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Graphene aerogel prepared through double hydrothermal reduction as high-performance oil adsorbent

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ABSTRACT

Cork-like graphene aerogels were synthesized via EDA-ammonia double hydrothermal reduction approach. The synthesized porous aerogels displayed high porosity, hydrophobicity and excellent mechanical properties. Its adsorption efficiency for oil is significantly higher than that of conventional adsorbents, having oil capacity (130.10 g/g) for pure diesel and continuous treatment capacity (71.67 g/g) for emulsified oil in oil-contaminated water. Besides, its recycling performance was evaluated by mechanical extrusion, ethanol washing and calcined regeneration, and for emulsified oil, the adsorption process follows a pseudo-second-order kinetic model and adsorption isotherms are related well by the Freundlich model with a determination coefficient. (R^2) of 0.9994. Furthermore, a continuous aerogel-based water treatment process has been proposed to make the graphene-based aerogels have great potential applications for oil spill clean-up and water purification.

1. Introduction

Due to the exacerbation of the oil pollution and increasing concern on the preservation of environment, there is a growing and urgent need to develop novel porous materials which can effectively purify the water contaminated by the petroleum products and oily compounds [1–4]. Various techniques have been proposed and employed for such cleanup, including physical adsorption, surfactant-aided diffusion, mechanical recovery by oil skimmers, in-situ burning, enhanced biodegradation by microbes, and so on. Among the existing methods [5–8], physical adsorption by porous materials is probably the simplest and most effective technique. The principle behind this technique is that the non-polar compounds can be physically adsorbed by hydrophobic materials, and in general, a high surface area and porous structure of the adsorbents favor this process. Highly porous natural materials, such as perlite [6], zeolite [7] and wool [8], have been used to separate water-oil mixture. However, such “oil-removing” materials can be blocked by the oil during the adsorption process. This decreases the separation efficiency and the service life of the materials. Furthermore, such materials are not suitable for the gravity-driven removal of light oils (which are less dense than water) from mixed solutions because the water settles below the oil, creating a layer of water between the oil and the adsorbents [9]. A surface that is hydrophobic in air will generally need to have a very rough micro/nanoscale hierarchical structure or a re-entrant surface curvature, and will need to undergo rigorous chemical modifications to give it a high hydrophobicity.

Graphene-based materials were regarded as “ingenious materials” for the removal of oily pollutants from aqueous media due to their hydrophobic and oleophilic properties. As such, fabrication of graphene into monolithic materials with high surface area and controlled porosity is significantly attractive to material scientists and greatly desirable for oil-water separation. For example, Li et al. [10] prepared graphene-based aerogel by assembly of graphene oxide (GO) sheets and ethylenediamine (EDA), the material exhibited adsorption capacities for organic solvents ranging from 100 to 166 times of its own weight. Song et al. [11] reported the use of graphene aerogels form hydrothermal assembly of GO and dopamine. The material exhibited adsorption capacities for fuel oil ranging form 99 to 118 times of its own weight, much higher than those natural materials and polystyrene foam. Besides the high adsorption capacity of monolithic graphene aerogel, the adsorption capabilities of the materials can be easily restored by a simple thermal treatment and squeezing method. Shi et al. [12] prepared nitrogen-doped graphene aerogels by hydrothermal assembly of GO in the presence of pyrrole, and the product showed improved adsorption capacity resulting from its low density.

Although monolithic graphene-based frameworks, such as aerogels, foams and sponges, which exhibit continuously interconnected porous structures, high compressibility and large surface area, have been developed in recent years as new-generation oil adsorbents [13], there are still many items should be addressed to optimize their functional properties. For example, the adsorbates (i.e. oily compounds and petroleum products) generally lack well-defined characterization in the

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existent forms, which substantially limits the comprehension of adsorption for adsorbate by utilizing the porous structures in the material. Besides, work on adsorption mechanism for graphene-based aerogels is insufficient, which restrains the enhancement of progress in the preparation of materials. In addition, the conventional adsorption units are not matched with graphene-based aerogels, which possible limits the functional properties of those materials. Therefore, fabrication of hierarchical architectures in graphene-based aerogels by integrating porous channels and construction of suitable adsorption units by considering materials' functional properties are highly desirable.

Herein, we described a facile and novel two-step hydrothermal reduction method to fabricate porous, resilient graphene aerogels with the addition of traces of organic additives (EDA) and inorganic aqueous solution ($NH_3 \cdot H_2O$) for oil-water separation directly. A detailed comparison of graphene aerogels recovery methods, including thermal desorption, ethanol etching, squeezing were conducted in this work. Subsequently, several characteristics were investigated.

2. Materials and methods

2.1. Materials and reagents

Graphite powders, natural, briquetting grade, ~30 µm, 99.9995% (metals basis) were purchased from Sinopharm Chemical Reagent Co. Ltd. Hydrochloric acid (HCl, 36% wt), $NH_3 \cdot H_2O$, sulphuric acid (H_2SO_4, 98% wt), ethylenediamine (EDA), $NaNO_3$, $KMnO_4$, and H_2O_2 aqueous solution (30% wt) were purchased from Aladdin Industrial Corporation, and used directly without further purification. Kerosene, gasoline, 0# commercial diesel and straight-run diesel were purchased from China National Petroleum Corporation (Qingdao). Deionized water (DI water) was used throughout the study, unless otherwise stated.

2.2. Preparation of graphene oxide

Graphene oxide was synthesized based on the procedure established previously with some modifications [14]. Briefly, 5.0 g graphite powders and 2.5 g sodium nitrates were added into 115 ml concentrated sulfuric acid solution at room temperature, then the mixture was put into an ice bath for 10 min with mild agitation. Potassium permanganate (15.0 g) was then added slowly and kept the temperature of the suspension lower than 10 °C for another 100 min, The mixture were heated to 35 °C and kept for 60 min, next, 230 ml Deionized water was added and the temperature of the solution was kept at 98 °C for another 30 min, with the color of the aqueous solution turning from brown to yellow .The solution was diluted to 500 ml, and 45 ml H_2O_2 (30% wt) was added to reduce the left potassium permanganate. The resulting mixture was filtered and washed with HCl solution for 3 times, and then with water repeatedly to neutral state. The product was centrifuged at 10000 rpm for 10 min after each washing step. The resulting sample was dried in vacuum at 60 °C for 72 h.

2.3. Preparation of graphene aerogel

Graphene aerogel was synthesized via EDA-ammonia double hydrothermal reduction approach. In this procedure, aqueous GO dispersion (20 ml, 3 mg ml^{-1}) and 20 µL EDA were sealed in a Teflon-lined stainless-steel autoclave. Subsequently, the mixture were heated at 90 °C for 5 h, and a graphene hydrogel (GH) formed. Then the GH was immerged in the ammonia solution (14% v) for 1 h at 90 °C. Finally, the as-prepared hydrogel was washed with distilled water and then dried by freeze-drying. The resulting aerogels were denoted as EGA. The synthesis strategy of EGA materials is schematically illustrated in Fig. 1a. For comparison, aerogels prepared hydrothermally without EDA-ammonia double reduction were denoted as GA. Another samples prepared merely through EDA reduction were denoted as EA.

2.4. Characterization

The as-made samples were characterized with X-ray diffraction (XRD) (X'Pert PRO MPD, Holland) using Cu Ka radiation (k = 1.518 Å). The morphology of the samples was observed by a JSM 7401F (JEOL Ltd., Tokyo, Japan) SEM operated at 3.0 kV and a JEM 2010 (JEOL Ltd., Tokyo, Japan) TEM operated at 120.0 kV. The surface wettability of EGA was evaluated by contact angle measurement, using a Contact Angle System OCA (Data physics), combined with a high-speed camera. Water droplets deposited directly at the top surfaces of EGA, and the water contact angles (WCAs) were measured. XPS was performed using a K-Alpha XPS system with a monochromatic Al Kα X-ray source and a charge neutralizer. Raman spectra were obtained with a RenishawRaman system model 1000 spectrometer. The N_2 adsorption–desorption isotherms of the sample was measured at 77 K using specific surface porosity analyzer 3H-2000PS1. The oil content of oily water was measured by IR petroleum determination instrument. The drop sizes of oil-in-water emulsions were measured by polarized light microscopy (Motic, USA). The diameter distribution of emulsion was measured by Malvern Mastersizer 2000 (Malvern, UK).

2.5. Oil adsorption capacity and reusable performance of EGA

EGA was simply put into a 10 ml injection syringe own to the cylinder shape. The oil adsorption process was designed as followed [15]: Firstly, 12 mg monolithic EGA was put into the injector, then excess amount of oil (kerosene, gasoline, straight-run diesel or 0# commercial diesel) was added into the injection syringe and maintained for 120 min. Finally, the oil was decanted from the injector and hanged for 2 h so that the oil droplets dripped off by gravity. The adsorption capacity of EGA, q_1 (g/g) was calculated according to Eq. (1).

$$q_1 = \frac{m_1 - m_0}{m_0} \tag{1}$$

where m_0 and m_1 designate the mass of the EGA sample before and after adsorption, respectively. The reusable performance was conducted by three ways, including squeezing (Fig. 2a), ethanol washing and combustion up to 15 cycles. Re-adsorption capacities were also calculated by Eq. (1). All the adsorption tests for each kind of sample were repeated for three times at room temperature and the average value was recorded as the final oil adsorption value to ensure the accuracy.

2.6. Continuous treatment of oil-in-water emulsions

The schematic diagram of the continuous oil adsorption equipment of EGA was shown in Fig. 2b. Emulsion was prepared by dispersing certain amount of diesel oil into DI water of 500 ml homogeneously. The initial concentration of oily water was set at around 6000 mg/l for the first 3 h to reduce the experimental time, and then it was set at around 1500 mg/l to ensure the accuracy of the test. The emulsion was fed by pump into the column, at a rate of 5 ml/min, and the packed aerogels (0.2 g) was coated by polyethylene terephthalate (PET) non-woven fabric. The aim of the non-woven fabric coating was to prevent the leakage of peeling graphene sheets from the EGA, just like making tea by using disposable tea bag. The adsorbing capacity of non-woven fabric is very low and can be ignored owing to the significant difference from that of EGA. The concentration of liquid exiting from the column was measured every hour to obtain the adsorption efficiency. Furthermore, the total emulsified oil adsorption capacity of EGA, q_2 (mg/g), was calculated according to Eq. (2).

$$q_2 = \left(\frac{c_0 t_0 - S_{area}}{m_0}\right) \times V \tag{2}$$

where c_0 (mg/L) is the initial concentration of the oily water, t_0(h) is the delivery time. S_{area} is the total areas under curve of continuous treatment, which can be achieved by integration. V (L/h) is the delivery rate,