Polyaniline deposition to enhance the specific capacitance of carbon nanotubes for supercapacitors

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Recent application of carbon nanotubes (CNTs) as electrode material for supercapacitor has ignited significant worldwide investigation [1–4]. The CNTs for supercapacitors exhibit a unique pore structure and high usage efficiency of specific surface area [5]. However, the small specific surface area of CNTs leads to a fairly low-specific capacitance value. It is necessary to improve the capacitance of CNTs for practical applications. Polyaniline (PANI) has been considered promising electroactive material with high-faradic pseudocapacitance for supercapacitor owing to the existence of several different oxidation-state structures [6–10]. The deposition of PNAI on the surface of CNTs is a simple and cheap method to enhance the specific capacitance of CNTs. We report here the preparation of CNTs–PANI nanocomposite and its application as electrode material for supercapacitor.

Carbon nanotubes were produced catalytically with Ni particles as the catalyst. Nitric acid treatment was employed to remove the catalyst particles before use. For the preparation of CNTs–PANI nanocomposite, a solution of 1 mol l^{-1} HCl containing CNTs was sonicated at room temperature. The aniline monomer in 1 mol l^{-1} HCl was added to the CNTs solution. An oxidant solution containing 0.125 mol l^{-1} $(NH_4)_2S_2O_8$ in 1 mol l^{-1} HCl was slowly added into the solution. The mixture was left for polymerization for 2 h at about 0 °C under constant stiring. The CNTs–PANI nanocomposite was obtained by filtering and rinsing the reaction mixture with deionized water followed by drying of the remaining powder under vacuum at 60 °C for 24 h. PANI was also prepared using method mentioned above without addition of CNTs. Transmission electron Microscopic studies of the CNTs and the CNTs–PANI composite were performed using a TEM-100CX microscope. Fourier transform infrared spectroscopy (FT-IR) measurements of the PANI and the CNTs–PANI composite were also carried out.

Electrodes (12 mm in diameter) for supercapacitors were formed by pressing a mixture of the CNTs or the CNTs–PANI nanocomposite (95 wt%) and the polytetrafluoroethylene (5 wt%) under 15 MPa at 25 °C for about 5 min. If a two-electrode system was used, two electrodes of the same type were mounted face-to-face into the holder with a glass-fibre separator in between. Before the electrochemical measurements were conducted, all electrodes were vacuum-wetted. The electrolyte used in all experiments was 1 mol l^{-1} $NaNO_3$.

Cyclic voltammetric measurement was performed with a potentiogalvanostat (TOHO PS-14, Japan). A platinum plate (40×30 mm) and a saturation calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. Galvanostatic charge-discharged of the supercapacitor cell was conducted at different current densities. Specific capacitance of the active materials can be calculated from the discharge curves using equation $C = (2I\Delta t)/(m\Delta V)$. Where I is the discharge current, t the time, V the voltage and m is the amount of active material in one electrode.

Figs 1 and 2 are the TEM images of the CNTs and the CNTs–PANI composite, respectively. As shown in Fig. 1, the diameter of the CNTs is in the range of 10–30 nm and no catalyst particle is visible after nitric acid treatment. Fig. 2 reveals that the surface of CNTs was quite uniformly coated with PANI, indicating that *in situ* chemical polymerization of PANI was effectively achieved.

Fig. 3 shows the FT-IR spectra of the PANI and the CNTs–PANI nanocomposite. For the CNTs–PANI nanocomposite, the peaks appearing at 3435, 1561, 1479, 1294, 1128, and 812 cm^{-1} indicate the formation of PANI. However, compared with the spectra of the PANI, the peaks of the CNTs–PANI nanocomposite shifted in the direction of low wave number. This may be attributed to the interaction between the CNTs and the PANI. What's more, owing to the introduction of the CNTs, the intensity of the peaks of the CNTs–PANI nanocomposite decreased.

Fig. 4 presents the cyclic voltammetric behaviors of the CNTs and the CNTs–PANI nanocomposite electrodes in 1 mol l^{-1} $NaNO_3$. Cyclic voltammetric measurements were performed in the potential range of –0.2–0.8 V with a scan rate of 10 mV s^{-1}. The cyclic voltammograms of the CNTs electrode is in the form of rectangular shape, which is the characteristic of an ideal double-layer capacitor. Just as the CNTs electrode, no obvious redox peak is found in the cyclic voltammograms of the CNTs–PANI composite electrode. This result indicates that the CNTs–PANI composite shows the capacitive-like characteristic in $NaNO_3$ solution

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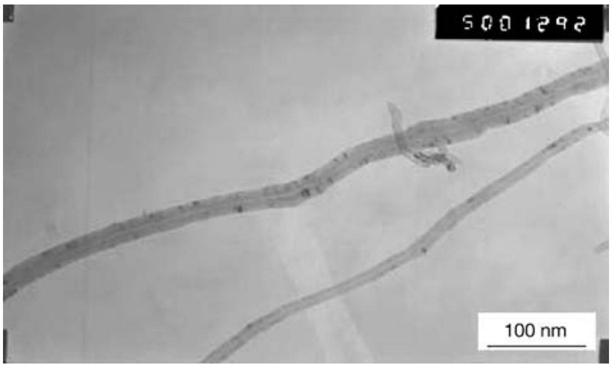

Figure 1 TEM image of the CNTs.

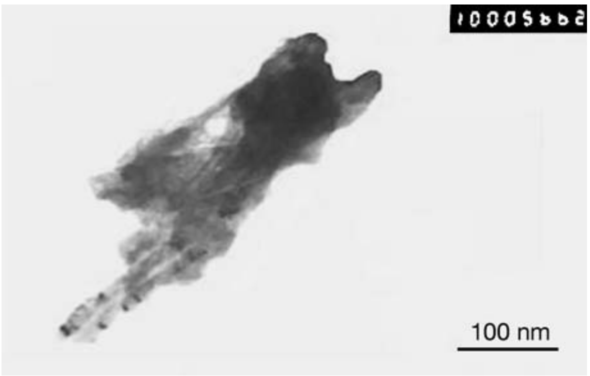

Figure 2 TEM image of the CNTs–PANI nanocomposite.

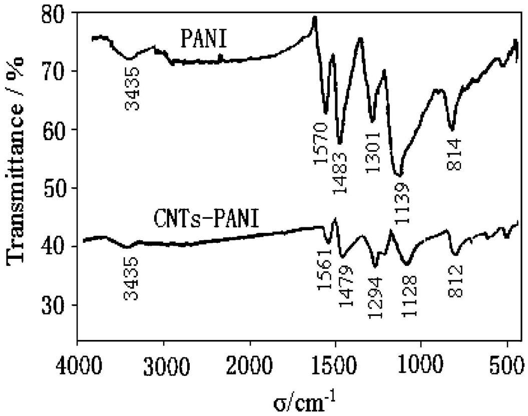

Figure 3 FT-IR spectra of the PANI and the CNTs–PANI nanocomposite.

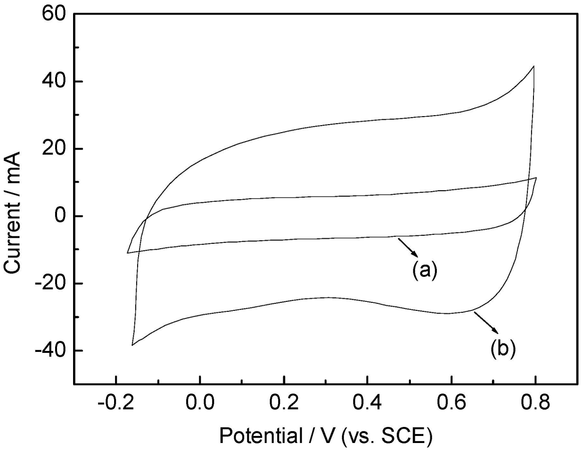

Figure 4 Cyclic voltammogram of (a) the CNTs and (b) the CNTs–PANI nanocomposite electrodes in 1 mol l^{-1} $NaNO_3$ with a scan rate of 10 mV s^{-1}.

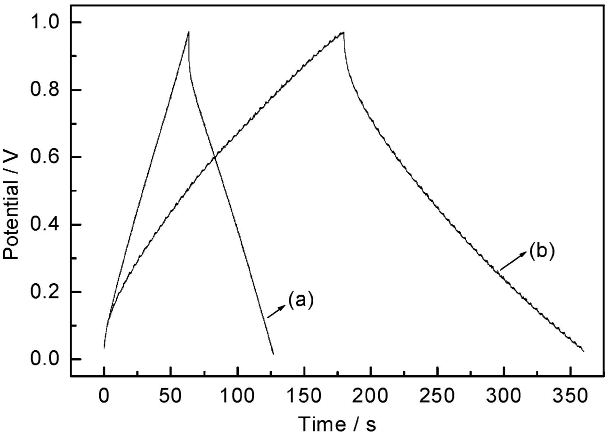

Figure 5 Galvanostatic charge/discharge of (a) the CNTs and (b) the CNTs–PANI nanocomposite supercapacitors at a current density of 5 mA cm^{-2}.

and thus is suitable for the application of electrochemical supercapacitors. Furthermore, the much higher response current of the CNTs–PANI composite electrode indicates that the specific capacitance of the CNTs–PANI composite is much higher than that of the CNTs.

Fig. 5 shows the galvanostatic charge–discharge of the CNTs and CNTs–PANI nanocomposite supercapacitors at a current density of 5 mA cm^{-2}. It can be found that the charge curves are very symmetric to their corresponding discharge counterparts in the whole potential range. The measured specific capacitance for the CNTs and the CNTs–PANI nanocomposite were 47 and 183 F g^{-1}, respectively. The much higher specific capacitance of the CNTs–PANI nanocomposite mainly arises from the pseudocapacitance given by the uniformly coated PANI. During the process of charging and discharging, electrochemical oxidation and reduction reactions happen in the PANI. The reactions are accompanied by doping and undoping of counter anions. These reactions facilitate the charge storage in PANI and thus result in pseudocapacitance. Furthermore, unlike most metal oxides, whose redox reactions are primarily surface mechanisms, the process involving the conducting polymer material is more of a bulk process and therefore can achieve a very high specific capacitance [11]. Moreover, for the CNTs–PANI nanocomposite, the CNTs serve as a nanosized backbone for polymerization of aniline so as to increase the surface area of the coated PANI and therefore the active sites on the PANI chains. So, the specific capacitance of the CNTs–PANI nanocomposite is significantly higher than that which is computed taking into account the capacitance of the two components and their relative amount.

Fig. 6 is the Ragone plot of the CNTs and the CNTs–PANI supercapacitors. Energy density and power density are calculated using equations $E = (UIt)/2$ m and $P = (UI)/m$, respectively. Where U is the working voltage, I the discharge current, t the discharge time and m is the total weight of the two electrodes of a capacitor cell. It can be found that the CNTs and the CNTs–PANI supercapacitors achieved an energy density of 1.65 and 6.34 Wh kg^{-1}, respectively. Supercapacitors based on both the CNTs and the CNTs–PANI

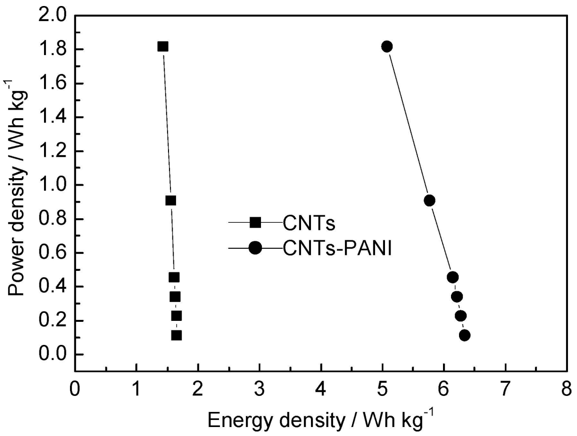

Figure 6 Ragone plot of the CNTs and the CNTs–PANI supercapacitors.

nanocomposite have an excellent power performance. However, with the increase of the power density, the energy density of the CNTs–PANI nanocomposite supercapacitor decreased a little faster than that of the CNTs supercapacitor. The reason is that the speed of the redox reactions within the PANI is not so fast as the formation of the electric double-layer in the CNTs electrode.

In conclusion, CNTs–PANI nanocomposite was prepared by coating PANI on the surface of the CNTs. At a current density of 5 mA cm^{-2}, the CNTs and the CNTs–PANI nanocomposite achieved a specific capacitance of 47 and 183 F/g, respectively. Supercapacitors based on the CNTs–PANI nanocomposite exhibited excellent power performance. All these indicate that PANI addition is a simple, cheap, and effective method to increase the specific capacitance of the CNTs.

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