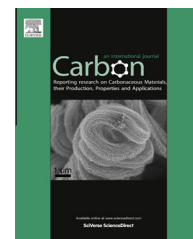


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Graphene–terpyridine complex hybrid porous material for carbon dioxide adsorption

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ABSTRACT

A graphene-based porous material for carbon dioxide sorption was designed and fabricated through an azide–alkyne click reaction between alkynyl group modified graphene oxide (alkynyl-GO) and azido-terpyridine complex. In the preparation of graphene terpyridine complex hybrid porous materials (GTCF), alkynyl-GO sheets were synthesized and used as the building blocks, which were then cross-linked with azido-terpyridine complexes through a copper (I) ion-catalyzed click reaction (Huisgen cycloaddition reaction). The incorporation of the non-planar terpyridine complexes between graphene sheets increases the porosity in the GTCF materials. Meanwhile, three kinds of nitrogen-containing groups (amine, triazole, and terpyridine groups) were introduced or formed during the modification and cross-linking, which offer more basic sites for the acidic gas sorption. Gas sorption analysis shows that the GTCF hybrid porous materials possess high specific surface area and their carbon dioxide capacity could reach up to 11.7 wt.% at 273 K.

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1. Introduction

Graphene-based hybrid materials could be prepared through covalent and non-covalent cross-linking methods [1,2], and are widely investigated in energy storage and conversion applications [3] such as supercapacitor [4], lithium ion battery [5], hydrogen storage [6], and solar cell [7]. GO-based supramolecular hydrogel has been prepared through the noncovalent interaction between triblock copolymers poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO) modified GO and α -cyclodextrin, i.e., PEO chains penetrate into the cyclodextrin cavities [8]. Meanwhile, the oxygen containing groups on GO sheets, which could react with many groups, such as amido, hydroxyl, and isocyanato groups, provide a wide variety of reactions for covalent modification of GO sheets [9,10]. Up to date, graphene-based porous materials were mostly prepared by noncovalent modification

of graphene sheets, and there are only several reports on graphene-based hybrid porous materials constructed through covalent cross-linking method. We have previously reported a kind of GO hybrid porous materials through the cross-linking of GO sheets with organic diisocyanates by using the reaction of diisocyanate with the carboxyl and hydroxyl groups on both sides of the GO sheets [2]. Srinivas et al. synthesized porous GO frameworks through the reaction between GO and linear boronic acid, in which boronate-ester was formed as a result of B–O bonding between boronic acids and oxygen functional groups on the GO layers [11]. Besides the increase in the porosity, the cross-linking would also enhance the mechanical and thermal stability of the hybrid material. The glutaraldehyde cross-linked GO paper exhibits higher mechanical properties in comparison with GO paper owing to the better interlayer adhesions [12].

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Besides covalent bonding, the coordination bonds between the carboxyl groups on the GO layer and transition metal ions (i.e., Zn^{2+} , or Cu^{2+}) make it possible to fabricate graphene-based metal-organic framework (GMOF) hybrid materials or other porous materials [13]. Furthermore, benzoic acid groups were functionalized on GO sheets in order to increase the number of the carboxyl groups on the GO layer prior to the fabrication of GMOF hybrid materials. In this method, metal-organic framework nanowire on benzoic acid-functionalized graphene was fabricated and the hybrid material possesses a specific surface area of $810 \text{ m}^2 \text{ g}^{-1}$ [14].

Click chemistry is a fast, efficient, and reliable approach to the construction of carbon-heteroatom bonds and has become an important tool for material scientists [15,16]. The azide-alkyne click reaction, which is also named Huisgen cycloaddition reaction, could be catalyzed by copper (I) ions (Cu(I)) and results in the formation of 1,2,3-triazole, and has become the powerful pathway in click chemistry due to its efficiency, reliability, specificity, and biocompatibility [17]. Therefore, click reaction has been widely used in the field of organic synthesis, polymer science, and surface modification on nanomaterials [16,17]. Polymer chains containing an azide group have been modified on alkyne-modified GO sheets through azide-alkyne click reaction. The modified GO dispersed well in various kinds of solvents. The modification of GO through click reaction can proceed very easily and with high yields, thus could be expanded to other material preparations [18,19].

Herein, we designed a kind of graphene-based porous material by azide-alkyne click reaction between alkynyl group modified GO (alkynyl-GO) and azido-terpyridine complex, in which alkynyl-GO sheets were synthesized as the building blocks and cross-linked by the non-planar terpyridine complex. The as-prepared graphene-terpyridine complex hybrid porous materials (GTCTF) were obtained with high porosity and carbon dioxide sorption capacity.

2. Experimental

2.1. Materials

Natural flake graphite with an average particle diameter of $20 \mu\text{m}$ (99 wt.% purity) was obtained from Yingshida graphite Co. Ltd., Qingdao, China. Iron(II) sulfate hydrate ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$), copper sulfate hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sulfuric acid (98 wt.%), hydrogen peroxide (30 wt.%), sodium nitrate, chloroacetic acid, *N,N*-dimethylformamide (DMF) and ethanol were purchased from Beijing chemical works, China. *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl), propargylamine, and L-sodium ascorbate (VCNa) were purchased from Acros Organics. All these reagents were of reagent grade and used without further purification. Ultra-pure water ($18.2 \text{ M}\Omega \text{ cm}$) was obtained by the Millipore-ELIX water purification system. 4'-Azido-2,2':6',2''-terpyridine (azido-tpy) and its complex with iron(II) were synthesized according to the reported procedures [20–22].

2.2. Preparation of alkynyl-GO

Aqueous GO dispersion was prepared by chemical exfoliation of the natural flake graphite by a modified Hummers' method

[23]. Alkynyl-GO is prepared through carboxylation and alkylation of GO. In the carboxylation process, NaOH (2.5 g) and chloroacetic acid (2.5 g) were added into aqueous GO dispersion (2 mg mL^{-1} , 60 mL), and then the mixture was sonicated for 3 h. The resulted black dispersion was neutralized by HCl (1.0 M), and purified by centrifugation, and the black dispersion was named as GO-COOH [24]. EDC·HCl was added to the as-prepared GO-COOH to give a concentration of about 3 mg mL^{-1} . After the addition of propargylamine (1 mL), the mixture was stirred overnight [19]. The alkynyl-GO was purified by centrifugation and washed with water [25]. Alkyne-GO dispersion in DMF was obtained by solvent exchange method [26,27]. In the solvent exchange process, aqueous alkynyl-GO dispersion was centrifuged, then the supernatant liquid was removed and the black solid was redispersed in DMF. The solvent exchange process was repeated for five times.

2.3. Preparation of GTCTF

Alkynyl-GO dispersion in DMF (2 mg mL^{-1} , 20 mL) was sonicated for 30 min (120 W) prior to reaction, (azido-tpy)₂-Fe(II) complex was dispersed in DMF (10 mL) and then added into alkynyl-GO dispersion. After stirred for 2 h, the green mixture of CuSO_4 (5 mg) and VCNa (10 mg) in DMF (2 mL) was added into the mixture. The reaction was conducted for 2 h at 80°C , and the black product was collected by filtration and washed with water and ethanol and dried at 60°C .

GTCTF-1–4 were prepared with a different weight ratio of alkynyl-GO to azido-(tpy)₂-Fe(II) complex, which were 16:1, 12:1, 8:1, and 4:1, respectively.

2.4. Instrumental characterization

Absorption spectra were obtained using a Perkin-Elmer Lambda 950 ultraviolet-visible-near infrared spectrophotometer (Perkin-Elmer Instruments Co. Ltd, USA) and quartz cells with a 1 cm path length. Raman spectra were recorded with a Renishaw inVia Raman spectrometer (Renishaw plc, UK). All samples were tested in powder form on silica wafer without using any solvent. The laser excitation was provided by a regular model laser operating at 633 nm. Infrared (IR) spectra were recorded in potassium bromide pellets using a Spectrum One Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer Instruments Co. Ltd, USA).

Scanning electron microscopy (SEM) observations were carried out using a Hitachi S-4800 microscope (Hitachi Ltd., Japan) at an accelerating voltage of 6.0 kV and equipped with a Horiba energy dispersive X-ray spectrometer (EDX). The SEM sample on carbon tape was subject to the observation without any sputter-coating because it shows good electronic conductivity. Thermal gravimetric analysis (TGA) was performed on a Pyris Diamond thermogravimetric/differential thermal analyzer by heating the samples at 5°C min^{-1} to 800°C in the atmosphere of nitrogen. X-ray diffraction (XRD) patterns of the samples were measured from 0.5 to 90° by a Philips X'Pert PRO X-ray diffraction instrument with $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation (40 kV, 30 mA).

Nitrogen sorption isotherms and carbon dioxide sorption isotherms were obtained with a Micromeritics TriStar II 3020 accelerated surface area and porosimetry analyzer. Nitrogen

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