ARTICLE IN PRESS

Materials Science and Engineering B xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Thermal reduction of graphene-oxide-coated cotton for oil and organic solvent removal

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ARTICLE INFO

Article history:
Received 22 December 2015
Received in revised form 5 May 2016
Accepted 8 June 2016
Available online xxxx

Keywords:
Natural cotton
Oil sorbent
Reduced-graphene-oxide-coated cotton
Hydrophobic cellulose
Oil spill cleanup

ABSTRACT

The reduced-graphene-oxide (RGO)-coated cotton sponge (RGO-Cot) was prepared by simply heating a graphene-oxide (GO)-coated cotton sponge, which was fabricated by dipping a commercial cotton sponge into a GO dispersion, under vacuum at 200 °C for 2 h. The thus prepared RGO-Cot sponges exhibited superhydrophobicity and superoleophilicity, with a water contact angle of 151°. These RGO-Cot sponges could be used for removal of many types of oils and organic solvents as they exhibit absorption capacities in the range of 22–45 times their weight and good absorption recyclability.

1. Introduction

The water pollution due to contaminated oils and organic solvents is one of the urgent environmental problems that the world is facing [1,2]. Oil spills during exploration, production, and transportation of crude oil and chemical leakages are the main causes of this pollution. Therefore, awareness of environmental protection and water recycling should be a significant concern. There have been several methods devised for removing oils and organic solvents from contaminated water, including skimmers, dispersants, and absorbents [3]. Among them, absorbents have emerged as potential materials for effective removal of organic solvents and oils from oceans and rivers because they meet the demands of water purification and oil spill cleanup [4–9]. Generally, absorbent materials that have been investigated for use in organic solvent and oil removal include polymeric sponges [10–13], inorganic-based materials [14–21], and carbon-based materials [22–30].

With outstanding hydrophobicity, graphene and reduced-graphene-oxide (RGO) are promising candidates for selective removal of oils and organic solvents [31–37]. Graphene/RGO sponges and aerogels can be prepared via physical and chemical methods. These materials exhibit high specific surface area, good chemical stability, and high absorption capacity. The use of graphene/RGO sponges and aerogels for oil and solvent removal is very attractive and effective; however, the preparations of these materials are expensive, difficult to scale up, and result in brittle materials. The use of commercial sponges coated with graphene/RGO has attracted attention because of their low cost, flexibility, and recyclability [29,38–42]. Most of these methods use a facile dipping method for the preparation of graphene/RGO-coated commercial sponges.

Cotton is a cheap and porous commercial sponge that absorbs both organic solvents and water. To use commercial cotton as selective sorbent, it should be hydrophobically modified [43–48]. In very recent years, the fabrication of graphene/RGO-coated cotton has been investigated [40,41]. This material showed fairly good selective absorption capacities for various types of oils and organic solvents. For example, Ge and co-workers [42] used a self-assembly technique for the preparation of RGO-coated cotton (RGO-Cot) sponges, which formed after chemical reduction of a GO dispersion in the presence of commercial cotton and a reducing agent. The RGO-Cot obtained by Ge's method showed superhydrophobicity with a water contact angle (WCA) of 152.6°. In another study [41], the RGO-Cot sponge was fabricated by dipping commercial cotton into an RGO dispersion prepared from chemical reduction of a GO dispersion. The RGO-Cot sponge prepared by Sun's method should be coated by polydimethylsiloxane (PDMS) to acquire the WCA of 152°.

In the two above mentioned methods, the formation of RGO from GO was conducted using hydrazine hydrate as reducing agent. Furthermore, in Sun' method the RGO-Cot prepared after dipping cotton into RGO dispersion exhibited low hydrophobicity and the hydrophobic polymer should be used to gain the superhy-

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http://dx.doi.org/10.1016/j.mseb.2016.06.007
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Please cite this article in press as: N.T. Hoai et al., Thermal reduction of graphene-oxide-coated cotton for oil and organic solvent removal, Mater. Sci. Eng. B (2016), http://dx.doi.org/10.1016/j.mseb.2016.06.007

drophobic RGO-Cot. In this study, we propose a facile method for the preparation of a RGO-Cot sponge with the WCA of 151° without using any reducing agents or hydrophobic polymers. The major difference between this study and previous studies of Ge et al. and Sun et al. is that the reducing agent and hydrophobic polymer were not used in this study to obtain superhydrophobic RGO-Cot. The GO-Cot was first prepared by dipping commercial cotton into a GO dispersion. The RGO-Cot was then fabricated by heating the GO-Cot under vacuum at 200 °C for 2 h. The thus prepared RGO-Cot sponge was characterized using water contact angle, Raman spectroscopy, scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and absorption capacity measurements.

2. Experimental

2.1. Materials

Graphite powder, $K_2S_2O_8$, P_2O_5, and $KMnO_4$ were supplied by Sigma-Aldrich. Concentrated H_2SO_4, concentrated HCl, and 30% H_2O_2 solution were purchased from Xilong Chemical (China). Natural cotton was supplied by Bach Tuyet Cotton Corp. (Vietnam). Cooking oil was supplied by Tuong An Vegetable Oil JSC (Vietnam). Motor oil was purchased from Castrol Vietnam. Crude oil was received as a gift from Research and Engineering Institute (R&EI), Vietsovpetro JV (VSP). Acetone, ethanol, hexane, toluene, and chloroform were purchased from Xilong Chemical Co., Ltd.

2.2. Preparation of graphene-oxide

Graphene oxide (GO) was synthesized from graphite powder (Sigma-Aldrich) by the modified Hummers method [49]. Graphite powder (10 g) was added to an 80 °C concentrated H_2SO_4 solution (15 mL), then 10 g of $K_2S_2O_8$ and 10 g of P_2O_5 were also added. The resulting dark blue slurry was heat isolated and cooled to room temperature over 6 h. The slurry was then diluted with distilled water, filtered, and washed until rinse water became neutral. The product was dried under vacuum at room temperature for 1 day and referred to as preoxidized graphite. The preoxidized graphite was then oxidized by Hummers' method [50]. To 230 mL of cold concentrated H_2SO_4, 10 g of preoxidized graphite powder was added, followed by the gradual addition of 30 g of $KMnO_4$ with stirring and cooling to prevent the temperature of mixture from reaching 20 °C. The mixture was then stirred at 35 °C for 4 h. Then, 460 mL of water was then added to the mixture and allowed to stand for 30 min. The reaction was terminated by adding a large amount of distilled water (1.4 L) and 25 mL of 30% H_2O_2 solution. The resulting bright yellow mixture was washed with 2.5 L of 1:10 HCl solution. The mixture was then subjected to centrifugation (9000 rpm, 90 min) and washed with distilled water. The centrifugation procedure was repeated until the rinse water became neutral. During the addition of water, the supernatant layer was collected and the GO film was formed after evaporation of water at ambient temperature for 2 weeks. The GO dispersions for preparation of GO-coated cotton were achieved by dissolving appropriate amounts of GO film into 40 mL of distilled water followed by sonication for 15 min.

2.3. Preparation of GO-coated cotton and RGO-coated cotton

For various concentrations of graphene oxide in distilled water (0.05, 0.1, 0.2, 0.3, and 0.5% w/v), 0.4 g of natural cotton samples were immersed in the mixtures for 1 day to allow maximum coating of GO onto the cotton surfaces. The GO-coated cotton was achieved by gently pressing the cotton samples and drying under vacuum for 2 days at ambient temperature. The RGO-coated cotton samples were prepared by heating GO-coated cotton samples under vacuum at 200 °C for 2 h.

2.4. Measurements

The morphology of the material was examined using a field-emission scanning electron microscope (FE-SEM, JSM-6701F). The water contact angles (WCAs) of the cotton sponges were measured using an optical contact angle meter (OCA, Data Physics) with 4 µL water droplets. Raman spectra were measured using a HORIBA JobinYvonLabRAM 200. The atomic force microscopy (AFM) images were measured using a Nanotec instrument with WSxM 5 software. The X-ray diffraction (XRD) profiles were measured using a Bruker powder X-ray diffractometer and Cu-Kα irradiation. The X-ray photoelectron spectroscopy (XPS) results were confirmed by an AES-XPS ESCA2000 instrument with an Al-Kα source. The absorption capacities of the cotton sponges for oils and organic solvents were measured by immersing the modified cotton samples into various organic solvents and oils for 30 min until they were saturated. The absorption capacity, A, was determined by the equation $A = (W_{\text{saturated}} - W_{\text{initial}})/W_{\text{initial}}$, where $W_{\text{saturated}}$ and W_{initial} are the weights of the modified cotton before and after absorption. For the recyclability tests, the organic solvents absorbed by RGO-coated-cotton were desorbed by distillation using vacuum at ambient temperature.

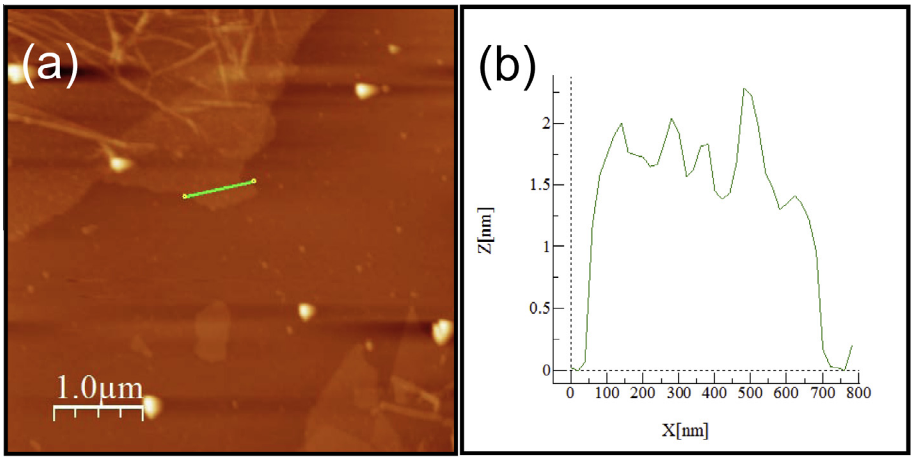

Fig. 1. (a) A typical AFM image of GO nanosheets. (b) Thickness of GO nanosheet of approximately 2 nm.

Please cite this article in press as: N.T. Hoai et al., Thermal reduction of graphene-oxide-coated cotton for oil and organic solvent removal, Mater. Sci. Eng. B (2016), http://dx.doi.org/10.1016/j.mseb.2016.06.007