STRETCHABLE AND FLEXIBLE CONDUCTIVE FIBERS

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OCTOBER 2017

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by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

Indian Institute of Technology Delhi

October 2017

Dedicated to My Parents, Prof. Manjeet Jassal &

Prof. Ashwini K. Agrawal

You showed me light when I was in dark
In my life you have left a very big mark
In every step, you were my guide
My every success is your pride

CERTIFICATE

This is to certify that the thesis titled '**Stretchable and Flexible Conductive Fibers',** being submitted by **Ms. Kiran Yadav** to the **Indian Institute of Technology Delhi** for the award of degree **Doctor of Philosophy**, is a record of bonafide research work carried out by her. She has worked under my guidance and supervision and fulfilled the requirements for the submission of thesis, which has attained the standard required for a PhD. degree of this Institute.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

Dr. Manjeet Jassal

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ACKNOWLEDGEMENTS

It gives me immense pleasure in expressing my deepest gratitude to my supervisor Prof. Manjeet Jassal, Department of Textile Technology, IIT Delhi, for her constant guidance, support, care, motivation and providing me excellent research atmosphere during the tenure of this PhD. I will always be grateful to her for her invaluable suggestions and untiring help, which she have shown right from the beginning till the successful completion of this endeavour. She has made me what I am, letting me know my capabilities and bringing the best out of me. She was always there for me.

I am also very thankful to Prof. Ashwini K. Agrawal, who always brought positivity, provided relentless support, unremitting encouragement and guidance throughout the course of this research work. He taught me to look at the new dimensions of research and life. He helped me identify and utilize my potential to maximum extent. His motivatioval and encouraging words were acted as stimulus to solve problems.

I am thankful to the present Head, Department of Textile Technology, Prof B. K Behara and previous Heads of Department- Prof. R. Chattopadhyay and Prof. Kushal Sen for providing their cooperation for smooth completion of this research work. I would like to express my thanks to my SRC members- Prof. S. N. Maiti , Prof. Bhanu Nandan and Prof. Mangala Joshi for their valuable suggestions.

I would like to acknowledge Ministry of Human Resource Development (MHRD), Govt. of India, for the financial support. I would also like to thank Department of Science and Technology (DST) for providing necessary research facilities through various research grants

to SMITA Research Lab and Nanoscale Research Facility, IIT Delhi for providing instrumental facilities .

I would also take this opportunity to thank Mr. A. K. Sehgal, Mr. Om Praksah, Mr. B. Biswal, Mr. Amarjit, Mr. Raj Kumar, Mr. Ashok Tanwar, Mr. V. K. Kala, and all other supporting staff members of the department for their sincere help.

I am also thankful to my parents (Mr. C.B. Yadava and Mrs. Urmila Yadav), brother Mr.Atul and sister Ms. Sarita for their whole hearted support and love. My two little nieces (Agamya Kritya and Agamya Sidhya) were there to bring energy in my life.

I am also thankful to my friends and labmates especially Dr. Ratyakshi Nain, Dr. Dhirendra, Singh, Ms Surabhi Jha, Dr. Kamlesh Panwar, Dr. Deepika Gupta, Dr Siddharth Sirohi, Mr. Raghav Mehra, Dr Bhavana Sharma, Ms. Suchismita Bhabani, Dr Prashant Panda, Mr. Shiven Kaushal, Mr. Hardeep, Ms. Nayana , Mr. Dhruv Gaur, Ms. Neeta Prajapati, Ms. Rashi Agrawal, Ms Kumud Arora and all other members of SMITA research group for the stimulating discussions and their constant support and encouragement. I am also thankful to Ms. Iqra and Mr. Harikrishnan for providing research related help.

I would like to thank my friends who were always there to support me through all ups and downs of my life, Ms. Anukriti Bansal, Ms. Sanchi Arora, Ms. Chhanda Sen, Ms. Arunima Shukla, Ms. Shweta Kandpal and Mr. Rana Chetan Singh.

Lastly, I express my sincere thanks to almighty God and all those who have helped me directly or indirectly during the course of my research work.

Kiran Yadav

ABSTRACT

Technological advancement in the area of electronics demands light, bendable, foldable, conformable and portable devices. In order to meet these requirements, the development is moving towards flexible and stretchable solutions. Literature reports various conducting nanomaterials for creating the conductive paths in film and fiber configuration. Fibers are mechanically stronger and more flexible compared to films for their use in various applications and they could also be integrated into textiles.

Silver nanowires (AgNWs) are a promising candidate for making flexible and stretchable electronics due to the highest electrical conductivity of silver in its bulk state. In the present study, synthesis of AgNWs using template-less approaches has been studied. AgNWs with aspect ratio of ~164 having diameter of 55 ± 9 nm were synthesized following glycerol mediated solvothermal method. The dispersion behavior of isolated and wet AgNWs in different solvents namely, ethanol, acetone and dimethyformamide was also investigated.

The incorporation of wet AgNWs in electrospun fibers through electrospinning was explored. PVA nanofibers having uniformly distributed, well aligned, and highly inter-connected AgNWs were electrospun. Using this approach, a very high amount of nanowires (up to 34.5 wt%) could be successfully incorporated into the nanofibers. The incorporation and alignment of AgNWs was attributed to the interaction of AgNWs with PVA and the polarization of long nanowires during the electrospinning process. A free standing, highly conducting nanoweb was fabricated with conductivity of approximately 654.85 S/cm. These conductive nanowebs are of interest for a number of electronic devices such as sensors or energy storage systems requiring flexibility and high surface area.

A new approach for making stable, flexible and conductive hollow fibers using dry-jet-wet spinning technique was investigated using poly(acrylonitrile) (PAN) as the polymer. The inner surface of the AgNW-PAN hollow fibers was deposited with AgNWs using its dispersion in the bore fluid. The bore fluid was found to play a crucial role in determining the morphology and flexibility of the hollow fibers and entrapment of long AgNWs on the inner walls. Highly conducting fibers with conductivity of ~10^4 S/cm could be obtained with the use of ~2 wt% of AgNWs. Using the above approach, highly stretchable, flexible conducting hollow fibers were also solution spun using intrinsically stretchable polyurethane. The influence of AgNWs concentration and bore fluid flow rate on the conductivity and stretchability of the hollow fibers was investigated. These fibers showed very high conductivity of ~1.52×10^4 S/cm at a very low concentration of AgNWs dispersion (~0.46 wt%). They also showed good retention of conductivity even at 100% strain, which remained stable with repeated cycling. These properties were mainly attributed to the deposition of AgNWs in the form of three distinct layers, namely embedded, anchoring and topmost AgNWs clusters.

Finally, the feasibility of the spun conductive hollow fibers as an electrode material for flexible supercapacitor was explored. The conducting fibers were successfully assembled into coaxial configuration to yield highly stable, flexible supercapacitors with capacitance value of 128 F/cm^3. The unique morphology of these conductive hollow fibers opens the possibility of making flexible and stable devices for wearable electronics.

The work discussed in this dissertation conclusively showed the significance of the preparation of desirable nanomaterials and the design of effective nanostructured electrodes for supercapacitor energy storage applications.

सार

इलेक्ट्रॉनिक्स के क्षेत्र में तकनीकी उन्नति, हलके, वक्रीय, आकृति अनुरूप और वहनीय उपकरणों की मांग करती है। इन आवश्यकताओं को पूरा करने के लिए, विकास लचीले और खींचने योग्य समाधान की ओर बढ़ रहा है। फिल्म और फाइबर कॉन्फिगरेशन में प्रवाहकीय पथ बनाने के लिए साहित्य विभिन्न नैनो- मटेरियल्स की रिपोर्ट करता है। रेशे, फिल्मों की तुलना में यंत्रवत् रूप से मजबूत और अधिक लचीले होने के कारण विभिन्न अनुप्रयोगों में उपयोग किए जाते हैं तथा वे वस्त्रों में एकीकृत भी हो सकते हैं। रजत नैनोवायर्स (AgNWs) अपने थोक अवस्था में चांदी के उच्चतम विद्युत चालकता के कारण लचीले और खिंचावयोग्य इलेक्ट्रॉनिक्स बनाने के लिए एक आशाजनक उम्मीदवार हैं। वर्तमान अध्ययन में, टेम्पलेट-मुक्त दृष्टिकोण का उपयोग करते हुए AgNWs के संश्लेषण का अध्ययन किया गया है। ग्लिसरॉल मध्यस्थता वाले सॉल्वैथर्मल विधि के अनुसार 55 ± 9 nm के व्यास वाले ~164 के पहलू अनुपात के साथ AgNWs संश्लेषित किए गए हैं। अलग-अलग सॉल्वैंट्स जैसे इथेनॉल, एसीटोन और डाइमिथाइल फॉर्मैमाइड (DMF) में पृथक एवं गीले AgNWs के फैलाव व्यवहार की जांच भी की गई।

इलैक्ट्रोस्पिनिंग के माध्यम से इलैक्ट्रोस्पन रेशे में गीले AgNWs के समावेश का पता लगाया गया है। AgNWs को PVA के अतिसूक्ष्म रेशो मे समान रूप से वितरित, पंक्तिबद्ध और अत्यधिक अंतःपरस्पर जुड़े हुए पाया गया। इस दृष्टिकोण का उपयोग करते हुए, नैनोवायर की एक बहुत बड़ी मात्रा (34.5 wt%) को सफलतापूर्वक नैनोफाइबर्स में शामिल किया जा सका। AgNWs के निगमन और संरेखण को PVA के साथ AgNWs के संपर्क और इलेक्ट्रोस्पिनिंग प्रक्रिया के दौरान लंबे नैनोवायर्स के ध्रुवीकरण का श्रेय दिया गया। एक स्वतंत्र, अत्यधिक संचालन लगभग 654.85 S/cm की चालकता के साथ नैनोवेब गढ़ा गया

था। ये प्रवाहकीय नैनोवेब कई ऐसे इलेक्ट्रॉनिक उपकरणों के लिए दिलचस्प हैं जिन प्रणालियों को लचीलेपन और उच्च सतह क्षेत्र की आवश्यकता होती है जैसे सेंसर या ऊर्जा भंडारण।

ड्राय-जेट-वेट कताई तकनीक का उपयोग करके स्थिर, लचीले और प्रवाहकीय खोखले रेशे बनाने के लिए एक नए दृष्टिकोण के उपयोग से पाली (एक्रिलोनिट्राइल) (PAN) बहुलक की जांच की गई। AgNW-PAN खोखले फाइबर की आंतरिक सतह बोर द्रव में फैलाव का उपयोग करते हुए AgNWs के साथ जमा की गई थी। बोअर द्रव का खोखले फाइबर की आकृति विज्ञान, लचीलेपन और आंतरिक दीवारों पर लंबे समय तक AgNWs के फंसाने में महत्वपूर्ण भूमिका अवलोकित हुई। AgNWs के ~2% के प्रयोग से ~10^4 S/cm की चालकता के साथ उच्च चलित तंतुओं को प्राप्त किया जा सका। उपर्युक्त दृष्टिकोण का उपयोग, उच्च फैलने योग्य, आंतरिक रूप से खिंचाव वाले पॉलीयुरेथेन का इस्तेमाल करते हुए संचालन करने योग्य खोखले, फाइबर की संरचना के लिए किया गया। AgNWs की एकाग्रता और खोखले फाइबर के प्रवाहकत्त्व पर प्रवाह द्रव प्रवाह दर का प्रभाव जांच कर लिया गया। इन फाइबर में AgNW के फैलाव (~0.46 wt%) की बहुत कम एकाग्रता में ~1.52×10^4 S/cm की बहुत अधिक चालकता दिखायी गयी। उन्होंने 100% तनाव पर भी चालकता का अच्छा प्रतिधारण दिखाया, जो साइक्लिंग के साथ स्थिर रहा। इन गुणों को मुख्य रूप से AgNW के तीन अलग-अलग परतों, अर्थात् एम्बेडेड, एंकरिंग और सबसे ऊपर के AgNWs क्लस्टर में जमा होने की वजह से पाया गया।

अंत में, लचीला सुपरकैपेसिटर के लिए इलेक्ट्रोड सामग्री के रूप में प्रवाहकीय खोखले फाइबर की व्यवहार्यता का पता लगाया गया। संचालन फाइबर को सफलतापूर्वक समाक्षीय कॉन्फ़िगरेशन में इकट्ठा किया गया था, जो 128 F/cm^3 के समाई मूल्य के साथ अत्यधिक

स्थिर, लचीला सुपरकैपेसिटर उत्पन्न करते हैं। इन प्रवाहकीय खोखले फाइबर के अद्‌वितीय आकारिकी, पहनने योग्य इलेक्ट्रॉनिक्स के लिए लचीला और स्थिर उपकरण बनाने की संभावना को खोलते हैं।

इस निबंध में चर्चा की गई कार्यवाही ने वांछनीय नैनो-मटेरियल्स की तैयारी का महत्व और सुपर-कैपेसिटर ऊर्जा भंडारण अनुप्रयोगों के लिए प्रभावी नैनोस्ट्रक्चर्ड इलेक्ट्रोड की रचना को दिखाया।

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Symbol/Abbreviation	Expanded Form/Term
EDOT	3,4-Ethylenedioxythiophene
Ag-Py	Ag-Pyridine
AFM	Atomic force microscope
BFFR	Bore fluid flow rate
BMI	Brain machine interface
CNFs	Carbon nanofibers
CNTs	Carbon nanotubes
CMC	Carboxymethyl cellulose
CTAB	Cetyltrimethyl ammonium bromide
CVD	Chemical vapor deposition
$CuCl_2$	Copper chloride
DMF	Dimethylformamide
EDX	Energy dispersive X-ray
EG	Ethylene glycol
$FeCl_3$	Ferric chloride
$Fe(NO_3)_3$	Ferric nitrate
FE-SEM	Field emission- scanning electron microscope
GNP	Graphite nanoplatelets
HDPE	High density polyethylene
MEV	Minimum electrospinning voltage
MTPs	Multiply twinned particles

MWNTs	Multi-walled nanotubes
NP	Nanoparticles
NWs	Nanowires
OLEDs	Organic light-emitting diodes
H_3PO_4	Phosphoric acid
PEDOT: PSS	Poly(3,4-ethylenedioxythiophene):polystyrene sulphonate
PAN	Poly(acrylonitrile)
PET	Poly(ethylene terphthalate)
PVA	Poly(vinyl alcohol)
PVDF-HFP	Poly(vinylidene fluoride-*co*-hexafluoropropylene)
PVP	Poly(vinylpyrrolidone)
Pani	Polyaniline
PC	Polycarbonate
PDMS	Polydimethylsiloxane
PP	Polypropylene
Ppy	Polypyrrole
PS	Polystyrene
PU	Polyurethane
AgCl	Silver chloride
AgNP	Silver nanoparticle
AgNWs	Silver nanowires
$AgNO_3$	Silver nitrate
SWCNTs	Single-walled carbon nanotubes

NaCl	Sodium chloride
NaOH	Sodium hydroxide
SBS	Styrene butadiene styrene
SEBS	Styrene-ethylene-butadiene-styrene
SERS	Surface enhanced Raman scattering
TEM	Transmission electron microscope
Fe(acac)3	Tris(aceylactonato) iron(III)
UV	Ultraviolet
ZnO	Zinc oxide
σ	Conductivity
G	Conductance