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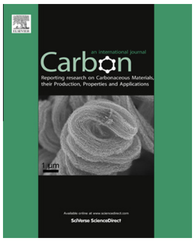

Ultralight, high-surface-area, multifunctional graphene-based aerogels from self-assembly of graphene oxide and resol

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ABSTRACT

The self-assembly between graphene oxide sheets and resol-type phenolic prepolymers was investigated as a method to form three-dimensional porous carbon objects with high surface areas and low densities. After freeze-drying and subsequent pyrolysis of the assembled hydrogels, ultralight graphene/carbon composite aerogels with high surface areas and porosity, good conductivity, and well-defined bulk shape were obtained. By adjusting the amount of graphene oxide and resol in the precursor mixture, aerogels with a density as low as 3.2 mg/cm^3 or a surface area as high as 1019 m^2/g could be prepared. It is proposed that resol molecules are first adsorbed on the surface of graphene oxide sheets, and then the surface-coated sheets are crosslinked by the polymerization of resol prepolymers. The absorption performance was evaluated for the aerogel with the lowest density. Due to the high porosity, the aerogel displayed fast absorption rates for organic solvents as well as high absorption efficiencies. The high conductivity of the aerogels permits good performance as binderless monolithic electrodes for supercapacitors.

1. Introduction

Graphene consists of two-dimensional, one-atom-thick sheets of sp^2-hybridized carbon atoms and has attracted tremendous interest in a variety of fields, due to its outstanding electronic, thermal, and mechanical properties [1,2]. As such, fabrication of graphene into three-dimensional (3D) materials with high surface area and porosity that also maintain some of these properties is tremendously attractive to materials scientists and greatly desirable in advanced applications, such as absorption and energy storage. One approach to assemble graphene sheets into 3D bulk objects is to prepare them as aerogels.

Aerogels are a class of light-weight, porous solids with large surface areas and pore volumes. They have been widely studied in various applications including thermal insulation, absorption, and catalyst supports [3,4]. It was recently found that carbon aerogels composed of interconnected graphene sheets can be obtained by simple assembly of graphene oxide (GO) sheets [5–13]. Compared to traditional carbon aerogels which are typically polymer-derived glassy carbon [14], graphene-based aerogels permit the opportunity to achieve ultralow density, high surface area and porosity, combined with good conductivity for improved absorption, catalytic, and electrochemical performance [10,11,15–17]. Bi et al. reported the use of graphene aerogels obtained from hydrothermal assembly of GO as sorbent materials with an absorption capacity of 86 g/g for chloroform, much higher than that obtained with natural products and polymeric foams [18]. The absorption capabilities of the graphene aerogels can be easily restored by a simple heat treatment. Zhao et al. prepared N-doped graphene aerogels by hydrothermal assembly of GO in the

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presence of pyrrole, and the product showed improved absorption capacity (~480 g/g for chloroform) resulting from its low density (density = 2.1 mg/cm^3) [11]. In addition, it also exhibited a high conductivity of 1200 S/m and superior capacitance of 484 F/g due to the N-doped graphene structure. The least dense graphene-based aerogel up to date, reported by Sun et al., was prepared by assembly of carbon nanotubes and giant GO sheets, had a density of 0.16 mg/cm^3, and exhibited a very high absorption capacity of 568 g/g for chloroform [13]. Although the materials were ultralight, the surface areas of the above aerogels were all less than 300 m^2/g, far less than the theoretical value of single-layered graphene (2600 m^2/g). High-surface-area graphene-based aerogels were obtained with resorcinol and formaldehyde to provide crosslinks, the highest reported surface area being 763 m^2/g for these systems, but their densities were all above 10 mg/cm^3 [6,19]. Even though a number of methods have been reported for the preparation of graphene aerogels, it is still challenging to achieve ultralight graphene-based aerogels (<10 mg/cm^3) with high surface areas (>1000 m^2/g) and good bulk electrical conductivity (>10 S/m). Tunability of the physical properties of graphene-based aerogels is rarely studied, so it is of great interest to explore preparations of ultralight, high-surface-area graphene-based aerogels with controlled properties.

Here we report the preparation of graphene/carbon composite aerogels with densities as low as 3.2 mg/cm^3 or specific surface areas as high as 1019 m^2/g from the assembly of graphene oxide and a resol-type phenolic resin, and control the properties of the resulting graphene/carbon composite aerogels by adjusting the amounts of GO and resol precursor. Use of resol resin as the mediating agent for the assembly of GO also offers better control of the shape of the aerogel because the volume of the original precursor mixture is nearly retained, and the aerogels replicate the interior shape of the reactor. We also propose an adsorption–assembly mechanism to explain the gelation mechanism of the GO–resol mixture and the difference in textural properties of the aerogels. Due to their highly porous structure, the aerogels have outstanding absorption efficiencies and can absorb hydrocarbons and chloroform up to 400 times their weight, which ranks among the best absorbing materials. The aerogels also display reasonably good electrochemical performance as binderless monolithic electrodes for supercapacitors with specific capacitance values of 99 and 80 F/g at current densities of 100 mA/g and 2 A/g, respectively.

2. Experimental

2.1. *Materials*

The following chemicals were used as received: natural graphite flakes (SP-1, 45 μm) from Bay Carbon, Inc.; $NaNO_3$ and $KMnO_4$, and formaldehyde (37%) from Fisher Scientific; H_2SO_4 and HCl from VWR International; H_2O_2 (30%) and KOH from Macron Fine Chemicals; phenol from Sigma–Aldrich.

2.2. *Synthesis of graphene oxide and phenolic resol resin*

Graphene oxide was synthesized according to the Hummers method, as reported elsewhere [20,21]. The resulting slurry was centrifuged and washed with 2 M HCl until it was SO_4^{2-}-free. The acid-washed GO was redispersed in water to form a brown dispersion. The pH of the dispersion was then adjusted to 5–6 with concentrated ammonia solution to promote exfoliation of GO, and unoxidized graphite impurities were removed by centrifugation at 4000 rpm. The pH of the resulting supernatant was adjusted back to 3, and the supernatant was dialyzed several times in deionized (DI) water until its pH became close to 5 and remained unchanged. The dispersion was then diluted to obtain a GO concentration of 1 mg/mL.

Resol resin was prepared according to a literature procedure [22]. A clear orange solution with 50 wt.% of resol in ethanol was obtained for further use.

2.3. *Preparation of graphene/carbon composite aerogels*

In a typical synthesis, 15 mL GO aqueous dispersion (1 mg/mL) was adjusted to pH 3 using 0.1 M HCl, and then 0.30 g of resol solution (50 wt.% in ethanol) was added while stirring. The mixture was then transferred to a 23 mL autoclave with a Teflon liner and hydrothermally treated at 180 °C for 24 h. A graphene/phenolic polymer composite aerogel was obtained after freeze-drying of the resulting hydrogel and was denoted as G1P2 aerogel. A graphene/carbon composite aerogel was obtained after pyrolysis at 900 °C for 2 h in flowing nitrogen and was denoted as G1C2 aerogel. Aerogels with various precursor compositions were also prepared, and they were denoted as G*x*P*y* aerogels, where *x* is the concentration of GO dispersion in units of mg/mL, and *y* is the number of aliquots of 0.15 g of resol solution; these materials correspond to the G*x*C*y* aerogel after pyrolysis. Syntheses using only resol prepolymers or GO were conducted similarly. The freeze-dried and pyrolyzed products using only the resol prepolymers were denoted as PF–HT and PFC, respectively, where PF stands for phenol–formaldehyde polymer and HT stands for hydrothermal treatment. Freeze-dried and pyrolyzed products obtained using only GO were denoted as GO–HT and GS, respectively.

2.4. *Characterization*

Scanning electron microscopy (SEM) images were taken using a JEOL 6500 FEG–SEM with an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai T12 microscope using an accelerating voltage of 120 kV. Samples were sonicated in ethanol and then dropped onto a Cu grid. X-ray diffraction (XRD) patterns were acquired using a PANalytical X-Pert Pro MPD X-ray diffractometer equipped with a Co source (45 kV, 40 mA, $\lambda = 1.790$ Å) and an X-Celerator detector. Small-angle X-ray scattering (SAXS) patterns were acquired using a Rigaku RU-200BVH 2D SAXS instrument with a Cu X-ray source (45 kV, 40 mA, $\lambda = 1.542$ Å) and a Siemens Hi-Star multi-wire area detector with a sample-to-detector distance of 70 cm. For atomic force microscopy (AFM) measurements, graphene oxide was spin-coated at a rate of 100 L/0.5 in.^{2} of substrate from a 0.5 mg/mL dispersion in water at 3000 rpm for 30 s on top of freshly cleaved V-5 muscovite, and then dried under vacuum overnight at room temperature. The AFM imaging was performed in contact mode to record GO sheet thickness