

Hierarchically Porous Carbon/Polyaniline Hybrid for Use in Supercapacitors

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A hierarchically porous carbon (HPC)/polyaniline (PANI) hybrid electrode was prepared by the polymerization of PANI on the surface of the HPC *via* rapid-mixing polymerization. The surface morphologies and chemical composition of the HPC/PANI hybrid electrode were characterized using transmission electron microscopy and X-ray photoelectron spectroscopy (XPS), respectively. The surface morphologies and XPS results for the HPC, PANI and HPC/PANI hybrids indicate that PANI is coated on the surface of HPC in the HPC/PANI hybrids which have two different nitrogen groups as a benzenoid amine (–NH–) peak and positively charged nitrogen (N⁺) peak. The electrochemical performances of the HPC/PANI hybrids were analyzed by performing cyclic voltammetry and galvanostatic charge–discharge tests. The HPC/PANI hybrids showed a better specific capacitance (222 F/g) than HPC (111 F/g) because of effect of pseudocapacitor behavior. In addition, good cycle stabilities were maintained over 1000 cycles.

Keywords: Supercapacitor, Polyaniline, Porous Carbon, Hybrid.

1. INTRODUCTION

The increasing demand for energy storage devices has resulted in noticeable interest in supercapacitors owing to their high power density and good cycle stability.¹ Supercapacitors can be classified according to their energy storage mechanism into two categories: electrochemical double-layer capacitors (EDLCs) and pseudocapacitors. In EDLCs, electrons are stored on the surface of the electrode material. Therefore, electrode materials that have large specific surface area are important for increasing the specific capacitance of EDLCs. Carbon materials are widely used as electrode materials for EDLCs because of their high surface area, low density, and good electroconductivity.^{2,3} However, the specific capacitance of carbon-based electrodes is dependent on their surface area, and this dependence is a limitation of the carbon-based materials when high capacitances need to be achieved. For example, the theoretical surface area of carbon nanotubes is up to 1315 m/g.^{4,5} Pseudocapacitors are a type of supercapacitor in which energy is stored by redox reactions. The specific capacitance of pseudocapacitors exceeds that of EDLCs based on carbon materials.¹ However, pseudocapacitive materials such as metal oxides and

conducting polymers have poor cycle stability. Therefore, hybrid systems with advanced electrodes prepared from carbon-based materials are required.^{6,7}

Recently, carbon-based electrode materials with nitrogen groups have been reported.^{8–10} The nitrogen groups enhance specific capacitance by pseudocapacitive effects. These results suggest that a hybrid EDLC-based electrode materials and pseudocapacitive materials could be suitable for high-performance supercapacitors.

In this study, hierarchically porous carbon (HPC)/ polyaniline (PANI) hybrids were prepared by polymerization of PANI on the surface of HPC. The synergistic effects of the EDLC performance of HPC and the pseudocapacitive effects of PANI led to good electrochemical performances of the hybrid electrodes in 1 M H₂SO₄ electrolyte.

2. EXPERIMENTAL DETAILS

2.1. Preparation of HPC

NaOH and urea are dissolved in water at –12 °C. The mixture solutions were maintained under stirring for 2 h. Cotton cellulose (Aldrich) was dispersed in the mixture solution and then vigorously stirred. The NaOH/urea/cellulose solution was frozen at –196 °C and then freeze-dried for 5 days. The cryogel was then

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carbonized from 25 °C to 800 °C for 2 h. The heating rate was 5 °C/min with a N₂ flow rate of 200 mL/min. After carbonization, the sample was washed repeatedly using distilled water and ethanol, and then, dried in an oven at 60 °C for 24 h.

2.2. Preparation of HPC/PANI Hybrids

HPC/PANI hybrids were prepared by rapid-mixing polymerization, and the procedure is described as follows. The HPC suspension in 40 mL of 1 M HCl was obtained by ultrasonication in an ultrasonic bath. Then, 40 mg of aniline were added into the above suspension, and it was sonicated for approximately 10 min. Ammonium persulfate (100 mg) was then dissolved in 40 mL of 1 M HCl. This ammonium persulfate solution was rapidly added into the above suspension and stirred for 2 h at 5 °C. Lastly, the HPC/PANI hybrid was washed using distilled water and then dried in an oven at 60 °C for 24 h.

2.3. Characterization

The morphology and the composition of the HPC/PANI hybrids were characterized by transmission electron

microscopy (TEM, CM200, Philips, USA) and X-ray photoelectron spectroscopy (XPS, AXIS-HIS, Kratos Analytical, Japan). XPS was employed with a dual-chromatic Mg K α X-ray source at 1500 eV. The electrochemical performances of the HPC/PANI hybrids were analyzed by cyclic voltammetry (CV) and constant current charge–discharge tests.

The electrochemical properties were investigated in a three-electrode test cell by an electrochemical analyzer (AutoLab PGSTAT12, Eco Chemie) with a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was prepared as follows. The HPC/PANI hybrids and polytetrafluoroethylene (PTFE) were mixed in a mass ratio of 9:1, dispersed in ethanol to produce a homogeneous paste, and then, ethanol was evaporated in an oven at 80 °C. The resulting mixtures were coated onto a nickel mesh (1 × 1 cm) and dried at 80 °C for 1 h. Cyclic voltammetry (CV) tests were conducted with scan rates of 5 mV/s. Galvanostatic charge–discharge curves were measured at current densities of 1 A/g. The cyclic voltammetry and the galvanostatic charge–discharge potential range was –0.2 to 0.8 V in a 1 M H₂SO₄ electrolyte.

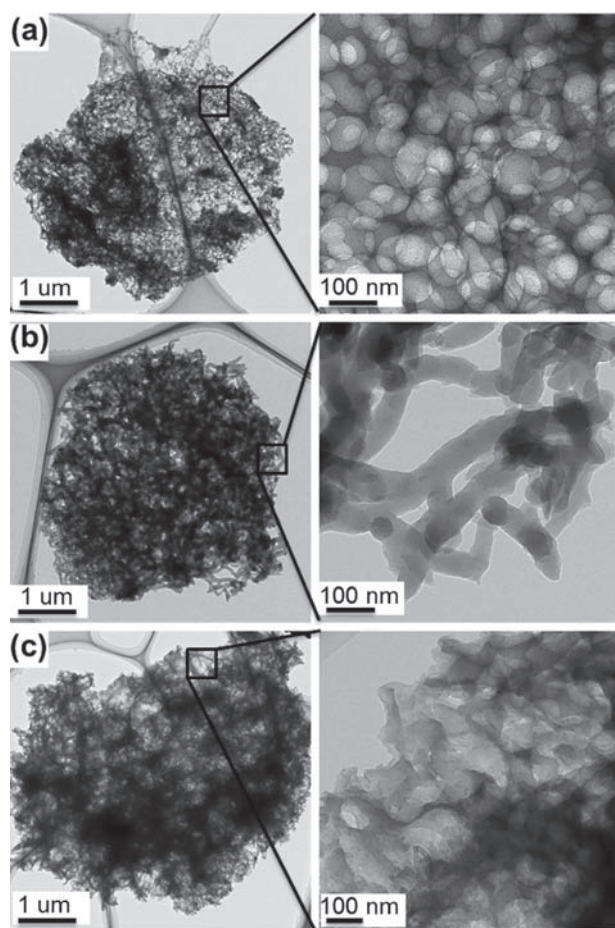


Figure 1. TEM images of the (a) HPC, (b) PANI, and (c) HPC/PANI hybrids.

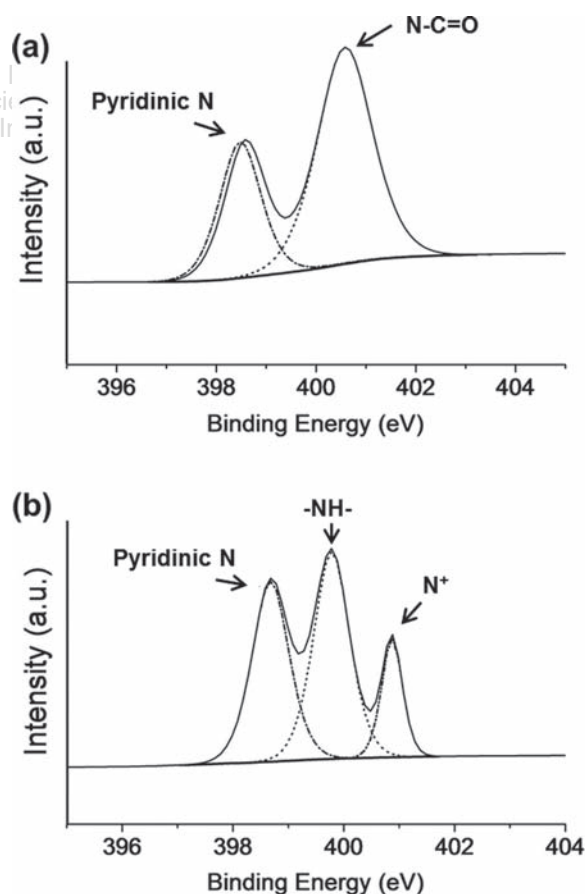


Figure 2. The N1s core-level XPS spectra of the (a) HPC and (b) HPC/PANI hybrid.

3. RESULTS AND DISCUSSION

The surface morphology of the HPC, PANI, and HPC/PANI hybrids were characterized by TEM. Figures 1(a) and (b) show the hierarchically porous morphology of the HPC, which is advantageous for ionic diffusion. In addition, the porous morphology results in a large specific surface area, which makes HPC useful as a template. PANI is most commonly available in the form of nanofibers,¹² as shown in Figures 1(c) and (d). The PANI nanofibers are tangled. Figures 1(e) and (f) show the TEM image of the HPC/PANI hybrid. At low magnification, the morphology of the HPC/PANI hybrid is similar to that of HPC [Figs. 1(a) and (e)]. However, a comparison at higher magnification shows a difference: i.e., the surfaces of the pores of the HPC/PANI hybrid are coated with PANI [Figs. 1(b) and (f)]. The surface of pure PANI is smooth, but the morphology of coated PANI is very rough. The HPC has well-defined pores. In contrast, even when PANI coated the surface of the HPC, a porous structure was maintained, which is advantageous for its use as an electrode for capacitors.¹

In order to confirm the presence of PANI on the surface of the HPC, XPS analysis was carried out. The N1s core-level XPS spectra of HPC are shown in Figure 2(a). The pyridinic N peak was centered at 398.58 eV, and the amide group peak was centered at 400.58 eV.¹¹ Figure 2(b) shows the N1s core-level XPS spectra of the HPC/PANI

hybrid. The peaks centered at 399.78 eV (benzenoid amine, $-\text{NH}-$) and 400.87 eV (positively charged nitrogen, N^+) revealed the presence of PANI on the surface of the HPC.¹³ An additional peak centered at 398.68 eV (pyridinic N) shows the presence of the HPC.¹¹

The electrochemical performances of the HPC/PANI hybrids were analyzed in 1 M H_2SO_4 aqueous solution as the electrolyte. The cyclic voltammogram curves of the HPC (black) and HPC/PANI hybrid (red) from -0.2 to 0.8 V versus SCE at a scan rate of 5 mV/s are shown in Figure 3(a). The cyclic voltammogram curves of the HPC and HPC/PANI hybrid were nearly rectangular because HPC and the HPC/PANI hybrid show electrochemical double-layer capacitor (EDLC) behavior because of the rough surface and porous structure. However, a comparison of the HPC and the HPC/PANI hybrid shows that the HPC/PANI hybrid electrodes show pseudocapacitor behavior. This effect appears to be due to the contribution of the coated PANI on the HPC surface.

Figure 3(b) shows the galvanostatic charge–discharge curves of the HPC (black) and the HPC/PANI hybrid (red) tested at a current density of 1 A/g. The curve of the HPC/PANI hybrid was almost triangular, indicative of the reversible behavior of the ideal capacitor. The curve of the HPC/PANI hybrid was nonlinear in a specific section because of the pseudocapacitor behavior of the coated PANI. The discharge curve of the HPC/PANI hybrid can

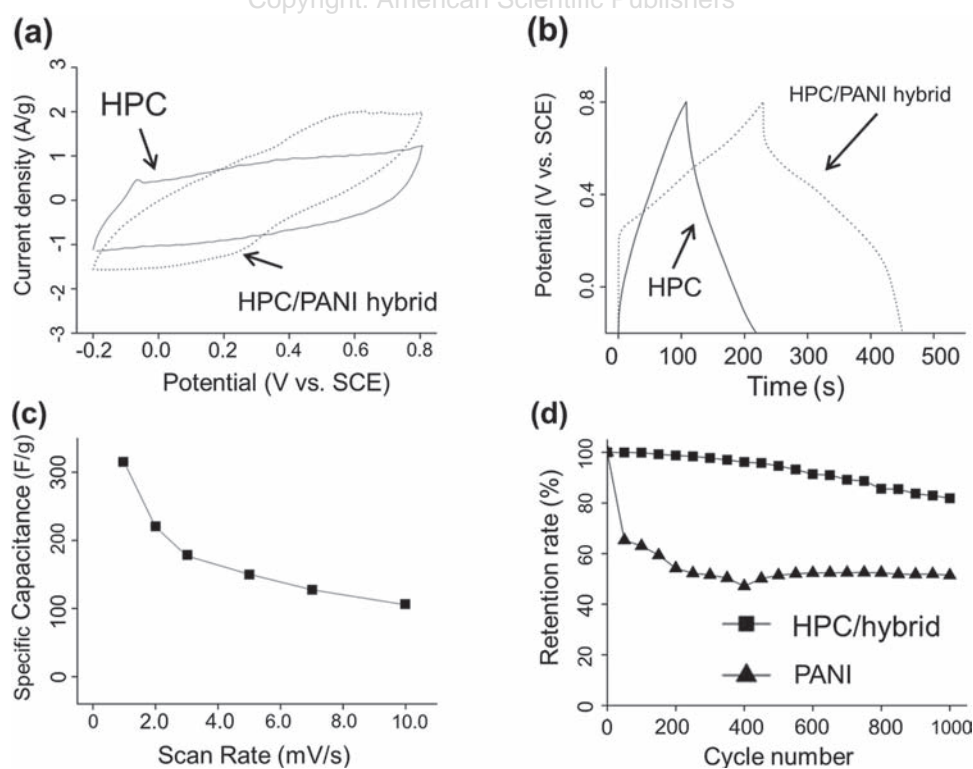


Figure 3. (a) Cyclic voltammograms at a scan rate of 5 mV/s, (b) galvanostatic charge–discharge curves in the potential window of -0.2 to 0.8 V at a current density of 1 A/g, (c) specific capacitance of HPC/PANI hybrid for different scan rates in the potential window of -0.2 to 0.8 V, and (d) variations of the specific capacitance as a function of cycle number at 50 mV/s.

be divided into two sections. The first section corresponds to a fast potential drop. This section is similar to the discharge curve of the HPC due to the EDLC behavior of the HPC/PANI hybrid. In the second section, the potential is slowly reduced. The slow decline is a result of the combination of EDLC and pseudocapacitor behaviors of the HPC/PANI hybrid.¹⁴ The specific capacitance was calculated from the discharge curves using the following equation:

$$C = \frac{I \times t}{W \times \Delta E}$$

where I is the discharge current, t the discharge time, W the mass of the electrode, and ΔE the potential difference in discharge.¹⁵ The specific capacitance of the HPC/PANI hybrid was 221.6 F/g at a current density of 1 A/g, which is much higher—almost 100% higher—than that of the HPC (111.4 F/g).

The specific capacitances of the HPC/PANI hybrid from -0.2 to 0.8 V versus SCE at scan rates from 10 to 100 mV/s are shown in Figure 3(c). At scan rates from 10 to 100 mV/s, the HPC/PANI hybrid has a capacitance retention of 33%, and its specific capacitance was 105 F/g at a scan rate of 100 mV/s.

The cycle stability, which is an important characteristic for capacitors, is shown in Figure 3(d) as a function of the charge–discharge cycle number at a scan rate of 50 mV/s. The specific capacitance of PANI decreased to 51% after 1000 cycles. However, the specific capacitance of the HPC/PANI hybrid was almost 82% after 1000 cycles. These results are attributed to the use of the HPC as a template for the coated PANI, which prevents the coated PANI from swelling and shrinking for many repeated redox process, which leads to the degradation of PANI.

4. CONCLUSIONS

An HPC/PANI hybrid electrode for use in supercapacitors was prepared by rapid-mixing polymerization. The surface and composition of the HPC/PANI hybrid were characterized by TEM and XPS. The electrochemical properties were investigated by cyclic voltammograms

and galvanostatic charge–discharge tests. The HPC/PANI hybrid electrode exhibited better specific capacitance than the HPC electrode did, owing to the pseudocapacitance effect of PANI: the HPC/PANI hybrid electrode exhibited a high capacitance of 221.6 F/g at a current density of 1 A/g, and the initial capacitance was maintained at 82% after 1000 cycles.

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