



Enhancing the cycling stability of the polyaniline hybrids benefited from the hollow manganese dioxide/acetylene black skeleton



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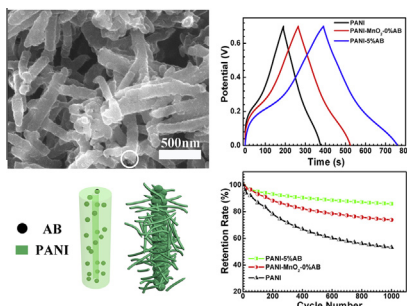
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HIGHLIGHTS

- The novel 1D PANI–AB nanocomposites can be fabricated by MnO₂ nanotubes.
- The obtained hollow PANI–AB nanocomposites possess 1D branched structure.
- HOLLOWED PANI–AB hybrid nanostructures exhibit good long-term cycling stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Polyaniline (PANI) can be regarded as the most promising pseudocapacitive material for using as supercapacitor electrodes. However, its poor cycling stability has become the major obstacle limiting its practical applications. In this study, we have successfully improved the cycling stability of PANI-based supercapacitor by designing the PANI-acetylene black (PANI–AB) hybrid nanostructures assisted by MnO₂ nanotubes as sacrificial templates with a simple and low-cost method. The hybrid nanocomposites can exhibit good long-term cycling stability and 86% of the capacitance can be retained after 1000 cycles by CV test at a scan rate of 50 mV s⁻¹ compared to that of pure PANI-based supercapacitors. Furthermore, the PANI–5%AB hollowed hybrids also exhibit much better electrochemical performance (520 F g⁻¹ at 1 A g⁻¹) than that of pure PANI pseudocapacitors (271 F g⁻¹ at 1 A g⁻¹). The as-prepared full cells based on the hybrid structures can be further demonstrated that the PANI–5%AB based electrodes can have promising performance with high power density of 1361 W kg⁻¹ and energy density of 17.8 W h kg⁻¹ at current density of 2 A g⁻¹, even 6.32 kW kg⁻¹ and 14.1 W h kg⁻¹ at high current density of 10 A g⁻¹. The supercapacitor performances demonstrate that PANI–5%AB hybrid nanocomposites are very promising for high-performance electrochemical supercapacitor application.

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1. Introduction

Supercapacitors (also called ultracapacitor) with ultrahigh work density and long cycling ability (>50,000 cycles) have been

regarded as a most promising energy source for high power supplies, electric and hybrid vehicles, and portable electronics [1–5]. A typical supercapacitor can be composed of two electrodes, electrolyte, and a separator between two electrodes, in which the electrode materials determine the whole supercapacitor performance [6]. Polyaniline (PANI) as supercapacitor electrode materials can greatly enhance the energy storage capacity due to the additional

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capacitance contribution from fast and reversible redox reactions in the supercapacitors [5,7]. However, its poor cycling stability greatly restricts its rapid development in supercapacitors (usually < 50% capacitance retention after 1000 charge–discharge cycles in aqueous electrolytes), which mainly results from its poor mechanical stability (swelling, shrinkage, cracks, or breaking) during the charging and discharging process [8–10].

One of the most effective strategy for prolonging the cycle life of PANI-based supercapacitors is to rationally design their structures by combining the advantages of PANI with high pseudo-capacitance and carbon electrode materials with excellent mechanical properties and cycle durability [11–13]. With this consideration, several different types of hybrid structures (such as porous carbon/PANI [14–16], carbon nanotube/PANI [17–19], carbon fiber/PANI [12,20,21] and graphene/PANI composites [6,22–24]) have been explored to improve the electrochemical performance in achieving long cycle life together with energy density. Among of these developed hybrid structures, one-dimensional (1D) nanocomposites can be as an ideal structure for electrode materials due to 1D structure nature which can facilitate for efficient charge transport and reducing ions-transport length [9,25]. Up to now, a great deal of efforts have demonstrated that 1D PANI–carbon hybrids (carbon served as the matrix/scaffolds for the PANI active component) used as electrode materials can exhibit excellent mechanical properties and cycle durability. For example (Table S1), Zhou et al. have prepared 1D PANI/carbon nanotube nanocomposites by in situ polymerization of aniline on carbon nanotubes with capacity retention of 80.7% after 1000 cycles [26]. Li et al. have fabricated PANI/carbon nanotube with ternary coaxial structures as supercapacitor electrodes via a simple wet chemical method, which obtained the capacity retention of 77% after 1000 cycles [27]. Kotal et al. have synthesized 1D PANI/carbon nanofiber nanocomposites by a chemical grafting approach with the capacity retention of 86% after 2000 cycles [20]. Sun and Liu have reported fibrous structure of MnO₂ and PANI deposited on carbon cloth with 76% capacitance retention after 1200 cycles [28]. However, despite these efforts on the fabrication of various 1D PANI–carbon nanocomposites, their cycling performances are still far from satisfactory, and at the same time it is needed to point out that the carbon materials used were relatively expensive (carbon nanotube, graphene or carbon cloth), which greatly restrict their commercial applications.

In this study, a simple and effective route to improve the cycling stability of 1D PANI–carbon electrode materials by in situ chemical polymerization of aniline on MnO₂–AB nanotubes as the sacrificial template has been reported. The obtained PANI–AB hybrid nanocomposites with desired 1D hollowed branched structure can increase the effective utilization of active materials throughout the whole electrode matrix and reduced the effective diffusion distance of protons and electrons, leading to excellent cycle durability as well electrochemical performance. The used MnO₂ nanotubes can play two roles in the preparation of hybrid electrode material: (1) acting as an ideal template for directing, growing and anchoring carbon–PANI composites on it to form 1D nanostructure, (2) functioning as sacrificial template facilitating the formation of hollow-like 1D nanostructure. Compared to pure PANI nanofibers prepared by polymerization of aniline without adding the MnO₂ template and AB, the improvement on the electronic conductivity, specific capacitance and cycling stability can be achieved from the 1D PANI–5%AB hybrid nanocomposites due to their increased surface area, higher conductivity and more accessible sites for redox reactions. The hybrid electrode exhibited excellent cycling stability with 86% capacitance retention after 1000 charge–discharge cycles. Moreover, the full cells based on the hybrid 1D nanocomposites further demonstrated remarkable high the power density

of 1361 W kg⁻¹ and energy density of 17.8 W h kg⁻¹ at current density of 2 A g⁻¹, even 6.32 kW kg⁻¹ and 14.1 W h kg⁻¹ at higher current density of 10 A g⁻¹.

2. Experimental

2.1. Raw materials

All the reagents such as aniline monomer (AN), ammonium persulfate (APS), potassium permanganate (KMnO₄), and manganese-sulfate (MnSO₄) used in this study were of analytical grade and were used as received without any further purification. The acidified AB can be obtained after original AB nanoparticles were treated with concentrated nitric acid for 6 h, and washed with deionized water, then dried at 60 °C. All solutions were prepared by using deionized water. Prior to prepare the working electrode, the stainless steel mesh was cleaned with acetone by ultrasound for 10 min, and washed with deionized water, then followed by drying at 60 °C for later use.

2.2. Preparation of MnO₂ nanotubes

MnO₂ nanotubes were prepared by a facile hydrothermal reaction [29] via the following reaction: $2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$. In a typical process, 0.237 g KMnO₄ was firstly dissolved into 30 mL NaOH aqueous solution (2 mM) prior to add 0.380 g MnSO₄·H₂O. Then, the solution was transferred into a Teflon lined stainless steel autoclave for hydrothermal process after 2 h stirring at room temperature and was kept in an electrical oven for 4 h at the temperature of 140 °C. After the autoclave was cooled down to room temperature, the black precipitate was washed with deionized water for several times by centrifugation until the solution pH was ~7. Finally, the raw powders were dried in a vacuum furnace at 80 °C for 24 h.

2.3. Synthesis of the PANI–AB ternary composites

The hybrid nanocomposites were synthesized by aqueous polymerization route. Firstly, suspension A was prepared by dispersing 1.369 g APS and 0.056 g MnO₂ nanotubes in 20 mL of 1 M HCl solution under ultrasonic treatment for 1 h, which was placed in an ice bath and stirred slowly. Subsequently, solution B was prepared by adding 540 μL aniline and a certain amount of acidified AB (0.014 g, 0.028 g, and 0.042 g) into 20 mL of 1 M HCl solution, respectively. After it was cooled to 0 °C in an ice bath, solution B was slowly added to solution A placed in the ice bath followed by stirring for 24 h to synthesize the hybrids. The resulting products were washed with deionized water and ethanol for three cycles using centrifugation method. Finally, the products were dried under vacuum at 60 °C for 24 h and three PANI–AB composites (PANI–2.5% AB, PANI–5%AB and PANI–7.5%AB) with varying contents of AB were obtained. For comparison, pure PANI nanofibers (or PANI–MnO₂–0%AB) hybrids were synthesized with using the same route as that of the PANI–AB hybrids without introducing the components of MnO₂ and AB (or AB). The fabrication procedure for PANI–AB hybrids is illustrated in Fig. 1.

2.4. Characterizations

The morphologies and structures of the hybrids were investigated by powder X-ray diffractometer (XRD) using a monochromatized Cu target radiation resource ($\lambda = 1.54 \text{ \AA}$), scanning electron microscopy (SEM, Magellan 400) operated at 10 kV equipped with an energy-dispersive X-ray analyzer, and transmission electron microscopy (TEM, JEM-2100F) at 200 kV, respectively.

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