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Reactive Template Fabrication of Uniform Core–Shell Polyaniline/Multiwalled Carbon Nanotube Nanocomposite and Its Electrochemical Capacitance

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Uniform core–shell PANI/MWCNT nanocomposite was synthesized by an efficient reactive template method based on the MnO_2/MWCNTs as a template and an oxidant. Such nanocomposite presents a high specific capacitance of $296\,F\,g^{-1}$ at $2\,A\,g^{-1}$ and even $220\,F\,g^{-1}$ at $5\,A\,g^{-1}$ and long cycling stability (84% capacity retention after 1000 cycles), indicating a promising candidate for electrochemical capacitors.

Recent research efforts have been focused on conducting polymer (CP)-based electrochemical capacitors (ECs) owing to their high supercapacitance and low material cost.[1–3] Among various CPs, polyaniline (PANI) is a unique and promising candidate for practical applications due to good processability, environmental stability, low cost, and reversible control of electrical properties by both charge-transfer doping and protonation. Multiwalled carbon nanotubes (MWCNTs) with high surface area, excellent electrical conductivity, and interconnectivity have been predicted as excellent filler for PANI in improving its electric conductivity and mechanical properties for application in ECs.[1,3–8] An efficient utilization of the MWCNTs is achieved only with homogeneous dispersion within the matrices, without damaging their integrity. Such dispersibility can be optimized by coating the individual MWCNTs with a thin PANI layer, creating a core–shell microstructure. It still keeps the mesoporous and conducting network of the MWCNT backbone, increases the PANI/electrolyte interfaces, and maintains the charge-transport kinetics in thin PANI layer, which facilitates better accessibility of ions and electrons to the rich electrochemically active surface of PANI, responsible for its larger specific capacitance (SC) at high rates.[2,4–7,9] In this work, core–shell PANI/MWCNT nanocomposite with a thin PANI shell was synthesized by a reactive template,[7] where the uniform MnO_2/MWCNTs acted as a chemical oxidative initiator for aniline polymerization and a template.

Uniform MnO_2/MWCNT composite was synthesized according to our previous work.[4] In a synthesis of PANI/MWCNTs, solution **a** was prepared by dispersing 79 mg MnO_2/MWCNTs in 30 mL of deionized (DI) water by using ultrasonication and then placing in an ice bath. Solution **b** was prepared by adding 90 mL of aniline monomer into a mixed solution of 2.8 mL of sulfuric acid and 17.2 mL of DI water. After cooling to room temperature, **b** was mixed with solution **a** quickly with stirring. The reaction was carried out for 8 h. The product was collected and dried at 60 °C. The morphology and structure of the sample were examined by a transmission electron microscope (TEM, FEI TECNAI-20) and a Fourier transform infrared (FTIR) spectrometer (360 Nicolet AVATAR). The electrical conductivity of the sample was evaluated by a four-point probe meter (SDY). The working electrode was prepared with the electroactive materials with acetylene black and poly(tetrafluoroethylene) in a weight ratio of 5:1.5:0.5. A little water was added to this mixture to form a homogeneous coating slurry, which was smeared onto graphite substrates. Electrochemical measurements were performed in 2 M H_2SO_4 solution with a CHI660C electrochemical workstation. All experiments were carried out in a three-compartment cell with a working electrode, a platinum plate counter electrode, and a saturated calomel electrode (SCE) as a reference electrode.

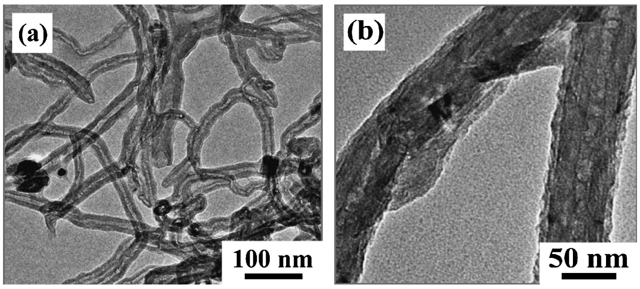

Figure 1. TEM images of the core–shell PANI/MWCNT nanocomposite with different magnification.

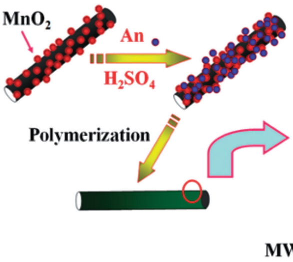

Figure 2. Scheme showing the preparation of the core–shell PANI/MWCNT nanocomposite.

Figure 1 shows typical TEM images for the PANI/MWCNT nanocomposite. It is easy to observe that a thin and uniform layer was coated on the side wall of MWCNTs with obvious nanotubular morphology, rather than the simple aggregations of PANI and the MWCNTs randomly coexisting in a mixture. Moreover, the loading of PANI can be estimated as 20–25 wt % at the most based on the thickness of PANI shell shown in Figure 1b.[5] As shown in Figure 2, the existence of MnO_2 nanoparticles (NPs) plays a great role in the formation of core–shell PANI/MWCNT composite. Specifically, the oxidative MnO_2 NPs were well dispersed onto the surfaces of the MWCNTs and used as a chemical oxidative initiator for aniline polymerization in the H_2SO_4 solution.[7] This effect causes the MnO_2 to be spontaneously removed and a thin PANI layer to

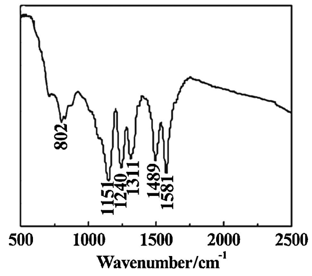

Figure 3. FTIR spectrum of the PANI/MWCNT nanocomposite.

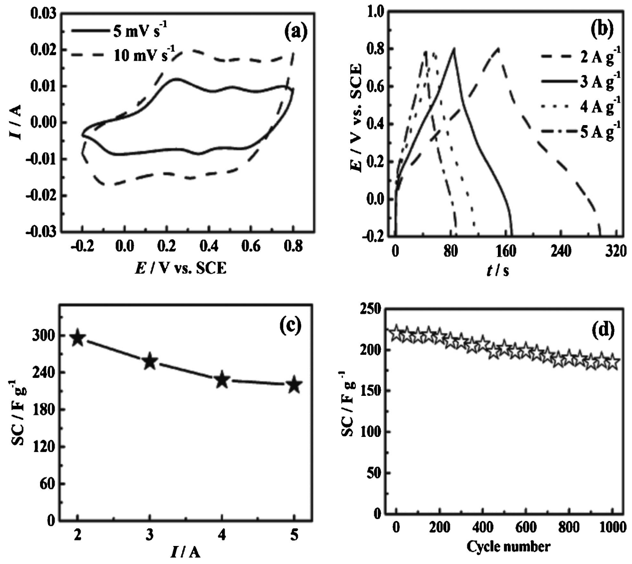

Figure 4. (a) CV curves at different scan rates, (b) typical CP curves at various current densities, (c) the SCs versus discharge current, and (d) the cycling performance of the core–shell nanocomposite.

uniformly coat on the surface of individual MWCNTs, because MnO_2 NPs are reduced into soluble Mn^{2+} ions, whereas the aniline monomer is oxidatively polymerized to a thin PANI coating layer. If the MnO_2 NPs were absent, the great phase separation of electroactive PANI and MWCNTs could be formed, which has been confirmed in our previous work.[5] Such nanostructure maintains the immanent three-dimensional mesoporous structure of the MWCNTs, enhances the dispersion of PANI and ensures sufficient electroactive interfaces for energy storage at high rates.[2,4–7]

Figure 3 shows the FTIR spectrum of the nanocomposite. The absence of peaks at 515 and 587 cm^{-1} contributed by the Mn–O vibrations confirms the pure PANI.[4] Peaks at 1311, 1489, and 1581 cm^{-1} are attributed to Ph–N, the benzenoid, and the quinoid structures of PANI, respectively. Notably, the intensity of the band at 1151 cm^{-1} is larger than that of PANI reported before,[4] suggesting a strong π-stacking interaction between the PANI and MWCNTs, which is responsible for the good conductivity of the nanocomposite (12 S cm^{-1}).[6,10]

Electrochemical performance of the core–shell PANI/MWCNT nanocomposite was studies by cyclic voltammograms (CV) and chronopotentiometry (CP). The CV curves of the core–shell composite within the potential range from -0.2 to 0.8 V at various scan rates are shown in Figure 4a. Two pairs of redox peaks and large electrochemical response currents observed in Figure 4a reveal the large Faradaic capacitance of the composite. The CP curves of the nanocomposite (Figure 4b) at large mass-normalized currents (2–5 A g^{-1}) are also demonstrated to qualify its SCs. The SCs can be calculated according to the following equation: $SC = It/\Delta Vm$, where I, t, ΔV, and m are the discharge current, the discharge time, the discharge potential range, and the mass of active material in the electrode, respectively. The discharge SC of the core–shell composite can be calculated as 296 F g^{-1} at 2 A g^{-1}, much larger than those for the MWCNTs,[4,5] pure PANI,[4,5] and even for activated carbon.[11] Moreover, such core–shell nanocomposite not only exhibits large SCs but also maintains them well at higher current densities. Specifically, the SC reduces to 220 F g^{-1} at 5 A g^{-1}. The capacitance retention is about 74%, with growth of current densities from 2 to 5 A g^{-1} (Figure 4c), suggesting a good rate capability of the nanocomposite. The good electrical conductivity and rich mesporous structure facilitate ions and electrons to access rich electroactive surfaces of the thin PANI layer with fast charge-transport kinetics, responsible for its higher SCs at large current densities. The electrochemical stability of the nanocomposite was examined by continuous charge–discharge cycling at a 5 A g^{-1}. The SC loss after 1000 consecutive cycles is about 16% (Figure 4d), indicating its long-term electrochemical stability. The strongly conjugated interaction is greatly helpful for the charge-transfer reactions between the thin PANI layer and MWCNTs. As a result, nanometer-sized PANI layer is possible for better accommodation of the volumetric changes during the charge–discharge cycling, contributing to good cycling performance.[2,5–7]

In conclusion, we have proposed a reactive template synthesizing uniform core–shell PANI/MWCNT nanocomposite. The nanocomposite presents a large SC, excellent rate capability, and long cycling stability, indicating a promising candidate for ECs. Our method for synthesizing core–shell PANI/MWCNTs is expected to be a versatile method to synthesize other core–shell CPs/MWCNTs.

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