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# Fabrication of sandwich nanostructure graphene/polyaniline hollow spheres composite and its applications as electrode materials for supercapacitor

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ABSTRACT

A novel three-dimensional (3D) reduced graphene oxide/polyaniline hollow spheres (RGO/PANI-HS) composite, in which PANI-HS were inserted between RGO layers, has been fabricated as electrode materials for supercapacitor applications. This 3D nanostructure was constructed by electrostatic interaction between $SiO_2$@polyaniline core–shell spheres and graphene oxide, reduction of graphene oxide and removal of $SiO_2$ in sequence. Due to its tailored nanostructure and over-all conductive network, RGO/PANI-HS electrode exhibits a high specific capacitance of 529 F $g^{-1}$ at 0.5 A $g^{-1}$ and excellent rate capability (remains 72% even at 10 A $g^{-1}$), which is much higher than that of PANI-HS electrode (424 F $g^{-1}$ at 0.5 A $g^{-1}$, 62% retention at 10 A $g^{-1}$) in 1 M $H_2SO_4$ aqueous solution. More importantly, RGO/PANI-HS composite can maintain 85% of its initial specific capacitance well above 51% for PANI-HS after 1000 cycles, suggesting a superior electrochemical cyclic stability.



## 1. Introduction

Supercapacitors, also called as electrochemical capacitors or ultracapacitors, have attracted more and more interests of researchers due to its high power density, excellent cycling stability, fast charging–discharging rate and operational security compared with other secondary batteries [1–3]. In principle, supercapacitors are divided into two types based on their charge storage mechanism: electrochemical double-layer capacitors (EDLCs) and pseudo-supercapacitors [4,5]. As for EDLCs, in which carbon-based active materials are generally used as electrode materials due to their high surface area and conductivity, its energy storage is generated by the rapid electrostatic charge accumulation at electrode/electrolyte interfaces, possessing the advantages of high power density and long cycle life, but relatively low specific capacitance due to the limited available electrochemically surface area [6,7]. While for pseudocapacitors, the charge storage mainly occurs through the faradic charge transfer reactions or reversible redox of the transition metal oxides or conducting polymers on the surface of the electrode [8]. The specific capacitance is generally high but the disadvantages of slow response and poor stability during the charge–discharge cycling limit its development in practical applications [4,9]. Accordingly, in order to overcome the disadvantages of a single phase material and integrate the benefits of EDLCs materials and pseudo-supercapacitors materials, researchers are devoting to preparing the composites, which are composed of conductive substrates and pseudocapacitive materials, to obtain the rapid charging–discharging rate, high overall capacitances and long cycling life [10,11].

Among the pseudocapacitive materials, polyaniline (PANI) has been considered as one of the most promising candidate materials due to its excellent environmental and chemistry stability, extraordinarily fast redox rate, remarkable electric conductibility, high theoretical specific pseudocapacitance, low cost and facile synthesis [8,12,13]. However, during the doping/dedoping processes, the swelling/shrinkage of PANI result in volume changes and damages the backbone of polymer, which seriously weakens the cycle stability of PANI and consequently hinders its application in supercapacitor [8]. In order to improve the cycle stability and maximize the specific capacitance value of PANI, many studies have concentrated on the fabrications of composites that combine PANI with carbon materials (e.g., carbon nanotubes [14], graphene [12,15]) or metallic oxides (e.g., $SnO_2$ [16], $MnO_2$ [17], $TiO_2$ [18,19]). Compared with other composites, PANI/graphene composites have attracted considerable attention due to the outstanding performances of graphene. Graphene, a single layer of two-dimensional

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carbon atoms, emerges as an excellent electrode material owing to its extraordinary electrical conductivity, high specific surface area, remarkable mechanical stiffness and good chemistry stability [20–22]. Hence, PANI/graphene composites have been widely researched as promising active electrode materials for supercapacitor because of its high specific surface area, excellent electric conductivity and two kinds of energy storage mechanisms. It is generally believed that the approach where the PANI combines with graphene can greatly affect the capacitance value of composite [12]. Various types of PANI nanostructures have been designed and synthesized by different methods, such as nanospheres [12], nanowires [23,24], nanofibers [25,26], nanorods [8,27], nanoparticles [28], etc. The electrochemical performance of those PANI/graphene composites is significantly enhanced relative to single nanomaterials owing to their high surface area and low electrolyte transport resistance. However, until now, the studies about hollow structured PANI/graphene composite are still limited.

In energy-related fields, hollow micro-/nano-structured materials are one kind of attractive candidate materials for practical applications [29]. Compared with other type nanostructures, the special hollow structure of PANI provides prominent advantages for supercapacitor applications owning to its enhanced specific surface area and reduced transport lengths for both mass and charge transport [30,31]. In this work, we fabricate reduced graphene oxide/polyaniline hollow spheres (RGO/PANI-HS) composite with a novel three-dimensional (3D) nanostructure, in which the PANI-HS were inserted between the RGO layers forming a unique sandwich structure. The results of electrochemical measurements indicate that the RGO/PANI-HS composite can deliver a high specific capacitance of 529 F $g^{-1}$ at 0.5 A $g^{-1}$ and maintain 85% of its initial capacitance even after 1000 cycles. The RGO/PANI-HS composite possesses excellent electrochemical performance as well as its relatively easy preparation method, which indicates that this composite could be promising electrode materials for high-performance supercapacitor applications.

## 2. Experimental

### 2.1. Materials

Graphite powder (chemically pure) was supplied by Sinopharm Chemical Reagent Co., Ltd. (SCRC). Aniline, ammonium peroxydisulfate (APS), hydrofluoric acid (HF), hydrochloric acid (HCl), tetraethoxysilane, ammonia solution (25–28%), and ethanol were all purchased from Chuandong Chemical Reagent Company (Chengdu, China). γ-Aminopropyltriethoxysilane (APTES) was obtained from Yanxin Chemical Reagent Co., Ltd. (Shanghai, China). Distilled water was produced by Water Purification System.

### 2.2. Fabrication of graphene oxide (GO) and reduced graphene oxide (RGO)

GO was synthesized using natural graphite powder by a modified Hummers method [32]. RGO was prepared by the reduction of GO with hydrazine as described elsewhere [33].

### 2.3. Fabrication of silica microspheres ($SiO_2$) and modified with APTES

Solid silica spheres ~430 nm in diameter were prepared using a sol–gel procedure originally described by Stober et al. [34]. Then the as-prepared $SiO_2$ spheres were modified with APTES, and specific steps are as follows: 0.8 g $SiO_2$ spheres were dispersed in 25 mL of toluene containing 0.4 g APTES under the aid of ultrasonic, then the mixed solution was refluxed for 6 h at 105 °C. For purification, the product was washed with toluene and ethanol three times, respectively, and then dried at 40 °C for 12 h.

### 2.4. Fabrication of PANI-HS

0.1 g of modified $SiO_2$ was dispersed in 80 mL 1 M HCl solution containing 0.2 mL aniline through ultrasonic treatment for half an hour and stirred for another 6 h. 0.4902 g ammonium peroxydisulfate dispersed in 40 mL of 1 M HCl aqueous solution was added dropwise to the mixture solution, and the reaction was allowed to proceed for 12 h under ice bath condition. For purification, the product was washed with 1 M HCl and ethanol three times, respectively. After that, the PANI-coated $SiO_2$ particles were treated with 2 M HF + 8 M $NH_4F$ solution at room temperature for 30 min to produce PANI-HS, washed with deionized water three times, and then dried at 40 °C for 12 h.

### 2.5. Fabrication of RGO/PANI-HS composite

RGO/PANI-HS composite was obtained as follows: 40 mg $SiO_2$@PANI powders were added into 140 mL deionized water and re-dispersed by ultrasound for 0.5 h. Next, 40 mL GO solution (0.5 mg $mL^{-1}$) was added dropwise to the above solution with the aid of ultrasonication (within 0.5 h), and the resulting mixture solution was dispersed evenly by ultrasound for another 0.5 h. Subsequently, 0.83 mL ammonia solution and 20 μL hydrazine solution ($N_2H_4$, 80 wt% in water) was added, and the mixture solution was heated at 98 °C for 1 h. The above production was dispersed in 2 M HF + 8 M $NH_4F$ solution at room temperature for 30 min, washed with deionized water three times, and then dried at 40 °C for 12 h.

### 2.6. Material characterizations

The zeta potential of $SiO_2$@PANI and of GO was measured using the Zetasizer Nano (ZEN3690) to determine the effect of surface charge on $SiO_2$@PANI and GO dispersions. The morphologies of materials were examined by field-emission scanning electron microscope (FE-SEM, JEOLJSM-6335F), transmission electron microscopy (TEM, JEM 1200EX) and atomic force microscopy (AFM, Asylum Research MFP-3D). Fourier transform infrared spectra (FTIR) of the materials were obtained by using FTIR spectrophotometer (NICOLET-5700) in the range from 4000 to 500 $cm^{-1}$ with the KBr pellet method. X-ray diffraction (XRD) patterns were confirmed by PANalytical Empyrean diffractometer with Cu (Ka) radiation at 40 kV and 30 mA. Raman spectra were recorded with LabRAM HR evolution Raman spectrometer.

### 2.7. Electrochemical characterization

The supercapacitor electrodes were prepared by coating the homogeneous slurry containing 80 wt.% active materials, 10 wt.% acetylene black and 10 wt.% polytetrafluoroethylene in the presence of *N*-methylpyrrolidone onto the surface of carbon paper. The mass of the active material loaded on the carbon paper (1.0 $cm^2$) is approximately 1.6 mg. Then, the as-prepared electrodes were dried at 40 °C for 12 h before use. All electrochemical measurements were carried out by introducing a three-electrode test system using the as prepared electrode as the working electrode, the platinum sheet as counter electrode, and the saturated calomel electrode (SCE) as reference electrode immersed in 1.0 M $H_2SO_4$ solution. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured by electrochemical workstation (CHI 604). The scan rate of CV between −0.2 and 1.0 V (vs. SCE) was tested in the range from 10 to 100 mV $s^{-1}$. The frequency range for EIS was 100 kHz–0.01 Hz at open circuit potential with an AC perturbation voltage of 5 mV. Galvanostatic charge/discharge (GCD) tests were measured in a voltage range from 0 to 0.8 V using Autolab 72092.