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Three-dimensional paper-like graphene framework with highly orientated laminar structure as binder-free supercapacitor electrode

Yidan Gao[a,b], Yaoyao Zhang[a,c], Yong Zhang[a], Lijing Xie[a], Xiaoming Li[a], Fangyuan Su[a], Xianxian Wei[a,d], Zhiwei Xu[c,*], Chengmeng Chen[a,*], Rong Cai[a,e]

[a] *Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, Shanxi, China*
[b] *University of Chinese Academy of sciences, Beijing 100049, China*
[c] *State Key Laboratory of Separation Membranes and Membrane Processes, School of Textiles, Tianjin Polytechnic University, Tianjin 300387, China*
[d] *Taiyuan University of Science and Technology, Taiyuan 030024, Shanxi, China*
[e] *Academy of Opto-Electronics, Chinese Academy of Sciences, Beijing 100094, China*

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ABSTRACT

A free-standing paper-like three-dimensional graphene framework (3DGF) with orientated laminar structure and interconnected macropores, was obtained by the hard template-directed ordered assembly. As the sacrificial templates, polystyrene (PS) latex spheres were assembled with graphene oxide (GO) to build up a sandwich type composite film, followed by heat removal of which with a simultaneous reduction of GO. The 3DGF exhibited high specific surface area of 402.5 m^2/g, controllable pores and mechanical flexibility, which was employed as the binder-free supercapacitor electrode and shows high specific gravimetric capacitance of 95 F/g at 0.5 A/g, with enhanced rate capability in 3 electrode KOH system.

1. Introduction

Supercapacitors are attracting increasing attention from industry due to their potential in load cranes, forklifts, electric vehicles, consumer electronics and mobile electrical systems [1–3]. Comparing with batteries, supercapacitors show irreplaceable properties such as high power density, fast charging/discharging rate, long cycle life (>100,000 cycles) and high reliability [1,4–8]. Recently, graphene has been highly concerned for application in electrochemical energy storage, due to its large theoretical surface area (2630 m^2/g), good electronic conductivity, and high electrochemical stability [9–11]. However, the graphene nanosheets tend to re-stack into irreversible agglomerates due to their strong interlayer van der Waals forces [12–14]. Obviously, this π–π stacking of graphene will decrease the accessibility of surface to the electrolyte so as to affect the performance of the electrode [7,13–15]. In a typical process when preparing an electrode of powder form graphene, the insulating polymer binder is usually involved. The binder will increase the electronic resistance and wrap the surface of the electrode material, so as to impede the electron transportation and ion diffusion, as well as complicate the fabrication of the device [1,2,16]. To address these challenges, the binder-free electrodes should be developed to utilize the ultimate property of graphene for high performance supercapacitors.

In the past few years, self-supported three-dimensional (3D) architectures with continuously interconnected macropores (such as aerogels [17–19], foams [20] and sponges [21], and hierarchical porous hybrid paper [22–25]) have been demonstrated to be effective in preventing graphene from aggregating [26]. The energy storage performance of the materials is significantly improved, which is attributed to the large surface area, high accessibility to reaction sites, facilitated ion transport, increased mechanical integrity, and/or synergistic effects among multicomponents [27–31]. These macroscopic materials are randomly assembled with graphene as the basic building blocks in a sol-gel or hydrothermal process. Without the assistance of templates, pores in the materials are randomly distributed and uncontrollable. Besides, the absent of external orientation during assembly will result in isotropic inter-connection of graphene to affect the macroscopic performance of the resulting material. Therefore, to assemble the graphene sheets in a precisely controllable manner for smarter energy storage still remain a challenge.

Recently, the template-directed method using polymer microspheres as sacrificial templates has been developed for fabricating a pore-structure and porosity controlled 3D macroporous graphene architecture. In previous works, Choi et al. [32,33] have fabricated the 3D hierarchical metal oxide/chemical modified graphene hybridized films using PS spheres (2 μm) as structural guiding templates.

* Corresponding author. Tel./fax:+ 86 22 83955231
E-mail addresses: xuzhiwei@tjpu.edu.cn (Z. Xu), ccm@sxicc.ac.cn (C. Chen).

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During the process, the hydrazine is employed to reduce graphene oxide followed by removal of template by toluene. The method involved is considered to be toxic and complex. In our previous report, polymethyl methacrylate latex spheres was used, followed by one step thermal reduction and template removal, to obtain a self-standing macroporous graphene film for binder-free electrode. However, the surface area of the resulting material is only 128.2 m^2/g, which is due to the overlarge diameter (as high as 500 nm) of the templates [34]. Afterwards, Wang et al. [35] used PS microspheres templates (Φ280 nm) to prepare the macroporous graphene structure by a similar approach. However, the resulting material is still in powder form, and thus polymer binders are inevitable during the subsequent electrode preparation.

In this contribution, a free-standing paper-like 3DGF with higher surface area, smaller pore size and highly orientated laminar structure was fabricated by a facile template method with PS microspheres as the sacrificial templates followed by thermal annealing. After systematical characterization, the material was evaluated as binder-free supercapacitor electrode which shows enhanced energy and power density. Besides, the electrochemical performance was further correlated to the microstructure of 3DGF.

2. Experimental

2.1. Synthesis of polystyrene nanospheres

Polystyrene nanospheres with the size of 150 nm were synthesized by emulsifier-free emulsion polymerization in a 250 mL three-necked round bottom flask. In a typical process, the sodium dodecylbenzene sulfonate (0.07 g) and potassium persulfate (0.09 g) were firstly dissolved in 80 mL and 20 mL deionized water, respectively. Then, the solution and styrene monomer (5 mL) were poured into the three neck flask in Ar atmosphere. After about 30–40 min, the obtained mixture was stirred at approximately 350 rpm and heated to 70 °C. After reaction for 8 h, the desired polystyrene nanospheres were obtained by centrifugation and washing with deionized water and ethanol several times. The resultant polystyrene nanospheres were re-dispersed in deionized water to obtain an aqueous suspension (30 mg/mL) for further application.

2.2. Fabrication of the binder-free 3DGF

Graphite oxide was prepared by a modified Hummers' method, followed by ultrasonication (100 W, 30 min) in deionized water to get the graphene oxide hydrosol (3 mg/mL). The graphene oxide hydrosol (10 mL) was mixed with polystyrene nanospheres suspension (3.5 mL) and sonicated for 15 min to get a homogeneous colloidal suspension, which was then filtrated on a vacuum millipore filter to realize the sandwich type assembly of polystyrene nanospheres and graphene oxide sheets. The above composite film was peeled off from the filter and air dried at 50 °C overnight, and the weight ratio of GO and PS in the film was 1:3.5. The composite films were annealed to 800 °C (heating rate 10 °C/min) for 0.5 h under Ar atmosphere in a tubular furnace. GO within the composite film was thermally reduced into graphene, while the polystyrene nanospheres templates were removed simultaneously, so as to get the 3DGF. At the same time, the control sample was prepared by a similar procedure but with no polystyrene nanospheres template, resulting in the compact graphene film (GF800).

2.3. Characterization

The morphologies and microstructure of the samples were examined by field emission scanning electron microscopy (FESEM, JEOL JSM-7001F, Japan), transmission electron microscope (TEM, JEM-2010, Japan), X-ray diffraction measurements (XRD, Rigaku, D/Max-2400, Japan) and nitrogen adsorption and desorption experiments (BELSORP-max, Japan). The specific surface area was obtained using Brunauer Emmett Teller (BET) method and the pore size distribution was calculated from the adsorption branch of the nitrogen isotherm using the Barrett Joyner Halenda (BJH) model. Thermogravimetric analysis (TGA, STA 409PC, NETZSCH, Germany) was carried out under Ar purge at a heating rate of 10 °C/min from room temperature to 1000 °C. The reduction of GO was confirmed using an Elementar (vario Macro cube, Germany).

2.4. Electrochemical measurements

The electrochemical properties of 3DGF and GF800 were measured in a 6 M KOH solution as electrolyte. All electrochemical measurements were carried out on a CHI760D electrochemical working station (CH Instrument). The prepared 3DGF was utilized as working electrodes without adding polymeric binders or conducting additives. Hg/HgO electrode and platinum plate were used as the reference electrode and counter electrode, respectively. The specific capacitance was calculated from the results of galvanostatic charge–discharge tests using equations:

$$C_{sp,galvanostatic} = \frac{i\Delta t}{m\Delta E} \quad (1)$$

where C is the specific capacitance (F/g), i is the discharge or charge current, Δt is the time discharge time, m is the mass of a part of electrode, and ΔE is the potential window (–0.9–0 V).

3. Results and discussion

The Schematic illustration for the fabrication of 3DGF is shown in Fig. 1. PS microspheres and GO nanosheets were assembled owing to

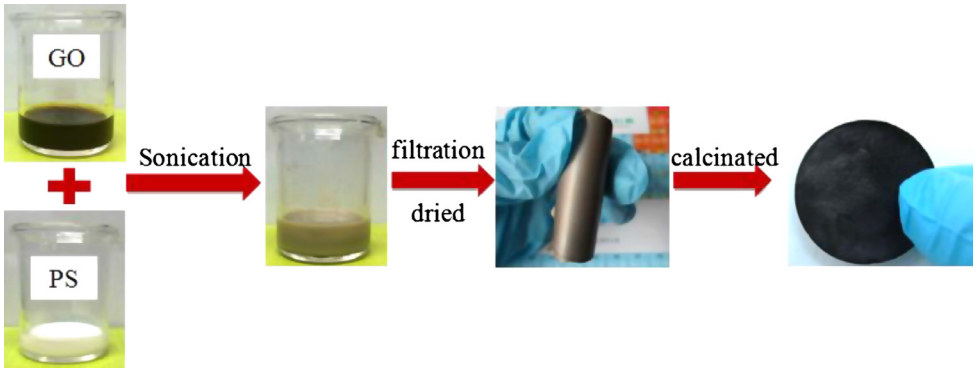

Fig. 1. Schematic illustration for the fabrication of 3DGF.