1D Electrospun Nanofibers Supported Metal Oxide-based Nanostructures for Supercapacitor Applications

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Dedicated to my

Family

CERTIFICATE

This is to certify that the thesis entitled "**1D Electrospun Nanofibers Supported Metal Oxide-based Nanostructures for Supercapacitor Applications**," being submitted by **Ms. Vaishali Tanwar** to the **Indian Institute of Technology, Delhi,** for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which, to my knowledge, has reached the requisite standard for submitting the thesis. The results in this thesis have not been submitted to any other university or institute, whether in part or full, for the awards of any other degree or diploma.

Prof. Pravin P. Ingole

Professor

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ABSTRACT

The rapid depletion of conventional energy resources, coupled with escalating environmental concerns and increasing global energy demand, has elevated the pursuit of clean and renewable energy alternatives. However, the intermittent availability of renewable energy sources and the growing consumer market highlight the crucial need to develop sustainably advanced energy storage systems capable of efficiently meeting peak power demands. Recently, Electrochemical supercapacitors (SCs) have gained considerable attention due to their superior energy densities compared to conventional capacitors, as well as higher power densities, longer cycle life, and enhanced safety features compared to batteries. They are emerging as promising solutions for substantial and advanced storage systems, with potential applications in electric vehicles, backup power sources, and pulse power providers, poised to attract significant consumer interest in the coming years. Despite these advancements, challenges such as inferior energy density (<10 Wh kg^{-1}), limited nanostructured electrode designs and scalability issues hinder their widespread commercialization. To address these challenges, this thesis aims to synthesize innovative nanoarchitectures, particularly 1D nanofibers supported metal oxide (MO) based composites, for enhanced electrochemical performance. This includes achieving high energy densities while maintaining robust power densities, thereby advancing the practicality and application of SCs in various energy storage applications. The thesis systemically focuses on the nanoscale engineering of electrode materials using scalable approaches such as electrospinning to generate advanced hybrid materials with optimized morphology and composition. It is structured into eight chapters.

Chapter 1 provides a comprehensive overview of global energy scenarios and the various energy storage systems that have been widely studied, highlighting their respective advantages and disadvantages. It introduces supercapacitors (SCs), explains their fundamental operational principles and components, and discusses their classification and energy storage mechanisms. The chapter extensively reviews the literature on carbon-based materials, metal oxides, and their hybrid composites as electrodes for SCs, focusing on their electrochemical performance. Special attention is given to developing electrode materials using scalable approaches such as electrospinning and subsequent treatments to create highly efficient hybrid structures of metal oxides and polymer fibers. The chapter also outlines the motivation for the thesis work and articulates its objectives clearly.

Chapter 2 details the methodology for synthesizing 1D nanofiber-supported metal oxide-based composites. Additionally, the chapter outlines the experimental methodologies employed for

material investigation and highlights various characterization techniques crucial for establishing structure-property relationships. It provides a comprehensive explanation of the electrochemical methodologies used to evaluate the electrochemical performance, discussing key parameters for assessing the supercapacitive performance of the synthesized materials.

Chapter 3 introduces W-PAN, a high-performance hybrid electrode material fabricated by decorating 1D electrospun PAN nanofibers with WO_3 nano petals. This approach enhances WO3's electrochemical capabilities through a tailored support structure. The study elucidates the charge storage mechanisms of W-PAN, highlighting synergies between WO_3 and PAN fibers that lead to superior electrochemical properties. W-PAN exhibits extended discharge times, higher specific capacitance (C_{sp}), and enhanced cyclic durability compared to pristine WO3 and PAN. The fibrous PAN matrix supports WO_3 deposition, facilitating strong interactions and contributing to its pseudocapacitive behavior. Comprehensive analysis reveals dual charge storage mechanisms-double-layer and pseudocapacitive underscoring W-PAN's effectiveness in energy storage.

Chapter 4 meticulously details the synthesis and optimization of WO_3 nanoparticles grown onto PVP-modified carbon nanofibers (m-CNFs) to create advanced hybrid supercapacitor materials. The chapter discusses the strategic use of phase-separation mediated electrospinning of PAN and PVP polymers, followed by controlled thermal treatment, to prepare m-CNFs. This approach allows for precise PAN to PVP ratio adjustment, providing insights into how the polymer-derived supports influence ion transport efficiency and enhance the utilization of electrode materials. Key findings highlight the significant role of m-CNFs in establishing intimate interfaces with WO_3 nanoparticles. This structural integration enhances electron and ion transfer rates, thereby boosting the pseudocapacitive charge storage capacity of the hybrid material.

Chapter 5 explores the development of hierarchical multi-metal oxide (WO_3/SnO_2) @carbon-based nanostructures as advanced supercapacitor electrode materials. The chapter emphasizes the strategic design of these nanostructures to enhance charge storage capabilities through induced lattice defects and heterointerface interactions. The synthesis method involves single-spinneret electrospinning followed by controlled calcination, ensuring a scalable and efficient approach to fabricate $WO_3/SnO_2@C$ hybrids. It also highlights the superior electrochemical performance of $WO_3/SnO_2@C$ compared to individual WO_3 and SnO_2 materials. This exceptional electrochemical performance is attributed to the synergistic effects of the hierarchical morphology and induced lattice defects, which facilitate efficient charge transfer and minimize degradation over extended cycling. The chapter also elucidates the charge storage mechanisms of $WO_3/SnO_2@C$, emphasizing the capacitive adsorption/desorption of $H+$ ions as the primary contributor to its electrochemical capacitance.

Chapter 6 comprehensively explores the synthesis strategy, structural characteristics, and electrochemical performance of 1D SnO_2- fibers. The chapter highlights the synthesis process involving electrospinning a SnO_2 precursor solution with polyvinylpyrrolidone (PVP). This approach enables the formation of uniform and highly porous 1D nanostructures of SnO_2, which is crucial for optimizing the material's electrochemical performance. Key to the methodology is PVP as a soft carbon template in facilitating the creation of a fibrous morphology with a high surface area composed of densely packed small spheroidal nanoparticles of SnO_2. This structural configuration enhances the active electrochemical surface area, promoting efficient ion intercalation and de-intercalation processes at the electrode/electrolyte interface during charge-discharge cycles. The study demonstrates that SnO_2 nanocomposites are promising electrode materials, offering ultra-high energy and power densities suitable for various practical energy storage needs.

Chapter 7 explores a novel approach to enhance the energy storage capabilities of hybrid electrode materials by synthesizing bimetallic oxides (Bi_2O_3 and SnO_2) embedded in carbon fibers (CFs), termed BS/NCFs-based 1D nanostructures. The chapter details a straightforward method involving the electrospinning of polyacrylonitrile (PAN) combined with a metal precursor mixture, followed by controlled calcination to achieve the desired composite structure. A strategic PAN carbonization facilitates the in-situ nucleation of Bi_2O_3 and SnO_2 nanoparticles within the CF matrix. A highly porous 1D structure characterized by mesoporous pore sizes and a high specific surface area enhances electrolyte accessibility, promotes rapid electron transport, and facilitates effective charge storage mechanisms crucial for supercapacitive performance. The chapter emphasizes the structure-property relationships of BS/NCFs, highlighting the benefits of optimal MO composition and calcination temperature in achieving enhanced electrochemical properties.

Chapter 8 serves as the culmination of the thesis, presenting a comprehensive summary and conclusion of the investigations conducted throughout the study. This final chapter is pivotal in synthesizing the key findings, discussing their implications, and outlining future prospects for advancing efficient SC electrode materials.

अतिक्रमण

पारंपरिक ऊर्जा संसाधनों की तेजी से कमी, बढ़ती पर्यावरणीय चिंताओं और बढ़ती वैश्विक ऊर्जा मांग ने स्वच्छ और नवीकरणीय ऊर्जा विकल्पों की खोज को बढ़ा दिया है। हालांकि, अक्षय ऊर्जा स्रोतों की रुक-रुक कर उपलब्धता और बढ़ता उपभोक्ता बाजार बिजली की चरम मांगों को कुशलता से पूरा करने में सक्षम स्थायी रूप से उन्नत ऊर्जा भंडारण प्रणालियों को विकसित करने की महत्वपूर्ण आवश्यकता को उजागर करता है। हाल ही में, इलेक्ट्रोकेमिकल सुपरकैपेसिटर (SC) ने पारंपरिक कैपेसिटर की तुलना में अपनी बेहतर ऊर्जा घनत्व के साथ-साथ उच्च शक्ति घनत्व, लंबे चक्र जीवन और बैटरी की तुलना में बेहतर सुरक्षा सुविधाओं के कारण काफी ध्यान आकर्षित किया है। वे इलेक्ट्रिक वाहनों, बैकअप बिजली स्रोतों और पल्स बिजली प्रदाताओं में संभावित अनुप्रयोगों के साथ पर्याप्त और उन्नत भंडारण प्रणालियों के लिए आशाजनक समाधान के रूप में उभर रहे हैं, जो आने वाले वर्षों में महत्वपूर्ण उपभोक्ता रुचि को आकर्षित करने के लिए तैयार हैं। इन प्रगति के बावजूद, निम्न ऊर्जा घनत्व (<10 Wh kg^{-1}) सीमित नैनोस्ट्रक्चर्ड इलेक्ट्रोड डिजाइन और मापनीयता के मुद्दे जैसी चुनौतियां उनके व्यापक व्यावसायीकरण में बाधा डालती हैं। इन चुनौतियों का समाधान करने के लिए, इस शोध प्रबंध का उद्देश्य विद्युत रासायनिक प्रदर्शन को बढ़ाने के लिए नवीन नैनोआर्किटेक्चर, विशेष रूप से 1डी नैनोफाइबर समर्थित धातु ऑक्साइड (MO) आधारित कंपोजिट को संश्लेषित करना है। इसमें मजबूत बिजली घनत्व बनाए रखते हुए उच्च ऊर्जा घनत्व प्राप्त करना शामिल है, जिससे विभिन्न ऊर्जा भंडारण अनुप्रयोगों में अनुसूचित जातियों की व्यावहारिकता और अनुप्रयोग को आगे बढ़ाया जा सकता है। थीसिस व्यवस्थित रूप से इलेक्ट्रोड सामग्री के नैनोस्केल इंजीनियरिंग पर केंद्रित है, जिसमें इष्टतम आकृति विज्ञान और संरचना के साथ उन्नत संकर सामग्री उत्पन्न करने के लिए इलेक्ट्रोस्पिनिंग जैसे स्केलेबल दृष्टिकोण का उपयोग किया जाता है। इसे आठ अध्यायों में संरचित किया गया है।

अध्याय 1 वैश्विक ऊर्जा परिदृश्यों और विभिन्न ऊर्जा भंडारण प्रणालियों का एक व्यापक अवलोकन प्रदान करता है जिनका व्यापक रूप से अध्ययन किया गया है, उनके संबंधित लाभ और नुकसान को उजागर करता है। यह सुपरकैपेसिटर (SC) का परिचय देता है जो उनके मौलिक परिचालन सिद्धांतों और घटकों की व्याख्या करता है, और उनके वर्गीकरण और ऊर्जा भंडारण तंत्र पर चर्चा करता है। इस अध्याय में कार्बन-आधारित सामग्रियों, धातु ऑक्साइड और उनके संकर यौगिकों पर साहित्य की व्यापक रूप से समीक्षा की गई है, जो अनुसूचित जातियों के लिए इलेक्ट्रोड के रूप में उनके विद्युत रासायनिक प्रदर्शन पर ध्यान केंद्रित करते हैं। धातु ऑक्साइड और पॉलिमर फाइबर की अत्यधिक कुशल संकर संरचनाओं को बनाने के लिए इलेक्ट्रोस्पिनिंग और बाद के उपचारों जैसे स्केलेबल दृष्टिकोण का उपयोग करके इलेक्ट्रोड सामग्री विकसित करने पर विशेष ध्यान दिया जाता है। यह अध्याय शोध प्रबंध कार्य के लिए प्रेरणा को भी रेखांकित करता है और इसके उद्देश्यों को स्पष्ट रूप से व्यक्त करता है।

अध्याय 2 में 1D नैनोफाइबर-समर्थित धातु ऑक्साइड-आधारित यौगिकों के संश्लेषण की कार्यप्रणाली का विवरण दिया गया है। इसके अतिरिक्त, अध्याय सामग्री जांच के लिए नियोजित प्रयोगात्मक पद्धतियों की रूपरेखा तैयार करता है और संरचना-संपत्ति संबंधों को स्थापित करने के लिए महत्वपूर्ण विभिन्न लक्षण वर्णन तकनीकों पर प्रकाश डालता है। यह इलेक्ट्रोकेमिकल प्रदर्शन का मूल्यांकन करने के लिए उपयोग की जाने वाली इलेक्ट्रोकेमिकल पद्धतियों की एक व्यापक व्याख्या प्रदान करता है, जिसमें संश्लेषित सामग्री के सुपरकैपेसिटिव प्रदर्शन का आकलन करने के लिए प्रमुख मापदंडों पर चर्चा की जाती है।

अध्याय 3 में W-PAN का परिचय दिया गया है, जो एक उच्च प्रदर्शन वाली संकर इलेक्ट्रोड सामग्री है जिसे WO_3 नैनो पंखुड़ियों के साथ 1डी इलेक्ट्रोस्पन पैन नैनोफाइबर को सजाकर बनाया गया है। यह दृष्टिकोण एक अनुरूप समर्थन संरचना के माध्यम से WO_3 की विद्युत रासायनिक क्षमताओं को बढ़ाता है। अध्ययन डब्ल्यू-पैन के चार्ज भंडारण तंत्र को स्पष्ट करता है, जो WO_3 और PAN फाइबर के बीच तालमेल को उजागर करता है जो बेहतर विद्युत रासायनिक गुणों की ओर ले जाता है। W-PAN प्राचीन WO_3 और W-PAN की तुलना में विस्तारित निर्वहन समय, उच्च विशिष्ट धारिता (C_{sp}) और बढ़ी हुई चक्रीय स्थायित्व प्रदर्शित करता है। रेशेदार PAN मैट्रिक्स WO_3 निक्षेपण का समर्थन करता है, जो मजबूत अंतःक्रिया को सुविधाजनक बनाता है और इसके छद्म कैपेसिटिव व्यवहार में योगदान देता है। व्यापक विश्लेषण से दोहरे चार्ज भंडारण तंत्र-दोहरी-परत और छद्म कैपेसिटिव का पता चलता है जो ऊर्जा भंडारण में डब्ल्यू-पैन की प्रभावशीलता को रेखांकित करता है।

अध्याय 4 उन्नत संकर सुपरकैपेसिटर सामग्री बनाने के लिए पीवीपी-संशोधित कार्बन नैनोफाइबर (m-CNFs) पर उगाए गए WO_3 नैनोकणों के संश्लेषण और अनुकूलन का सावधानीपूर्वक विवरण देता है। इस अध्याय में m-CNFs तैयार करने के लिए PAN और PVP पॉलिमर के चरण-पृथक्करण मध्यस्थता इलेक्ट्रोस्पिनिंग के रणनीतिक उपयोग पर चर्चा की गई है, जिसके बाद नियंत्रित थर्मल उपचार किया गया है। यह दृष्टिकोण सटीक पैन से पीवीपी अनुपात समायोजन की अनुमति देता है, जो इस बात की अंतर्दृष्टि प्रदान करता है कि बहुलक-व्युत्पन्न समर्थन आयन परिवहन दक्षता को कैसे प्रभावित करता है और इलेक्ट्रोड सामग्री के उपयोग को बढ़ाता है। प्रमुख निष्कर्ष WO_3नैनोपार्टिकल्स के साथ अंतरंग इंटरफेस स्थापित करने में m-CNFs की महत्वपूर्ण भूमिका पर प्रकाश डालते हैं। यह संरचनात्मक एकीकरण इलेक्ट्रॉन और आयन स्थानांतरण दरों को बढ़ाता है, जिससे संकर सामग्री की छद्म कैपेसिटिव चार्ज भंडारण क्षमता को बढ़ावा मिलता है।

अध्याय 5 उन्नत सुपरकैपेसिटर इलेक्ट्रोड सामग्री के रूप में पदानुक्रमित बहु-धातु ऑक्साइड (WO_3/SnO_2)@C-आधारित नैनोस्ट्रक्चर के विकास की पड़ताल करता है। यह अध्याय प्रेरित जाली दोषों और हेटेरोइंटरफेस इंटरैक्शन के माध्यम से चार्ज स्टोरेज क्षमताओं को बढ़ाने के लिए इन नैनोस्ट्रक्चरों के रणनीतिक डिजाइन पर जोर देता है। संश्लेषण विधि में एकल-स्पिनरेट इलेक्ट्रोस्पिनिंग के बाद नियंत्रित कैल्सीनेशन शामिल है, जो WO_3/SnO_2@C हाइब्रिड बनाने के लिए एक स्केलेबल और कुशल दृष्टिकोण सुनिश्चित करता है। यह व्यक्तिगत WO_3 और SnO_2 सामग्रियों की तुलना में WO_3/SnO_2@C के बेहतर विद्युत रासायनिक प्रदर्शन पर भी प्रकाश डालता है। इस असाधारण विद्युत रासायनिक प्रदर्शन का श्रेय पदानुक्रमित आकृति विज्ञान और प्रेरित जाली दोषों के सहक्रियात्मक प्रभावों को दिया जाता है, जो कुशल चार्ज हस्तांतरण की सुविधा प्रदान करते हैं और विस्तारित साइक्लिंग पर क्षरण को कम करते हैं। अध्याय WO_3/SnO_2@C के चार्ज स्टोरेज तंत्र को भी स्पष्ट करता है, जो इसके विद्युत रासायनिक धारिता में प्राथमिक योगदानकर्ता के रूप में H^+ आयनों के कैपेसिटिव एडसोर्प्शन/डिसॉर्प्शन पर जोर देता है।

अध्याय 6 1D एसएनओ2-फाइबर की संश्लेषण रणनीति, संरचनात्मक विशेषताओं और विद्युत रासायनिक प्रदर्शन की व्यापक रूप से पड़ताल करता है। यह अध्याय पॉलीविनाइलपाइरोलिडोन(PVP) के साथ एक SnO_2अग्रदूत समाधान को इलेक्ट्रोस्पिनिंग से जुड़ी संश्लेषण प्रक्रिया पर प्रकाश डालता है। (PVP). यह दृष्टिकोण SnO_2 के समान और अत्यधिक छिद्रपूर्ण 1D नैनोस्ट्रक्चर के गठन को सक्षम बनाता है, जो सामग्री के विद्युत रासायनिक प्रदर्शन को अनुकूलित करने के लिए महत्वपूर्ण है। SnO_2 के घने पैक किए गए छोटे गोलाकार नैनोकणों से बने उच्च सतह क्षेत्र के साथ एक रेशेदार आकृति विज्ञान के

निर्माण को सुविधाजनक बनाने में एक नरम कार्बन टेम्पलेट के रूप में कार्यप्रणाली की कुंजी पी. वी. पी. है। यह संरचनात्मक विन्यास सक्रिय विद्युत रासायनिक सतह क्षेत्र को बढ़ाता है, चार्ज-निर्वहन चक्रों के दौरान इलेक्ट्रोड/इलेक्ट्रोलाइट इंटरफेस पर कुशल आयन इंटरकेलेशन और डी-इंटरकेलेशन प्रक्रियाओं को बढ़ावा देता है। अध्ययन से पता चलता है कि SnO_2नैनोकंपोजिट आशाजनक इलेक्ट्रोड सामग्री हैं, जो विभिन्न व्यावहारिक ऊर्जा भंडारण आवश्यकताओं के लिए उपयुक्त अति-उच्च ऊर्जा और शक्ति घनत्व प्रदान करते हैं।

अध्याय 7 कार्बन फाइबर (CFs) में एम्बेडेड बाइमेटेलिक ऑक्साइड (Bi_2O_3 और SnO_2) को संश्लेषित करके संकर इलेक्ट्रोड सामग्री की ऊर्जा भंडारण क्षमताओं को बढ़ाने के लिए एक नए दृष्टिकोण की पड़ताल करता है जिसे बीएस/एनसीएफ-आधारित 1D नैनोस्ट्रक्चर कहा जाता है। अध्याय में एक सीधी विधि का विवरण दिया गया है जिसमें एक धातु अग्रदूत मिश्रण के साथ संयुक्त पॉलीएक्रिलोनाइट्राइल (PAN) की इलेक्ट्रोस्पिनिंग शामिल है, जिसके बाद वांछित समग्र संरचना को प्राप्त करने के लिए नियंत्रित कैल्सीनेशन किया जाता है। एक रणनीतिक पैन कार्बोनाइजेशन सीएफ मैट्रिक्स के भीतर Bi_2O_3 और SnO_2 नैनोकणों के इन-सीटू न्यूक्लिएशन की सुविधा प्रदान करता है। एक अत्यधिक छिद्रपूर्ण 1डी संरचना जिसकी विशेषता मेसोपोरस छिद्र आकार और एक उच्च विशिष्ट सतह क्षेत्र है, इलेक्ट्रोलाइट की पहुंच को बढ़ाती है, तेजी से इलेक्ट्रॉन परिवहन को बढ़ावा देती है, और सुपरकैपेसिटिव प्रदर्शन के लिए महत्वपूर्ण प्रभावी चार्ज भंडारण तंत्र की सुविधा प्रदान करती है। यह अध्याय BS/NCFs के संरचना-संपत्ति संबंधों पर जोर देता है, जो उन्नत विद्युत रासायनिक गुणों को प्राप्त करने में इष्टतम एमओ संरचना और कैल्सीनेशन तापमान के लाभों पर प्रकाश डालता है।

अध्याय 8 शोध प्रबंध की पराकाष्ठा के रूप में कार्य करता है, जो पूरे अध्ययन में की गई जांचों का एक व्यापक सारांश और निष्कर्ष प्रस्तुत करता है। यह अंतिम अध्याय प्रमुख निष्कर्षों को संश्लेषित करने, उनके प्रभावों पर चर्चा करने और कुशल एससी इलेक्ट्रोड सामग्री को आगे बढ़ाने के लिए भविष्य की संभावनाओं को रेखांकित करने में महत्वपूर्ण है।

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ABBREVIATIONS AND SYMBOLS

ASC	Asymmetric Supercapacitor
BJH	Barrett-Joyner-Halenda
B.E.	Binding Energy
BET	Brunauer–Emmett–Teller
CNFs	Carbon nanofibers
CL	Core Level
CV	Cyclic voltammetry
DTA	Differential Thermal Analysis
EDLC	Electrochemical double-layer capacitance
EESS	Electrochemical energy storage systems
EIS	Electrochemical impedance spectroscopy
ES	Electrospinning
ESR	Equivalent Series Resistance
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
GCD	Galvanostatic Charge Discharge
MO	Metal oxide
NS	Nanostructures
NCFs	Nitrogen-doped carbon fibers
1D	One dimensional
O_{vac}	Oxygen Vacancy
OCP	Open circuit potential
PVP	Polyvinylpyrrolidone
PAN	Polyacrylonitrile
SAED	Selected Area Electron Diffraction
STEM	Scanning Tunneling Microscopy
SEM	Scanning Electron Microscopy
SC	Supercapacitor
SSA	Specific Surface Area
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
XPS	X-ray Photon Electron Microscopy
C_a	Areal Capacitance
E_d	Energy Density
P_d	Power Density
C_{sp}	Specific Capacitance
h	hour
min	minute
s	second
g	gram

eV	Electron volt
°C	degree centigrade
M	molar
R_{ct}	charge transfer resistance
R_s	solution resistance
σ	Warburg coefficient
t	time
V	voltage
V_{drop}	voltage drop/IR drop
ε_0	permittivity of vacuum
ε_r	relative dielectric constant