



Highly efficient, rapid and selective CO₂ capture by thermally treated graphene nanosheets

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ABSTRACT

Graphene, by virtue of its unique molecular structure and many interesting properties, is receiving considerable attention as an adsorbent for separation and purification of gases. In this study, graphene nanosheets were subjected to heat treatment in the temperature range of 200–800 °C under flowing N₂ to improve their textural characteristics (surface area, pores size, and total pore volume) for efficient removal of CO₂ from flue gases. The resulting graphene materials showed highly ordered structure, large surface area (up to 484 m² g⁻¹) and interconnected hierarchical pore networks with narrow pore size distribution in the large-micropore/small-mesopore range. As a consequence, the heat-treated graphene samples demonstrated significantly greater CO₂ uptake capabilities (up to 2.89 mmol g⁻¹) compared to pristine graphene (0.81 mmol g⁻¹) at 0 °C and 1 bar. More importantly, the materials displayed rapid adsorption kinetics with ultrahigh selectivity for CO₂ over N₂, as well as stable and readily reversible adsorption/desorption cycling behavior. The isosteric heat of adsorption had an unusual dependence on surface loading because of the presence of attractive intermolecular forces between the adsorbed quadrupolar CO₂ molecules. These findings demonstrate for the first time that thermal treatment at high-temperatures can have a positive influence on the single component CO₂ adsorption characteristics of graphene sheets and should be explored further as an effective strategy in the design and development of graphene-based porous solid adsorbents for CO₂ abatement.

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1. Introduction

The effective capture of CO₂ from fossil-fuelled power plants and large industrial sources (such as steel, cement and fertilizer production) is a top global priority to reduce the impacts of global warming on our climate system and the natural environment [1]. Among the various strategies (i.e., pre-combustion, post-combustion and oxy-fuel combustion) and numerous technologies (e.g., absorption, adsorption and membrane separation) that are currently being explored to curb CO₂ emissions [2,3], post-combustion capture using solid adsorbents is an attractive option because of its ease in retrofitting existing CO₂ sources, less energy requirements, simplicity of operation, applicability over a wide range of temperature and pressure conditions, facile regeneration of the spent adsorbents, and low capital costs [4]. As a result, several different classes of adsorbent materials have been examined for separation of CO₂ from flue gases and other industrial exhaust streams. These include zeolites, porous silica, porous polymers, metal oxides, alumina, activated carbons, carbon

fibers, ion-exchange resins, and metal organic frameworks (MOFs) [4–8]. While some of those adsorbents have low adsorption capacities and/or require long time to reach saturation due to slow adsorption kinetics, or sometimes poor selectivity relative to other gases, most of them exhibit reduced activity in the presence of moisture, low chemical and thermal stability, or weak mechanical properties that lessen their suitability for on-site application [8]. There is therefore a pressing need to develop advanced solid adsorbents that can adequately address the inherent requirements of real-world CO₂ capture systems.

Recently, graphene-based materials have received a great deal of attention for the development of next-generation energy efficient and high volume CO₂ adsorbents [9–16], due to their exceptional surface area (theoretical value of 2630 m² g⁻¹), excellent thermal conductivity (up to 5000 W m⁻¹ K⁻¹), outstanding mechanical strength (Young's modulus of about 1 TPa), and remarkable chemical stability [17]. However, graphene as a bulk material has the tendency to form irreversible agglomerates, behaving as particulate graphite platelets, due to strong van der Waals force between the large and planar basal planes, causing a significant decrease of the ultrahigh surface area of two-dimensional graphene sheets [18]. Since gas adsorption behavior

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is mainly governed by the surface area and pore characteristics of the adsorbent material [10], the introduction of nanopores into graphene sheets has been identified as one of the most effective methods for improving the adsorption performance of graphene materials [19]. Because of their porous structure, such holey graphene scaffolds have a higher surface area and much more “space” for capturing and storing CO₂ compared to pristine graphene [15]. For example, Srinivas et al. [9] fabricated highly porous graphene-based adsorbents with large specific surface area (1900 m² g⁻¹) and high pore volume (1.65 cm³ g⁻¹), via KOH activation of exfoliated graphene oxide (GO) precursors, that could adsorb up to 16.38 mmol CO₂ per gram at 27 °C and 20 bar. Likewise, several processes have been considered to obtain graphene architectures with porous morphologies for enhanced adsorption and recovery of CO₂, including cross-linking [10,11], template directed chemical vapor deposition [12], chemical etching [13], physical activation [14,15], hydrothermal reduction [16], and combinations thereof. Nevertheless, most of these methods are expensive, time-consuming, chemically hostile, complex processes with potentially negative environmental impacts. In addition, the precise control over the surface area, pore structure, pore size and pore size distribution still remains a large scientific and technological challenge [18].

Thermal treatment/reduction is an efficient and convenient alternative for preparation of porous graphene nanostructures because of its (i) simplicity; (ii) scalability; and (iii) sustainability (since it does not involve the use of toxic chemicals or hazardous substances) [20,21]. By varying the process conditions, graphene with various pore size and morphology can be easily obtained. Zhang and co-workers have recently shown that thermal treatment at low-temperature can lead to crumpling rather than stacking of graphene layers, resulting in a bimodal macro/mesoporous structure with large surface area (429 m² g⁻¹) [22]. As a consequence, these structural defects onto graphene provided a high density of ion diffusion channels, which facilitated rapid charge storage and transport for high-performance energy storage applications. Thermal processing therefore seems to be a promising research direction for the design and synthesis of porous graphene materials with high surface area and pore volume for CO₂ capture applications. However, till date, the effects of thermal treatment on the CO₂ adsorption performance of graphene remain unexplored.

In this work, we present the facile synthesis of robust graphene-based porous adsorbents with large accessible surface area and well-defined tunable pore morphology through direct thermal treatment of graphene nanosheets at high-temperatures. The prepared graphene materials show an excellent CO₂ removal ability from flue gases, specifically in terms of high capacity, excellent selectivity, rapid kinetics, low initial isosteric heat, easy regeneration, as well as superior long-term stability over multiple adsorption–desorption cycles. Most importantly, these nanoporous carbons are essentially hydrophobic and hence merit further consideration for the development of post-combustion CO₂ adsorption modules. To the best of our knowledge, this is the first report describing the mechanism of surface modification of graphene nanosheets via heat treatment and its effects on pore development and CO₂ uptake.

2. Experimental

2.1. Materials

Graphite powder (<20 µm) was purchased from Sigma–Aldrich and used as received. Sulfuric acid (H₂SO₄, 98 wt.%, Merck), phosphoric acid (H₃PO₄, 85 wt.%, J.T. Baker), potassium permanganate (KMnO₄, Acros Organics), hydrogen peroxide (H₂O₂, 30 wt.%,

Sigma–Aldrich), and hydrazine hydrate (N₂H₄, 50–60 wt.%, Sigma–Aldrich) were used as obtained from the supplier without any further purification. Deionized water was used during the experimental process.

2.2. Synthesis of graphene oxide

GO was prepared from natural graphite powder using an improved Hummer's method [23]. In brief, a 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (360:40 mL) was added to a mixture of graphite powder (3 g, 1 wt. equiv.) and KMnO₄ (18 g, 6 wt. equiv.), producing a slight increase in the temperature to 35–40 °C. The reaction mixture was further heated to 50 °C and stirred for 12 h. It was then cooled to room temperature and poured onto ice (~400 mL) with 3 mL H₂O₂. The mixture was finally centrifuged and the supernatant was decanted away. The remaining solid material was rinsed repeatedly with deionized water until the pH of the solution was neutral. After filtration and drying in air at room temperature, GO was obtained.

2.3. Synthesis of graphene

Graphene was synthesized by hydrazine reduction of GO. In a typical procedure, GO (0.025 g) was suspended in deionized water (40 mL), yielding an inhomogeneous yellow-brown dispersion. This dispersion was then sonicated until it became clear with no visible particulate matter. To this solution, N₂H₄ (10 mL) was added and the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and kept at 100 °C for 24 h followed by cooling to ambient temperature naturally. The resulting black precipitate was isolated by filtration, washed copiously with deionized water and ethanol, and dried at 100 °C.

2.4. Thermal treatment of graphene

Thermal treatment of the as-synthesized graphene (GPN) sheets was carried out at four different temperatures (200, 400, 600 and 800 °C) in a horizontal tube furnace (TMH12, Elite Thermal Systems Ltd., UK). A weighed amount of GPN was first loaded on a ceramic boat, placed at the center of the tube furnace, and then heated under a continuous flow of N₂ (500 mL min⁻¹) at a rate of 5 °C min⁻¹, with a holding time of 2 h at the desired temperature. Following the heat treatment, the sample was allowed to cool down to room temperature in the furnace. The materials thus obtained were labeled GPN-X, where X is the temperature of thermal treatment.

2.5. Characterization methods

Wide angle X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE (Bruker Co., Germany) X-ray diffractometer equipped with Ni-filtered Cu K α radiation ($\lambda = 0.15$ nm) operating at 40 kV and 40 mA. The diffraction patterns were collected over a 2 θ range of 5–70°. The interlayer spacing was then calculated using the Bragg's equation. X-ray photoelectron spectroscopy (XPS) data was acquired using a VG ESCA 220i-XL imaging system (Thermo VG Scientific Ltd., UK). Monochromatic Al K α X-ray ($h\nu = 1486$ eV) was employed for analysis with photoelectron take-off angle of 90° to the surface plane. The analysis area was approximately 700 nm in diameter while the maximum analysis depth was in the range of 4–8 nm. Field emission scanning electron microscopy (FESEM) was performed on a JEOL JSM-6700F (JEOL Ltd., Japan) field emission microscope operated at an electron accelerating voltage of 15 kV. The samples were mounted on an aluminium stub with carbon adhesive tape and coated with a thin layer of platinum under high vacuum (10^{-3} – 10^{-7} Mbar) conditions using a Hitachi E-1030 ion

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