

Preparation and characterization of ternary hierarchical carbon nanofibers surface-grafted with CNTs and coated with conductive polymer

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ABSTRACT

This study reports the fabrication and structural characterization of novel ternary hierarchical carbon nanofibers (CNFs) surface-grafted with carbon nanotubes (CNTs) and then coated with conductive polymer. During the process, CNFs were produced by carbonization of as-electrospun polyacrylonitrilenanofibers with the diameter of ~200-400 nm, followed by CNT-growth via chemical vapor deposition (CVD). Ultrathin PANI film was further deposited onto the porous CNT-grafted CNFs via in-situ polymerization of anilines in aqueous solution. Such nanostructures can be used as electrodes for use in supercapacitors, in which the PANI films supported by conductive CNT/CNF scaffolds can trigger favorable pseudocapacitive effect and meanwhile the carbon substrate keeps low electrical resistance during cycling. These unique hierarchal nanostructures are excellent candidates for use as electrodes in high-performance supercapacitors for energy storage and management.

Keywords: polyaniline nanowires, carbon nanofibers, carbon nanotubes, electrospinning, polymerization

1 INTRODUCTION

Development of novel energy conversion and storage materials is one of the solutions to meet today's societal and environmental demands, which have become more and more relying on sustainable, clean and renewable energy resources. Among various energy conversion and storage devices, electrochemical capacitors (i.e., supercapacitors or ultracapacitors) are deemed as an efficient, competitive solution to the increasing need for high-power density energy storage devices. Yet, supercapacitors usually carry relatively low energy density compared to rechargeable batteries, which need to be further improved via developing new types of electrode materials. To date, conductive polymers (e.g., polyaniline and polypyrrole) have attracted substantial interest as promising electrode materials for supercapacitors because of their enhanced conductivity, high pseudocapacitance, and sound environmental stability. It has been reported that the pseudocapacitance of PANI gained from a reversible oxidation and reduction of the conjugated double bonds can reach the specific capacitance as high as 190 F/g [1]. Nevertheless, conductive polymers

as monolithic electrodes may not meet the practical requirements since the pseudocapacitance of conductive polymers is limited by a number of factors, such as the redox switching, poor cyclic stability, and low life limit, among others [2].

In order to suppress these drawbacks of conductive polymers for use in electrodes, herein we report the preparation of a new type of ternary hierarchical carbon nanofibers (CNFs) surface-grafted with carbon nanotubes (CNTs) and then coated with PANI thin films. During polymerization of anilines, the percolating network of CNT-grafted CNFs provides a large, porous surface for the active sites of anilines, resulting in long ordered PANI nanowires grown on the surface of CNTs and CNFs. In addition, the morphology and structure of the porous PANI/CNT-grafted CNFs were characterized by means of Scanning electron microscopy (SEM), Raman spectroscopy, and Fourier transform infrared spectrometry (FT-IR).

2 EXPERIMENTS

2.1 Materials

Polyacrylonitrile (PAN, $M_w=150,000$), nickel (II) acetylacetonate [$\text{Ni}(\text{AcAc})_2$, 95%], *N,N*-dimethylformamide (DMF, 99%), aniline (99%), and ammonium persulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98%] were purchased from Sigma-Aldrich, Corp., St. Louis, MO. The materials were used without further purification.

2.2 Preparation of CNT-grafted CNFs

The PAN/ $\text{Ni}(\text{AcAc})_2$ (ratio 5:2 by weight) composite nanofibers were fabricated by electrospinning. During the process, PAN and $\text{Ni}(\text{AcAc})_2$ powders were dissolved in DMF to prepare a 10% wt. electrospinnable solution, which was then placed into a 10-ml plastic syringe installed with a stainless steel spinneret. Electrospinning was performed in a DC electric field of 90 kV/m, which was generated via applying a positive 18 kV voltage to a 20-cm gap between the spinneret and nanofiber collector.

The stabilization and carbonization of as-electrospun PAN/ $\text{Ni}(\text{AcAc})_2$ nanofibers were performed in a tubular furnace. The as-electrospun PAN/ $\text{Ni}(\text{AcAc})_2$ nanofibers were first annealed at 215°C for 1h in air for oxidative stabilization, followed by heating up to 500 °C at a rate of 5 °C/min in Ar atmosphere. Subsequently, the CNFs were further annealed at

500 °C in a mixed H₂ and Ar (H₂/Ar=1/2) flow for 1h to reduce Ni²⁺ to Ni atom. Ni atoms then aggregated onto CNF surface to form catalytic nanoparticles; these Ni nanoparticles functioned as catalyst to decompose hydrocarbon molecules into carbon atoms. Thereafter, the Ni/CNFs were heated up to 900 °C at a rate of 5°C/min and annealed for 30 min in Ar flow for full carbonization. After that, the furnace was cooled down to 650°C in Ar and maintained at this temperature for 1h to grow CNTs by adopting a mixture flow of Ar and C₂H₄ (Ar/C₂H₄=1).

2.3 Polymerization of aniline on CNT-grafted CNF mats

In-situ polymerization of aniline on CNT-grafted CNFs was prepared to follow the following route. A 0.03 M aniline solution in 200 mL 1 M sulfuric acid (H₂SO₄) was prepared first and cooled down to 0-5°C in a 500 mL flask. As-prepared CNT-grafted CNF mats (0.06 g dry weight) were then added to the aniline/sulfuric acid solution for 1 h. Then, a 0.0075 M ammonium persulfate in 200 mL sulfuric acid solution was added in. The molar ratio of aniline/ ammonium persulfate was 4/1. The mixture solution was continuously stirred for 5 h polymerization at the same temperature of 0-5°C in an ice-bath [3]. During this period, the color of the solution was slowly changed to dark green. After polymerization, CNT-grafted CNF mat coated with PANI was filtered, and washed sequentially with deionized water and acetone. The product of PANI/CNT-grafted CNFs weighted 0.12 g after drying at a temperature of 70 °C for 3 h.

2.4 Characterization of as-prepared materials

SEM (JEOL JSM-7600F, Japan) was used to observe the morphologies and structures of CNT-grafted CNFs and PANI/CNT-grafted CNFs without coating any other electrically conductive material, such as gold. FT-IR data were recorded in a Vertex 70 Fourier transform infrared spectrometer. Raman spectra of the samples were obtained from a laser confocal Raman spectrometer (Nicolet NXR 9650 FT-Raman spectrometer) with a laser excitation 632.8 nm.

3 RESULTS AND DISCUSSION

3.1 Morphology characterization

Figs 1A and B are the SEM micrographs of the surface morphology and structures of the as-prepared CNT-grafted CNFs. It can be found that the diameter of CNFs is in the range of 300 nm to 500 nm; the entangled CNTs with the diameter of 20-30 nm were randomly grown on the surface of CNFs. The length of CNTs is about a few microns. The diameter and length of the grown CNTs can be controlled by tuning the process and material parameters such as the

catalyst, carbon sources, temperature, and duration of the reaction [4-5]. The CNT-grafted CNFs prepared by electrospinning and subsequent chemical vapor deposition CVD were highly porous with a rather rough surface layer compared to CNF surface. This can also be considered as evidence to enhance the specific surface area and electrical conductivity of the hierarchical materials.

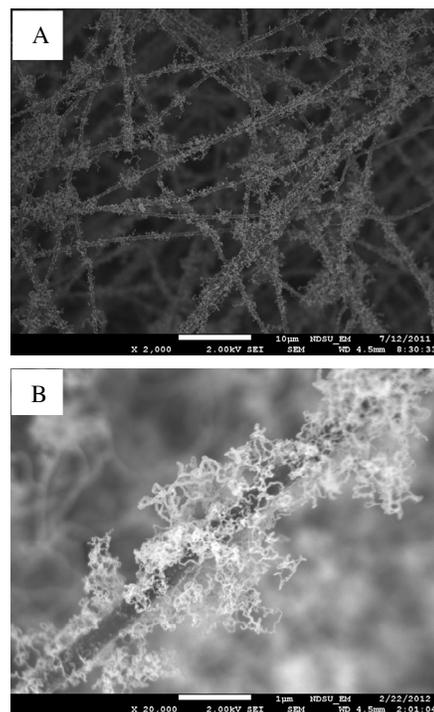


Figure 1: SEM micrographs of CNT-grafted CNFs (A), a typical single CNT-grafted CNF (B).

In-situ polymerization based on aniline as the monomer and ammonium persulfate as catalyst to coat PANI onto the surface of CNT-grafted CNFs can lead to the favorable pseudocapacitance of the resulting porous nanomaterials for use in electrodes of supercapacitors. Such materials also carry both high specific surface area and excellent electrical conductivity. Figs. 2A and B are the SEM micrographs of PANI-coated CNFs and CNT-grafted CNFs, respectively. It can be observed that an ultrathin layer of needle-like PANI was covered on their surface. PANI particles were not detected in SEM examination; however, as shown in Fig. 2A, PANI nanowires with the diameter ranging from 50 nm to 80 nm and the length of ~150 nm were detected. The diameter and length of the PANI nanowires could be tailored by adjusting the concentration of aniline, temperature and duration of polymerization. Furthermore, PANI coated CNT-grafted CNFs also exhibited a hierarchical nano-architecture, which was generated via assembling nano-scaled CNTs with ultrathin PANI film (Fig. 2B). Such process altered the surface morphology and provided a rougher surface. Moreover, when used as porous electrodes in supercapacitors, the grafted CNTs also functioned as excellent current-delivery channel to suppress the electrical contact

resistance of the electrodes due to high electrical conductivity and connectivity.

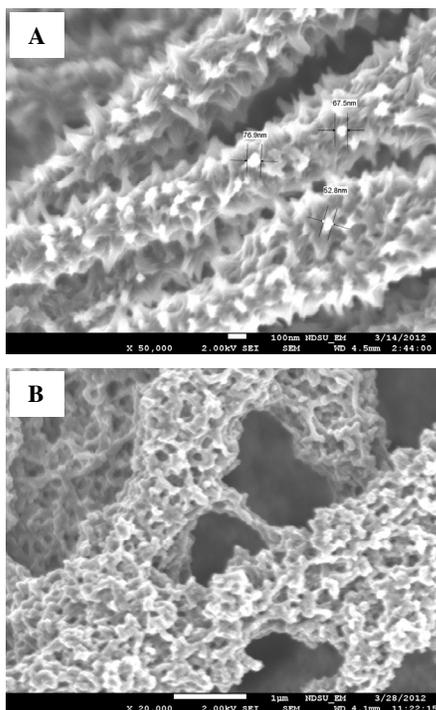


Figure 2: SEM micrographs of PANI/CNFs (A), and PANI/CNT-grafted CNFs (B).

3.2 IR and Raman spectra

Fig. 3 shows a typical FT-IR spectrum of the PANI/CNT-grafted CNFs. The absorption peaks at 1564 cm^{-1} and 1465 cm^{-1} corresponds to the C-C stretching deformation mode of the quinoid (Q) and benzenoid (N) rings of PANI, respectively [6]. The peak at 3420 cm^{-1} is due to the N-H stretching vibration of PANI, while peaks at 1231 and 1294 are attributed to the C-N stretching vibration of an aromatic conjugation. The N-Q-N stretching band at 1087 is the characteristic band of PANI salt [7]. Thus, intensities of these peaks imply the formation of PANI layer on the surface of CNT-grafted CNFs. On the other hand, a characteristic band of CNT-grafted CNFs associated with C-C symmetric stretching was observed at 790 cm^{-1} . The resonance Raman spectra of PANI/CNT-grafted CNFs at 632.8 nm exciting radiation is shown in Fig. 4. The characteristic bands by the vibration of the benzene ring at 1581 cm^{-1} and 1151 cm^{-1} are attributed to the $\nu\text{C-C}$ stretch and $\beta\text{C-H}$ angular deformation, respectively. The amine group is characterized by $\nu\text{C-N}$ stretch at 1210 cm^{-1} . Another characteristic peak of PANI base is the stretch of C=N bond at 1479 cm^{-1} [8].

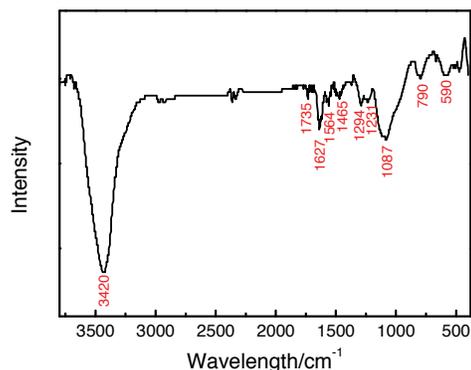


Figure 3: FT-IR spectra of PANI coated CNT-grafted CNFs.

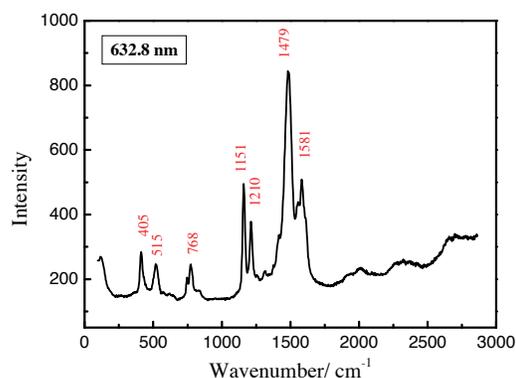


Figure 4: Raman spectra of PANI coated CNT-grafted CNFs.

4 CONCLUDING REMARKS

By consecutively utilizing electrospinning, carbonization, and in-situ polymerization technology, ultrathin PANI films were successfully synthesized and deposited on CNT-grafted CNFs. It has been found that such composite could be a novel type of ternary hierarchical nanomaterials for use in porous electrodes of supercapacitors due to its superior effective pseudocapacitance and high specific surface area. Owing to their excellent electrical conductivity and connectivity, the carbonized electrospun nanofibers grafted with CNTs and then coated PANI carry very low intrinsic contact electric resistance. The present experimental study expects a unique low-cost technical route to synthesize novel ternary hierarchical nanostructures, which can be excellent candidates for use as electrodes in high-performance supercapacitors for energy storage and management.

ACKNOWLEDGMENT

This research was supported by the North Dakota DoE EPSCoR-Sustainable Energy Seed Grant Initiative Program (SUNRISE).

REFERENCES

- [1] Y. K. Zhou, B. L. He, W. J. Zhou, J. Huang, X. H. Li, B. Wu, and H. L. Li, *Electrochim. Acta*, 49, 257, 2004.
- [2] X. Zhao, B. M. Sanchez, P. J. Dobson, and P. S. Grant, *Nanoscale*, 3, 839, 2011.
- [3] S. J. He, X. W. Hu, S. L. Chen, H. Hu, M. Hanif, and H. Q. Hou, *J. Mater. Chem.*, 22, 5114, 2012.
- [4] C. L. Lai, Q. H. Guo, X. F. Wu, D. H. Reneker, and H. Q. Hou, *Nanotech.*, 19, 1, 2008.
- [5] Z. P. Zhou, X. F. Wu, and H. Fong, *Appl. Phys. Lett.*, 100, 023115, 2012.
- [6] W. Tang, J. H. Wu, X. M. Sun, Q. H. Li, J. M. Lin, *Langmuir*, 25, 5253, 2009.
- [7] D. S. Yuan, T. X. Zhou, S. L. Zhou, W. J. Zou, S. S. Mo and N. N. Xia, *Electrochem. Commun.*, 13, 242, 2011.
- [8] C. M. S. Izumi, G. F. S. Andrade, and M. L. A. Temperini, *J. Phys. Chem. B*, 112, 16334, 2008.