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Electrospun carbon nanofibers surface-grafted with vapor-grown carbon nanotubes as hierarchical electrodes for supercapacitors

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This letter reports the fabrication and electrochemical properties of electrospun carbon nanofibers surface-grafted with vapor-grown carbon nanotubes (CNTs) as hierarchical electrodes for supercapacitors. The specific capacitance of the fabricated electrodes was measured up to 185 F/g at the low discharge current density of 625 mA/g; a decrease of 38% was detected at the high discharge current density of 2.5 A/g. The morphology and microstructure of the electrodes were examined by electron microscopy, and the unique connectivity of the hybrid nanomaterials was responsible for the high specific capacitance and low intrinsic contact electric resistance of the hierarchical electrodes. © 2012 American Institute of Physics. [doi:10.1063/1.3676193]

Due to fast consumption of fossil fuels and growing concern of climate change, today's society has become more and more relying on sustainable/renewable energy resources (e.g., solar, wind, geothermal, biomass energy, etc.), in which innovative materials and technologies for efficient storage and conversion of energy play a crucial role.¹ With the high specific power density, superior efficiency, fast charge/discharge rate, and long lifetime in harsh conditions, supercapacitors have been considered as a promising type of energy-storage devices supplemental to rechargeable batteries and, hence, have attracted extensive interests in recent years.^{2–6} Several types of supercapacitors (including pseudo-supercapacitors) have been developed based on a variety of porous electrodes made of activated carbon, carbon nanotubes (CNTs), graphene, and carbon nanofibers (CNFs) surface-attached with metal (or metal oxide) nanoparticles or conductive polymers.^{1–6} Among these, continuous CNFs (prepared via carbonization of polymer nanofiber precursors made by the technique of electrospinning^{7–9}) have shown the great potential for the development of mechanically flexible/resilient, cost-effective, and property-tailorable electrodes for supercapacitors and rechargeable batteries.^{10–14} When measured in KOH aqueous solution, the specific capacitance of the electrodes made of carbonized electrospun polyacrylonitrile (PAN) nanofibers (with diameters of 200–400 nm) was 173 F/g at a low charge/discharge current density of 10 mA/g, and 120 F/g at a high charge/discharge current density of 1000 mA/g.¹⁰ The electrochemical performance of such electrodes can be further enhanced via improving the specific surface area of the CNFs through post-electrospinning treatment and/or via attaching metal (or metal oxide) nanoparticles on the CNFs to induce the pseudo-capacitive effect.^{12–14} Herein, we report the fabrication of a type of hierarchical electrodes for solid-state supercapacitors with high specific surface area and superior intrinsic connectivity via grafting CNTs onto electrospun PAN-based CNFs.¹⁵ The electrochemical performances and microstructures of the hierarchical electrodes were investigated.

During this study, the electrospinning technique^{7–9} was utilized to fabricate continuous PAN nanofibers that were subsequently used as the precursor for making CNFs. The powders of PAN (MW = 150 000) and Ni(AcAc)₂ (purchased from the Sigma-Aldrich, Corp., St. Louis, MO) were dissolved in dimethylformamide (DMF) at the room temperature to prepare a solution with concentrations of PAN and Ni(AcAc)₂ being 13 wt. % and 5 wt. %, respectively. The solution was then filled into a 10 ml plastic syringe installed with a stainless steel needle (with the inner diameter: 0.48 mm). The electrospinning was carried out by applying a positive DC voltage of 18 kV (using an ES30P power supply purchased from the Gamma High Voltage Research, Inc., Ormond Beach, FL) between the spinneret and the collector (with the separation distance of 20 cm). The solution flow rate was set at 1.5 ml/h by a digital syringe pump (model number: KDS 200) purchased from the KD Scientific, Inc. (Holliston, MA).

The stabilization and carbonization of as-electrospun PAN/Ni(AcAc)₂ composite nanofibers (with diameters of 200–400 nm), as well as the growth of CNTs on the CNFs, were performed in a tubular reaction furnace purchased from the Atomate, Inc. (Santa Barbara, CA). The composite nanofibers were first stabilized in air to 215 °C at a heating rate of 1 °C/min followed by holding the temperature at 215 °C for 1 h. Subsequently, the stabilized composite nanofibers were further carbonized in Ar to 500 °C at a rate of 5 °C/min. During this process, Ni(AcAc)₂ was decomposed into NiO. Thereafter, the carbonized nanofibers were treated at 500 °C for 1 h in a mixture flow of H₂ and Ar (H₂/Ar = 1/2) to reduce NiO into elemental Ni, which would diffuse and aggregate into Ni nanoparticles on the nanofiber surface. The Ni nanoparticles served as a catalyst for the growth of CNTs on the surface of CNFs. The sizes of Ni nanoparticles could be tuned via adjusting the temperature and duration of the process. After that, the samples were heated to 650 °C at 5 °C/min in an Ar flow and maintained at this temperature for 30 min; the Ar flow was then replaced with a mixture flow of Ar and C₂H₂ (Ar/C₂H₂ = 1) to grow CNTs. After reaction for 1 h, the C₂H₂ gas was turned off, and the furnace was cooled down to ambient temperature in Ar flow. Upon the

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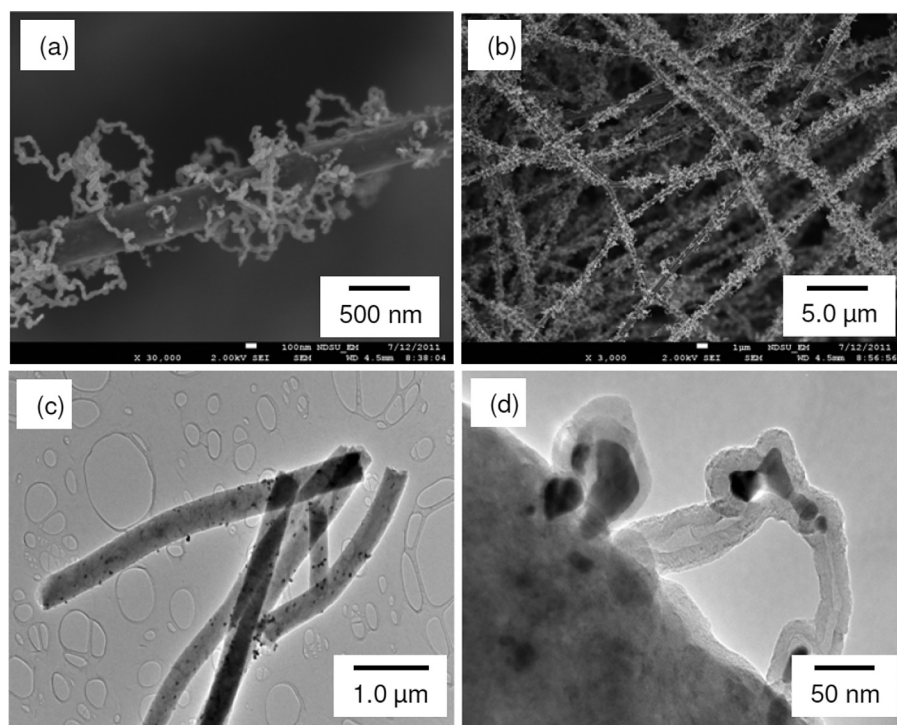


FIG. 1. SEM micrographs (a) and (b) of CNT-grafted CNFs; TEM micrographs (c) and (d) of Ni nanoparticles in CNT-grafted CNFs.

above process, as-electrospun PAN/ $\text{Ni}(\text{AcAc})_2$ nanofibers were finally converted into CNFs surface-grafted with CNTs (Fig. 1). During the conversion of NiO into Ni nanoparticles, it was expected that the reducing agent of H_2 would result in the formation of H_2O , which would further react *in situ* with CNFs to generate tiny pores. This process would enhance the specific surface area of the CNFs.

Prototype solid-state supercapacitors were then fabricated by using the above CNT-grafted CNFs as electrodes. In this process, two CNT-grafted CNF mats with thickness of $\sim 200\ \mu\text{m}$ were used to sandwich a thin layer of polymer electrolyte; the electrolyte was a mixture of poly(vinyl alcohol) (PVA) and H_3PO_4 (10 wt. %),^{16,17} as shown in Fig. 2. In addition, a mat of electrospun PAN nanofibers (with the diameters of 300–400 nm) was used as the separator to isolate the two hierarchical electrodes. Two pieces of copper foil were used as current collectors of the supercapacitors. The cyclic voltammetry and galvanostatic charging/discharging behavior were studied to evaluate the capacitive behavior and specific capacitance of the hierarchical electrodes, respectively, by using a supercapacitor tester (BT2000, Arbin Instruments, TX).

The morphology and microstructure of CNT-grafted CNFs were characterized with JEOL JSM-7600F/JEM-2100 scanning/transmission electron microscopes (SEM/TEM). The SEM micrographs [Figs. 1(a) and 1(b)] showed that CNTs were grafted on the surface of CNFs. In principle, pri-

mary factors that influence the specific capacitance of electric double-layer capacitors (EDLCs) are the specific surface area and electrical conductivity of the electrodes. The adopted method based on C_2H_2 as the carbon source and $\text{Ni}(\text{AcAc})_2$ as the catalyst precursor to graft CNTs onto the surface of electrospun PAN-based CNFs can substantially increase the specific surface area and electrical conductivity of the hierarchical electrodes. In addition, at the reaction condition of 650°C in Ar, the formation of Ni nanoparticles on the CNF surface could be observed in the TEM micrograph [Fig. 1(c)]. The sizes of Ni nanoparticles were in the range of 10–30 nm. The C_2H_2 gas was carried into the tubular reaction furnace and decomposed on the surface of Ni nanoparticles, where tubular nanostructure of multi-wall CNTs grew consequently on the electrospun CNFs.¹⁵ The TEM image [Fig. 1(d)] shows the growth of CNTs with the outer diameters of 20–40 nm and the lengths of several microns. The diameter and length of the grafted CNTs could be tailored by adjusting the temperature, duration of the reaction, and carbon sources.¹⁸ The Ni nanoparticles could be identified at the tip and middle locations of the CNTs due to different growth mechanisms.¹⁸ The presence of Ni nanoparticles in CNFs could be advantageous to the performance of supercapacitors, because the Ni nanoparticles might carry the potential pseudo-capacitive effect.

Electrochemical properties of the hierarchical electrodes were characterized in the gel electrolyte of PVA with 10 wt. % H_3PO_4 by cyclic voltammetry. Fig. 3 shows the current-voltage (CV) curves of the electrodes at several scanning rates (e.g., 5, 10, 30, and 50 mV/s). At the low scanning rates (e.g., 5 mV/s and 10 mV/s), the shapes of CV curves were nearly rectangular, i.e., the electrodes were stable in the gel electrolyte (see the inserted cyclic CV diagram at scanning rate of 10 mV/s in Fig. 3). In contrast, at the high scanning rates (e.g., 30 mV/s and 50 mV/s), the CV curves had been



FIG. 2. (Color online) Schematic of a prototype supercapacitor made of hierarchical electrodes.

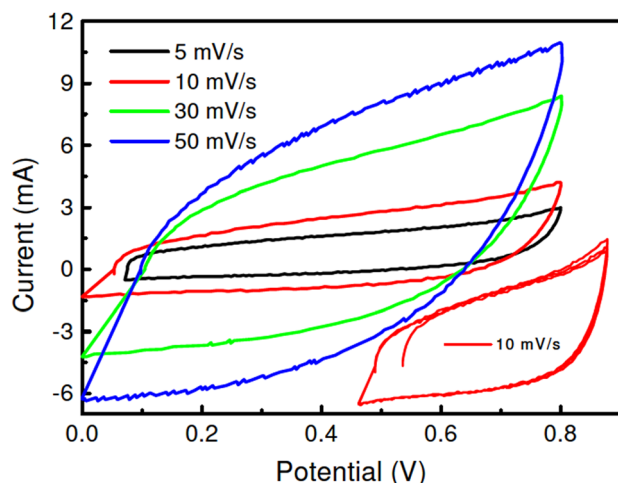


FIG. 3. (Color online) Cyclic voltammograms of the hierarchical electrodes at varied scanning rates.

distorted with oblique angles. This indicated that high contact electric resistance existed between the electrodes and current collectors. The pseudo-capacitive behavior of Ni nanoparticles was not clearly identified from Fig. 3 (i.e., the Ni nanoparticles in this study exhibited the specific capacitance similar to that of carbon). In principle, the high specific surface area of the electrodes, the low volume fraction of Ni,¹⁹ and the well-capsulation of Ni nanoparticles by the surrounding carbon might have shielded the pseudo-capacitive effect of Ni nanoparticles.

The typical potential-time discharge curves (chronopotentiograms) of the hierarchical electrodes tested in the PVA/H₃PO₄ gel electrolyte at 625 mA/g and 1875 mA/g, respectively, are plotted in Fig. 4. No significant IR drop was observed at the low discharge current of 625 mA/g, reflecting a low equivalent series resistance (ESR) of the electrodes. These results suggest that the unique connectivity of continuous CNFs surface-grafted with CNTs effectively improved the electric conductivity of the hierarchical electrodes; in contrast, the IR dropped noticeably with increase discharge current density.²⁰ The specific discharge capacitance (C) of the electrodes can be calculated using the relation

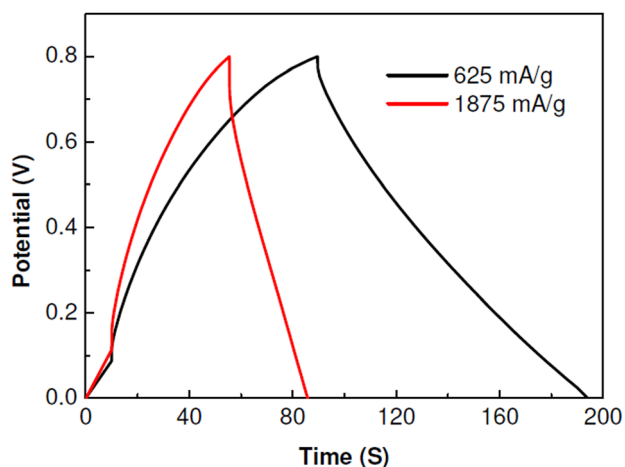


FIG. 4. (Color online) Potential-time discharge curves.

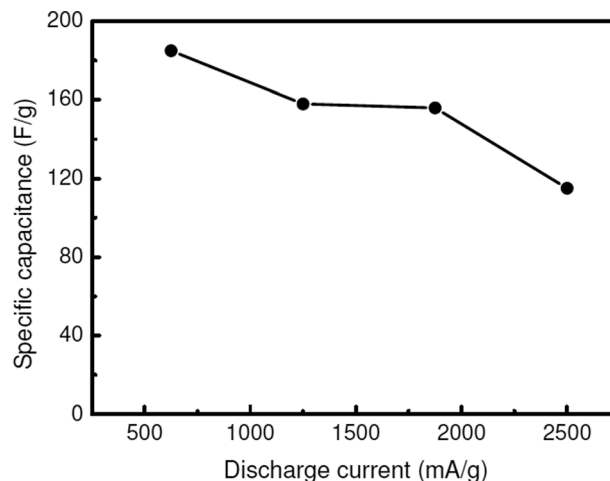


FIG. 5. Dependence of specific capacitance on discharge current density.

$$C = 2 \times \frac{I \times \Delta t}{M \times \Delta V}, \quad (1)$$

where I , Δt , and ΔV are the applied discharge current, time duration, and voltage change, respectively; M is the mass of the two electrodes. Fig. 5 shows the variation of the specific capacitance with respect to the discharge current density of the hierarchical electrodes in the PVA/H₃PO₄ gel electrolyte. The specific capacitance was up to 185 F/g at the discharge current density of 625 mA/g. Due to the high conductivity and large specific surface area of the hierarchical electrodes, the specific capacitance value of 114 F/g could be maintained even at the discharge current density as high as 2.5 A/g.

In summary, electrospun PAN-based CNFs surface-grafted with vapor-grown CNTs could be a type of hybrid nanomaterials to fabricate hierarchical (supercapacitor) electrodes with high specific surface area and superior capacitive performance. Unlike discrete CNTs and/or CNTs coated with conductive polymers or attached with nanoparticles of metals (or metal oxides), the excellent connectivity of the developed nanofibrous materials could result in remarkable reduction of intrinsic contact electric resistance. Albeit the pseudo-capacitive effect of Ni nanoparticles was not noticeably identified in this study, such effect could be further explored through exposure of Ni nanoparticles to electrolyte via chemical or physical methods.

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