



ELSEVIER

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Organic solvents-enabled hydrothermal preparation of graphene hydrogels

Hai Li^{a,b}, Baoping Zhang^b, Chunxiang Lu^{b,*}^a Shanghai Shanshan Tech Co., Ltd, Shanghai 201209, China^b National Engineering Laboratory for Carbon Fiber Technology, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

ARTICLE INFO

Article history:

Received 22 January 2014

Accepted 2 May 2014

Available online 10 May 2014

Keywords:

Carbon materials

Sol-gel preparation

Hydrothermal reduction

Graphene hydrogels

Organic solvents

ABSTRACT

The graphene hydrogels (GHGs) could be prepared via hydrothermal process using graphene oxide (GO) hydrosol. However, the formation of GHGs is unavailable when the GO concentration is low. In this work, we successfully address this problem with the aid of some organic solvents such as tetrahydrofuran, acetone and ethanol. The as-obtained GHGs have different mesopore structure and interior micro-structure depending on the organic solvents used. Ethanol-enabled GHGs (eGHGs) show a cross-linked three-dimensional (3D) network structure composed of random dispersed graphene, and greatly enhance the cycling stability of Si nanoparticles as an anode material for lithium ion batteries. This work extends the possibility of synthesizing network graphene macroform.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Graphene has gained special attention due to its extraordinary properties, such as large specific surface area, excellent electronic conductivity and superior mechanical properties [1]. These unique properties make graphene a promising material in various technological fields including energy storage [2], catalysis [3], and composites [4,5]. Assembling two-dimensional (2D) graphene sheets into three-dimensional (3D) network structure could bring some additional applications. 3D graphene network structure could be prepared by template method [6,7] and chemical vapor deposition (CVD) method [8]. But these methods are complicated.

Recently, Xu et al. reported self-assembled 3D graphene hydrogels (GHGs) prepared by simple hydrothermal reduction of graphene oxide (GO) aqueous dispersion [9]. However, the formation of GHGs strongly depends on the GO concentration. For example, when GO concentration was 0.5 mg mL⁻¹, only a black powdery material was produced. Herein, we demonstrate that some organic solvents such as tetrahydrofuran, acetone and ethanol can enable the formation of GHGs at a low GO concentration of 0.5 mg mL⁻¹, thus extending the diversity of preparation methods. The micro-structure of these GHGs is associated with the solvents used. As an application, the ethanol-enabled GHGs (eGHGs) greatly enhance

the cycle performance of Si nanoparticles as an anode material for lithium ion batteries.

2. Experiments

40 mg GO (Nanjing XFNANO Materials Tech Co.,Ltd) was dispersed in 40 mL of deionized water to form 1 mg mL⁻¹ of homogeneous hydrosol by sonication. A 40 mL portion of deionized water, ethylene glycol, tetrahydrofuran, acetone, or ethanol was added into the GO hydrosol to obtain 0.5 mg mL⁻¹ of GO dispersion. Moreover, 40 mg GO was dispersed in 80 mL of tetrahydrofuran to form another 0.5 mg mL⁻¹ of GO dispersion. The above six kinds of GO dispersion was sealed in a 100-mL Teflon-lined autoclave and maintained at 200 °C for 12 h, respectively. Then the autoclave was naturally cooled to room temperature. Some black suspended matters or some GHGs were produced. The GHGs were lyophilized and subsequently annealed in N₂ atmosphere at 1000 °C for 1 h. The eGHGs were employed to prepare Si/eGHGs composite by dispersing grinded eGHGs and commercial Si nanoparticles (1:3 w/w) in ethanol solution and slowly drying at 30 °C with constant stir.

Field emission scanning electron microscopy (FESEM) was used to observe the morphology of GHGs and eGHGs/Si composite. To investigate the application of eGHGs in lithium ion batteries, the working electrode composed of 70 wt% Si/eGHGs composite, 20 wt% acetylene black and 10 wt% sodium carboxymethylcellulose (CMC) was prepared. The eGHGs/Si, acetylene black and CMC were

* Corresponding author. Tel.: +86 351 4250093; fax: +86 351 4166215.

E-mail address: chunxl@sxicc.ac.cn (C. Lu).

mixed homogeneously in deionized water and then pasted onto Cu foil. The electrodes were dried under vacuum at 100 °C for 12 h. CR2016-type coin cells were assembled in an argon-filled glove-box. Lithium metal foil was used as the counter electrode and the reference electrode and microporous polypropylene (Celgard2400) as the separator. The electrolyte was 1 M LiPF₆ in EC/DMC (1:1 v/v) plus 5 v% vinylene carbonate (VC). The discharge and charge measurements of the cells were performed in a voltage range between 0.01 and 2 V at a current density of 500 mA g⁻¹.

3. Results and discussion

Fig. 1a–f shows the photographs of the six hydrothermal products. Under the same GO concentration of 0.5 mg mL⁻¹ and process conditions, the products with two kinds of appearance were obtained. The products from pure water (Fig. 1a), pure tetrahydrofuran (Fig. 1b) and water/ethylene glycol (Fig. 1c) are suspensions of black powdery materials, similar to a previous report [10]. While the products from mixed solvents of water/tetrahydrofuran (Fig. 1d), water/acetone (Fig. 1e) and water/ethanol (Fig. 1f) are GHGs. They are denoted as tGHGs, aGHGs, and eGHGs (mentioned above), respectively. The apparent size of these GHGs changed little after lyophilization and annealing (Fig. 1g–i), indicating the strong cross-links between graphene sheets. The formation of GHGs cannot be realized in water/1-methyl-2-pyrrolidone (water/NMP, not shown here) under the same preparation

condition. It seems that high pressure plays an important role in the formation of GHGs, considering the facts that tetrahydrofuran, acetone and ethanol have higher vapor pressure than water while ethylene glycol and NMP have lower one than water. After hydrothermal reduction, the GO sheets became hydrophobic due to their restored conjugated domains. When the vapor pressure of solvents is high enough, it could press the flexible graphene sheets into GHGs with the aid of hydrophobicity and π - π interactions. Therefore, it is believed that some other solvents with high vapor pressure could likely enable the formation of GHGs. However, the GHGs are unavailable in pure tetrahydrofuran (Fig. 1b). This indicates that high pressure is the essential condition, though not the sufficient one, for the formation of GHGs. These phenomena can be explained as follows. When GO sheets were hydrothermally reduced, the oxygen functional groups diminished, leading to the incompatibility between graphene sheets and the solvents. Therefore, no homogenous graphene dispersion can be obtained in all solvents used. In pure water, the GO concentration of 0.5 mg mL⁻¹ is not enough to make the crosslinking of the graphene sheets occurs [9]. In the case of water/ethylene glycol and water/NMP, the vapor pressure is too low to effectively drive graphene sheets to form aggregation with large size. For the solvents of water/tetrahydrofuran, water/acetone or water/ethanol, the high vapor pressure originating from these organic solvents can enable the formation of GHGs. The dispersibility of GO in pure tetrahydrofuran is poorer than that in water, leading to insufficient interconnection and rearrangement of graphene

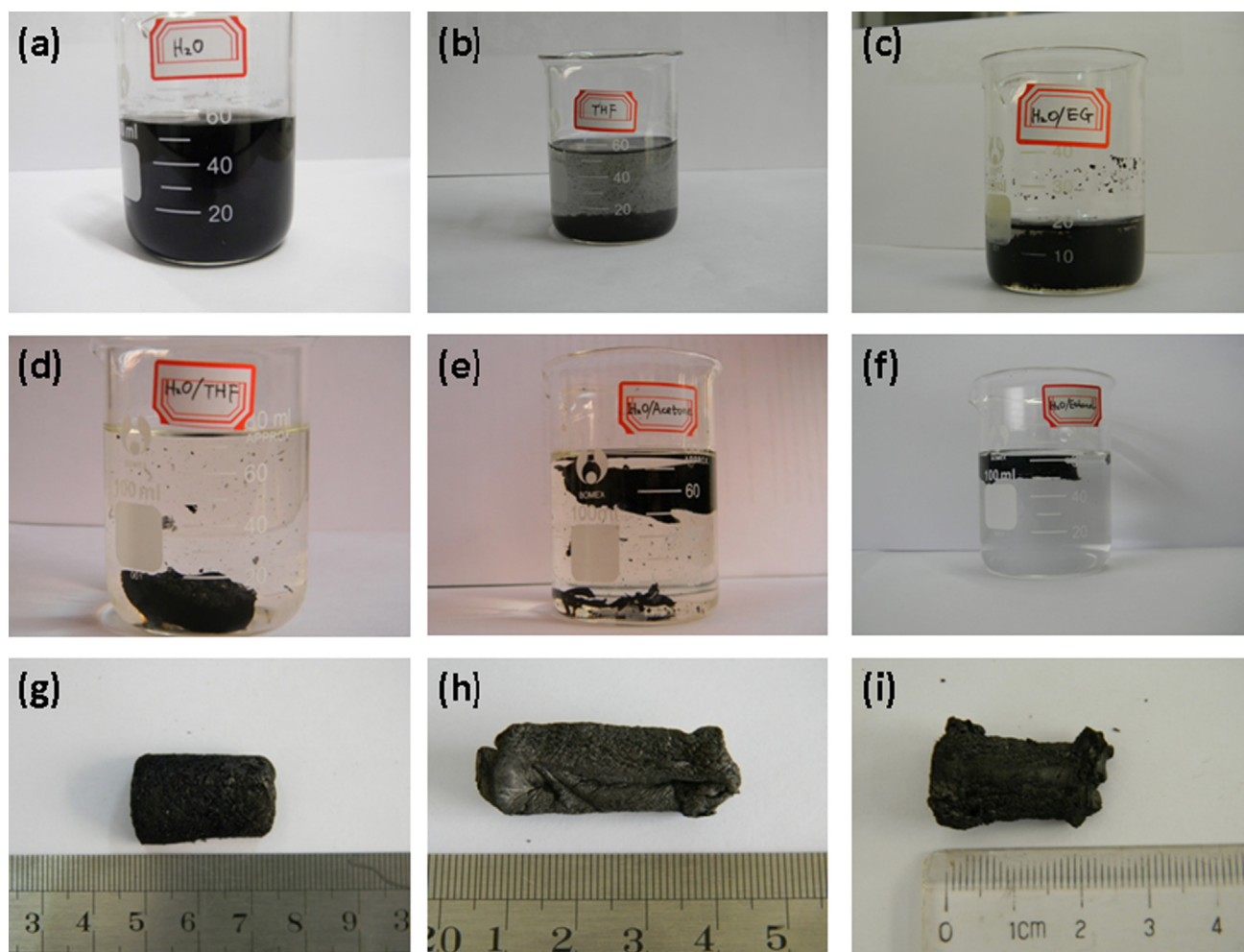


Fig. 1. (a)–(f) Photograph of the hydrothermal products in the solvents of water, tetrahydrofuran, water/ethylene glycol, water/tetrahydrofuran, water/acetone and water/ethanol, respectively. (g)–(i) Photograph of the lyophilized tGHGs, aGHGs and eGHGs, respectively.

Download English Version:

<https://daneshyari.com/en/article/1643988>

Download Persian Version:

<https://daneshyari.com/article/1643988>

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