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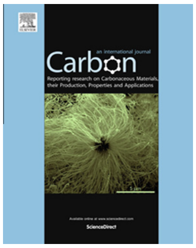

Effect of surface chemistry and textural properties on carbon dioxide uptake in hydrothermally reduced graphene oxide

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ABSTRACT

We developed a facile method to obtain bulk quantities of three-dimensional porous materials through hydrothermal treatment of aqueous graphene oxide (GO) dispersion at different temperatures. The morphology and textural properties of hydrothermally reduced GO (HRGO) were characterized by scanning electron microscopy, X-ray diffraction, and nitrogen adsorption–desorption measurements. X-ray photoelectron spectroscopy, Raman spectroscopy, and infrared spectroscopy were used to analyze their chemical properties. The as-prepared HRGO not only exhibited three-dimensional porous network structure, but also possessed high specific surface area and large pore volume. Controllable surface functionalities on graphene sheets and textural properties enabled the HRGO to show an excellent carbon dioxide capture performance. The HRGO prepared at 100 °C exhibited higher carbon dioxide adsorption capacity (2.4 mmol g^{-1} at 1.0 bar and 273 K) than those of the other two porous materials prepared at 80 and 120 °C. It was found that in addition to textural properties, the excellent adsorption performance can also be ascribed to various surface interactions between carbon dioxide and HRGO, including acid–base interaction, polar interaction, and hydrogen bonding. This study can be helpful to the development of porous materials for carbon dioxide uptake and separation.

1. Introduction

Global carbon dioxide emissions largely resulting from the combustion of fossil fuels have increased steadily in the past few decades and have partly led to global warming and some environmental issues. It is reported that the concentration of carbon dioxide in the atmosphere has increased from 270 ppm before the industrial revolution to more than 390 ppm today [1]. Therefore, to deal with the problem of global warming, the storage and separation of carbon dioxide gas from the atmosphere is currently a serious challenge. To date, many types of sorbents have been proposed as potential sorbents for carbon dioxide, including metal–organic frameworks [2–5], zeolitic imidazolate frameworks [6,7], microporous organic polymers [8,9], mesoporous silicas [10,11], and porous carbons [12,13]. These materials generally possess high specific surface area and permanent porosity, which make them highly competitive in carbon dioxide uptake.

Microporous carbons are considered to be ideal solid adsorbents for carbon dioxide owing to their intriguing properties, such as high porosity, low cost, and easy regeneration. It has been shown that micropores less than 1 nm play an

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important role in carbon dioxide uptake, especially at ambient conditions. KOH activation is a well-known method to produce microporous carbons with high porosity and their surface area can be up to 3000 $m^2 g^{-1}$ [14,15]. Many research groups have reported that microporous carbons possess excellent adsorption performance for carbon dioxide, and their adsorption capacities can reach 5.8 mmol g^{-1} [16], 6.2 mmol g^{-1} [17], 7.0 mmol g^{-1} [14], and 8.9 mmol g^{-1} [15] at 1 bar and 273 K. Graphene, a class of two-dimensional carbon nanomaterials, has attracted extensive concern for its potential use in various applications, such as hydrogen storage [18–21], carbon dioxide capture [22–24], and electrode material in electrochemical energy devices [25–27]. Chemical reduction of exfoliated graphite oxide is considered to be a common method to prepare graphene in a large scale [28]. Graphene oxide (GO) is an intermediate during the synthesis of graphene starting from graphite by a solution chemistry method and possesses various polar functional groups, such as hydroxyl, epoxy, carbonyl, and carboxyl [29]. Recently, there have been extensive researches focusing on exploring the preparation of graphene-based porous materials via chemical activation in order to expand their practical applications into carbon dioxide uptake and separation. Srinivas et al. reported the synthesis of a range of highly porous carbons from GO precursor with KOH chemical activation. They showed that the as-prepared porous materials exhibited excellent adsorption ability (16.4 mmol g^{-1}) for carbon dioxide at 300 K and 20 bar [13]. Chandra et al. reported the preparation of a nitrogen-doped porous carbon via chemical activation of a polypyrrole–graphene composite and the resulting nitrogen-doped porous carbon possessed high carbon dioxide adsorption capacity (4.3 mmol g^{-1}, 1.0 bar) and selectivity (16) of carbon dioxide over nitrogen at 298 K [12]. A nitrogen-doped microporous carbon, prepared by Saleh et al. via chemical activation of polyindole-modified GO sheets, showed high carbon dioxide adsorption capacity of 3.0 mmol g^{-1} at 298 K and 1.0 bar [30]. Graphene-based microporous carbon materials are highly promising in the field of carbon dioxide uptake due to their large surface area, easy surface modification, and being low cost.

In the recent years, theoretical studies reported by Wood et al. using density functional theory (DFT) have shown that polar groups may be promising candidates for enhancing carbon dioxide adsorption capacity by strengthening adsorption and activating exposed edges and terraces to introduce additional binding sites [31]. It is well-known that there are many polar groups existing in the basal plane and edge of GO sheets [29]. Thus, GO sheet with a large number of oxygen-containing groups can be considered as a useful building block to construct porous materials with excellent carbon dioxide capture capacity. The work on carbon dioxide capture of GO-based porous materials is still limited [32–34]. This is likely due to the difficulties in preventing the restacking of GO sheets and increasing the specific surface area of GO-based porous materials. Recently, pillaring molecular structures have been applied to keep GO layers apart to obtain porous materials with high accessible surface area [35]. Burress et al. reported the synthesis of porous GO frameworks through a well-known reaction between boronic acids and hydroxyl groups of GO sheets [32]. In a similar way, Srinivas et al. reported the detailed synthesis of porous GO frameworks by reacting GO sheets with linear boronic acid pillaring units in a solvothermal reaction. They demonstrated that the resulting porous GO frameworks exhibited high isosteric heat of adsorption (Q_{st}) and adsorption capacity for hydrogen [33].

In our work, we prepared three-dimensional (3D) porous materials with controllable C/O ratios through a facile hydrothermal treatment of aqueous GO dispersion at different temperatures. The as-prepared porous materials exhibited high surface area and large pore volume. The advantage of functionalized graphene materials was demonstrated by their enhanced performance as carbon dioxide adsorbents. We compared the uptake capacity, Q_{st}, and selectivity of carbon dioxide over nitrogen for the as-prepared porous materials and further discussed the effect of surface chemistry and textual properties of HRGO on carbon dioxide uptake, which may be useful for the preparation of porous materials with enhanced carbon dioxide storage and separation capacity.

2. Experimental section

2.1. *Materials*

Natural flake graphite (average particle diameter of 20 μm, 99 wt% purity) was obtained from Yingshida graphite Co. Ltd., Qingdao, China. Sulfuric acid (98 wt%), hydrogen peroxide (30 wt%), potassium permanganate, sodium nitrate, hydrochloric acid, *tert*-butanol, and ethanol are of analytical grade and were purchased from Beijing Chemical Reagents Company. All these chemical reagents were used directly without further purification. Ultra-pure water (18 MΩ cm) used in all experiments was obtained from a Millipore-ELIX water purification system.

2.2. *Preparation*

GO was prepared by a modified Hummers' method using natural flake graphite as starting material [36–39]. Aqueous GO dispersion was sonicated for 60 min before using. A total of 20 mL of aqueous GO dispersion (10 mg mL^{-1}) was sealed in a Teflon-lined stainless-steel autoclave and heated at different temperatures (80, 100, and 120 °C) for 16 h. The autoclave was then cooled to room temperature. The hydrothermally treated GO dispersion was found to form a hydrogel. The as-made hydrogels were washed with *tert*-butanol before freeze-drying to replace water within the network of hydrogels. This is because *tert*-butanol is easier to be sublimated than water. Finally, the as-prepared hydrogels were freeze-dried under vacuum (less than 20 Pa) for 24 h to completely remove the solvent. The obtained porous materials were denoted as HRGO-*x*, wherein *x* represented the hydrothermal temperature.

2.3. *Instrumental characterization*

Scanning electron microscopy (SEM) images were observed by using a Hitachi S-4800 microscope (Hitachi Ltd., Japan) equipped with a Horiba energy dispersive X-ray (EDX) spectrometer at an accelerating voltage of 4–8 kV. X-ray diffraction