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The molecular level control of three-dimensional graphene oxide hydrogel structure by using various diamines

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HIGHLIGHTS

- The well-controlled three-dimensional networks of graphene oxide hydrogels (GOHs) are realized.
- Amide linkages are formed between two graphene oxide sheets by the condensation reaction.
- GOHs fabricated by using pPDA facilitate the removal of organic dyes such as methylene blue.

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ABSTRACT

The well-controlled and covalently cross-linked three-dimensional networks of graphene oxide hydrogels (GOHs) are realized by using two different diamines, such as *o*-phenylene diamine (oPDA) and *p*-phenylene diamine (pPDA). Amide linkages are formed between two graphene oxide (GO) sheets due to the condensation reaction between diamines and carboxylic acids on the GO sheets. The surface area and pore volume of pPDA-GOH are twice the size of those of oPDA-GOH due to the longer amine-to-amine distance. Aromatic amine-based hydrogels exhibit enhanced mechanical strength compared to that of aliphatic amine due to the presence of an aromatic ring between amide linkages. Highly-developed 3D networks of GOH fabricated by using pPDA facilitate the removal of organic dye such as methylene blue in aqueous solutions at various pH conditions. It also shows improved regeneration ability in repeated adsorption tests.

1. Introduction

Graphene, which is one of the most promising candidates for the next generation active materials of electronics, polymer composites, sensors, catalysis, pollution controls, energy conversion and storage devices, has been explored extensively due to its outstanding electrical, thermal, and mechanical properties [1–7]. However, the relatively low surface area of the final product, which is caused by its strong van de Waals force between two-dimensional (2D) graphene sheets, is considered to be one of the most significant issues that needs to be solved prior to use in applications in which the performance of the device is generally proportional to the surface area of the active materials. The large surface area three-dimensional (3D) graphene structure can be fabricated either by assembling 2D graphene oxide (GO) nanosheets by flow-directed assembly, evaporation induced self-assembly, the Langmuir–Blodgett technique, layer-by-layer deposition and one-step hydrothermal reduction of aqueous GO dispersion, or by chemical bonding between GOs with multifunctional crosslinking agents such as ethylene diamine (EDA), and generally the chemically bonded 3D structures show better robustness than physically assembled structures [8–13].

In general, dye-containing wastewater should be treated by particular methods such as membrane filtration, ion-exchange and physicochemical adsorption, as the organic dyes are commonly non-degradable with UV and visible light and are stable for physical, biological and chemical treatments [14]. In this regard, the self-assembled 3D structured GO can be effectively used for the treatment of organic dye containing wastewater due to its large surface area and strong interactions between GOs and dye molecules [14].

In this work, we designed and fabricated 3D GO structures at a molecular level using different aromatic diamines such as *o*-phenylene diamine (oPDA) and *p*-phenylene diamine (pPDA) as the crosslinking agents, and compared the physical and mechanical properties between them according to the structures of the diamines. In addition, the adsorption capability of organic dye was

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tested according to the different hydrogel structures fabricated under various conditions. By changing the diamine structure, we can precisely control the properties of the final 3D GO hydrogel structures at a molecular level and can effectively use them as well-designed and excellent adsorbents for organic dye removal applications.

2. Experimental

2.1. Chemicals

Expandable graphite (Grade 1721) was purchased from Asbury Carbon Co. (USA). The EDAs, oPDA, pPDA, methylene blue (MB), concentrated sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrochloric acid (HCl), nitric acid (HNO_3), ethanol (C_2H_5OH) and hydrogen peroxide (H_2O_2) were purchased from Sigma–Aldrich Co. (USA). All of the chemicals were used as received without further purification steps.

2.2. Preparation of GOs

The expandable graphite was mixed with HNO_3 and $KMnO_4$ after thermal expansion by microwave heating for 1 min. GO was prepared from expanded graphite using the modified Hummer's method described in our previous report [13,15]. Firstly, 500 mL of concentrated H_2SO_4 was charged into a 3 L beaker equipped with a Teflon impeller, and 5 g of expanded graphite was slowly added under stirring at 0 °C. Then 30 g of $KMnO_4$ was slowly added while the temperature was maintained below 20 °C, and the suspension was stirred for 2 h at 35 °C to oxidize and exfoliate the expanded graphite. To dilute the suspension, 6 L of deionized water was slowly added while the temperature was maintained below 70 °C and was stirred for 1 h, and 50 mL of H_2O_2 (30 wt%) was slowly added and vigorous bubbles were observed accompanied by a color change from dark brown to yellow. The suspension was centrifuged and washed four times with a 10% HCl solution to remove metal ions, followed by centrifugation at 10,000 rpm and washing with deionized water to completely remove the acid until the pH of the GO suspension reached 7. The concentration of the GO was adjusted to 10 mg mL^{-1} in the aqueous solution for further experiments.

2.3. Synthesis of 3D GO hydrogel

20 mg of oPDA or pPDA was dispersed into 10 mL of the GO solution with various concentrations of 1, 2.5 and 5 mg mL^{-1} followed by ultrasonication at 10 °C for 2 h. The crosslinking reaction was performed at 90 °C for 8 h. The resulting GO hydrogel (GOH) was submerged into 2 L deionized water 5 times for 1 h each time in order to remove the unreacted oPDA or pPDA. To remove water without destroying the 3D networks, the GOH was freeze dried at −37 °C for 2 days.

2.4. Characterization

The chemical and physical structures of GO and GOH were characterized by scanning electron microscope (SEM, JOEL JSM-6500FE), X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific ESCALAB 250Xi) using an Al Kα X-ray source (1486.6 eV), an X-ray diffraction system (XRD, Rigaku, D/MAZX 2500 V/PC) using a high power X-ray diffractometer with Cu Kα radiation (35 kV, 20 mA, λ = 1.5418 Å) at a scan rate of 2° (2θ) per minute, and a Raman spectrometer using a confocal Raman microscope (WITec, Alpha300S) at a 532 nm wavelength of incident laser light. Fourier transform infrared spectroscopy (FT-IR) was conducted using a Nicolet 380 FT-IR spectrometer (Thermo Scientific) at a resolution of 4 cm^{-1}. Thermal gravimetric analysis (TGA, TA Instruments, Q50) was also performed under a nitrogen atmosphere with a heating rate of 10 °C per minute. The mechanical properties were tested by a texture analyzer system (AMETEX).

2.5. Adsorption test

The adsorption of MB dye in an aqueous solution was examined with 10 mg GOH absorbents in 100 ml of MB solution (25 mg L^{-1}). The mixture was stirred in the bath with a magnetic bar at room

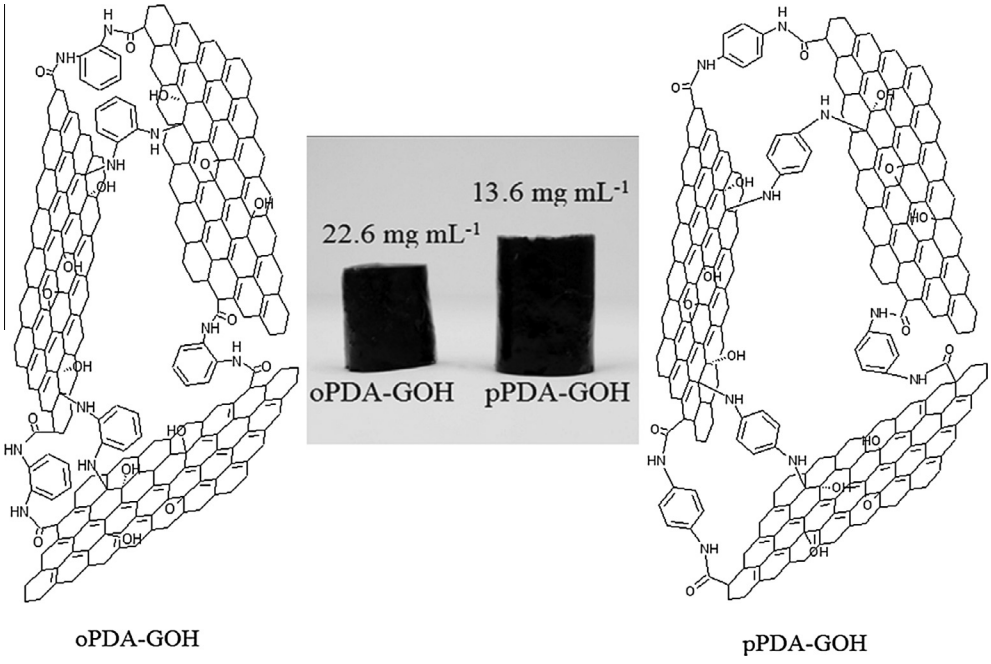

Fig. 1. Optical images and bulk density of the GOH holding weight after freeze-drying (center), and schematics of 3D network formed by the chemical reactions between epoxy and carboxylic acid groups of GO and two diamines (oPDA and pPDA).