Materials Research Bulletin 73 (2016) 401–408

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Self-assembled three-dimensional graphene/Fe_3O_4 hydrogel for efficient pollutant adsorption and electromagnetic wave absorption

Yue Yang[a], Yanrong Zhao[a], Shihan Sun[a], Xueyu Zhang[a], Lianfeng Duan[a], Xin Ge[b,*], Wei Lü[a,*]

[a] Key Laboratory of Advanced Structural Materials, Ministry of Education, Changchun University of Technology, Changchun 130012, China
[b] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

ARTICLE INFO

Article history:
Received 31 July 2015
Received in revised form 25 September 2015
Accepted 30 September 2015
Available online 9 October 2015

Keywords:
Surface properties
Solvothermal
Magnetic materials
Magnetic properties
Microporous materials

ABSTRACT

3D composite hydrogels composed of graphene sheets and Fe_3O_4 nanoparticles (G/Fe_3O_4) were prepared via a simple hydrothermal method. The composite has an interconnected 3D porous network, and the Fe_3O_4 nanoparticles with the size of ~13 nm are uniformly dispersed onto the graphene sheets. Due to the synergistic effects of the assembled graphene sheets and Fe_3O_4 nanoparticles, the resultant G/Fe_3O_4 exhibited efficient adsorption for organic pollutant using Rhodamine B as the adsorbate and electromagnetic wave absorption. The maximum removal ratio of Rhodamine B was 99.6%, and the G/Fe_3O_4 hydrogel demonstrated wide and strong wave absorption achieved in the frequency range of 2–20 GHz. Present work shows a way to design and prepare lightweight and high performance materials for both electromagnetic wave absorption and wastewater treatment based on 3D graphene and Fe_3O_4 nanomaterials.

1. Introduction

The integration of nanoscaled materials into macroscopic size by the self-assembly method has been recognized as one of the most effective strategies to realize the practical applications of nanomaterials. Recently, researchers have exhibited remarkable progress in self-assembly of nanomaterials into three-dimensional (3D) structures such as hydrogels, aerogels, and mesopores frameworks [1,2]. Graphene as a typical two-dimensional material with unique electrical, mechanical, thermal, optical properties and huge theoretical specific area has received intense interest. Graphene oxide (GO) is a precursor of graphene with oxygen-containing functional groups on the basal plane and the sheet edge. Some reports have shown that GO could form 3D hydrogel structure by various supramolecular interactions [3,4]. Such graphene-based 3D macrostructures with desired properties take the key advance to realize their extensive potential applications. Previous works have shown the preparation of the 2D graphene functional structures using GO and various metal oxides such as TiO_2, MnO_2, ZnO, Fe_2O_3, Fe_3O_4, CuO as precursors. Among them, Fe_3O_4 nanocrystals (NCs) have attracted a large number of investigations due to their excellent magnetic properties, chemical stability, non toxicity, and low magnetocrystalline anisotropy [5–10]. The integration of 2D graphene/Fe_3O_4 (G/Fe_3O_4) composites into 3D structures would induce porous network and therefore increased specific surface area. This will realize their extensive potential applications specially for pollutant adsorption and electromagnetic (EM) wave absorption. Nowadays, to improve living environment has become increasingly important. Water pollution has become increasingly important, and the rapid development of EM wave devices produces a highly harmful living environment for human beings. The 3D G/Fe_3O_4 system would be efficient in both pollutant adsorption and EM wave absorption. Although a few of reports about applications of 3D G/Fe_3O_4 for electrocatalyst [11], supercapacitor [12–14], EM wave absorption [15–17] have been exhibited, the investigation of multifunctional applications of 3D G/Fe_3O_4 for both pollutant adsorption and EM wave absorption is still limited.

In this work, we investigate the multifunctional applications of 3D/Fe_3O_4 hydrogels prepared by a simple hydrothermal strategy. Due to the synergistic effects of the assembled graphene nanosheets and Fe_3O_4 nanoparticles, the resultant 3D G/Fe_3O_4 exhibited efficient adsorption for organic pollutant using Rhodamine B (Rh.B) as the adsorbate and EM wave absorption. The maximum

* Corresponding authors. Fax: +86 431 85716426.
E-mail addresses: xge@ciac.ac.cn (X. Ge), lw771119@hotmail.com (W. Lü).

http://dx.doi.org/10.1016/j.materresbull.2015.09.032
0025-5408/

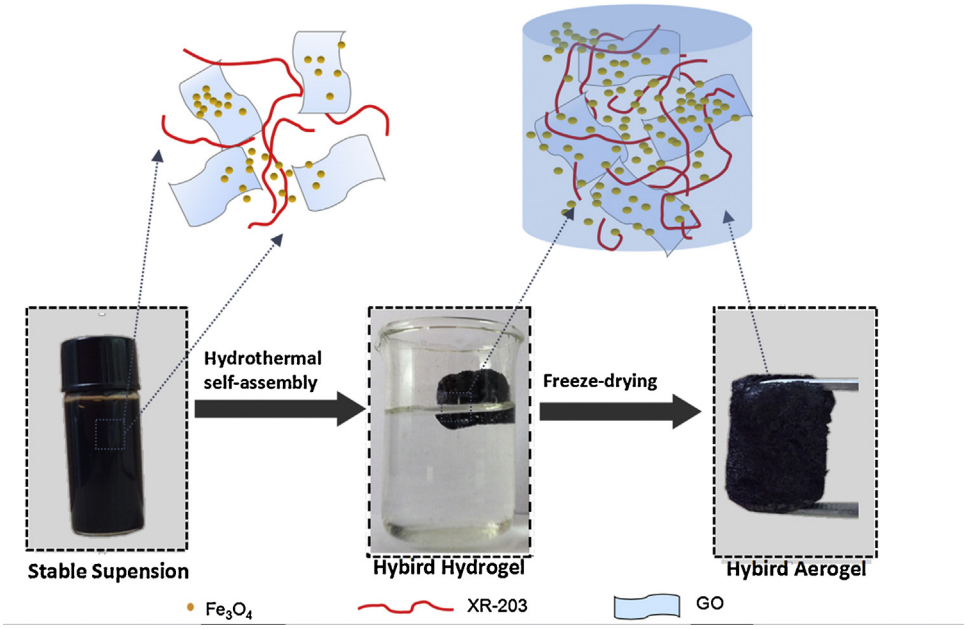

Fig. 1. Fabrication procedures of 3D G/Fe_3O_4 hydrogel.

removal ratio of Rh.B gets to 99.6%. The G/Fe_3O_4 hydrogel has both wide and strong wave absorption achieved in the frequency range of 2–20 GHz.

2. Experiments

2.1. Chemicals

Iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate, hydrazine hydrate, graphite powder, Rh.B were purchased from Aladdin. Water crosslinking agent is commercial water-based acrylic ink crosslinking agent (XR-203). All the reagents used for the experiments were analytical grade. Water used in all experiments was doubly distilled and purified by a Milli-Qsystem.

2.2. Characterization

Transmission electron microscopy (TEM) images were obtained using a JEOL2010 transmission electron microscopy. Scanning electron microscopy (SEM) images were obtained using a JSM-5500LV. The X-ray diffraction (XRD) measurements were performed using a D-MAXIIA X-ray diffractometer. The concentrations of dye solutions were measured using UV-2501 spectrophotometer. The magnetic properties were measured by a vibrating sample magnetometer (VSM) at room temperature.

2.3. Synthesis of Fe_3O_4 NCs and G/Fe_3O_4 hydrogels

GO was synthesized from natural graphite powder according to a modified Hummers method [18]. The purified GO powders were collected by centrifugation and air drying at room temperature.

For fabrication of Fe_3O_4 NCs, a solution including 0.884 g $FeCl_2{\cdot}4H_2O$ and 0.533 g $FeCl_3{\cdot}6H_2O$ was prepared. Then, hydrazine hydrate was added and heated to 80 °C, and the solution was left to stir for 1 h. After cooling to room temperature, the resulted Fe_3O_4 NCs were isolated with the help of a magnet field and thoroughly washed by deionized water.

For fabrication of 3D G/Fe_3O_4 composites, in a typical experiment, 85 mg GO was dispersed in 20 ml DI-water by ultrasonic processing for 2 h to obtain a homogeneous solution as shown in Fig. 1(a). Then, 2 ml hydrazine hydrate and 100 ul water crosslinking agent were added, and ultrasonic for 20 min. After that, Fe_3O_4 NCs were added into the mixed solution, which was left to ultrasonic for another 30 min. Subsequently, the homogeneous black solution was transferred into a 50 ml Teflon-lined autoclave and maintained at 180 °C for 12 h to form a graphene-based 3D hydrogel as shown in Fig. 1(b). The as-prepared hydrogel was freeze–dried to acquire 3D G/Fe_3O_4 structure as shown in Fig. 1(c). Three hydrogels with different weight ratios of GO to Fe_3O_4 NCs were prepared: 1:1 (sample 1), 1: 2.5 (sample 2) and 1: 4 (sample 3).

2.4. Adsorption experiments

The removal of Rh.B from aqueous solutions by the G/Fe_3O_4 hydrogel was carried out as follows: 3D G/Fe_3O_4 (2–16 mg) was added to 20 ml Rh.B solution (20 mg/l); After 1 h, the magnetic graphene nanocomposite was removed from the solution by magnetic separation using a permanent magnet and the equilibrium concentration of the dyes in the solution was determined with UV–vis spectrophotometer at the wavelength of 554 nm (λ_{max}).

2.5. Absorption of EM wave experiments

The electromagnetic parameters of the samples were measured with a vector network analyzer. The measured samples were prepared by mixing 30 wt% of the sample with a paraffin matrix. The mixture was then made into toroidal shape with an outer diameter of 7.00 mm and inner diameter of 3.04 mm.

3. Results and discussion

Fig. 2 shows the XRD patterns of as-prepared G, Fe_3O_4 NCs and G/Fe_3O_4 hydrogels (samples 1, 2 and 3). The XRD pattern of G shows a broad peak between 20°–30° corresponding to the (0 0 2) reflection of graphene, indicating that the samples are very poorly ordered along the stacking direction. The position of all diffraction peaks of G/Fe_3O_4 hydrogels match well with data of the JCPDS card for Fe_3O_4 and can be assigned to be the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) of crystal planes of Fe_3O_4. The XPS spectrum of