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Facile synthesis of 3D reduced graphene oxide and its polyaniline composite for super capacitor application

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ABSTRACT

We propose a facile and environmentally-friendly strategy for fabricating three-dimensional (3D) reduced graphene oxide (3D-rGO) porous structure with one step hydrothermal method using glucose as the reducing agent and $CaCO_3$ as the template. The reducing process was accompanied by the self-assembly of two-dimensional graphene sheets into a 3D hydrogel which entrapped $CaCO_3$ particle into the graphene network. After the removal of $CaCO_3$ particle, 3D-rGO with interconnected porous structure was obtained. The 3D-rGO was further composted with PANI nanowire. The structure and the property of 3D-rGO and 3D-rGO/PANI composite have been characterized by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, transmission electron microscopy, cyclic voltammetry, galvanostatic charge–discharge test and electrochemical impedance spectroscopy. Electrochemical test reveals that the 3D-rGO/PANI has high capacitance performance of 243 $F g^{-1}$ at current charge–discharge current density of 1 $A g^{-1}$ and an excellent capacity retention rate of 86% after 1000 cycles.

1. Introduction

With a fast-growing market for portable electronic devices and development of hybrid vehicles, there has been an increasing demand for high efficient, low cost and environmentally benign energy storage devices. Among various energy storage, super capacitors have attracted great attention because of their high power density, fast charge–discharge process and long cycling life [1–5]. In principle, super capacitor can be divided in two categories based upon the charge–storage mechanism: the electrical double-layer capacitors (EDLCs), where capacitance arises from the pure electrostatic accumulated at the electrode–electrolyte interface, such as carbon materials; and the pseudocapacitance, in which fast and reversible oxidation/reduction or faradaic charge reaction of the electroactive species take place on the surface of the electrode, such as metal oxides and conductive polymer [6].

Recently, graphene, a one-atom-thick 2D single layered carbon material, has attracted great interest for EDLC application due to its many advantages, such as extraordinarily high thermal and electrical conductivity, superior mechanical strength, and high theoretical specific areas (over 2600 $m^2 g^{-1}$) [7]. As an essential characteristic of an electrode material, the very large electrochemically active surface area of graphene is the most notable feature, which determines the capacitance. However, because of the aggregation of graphene sheets due to the strong π–π interaction, the large surface area cannot be fully utilized. A key issue is how to avoid the aggregation of graphene sheets during the electrode preparation [8–11]. Thus, 3D graphene materials have been developed to resolve the restacking problem of graphene sheets and a high rate of performance in super capacitors was obtained. For example, using a CVD and template method, Cheng et al. prepared graphene networks [12], Shi and co-workers synthesized graphene hydrogel by a hydrothermal method [13] and Wei and co-workers prepared 3D graphene film through a templating way [14]. However, these methods are either complicated or need to use strong reducing agents such as hydrazine, which is not good for low-cost, mass production and environmentally friendly.

One the other hand, PANI has been considered as an important and highly promising electrode material for energy storage application. It possesses the largest theoretical pseudocapacitance (~2000 $F g^{-1}$) among all of the conducting polymers owing to its

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multiple redox states [15]. It can be cheaply and easily fabricated into various nanostructures. However, its poor cycling stability and conductivity severely hamper its potential application [16]. Composite of PANI with graphene are promising because graphene is an excellent to host active polymer. Graphene can sever as a stable and underlying conductive network, where good electrical conductivity and improved cycling stability can be achieved. PANI can promote the electrochemical capacitance of graphene, and it also can sever as an intercalated spacer to further improve the specific area of graphene. Thus, great improvement in their properties and performances can be achieved due to the synergistic effect between two components [17–19].

Here, we describe the design and preparation of 3D reduced graphene oxide (3D-rGO) porous material with facial hydrothermal method using graphene oxide (GO) as a 3D-rGO precursor, glucose as the reducing agent and $CaCO_3$ as the template. The reducing ability of glucose can be greatly enhanced to reduced graphene oxide under hydrothermal condition [20], which makes this process green. The reduced graphene sheets assemble into 3D hydrogel, and wrap $CaCO_3$ particles in graphene network under hydrothermal condition. The $CaCO_3$ particle can be removed easily by dilute acidic solution to generate 3D-rGO with interconnected porous structure. This kind of interconnected 3D porous network will facilitate the access of electrolyte ions into the internal surface of graphene sheets for a higher charge–discharge rate. It will also composite with other functional materials easily. 3D-rGO/PANI nanowire composite is prepared by in situ dilute polymerization to combine the advantage of both materials, which exhibits high capacitance while keeping the excellent rate performance and cycling stability.

2. Experimental

2.1. Materials

Graphite powder (40–400 nm) was obtained from Qingdao Henglide Graphite Co., Ltd. Concentrated H_2SO_4 (98%), HCl (36%), $HClO_4$, glucose, $KMnO_4$ and H_2O_2 (30%) solution were purchased from Sinopharm Chemical Reagent Co., Ltd. Na_2CO_3 and $CaCl_2$ was purchased from TCI Co., Ltd. All of the reagents were used as received without further purification.

2.2. Synthesis

2.2.1. Preparation of graphene oxide (GO)

GO was prepared from natural flaked graphite according to a modified pressurized oxidation [21]. 2.0 g of graphite was added into 60 ml H_2SO_4 (98%) in an ice bath followed by slowly adding 7 g K_2MnO_4 with vigorous stirring. The resulting solution was poured into a teflon-lined autoclave, which was kept at −2 to 2 °C for 1 h and then 150 °C for another 1 h. The obtained mixture was diluted with 1 L deionizer water, followed by adding 30% H_2O_2 (25 mL) to change the color of the mixture to bright yellow. Then, 600 mL of 5% HCl solution was added, and the mixture was left undisturbed for 2 days or longer. The precipitate was centrifuged and then washed successively with 1 M HCl solution and deionized water. Finally, GO was obtained by lyophilizing at −48 °C, 18 Pa.

2.2.2. Preparation of three-dimensional reduced graphene oxide (3D-rGO)

The mixture of $NaCO_3$ (530 mg) and ethanol (5 mL) was slowly dropped into 10 mL solution of $CaCl_2$ (550 mg) with stirring to form part A. On the other hand, 10 mL homogeneous GO aqueous dispersion with 120 mg of GO was prepared by sonication and vigorous stirring. Then, 100 mg of glucose and 1 mL of ammonium hydroxide were added into the above mentioned GO solution to get part B. Subsequently, the mixture of parts A and B was poured into a teflon-lined autoclave and heated at 120 °C for 12 h to form GO–$CaCO_3$ hydrogel. The resulting hydrogel was dried by lyophilizing at −48 °C, 18 Pa. Then, the dried hydrogel was placed into 50 mL of 1 M HCl solution, followed by filtering, washing and lyophilizing at −48 °C, 18 Pa to obtain the freestanding three-dimensional reduced graphene oxide (3D-rGO). For comparison, rGO powder was also prepared through the above-mentioned chemical process without adding of part A.

2.2.3. Preparation of 3D reduced graphene oxide/polyaniline composite (3D-rGO/PANI)

3D-rGO/PANI composite was synthesized using in situ dilute polymerization [22] in the presence of 3D-rGO. 0.93 g aniline monomer was slowly dropped into 100 mL of 1 M $HClO_4$ aqueous solution in an ice bath with vigorous stirring. Then, 3D-rGO was added, and the monomer solution was stirred for 30 min. A pre-cooled oxidant solution with 0.114 g ammonium persulfate (APS) oxidant and 50 mL of 1 M $HClO_4$ aqueous solution was added to the monomer solution. The polymerization proceeded for 12 h in an ice bath with stirring. Finally, 3D-rGO/PANI was filtrated, washed with distilled water and ethanol, and dried by lyophilizing at −48 °C, 18 Pa.

2.3. Characterizations

X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI 5000 VersaProbe analyzer (UlVAC-PHI Ltd., Japan). Fourier transform infrared spectrometer (FTIR) of the samples were recorded with an IRPrestige-21 FT-IR spectrometer. X-ray diffraction (XRD) was performed with an X'Pert Pro (PANalytical) diffractometer using monochromatic Cu Kα1 radiation (λ = 1.5406 Å) at 40 kV. The morphology of as-prepared samples was characterized by a scanning electron microscope (SEM, Hitachi S-4800 field emission) and transmission electron microscope (TEM, JEOL-JEM-2100F operating at 100 kV).

2.4. Evaluation of the electrochemical properties

The capacity properties and electrochemical impedance spectra (EIS) of the as-prepared samples were characterized with a CHI 660A electrochemical workstation (Chenhua, Shanghai). Cyclic voltammetry (CV), galvanostatic charge–discharge, electrochemical impedance spectroscopy and cycling stability were carried out in a conventional three-electrode cell and the working electrode was prepared by dropping the sample onto a glassy electrode. A platinum sheet was used as the counter electrode and an AgCl/Ag electrode was used as the reference electrode. A solution containing 1.0 M H_2SO_4 served as the electrolyte at room temperature. The potential window of cyclic voltammograms curves ranged from 0 to 1.0 V at various scan rates and that of galvanostatic charge–discharge testing (GV) were recorded between 0 and 0.8 V at different current densities.

3. Results and discussion

3.1. Preparation and characterization of samples

The procedures for the preparing of 3D-rGO and 3D-rGO/PANI composite are illustrated in Scheme 1. The GO dispersion which contains glucose as well as $CaCO_3$ particles was put into an autoclave and heated. At first, the starting material GO sheets were randomly dispersed in water, due to their strong hydrophilicity and electrostatic repulsion effect. Under the hydrothermal condition, the GO sheets were reduced by glucose, and became regionally hydrophobic due to diminish of oxygenated functional groups. The