Materials Research Bulletin 48 (2013) 3553–3558

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Graphene oxide foams and their excellent adsorption ability for acetone gas

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ARTICLE INFO

Article history:
Received 18 May 2012
Received in revised form 9 May 2013
Accepted 15 May 2013
Available online 23 May 2013

Keywords:
A. Microporous materials
C. Thermogravimetric analysis (TGA)
D. Microstructure

ABSTRACT

Graphene oxide (GO) and reduced graphene oxide (RGO) foams were prepared using a unidirectional freeze-drying method. These porous carbon materials were characterized by thermal gravimetric analysis, differential scanning calorimetry, X-ray photoelectron spectroscopy and scanning electron microscopy. The adsorption behavior of the two kinds of foams for acetone was studied. The result showed that the saturated adsorption efficiency of the GO foams was over 100%, and was higher than that of RGO foams and other carbon materials.

1. Introduction

Graphene is a nano-scale carbon material which was first isolated by a micro-mechanical cleavage method in 2004 [1]. Since then it also has received a great deal of attention because of its unique properties [2–4] and potential applications [5–9]. Graphene is a monolayer of carbon atoms, with a thickness of about 0.335 nm [10–13]. It can exist as a free-standing form and exhibits many unusual and intriguing physical, chemical and mechanical properties [1,11]. The theoretical surface area of a single graphene calculated by McAllister et al. is 2630 m^2/g [14] which is more than twice that of activated carbon. Its huge surface area endows it with potential adsorption abilities [15,16]. For example, Lamari determined the potential for hydrogen adsorption on functionalized graphene using molecular modeling [17].

Besides the micro-mechanical cleavage method, there are several ways to prepare graphene [18–20], such as liquid-phase exfoliation, solvothermal synthesis, and unzipping carbon nanotubes. Liquid-phase exfoliation (usually the oxidative treatment of graphite to produce graphene oxide (GO) followed by chemical reduction) is a common way to prepare graphene on a large scale. GO is an important derivative of graphene. GO nanosheets have a large number of functional groups, such as –OH, –COOH, –O–, and C=O on their surfaces. These groups make graphene hydrophilic, dispersible in solvents, and easily modified to be compatible with a polymer matrix [12]. GO is usually produced by the oxidative treatment of graphite [21] using a “Brodie” [22], “Hummers” [23], or “Staudenmaier” [24] method. The Hummers method is the most popular. Since GO is prepared from low-cost graphite, it has an outstanding cost advantage and more versatile applications compared with CNT [25]. Although GO is an electrically insulating material [26], this can be changed by using chemical or thermal methods to reduce GO to restore its electrical conductivity [27].

Polymers and some inorganic materials can be easily made into highly porous structures. These porous materials can be used as catalyst carriers, scaffolds for cell cultures or absorbents for chemicals [28,29], such as CO_2 gas [30,31] which controlling and reducing the concentration of CO_2 in the atmospheric has been gaining significant public and scientific attention [32]. A sponge-like bulk CNT material, with a density close to the lightest foams and with a porosity of >99%, has been reported [33]. The sponge consists of CNT self-assembled into a porous, interconnected, three-dimensional framework. The light-weight, high porosity, and large surface area make it a promising candidate for environmental applications such as sorption, filtration and separation, or use as a catalytic carrier.

Herein, highly porous GO or reduced graphene oxide (RGO) foams were prepared by a unidirectional freeze-drying method, and, for the first time, their adsorption behavior for acetone was studied.

2. Experimental

2.1. Materials

Graphite was from Huadong Graphite Factory, China. Activated carbon (AC, BET surface area: about 280 m^2/g, average pore size: 3 nm); bamboo charcoal (BC, BET surface area: about 245 m^2/g, average pore size: about 180 nm) were supplied by Tianjin Activated Carbon Co., China, multiwalled carbon nanotubes (CNTs,

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0025-5408/$ – see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.materresbull.2013.05.056

BET surface area: 320 m^2/g, inner diameter: 10 nm) were supplied by Nanotech Port Co., Shenzhen, China, and all other reagents were from Tianjin Chemical Reagent Co. All the chemicals were used as received.

2.2. Preparation of GO nanosheets

GO was prepared from purified natural graphite according to the method reported by Hummers and Offeman [23]. Briefly, concentrated H_2SO_4 (23 mL) was added into a 250-mL flask filled with graphite (1 g) at 0 °C (ice bath), followed by the addition of $NaNO_3$ (0.5 g). Then solid $KMnO_4$ (3 g) was added gradually with stirring and the temperature of the mixture was kept below 20 °C. The mixture was stirred with a mechanical stir bar for 2 h. The temperature was then increased to 35 °C and maintained at this temperature for half an hour. Then excess deionized water was added to the mixture and the temperature was increased to 90 °C and the mixture was stirred for 0.5 h. Finally 30% H_2O_2 was added until the color turned to brilliant yellow and there was no gas being produced. The product was filtered and rinsed three times with 5% HCl solution to remove the metal ions and then filtered and rinsed with deionized water to remove the acid. The resulting filter cake was dried in air, and different amounts of the cake were dispersed into deionized water by sonicating for 3 h to obtain GO suspension with different concentration.

2.3. Preparation of GO foams

One of the above GO suspensions was injected into a plastic tube 20 mm in diameter and 50 mm long. The tube was then placed in an insulated Styrofoam container with only the bottom surface of the plastic tube exposed to the air. The Styrofoam container was placed on the surface of a 6-cm-diameter disk of copper, which in turn rested on a 6-cm-deep pool of liquid nitrogen to create a uniaxial thermal gradient [34]. When the liquid nitrogen evaporated, the homogeneous GO suspension was unidirectionally frozen from the bottom to the top. The solidified GO/water system was then transferred into a freeze-drying vessel (Alpha1-2, Christ, Germany) under vacuum (<20 Pa) and freeze-dried for 48 h to give GO foams that were then further dried in a freeze dryer for 6 h. The samples were then removed and stored in a desiccator.

2.4. Thermal reduction of GO foams

To prepare the RGO foams, the GO foams were heated in an oven for 60 min at 100 °C, 60 min at 150 °C, and then 120 min at 200 °C in an atmosphere of N_2.

2.5. Characterization

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed by a standard method on a STA 409 PC. Elemental analysis was performed using X-ray photoelectron spectroscopy (XPS) (PHI1600 ESCA System, PERKIN ELMER, USA). Scanning electron microscopy (SEM) was conducted with a JEOL-6700F ESEM instrument after sputter coating the samples with gold.

2.6. The volume fraction (VF) of GO in the GO foams

The approximate VF of GO in the GO foams was calculated according to the following formula.

$$\mathrm{VF}\,(\%) = \frac{V_\mathrm{p}}{V_\mathrm{m}} \times 100 = \frac{W_\mathrm{m}/\rho}{V_\mathrm{m}} \times 100 \qquad (1)$$

where V_m is the total volume of the GO foams (cm^3), V_p is the volume occupied by GO (cm^3), W_m is the mass of the GO foams (g), and ρ is the density of the GO (g/cm^3).

2.7. Water adsorption ability of GO and RGO foams in distilled water

The above prepared GO or RGO foams (the weight was M_0) was put into distilled water at 25 °C for water adsorption test. They were taken out and their weight was measured in a certain time interval until the weight was constant, at which the water adsorption equilibrium was reached. They were then taken out and their weights were measured (M_t). The water adsorption of the GO or RGO forms was defined as: water adsorption (g/g) = $(M_\mathrm{t} - M_0)/M_0$. To calculate the average results, three parallel experiments were taken for GO or RGO.

2.8. Adsorption of the foams for acetone gas

The GO foams were heated at 50 °C for 1 h under vacuum to remove moisture, and then they were packed into a glass column in an adsorber equipped with vacuum pump and exposed to acetone gas at room temperature. The apparent adsorption efficiency (Ad) of the GO foams for acetone was calculated with the following formula:

$$\mathrm{Ad}\,(\%) = \frac{W'_\mathrm{t} - W_\mathrm{t}}{W_0} \times 100 \qquad (2)$$

where W_0 represents the weight of the foams before the adsorbing test, W_t and W'_t are the total weights of the GO foams (g) and the glass column before and after adsorbing acetone for a given time, respectively. Ad is the apparent adsorption efficiency of the foams at a given time. The Ad is equal to the saturation adsorption efficiency (Ade) if the adsorption period is long enough. All data is the mean value of three independent measurements. The adsorption behavior of RGO, activated carbon, bamboo charcoal and CNT were determined in the same way.

3. Results and discussion

3.1. Characterization of GO foams

The porous GO foams were prepared from homogeneous and stable GO suspension (see Fig. S1) by a unidirectional freeze-drying method. Under illumination, the foam is shiny, yellowish, and has visible textures that indicate the direction of the pores (Fig. 1). The porous GO foam turned black but kept its shape after it was

Fig. 1. Optical photos of porous GO (left) and RGO foams (right).