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Preparation of porous nanorod polyaniline film and its high electrochemical capacitance performance

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ABSTRACT

Nano-sized polyaniline (PANI) films were electrochemically deposited onto an ITO substrate by a pulse galvanostatic method (PGM) in an aqueous solution. The morphology of the as-prepared PANI film was characterized using a field emission scanning electron microscope (FESEM). It was observed that the as-prepared PANI films were highly porous, and showed a nano-sized rod-like or coralline-like morphology depending on the charge loading performed in the electropolymerization process. Furthermore, the PANI films were electrochemically measured by the galvanostatic charge–discharge (GCD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests in 1 mol L^{-1} $HClO_4$ solution. The results showed that such PANI films had a favorable electrochemical activity and an excellent capacitance. The rod-like PANI film prepared with the charge loading of 1000 mC showed the highest discharge capacitance of 569.1 F g^{-1} at a low current density of 1 A g^{-1}. The discharge capacitance retained 97.7% after 1000 cycles at a large current density of 10 A g^{-1}.

1. Introduction

Supercapacitor is also called electrochemical capacitor, electrical double-layer capacitor, golden capacitor or Faradaic capacitor, and possesses the properties of ordinary capacitor and battery. Its specific capacitance is higher than conventional capacitor, and the specific power and cycle life is also better than the battery. Since it exhibits a long cycle life, high efficiency, excellent charge–discharge performance, and is also environmentally friendly. It has been especially attended in electric vehicle with green power as a drive [1–5].

As a new kind of energy storage device with a prospect for broad application, much research work has been conducted into the supercapacitors [1,3–5]. One dimension (1D) nano-sized polyaniline has a very high conductance, a reverse oxidation/deoxidization property, and a large specific area, with these benefits making it very useful for application in battery electrode materials, biochemistry sensors, antiseptic coating, and supercapacitors [6–16].

Over the past several years, a hard-template [17,18] and soft-template [19,20] were widely employed in the synthesis of 1D nano-sized PANI. However, simple, efficient, and controlled synthesis methods for preparing of the 1D nano-sized PANI are still lacking. Our previous work reported that PANI nanofibers with a diameter of about 100 nm were successfully prepared by a pulse galvanostatic method (PGM) on stainless steel substrate [21].

In this work, PANI nanorods are attempted to be electrochemically deposited onto an ITO substrate by PGM in the HNO_3 solution. The morphology, electrochemical properties and capacitance performance of the as-prepared PANI films are fully investigated.

2. Experimental

PANI films were obtained from electrochemical polymerization in a 1.0 mol L^{-1} HNO_3 + 0.2 mol L^{-1} aniline aqueous solution through a pulse galvanostatic current technique with a two-electrode configuration. An ITO substrate (1.0 × 1.0 cm) was used as the working electrode, and a graphite rod with a diameter of 1 cm was used as the counter electrode. Polymerization was carried out at a mean current density of 2 mA cm^{-2} under a pulse period of t_{on}:t_{off} = 2 s:2 s for the charge loading of 4000 mC, 2000 mC and 1000 mC, respectively. After electropolymerization, the working electrode was taken out of the aqueous solution, washed by deionized water, and then dried under the air for further characterization.

The mass of the deposited PANI was calculated by the Faraday's law shown in Eq. (1) assuming the current efficiency is 100%.

$$Q = \frac{m}{M} zF \quad (1)$$

where Q is the charge loading; m the mass of the deposited PANI; M molar mass of aniline monomer; F Faraday constant; and z is the

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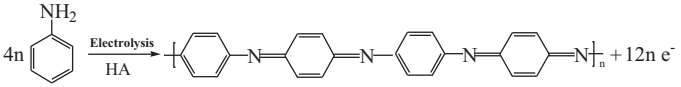

Scheme 1. The electropolymerization reaction for synthesizing of PANI.

exchanged number of electron which is based on the reaction to form pernigraniline shown in Scheme 1.

The electrochemical performance of the as-prepared PANI was evaluated by galvanostatic charge–discharge (GCD), cyclic voltammetry (CV, CHI 1140A) and electrochemical impedance spectroscopy (EIS, Solatron 1287/1255B) tests in a 1 mol L^{-1} $HClO_4$ aqueous solution. Typically, the tests were carried out with a three-electrode cell, with the working electrode consisting of the as-prepared PANI film, and using a graphite rod and a saturated calomel electrode (SCE) as the counter and reference electrode, respectively. The morphology of the as-prepared PANI film was characterized through a field emission scanning electron microscope (FESEM, JEOL, JSM-6701F).

3. Results and discussion

Fig. 1 shows FESEM images of the as-prepared PANI film with an electropolymerization charge loading of 1000 mC. From reference to the low magnification image (Fig. 1a), it clearly illustrates that the PANI film is highly porous and relatively uniform nanorods agglomerating into interconnected networks. At a higher magnification (Fig. 1b), it can be seen that the diameter of the PANI rod is around 100 nm.

The effect of the charge loading on the morphology of the PANI film was investigated as well. The corresponding FESEM images are shown in Fig. 2. An interesting result is that the PANI rod has

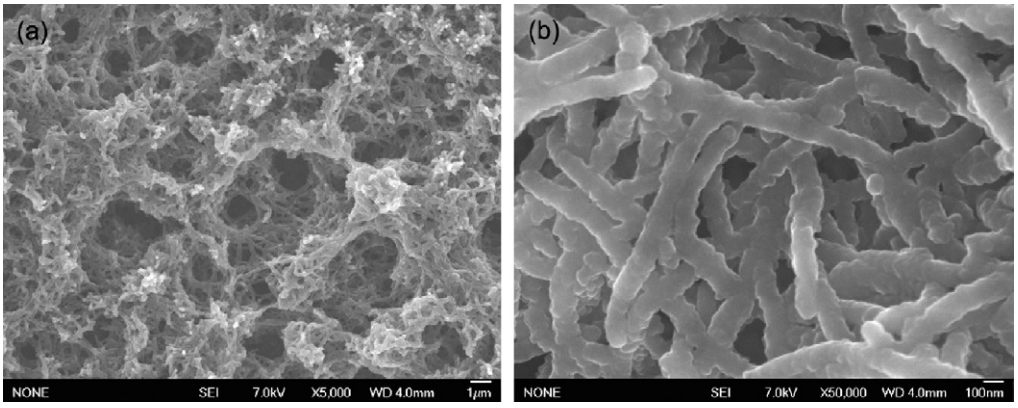

Fig. 1. FESEM images of PANI film deposited by PGM in HNO_3 aqueous solution at the charge loading of 1000 mC. (a) 5000× and (b) 50,000×.

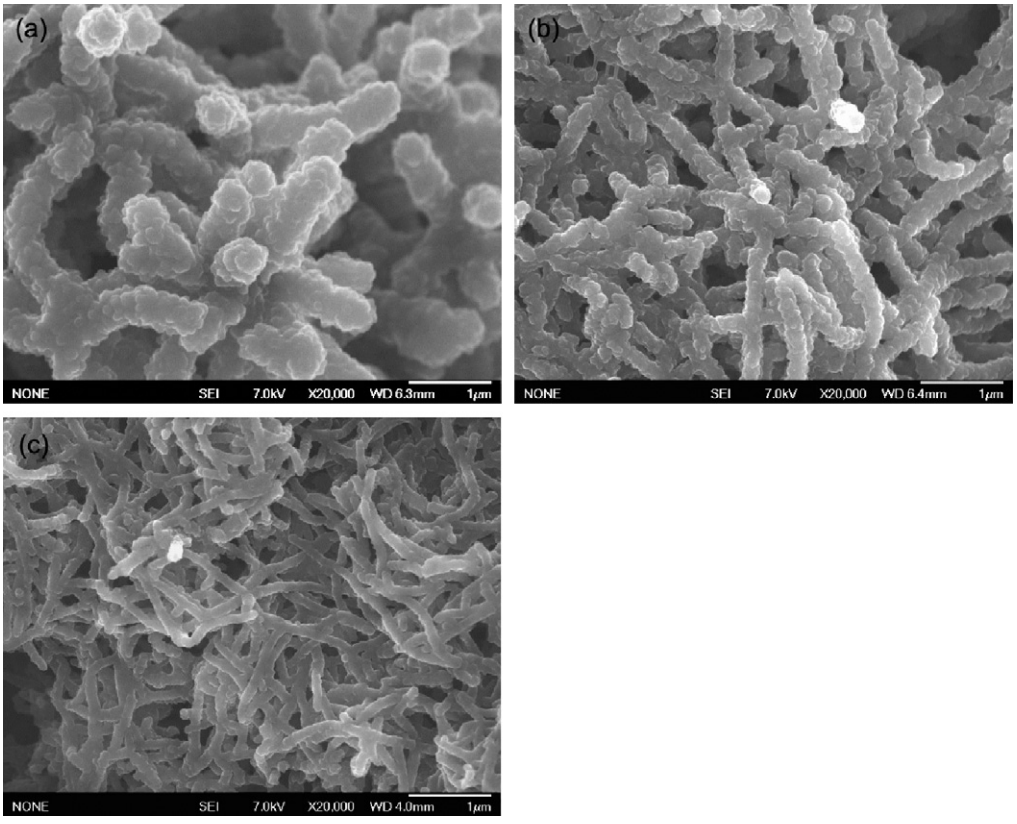

Fig. 2. FESEM images of PANI film deposited by PGM in HNO_3 aqueous solution, with the charge loading of (a) 4000 mC, (b) 2000 mC and (c) 1000 mC, respectively.

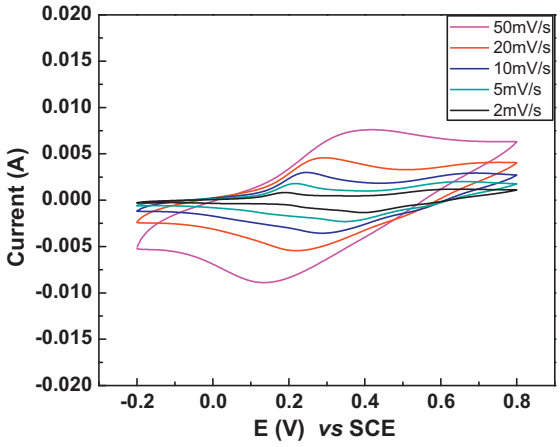

Fig. 3. CV curves of the prepared nanorod PANI film at different scan rates.

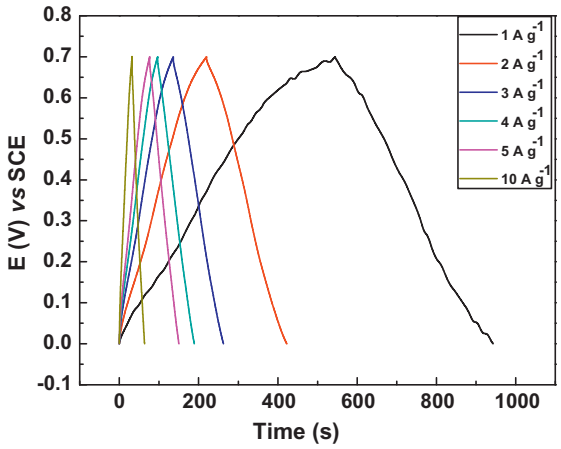

Fig. 5. Typical galvanostatic charge–discharge curves of nanorod PANI film at various current densities.

grown in diameter from 100 nm (Fig. 2c) to 200 nm (Fig. 2b) by increasing the charge loading from 1000 mC to 2000 mC. Moreover, a coralline-like PANI film was synthesized and shown in Fig. 2a is when the charge loading increased up to 4000 mC.

Since the nanorod PANI film possesses a large specific area and a porous configuration, this may enable the electrochemical accessibility of electrolyte through the PANI phase. To further understand electrochemical activity of the as-prepared nanorod PANI film, some of electrochemical measurements were carried out. The CV curve of PANI film at different scan rates is shown in Fig. 3. The results indicate that the nanorod PANI film has obvious capacitance performance, with a couple of Faradaic peaks also relating to the protonation/deprotonation processes. Fig. 4 is a typical Nyquist plot of the as-prepared nano-PANI electrode tested in the 1 mol L^{-1} $HClO_4$ aqueous solution with a frequency loop from 100 kHz to 1 mHz using a perturbation amplitude of 5 mV. EIS has been used to study the redox processes of PANI film and also to evaluate its conductivity [11,14]. In the low frequency region, a line almost vertical to the real axis in the imaginary part of the impedance is attributed to the Faradaic pseudo-capacitance of the PANI electrode. It is indicating that this PANI film could be an ideal capacitor material. Furthermore, it exhibits a semicircle in the high frequency region which is indicative of the charge transfer phenomena by a Faradaic process. The numerical value of the semicircle diameter on the Z' axis is approximately equal to the charge transfer resistance (R_{ct}). In the medium frequency region, the 45° straight line is attributable to the semi-infinite diffusion of ions into the porous structure of the nano-PANI interface, which is called as Warburg diffusion (Fig. 4 inset). These properties suggest that the observed rod-like structure of PANI film is responsible for the enhanced reaction kinetics.

Galvanostatic charge–discharge tests were then carried out to evaluate the capacitance of nano-sized PANI films at various current densities using a potential window 0–0.7 V versus SCE. It is observed in Fig. 5 that PANI films show typical capacitance char-

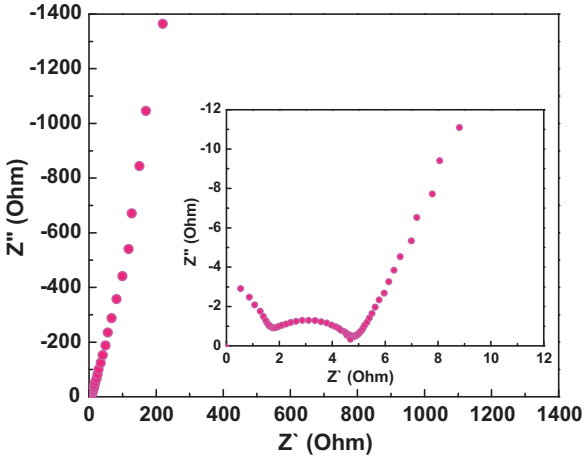

Fig. 4. The Nyquist plots of the as-prepared nanorod PANI film in the frequency range between 100 kHz and 1 mHz. Inset: an enlarged curve in the medium-to-high frequency region.

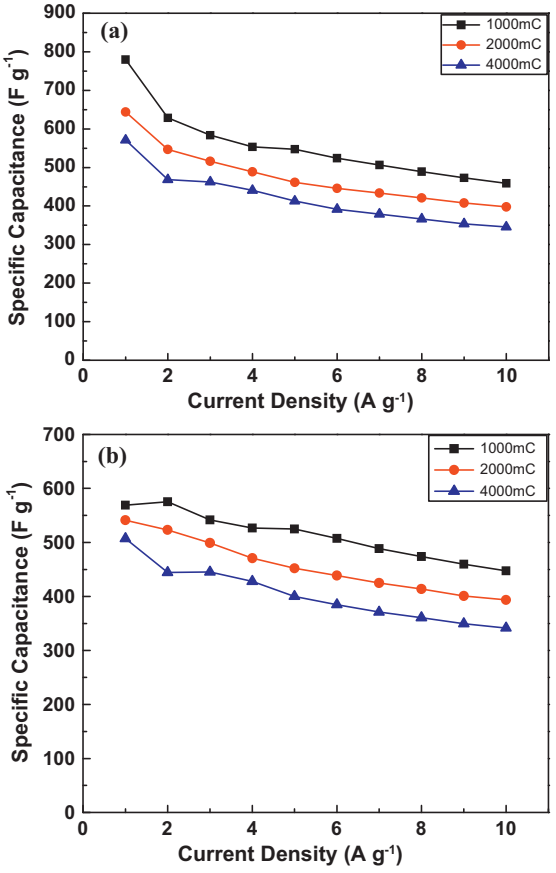

Fig. 6. Electrochemical capacitance behavior of the as-prepared PANI films in $HClO_4$ aqueous solution: (a) charge specific capacitances, and (b) discharge specific capacitances in different current densities.

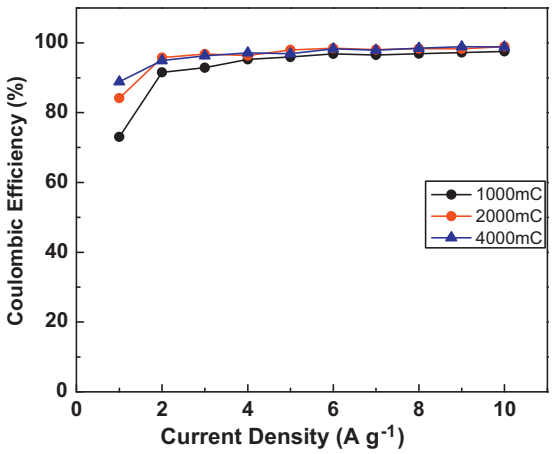

Fig. 7. Coulombic efficiencies of the as-prepared PANI films in different current densities.

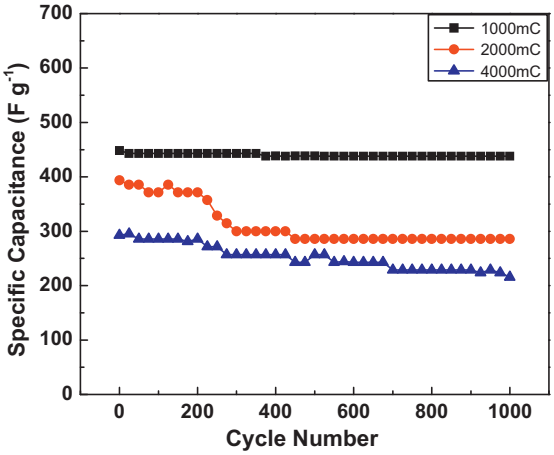

Fig. 8. Cycle stability of the as-prepared PANI films.

acteristics. The specific capacitance can be calculated according to Eq. (2) [22]:

$$C_m = \frac{C}{m} = \frac{I \times t}{\Delta V \times m} \quad (2)$$

where C_m is specific capacitance [$F g^{-1}$], I and t are charge–discharge current and time, respectively, ΔV is 0.7 V in our measurement, and m is the mass of active material within the substrate electrode.

The charge and discharge specific capacitances of the as-prepared PANI films as a function of different current densities are shown in Fig. 6(a) and (b), with different charge loadings of 4000 mC, 2000 mC and 1000 mC. It is observed that the charge and discharge specific capacitances for those PANI films decrease with increasing of current density. The rod-like PANI film prepared at the charge loading of 1000 mC shows the highest charge and discharge capacitance of 779.5 $F g^{-1}$ and 569.1 $F g^{-1}$ in the first cycle at the current density of 1 $A g^{-1}$. This is because the rod-like PANI film prepared at the charge loading of 1000 mC has a highly porous structure and larger specific area.

Furthermore, the coulombic efficiency (charge capacitance/discharge capacitance) at different current densities is presented in Fig. 7. It can be seen that the coulombic efficiency of the nano-sized rod-like PANI film is less than 90% at the current density of 1 $A g^{-1}$, but up to 99% at the current density of 10 $A g^{-1}$.

The cycle stability of the as-prepared PANI films electrodes were examined at a large charge–discharge current density of 10 $A g^{-1}$. As shown in Fig. 8, the rod-like PANI film prepared with the charge loading of 1000 mC shows the best cycle stability, with the discharge capacitance retained at 97.7% after 1000 cycles. This result indicates that the as-prepared rod-like PANI film has long-term cycle stability and could be used as electrode materials for supercapacitor working at a high charge–discharge current density.

4. Conclusions

In this work, nanorod PANI films were electrochemically polymerized onto an ITO substrate by pulse galvanostatic method in an aqueous solution. Further investigatory work showed that the produced nanorod PANI films had significant capability to be used as high performance supercapacitor electrode materials. The specific capacitance of such PANI was measured in $HClO_4$ solution. The highest specific capacitance of PANI nanorod arrays was 569.1 $F g^{-1}$ at a low current density of 1 $A g^{-1}$ and kept as high 458.9 $F g^{-1}$ at a large charge–discharge current density (10 $A g^{-1}$). The cycle stability of the prepared nanorod PANI film was investigated, with the result showing that it had a low fading rate for its specific capacitance after 1000 cycles.

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