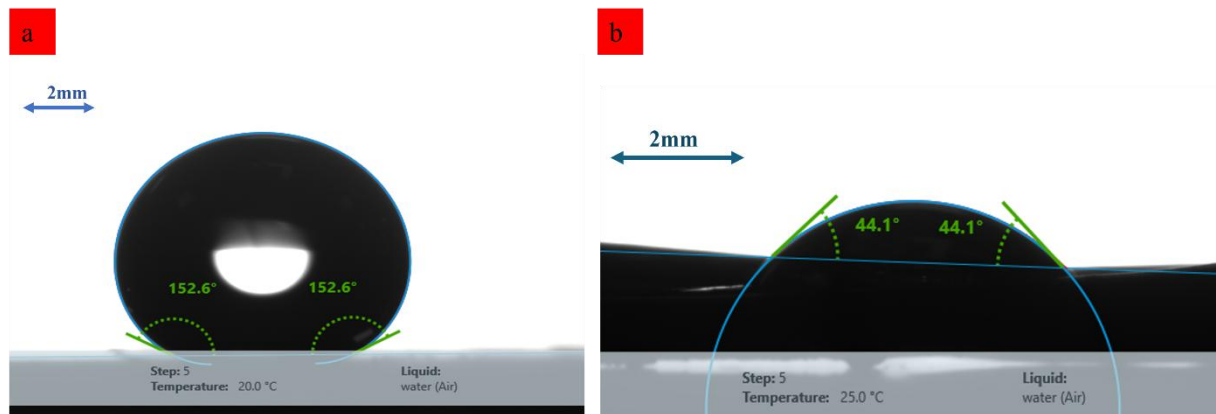


Figure 7.4 CA for moth-eye textured PS at optimized process parameters: 5 MPa embossing pressure, 120°C temperature, and 1 min holding time, (b) CA for nanoholes textured PS at 3 MPa embossing pressure.

7.2 Anti-reflective polystyrene surface

A nanotextured polystyrene hole and moth-eye textured NPs made by AAO and AAO/CNPs in hot embossing were characterized for UV-reflectance. Hexagonal patterned nanoholes of size 80 nm circular morphology were obtained as discussed in section 6.4. The reflectance measurements for nanohole-textured polystyrene were recorded across the visible spectrum and benchmarked against finite-difference time-domain (FDTD) simulations. The hexagonal

unit cell of nanoholes with 80 nm diameter, 150 nm depth, and a refractive index of nanoholes textured polystyrene based on the effective medium theory of Equation 1.5, which comes out as 1.34. As shown in Figure 7.5, texturing reduces the minimum reflectance to 5%, compared with 25% for the untextured (plain) polystyrene.

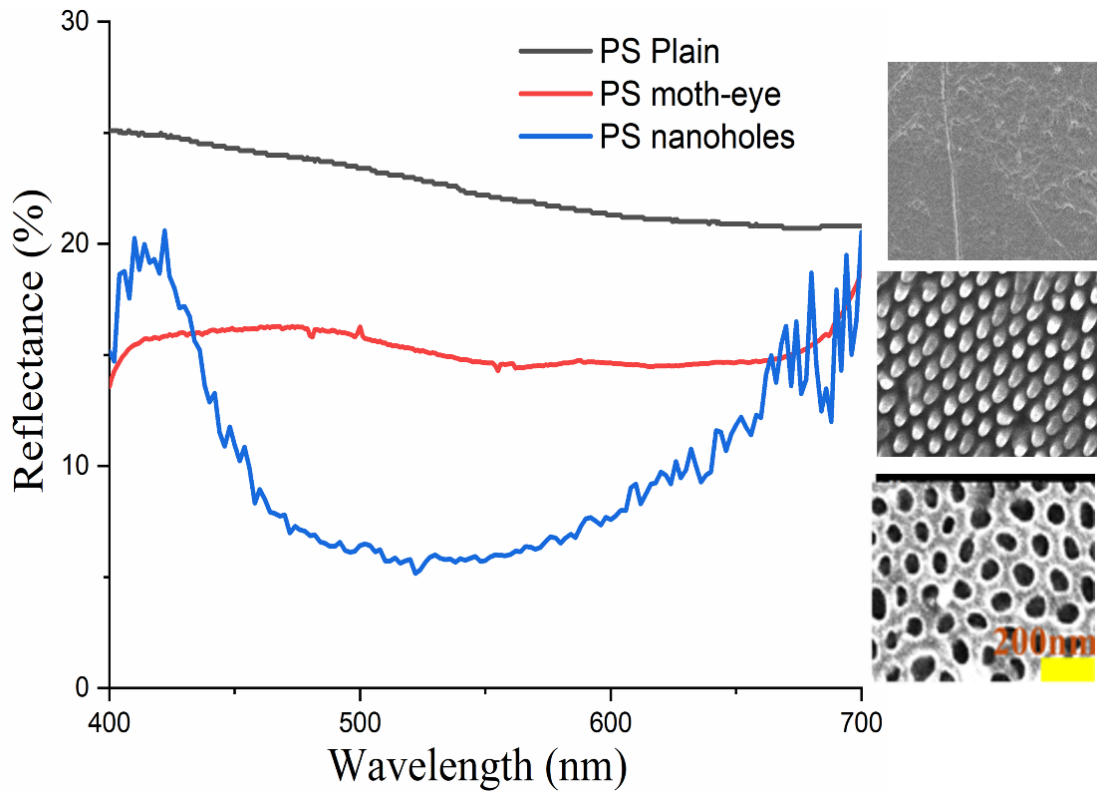


Figure 7.5 UV spectrum of plain PS, PS moth-eye, and PS nanoholes.

A comparable spectral response was simulated in Lumerical FDTD using a plane-wave source with perfectly matched layers along the propagation direction and periodic boundary conditions laterally. The simulation predicts a minimum reflectance approaching 3% and a peak near 430 nm of 15%, whereas the experiment shows a corresponding peak of 19% at the same wavelength. The antireflection behaviour originates from two complementary effects. First, the nanohole array forms a graded-index transition from air to polymer, which reduces the Fresnel mismatch and thereby suppresses specular reflection. Fresnel reflection calculated from Equation 1.6 is $\sim 2.2\%$, which is validated with FDTD simulation of minimum reflection of

~3.5%. However, this variation in simulated and mathematical mismatch depends on the reflective index of polystyrene, due to solvent-based, self-prepared sheets showing less transparency compared to the commercially available hot moulded PS sheet. Second, the holes promote multiple internal reflections and lateral scattering, increasing the optical path length within the textured layer. This further lowers the probability that light will couple back into free space as reflected power. Depending on the hole depth-to-diameter ratio and pitch, weak cavity/guided-mode resonances can also occur, shaping the spectrum and producing features such as the reflectance maximum observed for lower wavelength around 430 nm, as shown in Figure 7.6.

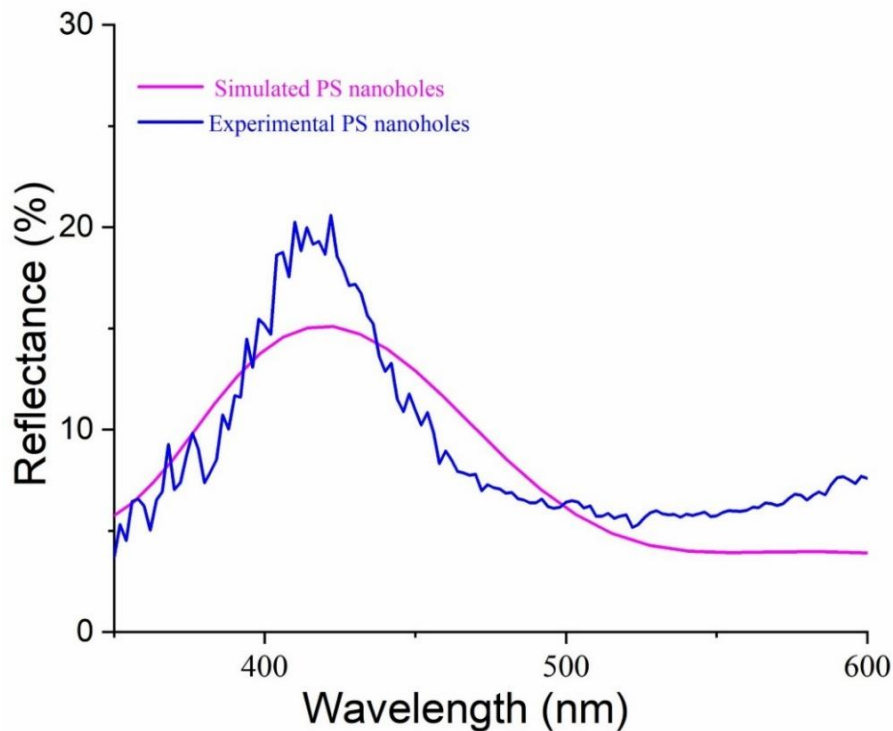


Figure 7.6 Reflectance of simulated and experimental textured PS nanohole.

The small discrepancies between measurement and simulation are expected and can be attributed to practical factors not fully captured in the idealized model, including rounding/tapering of hole sidewalls, slight deviations in hole diameter or depth across the field, surface contamination or oxidation layers, and the finite sample size compared with the periodic array assumption. Despite these differences, the close agreement in both trend and

feature positions validates the design rationale and confirms that nanohole texturing is an effective route to reduce visible reflectance on polystyrene. According to Mie theory, the dimensionless size parameter (x), which determines the scattering regime, is given by $\frac{2\pi a}{\lambda}$, where a is the nanofeature diameter, and λ is the incident wavelength. For nanohole arrays, when the incident light wavelength approaches the characteristic hole size of 80 nm, strong light–matter interaction occurs. At this scale, the nanoholes act as scattering centers, leading to reflection enhancement. This implies that when nanohole size is more than 80 nm, it will lead to scattering/reflecting light at higher wavelengths, thereby encouraging its effectiveness for antireflective applications within the visible spectrum.

7.3 SERS application of AAO/CNPs@Au substrate

SERS is a powerful analytical technique that exploits the LSPR of noble metal nanostructures to amplify weak Raman signals. The gold nanostructures are particularly attractive due to their chemical stability and strong plasmonic activity in the visible range, which overlaps well with the excitation wavelength used for the analyte, rhodamine 6G (R6G). When Au is deposited on highly aligned AAO/CNP substrates, intense electromagnetic “hot spots” are generated at sharp edges, junctions, and nanoscale gaps, drastically enhancing Raman scattering efficiency. The ordered porous framework of AAO, combined with the conductive network of carbon nanopillars, provides a robust and reusable platform for uniform Au decoration. This hybrid nanostructure enables reproducible detection of R6G at very low concentrations, demonstrating the potential of AAO/CNPs@Au substrates for reliable and sensitive SERS applications.

7.3.1 Surface morphology

The morphology of the self-organized, hexagonally arranged nanoporous AAO was examined using FESEM, and the corresponding images are presented in Figure 7.7(a–e). Figure 7.7(a) illustrates the surface morphology of the as-anodized AAO prepared at 45 V, 10°C in 0.3 M oxalic acid. From the FESEM analysis, the average widened pore diameter and interpore

spacing were determined using ImageJ software to be 75 nm and 130 nm, respectively, assuming a circular pore geometry, as depicted in Figure 7.7(b). The successful incorporation of CNPs is shown in Figure 7.7(c), where CNPs were exposed from AAO with an average diameter of 78 ± 4 nm. Surface-Enhanced Raman Scattering from Au-nanorod arrays with sub-5-nm gaps [138]. However, interpillar spacing was calculated as a sub-10 nm range by using ImageJ software, as illustrated in Figure 7.7(d). Further validation of the presence of carbon inside AAO was done by EDX spectroscopy, as shown in Figure 7.7(e, f).

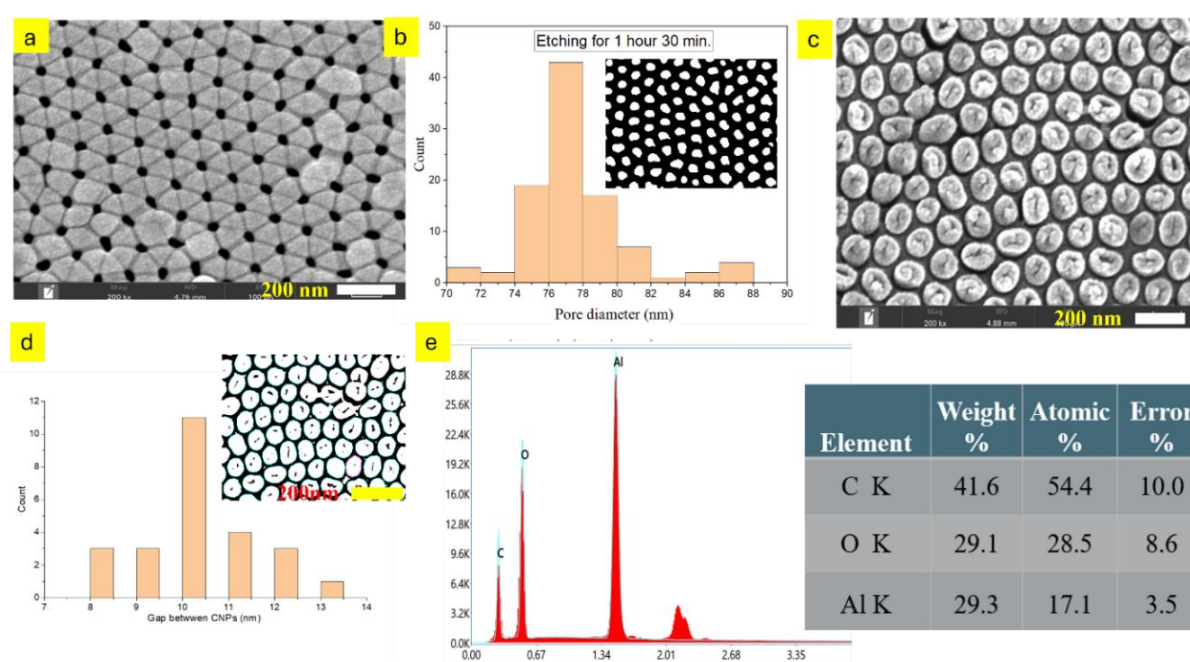


Figure 7.7 (a) FESEM image of as-grown AAO top surface, (b) pore diameter vs pore count histogram by Image J software, (c) FESEM image of 2 min etched AAO/CNPs, (d) CNPs gap vs pore count histogram by ImageJ software, (e) EDX of AAO/CNPs.

A deposition time of 1 min produced a 10 nm gold coating. The resulting ordered arrangement of Au nanoparticles is crucial for the formation of nanoscale “hot spots” between neighbouring CNP@Au structures. With 3 min of sputtering, the gold layer became thinner while still conforming to the protruding geometry of the CNPs. At 5 min, however, the density of Au nanoparticles increased markedly, leading to a reduction in the uniformity of the decorated caps. By 7 min of deposition, the gaps between adjacent nanopillars were almost completely

bridged by gold, eliminating the nanoscale gaps that typically act as SERS hot spots. Overall, it was observed that the inter-pillar spacing progressively decreased with deposition time, and an optimal balance between particle density and gap size is critical for maximizing SERS enhancement. The FESEM images of the AAO/CNP@Au are shown, where Figure 7.8 (a-d) illustrates the morphology after 3, 5, and 7 min of deposition, respectively.

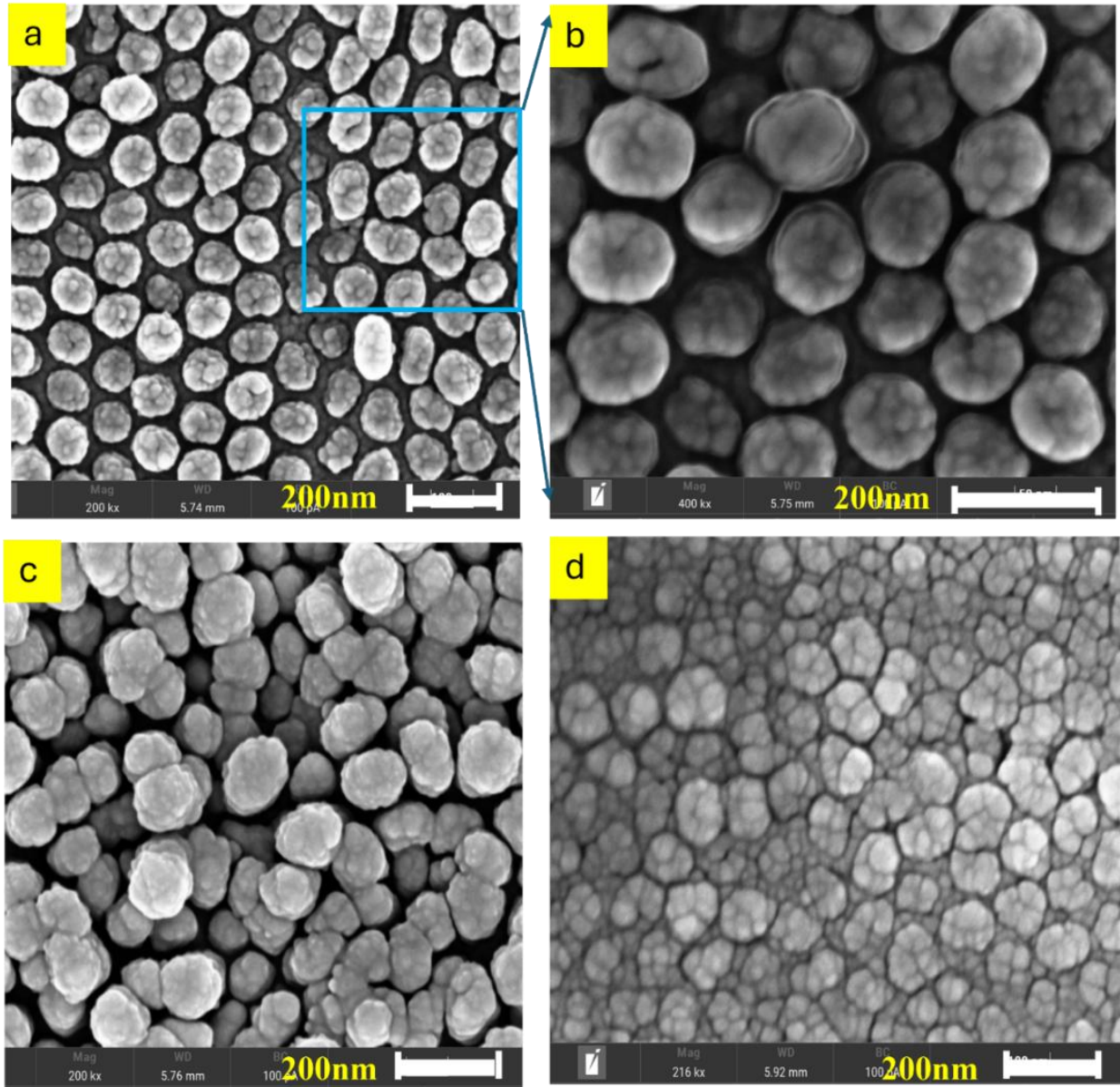


Figure 7.8 FESEM image of AAO/CNPs with sputtered gold deposition for (a, b) 3 min, (c) 5 min, (d) 7 min.

The elemental composition of the Au-decorated AAO/CNP hybrids was examined using energy-dispersive X-ray spectroscopy (EDX), as shown in Figure 7.9(a–f). The spectrum clearly confirmed the successful incorporation of gold, displaying a strong Au peak near 2.1 keV, along with signals corresponding to carbon from the CNPs and aluminium from the AAO matrix. The presence of a distinct Au peak provides direct evidence that the sputtering process has resulted in a uniform and appreciable gold coating.

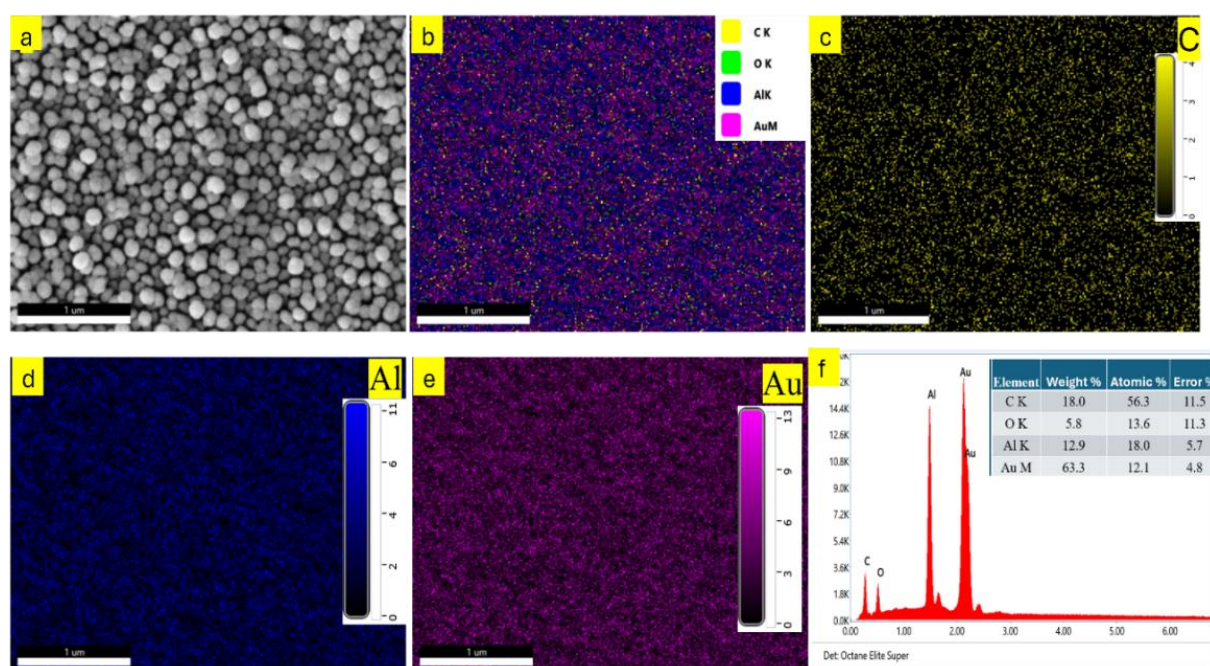


Figure 7.9 (a)FESEM image for EDX mapping, (b–f) EDX elemental mapping of AAO/CNP@Au.

In order to investigate the SERS performance, the vertically aligned CNPs were employed, which offer additional advantages by trapping incident light within their patterned array and thereby reinforcing electromagnetic field localization in the CNP@Au hybrid pillars. Following 3 min of sputtering, Au caps with diameters in the 80–90 nm range were deposited along the pillar sidewalls, effectively reducing the inter-pillar spacing. The as-prepared AAO/CNP@Au substrates were then evaluated for R6G dye as a probe molecule. Figure 7.10(a) illustrates the schematic representation of Raman signal amplification in the Au-decorated CNP hot spots. The optical response of these substrates was further analyzed through

UV–Vis absorption measurements, as presented in Figure 7.10(b, c). A pronounced absorption band appeared in the visible region of 350–1000 nm. The bare 2 min etched CNPs sample exhibited strong absorption, attributed to the inherent anti-reflective behaviour of carbon nanostructures. Upon Au decoration, the absorption peak progressively shifted toward shorter wavelengths or blue shift with increasing deposition thickness, although a reduction in overall absorption intensity was also noted due to altered light matter interaction within the hybrid structure. Reflection spectra of CNP@Au revealed a corresponding red shift, as illustrated in Figure 7.10(c). The intrinsic absorbance of CNPs leads to low reflection; however, upon Au deposition, the reflection increases due to the excitation of LSPR modes at the Au nanostructure interface. A similar spectral shift was previously reported for PDMS-infiltrated AAO templates coated with Au, where the plasmon resonance peak was observed between 515–530 nm, governed by the aspect ratio of the nanorods [139]. The intrinsic absorption trend of the pristine AAO/CNPs structure at shorter wavelengths was further validated through comparative spectra [140]. Raman spectra of bare CNPs and CNP@Au samples are shown in Figure 7.10(d). Distinct CNP peaks at 1333 cm^{-1} (D-band) and 1595.8 cm^{-1} (G-band) were identified, consistent with typical CNT features [141]. The G-band corresponds to the E_{2g} stretching vibration of sp^2 carbon atoms (non-dispersive mode), while the D-band originates from breathing vibrations of K-point phonons, associated with lattice defects and disorder in CNTs [142]. Upon Au decoration, a blue shift of $\sim 3.7\text{ cm}^{-1}$ in the G-band and a red shift of $\sim 2.9\text{ cm}^{-1}$ in the D-band were detected, indicating strong CNP@Au interactions. This was further supported by a decrease in the intensity ratio (I_G/I_D) from 1.3 for bare CNPs to 1.2 for 30 nm Au deposition, and 1.1 for 50 nm Au deposition. Since thin Au films are inherently Raman inactive, excessive gold loading reduced the enhancement effect. The optimum wavelength was identified using Raman spectroscopy with a 514 nm excitation source, where all samples showed absorption peaks around 540 nm.

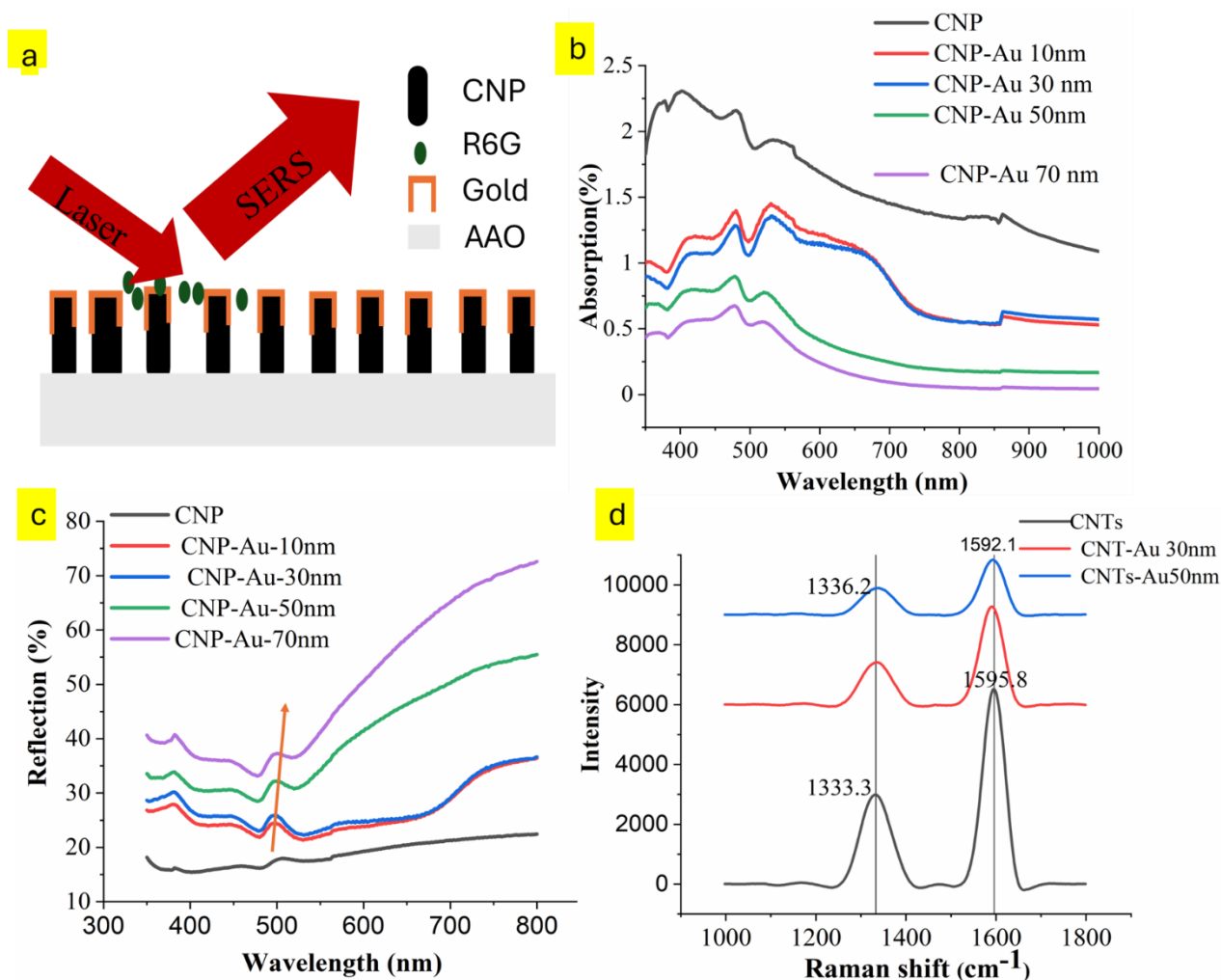


Figure 7.10 (a) Schematic of SERS process, (b) UV-Vis absorption spectra for different Au deposition thickness, (c) UV-vis reflection plot, (d) Raman spectrum for different CNP-Au nanocomposites.

The CNP pillar diameter after the 3 min deposition of Au, was analysed with Image J software, and obtained a average diameter of 82 nm as shown in Figure 7.11(a). Finally, the SERS activity of CNP@Au substrates was tested with a fixed concentration of 1 μM R6G. Significant signal enhancement was observed across all gold-coated samples, with the maximum enhancement achieved for CNP@Au substrates coated with 30 nm Au, as shown in Figure 7.11(b, c). The most prominent R6G Raman feature appeared at 1352 cm^{-1} under 1 mW laser excitation with a value of 2800 ± 100 for 30 nm Au sputtering. The SERS performance of the optimized CNP@Au 30 nm substrate was further examined for detecting R6G at lower concentrations.

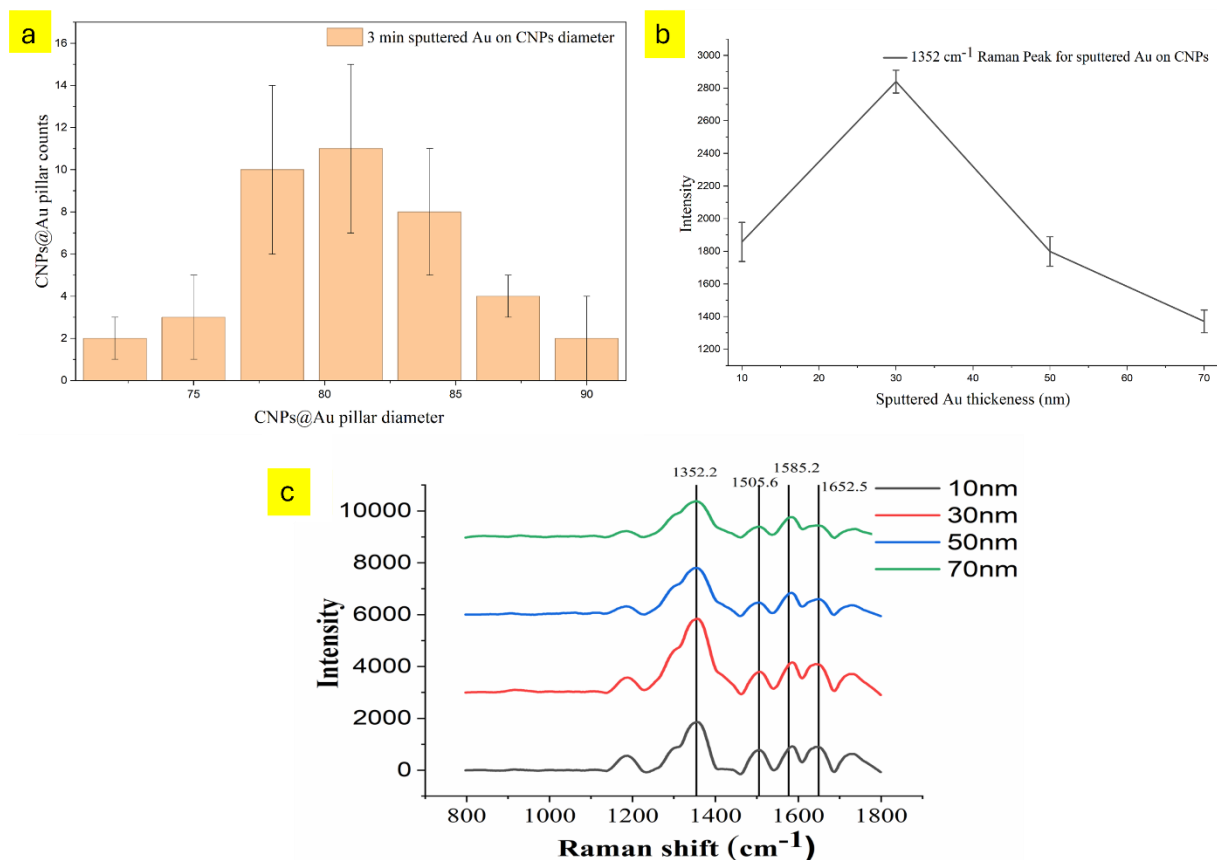


Figure 7.11 (a) Image J analysis for CNP diameter after 3 min Au sputtering for n=3, (b) variation of 1352cm⁻¹ Raman peak intensity for different Au thickness. (c) AAO/CNP@Au deposition dependent SERS spectra for 10⁻⁶M concentration of R6G dye.

Figure 7.12(a) presents the concentration-dependent spectra, where characteristic vibrational bands of R6G at 1648, 1582, 1505, 1352, and 1186 cm⁻¹ are clearly visible as the concentration decreases from 10⁻⁴ M down to 10⁻¹⁰ M. The band at 1352 cm⁻¹ partially overlaps with the CNP D-band (normally centered near 1332 cm⁻¹), resulting in a slight shift due to spectral overlap.[143] This 1352 cm⁻¹ feature was selected for quantitative analysis, and its intensity was plotted against concentration to construct a calibration curve, shown in Figure 7.12(b). The resulting linear relationship demonstrates a strong correlation with an adjusted R² value of 0.96, confirming the reliability of the substrate for quantitative sensing. The observed vibrational peaks align well with the fundamental bands of the R6G spectrum, including C=C stretching (1648 cm⁻¹), C-H bending of the CCH group (1352 cm⁻¹), aromatic C-H stretching (1582, 1505

cm^{-1}), C–C bridge vibrations, and aromatic C–H bending (1186 cm^{-1}).^[144,145]. Based on these measurements, the experimental limit of detection (LOD) for the CNP@Au SERS substrate was determined to be 10^{-9} M for R6G, highlighting its high sensitivity and strong enhancement capability. The SERS enhancement factor R6G was estimated to be

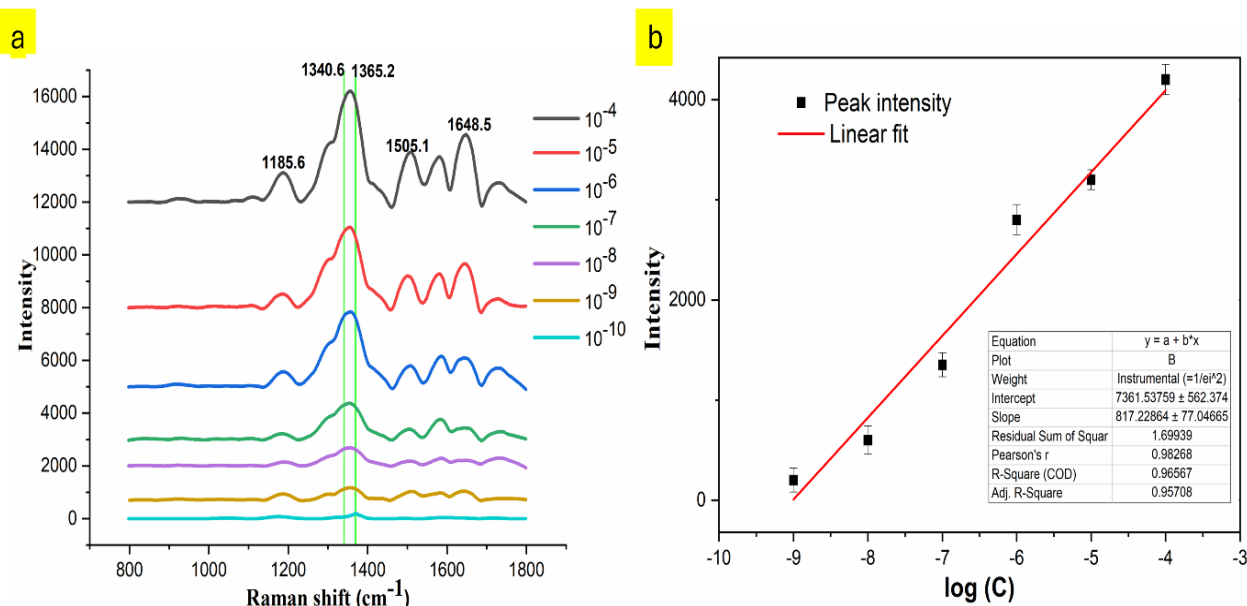


Figure 7.12 (a) SERS of R6G dye for different concentrations from 10^{-4} to 10^{-10} M deposited on CNPs@Au, (b) Raman intensity plot vs log of concentration for 1352 cm^{-1} peak.

approximately 5.8×10^6 , indicating a substantial amplification of the Raman signal.

The N_{SERS} and N_{Raman} values were determined using Rhodamine 6G dye at concentrations of $1 \mu\text{M}$ and 100 mM , respectively. For the SERS analysis, $20 \mu\text{L}$ of the $1 \mu\text{M}$ dye solution can be carefully dispensed onto the AAO/CNPs@Au-30 nm substrate and allowed to air dry over several h. In contrast, for the standard Raman measurements, $10 \mu\text{L}$ of the 100 mM R6G solution can be drop-cast onto a bare silicon substrate. The value of N_{SERS} can be estimated by calculating the number of R6G dye molecules located within the laser-illuminated area on the SERS substrate. Similarly, N_{Raman} corresponds to the number of molecules present within the laser spot on the normal Raman substrate. The total number of dye molecules deposited on both the SERS and Raman substrates can be determined using the following relationship

$$N = C \times V \times N_A \times \frac{A_L}{A_S} \quad (7.3)$$

Here, C represents the concentration of the analyte, V is the volume of the solution dispensed onto the SERS substrate, and N_A denotes Avogadro's number. A_L refers to the area of the laser spot, while A_S is the total area of the SERS substrate. The substrate area can be considered 0.25 cm^2 , based on the silicon substrate dimensions of $0.5 \text{ cm} \times 0.5 \text{ cm}$. The laser spot size is determined using the following formula,

$d_{spot} = 1.22 \times \frac{\lambda}{N_{Aperture}}$ where d_{spot} is the diameter of the laser spot ($\sim 1 \mu\text{m}$), λ is the laser wavelength of 514 nm, and $N_{Aperture}$ is the numerical aperture of the objective lens, which is 0.75 for the objective lens of 50x.

Laser spot area, also termed as diffusion area, calculated using the simple formula for area of a circle, i.e., $A_L = \pi r^2$

In this context, r denotes the radius of the laser spot. With this, all necessary parameters are available for the calculation of the enhancement factor (EF) [35].

From the above formulas: $\frac{N_{SERS}}{N_{Raman}} \sim 5 \times 10^4$

Intensity counts for the Raman sample, it is approximately 30, and the SERS substrate calculated intensity comes out as 3500.

$$EF = \frac{3500}{30} \times 5 \times 10^4 = 5.8 \times 10^6$$

A FDTD simulation was used to determine the electric field distribution on CNP with and without the deposition of Au nanoparticles. The modelled unit cell comprised a CNP grown within the AAO template and decorated with a gold nanocap. For the simulation, the optical constants of the CNPs were considered analogous to those of CNTs. Specifically, the structure was represented as a CNP with a length of 100 nm and a diameter of 80 nm protruding from the AAO surface, capped with a 30 nm thick Au coating. In this configuration, the incident light was polarized perpendicular to the propagation axis and directed normally onto the substrate surface. The comparative simulation results with and without the Au nanocaps are

presented in Figure 7.13(a-c). As shown schematically in Figure 7.13(a), the modelled unit cell of the CNP@Au nanopillar array included an interparticle spacing of ~ 10 nm between adjacent gold caps. The corresponding electric field distributions obtained through FDTD simulations under 514 nm excitation are displayed in Figure 7.13(b, c). The results clearly demonstrate strong localization of the electric field at the interparticle junctions, forming nanoscale hotspots that are primarily responsible for the enhanced SERS response. In the case of bare CNPs (without Au coating), the field intensity is roughly twice that of the incident wave. By contrast, when Au nanocaps are introduced, the interparticle gaps induce plasmonic coupling, leading to an approximate 14-fold amplification of the local electric field relative to the incident field. The experimentally obtained EF for the prepared CNP@Au SERS substrate was calculated to be 5.8×10^6 . From the FDTD simulations, the localized electric field intensity was found to increase by nearly 13.7 times due to the formation of Au nanogaps.

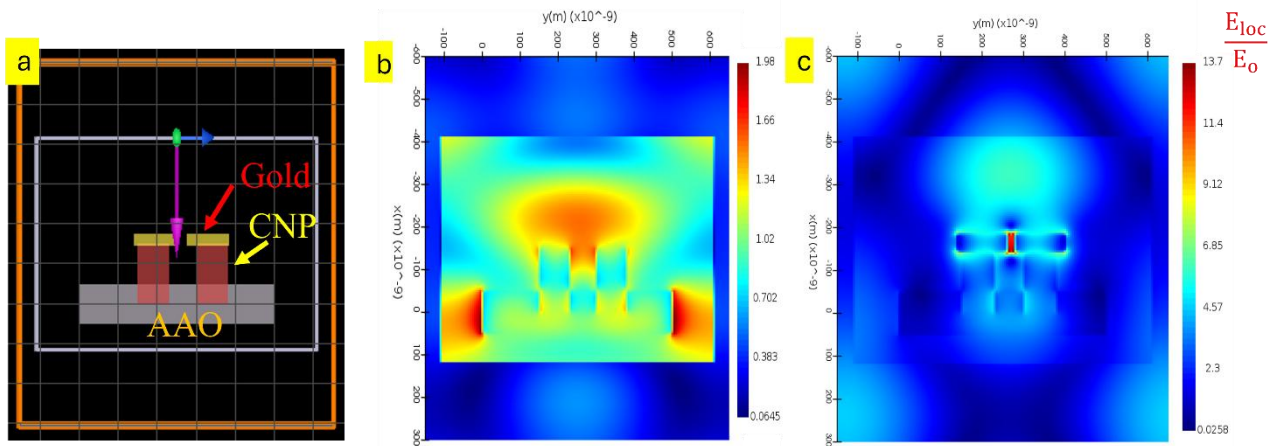


Figure 7.13 (a) Schematic for FDTD simulation for CNP-Au sample, (b) simulated electric field distribution for CNPs, (c) simulated electric field coupling between nano capped gold over CNPs.

Since the SERS enhancement is proportional to the fourth power of the electric field (E^4), the corresponding electromagnetic (EM) contribution to the EF is 0.3×10^6 . Thus, the overall experimental EF arises from the combined contributions of both electromagnetic (EM) and chemical mechanisms (CM). The difference between the simulated EM-driven enhancement

and the measured experimental EF can be attributed to the additional contribution of the CM mechanism, confirming its role in the overall SERS activity. In the CNP@Au-R6G system, the Fermi level of gold aligns with the π^* orbitals of R6G, enabling photoinduced charge transfer under excitation. The underlying CNPs, with electronic properties comparable to graphene, provide efficient electron mobility and act as a conductive channel to facilitate charge transfer to the R6G molecules. Upon illumination, hot electrons generated in Au nanocaps can transfer either directly to the LUMO of R6G or through the CNP support, enhancing chemical enhancement in SERS, as band diagram shown in Figure 7.14. This synergistic charge flow between Au, CNPs, and R6G contributes significantly to the overall signal amplification.

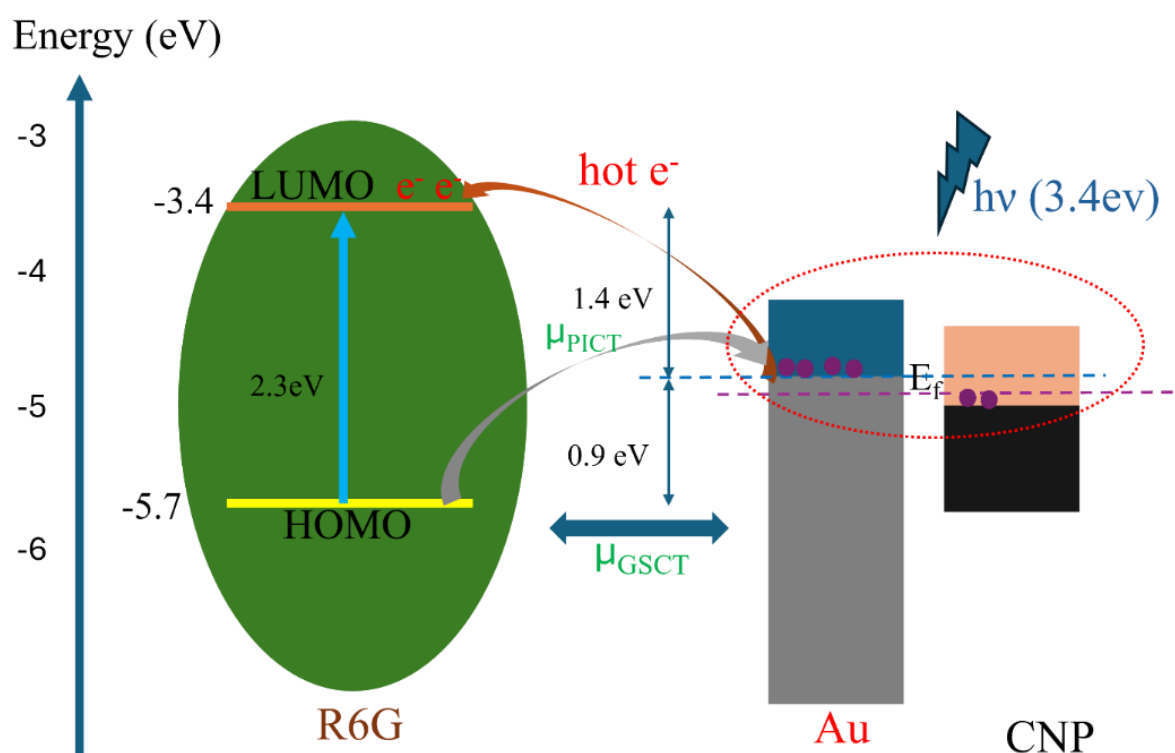


Figure 7.14 Band diagram for charge transfer mechanism in the Au-CNP@R6G sample.

The reproducibility of the fabricated CNP@Au SERS substrate was evaluated using a 10 nM R6G dye solution. Raman spectra were collected from 15 randomly chosen spots within a $10 \times 10 \mu\text{m}^2$ area to assess signal uniformity. The corresponding SERS intensity distribution is

shown in Figure 7.15(a), while Figure 7.15(b) presents the histogram of peak variations at 1350 cm^{-1} and 1585 cm^{-1} . The calculated relative standard deviations (RSD) for these peaks were 13.2% and 12.1%, respectively, both well below the 20% threshold commonly accepted for reliable and reproducible SERS substrates.

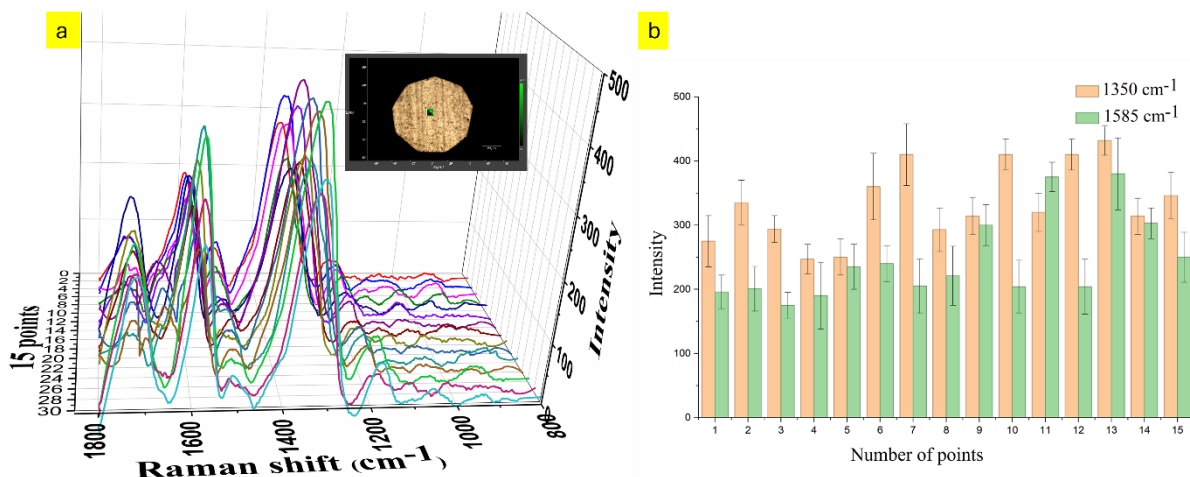


Figure 7.15 (a) SERS intensity plot of 1 μM for 15 different locations on the CNP-Au sample
 (b) Vibration intensity of 1350 cm^{-1} and 1585 cm^{-1} peak from 15 different locations on the CNP-Au sample.

7.4 AAO/CNPs sample as a supercapacitor

A supercapacitor is an advanced energy storage device that fulfils the bridge between battery and conventional capacitor by delivering high power density and excellent cyclic stability. Their energy storage mechanism is based on the separation of charge at the interface between the electrode material and the electrolyte, rather than through chemical reactions. For optimal design, supercapacitors require electrodes with high surface area, good electrical conductivity, and chemical stability, as well as electrolytes with wide potential windows and low resistance. These devices find widespread applications in regenerative braking systems, backup power supplies, hybrid electric vehicles, wearable electronics, and renewable energy systems, where rapid energy delivery and long operational life are essential. In this study, supercapacitor electrodes were fabricated using AAO-templated carbon nanopillars to exploit their high surface area and vertical alignment, enabling efficient ion transport and charge storage. Two electrode configurations were

prepared: bare AAO/CNPs and ZnO-coated AAO/CNP. The AAO template was anodized at 45 V for 2 h at 10°C in 0.3 M oxalic acid, followed by CNP growth inside the pores via CVD at 20 sccm acetylene flow for 4 h. The FESEM micrographs of AAO/CNPs are presented in Figure 7.16(a, b). Figure 7.16(a) displays the surface morphology of the as-anodized AAO cross section, whereas (b) shows the cross section of CNP-grown AAO. The calculated pore density is about $8.9 \times 10^9 \text{ cm}^{-2}$, consistent with the ~35% porosity typically observed for oxalic acid anodization. Figure 7.16(c) illustrates the photograph of a supercapacitor connected to a potentiostat.

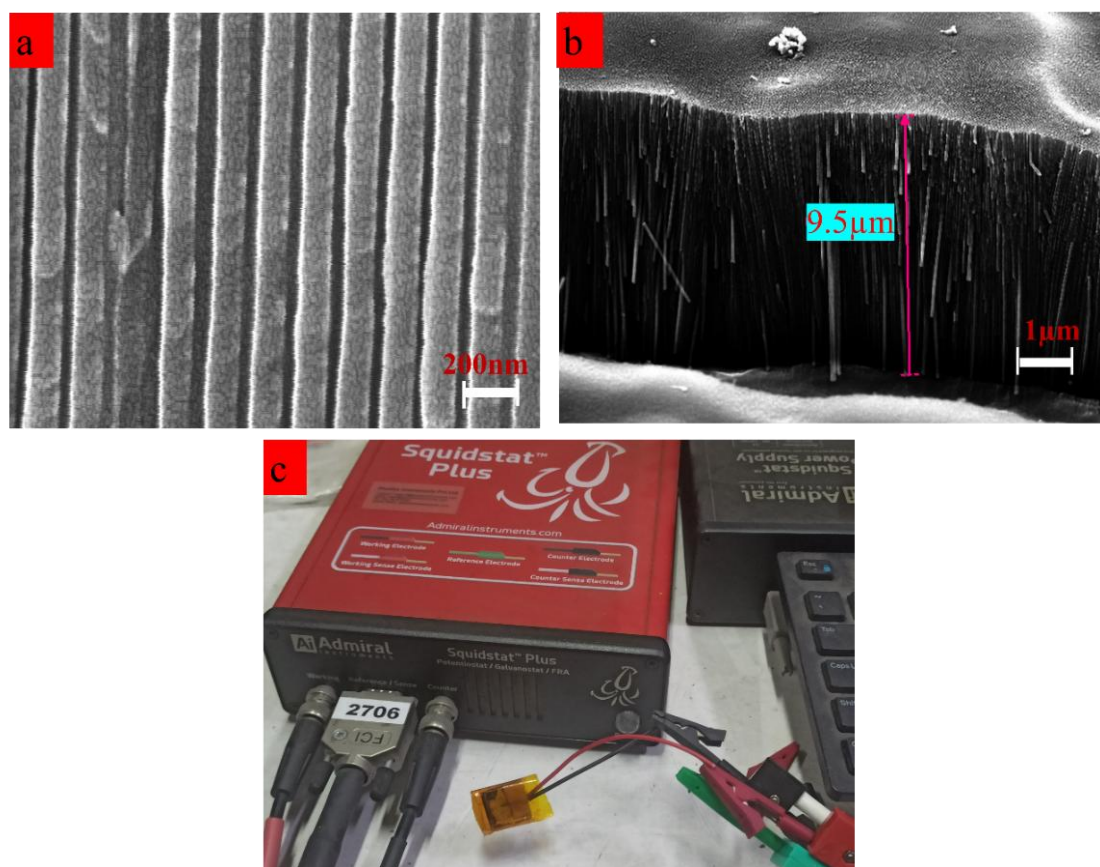


Figure 7.16 (a) FESEM of cross-section of AAO, (b) cross-section of AAO/CNPs, (c) photograph of the supercapacitor assembly.

The five-min etched CNP surface was employed as a template for ZnO nanosheet (NSs) growth, as illustrated in Figure 7.17(a, b). After 30 min of hydrothermal treatment at 120°C, no ZnO nanorods (NRs) were detected. However, extending the reaction time to 1 h led to the development of branched ZnO NRs on the ZnO NSs surface. This behaviour can be attributed

to the gradual release of OH^- ions under mildly alkaline conditions, which promotes lateral branching rather than preferential C-plane (0001) growth typical of the wurtzite ZnO structure. Figure 7.17(a) presents the FESEM image of ZnO grown for 1 h, while Figure 7.17(b) shows the FESEM image of cross-sectional AAO/CNP@ZnO, which highlights the intimate contact between the AAO/CNP framework and the ZnO morphology. Furthermore, the area elemental mapping shown in Figure 7.17(c–e) confirms the strong presence of zinc, carbon, aluminium, and oxygen elements in the hybrid structure.

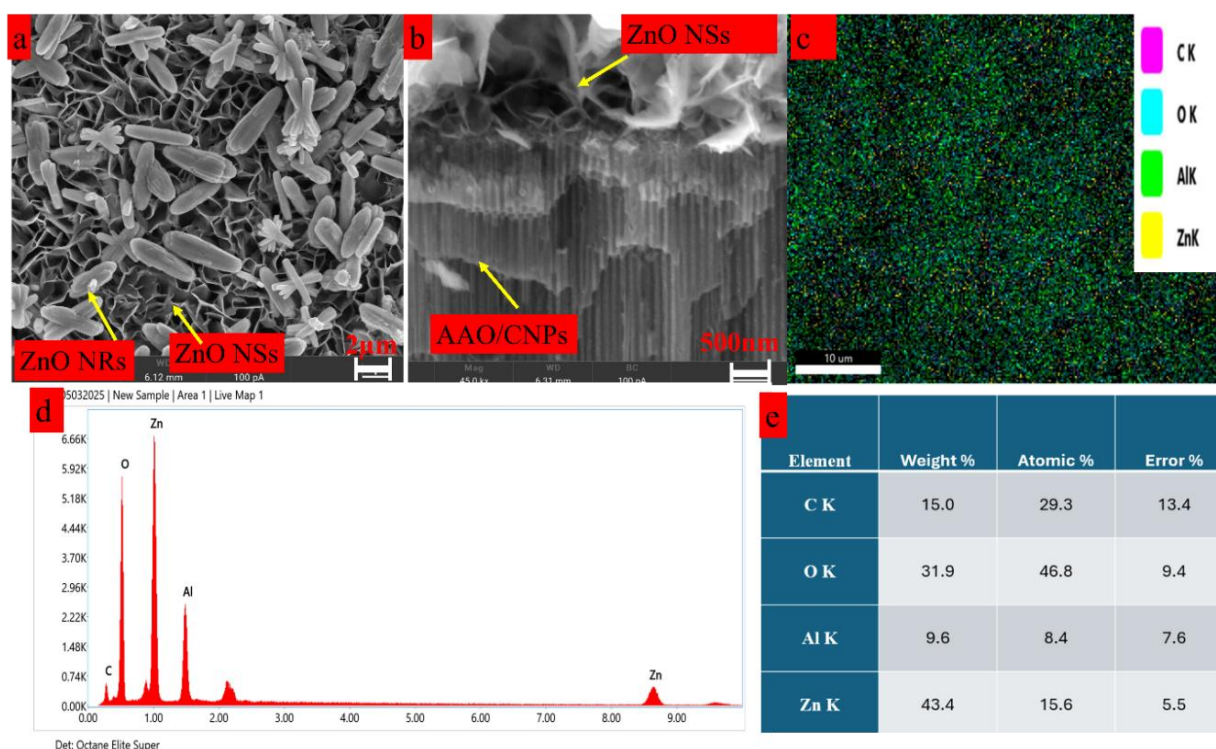


Figure 7.17 (a)FESEM image of ZnO NSs/NRs grown over AAO/CNPs, (b) cross-sectional view of AAO/CNP@ZnO, (c) area elemental mapping of AAO/CNPs/ZnO, and (d, e) EDX analysis of the as-prepared sample.

TEM analysis of CNPs confirmed their tubular morphology, showing an average diameter of 80 nm with a wall thickness of 10 nm, as shown in Figure 7.18(a). The structural characteristics of ZnO nanostructures grown on AAO/CNPs were further investigated using Raman spectroscopy. ZnO crystallizes in the hexagonal wurtzite phase and belongs to the C_{6v} symmetry group. Based on group theory, the Raman-active modes of ZnO include A_1 , E_1 , and

E_2 , while the B_1 modes remain silent. Both A_1 and E_1 modes can be further classified into longitudinal optical (LO) and transverse optical (TO) vibrations [146]. Figure 7.18(b) displays the Raman spectra of hydrothermally synthesized 3D-ZnO nanostructures deposited over AAO/CNPs, covering the spectral range up to 1800 cm^{-1} . The spectra exhibit two dominant features: the $E_2(\text{low})$ mode at 328.3 cm^{-1} , corresponding to Zn atom vibrations, and the $E_2(\text{high})$ mode at 434 cm^{-1} , related to oxygen atom vibrations. These peaks confirm the strong crystalline quality and hexagonal wurtzite nature of the ZnO NSs, consistent with prior reports. Additional modes observed include $A_1(\text{TO})$ (379.2 cm^{-1}), $E_1(\text{TO})$ (405.8 cm^{-1}), $E_1(\text{LO})$ (580 cm^{-1}), $A_1(\text{TO+LO})$ (1055.2 cm^{-1}), and $2E_1(\text{LO})$ (1146.3 cm^{-1}). The pronounced $E_2(\text{high})$ peak at 434 cm^{-1} further suggests preferential orientation along the c-axis (z-axis). Besides ZnO-related modes, distinct intrinsic Raman features of CNPs were also detected, including the D band at 1334 cm^{-1} , associated with disorder-induced vibrations, and the G band at 1590 cm^{-1} , corresponding to the E_{2g} in-plane stretching of carbon atoms. These findings validate the coexistence of ZnO NSs and graphitic carbon structures.

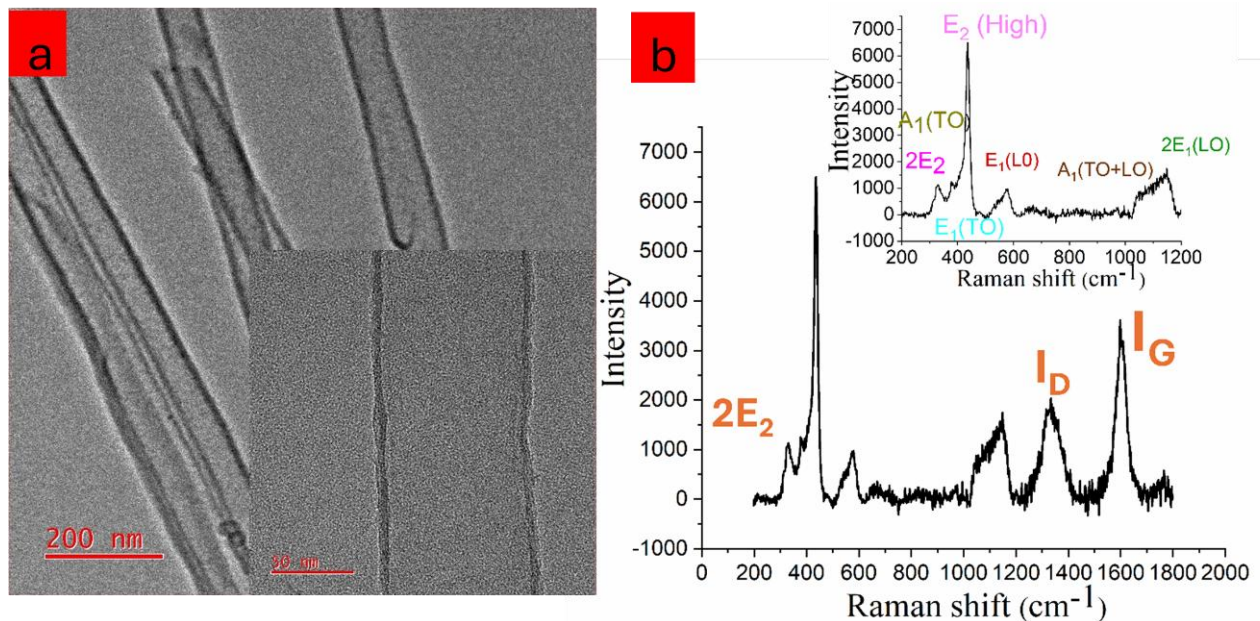


Figure 7.18 (a) HRTEM image of CNPs, inset shows the HRTEM image of CNP, (b) Raman spectrum of AAO/CNPs@ZnO, inset represents the optical vibrational response of ZnO in the Raman spectrum.

The electrochemical performance of the gel electrolyte-based AAO/CNPs@ZnO supercapacitor was assessed using CV, EIS, and GCD measurements. Figure 7.19(a) illustrates the CV profiles obtained for a 10 μm thick AAO/CNPs film subjected to different etching durations. Among the etched samples, the 5 min AAO etching condition yielded the highest current density, attributed to the well-preserved vertical alignment of the nanopillars. However, as the scan rate increases, the current density also rises, consistent with the characteristic capacitive relation ($i = C \frac{dv}{dt}$), as plotted in Figure 7.20(b). In order to further exploit the role of AAO/CNPs as current collectors, vertically branched ZnO nanostructures were grown on top of the 5 min etched samples and evaluated by CV. The incorporation of ZnO resulted in a pronounced increase in current density, reaching 1.8 mA/cm² at a scan rate of 500 mV/s, six times higher than the pristine AAO/CNPs electrode, as illustrated in Figure 7.19(c, d).

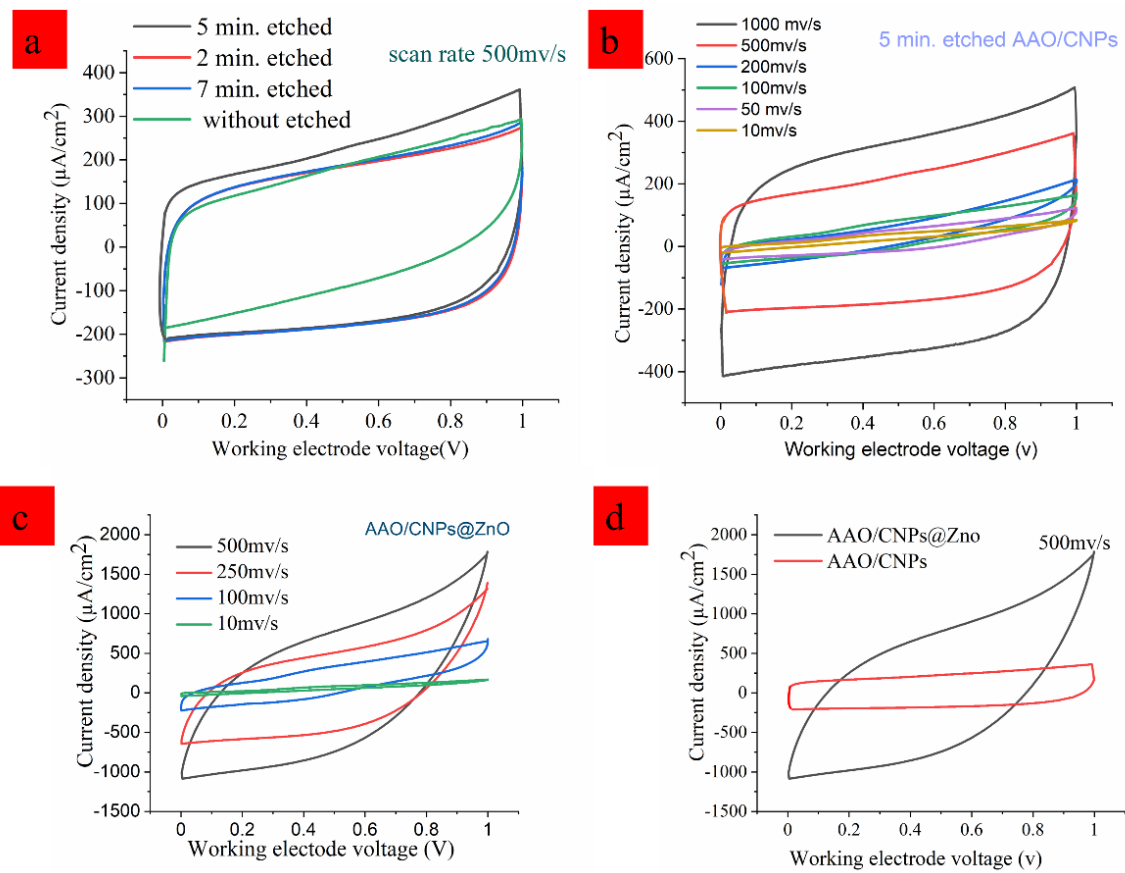


Figure 7.19 (a) CV scan of (a) AAO/CNPs for different etching durations, (b) different scan rates for 5 min. etched AAO, (c) different scan rate for AAO/CNPs@ZnO electrode, (d) at 500 mV/s scan rate for AAO/CNPs and AAO/CNPs@ZnO electrodes.

The CV curves exhibit a nearly rectangular shape without noticeable redox peaks, confirming the absence of faradaic reactions and the dominance of electric double-layer capacitance behaviour. This rectangular geometry, along with sharp current responses at the switching potential ends, is characteristic of an ideal EDLC. The areal specific capacitance was determined from the CV data. Based on the pore density, pore diameter, and AAO membrane thickness, the effective surface area of the CNPs was estimated to be 163 cm^2 per cm^2 of the Al electrode footprint. Using CV measurements, the average specific capacitance was found to be 0.8 mF/cm^2 , which translates to $4.96 \text{ }\mu\text{F/cm}^2$ when normalized to the CNP surface area. The obtained capacitance values are strongly dependent on electrode architecture and electrolyte composition. For comparison, reported $0.73 \text{ }\mu\text{F/cm}^2$ for AAO/CNTs integrated with a Si substrate [147], while in one more work demonstrated $3.1 \text{ }\mu\text{F/cm}^2$ using 33 nm CNTs in 0.5 M H_2SO_4 without a Si backing [148]. Similarly, it was achieved a $2.4 \text{ }\mu\text{F/cm}^2$ for AAO/CNTs in a ferrocyanide/KCl electrolyte system [149]. The higher capacitance values in this study can be ascribed to the superior quality of the carbon nanostructure and the presence of perforated barrier layers that enhance charge transport. Figure 7.20(a) presents the GCD profiles of the AAO/CNPs@ZnO electrode measured at various current densities within a 0–1 V potential window. At higher current densities, the GCD curves retain a nearly ideal triangular symmetry, confirming stable capacitive behaviour. In contrast, at lower current densities, the triangular profile becomes distorted, suggesting the presence of additional pseudocapacitive contributions. However, till 1000 cycles, no capacitance loss was observed in the GCD cycle, as shown in Figure 7.20(b). The specific capacitance for AAO/CNPs and AAO/CNP@ZnO was plotted against scan rate in Figure 7.20(c). The specific capacitance for AAO/CNP@ZnO was obtained as 3.1 mF/cm^2 , which is 215% increased from AAO/CNPs. The cyclic stability of the electrode was further assessed over 1500 continuous charge–discharge cycles at a current density of 0.5 mA/cm^2 . An initial drop of about 8–10% in capacitance was observed during the

early cycles, after which the device maintained stable performance throughout the remaining cycles, demonstrating robust long-term durability of 84%, as shown in Figure 7.20(d).

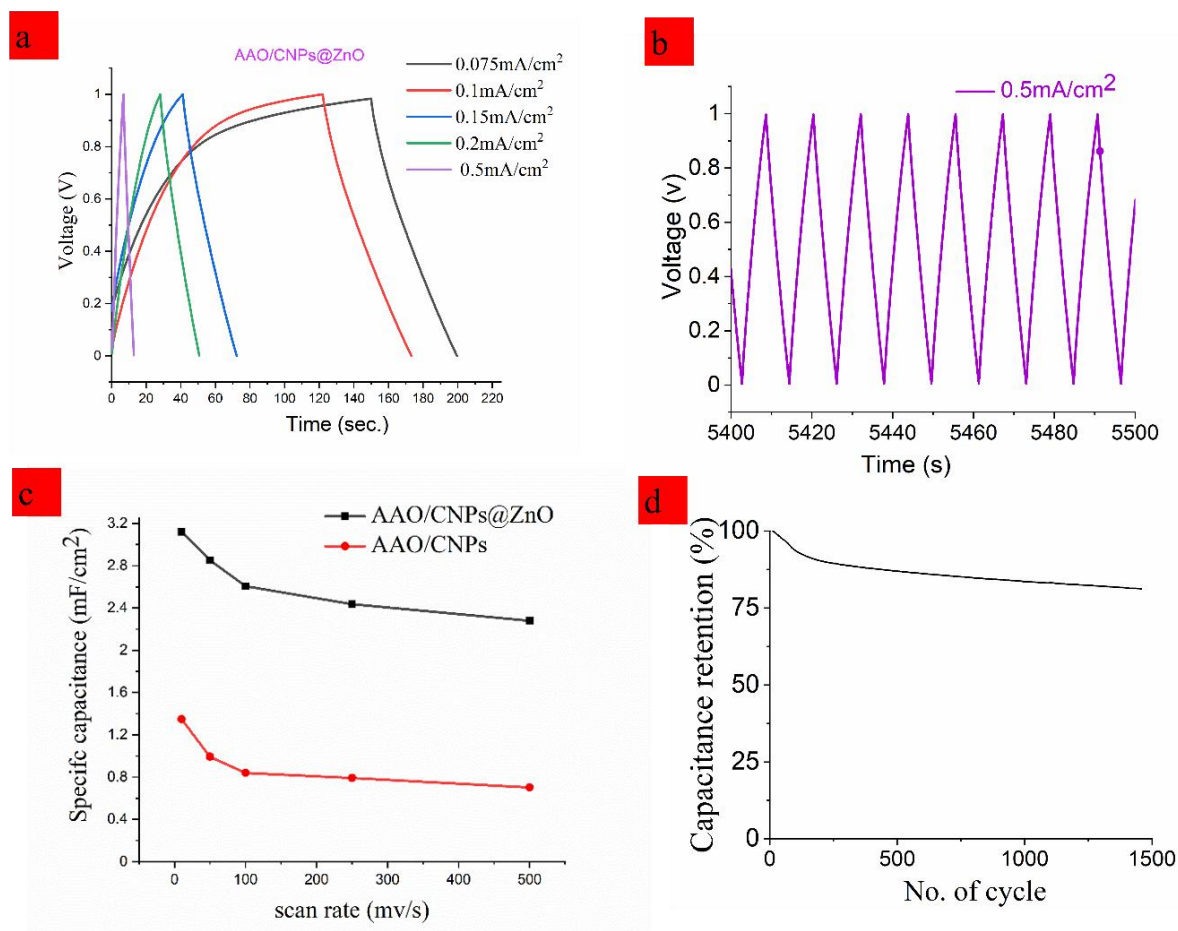


Figure 7.20 (a) GCD scan of AAO/CNPs@ ZnO for different scan rates 0.075, 0.1, 0.15, 0.2, 0.5 mA/cm² (b) GCD plot after 1000 cycles (c) specific capacitance vs scan rate plot for AAO/CNPs and AAO/CNPs@ZnO (d) specific capacitance retention of AAO/CNPs@ZnO for 1500 cycles at 0.5 mA/cm².

EIS was then conducted for AAO/CNPs@ZnO, as shown in Figure 7.21(a), whereas (b) shows for higher frequency range. The high-frequency intercept of the real impedance axis indicated an ohmic resistance of $3.8 \Omega \cdot \text{cm}^2$, confirming efficient electrical connectivity to the CNPs and successful removal of the oxide barrier. At low frequencies, the impedance profile approached the expected 90° slope of an ideal capacitor, while the measured phase angle of 76° in the 100 kHz–10 mHz range further supported the ideal capacitive behaviour of the assembled supercapacitor. The enhanced charge storage characteristics of the hybrid electrode stem from

the dual contribution of its components. The vertically aligned CNPs act as highly conductive pathways while simultaneously contributing to EDLC through the electrostatic adsorption of K^+ and OH^- ions from the PVA/KOH gel electrolyte, ensuring fast electron transport and high-power delivery. On the other hand, the ZnO nanosheets provide faradaic pseudo capacitance via surface redox reactions in equation 7.4, primarily following the reversible reaction kinetics. A comparative study with existing work is illustrated in Table 7.3.

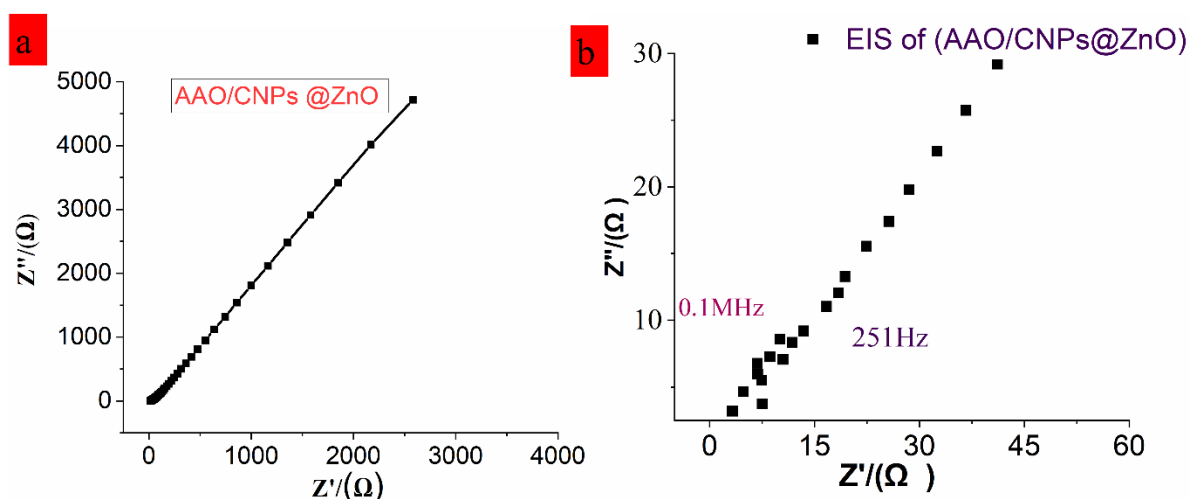


Figure 7.21 (a, b) Nyquist plot of AAO/CNPs@ZnO for 100KHz to 10mHz frequency.

Table 7.3 Comparative results of supercapacitor performance with existing studies

AAO/CNPs used as current collector	Specific capacitance	Cyclic stability/retention capacity	References
AAO/CNPs as flexible foil	$400\mu F/cm^2$	10,000	[111]
0.1 M KCl electrolyte	$2.4\mu F/cm^2$		[149]
0.5 M H_2SO_4 electrolyte	$3.1\mu F/cm^2$		[148]
Al/AAO@CNP on Si wafer	$0.44\text{ mF}/cm^2$	1000/70	[150]
AAO/CNP@ZnO	$1.8\text{ mF}/cm^2$	2000/84	Our work

This mechanism enhances both the specific capacitance and energy density of the device. The strong interfacial bonding between ZnO nanosheets and the exposed CNP framework facilitates efficient ion diffusion and charge transfer, which is crucial for maintaining rapid charge

discharge Overall, the synergistic combination of EDLC from CNPs and pseudo capacitance from ZnO results in a hybrid electrode with improved capacitance retention, high-rate capability, and enhanced electrochemical stability, making the AAO/CNPs@ZnO structure a promising platform for next-generation high-performance supercapacitors.

7.5 Summary

This chapter mainly considers the application related to nanostructures. Self-cleaning or superhydrophobic study of polystyrene nanopillars was explained thoroughly. An antireflective property of polystyrene nanoholes was explained and simulated with FDTD simulation. Moreover, the AAO/CNPs@Au surface was explored for R6G detection due to patterned decoration of sputtered Au NPs. In addition to that, ZnO grown over AAO/CNPs was explored for its remarkable supercapacitance performance. Polystyrene nanopillars having an aspect ratio of (1-2) have a water contact angle of 110° , while the moth-eye structure having an aspect ratio of (4-6) shows the maximum contact angle of 153° . Further, for a higher aspect ratio, it decreases to 133° .

- Polystyrene nanoholes show the reflectance reduction from 25% to 5%, which was validated with a simulation with a minimum reflectance of $\sim 3\%$.
- AAO@CNPs with 30 nm sputtered exhibit the maximum plasmonic enhancement with a sub-10 nm hot-spot. R6G dye can be detected for low concentration 10^{-10} M
- FDTD simulation exhibits an electric field enhancement of 13.7 times, and a possibility of chemical enhancement was explained.
- Supercapacitor performance of AAO/CNPs@ZnO electrode shows 3.1 mF/cm^2 with a capacitance retention of 84%.

Chapter 8

Conclusion and scope of future work

The aim of this research work, a comprehensive study was conducted for the fabrication and function utilization of anodized aluminium oxide with the best obtained ordered pore structure in order to grow hexagonally patterned, vertically aligned carbon nanopillars. The influence of anodization parameters such as anodization temperature and duration was optimized to achieve uniform pore arrangement and high aspect ratios suitable for templated growth. Nanopillars and nanoholes were developed over a large area of polystyrene by using an AAO and an AAO/CNPs mould, respectively. The hot embossing process enabled the replication of nanostructures such as nanolenses, moth-eye, and high aspect ratio nanopillars. Moreover, nanotextured holes on polystyrene demonstrated remarkable self-cleaning performance and anti-reflectivity performance. In addition to the fabrication process, this facile approach for Au decoration was explored for label-free SERS sensors to detect carcinogenic dye. Beyond sensing, the same AAO/CNPs nanocomposite framework was extended to energy storage applications by growing 3D-ZnO nanosheets. The resultant AAO/CNP@ZnO electrodes exhibited a significant enhancement in specific capacitance and charge-discharge performance, underscoring their sustainability and suitability for next-generation supercapacitors. The major findings of this research work can be summarized as follows

- Well-ordered hexagonally patterned nanopores can be obtained by anodization of aluminium. These AAO pores can be successfully achieved under optimized anodization conditions of 10 °C temperature and 45 V applied voltage using a 0.3 M oxalic acid electrolyte.
- Two h of anodization produced an AAO membrane with a thickness of approximately 10 μm , and an average pore diameter of 75 nm obtained after a 90 min pore-widening treatment.

- An optimized growth condition of 20 sccm acetylene flow with 200 sccm carrier gas at 625 °C for 4 h was found ideal for uniform carbon infiltration within AAO nanopores, leading to the successful formation of vertically aligned carbon nanopillars without any overgrown carbon.
- The replication of a large area polystyrene nanostructure was performed in a hot embossing process with an AAO mould of 75 nm diameter. At 1 MPa, a nanolens array were replicated uniformly, while high pressures of 5 MPa, 10 MPa enabled the transfer of moth-eye structure and high aspect ratio NPs.
- The AAO/CNPs mould employed at 3 MPa pressure and 110 °C temperature proved effective for nanohole texturing on the polystyrene surface, where the resulting large-area nanostructured PS sheet exhibited a significant reduction in reflectance, from 25% for the plain surface to just 5%, proving exceptional antireflective properties.
- The AAO/CNPs structure decorated with a 30 nm Au film shows a strong Raman signal enhancement for 10^{-10} M R6G dye detection. The Au functionalization effectively transformed the AAO/CNPs into a highly sensitive SERS substrate, validating its effectiveness for ultrasensitive molecular detection and advanced sensing applications.
- The AAO/CNPs@ZnO nanosheet electrodes were demonstrated using CV and GCD analyses, exhibiting a specific capacitance of 3.2 mF/cm², a 215% improvement compared to pristine AAO/CNPs electrodes. The incorporation of ZnO notably enhanced the electrochemical characteristics, highlighting the strong potential of these hybrid structures for high-performance energy storage and supercapacitor applications.

Future research in the field of nanostructured materials should emphasize the transition from laboratory-scale demonstrations to scalable, cost-effective production suitable for industrial applications. There are the following scopes where this research can be explored further

1. Self-cleaning solar cell - Self-cleaning, and antireflective nanostructured surfaces can significantly boost the performance and lifespan of solar cell modules. By minimizing dust accumulation and reducing light reflection losses, these coatings allow more sunlight to transmit to the active photovoltaic layer, thereby enhancing energy conversion efficiency.
2. Plasmonic-based CO₂ electrolysis – The incorporation of copper-decoration plasmonic nanostructures may serve as a promising approach to enhance CO₂ electroreduction efficiency. This facilitates faster reaction kinetics and higher selectivity toward desired products, enabling more efficient and sustainable CO₂ conversion for fuel and chemical synthesis applications.
3. Single-layer graphene supported on AAO membrane may isolate the intrinsic defect sites, enabling the efficient charge separation and selective filtration. Such membranes' properties make them a promising material for high-temperature syngas separation and purification processes.
4. Barely explored carbon allotropes, such as diamond nanopillars, present potential opportunities for applications requiring high thermal resistance and stability. These structures can also serve as robust platforms for quantum computing, particularly through the exploitation of nitrogen-vacancy (NV) centers, enabling precise spin manipulation and sensing at the nanoscale.
5. AAO/CNPs structures can be further explored for field emission properties in flexible electronic scanning, corrosion-resistant applications, as their strong chemical stability and interfacial bonding scaffold make them suitable for harsh environments.
6. CFD simulations of gas flow and temperature distribution within the CVD reactor and FEM simulation validation of AFM-based nanoindentation will be focused in future study to better understand growth uniformity and optimize process parameters.

Appendix A

Standard Operating Procedures (SOP) for hot embossing

The hot embossing system used in this study is an indigenously developed, custom-built setup designed for precise control of temperature and applied load. The system incorporates a load cell-based strain gauge assembly for real-time force monitoring and feedback control. The embossing ram is driven by a stepper motor-actuated mechanism, enabling controlled displacement and uniform pressure application. The system is controlled by remotely controlled interface, allowing precise control of process parameters. A cartridge (pencil) heater is used for heating purpose, and a K-type thermocouple is placed near the embossing interface. The temperature control device handles a maximum operating temperature of 120°C, with a measurement sensitivity of 0.1°C. The load application system has a maximum load capacity of 1000 N, ensuring adequate pressure for micro/nano-pattern transfer.

Hot embossing process recipe equipment

- Hot embossing system: indigenously developed
- Maximum temperature capability: 120°C
- Maximum pressure capability: 10 MPa

Materials

- Substrate: (e.g., thermoplastic polymer film / Si wafer / PMMA sheet)
- Thickness: 0.1 mm- 5mm
- Mold material: AAO, AAO/CNP, AAO/Ni, Si NPs
- Mold surface treatment: liquid dipping in anti-adhesive silane agent or vapor phase deposition of silane
- Cleaning solvents: Acetone, IPA, DI water sequentially (avoid acetone for thermoplastic polymers)

Procedure of use

Prior to hot embossing, both the polymer sample and the mold were cleaned to remove dirt such as dust, grease, or other residual contaminants. Cleaning should be carried out using suitable organic solvents (e.g., acetone and isopropyl alcohol), followed by through drying to ensure contamination-free surface. Before experiment, verify all electrical connections of the indigenously developed hot embossing system. Particular attention should be given to the cartridge (pencil) heater, K-type thermocouple, load cell integrated with the strain gauge assembly, stepper motor drive mechanism, and the remote-control unit to ensure proper functionality and operational safety. Thereafter, the system should be preheated to the desired embossing temperature and allowed to stabilize for approximately 2-5 min to achieve uniform heat distribution throughout the bulk sample. After stabilization, the mold will be securely mount onto the lower platen integrated with the load cell assembly. The polymer sample then carefully aligned with the mold surface. Using the remote-control interface, the stepper motor-driven ram was gradually lowered until the target load was achieved, as monitored in real time

through the load cell display. The applied load was maintained for a holding time of approximately 2–10 min, depending on process requirements. Perform demolding carefully after partial cooling of the polymer. This approach, known as viscous demolding, enables easier separation between the mold and polymer due to the viscoelastic state of the material and reduces the risk of structural damage. Allow the embossed sample to cool completely to room temperature before further handling or characterization.

CVD SOP

Materials

- Quartz tube diameter 65 mm
- Kenthal heater
- Analog flow meter

CVD process recipe

- Maximum working temperature = 1000°C
- Maximum flow meter capacity = 500 sccm
- Safe flow rate of precursor gas < 100 sccm
- Always establish carrier gas flow before introducing the precursor gas to prevent sudden pressure buildup and potential tube rupture.

Prior to deposition, the substrates should be thoroughly cleaned according to the standard cleaning procedure. Check all the system connections such as inspect the furnace's power supply, vacuum pump, temperature controller, pressure gauges, gas flow controllers, and gas intake lines before the CVD process. Place the cleaned substrates in a quartz boat and load them into the quartz reactor tube, and close the chamber. Further to remove the residual air and moisture from the chamber, an inert gas purging (e.g., nitrogen/H₂ or argon) can be performed for specified duration. After thermal stabilization, introduce the precursor gas (Acetylene, ethylene) along with the carrier gas at the specified flow rates. Continue the deposition for the prescribed period while monitoring temperature, pressure, and gas flow rates to ensure stable operating environments. After completion of deposition, the precursor gas flow should be stopped, while maintain the inert gas flow to prevent unwanted reaction and contaminations. After this, allow the system to cool down at room temperature under an inert environment. Once the system reaches a safe temperature, gently vent the chamber and remove the samples. Store the deposited samples in a clean, dry environment prior to characterization.

Raw image/ data (for optimum conditions)

The raw characterization data corresponding to the optimized parametric conditions are provided in the Appendix for transparency and reproducibility. These datasets represent the best-performing samples obtained under the optimized process parameters

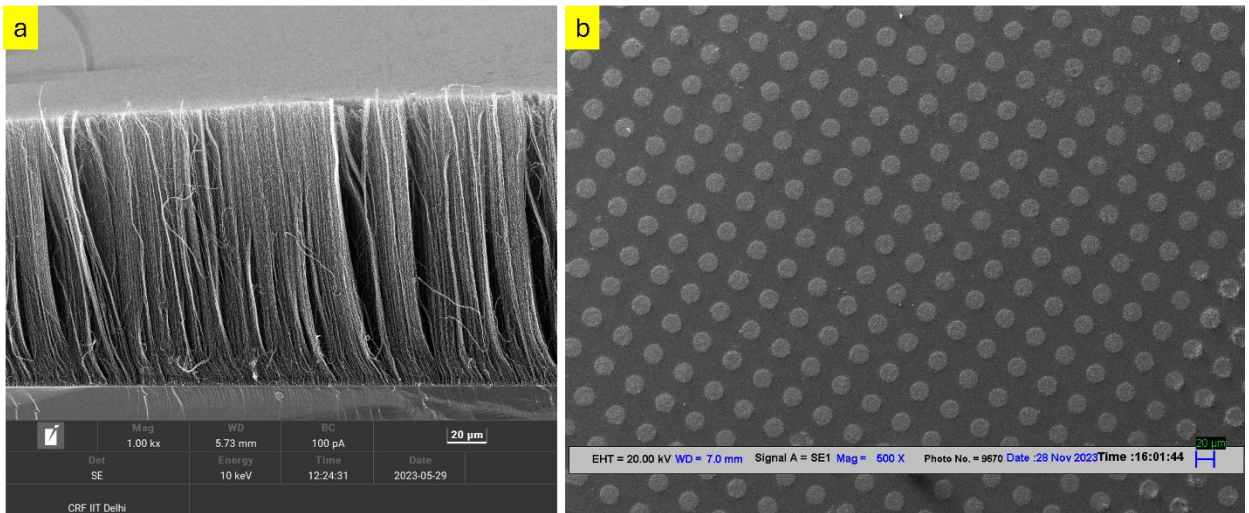


Figure A1 (a) FESEM image of maximum vertical CNTs growth obtained in CVD, (b) 20-micron CNTs pillars on Si wafer

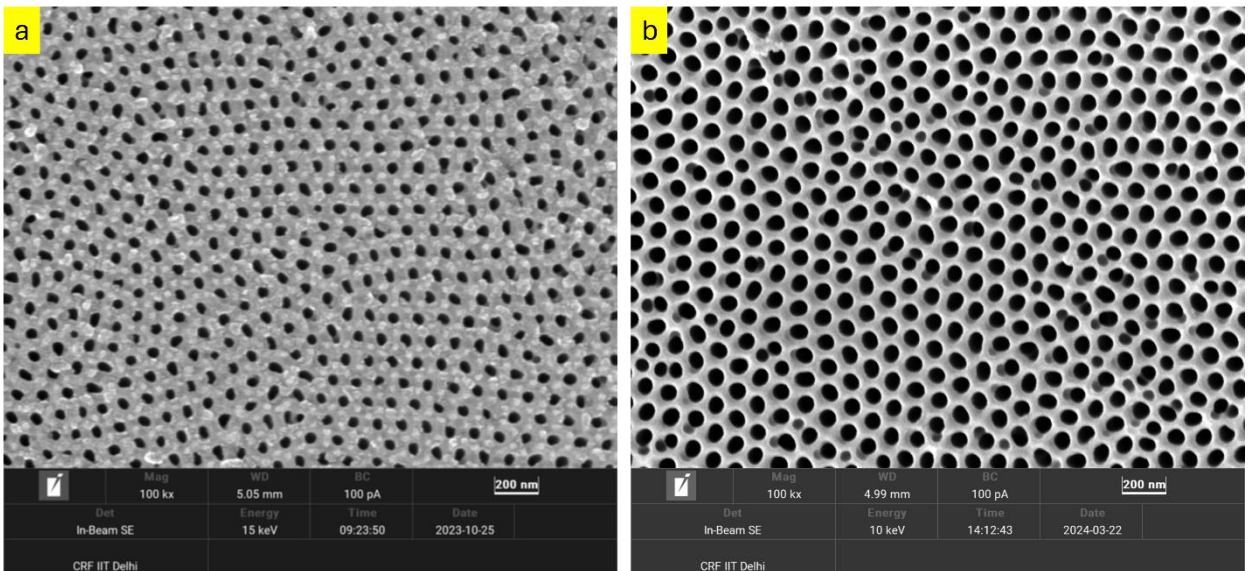


Figure A2 FESEM image of as-grown AAO at 10°C (b) 90 min etched AAO

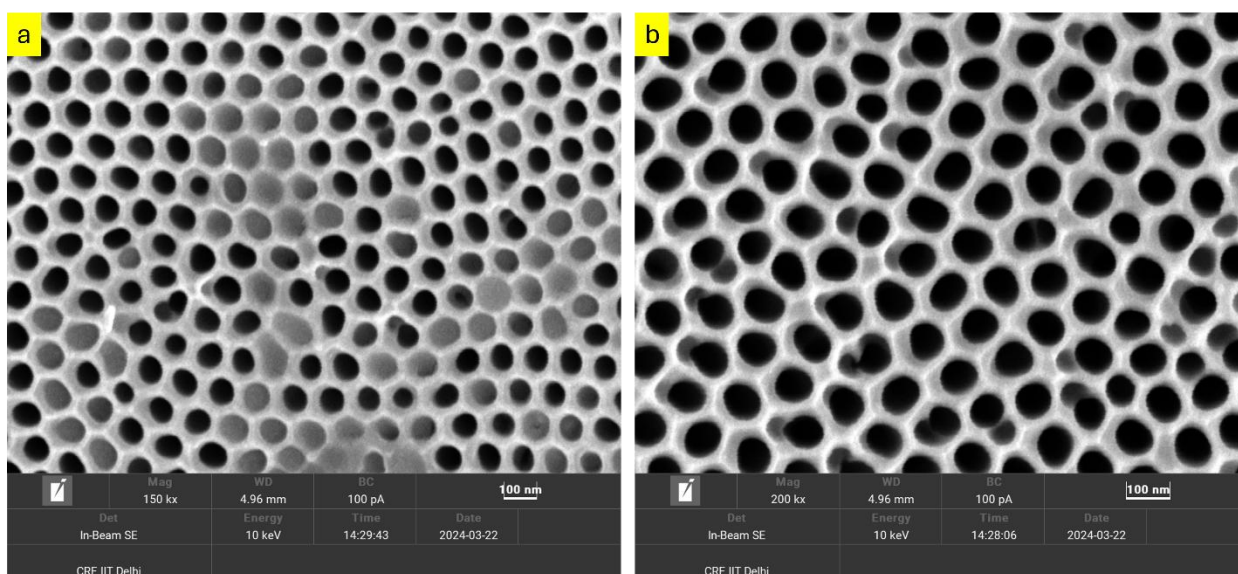


Figure A3 FESEM image of anti-adhesive silane-treated AAO for 10 min (b) 5 min treated.

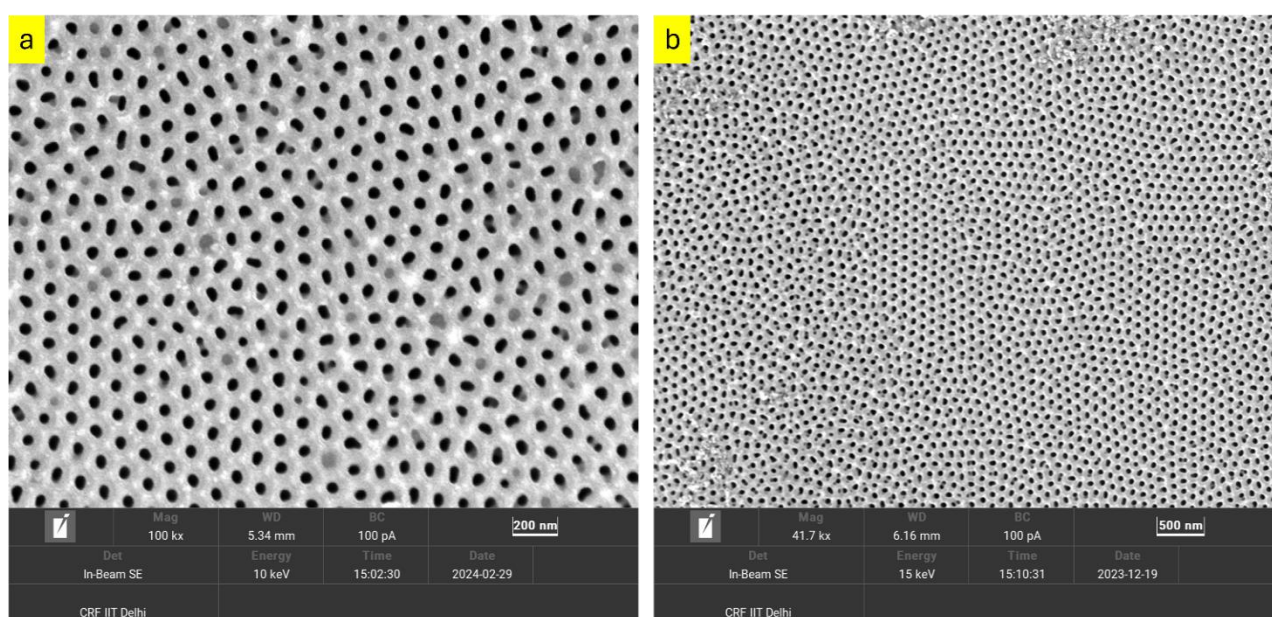


Figure A4 FESEM image of reused AAO moulds after multiple uses.

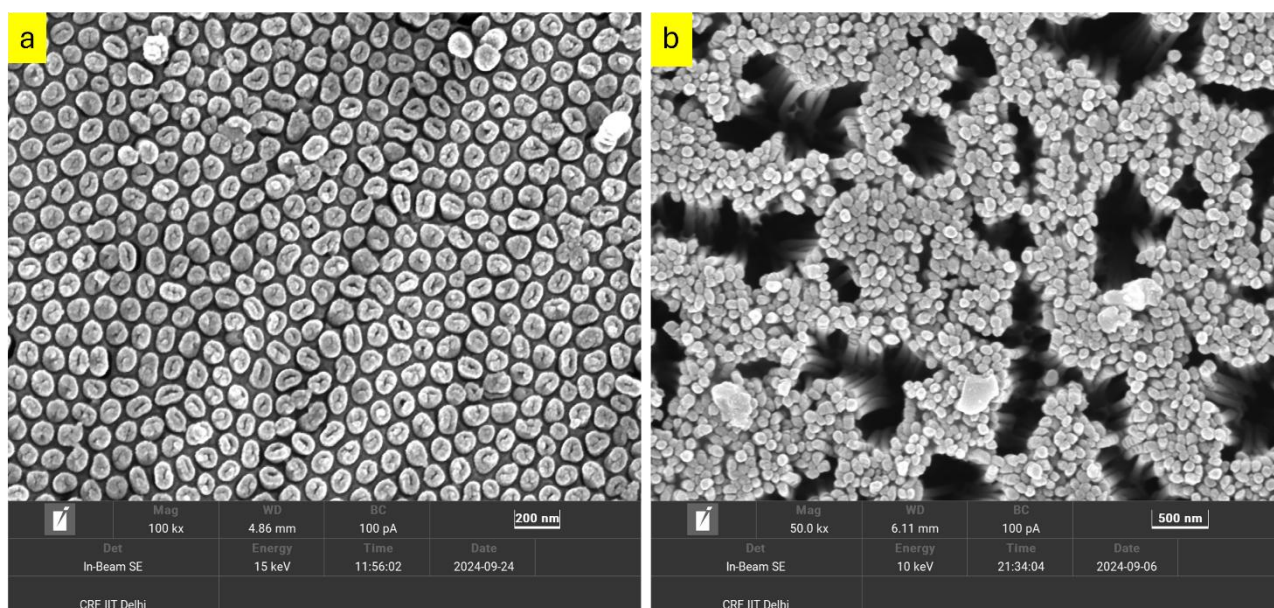


Figure A5 FESEM image of CNP expose from AAO mould for (a) 2 min, (b) 10 min

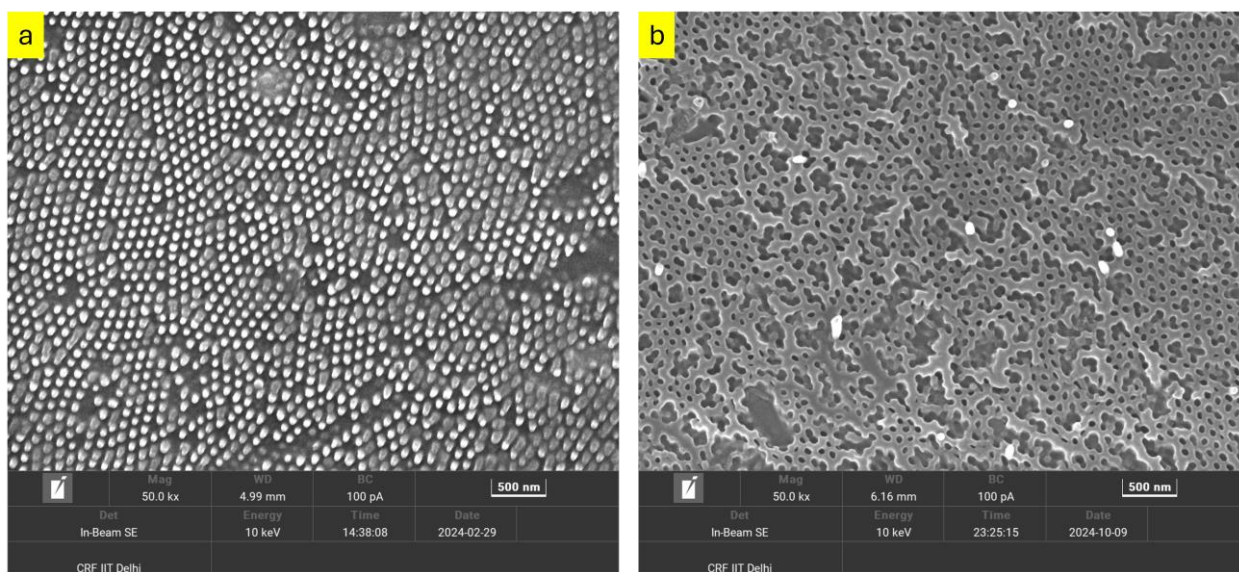


Figure A6 FESEM image of textured (a)moth-eye NPs, (b) nanohole array.

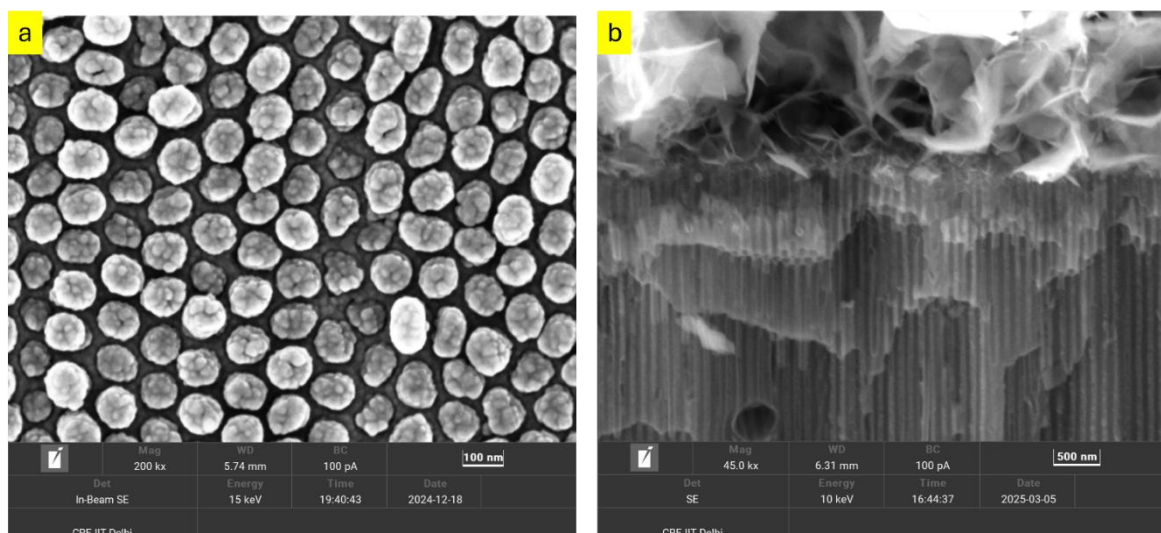


Figure A7 FESEM image of (a) AAO/CNP@3 min gold sputtered, (b) AAO/CNPs@ZnO cross-sectional view for supercapacitor.

References

- [1] D.J. BARBER, I.C. FREESTONE, an Investigation of the Origin of the Colour of the Lycurgus Cup By Analytical Transmission Electron Microscopy, *Archaeometry* 32 (1990) 33–45. <https://doi.org/10.1111/j.1475-4754.1990.tb01079.x>.
- [2] F.E. Wagner, S. Haslbeck, L. Stievano, S. Calogero, Q.A. Pankhurst, K.P. Martinek, Before striking gold in gold-ruby glass, *Nature* 407 (2000) 691–692. <https://doi.org/10.1038/35037661>.
- [3] I. Freestone, N. Meeks, M. Sax, C. Higgitt, A Roman Nanotechnology, *Gold Bull.* 40 (2007) 270–277.
- [4] S.K. Kulkarni, *Nanotechnology: Principles and Practices*, Springer Cham Heidelberg New York Dordrecht London, 2011.
- [5] T.A. Saleh, *Environmental Technology & Innovation Nanomaterials : Classification , properties , and environmental toxicities*, *Environ. Technol. Innov.* 20 (2020) 101067. <https://doi.org/10.1016/j.eti.2020.101067>.
- [6] N.A. Asli, N.E.A. Azhar, M.Z. Nurfazianawatie, K.M. Yusoff, H. Omar, F. Rosman, N.S.A. Malek, R. Akhir, I. Buniyamin, M.J. Salifairus, Z. Khusaimi, M.F. Malek, M. Rusop, S. Abdullah, N.E.A. Azhar, M.Z. Nurfazianawatie, K.M. Yusoff, H. Omar, Mechanism of vertically arrays of carbon nanotubes by camphor based catalysed in-situ growth, *Fullerenes, Nanotub. Carbon Nanostructures* 30 (2022) 476–486. <https://doi.org/10.1080/1536383X.2021.1958317>.
- [7] I. Karadzhov, B. Paulillo, J. Rombaut, K.W. Koch, P. Mazumder, Mechanically-Durable Antireflective Subwavelength Nanoholes on Glass Surfaces Using Lithography-Free Fabrication, (2024). <https://doi.org/10.1021/acsami.3c15391>.
- [8] G. Gupta, R.K. Tyagi, S.K. Rajput, P. Saxena, A. Vashisth, S. Mehndiratta, *Materials Today : Proceedings PVD based thin film deposition methods and characterization / property of different compositional coatings - A critical analysis*, *Mater. Today Proc.* 38 (2021) 259–264. <https://doi.org/10.1016/j.matpr.2020.07.132>.
- [9] X. Wang, J. Xu, X. Quan, Y. Li, Y. Wang, X. Cheng, *Microelectronic Engineering Fast fabrication of silicon nanopillar array using electron beam lithography with two-layer exposure method*, *Microelectron. Eng.* 227 (2020) 111311. <https://doi.org/10.1016/j.mee.2020.111311>.
- [10] A.U. Siddique, R. Xie, D. Horlacher, R. Warren, *Nanoscale Patterning of Surface Nanobubbles by Focused Ion Beam*, *LANGMUR* 40 (2024) 14613–14622. <https://doi.org/10.1021/acs.langmuir.4c01534>.
- [11] M.J. Haslinger, O.S. Maier, M. Pribyl, P. Taus, S. Kopp, H.D. Wanzenboeck, K. Hingerl, M.M. Muehlberger, E. Guillén, *Increasing the Stability of Isolated and Dense High-Aspect-Ratio Nanopillars Fabricated Using UV-Nanoimprint Lithography*, *Nanomaterials* 13 (2023) 1556. <https://doi.org/10.3390/nano13091556>.
- [12] Z. Li, Q. Fan, Y. Yin, *Colloidal Self-Assembly Approaches to Smart Nanostructured Materials*, (2022). <https://doi.org/10.1021/acs.chemrev.1c00482>.
- [13] C. Ku, *Advances in the Fabrication of Nanoporous Anodic Aluminum Oxide and Its*

- Applications to Sensors : A Review, *Nanomater. Rev.* 13 (2023) 2853.
- [14] G. Eddy, J. Poinern, N. Ali, D. Fawcett, Progress in Nano-Engineered Anodic Aluminum Oxide Membrane Development, 2011. <https://doi.org/10.3390/ma4030487>.
 - [15] A. Ruiz-Clavijo, O. Caballero-Calero, M. Martín-González, Revisiting anodic alumina templates: From fabrication to applications, *Nanoscale* 13 (2021) 2227–2265. <https://doi.org/10.1039/d0nr07582e>.
 - [16] K.S. Choudhari, C. Choi, S. Chidangil, S.D. George, Recent Progress in the Fabrication and Optical Properties of Nanoporous Anodic Alumina, *Nanomater. Rev.* 12 (2022) 444.
 - [17] A. Brudzisz, G.D. Sulka, A. Brzózka, Through-hole AAO-SA templates with a small pore diameter prepared by the voltage pulse detachment method, *Microporous Mesoporous Mater.* 283 (2019) 73–81. <https://doi.org/10.1016/j.micromeso.2019.03.052>.
 - [18] A. Terashima, M. Iwai, T. Kikuchi, Applied Surface Science Nanomorphological changes of anodic aluminum oxide fabricated by anodizing in various phosphate solutions over a wide pH range, *Appl. Surf. Sci.* 605 (2022) 154687. <https://doi.org/10.1016/j.apsusc.2022.154687>.
 - [19] L.N. Sacco, S. Vollebregt, Overview of Engineering Carbon Nanomaterials Such As Carbon Nanotubes (CNTs), Carbon Nanofibers (CNFs), Graphene and Nanodiamonds and Other Carbon Allotropes inside Porous Anodic Alumina (PAA) Templates, *Nanomaterials* 13 (2023). <https://doi.org/10.3390/nano13020260>.
 - [20] N. Turaeva, Y. Kim, I. Kuljanishvili, An extended model for chirality selection in single-walled carbon nanotubes, *Nanoscale Adv.* 5 (2023) 3684–3690. <https://doi.org/10.1039/d3na00192j>.
 - [21] A.O. Adeeyo, T.M. Ndou, M.A. Alabi, H.D. Mkoyi, E.M. Enitan, D.B. Beswa, R. Makungo, J.O. Odiyo, We are IntechOpen , the world ’ s leading publisher of Open Access books Built by scientists , for scientists TOP 1 %, Intech i (2016) 13. <https://www.intechopen.com/books/advanced-biometric-technologies/liveness-detection-in-biometrics>.
 - [22] A. Corletto, J.G. Shapter, Nanoscale Patterning of Carbon Nanotubes: Techniques, Applications, and Future, *Adv. Sci.* 8 (2021) 1–71. <https://doi.org/10.1002/advs.202001778>.
 - [23] C. Zhang, Z. Liu, C. Li, J. Cao, J.G. Buijnsters, Templated Synthesis of Diamond Nanopillar Arrays Using Porous Anodic Aluminium Oxide (AAO) Membranes, *Nanomaterials* 13 (2023). <https://doi.org/10.3390/nano13050888>.
 - [24] N. Swain, B. Saravanakumar, M. Kundu, L. Schmidt-Mende, A. Ramadoss, Recent trends in template assisted 3D porous materials for electrochemical supercapacitors, *J. Mater. Chem. A* 9 (2021) 25286–25324. <https://doi.org/10.1039/d1ta06122d>.
 - [25] S.H. Ng, Z.F. Wang, R.T. Tjeung, N.F. De Rooij, Development of a multi-layer microelectrofluidic platform, *Microsyst. Technol.* 13 (2007) 1509–1515. <https://doi.org/10.1007/s00542-006-0341-6>.
 - [26] W. Kim, D. Kim, S. Park, D. Lee, H. Hyun, J. Kim, Engineering lotus leaf-inspired micro- and nanostructures for the manipulation of functional engineering platforms, *J.*

- Ind. Eng. Chem. 61 (2018) 39–52. <https://doi.org/10.1016/j.jiec.2017.11.045>.
- [27] Y. Sugimoto, K. Kajikawa, D. Mayer, A. Offenhäusser, M. Toma, Metal Nanopillar Arrays Fabricated with Moth-Eye Films for Adjustable Plasmonic Colors and Colorimetric Plasmonic Sensing, *ACS Appl. Nano Mater.* 7 (2024) 26423–26433. <https://doi.org/10.1021/acsanm.4c00274>.
- [28] K. Daoudi, K. Ramachandran, S. Columbus, A. Tlili, M. Mahfood, M. Ali, E. Khakani, M. Gaidi, Tuning the nanostructural properties of silver nanoparticles for optimised surface enhanced Raman scattering sensing of SARS CoV-2 spike protein, *Adv. Nat. Sci. Nanosci. Nanotechnol.* 12 (2021) 035011.
- [29] A. Percot, M.C. Maurel, J.F. Lambert, E.L. Zins, *Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy* New insights into the surface Enhanced Raman Scattering (SERS) response of adenine using chemometrics, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 314 (2024) 124177. <https://doi.org/10.1016/j.saa.2024.124177>.
- [30] S. Sompech, S. Thaomola, Highly uniform core / shell structures AuR / Ag and AuR / Ag @ BSA with various shell thicknesses for surface-enhanced Raman scattering, *Adv. Nat. Sci. Nanosci. Nanotechnol.* 15 (2024) 015003.
- [31] H. Li, G. Liu, Y. Zhang, L. Hao, P. Zou, Y. Xu, M. Ji, X. Yu, J. Li, Study of SERS activity of different gold nanostructures prepared by electron beam lithography, *J. Mater. Sci. Mater. Eng.* 19 (2024). <https://doi.org/10.1186/s40712-024-00191-7>.
- [32] R. Sakalys, K.W. Kho, T.E. Keyes, A reproducible , low cost microfluidic microcavity array SERS platform prepared by soft lithography from a 2 photon 3D printed template ~, *Sensors Actuators B . Chem.* 340 (2021). <https://doi.org/10.1016/j.snb.2021.129970>.
- [33] J. Li, X. Chen, J.J. Zhu, DNA functionalized plasmonic nanoassemblies as SERS sensors for environmental analysis, *Aggregate* 4 (2023) 1–21. <https://doi.org/10.1002/agt2.271>.
- [34] F.Y. Alzoubi, A.A. Ahmad, I.A. Aljarrah, A.B. Migdadi, Q.M. Al-Bataineh, Localize surface plasmon resonance of silver nanoparticles using Mie theory, *J. Mater. Sci. Mater. Electron.* 34 (2023) 1–10. <https://doi.org/10.1007/s10854-023-11304-x>.
- [35] H. Hoang, C. Doanh, Q. Hoa, B. Pham, L. Thanh, T. Duy, Facile preparation of three-dimensional copper foam incorporated with Au / CuO nanorods as a durable , reusable and efficient SERS substrate, *Mater. Chem. Phys.* 329 (2025) 130067. <https://doi.org/10.1016/j.matchemphys.2024.130067>.
- [36] Q. Liang, Y. Wang, Y. Yang, T. Xu, Y. Xu, Y. Jeong, S. Yao, X. Song, Nanocellulose / two dimensional nanomaterials composites for advanced supercapacitor electrodes, (2022) 1–12. <https://doi.org/10.3389/fbioe.2022.1024453>.
- [37] X. Zhang, X. Zheng, X. Hu, X. Liu, Y. Xue, Three-Dimensional Carbon Nanomaterial/Aluminum Oxide/Aluminum Composite Current Collectors for Flexible Supercapacitors, *ACS Appl. Energy Mater.* 7 (2024) 3700–3708. <https://doi.org/10.1021/acsaem.4c00056>.
- [38] P. Gaikwad, N. Tiwari, R. Kamat, S.M. Mane, S.B. Kulkarni, A comprehensive review on the progress of transition metal oxides materials as a supercapacitor electrode, *Mater. Sci. Eng. B* 307 (2024) 117544. <https://doi.org/10.1016/j.mseb.2024.117544>.

- [39] M.T. Turchi Moghadam, M. Seifi, Fabrication and investigation of ZnO-CNT@Fe₃O₄/NF as supercapacitor electrode by using a novel preparation method of CNT, *Diam. Relat. Mater.* 125 (2022) 108962.
<https://doi.org/10.1016/j.diamond.2022.108962>.
- [40] J. Yu, N. Fu, J. Zhao, R. Liu, F. Li, Y. Du, Z. Yang, High Specific Capacitance Electrode Material for Supercapacitors Based on Resin-Derived Nitrogen-Doped Porous Carbons, (2019). <https://doi.org/10.1021/acsomega.9b01916>.
- [41] S. Ostmann, C.J. Kähler, A simple projection photolithography method for low - cost rapid prototyping of microfluidic chips, *Microfluid. Nanofluidics* 26 (2022) 1–7.
<https://doi.org/10.1007/s10404-022-02531-5>.
- [42] M.S.M. Saifullah, M. Asbahi, D.C.J. Neo, Z. Mahfoud, H.R. Tan, S.T. Ha, N. Dwivedi, T. Dutta, S. Dolmanan, Z. Aabdin, M. Bosman, R. Ganesan, S. Tripathy, D.G. Hasko, S. Valiyaveetil, Patterning at the Resolution Limit of Commercial Electron Beam Lithography, (2022). <https://doi.org/10.1021/acs.nanolett.2c02339>.
- [43] E. Gacka, P. Kunicki, A. Sikora, R. Bogdanowicz, M. Ficek, T. Gotszalk, I.W. Rangelow, K. Kwoka, Focused ion beam-based microfabrication of boron-doped diamond single-crystal tip cantilevers for electrical and mechanical scanning probe microscopy, *Measurement* 188 (2022) 110373.
<https://doi.org/10.1016/j.measurement.2021.110373>.
- [44] X. Feng, L. Sun, W. Wang, Y. Zhao, J. Shi, Construction of CdS @ ZnO core – shell nanorod arrays by atomic layer deposition for efficient photoelectrochemical H₂ evolution, *Sep. Purif. Technol.* 324 (2023) 124520.
<https://doi.org/10.1016/j.seppur.2023.124520>.
- [45] R. Cherry, J.J. Muhanga, H. Mehrabi, Monolithic light concentration by core – shell TiO₂ nanostructures templated by monodisperse polymer colloidal monolayers, *Nanotechnology* 34 (2023) 345601.
- [46] G. Geng, Z. Zhang, C. Li, R. Pan, Y. Li, H. Yang, Atomic Layer Assembly Based on Sacrificial Templates for 3D Nanofabrication, *Micromachines Rev.* 13 (2022) 856.
<https://doi.org/https://doi.org/10.3390/mi13060856>.
- [47] A.K. Eessaa, A.M. El-shamy, Microelectronic Engineering Review on fabrication , characterization , and applications of porous anodic aluminum oxide films with tunable pore sizes for emerging technologies, *Microelectron. Eng.* 279 (2023) 112061.
<https://doi.org/10.1016/j.mee.2023.112061>.
- [48] M.V. Singh, K. Tiwari, R. Gupta, Catalytic Chemical Vapor Deposition Methodology for Carbon Nanotubes Synthesis, 202204715 (2023).
<https://doi.org/10.1002/slct.202204715>.
- [49] Y. Xia, Z. Zhang, M. Gao, Y. Zheng, L. Chen, Y. Si, S. Mei, Enhancement in photoelectric performance of dye-sensitized solar cells with inverted pyramid structures based on nanoimprint lithography, *AIP* 11 (2021).
<https://doi.org/10.1063/5.0054147>.
- [50] A. Baji, S. Gangadoo, V. Khanh, M. Abtahi, A. Budiman, Fabrication of superhydrophobic polyvinylidene fluoride-co-hexafluoropropylene films enabled by nanoimprint lithography, *Mater. Lett.* 311 (2022) 131555.
<https://doi.org/10.1016/j.matlet.2021.131555>.

- [51] E. Vereshchagina, K. Milenko, F.T. Dullo, Microfluidic Surface-Enhanced Raman Scattering Sensors based on Nanoimprint Resist for Sensitive Detection of Pesticides in Water, 2023 IEEE SENSORS (n.d.) 1–4.
<https://doi.org/10.1109/SENSORS56945.2023.10324970>.
- [52] S. Fialkova, S. Yarmolenko, A. Krishnaswamy, J. Sankar, V. Shanov, M.J. Schulz, S. Desai, Nanoimprint Lithography for Next-Generation Carbon Nanotube-Based Devices, *Nanomater.* Artic. 14 (2024) 1011. <https://doi.org/https://doi.org/10.3390/nano14121011>.
- [53] V.J. Einck, M. Torfeh, A. McClung, D.E. Jung, M. Mansouree, A. Arbabi, J.J. Watkins, Scalable Nanoimprint Lithography Process for Manufacturing Visible Metasurfaces Composed of High Aspect Ratio TiO₂ Meta-Atoms, (2021).
<https://doi.org/10.1021/acsphotonics.1c00609>.
- [54] M.C. Turhan, R.P. Lynch, H. Jha, P. Schmuki, S. Virtanen, Anodic growth of self-ordered magnesium oxy-fluoride nanoporous/tubular layers on Mg alloy (WE43), *Electrochem. Commun.* 12 (2010) 796–799.
<https://doi.org/10.1016/j.elecom.2010.03.036>.
- [55] Y. Li, S. Chang, X. Liu, J. Huang, J. Yin, G. Wang, D. Cao, Nanostructured CuO directly grown on copper foam and their supercapacitance performance, *Electrochim. Acta* 85 (2012) 393–398. <https://doi.org/10.1016/j.electacta.2012.07.127>.
- [56] L. Zaraska, K. Gawlak, M. Gurgul, D.K. Chlebda, R.P. Socha, G.D. Sulka, Controlled synthesis of nanoporous tin oxide layers with various pore diameters and their photoelectrochemical properties, *Electrochim. Acta* 254 (2017) 238–245.
<https://doi.org/10.1016/j.electacta.2017.09.113>.
- [57] M. Martín-González, R. Martínez-Moro, M.H. Aguirre, E. Flores, O. Caballero-Calero, Unravelling nanoporous anodic iron oxide formation, *Electrochim. Acta* 330 (2020). <https://doi.org/10.1016/j.electacta.2019.135241>.
- [58] R. Kisslinger, S. Riddell, S. Savela, P. Kar, U.K. Thakur, S. Zeng, K. Shankar, Transparent nanoporous P-type NiO films grown directly on non-native substrates by anodization, *J. Mater. Sci. Mater. Electron.* 30 (2019) 11327–11335.
<https://doi.org/10.1007/s10854-019-01480-0>.
- [59] T.M. David, P.R. Dev, P. Wilson, P. Sagayaraj, T. Mathews, A critical review on the variations in anodization parameters toward microstructural formation of TiO₂ nanotubes, *Electrochem. Sci. Adv.* 2 (2022) 1–64.
<https://doi.org/10.1002/elsa.202100083>.
- [60] W. Lee, S. Park, Porous Anodic Aluminum Oxide : Anodization and Templated Synthesis of Functional Nanostructures, *Chem. Rev.* 114 (2014) 7487–7556.
<https://doi.org/dx.doi.org/10.1021/cr500002z>.
- [61] X. Sun, X. Guo, J. Zhang, J. Wu, Y. Shi, H. Sun, A new study on formation mechanism of ordered porous anodized metal oxides, *Rare Met.* 43 (2024) 5410–5418.
<https://doi.org/10.1007/s12598-024-02802-w>.
- [62] Y. Ni, J. Zhang, T. Gong, M. Sun, Z. Zhao, X. Li, H. Yu, Quantitative analysis of the volume expansion of nanotubes during constant voltage anodization, *Surfaces and Interfaces* 26 (2021) 101419. <https://doi.org/10.1016/j.surfin.2021.101419>.

- [63] X. Sun, X. Mo, L. Liu, H. Sun, C. Pan, Voltage-Driven Room-Temperature Resistance and Magnetization Switching in Ceramic TiO₂/PAA Nanoporous Composite Films, *ACS Appl. Mater. Interfaces* 11 (2019) 21661–21667. <https://doi.org/10.1021/acsami.9b02593>.
- [64] X. Du, D. Cai, Q. Ou, D. Chen, Z. Zhang, P. Liang, Surface & Coatings Technology Fabrication and characterization of the hierarchical AAO film and AAO-MnO₂ composite as the anode foil of aluminum electrolytic capacitor, *Surf. Coat. Technol.* 419 (2021) 127286. <https://doi.org/10.1016/j.surfcoat.2021.127286>.
- [65] H. Zhang, M. Zhou, H. Zhao, Y. Lei, Ordered nanostructures arrays fabricated by anodic aluminum oxide (AAO) template- directed methods for energy conversion, (n.d.).
- [66] F.A.S. Ribeiro, D. V Freitas, L. Pinto, L.B.C. Oliveira, L.J.L. Maciel, J.E. Kulesza, G. Machado, Optimization of TiO₂ Nanotubes Anodization Assisted by Response Surface Methodology for Enhanced Photoelectrochemical Performance, 03109 (2025). <https://doi.org/10.1002/slct.202503109>.
- [67] A. Apolinário, C.T. Sousa, G.N.P. Oliveira, A.M.L. Lopes, J. Ventura, L. Andrade, A. Mendes, J.P. Araújo, Tailoring the Anodic Hafnium Oxide Morphology Using Different Organic Solvent Electrolytes, *Nanomaterials* 10 (2020) 382. <https://doi.org/10.3390/nano10020382>.
- [68] B. Valdez-salas, J. Castillo-saenz, E. Beltr, J. Salom, One-step synthesis of freestanding and translucent ZrO₂ nanotube membranes by direct electrochemical anodization, 368 (2024) 10–13. <https://doi.org/10.1016/j.matlet.2024.136635>.
- [69] H. Yu, Z. Liu, T. Feng, G. Li, W. Zhang, X. Fu, R. Wang, Z. Tong, Y. Wang, K. Wang, Nitrogen-Doped α -Fe₂O₃ Nanosheets on Stainless-Steel Foils by Anodization for Self-Supported, Flexible, Binder-Free Supercapacitors, *ACS Appl. Energy Mater.* 8 (2025) 7963–7973. <https://doi.org/10.1021/acsaem.5c00168>.
- [70] J. Dong, C. Li, Y. Wang, Y. Fan, Q. Han, W. Gao, Y. Wang, K. Ren, J. Qi, E. He, *Spectrochimica Acta Part A : Molecular and Biomolecular Spectroscopy* Fabrication of complexed nanostructure using AAO template for ultrasensitive SERS detection, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 312 (2024) 124044. <https://doi.org/10.1016/j.saa.2024.124044>.
- [71] C.K. Chung, J. Electrochem, C. Soc, Role of Oxalate Anions on the Evolution of Widened Pore Diameter and Characteristics of Room-Temperature Anodic Aluminum Oxide Role of Oxalate Anions on the Evolution of Widened Pore Diameter and Characteristics of Room-Temperature Anodic Aluminum, (2017). <https://doi.org/10.1149/2.0681704jes>.
- [72] C.K. Chung, M.W. Liao, H.C. Chang, C.T. Lee, Effects of temperature and voltage mode on nanoporous anodic aluminum oxide films by one-step anodization, *Thin Solid Films* 520 (2011) 1554–1558. <https://doi.org/10.1016/j.tsf.2011.08.053>.
- [73] A.P. Leontiev, I. V. Roslyakov, K.S. Napolskii, Complex influence of temperature on oxalic acid anodizing of aluminium, *Electrochim. Acta* 319 (2019) 88–94. <https://doi.org/10.1016/j.electacta.2019.06.111>.
- [74] G.D. Sulka, W.J. Stepniowski, Structural features of self-organized nanopore arrays formed by anodization of aluminum in oxalic acid at relatively high temperatures,

- Electrochim. Acta 54 (2009) 3683–3691.
<https://doi.org/10.1016/j.electacta.2009.01.046>.
- [75] B. Tzaneva, I. Vrublevsky, Valentin Videkov, N. Lushpa, Role of electrode temperature in anodic growth of sulfuric acid alumina films, *J. Solid State Electrochem.* 29 (2025) 1459–1465. <https://doi.org/10.1007/s10008-024-06036-9>.
 - [76] Y. Pu, J. Hu, T. Yao, L. Li, J. Zhao, Y. Guo, Influence of anodization parameters on film thickness and volume expansion of thick- and large-sized anodic aluminum oxide film, *J. Mater. Sci. Mater. Electron.* 32 (2021) 13708–13718.
<https://doi.org/10.1007/s10854-021-05948-w>.
 - [77] C.A. Ku, C.C. Wu, C.W. Hung, C.K. Chung, Influence of Normal-to-High Anodizing Voltage on AAO Surface Hardness from 1050 Aluminum Alloy in Oxalic Acid, *Micromachines* 15 (2024). <https://doi.org/10.3390/mi15060683>.
 - [78] A.R. Grayeli, P. Balashabadi, M. Mojtahedzadeh, Structural and Hydrophilic Properties of Nanoporous Aluminium Oxide Film as a Function of Voltage Anodization, *ECS J. Solid State Sci. Technol.* 13 (2024) 113003.
<https://doi.org/10.1149/2162-8777/ad8bf2>.
 - [79] C.K. Chung, W.T. Chang, M.W. Liao, H.C. Chang, Effect of pulse voltage and aluminum purity on the characteristics of anodic aluminum oxide using hybrid pulse anodization at room temperature, *Thin Solid Films* 519 (2011) 4754–4758.
<https://doi.org/10.1016/j.tsf.2011.01.029>.
 - [80] Y. Liang, C. Wang, C. Kei, Y. Hsueh, W. Cho, T. Perng, Photocatalysis of Ag-Loaded TiO₂ Nanotube Arrays Formed by Atomic Layer Deposition, *J. Phys. Chem. C* 115 (2011) 9498–9502. <https://doi.org/10.1021/jp202111p>.
 - [81] Y. Zhang, M. Liu, B. Peng, Z. Zhou, X. Chen, S. Yang, Controlled Phase and Tunable Magnetism in Ordered Iron Oxide Nanotube Arrays Prepared by Atomic Layer Deposition, *Nat. Publ. Gr.* (2016) 1–8. <https://doi.org/10.1038/srep18401>.
 - [82] Q. Liu, Growth mechanism and kinetics of vertically aligned carbon nanotube arrays, (2021) 1–18. <https://doi.org/10.1002/eom2.12118>.
 - [83] M. Golshadi, L.K. Wright, I.M. Dickerson, M.G. Schrlau, High-Efficiency Gene Transfection of Cells through Carbon Nanotube Arrays, (2016) 3014–3020.
<https://doi.org/10.1002/sml.201503878>.
 - [84] F. Schütt, S. Signetti, H. Krüger, S. Röder, D. Smazna, S. Kaps, S.N. Gorb, Y.K. Mishra, N.M. Pugno, R. Adelung, networks, *Nat. Commun.* (n.d.) 1–10.
<https://doi.org/10.1038/s41467-017-01324-7>.
 - [85] O.I. Semenova, L.I. Fedina, A.K. Gutakovskii, S. V Sitnikov, N.N. Kurus, A.A. Dudin, A.A. Pavlov, D. V Sheglov, S. Branch, CVD SYNTHESIS AND THE STRUCTURE OF VERTICALLY ALIGNED CNT ARRAYS, 63 (2022) 1145–1152.
<https://doi.org/10.1134/S0022476622070095>.
 - [86] F. Wahida, A. Zulkifli, H. Yazid, A. Mutalib, Immobilization of carbon nanotubes decorated gold nanoparticles on anodized aluminium oxide (Au-CNTs-AAO) membrane for enhanced catalytic performance, *Mater. Chem. Phys.* 264 (2021) 124445. <https://doi.org/10.1016/j.matchemphys.2021.124445>.
 - [87] S. Jessl, S. Engelke, D. Copic, J.J. Baumberg, M. De Volder, Anisotropic Carbon

- Nanotube Structures with High Aspect Ratio Nanopores for Li-Ion Battery Anodes, (2021). <https://doi.org/10.1021/acsanm.1c01157>.
- [88] Y. Kim, K. Lee, J.S. Lee, G.Y. Jung, W.B. Kim, Nanoimprint lithography patterns with a vertically aligned nanoscale tubular carbon structure, (2008). <https://doi.org/10.1088/0957-4484/19/36/365305>.
- [89] C. Raksiri, P. Potejanasak, T. Dokyor, Fabrication of Nanogroove Arrays on Acrylic Film Using Micro-Embossing Technique, *Polymers (Basel)*. 15 (2023) 3804. <https://doi.org/10.3390/polym15183804>.
- [90] H. Hung, S. Lin, R. Lin, T. Huang, C. Wu, Fabrication of tunable Large-Area Moth-Eye nanostructures for antireflection and hydrophobicity via anodic aluminum oxide templates and nanoimprint lithography, (2025).
- [91] H. Lee, A. Yi, J.G. Choi, D.H. Ko, H. Jung Kim, Texturing of polydimethylsiloxane surface for anti-reflective films with super-hydrophobicity in solar cell application, *Appl. Surf. Sci.* 584 (2022) 152625. <https://doi.org/10.1016/J.APSUSC.2022.152625>.
- [92] T. Zhou, X. Su, X. Yao, G. Wang, X. Yang, Q. Yu, W. Guo, B. Zhao, X. Wang, Impact of process parameters on the flow behavior and filling accuracy of photoresist in hot embossing for microgroove array, *Mater. Today Commun.* 41 (2024) 110770. <https://doi.org/10.1016/j.mtcomm.2024.110770>.
- [93] Y. Song, K. Kim, K. Choi, B. Ki, J. Oh, Nano/micro double texturing of antireflective subwavelength structures on inverted pyramids, *Sol. Energy* 135 (2016) 291–296. <https://doi.org/10.1016/j.solener.2016.06.009>.
- [94] H. Zhang, Applied Surface Science Biomimetic high water adhesion superhydrophobic surface via UV nanoimprint lithography, *Appl. Surf. Sci.* 633 (2023) 157610. <https://doi.org/10.1016/j.apsusc.2023.157610>.
- [95] S.H. Lee, S. Yoon, H. Jeong, M. Han, S.M. Choi, J.G. Kim, J.W. Park, G.Y. Jung, B.K. Cho, W.B. Kim, Printable nanoscale metal ring arrays via vertically aligned carbon nanotube platforms, *Nanoscale* 5 (2013) 10653–10659. <https://doi.org/10.1039/c3nr02620e>.
- [96] S.H. Lee, S.M. Choi, S. Yoon, H. Jeong, G.Y. Jung, B.K. Cho, W.B. Kim, Transfer printing of metal nanoring and nanodot arrays for use in catalytic reactions, *Chem. Commun.* 50 (2014) 8472–8475. <https://doi.org/10.1039/c4cc02939a>.
- [97] A.M. Saleem, J. Berg, V. Desmaris, M.S. Kabir, Nanoimprint lithography using vertically aligned carbon nanostructures as stamps, *Nanotechnology* 20 (2009) 375302. <https://doi.org/10.1088/0957-4484/20/37/375302>.
- [98] J. Li, Y. Feng, L. Liang, F. Liao, W. Huang, K. Li, G. Cui, Z. Zuo, Flexible Multicavity SERS Substrate Based on Ag Nanoparticle-Decorated Aluminum Hydrous Oxide Nanoflake Array for Highly Sensitive In Situ Detection, *ACS Appl. Mater. Interfaces* 16 (2024) 35771–35780. <https://doi.org/10.1021/acsami.4c05642>.
- [99] A. Mukherjee, F. Wackenhut, A. Dohare, A. Horneber, A. Lorenz, H. MÜchler, A.J. Meixner, H.A. Mayer, M. Brecht, Three-Dimensional (3D) Surface-Enhanced Raman Spectroscopy (SERS) Substrates: Fabrication and SERS Applications, *J. Phys. Chem. C* 127 (2023) 13689–13698. <https://doi.org/10.1021/acs.jpcc.3c02410>.
- [100] X. Zhao, Y. Wang, Y. Yao, L. Chen, B. Lin, W. Zheng, Y. Zeng, L. Li, Y. She, L.

- Guo, One-Step, On-Site Chemical Printing of a 3D Plasmon-Coupled Silver Nanocoral Substrate toward SERS-Based POCT, *Anal. Chem.* 95 (2023) 6836–6845. <https://doi.org/10.1021/acs.analchem.2c05339>.
- [101] M. Fleischmann, RAMAN SPECTRA OF PYRIDINE ADSORBED AT A SILVER ELECTRODE, *Chem. Eng. J.* 26 (1974) 2–5.
- [102] U.S. Dinish, F. Chit, A. Agarwal, M. Olivo, Biosensors and Bioelectronics Development of highly reproducible nanogap SERS substrates : Comparative performance analysis and its application for glucose sensing, *Biosens. Bioelectron.* 26 (2011) 1987–1992. <https://doi.org/10.1016/j.bios.2010.08.069>.
- [103] S. Kalasung, I. Chatnuntaweche, V. Patthanasettakul, S. Limwichean, K. Lertborworn, M. Horprathum, N. Nuntawong, P. Eiamchai, K. Aiempnanakit, Au-decorated ZnO nanorod arrays for SERS-active substrates towards trace detection and classification of pentaerythritol tetranitrate, *Mater. Today Proc.* 47 (2021) 3517–3524. <https://doi.org/10.1016/j.matpr.2021.03.511>.
- [104] K. Sun, Q. Deng, H. Tang, AAO Template-Assisted Fabrication of Ordered Ag Nanoparticles-Decorated Au Nanotubes Array for Surface-Enhanced Raman Scattering Detection, *Sustainability* 14 (2022) 1305. <https://doi.org/10.3390/su14031305>.
- [105] A. Prasad, A. Chaichi, A. Mahigir, S.P. Sahu, D. Ganta, G. Veronis, M.R. Gartia, Ripple mediated surface enhanced Raman spectroscopy on graphene, *Carbon N. Y.* 157 (2020) 525–536. <https://doi.org/10.1016/j.carbon.2019.09.078>.
- [106] X. Liang, B. Liang, Z. Pan, X. Lang, Y. Zhang, G. Wang, P. Yin, L. Guo, Tuning plasmonic and chemical enhancement for SERS detection on graphene-based Au hybrids, *Nanoscale* 7 (2015) 20188–20196. <https://doi.org/10.1039/c5nr06010a>.
- [107] J. Zhang, X. Zhang, C. Lai, H. Zhou, Y. Zhu, Silver-decorated aligned CNT arrays as SERS substrates by high temperature annealing, *Opt. Express* 22 (2014) 21157. <https://doi.org/10.1364/oe.22.021157>.
- [108] Y. Wang, X. Xiao, H. Xue, H. Pang, Zinc Oxide Based Composite Materials for Advanced Supercapacitors, (2018) 550–565. <https://doi.org/10.1002/slct.201702780>.
- [109] N. Eswaramoorthy, S. Rajendran, B. Arjun Kumar, S. Nallusamy, M. Rengasamy, Y. Selvaraj, S. Sangaraju, T. Krishnan, G. Kumaresan, K. Rajaram, Influence of ZnO/MWCNTs based hybrid electrodes for boosting the performance of photovoltaic and supercapacitor devices, *Mater. Chem. Phys.* 316 (2024) 129049. <https://doi.org/10.1016/j.matchemphys.2024.129049>.
- [110] M. Saranya, R. Ramachandran, F. Wang, Journal of Science : Advanced Materials and Devices Graphene-zinc oxide (G-ZnO) nanocomposite for electrochemical supercapacitor applications, *J. Sci. Adv. Mater. Devices* 1 (2016) 454–460. <https://doi.org/10.1016/j.jsamd.2016.10.001>.
- [111] H.Y. Jung, M.B. Karimi, M.G. Hahm, P.M. Ajayan, Y.J. Jung, Transparent, flexible supercapacitors from nano-engineered carbon films, *Sci. Rep.* 2 (2012) 1–5. <https://doi.org/10.1038/srep00773>.
- [112] M.G. Hahm, A. Leela Mohana Reddy, D.P. Cole, M. Rivera, J.A. Vento, J. Nam, H.Y. Jung, Y.L. Kim, N.T. Narayanan, D.P. Hashim, C. Galande, Y.J. Jung, M. Bundy, S.

- Karna, P.M. Ajayan, R. Vajtai, Carbon nanotube-nanocup hybrid structures for high power supercapacitor applications, *Nano Lett.* 12 (2012) 5616–5621. <https://doi.org/10.1021/nl3027372>.
- [113] F. Rajab, Effect of the chemical vapor deposition process on the aspect ratio of vertically aligned carbon nanotubes (VACNTs), *MRS Adv.* 8 (2023) 343–348. <https://doi.org/10.1557/s43580-022-00392-2>.
- [114] N.T. Dee, M. Schneider, D.N. Zakharov, P.R. Kidambi, A.J. Hart, Automated processing of environmental transmission electron microscopy images for quantification of thin film dewetting and carbon nanotube nucleation dynamics, *Carbon N. Y.* 192 (2022) 249–258. <https://doi.org/10.1016/j.carbon.2022.02.019>.
- [115] M.J. Yadav, S. Aravindan, P. V. Rao, Enhanced control over size, areal density, and shape of substrate-supported Au and Ag nanoparticles by solid-state dewetting and alloying, *Nanotechnology* 35 (2024). <https://doi.org/10.1088/1361-6528/ad2e4c>.
- [116] J.K. Radhakrishnan, P.S. Pandian, V.C. Padaki, H. Bhusan, K.U.B. Rao, J. Xie, J.K. Abraham, V.K. Varadan, Growth of multiwalled carbon nanotube arrays by chemical vapour deposition over iron catalyst and the effect of growth parameters, *Appl. Surf. Sci.* 255 (2009) 6325–6334. <https://doi.org/10.1016/j.apsusc.2009.02.010>.
- [117] H. Gergeroglu, M.F. Ebeoglugil, Investigation of the effect of catalyst type, concentration, and growth time on carbon nanotube morphology and structure, *Carbon Lett.* 32 (2022) 1729–1743. <https://doi.org/10.1007/s42823-022-00381-3>.
- [118] P. Chowdhury, A.N. Thomas, M. Sharma, H.C. Barshilia, An approach for in situ measurement of anode temperature during the growth of self-ordered nanoporous anodic alumina thin films: Influence of Joule heating on pore microstructure, *Electrochim. Acta* 115 (2014) 657–664. <https://doi.org/10.1016/j.electacta.2013.10.178>.
- [119] L. Zaraska, W.J. Stępniewski, M. Jaskuła, G.D. Sulka, Analysis of nanopore arrangement of porous alumina layers formed by anodizing in oxalic acid at relatively high temperatures, *Appl. Surf. Sci.* 305 (2014) 650–657. <https://doi.org/10.1016/j.apsusc.2014.03.154>.
- [120] B. Sellarajan, M. Sharma, S.K. Ghosh, H.S. Nagaraja, H.C. Barshilia, P. Chowdhury, Microporous and Mesoporous Materials Effect of electrolyte temperature on the formation of highly ordered nanoporous alumina template, 224 (2016) 262–270.
- [121] K. Nielsch, J. Choi, K. Schwirn, R.B. Wehrspohn, Self-ordering Regimes of Porous Alumina : The 10 % Porosity Rule, (2002) 1–4.
- [122] D.A. Bograchev, T.B. Kabanova, A.D. Davydov, Electrodeposition of metals into nano/micropores of templates: a type of electrochemistry under confinement (review), Springer Berlin Heidelberg, 2025. <https://doi.org/10.1007/s10008-024-06118-8>.
- [123] S. Jeong, Carbon nanotubes based on anodic aluminum oxide nano-template, *Carbon N. Y.* 42 (2004) 2073–2080. <https://doi.org/10.1016/j.carbon.2004.04.015>.
- [124] E. Picheau, A. Impellizzeri, D. Rybkovskiy, M. Bayle, J.Y. Mevellec, F. Hof, H. Saadaoui, L. Noé, A.C. Torres Dias, J.L. Duvail, M. Monthieux, B. Humbert, P. Puech, C.P. Ewels, A. Pénicaud, Intense Raman D Band without Disorder in Flattened Carbon Nanotubes, *ACS Nano* 15 (2021) 596–603.

<https://doi.org/10.1021/acsnano.0c06048>.

- [125] J. Yuan, Y. Wang, M. Tang, X. Hao, J. Liu, G. Zhang, Y. Zhang, Effect of the pore structure of coal-based activated carbon and hydrogen addition on methane decomposition for the preparation of carbon nanotubes, *Vacuum* 207 (2023) 111584. <https://doi.org/10.1016/j.vacuum.2022.111584>.
- [126] P. Atz-Dick, A. Konrath, Y. Rátiva Melo, C. Radtke, L.F.P. Dick, Aluminum anodizing with simultaneous silanization for increased hydrophobicity and corrosion protection, *Appl. Surf. Sci.* 593 (2022). <https://doi.org/10.1016/j.apsusc.2022.153392>.
- [127] S.H. Lim, J.A. Lee, J.E. Kim, S. La, V.T. Huong, T. Tran, N.T. Ho, S.M. Noh, S.J. Son, S. Joo, Nanopatterned Polymer Molds Using Anodized Aluminum Templates for Anti-Reflective Coatings, *Polymers (Basel)*. 13 (2021) 1–10. <https://doi.org/10.3390/polym13193333>.
- [128] J. Schroers, G. Kumar, Bulk Metallic Glass in Micro to Nano Length Scale Applications, *Nano-Micro Interface Bridg. Micro Nano Worlds Second Ed.* 1–2 (2015) 159–188. <https://doi.org/10.1002/9783527679195.ch9>.
- [129] Y.J. Chang, R.Y. Chang, T.A. Osswald, Measurement and modeling of bulk viscosity for polystyrene melts, *Phys. Fluids* 33 (2021). <https://doi.org/10.1063/5.0055930>.
- [130] R. Melentiev, G. Lubineau, Large-scale hot embossing of 1 μm high-aspect-ratio textures on ABS polymer, *CIRP J. Manuf. Sci. Technol.* 38 (2022) 340–349. <https://doi.org/10.1016/j.cirpj.2022.05.011>.
- [131] J.J. Roa, G. Oncins, F.T. Dias, V.N. Vieira, J. Schaf, M. Segarra, AFM as an alternative for Young's modulus determination in ceramic materials in elastic deformation regime, *Phys. C Supercond. Its Appl.* 471 (2011) 544–548. <https://doi.org/10.1016/j.physc.2011.05.249>.
- [132] S. V. Kontomaris, A. Malamou, A. Stylianou, The Hertzian theory in AFM nanoindentation experiments regarding biological samples: Overcoming limitations in data processing, *Micron* 155 (2022) 103228. <https://doi.org/10.1016/j.micron.2022.103228>.
- [133] K. Enomoto, S. Kitakata, T. Yasuhara, N. Ohtake, T. Kuzumaki, Y. Mitsuda, Measurement of Young's modulus of carbon nanotubes by nanoprobe manipulation in a transmission electron microscope, *Appl. Phys. Lett.* 88 (2006) 2004–2007. <https://doi.org/10.1063/1.2195010>.
- [134] B. Lukić, J.W. Seo, E. Couteau, K. Lee, S. Gradečak, R. Berkecz, K. Hernadi, S. Delpeux, T. Cacciaguerra, F. Béguin, A. Fonseca, J.B. Nagy, G. Csányi, A. Kis, A.J. Kulik, L. Forró, Elastic modulus of multi-walled carbon nanotubes produced by catalytic chemical vapour deposition, *Appl. Phys. A Mater. Sci. Process.* 80 (2005) 695–700. <https://doi.org/10.1007/s00339-004-3100-5>.
- [135] D. Patil, A. Sharma, S. Aravindan, P.V. Rao, Development of hot embossing setup and fabrication of ordered nanostructures on large area of polymer surface for antibiofouling application, 14 (2019) 191–195. <https://doi.org/10.1049/mnl.2018.5462>.
- [136] J. Yeo, M.J. Choi, D.S. Kim, Robust hydrophobic surfaces with various micropillar arrays, *Robust Hydrophobic Surfaces with Var. Micropilla* 20 (2010) 025028. <https://doi.org/10.1088/0960-1317/20/2/025028>.

- [137] Y.J. Sheng, S. Jiang, H.K. Tsao, Effects of geometrical characteristics of surface roughness on droplet wetting, *J. Chem. Phys.* 127 (2007).
<https://doi.org/10.1063/1.2804425>.
- [138] P. Zhang, J. Wu, S. Wang, Fabrication of triangular Au / Ag nanoparticle arrays with sub-10 nm nanogap controlled by flexible substrate for surface-enhanced Raman scattering, *Nanotechnology* 34 (2023).
- [139] X. Jin, Q. Zhu, L. Feng, X. Li, H. Zhu, H. Miao, Z. Zeng, Y. Wang, Y. Li, L. Wang, X. Liu, G. Shi, Light-Trapping SERS Substrate with Regular Bioinspired Arrays for Detecting Trace Dyes, *ACS Appl. Mater. Interfaces* 13 (2021) 11535–11542.
<https://doi.org/10.1021/acsami.1c00702>.
- [140] X. Qu, L. Cao, F. Du, Fabrication of ordered arrays of CNT/TiO₂ nanotubes and their photocatalytic properties, *RSC Adv.* 5 (2015) 20976–20980.
<https://doi.org/10.1039/c4ra17002d>.
- [141] Z. Li, L. Deng, I.A. Kinloch, R.J. Young, Progress in Materials Science Raman spectroscopy of carbon materials and their composites : Graphene , nanotubes and fibres, *Prog. Mater. Sci.* 135 (2023) 101089.
<https://doi.org/10.1016/j.pmatsci.2023.101089>.
- [142] R. Trusovas, G. Rac, Recent Advances in Laser Utilization in the Chemical Modification of Graphene Oxide and Its Applications, (2016) 37–65.
<https://doi.org/10.1002/adom.201500469>.
- [143] W. Fang, Z. Zhang, N. Miao, R. Yang, Z. Xiao, X. Shen, Y. Cao, W. Xin, Highly Uniform Fabrication of Gold Nanoparticles on Carbon Nanotube Sheets for Sensors Based on Surface-Enhanced Raman Spectroscopy with Improved Reproducibility, *ACS Appl. Nano Mater.* 6 (2023) 9949–9957.
<https://doi.org/10.1021/acsanm.3c01989>.
- [144] A. Kaushik, J. Singh, R. Soni, J.P. Singh, MoS₂ – Ag Nanocomposite-Based SERS Substrates with an Ultralow Detection Limit, *Appl. NANO Mater.* 6 (2023) 9236.
<https://doi.org/10.1021/acsanm.3c00813>.
- [145] T. Van Nguyen, D.C. Vu, V.H. Pham, T.B. Pham, V.H. Pham, H. Bui, Optik Improvement of SERS for detection of ultra-low concentration of methyl orange by nanostructured silicon decorated with Ag nanoparticles, *Optik (Stuttg.)*. 231 (2021) 166431. <https://doi.org/10.1016/j.ijleo.2021.166431>.
- [146] A.S. Al-Asadi, L.A. Henley, M. Wasala, B. Muchharla, N. Perea-Lopez, V. Carozo, Z. Lin, M. Terrones, K. Mondal, K. Kordas, S. Talapatra, Aligned carbon nanotube/zinc oxide nanowire hybrids as high performance electrodes for supercapacitor applications, *J. Appl. Phys.* 121 (2017). <https://doi.org/10.1063/1.4979098>.
- [147] G.P. Scisco, K. Haynes, K.S. Jones, K.J. Ziegler, Single step bonding of thick anodized aluminum oxide templates to silicon wafers for enhanced system-on-a-chip performance, *J. Power Sources* 474 (2020) 228643.
<https://doi.org/10.1016/j.jpowsour.2020.228643>.
- [148] H.J. Ahn, J.I. Sohn, Y.S. Kim, H.S. Shim, W.B. Kim, T.Y. Seong, Electrochemical capacitors fabricated with carbon nanotubes grown within the pores of anodized aluminum oxide templates, *Electrochem. Commun.* 8 (2006) 513–516.
<https://doi.org/10.1016/j.elecom.2006.01.018>.

- [149] H. Zhan, D.J. Garrett, N. V. Apollo, K. Ganesan, D. Lau, S. Prawer, J. Cervenka, Direct fabrication of 3D graphene on nanoporous anodic alumina by plasma-enhanced chemical vapor deposition, *Sci. Rep.* 6 (2016) 384–388.
<https://doi.org/10.1038/srep19822>.
- [150] G.P. Scisco, K. Haynes, K.S. Jones, K.J. Ziegler, Single step bonding of thick anodized aluminum oxide templates to silicon wafers for enhanced system-on-a-chip performance, *J. Power Sources* 474 (2020) 228643.
<https://doi.org/10.1016/j.jpowsour.2020.228643>.

List of publications:

1. **Sahil Kumar Yadav**, Sivanandam Aravindan, P.V. Rao “Characterization of micro-textures created by hot embossing on polystyrene for probable use as an antireflective coating” Surface engineering, 41 (2025), 403-406
2. **Sahil Kumar Yadav**, Sivanandam Aravindan, P.V. Rao “Investigation of hot embossing parameters on the aspect ratio of polymer nanopillars fabricated using AAO mould” ASME, J. Micro Nano Sci. Eng., 13 (2025), 041005.
3. **Sahil Kumar Yadav**, Sivanandam Aravindan, P.V. Rao “Carbon nanostructure-based hot embossing template for fabrication of nanoholes over a large area of thermoplastic polymer for light trapping applications” Diamond and related materials, (2026), 161, 113140
4. **Sahil Kumar Yadav**, Sivanandam Aravindan, P.V. Rao “Highly ordered Au-decorated carbon nanopillars array for facile SERS substrate for detection of R6G dye”. Nanotechnology (2026),37,045303

Conferences attended:

1. **Sahil Kumar Yadav**, Sivanandam Aravindan, P.V. Rao “Process parameters optimization for patterned vertical aligned carbon nanotubes growth”. (ASMP 2024 conference, held at IIT Madras).
2. **Sahil Kumar Yadav**, Sivanandam Aravindan, P.V. Rao “Laser-assisted and UV-lithography-based patterning of vertically aligned carbon nanotubes over flexible polycarbonate polymers and silicon substrate”. (E-MRS 2025 conference, held in Strasbourg, France, May 26).

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