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Ultrasonic-microwave assisted synthesis of stable reduced graphene oxide modified melamine foam with superhydrophobicity and high oil adsorption capacities

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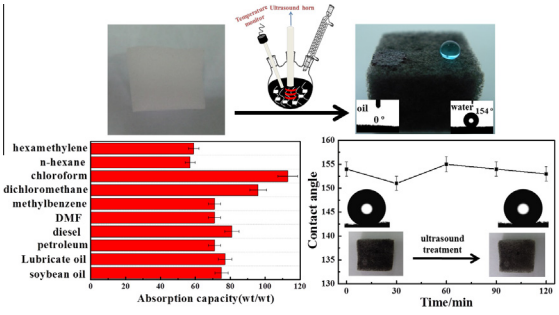
HIGHLIGHTS

- Ultrasonic-microwave synergistic method was used to produce the RGMF.
- The UMRGMF exhibited superhydrophobicity with water contact angle exceeding 150°.
- The UMRGMF showed a high oil adsorption capacity and excellent recyclability.
- The UMRGMF displayed high stability against cavitation erosion and corrosion liquids.

GRAPHICAL ABSTRACT

Superhydrophobic reduced graphene oxide modified melamine foam (RGMF) was prepared via a facile ultrasonic-microwave synergistic method and it showed high selectivity for collecting various oils and organic solvents from water and excellent recyclability and stability.



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ABSTRACT

We herein report the fabrication of recyclable, stable and cost-effective superhydrophobic reduced graphene oxide modified melamine foam (RGMF) through ultrasonic-microwave synergistic method for the first time. In the synthesis process, ultrasonic and microwave irradiation not only shortened the reduction time of graphene oxide (GO) with the existence of reducing agent, but also considerably enhanced the firmness of reduced graphene oxide (rGO) anchored onto the melamine foam (MF). The structure and property of the obtained RGMF were characterized by XRD, Raman, SEM and contact angle measurements. The results showed that the skeletons of MF were completely covered with rGO layers which were compact and full of wrinkles. The as-prepared RGMF was superhydrophobic without further modification. Besides, the RGMF showed excellent selective adsorption capacity of various oils and organic solvents from water. The maximum oil adsorption capacity was 112 times of the weight of the initial MF, and the adsorption capacity of the RGMF did not deteriorate after it was reused 20 times. More importantly, the RGMF showed good stability against cavitation erosion and corrosion liquids. All these features made the as-prepared material an ideal candidate for removal and collection of oils and organic solvents from water.

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1. Introduction

Over the years, considerable attention has been focused on oil spill and chemical leakage due to a series of major accidental releases of oil and chemical pollutants into the marine ecosystem [1]. Once oil spill and chemical leakage happened, numerous sea birds, mammals and seaweed will suffer sustained serious damage. The negative consequences of oil spills and chemical leakage also affect human health. As a result, the development of safe cleanup methods is extremely required.

Typical strategies to remediate accidental oil release include mechanical collection [2], chemical dispersants [3], bioremediation [4] and in situ burning [5]. However, those techniques are time-consuming, environmentally unfriendly, and expensive. Recently, filter materials and absorbents with special wettability for oil/water separation have received a high level of attention, because they can protect environment from secondary pollution and reduce the loss [6,7]. Filter materials have limitations to deal with oil spills, as they need to gather polluted water first and then filter it, whereas absorbents have the potential for cheap, simple, and fast cleanup of oil spills. So far, a wide variety of absorbents used for oil remediation have been reported, e.g., synthetic polymers [8], zeolites [9], clays [10] or natural materials (such as peat moss [11] and straw [12]). Although widely used in practical applications, these absorbents have many disadvantages, such as low adsorption capacity and separation efficiency, poor selectivity and stability. Therefore, it is urgent to find an ideal absorbent material to solve the problems.

Recently, the research on both superhydrophobic and superoleophilic porous 3D materials have attracted much attention for their outstanding application in selective adsorption of oils and organic solvents from water. A facile method to obtain such materials is to modify commercial foams with hydrophobic materials, including polydimethylsiloxane (PDMS) [13], lauryl methacrylate [14], carbon nanotubes (CNTs) [15] and reduced graphene oxide (rGO) [16–18]. rGO is a two-dimensional crystal with a single layer of carbon atoms [19]. It is intrinsically hydrophobic and oleophilic and can make superhydrophobic and superoleophilic surface by tailing its structure [20] and morphology [21]. Besides, the mechanical stiffness [22], high thermal stability [23], ultra-light and fire-resistant properties [24] also make rGO a good candidate to modify commercial foams. For instance, Zhu et al. prepared a rGO coated melamine foam by squeezed/released foam in the graphene oxide (GO) suspension for three times and heated at 180 °C for 6 h [25]. Zhao et al. reported an efficient and recyclable graphene coated melamine foam by immersing the foam in mixed solutions with GO and $NH_3{\cdot}H_2O/C_2H_5OH$ for 3 h and dried in a vacuum oven at 30 °C for 24 h [26]. However, these processes of preparing rGO modified foams are always time-consuming or complicated and the synthesized foams have poor stability, which are not suitable in industrial production.

Herein, we proposed a facile synthesis process of rGO modified melamine foam (RGMF) through ultrasonic-microwave synergistic method. Both ultrasonics sonochemistry and microwave chemistry have opened up new advances in synthesis of nanomaterials and nanocomposites [27,28]. They could accelerate reaction rate, reduce processing time, increase product yields, and strengthen the stability of composite materials. However, the reduction of GO to rGO by ultrasonic-microwave synergistic effect has not been reported. In this paper, the structure, morphology and surface wettability of the obtained RGMF were characterized. Then, the selective adsorption capacities of various oils and organic solvents from water were tested. Finally, the stability of the RGMF against cavitation erosion was investigated for the first time. These results may provide a potential scale-up approach to prepare superhydrophobic sponges for oil/water separation.

2. Experimental

2.1. Materials

Graphite powder (purity >99.95%) was procured from Aladdin (Shanghai, China). Ethylenediamine was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Melamine foams (MFs) were from Shanghai Foam Materials Co. In order to remove the surface contamination, MFs were immersed in ethanol with ultrasound treatment, and then dried in an oven before use. All reagents were analytical reagents and used without further purification.

2.2. Preparation of GO solution

GO was prepared from purified natural graphite by a modified Hummer's method [29]. Briefly, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (120:14 mL) was added to a mixture of graphite flakes (1.0 g) and $KMnO_4$ (6.0 g). The mixture formed above was then heated to 50 °C and stirred for 10 h. After that, the mixture was cooled to room temperature and poured onto ice (400 mL) with 30% H_2O_2 (4 mL). For purification, the mixture was washed in succession with distilled water, 30% HCl and ethanol. The resulting material was vacuum-dried overnight at room temperature and then dispersed into distilled water. GO solution was obtained after ultrasonic treatment.

2.3. Preparation of RGMFs

The synthesis of rGO modified melamine foam via ultrasonic-microwave synergistic method (UMRGMF) was conducted with a high-intensity ultrasonic and microwave horn (HX-300A, Beijing Xianghao Science and Technology Development Co., LTD, China). 50 mL GO solution (2 $mg{\cdot}mL^{-1}$) and 1 mL ethylenediamine were put into a 100 mL round-bottom flask. The mixture was heated up to 110 °C under microwave irradiation (2450 MHz, 300 W) and discontinuous ultrasonic irradiation (25 kHz, 750 W at 50% efficiency, 2 s insonation and 1 s interruption) for 30 min. The color of the solution turned black which indicated that rGO suspension was obtained. Then, MF was immersed into the rGO solution and continued reaction for another 30 min to obtain the UMRGMF. Finally, the UMRGMF was washed with copious amounts of distilled water and dried under vacuum at 60 °C for 24 h. For comparison, a dip coating method to fabricate rGO modified melamine foam (DRGMF) was conducted under the identical condition except for the absence of the irradiation of ultrasound and microwave.

Scheme 1 is a schematic illustration of the synthesis of UMRGMF. The white MF turned completely black under ultrasonic-microwave synergistic treatment, indicating that rGO was successfully anchored onto the MF.

2.4. Characterization

Scanning electron microscope image (SEM) was taken on a Hitachi S4800 operating at 5.0 kV. Powder X-ray diffraction (XRD) was carried out on Bruker axs D8 Discover (Cu Ka = 1.5406 Å) at a scan rate of 2°min^{-1} in the 2θ range of 10–30°. The Raman spectra were recorded by using a Horiba Jobin-Yvon LabRam HR800 Raman micro-spectrometer, with an excitation laser at 633 nm. The Fourier transform infrared spectroscopy (FTIR) spectra were collected by a Bruker Tensor 27 FT-IR spectrometer (Bruker, Germany) in a range of 400–4000 cm^{-1}. Static contact angles (CAs) of the as-prepared foams were measured by Dataphysics OCA 20 (Germany) contact angle measuring instrument. The sliding behavior of a water droplet on the UMRGMF was measured by electronic tilting