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Full Length Article

Improved interfacial floatability of superhydrophobic and compressive S, N co-doped graphene aerogel by electrostatic spraying for highly efficient organic pollutants recovery from water

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ABSTRACT

Sulfur and nitrogen co-doped graphene aerogel with Janus wettability of superhydrophobic/superhydrophilic was prepared with hydrothermal reduction combined with electrostatic spraying method. The upper surface exhibited an interconnected and porous 3D network with superhydrophobic property (water contact angle > 150°), while the under surface displayed a continuous membrane structure possessing rich wrinkles with superhydrophilicity (water contact angle < 5°). The hydrophobic mechanism was further demonstrated by FT-IR, XPS and theoretical calculations, resulting from the oxygen-containing functional groups decrease and the changes of surface electrostatic potentials and charge densities due to S, N co-doping into the graphitic network. More importantly, the Janus superwettability of the graphene aerogel enables it to stabilize at multiple interfaces, such as air/water, air/hexane, hexane/water and water/CCl_4 interfaces, resolving the floating problem under windy conditions for the ultralight and hydrophobic materials, which is vital for the practical applications. The as-synthesized graphene aerogel also exhibits remarkable compressibility with full recovery even at 90% strain, and remains over 50% of maximum stress even after 1000 cycles at 90% strain. With high BET surface area (406.80 m^2/g), high compressibility and robust structure, our graphene aerogel shows fast adsorption with high capacity and excellent recyclable performance, achieving up to about 65–192 times of its own weight for various oils and organic solvents.

1. Introduction

The fast development of modern transportation induces the increase of frequent accidents, such as discharge of the industrial oily wastewater, leakage of organic solvents, and spillage of crude oil, which have already caused serious global environmental crises [1–7]. Various methods have been developed to address these issues, such as in situ burning, using chemical agents (dispersants and solidifiers), bioremediation, and physical recovery (booms, skimmer vessels, and adsorbent materials) [5,8–12]. Among these methods and technology, the utilization of adsorbent materials is one of the most attractive processes due to its simple operation, low cost and in situ removal of oil and organic solvents from the water surface. The traditional adsorbents mainly include natural organic sorbents [13,14], inorganic sorbents [15,16], and synthetic organic sorbents [17–19], which usually possess the oil adsorption capacity of about 2–10 g/g, ~20 g/g and 15–25 g/g, respectively. Due to their low oil adsorption capacity and low oil/water separation efficiency, several efforts have been made to improve the porosity and hydrophobicity [15,19–21]. For example, the hydrophobic property of the traditional sorbents could be highly enhanced with surface modification strategy [20–22]. By using the surface modification method, the cost of the sorbents could be significantly reduced. However, the relatively low adsorption capacity and poor recyclability still limits their practical application. As attractive alternatives, the recently developed carbon-based adsorbents [23–25] and synthetic polymer materials [26–28] are considered as the promising candidates because of their intrinsic hydrophobicity, lipophilicity and high oil-sorption capacity.

As one promising carbon-based material, graphene displays significant potential for building porous, multifunctional, and high

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performance macroscopic three-dimensional aerogel [29–32] as a result of its remarkable blocking effect. Accordingly, graphene-based aerogel shows many dramatic properties, such as high specific surface area, ultralow density, superelasticity and chemical stability, making it the promising adsorbent for oil or organic solvent [29,30,33–39]. However, self-assembled graphene hydrogels using GO as the only precursor, which are driven by van der Waals force, hydrogen bonds and π-π stacking interactions of graphene sheets [40], are usually very weak and easily broken because of disappearance of these driven forces in the freeze-drying process. Therefore, cross-linking agents or polymers have been introduced into GO solution to enhance the interactions of graphene sheets to form porous 3D bulks, such as N-doped graphene aerogels [39,41–43], polymer-graphene sponges [44,45], and graphene@CNTs aerogels [33,37]. For N-doped graphene aerogels, the interaction between graphene sheets was enhanced by adding hydrazine [46], ethylenediamine [43], dopamine [41], melamine [42], and ammonium hydroxide [47], and so on. However, some of these aerogels still exhibit aggregation on the surface [41,43]. Furthermore, because of their ultralow density and hydrophobic property, the graphene-based adsorbents are difficult to float stably on the water surface in the practical application.

To address the above problems, a Janus structure of superhydrophobic/superhydrophilic S, N co-doped graphene aerogel/GO membrane (SNGA/GM) was designed, which has high specific surface area and superelasticity, and can stabilize at multiple interfaces. In the configuration, the co-doping of S and N enhanced the hydrophobicity and mechanical property, and the hydrophilic GO membrane (GM) makes it tightly cling to the water surface. Scheme 1 illustrates the preparation process of the Janus SNGA/GM materials, including that (a) SNGA was synthesized using a hydrothermal method and freeze-drying process, and then annealed at 800 °C for 1 h in the Ar atmosphere; and (b) superhydrophobic/superhydrophilic SNGA/GM was achieved by modifying one surface of SNGA with superhydrophilic GO membrane by electrostatic spraying method. The binary wettability of SNGA/GM makes it stable at the multiphase interfaces. Our experiments also demonstrated that SNGA/GM has high adsorption capacities for oils and organic solvents with about 65–192 times of its weight, and the adsorbates can be efficiently desorbed and recycled after squeezing due to its high compressibility.

2. Experimental section

2.1. Materials

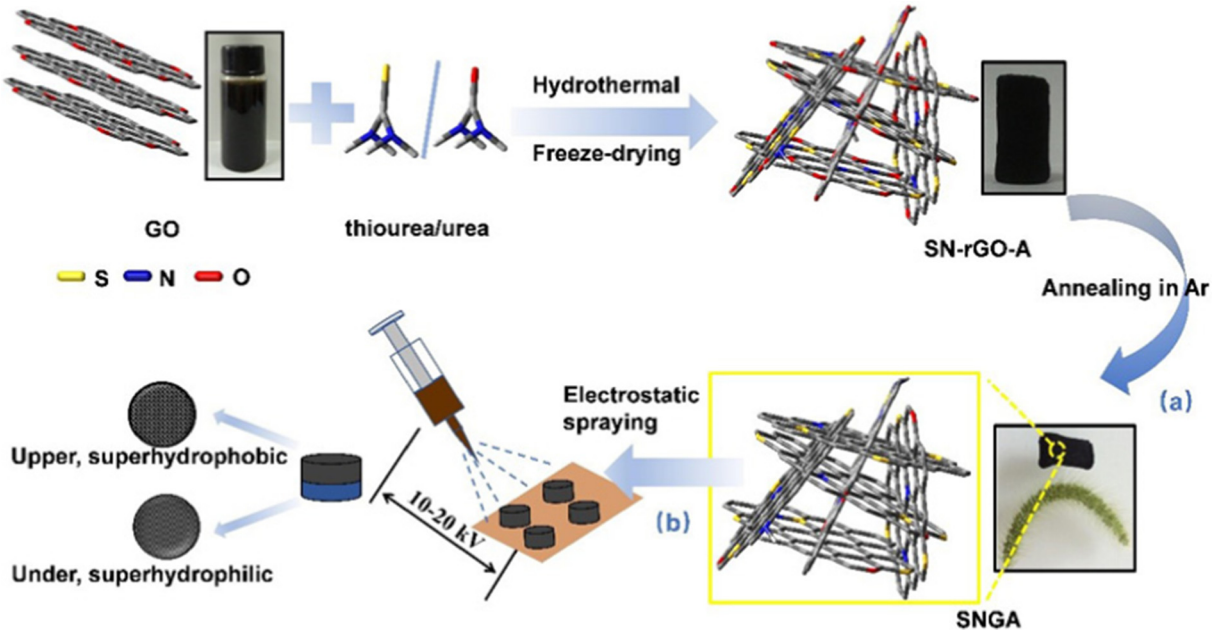
Expandable graphite was purchased from Henglide Graphite Company (Qingdao, China). Thiourea, urea, H_2SO_4, $NaNO_3$, $KMnO_7$, H_2O_2, and HCl were all purchased from Sinopharm Chemical Reagent Co., Ltd., China. Toluene, CCl_4, dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), acetone, ethanol, hexane, petroleum ether, Sudan red III and methylene blue were obtained from Sigma-Aldrich. Diesel were bought from China Petrochemical Corporation.

2.2. Preparation of GA, NGA, SNGA and SN-rGO-A

GO was synthesized with a modified Hummers method [48,49], and has been mentioned in the previous report [50]. The GA, NGA and SNGA were prepared via a hydrothermal reduction following by the carbonization method. In a typical synthesis, a mass of 1.8 g thiourea was added into a 40 mL GO water solution (1.5 mg·mL^{-1}). The mixture was then transferred into a 50 mL Teflon-lined autoclave and heated up to 180 °C for 12 h. The SN-rGO-A was obtained after vacuum freeze drying the washed formed hydrogels for 48 h. SNGA was achieved by annealing SN-rGO-A at 800 °C for 1 h under Ar atmosphere. For contrast, the NGA and GA were prepared using the same method as SNGA, with introducing urea instead of thiourea and without introducing any other reagent. Additionally, SGA was usually reported to be prepared by the solvothermal methods using ethanol as the solvent and diphenyl disulfide (DDS) as the sulfur source [51], or using dimethyl sulfoxide (DMSO) as the solvent as well as the sulfur source [52–54], which are not consistent with our preparation process by using water as the solvent for synthesizing other graphene-based aerogels (GA, NGA and SNGA). Therefore, in our work, SGA was obtained by sulfurizing graphene aerogel (GA) in the H_2S atmosphere with a flow rate of 0.2 L/min for 30 min at 450 °C.

2.3. Preparation of Janus SNGA/GM

Janus SNGA/GM was fabricated by modifying one surface of SNGA with GO membrane by an electrostatic spraying method. Briefly, the obtained SNGA was cut into small pieces with about 1 cm high and



Scheme 1. Schematic illustration of preparation of (a) SNGA and (b) SNGA/GM.