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High performance agar/graphene oxide composite aerogel for methylene blue removal

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ABSTRACT

A novel three-dimensional (3D) agar/graphene oxide (AGO) composite aerogel was prepared by a vacuum freeze drying method. The AGO aerogel was tested for its adsorption capacity of methylene blue (MB) and was found to have a maximum adsorption capacity of 578 mg/g, as determined from the Langmuir isotherm. The adsorption kinetic studies revealed that adsorption followed pseudo-second-order model. The thermodynamic parameters calculated from the Van't Hoff equation indicate that the adsorption was an endothermic and spontaneous process. The adsorption mechanism may be attributed to electrostatic interaction between MB and AGO aerogel. Furthermore, the AGO aerogel can easily be recycled with a dilute NaOH solution wash, retaining over 91% of the adsorption capacity after recycling three times.

1. Introduction

Graphene, a two-dimensional single-layered sheet of hexagonally arrayed sp^2-hybridized carbon atoms, has drawn tense attentions due to its unique electronic, thermal, and mechanical properties (Liang, Wu, Feng, & Müllen, 2009; Su, Pang, Alijani, Feng, & Müllen, 2009). Materials incorporating graphene and graphene derivatives have been investigated for applications as diverse as drug delivery (Yang, Li, Tan, Peng, & Liu, 2013), hydrogen storage (Paul et al., 2010), carbon dioxide capture (Zhou et al., 2012), solar cell (Li et al., 2010), water treatment (Wang et al., 2015; Zhang et al., 2014). As one of the derivatives of graphene, graphene oxide (GO) has become an attractive material because it is easily produced in bulk via a chemical exfoliation process of natural graphite (Dreyer, Park, Bielawski, & Ruoff, 2010; Park & Ruoff, 2009), and possesses large specific surface area and abundant oxygen-containing functional groups, which can be further functionalized (Li et al., 2012). The abundant oxygen-containing functional groups in GO have

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been exploited to produce a variety of materials including aerogels (Liu, Chung, Oh, & Seo, 2012; Shen, Fang, & Chen, 2015), fibers (Du et al., 2014; Li et al., 2014), and composites (Chang & Wu, 2013; Ge & Ma, 2015). In particular, 3D aerogels have grown in popularity and are the subject of much ongoing research.

Over the past several years, 3D graphene and graphene oxide aerogels have been prepared for various applications by a variety of methods including self-assembly approach (Hu, Zhao, Wan, Gogotsi, & Qiu, 2013; Zhao et al., 2014) and template-directed approach (Yan et al., 2014). Compared with template-directed growth, the self-assembly techniques, including vacuum freeze drying, and hydrothermal methods are simple and easily scalable. The hydrothermal method, first introduced by Xu, Sheng, Li, and Shi (2010), produced a graphene aerogel that was mechanically strong, electrically conductive, and thermally stable Sun, Xu, and Gao, (2013) used the freeze drying method to prepare a carbon areogel by mixing graphene and carbon nanotubes. Carbon nanotubes tightly adhere to the graphene surface and act as a support pillar to reduce the graphene sheets congregation.

The synthetic GO was used directly for dyes (Yang et al., 2011) and heavy metal ions adsorption (Wang et al., 2013). However, the dispersion and stability of GO sheets are very well in the natural aquatic environment, and the release of GO into the natural aquatic environment poses a potential secondary contamination risk (Chowdhury et al., 2013; Zhao et al., 2014). For this reason, agar was selected to reinforce the stabilizing of graphene oxide sheets to build the 3D microstructure because it is a biodegradable and non-toxic biopolymer with large number of oxygen-containing functional groups. It is suspected that the abundant oxygen-containing groups from agar and GO surface will both react via a dehydration reaction (Tao et al., 2014; Xie et al., 2013), and interact by hydrogen bonding (Cheng et al., 2012) as the hydrogel is forming. Herein, we synthesized a reusable 3D AGO composite aerogel using 2D GO sheets and agar as precursors (Scheme 1). The 3D AGO aerogel is expected to result in higher stability and good adsorption capacity for applications in water treatment. This is the first report of AGO aerogel to our knowledge.

Methylene blue (MB) is an important organic dye widely used in textile, dyeing, printing, pesticide, and coating for paper stock (Wu et al., 2009). Because of its aromatic ring, MB is highly toxic and very difficult to degrade (Hameed, Din, & Ahmad, 2007; Parida, Sahu, Reddy, & Sahoo, 2011). Consequently, MB must be removed from wastewater before discharging. As a 3D porous material, AGO aerogel is a promising adsorbent for such organic dyes as MB. The adsorption properties of MB and their dependence on a variety of parameters as well as adsorption isotherm, kinetic, and thermodynamic characteristics were determined for AGO aerogel.

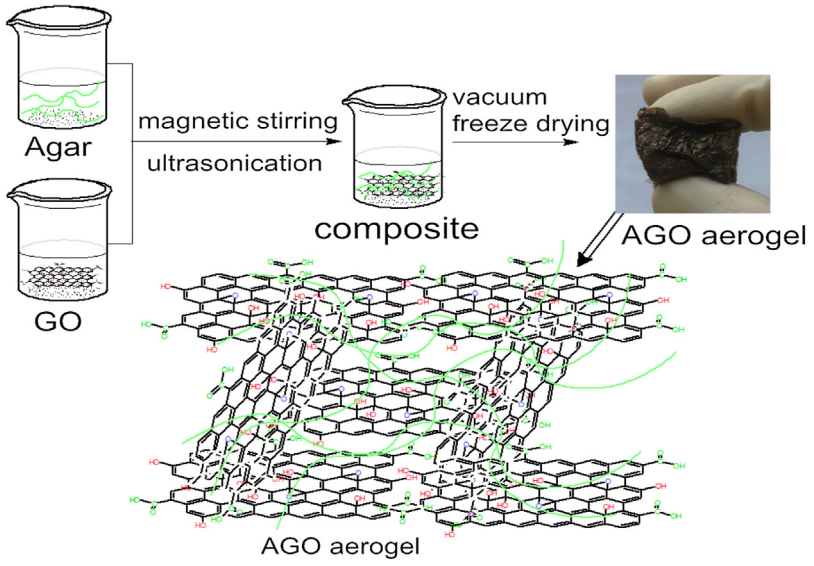
2. Materials and methods

2.1. Materials

The expandable graphite was purchased from Henglide Graphite Company (Qingdao, China). Methylene blue ($C_{16}H_{18}ClN_3S{\cdot}3H_2O$, >99% in purity) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Deuterated Dimethyl sulfoxide (99.9% atom% D) was purchased from Sigma-Aldrich Ltd., America. Agar (molecular formula: $(C_{12}H_{18}O_9)_n$, gel strength: 716.8 g/cm^2,) was purchased from Sinopharm Chemical Reagent Co., Ltd., China without further purification. Agar consists of two main components namely β-D-galactopyranose and 3,6 anhydro-α-L-galactopyranose. The ^{13}C NMR spectrum of agar was shown in Fig. S1 (Supporting information). All other reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China.

2.2. Preparation of GO

GO was prepared by modified Hummer method from expandable graphite (Hummers & Offeman, 1958). $KMnO_4$ (15 g) and $NaNO_3$ (2.5 g) were completely dispersed in H_2SO_4 (115 mL, 98 wt%) in ice bath under constant stirring followed by addition and complete dispersion of expandable graphite (2.5 g). The obtained mixture was maintained at 273 K for 24 h. Then, the mixture was heated to 308 K and waited at this temperature for 30 min with constant stirring. The temperature was slowly increased to 371 K as the solution was simultaneously diluted to 500 mL by adding deionized water drop by drop. The suspension was then maintained at 371 K for 15 min with constant agitation. The color of the mixture turned into yellow after about 5 mL 30% H_2O_2 was added. The mixture was then diluted with 3000 mL HCl solution (5%) to remove metal ions and rinsed with deionized water several times until the pH of the solution was neutral. Finally, the dry GO was prepared using vacuum freeze drying method.



Scheme 1. Synthetic scheme of AGO aerogel.