



Three-dimensional graphene-polyaniline hybrid hollow spheres by layer-by-layer assembly for application in supercapacitor



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ARTICLE INFO

Article history:

Received 28 February 2015
Received in revised form 7 May 2015
Accepted 10 May 2015
Available online 12 May 2015

Keywords:

reduced graphene oxide (RGO)
polyaniline
hybrid hollow sphere
layer-by-layer (LBL) assembly
supercapacitor

ABSTRACT

A novel kind of three-dimensional graphene-polyaniline hybrid hollow sphere (RGO-PANI HS) has been prepared via layer-by-layer (LBL) assembly of negatively-charged reduced graphene oxide (RGO) and positively charged polyaniline (PANI) on polystyrene (PS) microsphere, followed by the removal of the PS template. The hollow structure of the obtained RGO-PANI HS is confirmed by transmission electron microscopy (TEM). When used as the electrode materials for supercapacitor, the specific capacitance of the RGO-PANI HS reaches 381 F/g at a current density of 4.0 A/g, which is much higher than 251 F/g of the stacked RGO-PANI LBL film. The higher specific capacitance of RGO-PANI HS should be attributed to its unique hollow structure which provides a larger accessible surface area and facilitate the charge and ion transport. In addition, its specific capacitance can be facily tailored by changing the assembly cycle number. Furthermore, good cycling stability is also demonstrated with 83% of the original capacitance value maintained after 1000 charging/discharging cycles.

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1. Introduction

Supercapacitor, an electrochemical energy storage device, has attracted great interest due to its unique properties such as high power density, long cycle life, and fast charging-discharging rates. It is well-known that the energy storage mechanism is divided into two categories: faradaic pseudocapacitors and double-layer capacitors [1]. Graphene possesses outstanding electrical conductivity, high specific surface area, as well as good mechanical properties, and thus is considered as an ideal electrode material for double-layer capacitor [2,3]. On the other hand, polyaniline (PANI) is one of the most promising electrode materials for pseudocapacitors due to its high specific capacitance and electrical conductivity [4,5]. Based on the above-mentioned characteristics of graphene and PANI, hybrid nanomaterials of graphene and PANI are considered as promising electrode materials for supercapacitor combining the advantages of both materials with synergistic effects.

Up to now, considerable research interest has been dedicated to fabricating graphene-PANI hybrid materials and investigating their application in supercapacitors [6–26]. The reported synthesis

procedures of the graphene-PANI composites include in situ chemical polymerization or electropolymerization of aniline monomer in the presence of graphene or graphene oxide, or directly mixing the solutions of PANI and graphene. However, owing to the strong tendency of graphene to agglomerate and restack, it is difficult for these methods to realize the nanoscale uniform combination of graphene with PANI in a well-defined structure and composition, leading to a great sacrifice of the surface area of graphene sheets and intimate electrochemical interfaces which is important for many electronic devices such as supercapacitors and sensors. Layer-by-layer (LBL) assembly technique provides an attractive and straightforward strategy for fabricating graphene-PANI composite, which offers several advantages over the above-mentioned preparation methods, for example, nanometer-scale control over the compositions, architecture and properties of graphene-PANI composite. Moreover, the electrochemical behavior of graphene-PANI composite can be facily tuned by adjusting the assembling species as well as the numbers of assembling cycles. In recent years, the successful fabrication of graphene-PANI thin films via LBL assembly technique has been reported, which exhibited enhanced electrochemical performance [27–31].

Very recently, three-dimensional graphene-PANI hybrid structures, such as hollow structure and hydrogel/aerogel, have also been fabricated [32–36]. The hollow micro/nanostructured materials with the nanoscale shell, inner cavity and pore

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structures, offer particular advantages for application in supercapacitors owing to the enhanced specific surface area and shortened diffusion length for both charge and mass transport, which can greatly enhance the performance as electrode materials for supercapacitor. Liu et al. [33] reported a clever method to fabricate graphene–PANI hollow spheres by wrapping graphene oxide on a polyaniline hollow sphere via electrostatic interaction and subsequently electrochemical reducing GO to obtain the final hollow graphene–PANI hybrids. Choi et al. [34] reported a three-dimensional graphene–PANI hybrid hollow balls through the self-assembly of graphene oxide and poly(methyl methacrylate) particle, followed by the in situ polymerization of aniline and removal of the PMMA core. The resulted graphene–PANI hollow structures showed enhanced electrochemical performance, including high specific capacitance and good cycling stability. Considering the particular advantages of the LBL assembly technique, it is quite attractive to prepare hollow structured graphene–PANI hybrid via LBL assembly technique.

Herein, in this paper, a novel kind of graphene–PANI hybrid hollow spheres (RGO–PANI HS) was prepared using LBL self-assembly technique. Specifically, positively charged polyaniline and negatively charged reduced graphene oxide were used as building blocks to alternatively assemble on the surface of sulfonated polystyrene (PS) colloidal particles, followed by the removal of the PS particles. The obtained product was characterized by FTIR spectroscopy, Raman spectroscopy, TEM and SEM measurements, which demonstrate the successful preparation of hollow structured graphene–PANI hybrid materials. The electrochemical performance of the hybrid material as supercapacitor electrode was investigated by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy.

2. Experimental section

2.1. Materials

Natural graphite powder and N, N'-dimethylacetamide were purchased from Shanghai Aladdin Chemical Reagent Company. Polystyrene sulfonate (Mw 70 000) was purchased from Aldrich. Ammonium persulfate (APS), aniline and styrene were purchased from Sinopharm Chemical Reagent Co., Ltd. Styrene and aniline were purified by distillation, and other reagents were used as received. All solvents were of analytical grade. Graphene oxide (GO) was prepared from natural graphite powder using a modified Hummers method [37].

2.2. Synthesis of polystyrene templates

Uniform polystyrene (PS) particles were synthesized by dispersion polymerization of styrene in the presence of polyvinylpyrrolidone (PVP) according to Khan and Armes [38]. St (20 mL) and 3.2 g PVP were added to 125 mL of absolute ethanol, and 0.145 g azodiisobutyronitrile was then added to the flask under vigorous stirring with N₂. The above mixture was heated to 80 °C and the polymerization continued for 24 h at 80 °C. The resulting supernatant was purified by repeated centrifugation and rinsed with distilled water and ethanol. A white powder was finally obtained after drying. And the sulfonation of the obtained PS spheres was conducted using concentrated sulfuric acid at 45 °C for 24 h. The sulfonated PS templates were finally obtained by centrifugation, rinsed with a large amount of distilled water, and dried.

2.3. Preparation of aqueous dispersion of reduced graphene oxide (RGO)

The preparation of stable aqueous dispersion of negatively charged graphene has been reported in previous literature [39]. Typically, GO (100 mg) was dispersed in ultrapure water (100 mL) via ultrasonic treatment for about 30 min to obtain graphene oxide suspension. Polystyrene sulfonate (1 g) was then added into the above graphene oxide suspension and ultrasonicated for another 30 min. 1.5 mL of hydrazine hydrate was subsequently added, and the mixture was heated and stirred at 90 °C for 24 h. Finally, a stable black dispersion of negatively charged polystyrene sulfonate stabilized RGO was obtained.

2.4. Preparation of PANI dispersion

PANI aqueous dispersion was prepared according to previous literature [40]. Typically, aniline (0.931 g, 0.01 mol) and 0.1 mol/L sulfuric acid (100 mL) were mixed together and cooled to about 0 °C. Ammonium persulfate (2.28 g, 0.01 mol) was then added and stirred for 8 h. The synthesized PANI is emeraldine salt, which was transformed to emeraldine base after treating with ammonia (8% aqueous solution). The obtained PANI base was subsequently dissolved in dimethylacetamide (DMAc) under sonication and stirring. After filtering with 0.8 μm filter membrane, the solution was diluted 100 times with HCl aqueous solution (pH 3.1). Finally, the pH value of the PANI dispersion was adjusted to pH 2.5. The PANI dispersion was typically used within two days after preparation.

2.5. Preparation of RGO–PANI HS via LBL technique

RGO–PANI bilayers were deposited on the sulfonated PS templates by electrostatic interaction via LBL assembly technique. Initially, 2.36 g of the sulfonated PS templates were dispersed in 70 mL water. 45 mL of PANI dispersion was then added and stirred for 1 h. PANI wrapped PS (PANI@PS) was obtained by centrifugation and rinsed with water. Then PANI@PS was dispersed in water and negatively charged graphene dispersion was added and stirred for 1 h. After centrifugation and rinsed with water, (RGO–PANI)₁@PS was obtained. The above steps for PANI and graphene adsorption were repeated n times to obtain RGO–PANI hybrid multilayer encapsulated PS spheres ((RGO–PANI)_n@PS).

After the desired number of RGO–PANI hybrid layer has been coated on PS sphere, the sacrificial PS templates were etched to obtain hollow microspheres by exposing (RGO–PANI)_n@PS in tetrahydrofuran (THF) for 2 h. The product was collected by centrifugation, and washed with THF for three times to ensure the complete removal of the PS templates. After drying, the ultimate RGO–PANI HS was obtained. To simplify, the obtained RGO–PANI HS with different bilayers were designated as RGO–PANI HS-2bi, RGO–PANI HS-4bi, RGO–PANI HS-6bi and RGO–PANI HS-8bi, respectively.

As a control experiment, a conventional RGO–PANI LBL film was prepared on the ITO electrode using the same building blocks via LBL assembly technique according to our previous report [30].

2.6. Characterization and instruments

UV-vis spectrum was recorded on a TU-1901 spectro-photometer (Beijing Purkinje General Instrument Co., Ltd.). Bruker spectrometer was used for FTIR spectra analysis in the range of 400~4000 cm⁻¹ using pressed KBr pellets. Raman spectrum was recorded with a Micro-Raman-spectroscopy/invia-Reflex apparatus using an excitation laser with a wavelength of 514 nm. The zeta potential of the dispersion was determined using a ξ-potential analyzer (Zetasizer Nano ZS90, Brookhaven Instruments Corp.,

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