



Polyfurfuryl alcohol spheres template synthesis of 3D porous graphene for high-performance supercapacitor application



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ABSTRACT

In this work, a 3D porous graphene (3DrGO) was prepared by a hydrothermal assembly process of graphene oxide (GO) using polyfurfuryl alcohol (PFA) spheres as the template followed by thermal reduction. The introduction of PFA spheres can effectively enlarge the interspace between graphene sheets and suppresses their re-stacking in the thermal treatment. The 3DrGO was further composited with PANI nanowire. The structure and the property of 3DrGO and 3DrGO/PANI composite have been characterized by transmission electron microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, cyclic voltammetry, galvanostatic charge–discharge test and electrochemical impedance spectroscopy. Electrochemical test reveals that the 3DrGO has good capacitance performance of 104 F/g at current charge–discharge current density of 1 A/g and the capacitance performance increase to 530 F/g after further composited with PANI nanowire. Both 3DrGO and 3DrGO/PANI show excellent capacity retention rates of 95% and 88%, respectively, after 1000 cycles. All these impressive results demonstrate that the material obtained by this approach is greatly promising for application in high-performance supercapacitors.

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1. Introduction

Supercapacitors with high power density, excellent charging/discharging rate capability, and long life-cycles have become one of the most intensive research focuses in the electrical energy storage field [1–5]. In principle, supercapacitor 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 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 [6]. The most widely used materials for EDLCs are carbon-based materials, which usually have high power density but suffer from

low capacitance [7–9]. In contrast, pseudocapacitors, employing metal oxides or conducting polymers, could provide high specific capacitance but suffer from high cost and poor cycling stability arising from their low conductivity [10,11]. The development of new materials with higher specific capacitance and better cyclic life for supercapacitor electrodes is expected from the integration of conducting polymers or metal oxides and carbon materials [12–15].

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 a large theoretical specific surface area [16]. 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. Although the theoretical specific surface area of a single graphene sheet is as high as 2630 m²/g, experimentally accessible surface areas of graphene materials are far below this value because of the strong self-aggregation/stacking tendency of

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graphene sheets. Thus, numerous novel approaches have been developed to resolve the restacking problem of graphene sheets [17–20].

Recently, three-dimensional (3D) graphene aerogel with continuously interconnected porous network has been fabricated by the simple self-assembly of graphene oxide sheets under hydrothermal condition [21]. Solid nanostructure particles, such as CaCO_3 [22], metal oxides nanoparticles [23] and silica spheres [24] can also be involved into this procedure as hard-templates to synthesize 3D porous graphene with different pore sizes and morphologies. These three-dimensional (3D) porous graphene materials can better meet the need for high-performance electrodes, because they not only possess the intrinsic properties of two-dimensional graphene sheets, but also the porous structures which can greatly improve the accessibility of the electrolyte to the surface of the electrode and effectively promote charge transport. In addition, many efforts have been centered on the combination of graphene with conducting polymers for supercapacitor applications. Conducting polymer, such as polyaniline (PANI), has been considered as a highly promising electrode material since it possesses the largest theoretical pseudocapacitance ($\sim 2000 \text{ F/g}$) among all of the conducting polymers owing to its multiple redox states [25]. It is cheap and can be easily fabricated into various nanostructures. However, its poor cycling stability severely hamper its potential application [26]. Composite of PANI with graphene are promising because graphene can serve as a stable and underlying conductive network, where good electrical conductivity and improved cycling stability can be achieved. Meanwhile, PANI can promote the electrochemical capacitance of graphene, and serve 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 [27–30].

Here we describe the design and preparation of 3D reduced graphene oxide (3DrGO) porous material with facial hydrothermal method using graphene oxide (GO) as a precursor, and polyfurfuryl alcohol (PFA) spheres as the template. The GO sheets assemble into 3D hydrogel, and wrap PFA spheres in graphene network under hydrothermal condition. Subsequently, the reduction of graphene oxide (GO) to reduced graphene oxide (rGO) was fulfilled by thermal treatment under an N_2 flow. PFA spheres, which will pyrolysis into carbon, can help 3DrGO to maintain its interconnected porous structure through this thermal process. Our approach is simple and environmentally friendly compared with above mentioned template routes, because it requires no additional template etching process or the use of hazardous reductant. 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 be also composite with other functional materials easily. 3DrGO/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 μm) was purchased from Baichuan Graphite Ltd. (Qingdao, China). Concentrated H_2SO_4 (98%), fuming nitric acid, HCl (36%), KMnO_4 , P_2O_5 , H_2O_2 (30%) solution, and $\text{K}_2\text{S}_2\text{O}_8$, were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Furfuryl alcohol was purchased from Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Polyvinylpyrrolidone (PVP) was purchased from Shanghai Medical

Technology Co., Ltd. Unless otherwise specified, all reagents were used without further purification.

2.2. Synthesis

2.2.1. Preparation of graphene oxide (GO)

The GO aqueous dispersion was fabricated on the basis of method developed by Gao [31]. There are three steps in this process: first of all, 5 g natural graphite flakes (5 g), 150 mL 98% sulfuric acid and 50 mL fuming nitric acid were mixed and stirred at room temperature for 24 h. Then mixture was diluted and filtrated to get the graphite intercalated compounds. After washing, the graphite intercalated compounds were expanded at 1000 W by microwave irradiation for 90 s to get worm-like expanded graphite. Secondly, 5 g expanded graphite, 300 mL sulfuric acid, 4.2 g $\text{K}_2\text{S}_2\text{O}_8$ and 6.2 g P_2O_5 were added successively into a 500 mL flask and the mixture was kept at 80°C for 5 h. After cooling down, the pre-oxidized expanded graphite was obtained by filtered the diluted mixture, washed and dried at room temperature for 2 days. Finally, the pre-oxidized expanded graphite was added into 200 mL concentrated H_2SO_4 at 0°C , and then 15 g KMnO_4 was added slowly under continuous stirring. The mixture was heated to 35°C for 2 h, then added slowly into 2 L water. After cooling down, 10 mL H_2O_2 (30%) was added. The mixture was left undisturbed for 2 days and the nearly clear supernatant was decanted. The precipitate was centrifuged, and repeatedly washed with water, 1 M HCl solution and water successively. Finally, GO was obtained by lyophilizing at -48°C , 18 Pa.

2.2.2. Preparation of polyfurfuryl alcohol (PFA) spheres

PFA spheres were fabricated under the hydrothermal condition by using PVP as the template [32]. Briefly, 1 mL furfuryl alcohol was added into a mixture of 40 mL water and 1 g PVP drop by drop with stir to get a clear solution. Then the solution was transferred into a Teflon-lined autoclave and heated at 160°C for 12 h. The obtained PFA spheres were centrifuged, washed with water and ethanol, and dried at 60°C .

2.2.3. Preparation of three-dimensional reduced graphene oxide (3DrGO)

62.5 mg PFA spheres were dispersed in 15 mL H_2O by sonication form part A. Meanwhile, part B, 25 mL homogeneous GO aqueous dispersion with 250 mg of GO, was prepared by sonication and vigorous stirring. Subsequently, the mixture of part A and part B was poured into a Teflon-lined autoclave and heated at 160°C for 12 h to form 3D-GO/PFA hydrogel. The resulting hydrogel was dried by lyophilizing at -48°C , 18 Pa. Then the dried hydrogel was placed in a horizontal tube furnace, heated to 800°C at a heating rate of $5^\circ\text{C}/\text{min}$ and kept for 2 h under N_2 atmosphere to obtain the freestanding three-dimensional reduced graphene oxide (3DrGO). For comparison, rGO powder was also prepared through the above-mentioned process without adding of part A.

2.2.4. Preparation of 3D reduced graphene oxide/Polyaniline composite (3DrGO/PANI)

3DrGO/PANI composite was synthesized using in situ dilute polymerization in the presence of 3DrGO. 300 mg aniline monomer was slowly dropped into a mixture of 30 mL of 1 M H_2SO_4 aqueous solution and 30 mg 3DrGO with vigorous stirring. Then an oxidant solution 10 mL with 180 mg Ammonium persulfate (APS) oxidant was added to the monomer solution. The mixture was poured into a Teflon-lined autoclave and heated at 140°C for 12 h. The obtained 3DrGO/PANI was filtrated, washed with distilled water and ethanol, and dried by lyophilizing at -48°C , 18 Pa.

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