Polymer/reduced graphene oxide functionalized sponges as superabsorbents for oil removal and recovery

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ABSTRACT

Polyurethane dish-washing (PU-DW) sponges are functionalized sequentially with polyethylenimine (PEI) and graphene oxide (GO) to form PEI/reduced graphene oxide (RGO) PU-DW sponges. The PEI/RGO PU-DW sponge consists of PEI/RGO sheets having numerous pores, with diameters ranging from 236 to 254 nm. To further enhance hydrophobicity and absorption capacity of oil, PEI/RGO PU-DW sponge is further coated with 20% phenyltrimethoxysilane (PTMOS). The PTMOS/PEI/RGO PU-DW sponge absorbs various oils within 20 s, with maximum absorption capacity values of 880% and 840% for bicycle chain oil and motorcycle engine oil, respectively. The absorbed oils were released completely by squeezing or immersed in hexane. The PTMOS/PEI/RGO PU-DW sponge efficiently separates oil/water mixtures through a flowing system. Having the advantages of faster absorption rate, reusability, and low cost, the PTMOS/PEI/RGO PU-DW sponge holds great potential as a superabsorbent for efficient removal and recovery of oil spills as well as for the separation of oil/water mixtures.

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1. Introduction

Oil spills in sea and land have raised serious ecological concerns (Kirby and Law, 2010). Low-cost, effective, and high-speed approaches for removal of oil spills are thus important. With interesting features of lightweight, elasticity, and/or buoyancy, various absorbents, including silica aerogels (Reynolds et al., 2001), zeolites (Sakthivel et al., 2013), modified organophilic clays (Adebajo et al., 2003), cellulosic materials (Sun et al., 2002), exfoliated graphite (Toyoda and Inagaki, 2000), expanded perlite (Bastani et al., 2006), activated carbon (Ahmad et al., 2005) and graphene (Nguyen et al., 2012), have been used for removal of oil spills. Numerous processing steps, tedious pretreatments, and high costs for the production of the adsorbents are however problematic. Alternatively, synthetic polymers such as polypropylene (Wei et al., 2003), polyurethane (Shimizu et al., 1997), and polystyrene (Wu et al., 2012) have been used for cleanup of oil spills. However, these polymers with poor biodegradability cause various harmful problems on the ecosystem (Adebajo et al., 2003). In addition, cost for their production and handling of the used polymers is another concern. Low-cost and biodegradable natural absorbents have been used for oil recovery (Choi and Cloud, 1992); however, poor hydrophobicity and low oil absorption capacity limit their practicality. It is thus highly indispensable to develop eco-friendly, low-cost, and porous absorbents for rapid removal of oil spills.

Recently, composites and hydrogels of graphene oxide (GO) have become popular for water purification (Guo et al., 2015; Jiao et al., 2015; Wang et al., 2015). Having interesting properties of hydrophobic surfaces, large surface area, and high mechanical strength, reduced graphene oxide (RGO) has become one of the promising absorbent for removal of oils (Niu et al., 2012). Although direct reduction of GO by hydrazine formed smooth RGO sheets on the sponge surfaces, their stability was poor. Moreover, smooth morphology of the RGO sheets decreases their oil absorption efficiency. The preparation of rough and porous RGO sheets on the sponge surfaces through a cost-effective approach is a plausible solution for enhancing the stability and the oil absorption capacity. Nonetheless, conventional approaches that require hard and soft templates, expensive surfactants and toxic chemicals to form the pores on the RGO sheets should be avoided for safety. Though functional graphene/polypyrrole foams have been used for removing oils (Li et al., 2013), it is difficult to remove the oil from the RGO surface as a result of their strong absorption. Burning of these oil absorbed materials has been suggested, but it raises safety and ecological concerns.

Polyethyleneimine (PEI) is a polymer containing many amino groups and is soluble in hot water at low pH values or in chloroform. PEI can be used to modify various substrates through simple dynamic

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coating or covalent bonding. With its polycationic character, PEI has been used to modify the surfaces of cellulose paper to enhance its hydrophobicity (Koga et al., 2011). Through the formation of amide bonds between its amino groups and the carboxylic groups on the RGO surface, PEI has been used to provide positive charges on the surface of RGO (Cai et al., 2012). Having amino groups tethered on the backbone of PEI, the positive surface of PEI-modified RGO is ready for adsorption of anionic species.

The aim of this work is to prepare low-cost and effective absorbents for removal of oil spills and then recovery of the oil. To achieve these goals, a simple, hydrothermal approach was demonstrated for the preparation of PEI functionalized porous RGO sheets on polyurethane dish-washing (PU-DW) sponges. Hydrazine assisted hydrothermal treatment facilitates the cutting of smooth GO sheets by PEI and the removal of some functional groups of GO, producing rough and highly porous PEI/RGO sheets on PU-DW sponges. To further improve the capacity of the as-prepared PEI/RGO PU-DW sponge for absorption of oil and then to remove the oil from the sponge more efficiently, phenyltrimethoxysilane (PTMOS) that has been widely used as a sol-gel precursor for providing hydrophobic coatings was used to further modify its properties (Azenha et al., 2005). The PTMOS coating increased the hydrophobicity and thus increased diffusion rate of oil through the porous networks, leading to increased capacity and rate for absorption/desorption of oil.

2. Experimental

2.1. Materials

PU-DW sponge, PU packing sponge, PU car-washing sponge, and PU commercial sponge, melamine sponge, and cellulose sponge were purchased from a local super market. GO (5 g L^{-1}) dispersed in water was obtained from Graphene Supermarket (Calverton, NY, USA). Hydrazine monohydrate (80%) was obtained from Showa (Meguro, Tokyo, Japan). Acetone, diesel oil red O, ethanol, n-hexane, nitric acid and PEI aqueous solution (50-wt%) were received from Sigma Aldrich (St. Louis, MO, USA). Ethylenediaminetetraacetic acid (EDTA), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and PTMOS (>94%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Bicycle chain oil was obtained from a bicycle repairing shop, Taipei, Taiwan. Engine oil that had been used in a motorcycle for at least 1000 km was obtained from a motorcycle repairing shop, Taipei, Taiwan. All the cooking oils used in this study were purchased from a supermarket. All the oils were stained with oil red O before use in testing the oil absorption capacity of the sponges. Ultrapure water was obtained using a Milli-Q ultrapure (18.2 MΩ cm) system from Merck Millipore (Billerica, MA, USA).

2.2. Instrumentation

The morphologies and elemental compositions of PEI/RGO and PTMOS/PEI/RGO sheets were obtained using a JSM-1200EX II transmission electron microscope (JEOL, Tokyo, Japan) and a Hitachi S-2400 scanning electron microscope (Hitachi High-Technologies, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer, respectively. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images with in-situ EDS and elemental mapping were taken using Philips Tecnai F20 G2 FEI-TEM (Roanoke, VA, USA). For TEM, HAADF-STEM and X-ray photoelectron spectroscopy (XPS) measurements, PEI/RGO and PTMOS/PEI/RGO PU-DW sponges were soaked in 2 mL of ultrapure water prior to sonication for 5 min to remove the PEI/RGO and PTMOS/PEI/RGO sheets, respectively. The aqueous solution of PEI/RGO and PTMOS/PEI/RGO (2 μL) were separately placed onto formvar/carbon film Cu grids (200 mesh; Agar Scientific) and dried overnight under ambient conditions (27 °C, 1 atm). Each of the aqueous solutions of PEI/RGO or PTMOS/PEI/RGO (10 μL) was placed

on a Si substrate and dried overnight, which was then subjected to XPS measurements using a VG ESCA210 electron spectroscope from VG Scientific (West Sussex, UK). Prior to SEM measurements, each of the aqueous solutions of PEI/RGO or PTMOS/PEI/RGO (10 μL) was placed on Si substrates and dried overnight. UV–Vis absorption spectra of aqueous solutions of PEI/RGO taken at different time intervals were recorded using a Cintra 10e double-beam UV–Vis spectrophotometer (GBC Scientific Equipment, Victoria, Australia). Fourier transform infrared (FTIR) spectrum of PEI/RGO separated from the sponge through ultrasonication in aqueous solution was recorded using a Varian 640 FTIR spectro-photometer. Prior to FTIR analysis, aliquots (10 μL) of aqueous solution of PEI/RGO was dropped on CaF$_2$ disks and dried overnight. Raman spectra of GO and PEI/RGO samples prepared on silica wafers were recorded using a Raman spectroscopic system (Dongwoo Optron, KyungGiDo, Korea) equipped with a diode-pumped solid-state laser (operated at 532 nm and 100 mW) as the excitation source, with an accumulation time of 300 s. Contact angle measurements were made using a contact angle system (FTA 125) from First Ten Angstroms (Portsmouth, VA, USA). Bright-field images were acquired using an Olympus IX71 fluorescence microscope (Tokyo, Japan).

2.3. Preparation of PTMOS/PEI/RGO PU-DW sponges

PU-DW sponge blocks (2 × 2 cm) were washed with copious amounts of ultrapure water, and acetone through ultrasonication for 5 min prior to use. The clean sponge blocks were soaked in solutions containing PEI (5–50%), in which aliquots (19 mL) of mixtures of EDTA (4.49–9 mM), GO (0.1–2 mg mL^{-1}) and EDC (27.3–50 mM) were added to separately. After 24 h, the amino groups of PEI were cross-linked with the carboxyl groups of EDTA through the formation of covalent amide bond via EDC coupling. Then, aliquots (0.25–1 mL) of hydrazine were added separately into the mixtures, which were further heated at 95 °C for 3 h. During heating, reduction of GO by hydrazine and the cutting of GO sheets by PEI occurred in one step, leading to the formation of porous PEI/RGO sheets on the sponges. As a control, porous PEI/GO PU-DW sponge was prepared using the procedure same as that for functionalization of PEI/RGO PU-DW sponge, but in the absence of hydrazine at the ambient temperature (25 °C). The resulting mixture containing the sponge was left undisturbed at ambient temperature for at least 1 h to allow the amino groups of PEI to interact with the oxygen-containing groups on the surface and edge of the GO sheets. The as-obtained porous PEI/GO PU-DW sponges were dried overnight at 60 °C prior to use. To provide hydrophobic coating, the PEI/RGO PU-DW sponges were soaked separately in aliquots (20 mL) of PTMOS (5–20%)/n-hexane mixtures for 30 min and dried at 60 °C for at least 30 min. Similar synthetic procedures were applied for the preparation of porous PTMOS/PEI/RGO sheets on melamine sponges, PU car-washing sponges, and cellulose sponges. The oil absorption capacities of the bare PU-DW sponge, PTMOS PU-DW sponge and the PTMOS/PEI PU-DW sponge were tested as controls.

3. Results and discussion

3.1. Formation of PTMOS/PEI/RGO

Scheme 1 summarizes the formation of PTMOS/PEI/RGO PU-DW sponge through three steps, which include modification of the sponge with the porous PEI/GO sheets, reduction of PEI/GO sheets, and modification of PTMOS to provide hydrophobicity. To improve the stability of PEI/GO coating, the amino groups of PEI were cross-linked with the carboxylic groups of EDTA through the formation of amide bonds in the presence of EDC. The PEI polymer through its amino groups interacted with oxygen-containing groups (carboxyl,