



Synthesis of microspherical polyaniline/graphene composites and their application in supercapacitors



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ABSTRACT

Microspherical polyaniline/graphene (PANI/G-MS) composites are synthesized using sheet-like polyaniline/graphene oxide (PANI/GO) composites as raw materials via spray-drying and chemical reduction process, in which the granulated polyaniline (PANI) is in-situ grown on the surface of graphene oxide. For PANI/G-MS composites, PANI uniformly coats on the surface of graphene which can constitute a high conductive network to accelerate electronic transmission in the composites electrode for supercapacitors. Moreover, PANI/G-MS composites form numerous channels among their spherical particles during random stacking of sheet-like PANI/GO composites via spray-drying process. Due to the special structure, the electrochemical capacitance of the as-synthesized PANI/G-MS composite reaches 596.2 and 447.5 F g^{-1} at a current density of 0.5 and 20 A g^{-1} , respectively, indicating superior rate capability. Additionally, after 1500 cycles at a current density of 2 A g^{-1} , 83.7% of the initial capacitance is retained.

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1. Introduction

Supercapacitors, benefiting from the virtues of excellent power density, rapid charge/discharge rate and good cycling life, have a huge potential for the applications in portable electronic devices, electric vehicles and etc [1–4]. In order to further promote the development of supercapacitors, electrode materials which intimately affect the properties of supercapacitors should be taken into account [5,6]. Currently, electrode materials for supercapacitors can be divided into three types: carbon-based materials, conductive polymers and transition metal oxides [7–9]. As a typical representative of conductive polymers, polyaniline (PANI) enjoys some advantages for future practical application, such as high theoretical capacity, ease of synthesis and low cost [10,11]. However, when employed in supercapacitors, it suffers from some shortcomings of relatively low electrical conductivity and volumetric deformation that arises from the doping/dedoping of dopants during charging and discharging process [12–14]. These drawbacks affect the actual capacitance and the cycling stability of PANI, and then seriously restrict the use of PANI in supercapacitors. To conquer these obstacles, significant attentions have been focused on integrating PANI with high conductive carbon materials to obtain high-performance composite electrode materials. Many

carbon materials, for example, porous carbon [15], carbon aerogel [16], carbon nanotubes [17,18] and carbon nanofibers [19,20], have ever been utilized to hybridize with PANI. Recently, as a special monolayer nanostructure of carbon atoms network, graphene possesses a great superiority toward the above-mentioned carbon materials, e.g. excellent electrical and thermal properties, as well as high mechanical strength [21,22]. These outstanding properties render graphene as an extremely promising material for electrochemical energy storage, especially supercapacitors [23,24]. Therefore, a strategy for combining PANI with graphene would be an attractive method to overcome the drawbacks of PANI.

Many research works concerning various structures graphene/PANI composites have been carried out. Comparing to the lamellar structure, three-dimensional (3D) structures, such as 3D porous structures [21], sandwiched structure [25], tremella-like [26], spheres [27], hollow spheres [28], exhibit much more improved electrochemical performance. For instance, Stanciu et al. employed PANI nanoparticles as spacer to obtain sandwiched PANI/graphene nanocomposites and found it shows high specific surface area ($891 \text{ m}^2 \text{ g}^{-1}$) and specific capacitance (257 F g^{-1} at 0.1 A g^{-1}) [25]. Among those complicated structures, spheres structure is greatly conducive to improve the performance of electrode materials as well. Liu et al. have synthesized tremella-like PANI/graphene spherical composites by self-assembly of graphene nanosheets. Owing to the 3D porous spherical architecture, the specific capacity of 497 F g^{-1} at 0.5 A g^{-1} was achieved [26]. Moreover, Cao and his co-workers fabricated PANI/graphene nanocomposites

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through in situ polymerization using graphene microspheres as substrate. The final product exhibited an improved electrochemical capacitive performance [27]. However, due to the existence of concentration gradient of aniline between the surface and interior in graphene microspheres, the polymerization process tend to take place on the surface of graphene microspheres. In order to fully utilize the synergistic effect, graphene and PANI should well contact with each other. Therefore, designing a rational sphere structure of PANI/graphene composites with well contact between two components can enhance the performance of electrode materials.

Herein, 3D microspherical polyaniline/graphene (PANI/G-MS) composites have been synthesized by simple spray-drying and chemical reduction process. Spray-drying, as a simple technique of producing dry powders from dispersion solution or slurry, can be widely used for nanoparticles encapsulation or production of spherical particles which are resistant to aggregation [29,30]. As shown in Fig. 1, PANI/GO composites with a sheet-like morphology were acquired firstly through in-situ polymerization of aniline in the aqueous dispersion of GO, and then steps of spray-drying and chemical reduction were adopted to obtain PANI/G-MS composites from sheet-like PANI/GO suspension. The as-prepared PANI/G-MS composites have spherical structure which could form numerous channels inside the microspheres formed by random stacking of sheet-like PANI/GO composites. Moreover, PANI uniformly attaches to the surface of graphene inside the microspheres which could maximize the synergistic effect of the two components. The electrochemical tests indicated the specific capacitance can reach up to 596.2 F g^{-1} and 83.7% of the capacity retention after 1500 cycles was achieved. In addition, PANI/G-MS composites with different ratio of PANI and graphene prepared by controlling the concentration of aniline in GO suspension were investigated.

2. Experimental

2.1. Preparation of PANI/GO composites

Firstly, GO was prepared by a modified Hummers method and subsequent ultrasonic exfoliation process [31,32]. PANI/GO composites were synthesized through in-situ polymerization using GO nanosheets as substrate. Typically, 75 mg of GO was added to 300 ml 1 M H_2SO_4 aqueous solution with mechanical stirring and ultrasonic dispersion for 3 h. Then the mixture was moved into the ice bath. Subsequently, aniline monomer was poured into the GO suspension and stirred for 30 min. Then another 300 ml 1 M H_2SO_4 aqueous solution containing ammonium persulfate (APS) was added with vigorous stirring. The reaction was carried out in the ice bath for 24 h at nitrogen atmosphere. Finally, the product was filtered and washed with alcohol and deionized water. Various PANI/GO composites were synthesized by controlling the concentration of aniline in GO suspension ($C_{\text{AN}} = 0.02 \text{ M}$, 0.04 M and 0.06 M , respectively) and the molar ratio of aniline/APS was 4/1. For

comparison, the pure PANI ($C_{\text{AN}} = 0.04 \text{ M}$) was synthesized following the same process without GO nanosheets.

2.2. Preparation of PANI/G-MS composites

The PANI/G-MS composites were synthesized via spray-drying and chemical reduction process. Firstly, the as-prepared PANI/GO composites were re-dispersed in deionized water with sonication and then spray dried at 200°C to form PANI/GO-MS composites. Subsequently, the PANI/GO-MS composites were reduced by hydrazine hydrate (98%) and stirred at 95°C for 1 h. Then residual impurities were removed by filtration and repetitively washing with deionized water. Finally, the as-prepared products were added in 10 ml of 1 M H_2SO_4 solution containing 0.06 g of APS and stirred for 12 h at room temperature, followed by washing with deionized water and drying at 80°C for 12 h. It is worth noting that the hydrazine hydrate could reduce GO, along with the change of emeraldine salt, and the re-oxidation may convert the leucoemeraldine PANI back to emeraldine salt [33]. In addition, different PANI/G-MS composites were prepared from aforementioned various PANI/GO composites, and denoted as PANI/G-MS-2, PANI/G-MS-4 and PANI/G-MS-6, corresponding to $C_{\text{AN}} = 0.02 \text{ M}$, 0.04 M and 0.06 M , respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns were conducted on a D/MAX 2550VB/PC diffractometer (Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The Fourier-transform infrared (FT-IR) spectra were obtained on a Nicolet 5700 spectrometer (Thermo Electron, USA). Raman spectra were measured on an inVia Reflex Raman spectrometer (Renishaw, UK) with 514.5 nm wavelength laser excitation. Thermal gravimetric analysis (TGA) curves were measured with a thermogravimetric analyzer (PerkinElmer, USA) with a heating rate of $10^\circ\text{C}/\text{min}$ in an air flow of 100 ml/min. Transmission electron microscopy (TEM) measurement was carried out on a JEM-2100 (JEOL, Japan). Field emission scanning electron microscopy (FE-SEM) images were obtained on a Hitachi S-4800 instrument.

2.4. Electrochemical measurements

The three electrode system was used to assess the electrochemical performance of samples. The slurry mixture of 80% active materials, 10% acetylene black and 10% Polyvinylidene fluoride using 1-methyl-2-pyrrolidone as solvent was coated on carbon paper to prepare the working electrode. Ag/AgCl electrode and Platinum plate were used as the reference and counter electrode, respectively. The used electrolyte was 1 M H_2SO_4 aqueous solution at room temperature. All the electrochemical tests including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were carried out on an electrochemical workstation CHI 660D (Chenhua, China).

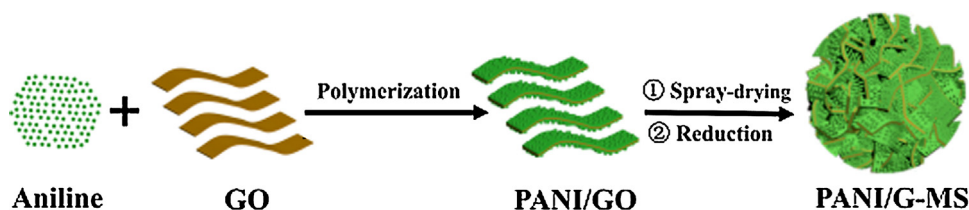


Fig. 1. Illustration of the preparation process of PANI/G-MS.

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