

FUNCTIONALIZED FIBROUS MATERIALS FOR HIGH PERFORMANCE AND FLEXIBLE SUPERCAPACITORS

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Functionalized Fibrous Materials for High Performance and Flexible Supercapacitors

by

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Submitted

In fulfillment of the requirements of the degree of
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Dedicated to

My Parents, Brothers, and My In-Laws

*Special thanks to my son, NAV, for his love and
support*

CERTIFICATE

This is to certify that the thesis entitled “Functionalized Fibrous Materials for High Performance and Flexible Supercapacitors”, submitted by Mrs. Ekta Vashishth to the Indian Institute of Technology Delhi in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy, is an authentic record of the research work carried out by her. She conducted this work under my guidance and supervision. She has satisfied all the requirements for the submission of this thesis, which, to the best of my knowledge, meets the requisite academic and research standards.



Prof. Bhanu Nandan

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Ekta Vashishth

ABSTRACT

Flexible supercapacitors represent one of the most promising next-generation electrochemical energy-storage technologies due to their exceptionally high-power density. Nevertheless, their long-term electrochemical stability is hindered by several critical challenges that contribute to performance degradation during repeated cycling. These limitations are largely attributed to the inherently low energy density of flexible supercapacitor systems. Consequently, such challenges significantly restrict their practical deployment and hinder large-scale commercialization. In response to these issues, this thesis focuses on the design and engineering of advanced functional fibrous architectures, and their strategic integration as high-value materials for the fabrication of high-performance flexible supercapacitors.

In this thesis, functionalized carbon cloth derived from waste cotton fabric is fabricated using simple and cost-effective synthesis approaches. These functionalized fibrous materials are investigated as electrode materials for flexible supercapacitors, with particular emphasis on metal-oxide-coated carbon cloth produced through various synthesis routes, as detailed in Chapters 4, 5, and 6. Chapter 4 presents the development of metal oxide-coated carbon cloth derived from waste cotton cloth prepared via solvothermal synthesis. Chapter 5 discusses the fabrication of MOF-derived metal oxides deposited on waste-cotton-derived carbon cloth using a straightforward dip-coating technique. Chapter 6 focuses on the synthesis of mixed metal oxides on carbon cloth through combined solvothermal and dip-coating methods to achieve high-performance flexible supercapacitors. Overall, each chapter introduces a novel electrode architecture based on purpose-designed fibrous materials, accompanied by the required structural and functional modifications to enhance their electrochemical performance.

First, a simple and efficient strategy is presented for designing a flexible electrode material by incorporating metal oxides as functional components onto waste cotton cloth. In this approach, carbon cloth microfibers are fabricated by growing Sn on the surface of waste cotton via solvothermal synthesis, followed by oxidation and carbonization to yield SnO₂@CC. The resulting SnO₂@CC, exhibiting a high specific surface area and predominantly microporous characteristics, delivers excellent electrochemical performance and is subsequently utilized as a freestanding, binder-free electrode for supercapacitor applications. Furthermore, the flexible

asymmetric full-cell supercapacitor assembled using this electrode demonstrates promising electrochemical behavior along with significant mechanical stability. Second, an advanced electrode design is proposed in which CoCo_2O_4 is synthesized from the metal–organic framework (MOF) ZIF-67. The $\text{CoCo}_2\text{O}_4@\text{NCC}$ composite is prepared by a simple dip-coating of waste cotton cloth in the ZIF-67 solution, followed by drying, calcination, and oxidation. The resulting CoCo_2O_4 integrated onto nitrogen-doped carbon cloth ($\text{CoCo}_2\text{O}_4@\text{NCC}$) serves as a collector-free, binder-free, and freestanding flexible electrode. Moreover, the $\text{CoCo}_2\text{O}_4@\text{NCC}$ based symmetric full-cell supercapacitor displays stable electrochemical performance under various bending conditions, confirming its excellent flexibility and mechanical robustness. This work highlights the development of a sustainable, high-performance flexible supercapacitor suitable for next-generation wearable energy-storage application. Third, a sustainable and scalable route is demonstrated to develop a mixed metal oxide SnO_2 and Co_3O_4 on the nitrogen doped carbon cloth ($\text{Co}_3\text{O}_4@\text{SnO}_2@\text{NCC}$) electrode material from waste cotton cloth. The combination to two metal oxides instead of one with superior electrochemical performance. This is mainly due to improved charge transfer capacity, improved electrical conductivity and enhanced specific capacitance. SnO_2 was coated on carbon cloth by simple solvothermal process and Co_3O_4 was coated on $\text{SnO}_2@\text{CC}$ by simple dip coating method by using waste cotton cloth. As a result, binary metal oxide incorporated nitrogen doped carbon cloth can display superior electrochemical performance. Based on these merits, $\text{Co}_3\text{O}_4@\text{SnO}_2@\text{NCC}$ used as waste cotton textile derived symmetric supercapacitor higher value of specific capacitance. Further, a flexible symmetric supercapacitor was fabricated with enhanced electrochemical performance compared to previously reported works.

In summary, the present thesis successfully demonstrates the development of flexible supercapacitors using novel fibrous architectures fabricated through cost-effective and scalable techniques, highlighting their potential for industrial applicability.

सार

लचीले सुपरकैपेसिटर अपनी असाधारण रूप से उच्च-शक्ति घनत्व के कारण अगली पीढ़ी की सबसे आशाजनक इलेक्ट्रोकेमिकल ऊर्जा-भंडारण तकनीकों में से एक हैं। फिर भी, उनकी दीर्घकालिक इलेक्ट्रोकेमिकल स्थिरता कई गंभीर चुनौतियों के कारण बाधित होती है, जो बार-बार उपयोग के दौरान उनके प्रदर्शन में गिरावट का कारण बनती हैं। इन सीमाओं का मुख्य कारण लचीले सुपरकैपेसिटर प्रणालियों का स्वाभाविक रूप से कम ऊर्जा घनत्व है। परिणामस्वरूप, ऐसी चुनौतियाँ उनके व्यावहारिक उपयोग को काफी हद तक सीमित करती हैं और बड़े पैमाने पर उनके व्यावसायीकरण में बाधा डालती हैं। इन समस्याओं के समाधान के रूप में, यह शोध-पत्र उन्नत कार्यात्मक रेशेदार संरचनाओं के डिज़ाइन और इंजीनियरिंग पर केंद्रित है, और उच्च-प्रदर्शन वाले लचीले सुपरकैपेसिटर के निर्माण के लिए उच्च-मूल्य वाली सामग्री के रूप में उनके रणनीतिक एकीकरण पर ज़ोर देता है।

इस थीसिस में, बेकार सूती कपड़े से प्राप्त फंक्शनलाइज्ड कार्बन क्लॉथ को सरल और किफायती संश्लेषण तरीकों का उपयोग करके तैयार किया गया है। इन फंक्शनलाइज्ड रेशेदार सामग्रियों की जांच लचीले सुपरकैपेसिटर के लिए इलेक्ट्रोड सामग्री के रूप में की गई है, जिसमें विभिन्न संश्लेषण मार्गों के माध्यम से उत्पादित धातु-ऑक्साइड-लेपित कार्बन क्लॉथ पर विशेष जोर दिया गया है, जैसा कि अध्याय 4, 5 और 6 में विस्तार से बताया गया है। अध्याय 4 में बेकार सूती कपड़े से प्राप्त धातु ऑक्साइड-लेपित कार्बन क्लॉथ के विकास को प्रस्तुत किया गया है, जिसे सॉल्वोथर्मल संश्लेषण के माध्यम से तैयार किया गया था। अध्याय 5 में एक सीधे डिप-कोटिंग तकनीक का उपयोग करके, बेकार सूती कपड़े से प्राप्त कार्बन क्लॉथ पर जमा किए गए धातु-कार्बनिक ढांचा-व्युत्पन्न धातु ऑक्साइड के निर्माण पर चर्चा की गई है। अध्याय 6 में उच्च-प्रदर्शन वाले लचीले सुपरकैपेसिटर प्राप्त करने के लिए, संयुक्त सॉल्वोथर्मल और डिप-कोटिंग विधियों के माध्यम से कार्बन क्लॉथ पर मिश्रित धातु ऑक्साइड के संश्लेषण पर ध्यान केंद्रित किया गया है। कुल मिलाकर, प्रत्येक अध्याय उद्देश्य-विशिष्ट रेशेदार सामग्रियों पर आधारित एक नई इलेक्ट्रोड वास्तुकला प्रस्तुत करता है, जिसके साथ उनके इलेक्ट्रोकेमिकल प्रदर्शन को बढ़ाने के लिए आवश्यक संरचनात्मक और कार्यात्मक संशोधन भी किए गए हैं।

सबसे पहले, बेकार सूती कपड़े पर कार्यात्मक घटकों के रूप में धातु ऑक्साइड को शामिल करके एक लचीला इलेक्ट्रोड सामग्री डिज़ाइन करने के लिए एक सरल और कुशल रणनीति प्रस्तुत की गई है। इस दृष्टिकोण में,

बेकार सूती कपड़े की सतह पर सॉल्वोथर्मल संश्लेषण के माध्यम से Sn उगाकर कार्बन कपड़े के माइक्रोफाइबर बनाए जाते हैं, जिसके बाद ऑक्सीकरण और कार्बनीकरण करके SnO₂@कार्बन कपड़ा प्राप्त किया जाता है। परिणामी SnO₂@कार्बन कपड़ा, जो एक उच्च विशिष्ट सतह क्षेत्र और मुख्य रूप से सूक्ष्म-छिद्रपूर्ण विशेषताएं प्रदर्शित करता है, उत्कृष्ट विद्युत रासायनिक प्रदर्शन प्रदान करता है और बाद में सुपरकैपेसिटर अनुप्रयोगों के लिए एक स्वतंत्र, बाइंडर-मुक्त इलेक्ट्रोड के रूप में उपयोग किया जाता है। इसके अलावा, इस इलेक्ट्रोड का उपयोग करके बनाया गया लचीला असममित पूर्ण-सेल सुपरकैपेसिटर, महत्वपूर्ण यांत्रिक स्थिरता के साथ-साथ आशाजनक विद्युत रासायनिक व्यवहार भी प्रदर्शित करता है। दूसरा, एक उन्नत इलेक्ट्रोड डिजाइन प्रस्तावित किया गया है जिसमें CoCo₂O₄ को मेटल-ऑर्गेनिक फ्रेमवर्क (धातु-कार्बनिक ढांचा) जियोलेटिक इमिडाज़ोलेट फ्रेमवर्क-67 से संश्लेषित किया जाता है। CoCo₂O₄@नाइट्रोजन-डोप्ड कार्बन कपड़ा कंपोजिट को बेकार सूती कपड़े को जियोलेटिक इमिडाज़ोलेट फ्रेमवर्क-67 घोल में साधारण डिप-कोटिंग द्वारा डुबोकर तैयार किया जाता है, जिसके बाद सुखाने, कैल्सीनेशन और ऑक्सीकरण की प्रक्रिया की जाती है। परिणामी CoCo₂O₄, जो नाइट्रोजन-डोप्ड कार्बन कपड़े (CoCo₂O₄@नाइट्रोजन-डोप्ड कार्बन कपड़ा) पर एकीकृत होता है, एक संग्राहक-मुक्त, बाइंडर-मुक्त और स्वतंत्र लचीले इलेक्ट्रोड के रूप में कार्य करता है। इसके अलावा, CoCo₂O₄@नाइट्रोजन-डोप्ड कार्बन कपड़ा -आधारित सममित पूर्ण-सेल सुपरकैपेसिटर विभिन्न मोड़ने की स्थितियों में स्थिर विद्युत रासायनिक प्रदर्शन प्रदर्शित करता है, जो इसकी उत्कृष्ट लचीलेपन और यांत्रिक मजबूती की पुष्टि करता है। यह कार्य एक टिकाऊ, उच्च-प्रदर्शन वाले लचीले सुपरकैपेसिटर के विकास पर प्रकाश डालता है, जो अगली पीढ़ी के पहनने योग्य ऊर्जा-भंडारण अनुप्रयोगों के लिए उपयुक्त है। तीसरा, बेकार सूती कपड़े से नाइट्रोजन-डोप्ड कार्बन कपड़े (Co₃O₄@SnO₂@नाइट्रोजन-डोप्ड कार्बन कपड़ा) इलेक्ट्रोड सामग्री पर मिश्रित धातु ऑक्साइड SnO₂ और Co₃O₄ विकसित करने के लिए एक टिकाऊ और मापनीय (विस्तार योग्य) मार्ग प्रदर्शित किया गया है। एक के बजाय दो धातु ऑक्साइड का यह संयोजन बेहतर विद्युत रासायनिक प्रदर्शन प्रदान करता है। इसका मुख्य कारण बेहतर चार्ज स्थानांतरण क्षमता, बेहतर विद्युत चालकता और बड़ी हुई विशिष्ट धारिता है। SnO₂ को साधारण सॉल्वोथर्मल प्रक्रिया द्वारा कार्बन कपड़े पर लेपित किया गया था, और Co₃O₄ को बेकार सूती कपड़े का उपयोग करके साधारण डिप-कोटिंग विधि द्वारा SnO₂@कार्बन कपड़ा पर लेपित किया गया था। परिणामस्वरूप, बाइनरी धातु ऑक्साइड-युक्त नाइट्रोजन-डोप्ड कार्बन कपड़ा बेहतर विद्युत रासायनिक प्रदर्शन

प्रदर्शित कर सकता है। इन खूबियों के आधार पर, बेकार सूती वस्त्र से प्राप्त सममित सुपरकैपेसिटर के रूप में उपयोग किए जाने वाले $\text{Co}_3\text{O}_4@\text{SnO}_2$ @नाइट्रोजन-डोप्ड कार्बन कपड़ा में विशिष्ट धारिता का मान उच्च होता है। इसके अतिरिक्त, एक लचीला सममित सुपरकैपेसिटर निर्मित किया गया, जिसका विद्युत-रासायनिक प्रदर्शन पूर्व में प्रकाशित कार्यों की तुलना में बेहतर था।

संक्षेप में, यह शोध-पत्र लागत-प्रभावी और मापनीय तकनीकों के माध्यम से निर्मित नवीन रेशेदार संरचनाओं का उपयोग करके लचीले सुपरकैपेसिटर के विकास को सफलतापूर्वक प्रदर्शित करता है, और औद्योगिक अनुप्रयोगों के लिए उनकी क्षमता को उजागर करता है।

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List of Symbols

s	Second
min	Minute
h	Hour
cm	Centimeter
cm ⁻¹	Centimeter inverse
cm ²	Centimeter square
cm ³ g ⁻¹	Centimeter cube per gram
nm	Nanometer
nm ⁻¹	Nanometer inverse
mm	Millimeter
m ² g ⁻¹	Meter square per gram
μm	Micrometer
A g ⁻¹	Ampere per gram
mA	Milliampere
°C	Degree centigrade
°C min ⁻¹	Degree centigrade per minute
°	Degree
g	Gram
g cm ⁻¹	Gram per centimeter
mg	Milligram
m ² g ⁻¹	Meter square per gram
mg cm ⁻²	Milligram per centimeter square
mL	Milliliter
F	Faraday
Fg ⁻¹	Faraday per gram

mFg^{-1}	Milli faraday per gram
F. s	Faraday second
Ω	Ohm
i	Current
ν	Scan rate
$\nu^{1/2}$	square root of scan rate
M	Molar
mM	Millimolar
V	Volt
mV	Millivolt
kV	Kilovolt
eV	Electron Volt
mVs^{-1}	Millivolt per second
W kg^{-1}	Watt per kilogram
Wh kg^{-1}	Watt-hour per kilogram
Hz	Hertz
kHz	Kilohertz
f_0	Frequency
τ_0	Reciprocal of frequency
ω	Angular frequency
%	Percentage

List of Abbreviations

EDLC	Electric double layer capacitance
ACC	Activated carbon cloth
NCC	Nitrogen doped carbon cloth
SnO ₂	Tin oxide
Co ₃ O ₄	Cobalt oxide
DMF	N, N-Dimethylformamide
DI	Deionized water
ASC	Asymmetric Supercapacitor
ZIF	Zeolitic imidazole framework
MOFs	Metal organic framework
Tin octoate	Tin (II) 2-ethylhexanoate
Co	Cobalt
Sn	Tin
O	Oxygen
C	Carbon
Ag	Silver
I _D /I _G	Intensity of defect band / intensity of graphitic band
WCC-SSC	Waste cotton cloth-derived symmetric supercapacitor
WCC-FSCC	Waste cotton cloth-derived flexible symmetric supercapacitor
AWCC-ASC	All-waste cotton cloth-derived asymmetric supercapacitor
FACS-AWCC	flexible all-waste cotton cloth-derived asymmetric supercapacitor
WCT-SYSC	Waste cotton textile-derived symmetric supercapacitor
WCT-FSYCC	Waste cotton textile-derived flexible symmetric supercapacitor
CV	Cyclic voltammetry
GCD	Galvanostatic charge-discharge
EIS	Electrochemical impedance spectroscopy
DI	Deionized
PVA	Poly vinyl alcohol
Co(NO ₃) ₂ .6H ₂ O	Cobalt nitrate hexahydrate
SEM	Scanning Electron Microscopy

TEM	Transmission Electron Microscopy
HRTEM	High resolution Transmission Electron Microscopy
EDX	Energy Dispersive X-ray Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
TGA	Thermogravimetric Analysis
FT-IR	Fourier Transform Infrared Spectroscopy
BET	Brunauer-Emmett-Teller
BJH	Barrett–Joyner–Halenda
LED	Light emitting diode
KOH	Potassium hydroxide
HCl	Hydrochloric acid
Na ₂ SO ₄	Sodium sulphate
R _{ct}	Charge transfer resistance
W	Warburg impedance
R _s	Equivalent series resistance