

Synthesis and Electrochemical Properties of Hollow Polyaniline Microspheres by a Sulfonated Polystyrene Template

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ABSTRACT: Hollow polyaniline microspheres (HMsPANI) for supercapacitors were prepared successfully with sulfonated polystyrene microspheres as the template. The prepared electrode materials of HMsPANI consisted of nanoparticles and, thus, had a hierarchical structure. The electrochemical behaviors of the materials were investigated with cyclic voltammetry and galvanostatic charge–discharge tests. A maximum specific capacitance of 421 F/g was achieved in a 1M H₂SO₄ solution, with the potential ranging from –0.2 to 0.8 V (vs a saturated calomel electrode), in a three-electrode glass cell at room temperature for the HMsPANI electrode. This suggested its potential application in electrochemical capacitors. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Supercapacitors, also called *electrochemical capacitors*, are unique energy-storage devices exhibiting 20–200 times greater capacitance values than conventional capacitors.¹ Therefore, a lot of research work has been done in the past few years to improve the performance of electrochemical capacitor electrodes. Various materials have been investigated for supercapacitors, including transition-metal oxides,^{2,3} conducting polymers,^{4–6} and carbonaceous materials.^{7–9} Conducting polymers have been regarded as promising pseudocapacitive materials because the kinetics of the charge–discharge processes of polymers with suitable morphology are fast, they can generally be produced at lower cost than noble metal oxides, and they are comparable to activated carbon.¹⁰

Recently, many attempts have been made to synthesize conducting polyaniline (PANI) chemically and to use it as an electrode material in supercapacitors. For examples, Subramania and Devi¹¹ prepared citric acid doped PANI nanofibers by a surfactant-assisted dilute polymerization technique. The specific capacitance behavior of the PANI nanofibers was characterized with cyclic voltammetry (CV), which exhibited a highest specific capacitance of 298 F/g. A hybrid-type supercapacitor was made by Park and Park¹² with conducting *p*-dopable PANI as the positive electrode material and activated carbon with a high specific surface area as the negative electrode material instead of a *n*-dopable conducting polymer. The specific capacitance of the

electrode material was 380 F/g. A copolymer of aniline (ANI) and pyrrole was synthesized with an inverted emulsion polymerization method by the oxidation of ANI and pyrrole with benzoyl peroxide in the presence of sodium laurylsulfate surfactant and *p*-toluenesulfonic acid. The values of the specific capacitance, energy, and power density for the poly(aniline-*co*-pyrrole)-*p*-toluenesulfonic acid system were calculated from charge–discharge studies and were found to be 21 F/g, 5.7 W h/kg, and 100 W/kg, respectively. Impedance analysis showed a specific capacitance value of 57 F/g at 0.01 Hz and 0.22 V.¹³

Now, a great number of different morphologies of PANI have been obtained by changes in the synthesis method, and the morphology can be directed by itself or templates.¹⁴ The templates include soft templates and hard templates. Wan et al.¹⁵ developed a template self-removing process to produce a PANI hollow structure with octahedral cuprous oxide as a template. Wu et al.¹⁶ fabricated a conducting PANI matrix based on a template of polystyrene (PS) latex. PS spheres as a hard template have spurred great interest because of the technical maturity of synthesis and because the size of the PS spheres can be controlled by the mass of the monomer, the temperature, the solvent, and so on.^{17–19} Moreover, its activity for reaction can be changed in further reaction.²⁰ Chu et al.¹⁸ reported a simple way to prepare hollow PANI and hollow polypyrrole microspheres in the size range of 2.2–3.4 μm in diameter. The template particles were prepared by simple sulfonation of dry PS

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Table I. Preparation of the PS Spheres by Dispersion Polymerization

Ingredient	Styrene (mL)	Azobisisobutyronitrile (g)	Ethanol (mL)	Water (mL)	Poly(<i>N</i> -vinyl pyrrolidone) (g)
Amount	20	0.2	95	3	1.5

Conditions: N₂, polymerization temperature = 70°C, and polymerization time = 12 h.

microspheres. ANI or pyrrole was oxidatively polymerized on the surface of sulfonated polystyrene (SPS). Dissolved with solvent, the SPS cores were removed from the core-shell particles, and uniform hollow PANI or polypyrrole microspheres were obtained. CV showed that the hollow PANI spheres maintained their oxidative stability and electrochemical properties after the cores were removed. It is a pity that the use of these advanced materials applied in the electrodes of supercapacitors is seldom reported in literature.

In this study, hollow polyaniline microspheres (HMSPANI) formed with nanoparticles were prepared and applied to the electrodes of supercapacitors. The effects of the weight ratio of ANI to SPS (*r*) on the PANI structure and the electrochemical properties were studied in detail. The specific capacitance of HMSPANI could be controlled by the ratio of the mass of ANI and SPS, and the maximum specific capacitance was 421 F/g in a 1M H₂SO₄ solution.

EXPERIMENTAL

Materials

Styrene and ANI monomer (analytical grade) were distilled until colorless under reduced pressure before use. Other chemicals were analytical grade and were used as received without further treatment.

Synthesis of the PS Microspheres

PS microspheres were produced by dispersion polymerization at 70°C for 12 h with magnetic stirring under a nitrogen atmosphere in a four-necked, round-bottom flask under the optimum conditions listed in Table I.

Preparation of the SPS Microspheres

The synthesized PS microspheres (2.0 g) were dispersed in concentrated sulfuric acid (30 mL, 98%) with the aid of ultrasound. The sulfonation took place at 45°C with magnetic stirring for 2.5 h.^{18,21} After they were diluted, the SPS spheres were separated by centrifugation and washed with ethanol and water three times, respectively. After the spheres were dried in a vacuum oven at 60°C for 24 h, a yellowish fine powder was obtained.

Preparation of the SPS/PANI Composite

The prepared SPS (2.0 g) was added to a glass container containing distilled water (30 mL) and dispersed for 0.5 h by ultrasonic dispersion; then, ANI monomer (0.4 g) was added with magnetic stirring for 0.5 h. (NH₄)₂SO₄ (0.98 g), dissolved in distilled water (20 mL), was added to the mixture solution. The polymerization of ANI was carried out at room temperature for 12 h. After the polymerization, a dispersion solution of the SPS/PANI composite was obtained by centrifugation and was washed with distilled water and ethanol until the pH of the fil-

trate solution was 7 and the filtrate solution was colorless. Finally, the composite was dried in a vacuum oven at 60°C.

Preparation of HMSPANI

The SPS/PANI composite (2.0 g) was added to tetrahydrofuran (THF: 50 mL) in a glass container, and the mixture was stirred with magnetic stirring at room temperature for 24 h. The powder was obtained by centrifugation, washed with distilled water and ethanol three times, and dried in a vacuum oven at 60°C for 24 h.

Structural Characterization

The morphologies and microstructures of PS, SPS, SPS/PANI, and HMSPANI were characterized with scanning electron microscopy (SEM: model JEM-6701F, JEOL, Japan). The IR spectra were recorded with a Fourier transform infrared (FTIR) spectrometer (Nexus 670, Nicolet Instrument Corporation, USA).

Electrode Preparation

A mixture containing 80 wt % HMSPANI powder, 7.5 wt % acetylene black, 7.5 wt % conducting graphite, and 5 wt % polytetrafluoroethylene was mixed well and then pressed at 10 MPa onto a stainless steel net for an electric connection. The electrode assembly was dried at 60°C for 12 h in air. Each electrode contained about 8 mg of electroactive material and had a geometric surface area of about 1 cm².

Electrochemical Tests

Electrochemical measurements were carried out with an electrochemical working station (CHI660C, Shanghai Chenhua, China) in a half-cell setup configuration at room temperature. A platinum gauze electrode and a saturated calomel electrode served as the counter electrode and the reference electrode, respectively. CV scans were recorded from -0.2 to 0.8 V at different scan rates in a 1M H₂SO₄ solution, and charge-discharge cycle tests were carried out in the potential range from -0.2 to 0.8 V in a 1M H₂SO₄ solution at different current densities.

RESULTS AND DISCUSSION

Preparation and Characterization of HMSPANI

The morphologies of the PS, SPS, SPS/PANI composite, and HMSPANI were characterized by SEM. As shown in Figure 1(a-d), the resulting HMSPANI basically replicated that of the SPS template and was spherical in shape, with a diameter of 4–5 μm. From the SEM images, we found that the surface of the obtained microspheres consisted of nanoparticles about 20–40 nm in size; this indicated that the as-synthesized PANI had a hierarchical structure. Figure 1(e-h) shows the SEM images of HMSPANI at different *r*'s. The lower ratio (*r* = 0.1) could lead the microspheres to structurally collapse. When the ratio was increased, hollow microspheres were obtained, and the

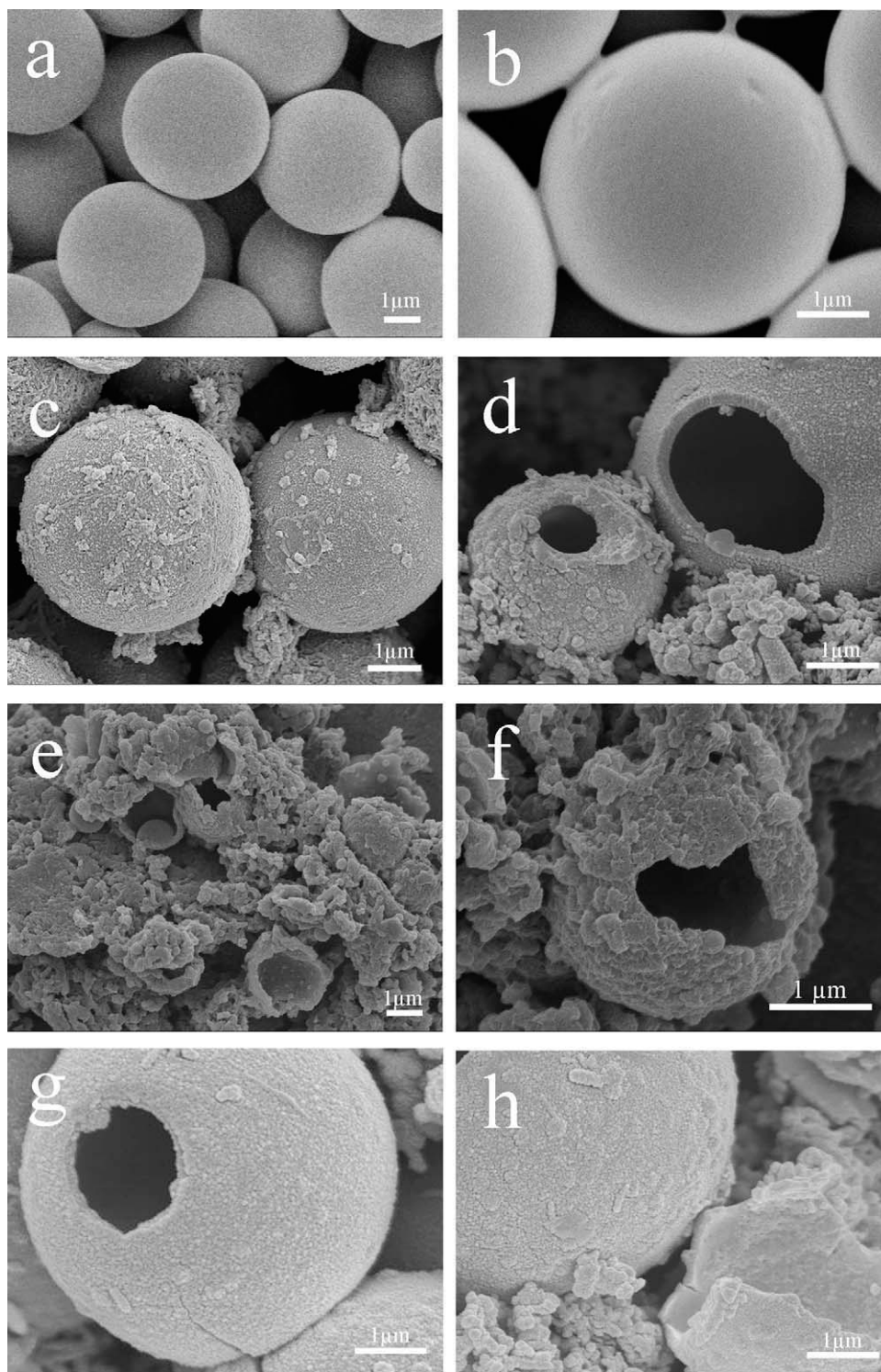


Figure 1. SEM images of (a) PS, (b) SPS, (c) SPS/PANI, (d) HMsPANI ($r_{\text{ANI/SPS}} = 1.0$), (e) HMsPANI ($r_{\text{ANI/SPS}} = 0.1$), (f) HMsPANI ($r_{\text{ANI/SPS}} = 0.4$), (g) HMsPANI ($r_{\text{ANI/SPS}} = 0.7$) and (h) HMsPANI ($r_{\text{ANI/SPS}} = 2.0$).

HMsPANI layer became thicker ($r = 1.0$). When the ratio exceeded 1.0, there were many PANI nanoparticles around the HMsPANI because a certain ANI polymerization did not react on the SPS surface.

The overall synthetic procedure is schematically summarized as Figure 2. As is well known, the SPS sphere contains a layer of hydrophilic $-\text{SO}_3\text{H}$ end groups, which serve as the dopant and provide hydrogen bonds at the same time. Thereby, $-\text{SO}_3\text{H}/$

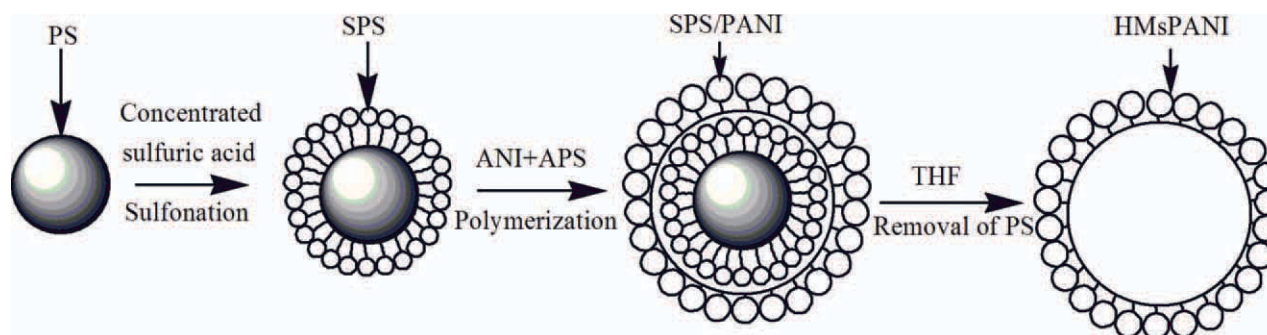


Figure 2. Synthetic procedure of HMSPANI.

ANI salt existed on the surface of the SPS sphere because of the acid–base reaction between SPS and basic ANI, which served as the templates in the formation of the microstructures of PANI. After the oxidant $(\text{NH}_4)_2\text{SO}_4$ was added drop by drop, ANI assembled and polymerized on the surface of the SPS spheres; thus, a layer of PANI nanoparticles formed on the SPS sphere surface. The process of the extraction of SPS was conducted with THF, and HMSPANI was eventually left behind.

Figure 3 shows FTIR spectra of the SPS/PANI composite and HMSPANI. The peaks shown in Figure 3(a) at 1600 and 1493 cm^{-1} corresponded to the vibrations of the C–C in the phenyl group; the strong absorbance peaks at 3082, 3026, 754, and 698 cm^{-1} corresponded to the vibrations of hydrogen in the phenyl groups of PS (Ar–H). The peaks at 1450 and 1028 cm^{-1} were attributed to the sulfonic acid groups of SPS.²⁰ C=C stretching vibrations of the quinoid and benzenoid rings at 1564 and 1480 cm^{-1} , respectively, C–N stretching at about 1300 cm^{-1} , N=Q=N absorption peaks (where Q represents the quinoid ring) at about 1130 cm^{-1} , and N–H stretching vibrations at 3437 cm^{-1} were all observed. As shown in Figure 3(b), all of the FTIR spectra were identical to those of PANI.²²

The material balance between the SPS/PANI composite and HMSPANI after SPS was dissolved with THF is presented in Table II. There was no residual SPS in HMSPANI after SPS was

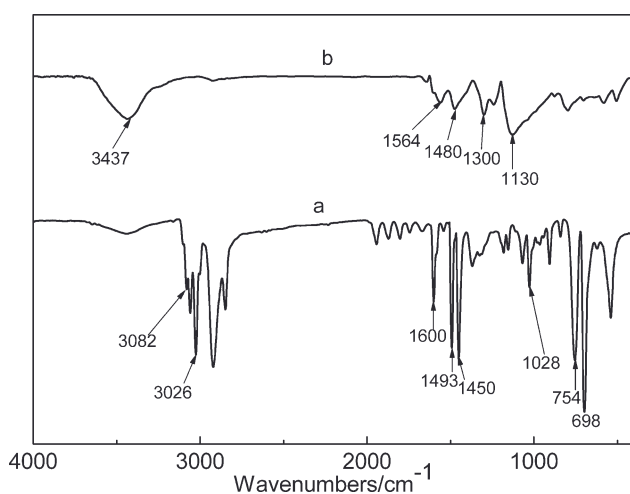


Figure 3. FTIR spectra of (a) SPS/PANI composite and (b) HMSPANI.

dissolved with THF because of the excessive use of THF, which was confirmed by FTIR spectroscopy. From Table II, we observed that the feeding ratios of ANI/SPS were close to the ratio calculated by the HMSPANI amounts after SPS was dissolved, and the mass of dissolving SPS was due to the high conversion of ANI.

Electrochemical Properties

Figure 4 shows the cyclic voltammograms of the HMSPANI in a 1M H_2SO_4 solution at different scan rates. All of the curves showed the obvious two peaks found on the positive and negative sweeps in the whole potential range and proved the redox reaction in this process. Peaks C_1 and A_1 were attributed to the redox transition of PANI between a semiconducting state (leucoemeraldine form) and a conducting state (polaronic emeraldine form). Peaks C_2 and A_2 were due to the emeraldine–pernigraniline transformation.²³ The output current increased when the scan rate increased, and the figures of all curves were similar. When the electrode potential was greater than 0.2 V, HMSPANI electrode oxidation began. The redox reactions were accompanied by energy storage and release.

Typical constant charge–discharge responses for HMSPANI are shown as Figure 5. On the four curves, the P – t responses of the anodic charge process showed that those were not similar mirror images of their corresponding cathodic discharge counterparts. From these, we observed that HMSPANI exhibited obvious pseudo-capacitance behavior in the 1M H_2SO_4 solution. The capacitance values were evaluated from charge–

Table II. Mass of HMSPANI Amounts before and after the Removal of SPS

$r_{\text{ANI/SPS}}$	PANI/SPS composites amount (g)	m_1 (g)	m_2 (g)	Calculated m_1/m_2 ratio
0.1	2	0.17	1.83	0.09
0.4	2	0.55	1.45	0.38
0.7	2	0.83	1.17	0.65
1.0	2	0.98	1.02	0.96
2.0	2	1.30	0.7	1.85

m_1 , HMSPANI amount after the dissolution of SPS; m_2 , mass of dissolving SPS.

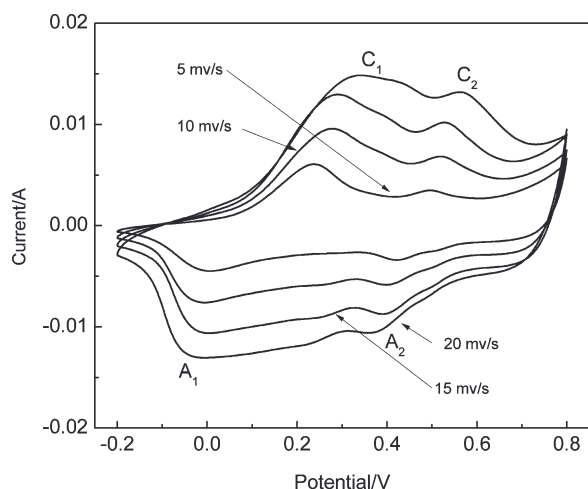


Figure 4. CV of HMsPANI in 1 M H₂SO₄ solution at different scan rates.

discharge cycling measurements, which are considered to be the most reliable. Specific capacitance values (C_s) were calculated according to Eq. (1).²⁴

$$C_s = I\Delta t / \Delta V m \quad (1)$$

where I is the discharge current, Δt is the discharge time corresponding to the voltage difference (ΔV), and m is the active electrode mass. In Figure 5, when the current density was 5 mA/cm², the discharge time was 550 s. On the basis of the previous equation, the specific capacitance for HMsPANI was shown to be 344 F/g. With the current density increased, the discharge time decreased, and the specific capacitance decreased. The specific capacitances at different current densities are shown in Table III. As shown in the table, when current density increased to 20 mA/cm², the specific capacitance dropped to 64% of the initial specific capacitance at a current density of 5 mA/cm².

As mentioned previously, ANI assembled and polymerized on the surface of the SPS spheres, and a layer of PANI shell

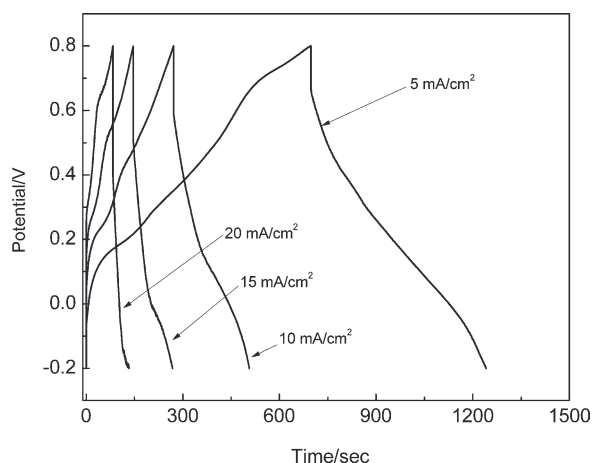


Figure 5. Galvanostatic charge–discharge curves of HMsPANI in 1 M H₂SO₄ solution at different current densities.

Table III. Specific Capacitance Values of HMsPANI in a 1M H₂SO₄ Solution at Different Current Densities

Current density (mA/cm ²)	5	10	15	20
Specific capacitance (F/g)	344	294	229	123

formed; thus, the feed ratio of ANI to SPS ($r_{\text{ANI/SPS}}$) affected the morphology and structure of PANI.¹⁸ The morphology and structure of PANI further made special contribution to the electrochemical performance. The relationship between the specific capacitance of HMsPANI and $r_{\text{ANI/SPS}}$ is plotted in Figure 6. As shown in the figure, a lower specific capacitance was obtained with lower $r_{\text{ANI/SPS}}$; the reason for this was that the PANI could not yet be coated on the SPS surface perfectly. An SEM image of PANI prepared under these conditions after the removal of the templates is shown in Figure 1. With increasing ratio, the specific capacitance of HMsPANI increased and reached a maximum of 421 F/g at 1.0. Under this situation, SPS could be coated by PANI completely and formed a hierarchical structure (see Figure 1). This structure and morphology contributed to the improved electrochemical performance. With a further increase in the ratio beyond 1.0, the specific capacitance resulted in a low decrease in the curve. This result implies that the excess ANI did not favor the expected structure of HMsPANI with hierarchy, which resulted in a decrease in the electrochemical performance.

The stability and reversibility of an electrode material are important for its use in an electrochemical supercapacitor. The cyclic performance was further examined by galvanostatic charge–discharge tests for 500 cycles with 10 mA/cm² of discharge current density, as shown in Figure 7. There was a decrease in the specific capacitance value in the first 200 cycles, and thereafter, the specific capacitance remained almost constant. The initial decrease was likely to be caused by the swelling and shrinking of PANI, which are known to cause degradation during cycling. After 500 charge–discharge cycles, the specific capacitance of the HMsPANI was obtained 45% of the initial capacitance. The results reveal that the HMsPANI electrode enjoyed good stability for a long cyclic life.

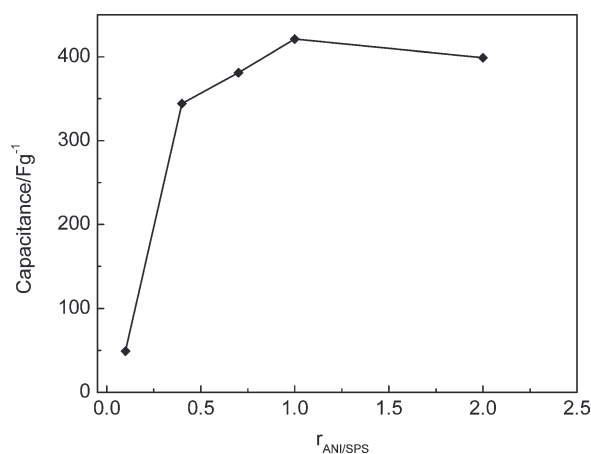


Figure 6. The relationship between specific capacitance of HMsPANI and $r_{\text{ANI/SPS}}$ at discharge current density of 5 mA/cm².

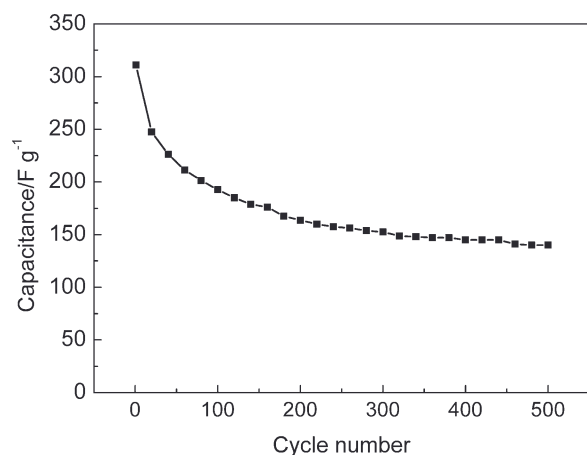


Figure 7. Cycle life of HMsPANI electrode at discharge current density of 10 mA/cm².

CONCLUSIONS

In summary, novel HMsPANI was successfully prepared by *in situ* chemical oxidative polymerization with SPS spheres as the template. The as-prepared electrode materials of PANI consisted of nanoparticles and, thus, had a hierarchical structure. This was effective for obtaining a very fast redox behavior, which contributed to the pseudo-capacitance. The specific capacitances of HMsPANI increased obviously with increasing loading ratio at low ratios in the curve; a further increase of $r_{\text{ANI/SPS}}$ beyond 1.0 resulted in a low decrease in the curve. Electrochemical tests showed that the HMsPANI electrode reached a maximum capacitance of 421 F/g in a 1M H₂SO₄ solution when $r_{\text{ANI/SPS}}$ was 1.0 and enjoyed good stability for a supercapacitor.

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