



Alcohol-dependent environments for fabricating graphene aerogels toward supercapacitors



Tingting Liu^a, Wei-Li Song^b, Li-Zhen Fan^{b,*}

^aSchool of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China

^bInstitute of Advanced Materials and Technology, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Article history:

Received 7 March 2015

Received in revised form 15 April 2015

Accepted 8 May 2015

Available online 11 May 2015

Keywords:

Graphene aerogel
alcohol
supercapacitors
hydrothermal reaction

ABSTRACT

Highly porous graphene aerogels with excellent flexibility were fabricated via simultaneous reduction and assembly of graphene oxides in various alcohols. Ethanol, isopropanol, and ethylene glycol of different steric environments for the alcohol groups were found to dominantly determine the porous structures, surface areas and chemical compositions. The observed different reduction degrees of the alcohols lead to different charge transfer ability and electrochemical capacitance. On the basis of physical and electrochemical properties, the mechanisms associated with the alcohol species have been discussed. Furthermore, the resultant supercapacitors assembled by the graphene aerogels exhibited effective specific capacitance up to 287 F g^{-1} (at current density of 0.1 A g^{-1}) with excellent cycle stability (>91% capacitance retention upon 8000 cycles). Combination of the alcohol-dependent energy storage performance and related mechanisms promises great potential for engineering and fabricating advanced graphene-based porous nanostructures of broad applications.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The increasing popularity of portable electronic devices and automobiles has stimulated great interests in the development of advanced energy storage and management devices. Supercapacitors have attracted growing attention owing to their ultrahigh power density, fast charging and long-life cycle [1]. Carbon-based materials of porous structures have been mostly considered as the ideal electrodes for electrical double layer capacitors. Amongst the carbonaceous materials, porous carbon materials with high specific surface area, such as activated carbon, carbon nanotubes and template porous carbon, have been widely used as the electrodes in supercapacitors because of their physicochemical stability, excellent electrical conductivity and long-term cycle [2,3].

With unique two-dimensional structure and outstanding electrochemical properties, graphene nanosheets have promised potential applications for energy storage [4,5]. Recently, for the unique porous 3D frameworks, graphene-based foams, hydrogels and aerogels have attracted increasing interests in the community since they possess ultrahigh specific surface area, moderate nano-

micro porous structure, high conductivity and multiple electronic transport pathways [6–14]. As a result, a variety of studies have been reported for preparing such porous 3D graphene aerogels and related structures, which indicates high specific capacitance and excellent cycling stability [6–9]. For a typical example, Duan and coworkers have fabricated flexible supercapacitors assembled by reduced graphene oxide (RGO) hydrogels, demonstrating enhanced specific capacitance up to 186 F g^{-1} with area specific capacitance of 372 F cm^{-2} (current density of 1 A g^{-1}) in a two-electrode system [9]. On this stage, further improvements including establishment of secondary holy channels in the continuous 3D RGO hydrogels for enhancing the ionic transport channels have been reported, exhibiting a specific capacitance up to 320 F g^{-1} along with 95% capacitance retention upon 10000 cycles in a two-electrode system [15].

Up to date, various explorative studies have been made in the design and generation of 3D graphene aerogels and related nanostructures via different strategies coupled with chemical or physical cross-linkers, such as organic binders [8,16], linkages [17,18] and ligands [19]. For instance, Pham et al. have fabricated RGO xerogels using iodine and toxic hypophosphorous acid, and the xerogels exhibited surface area up to $157.59 \text{ m}^2 \text{ g}^{-1}$ [22]. Moreover, the utilization of the other toxic reducing agents, such as hydrazine, NaBH_4 , LiAlH_4 , HI and etc., also suggest that the corresponding approaches are environmentally harmful and expensive. Meanwhile, unexpected impurities and elements may

* Corresponding author. Tel.: +86-13813084895; fax: +86-10-62334311.

E-mail addresses: liutingting@mail.njust.edu.cn (T. Liu), fanlizhen@ustb.edu.cn (L.-Z. Fan).

be introduced in the resulting RGO structures, which requires further complicated treatments in the purification [7,8,20–22].

In the present work, we select a green approach to fabricate graphene aerogels via self-assembly of GO sheets in the alcohol environments, where the by-products of the reaction are mostly water and, more importantly, both the by-products and residual alcohols could be easily removed. With the use of ethanol (EtOH), isopropanol (IPA), and ethylene glycol (EG) as reducing agents separately, the effects of the alcohols on the structures, surface areas and chemical compositions of the resulting graphene aerogels have been studied, which indicates that the chemical structures of the alcohols play the mainly role in the physical and chemical properties of the graphene aerogels. On this base, the as-prepared graphene aerogels can be used as the binder-free electrodes for supercapacitors, which suggests that alcohol is significantly responsible for the energy storage performance of the graphene aerogels. The fundamental mechanisms of the alcohol-dependent environments in the fabrication of graphene-based supercapacitors have been discussed.

2. Experimental section

First, graphene oxide (GO) was prepared according to the modified Hummers method [23]. Briefly, 2 g graphite (Aldrich) and 1 g NaNO₃ were added into a mixture of 120 mL of 98 % H₂SO₄ in the ice bath. The solution was kept at 0 °C for 1 h, followed by gradual addition of KMnO₄. After 2 h stirring, the solution was heated up to and kept at 30 °C for 30 min, followed by the slow addition of 150 mL of water. Then, 50 mL H₂O₂ (5%) was added. Finally, the solution was washed with water and HCl (5%).

In a typical preparation of the graphene aerogel, a well-dispersed mixture of alcohol (8 mL) (IPA, EtOH and EG for each batch separately) and aqueous graphene oxide solution (8 mL, 2 mg mL⁻¹) was treated by ultrasonication for 1 h, followed by transferred into an autoclave with a volume of 23 mL. The hydrothermal treatment was carried out at 180 °C for 18 h, and then the autoclave was naturally cooled to room temperature. The as-obtained graphene hydrogels were washed and freeze-dried to achieve corresponding graphene aerogels.

The structures of the as-prepared graphene aerogels were characterized by field emission scanning electron microscopy

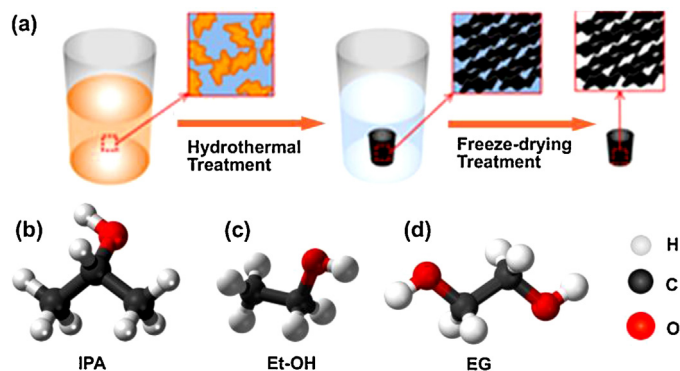


Fig. 1. (a) Schematic representation illustrating the fabrication of aerogels; (b)–(d) Ball-and-stick models for illustrating the chemical structures of the alcohols used for reduction.

(FESEM, JEOL JSM-6330) and transmission electron microscope (TEM, JEOL JSM-6330). Nitrogen adsorption/desorption isotherms were measured using a Quadrasorb SI analyzer at 77 K. The specific surface area was calculated using the Brumauer–Emmett–Teller (BET) method and the pore diameter was determined from the adsorption branch according to Barrett–Joyner–Halanda (BJH) method. X-ray photoelectron spectroscopy (XPS, PHI-5300) was applied to characterize the sample surface. Raman spectra were measured using micro-Raman spectrometer HR 800 (Jobin Yvon Horiba) at 514 nm wavelength incident laser light.

The electrochemical properties of the supercapacitors assembled by graphene aerogels was investigated in 6 mol L⁻¹ KOH electrolyte using three-electrode configuration by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge test. The working electrodes were prepared by pressing the graphene aerogel (~2 mg) on a piece of Ni foam without using any conductive agent and binder. Platinum foil and Hg/HgO electrodes were used as counter electrode and reference electrode, respectively. A galvanostatic charge–discharge test were tested at various current densities using a LAND-CT2001A cell test instrument with voltage window of $-1 \sim 0$ V (vs. Hg/HgO). CV and EIS were recorded using a CHI660C electrochemical workstation.

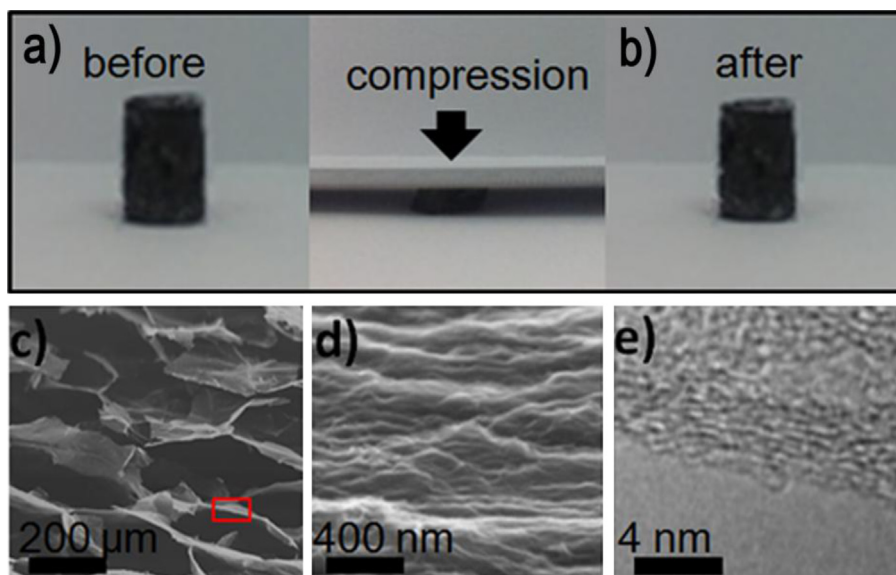


Fig. 2. Optical images showing the mechanical flexibility of aerogels: (a) as-fabricated aerogel and (b) dimensional recovery after compression; (c) FESEM image of cross section of graphene aerogel (ag-Et); (d) The magnified FESEM image of the selected area in (c); (e) TEM image of ag-Et.

Download English Version:

<https://daneshyari.com/en/article/183751>

Download Persian Version:

<https://daneshyari.com/article/183751>

[Daneshyari.com](https://daneshyari.com)