



# Nanoporous spongy graphene: Potential applications for hydrogen adsorption and selective gas separation



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## ABSTRACT

In the present work, a nanoporous (pore width ~ 0.7 nm) graphene-based sponge-like material with large surface area (~ 350 m<sup>2</sup>/g) was synthesized by wet chemical reduction of graphene oxide in combination with freeze-drying. Surface morphology and elemental composition were studied by scanning and transmission electron microscopy combined with energy dispersive X-ray spectroscopy. Surface chemistry was qualitatively examined by Fourier-transform infrared spectroscopy, while the respective structure was investigated by X-ray diffraction analysis. Textural properties, including Brunauer–Emmet–Teller (BET) surface area, micropore volume and surface area as well as pore size distribution, were deduced from nitrogen gas adsorption/desorption data obtained at 77 K and up to 1 bar. Potential use of the spongy graphene for gas storage and separation applications was preliminarily assessed by low-pressure (0–1 bar) H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> sorption measurements at different temperatures (77, 273 and 298 K). The adsorption capacities for each gas were evaluated up to ~ 1 bar, the isosteric enthalpies of adsorption for CO<sub>2</sub> (28–33 kJ/mol) and CH<sub>4</sub> (30–38 kJ/mol) were calculated using the Clausius–Clapeyron equation, while the CO<sub>2</sub>/CH<sub>4</sub> gas selectivity (up to 95:1) was estimated using the Ideal Adsorbed Solution Theory (IAST).

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## 1. Introduction

Graphene is considered one of the most promising nanomaterials for advanced applications in the fields of nanoelectronics and nanosensors [1,2], coatings and thin films technology [3,4], nanocomposite structures [5,6], catalytic chemistry [7,8], environmental engineering [9–11], gas separation and storage [10–13], as well as energy conversion and storage [14–17]. Visualized as a two-dimensional monolayer of sp<sup>2</sup>-bonded carbon atoms forming multiple hexagonal cells, this recently isolated [18,19] and extensively studied carbon allotrope combines a series of unique properties, including high electrical and thermal conductivity, remarkable strength and stiffness and an impressively large surface area relative to its mass [20–22]. Based on theoretical

calculations an individual graphene sheet can provide a specific surface area as high as 2630 m<sup>2</sup>/g (i.e. 1315 m<sup>2</sup>/g for each side) [23]. However, single planar graphene sheets are thermodynamically unstable and usually form few- or multi-layer stacks, as well as curved nanostructures (e.g. nanotubes, fibers, fullerenes, etc.).

Production of graphene has been widely reported over the past years mostly through micro-mechanical exfoliation/peeling of pyrolytic graphite [18,24], epitaxial growth by chemical vapor deposition or high-temperature segregation [25] and reduction of graphite- or graphene-oxide using thermal annealing, solvothermal/hydrothermal, electrochemical or microwave methods [26–30]. Especially the latter is considered the “bottleneck” in the development of graphene technology due to the need to optimize the reduction process and produce pristine graphene in high yield [31]. A plethora of porous graphene-based nanostructures, including nanosheets [32–34], sponges [35–40] and foams [41–43], have been synthesized with potential to be used as advanced nanoelectronic components for energy conversion and storage devices [29,33,34,37–39,43,48] and as highly-efficient adsorbents for liquid substances and gases [32,35,36,40–42,44–47]. Specifically, they

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have been proposed as electrodes and substrates for super-capacitors [29,43], batteries [33,34,38], fuel cells [39] and solar cells [48], as well as sorption materials for water purification from oils and organic solvents [35,36,41], sequestration of unwanted greenhouse emissions such as carbon dioxide (CO<sub>2</sub>) [45–47] and storage of highly-dense energy carriers such as methane (CH<sub>4</sub>) and hydrogen (H<sub>2</sub>) [32,40,42,44,45]. These nanoscale materials are considered attractive for the aforementioned applications as they combine low densities, large surface areas, tunable pore sizes and volumes, excellent thermal and chemical stability, environmental friendliness, non-toxicity and low production cost [16,49,50].

Focusing on materials-based gas storage applications, an intense research effort has been devoted towards the development of few-layer graphene or graphene oxide (GO) sorbents with narrow micropore sizes and large surface areas that can physically adsorb/store various gases (e.g. H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>) into their porous network [13]. Srinivas et al. [45] produced a series of nanoporous (1.2–2.6 nm) and high-surface area (916–1894 m<sup>2</sup>/g) GO-derived carbons by potassium hydroxide (KOH) activation that demonstrated a favorable behavior towards CO<sub>2</sub> and CH<sub>4</sub> adsorption. Lyth et al. [42] synthesized a high-surface area (1269 m<sup>2</sup>/g) graphene foam through the combustion of sodium ethoxide (C<sub>2</sub>H<sub>5</sub>ONa) that showed a significant H<sub>2</sub> storage capacity of 2.1 wt.% at 77 K and 10 bar. Recently, Sui et al. [47] prepared hydrothermally reduced GO samples with large surface areas (420–870 m<sup>2</sup>/g) and narrow-size micropores (~0.6 nm) that exhibited high CO<sub>2</sub> adsorption capacities up to 2.4 mmol/g at 273 K and 1 bar.

In the current study, we have prepared a nanoporous spongy derivative of GO by combining wet chemical reduction (i.e. hydrothermal treatment using a reducing agent) and freeze-drying methods. The as-prepared spongy material was extensively characterized with respect to its morphology, elemental composition, surface chemistry, texture/porosity and structure using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), Fourier-transform infrared spectroscopy (FT-IR), nitrogen (N<sub>2</sub>) adsorption at 77 K and X-ray diffraction (XRD), respectively. Great emphasis was placed on investigating its behavior towards H<sub>2</sub> cryo-adsorption at 77 K, as well as CO<sub>2</sub> and CH<sub>4</sub> adsorption at 273 K and 298 K, on the basis of systematic low-pressure (0–1 bar) measurements. The interaction strength of both CO<sub>2</sub> and CH<sub>4</sub> with the graphene surface as well as the CO<sub>2</sub> over CH<sub>4</sub> selectivity were two of the main gas sorption properties evaluated and discussed in this study within the context of potential gas storage and separation applications.

## 2. Materials and experimental methods

### 2.1. Graphene sponge synthesis

The graphene sponge-like material (denoted hereafter as GS) was synthesized by wet chemical reduction of GO using hydriodic acid (HI) followed by freeze drying. The original GO was prepared by oxidizing graphite powder (Sigma-Aldrich; <20 μm) using a modified Hummer's method, as already described in previous studies [37,51]. For the preparation of GS, about 120 mg of GO were easily dispersed in 60 ml aqueous solution by ultra-sonication for 30 min using a conventional ultra-sonic bath. Next, 1 ml of HI (Sigma-Aldrich; 30%) was added and the mixture was placed inside a polytetrafluoroethylene (PTFE)-lined stainless steel autoclave reactor for 12 h at 180 °C. A graphene hydrogel (GH) was subsequently collected from the reactor and was instantly submerged into de-ionized water for 24 h to remove any residual HI from its surface. Water was removed by 75 wt.% from the as-prepared GH through room temperature evaporation in order to obtain a final product with an enhanced surface area [37,40]. In a final step, the partially dried GH was freeze-dried with liquid N<sub>2</sub> and then freeze-dried in vacuum overnight to remove the excess water. By the end of this procedure, a black and fluffy powder was obtained.

### 2.2. Characterization techniques

Surface morphology was studied with a Quanta 200 (FEI) SEM using an acceleration voltage of 20 kV. The specimen was sputter-coated with silver (SC7640, Quorum Technologies) in argon atmosphere to avoid any charging effects during imaging. The elemental composition of the sample was subsequently analyzed using an EDVAC Genesis X-ray analysis probe at various sites and spectral patterns were generated for each session of analysis. High resolution images were obtained by a Philips CM-20 TEM with a lanthanum hexaboride (LaB<sub>6</sub>) filament using an acceleration voltage of 200 kV.

FT-IR spectra were collected by a Thermo Scientific Nicolet 6700 FT-IR spectrometer in the mid-infrared region of 4000–400 cm<sup>-1</sup>. The instrument was equipped with an attenuated total reflection (ATR) diamond crystal, a N<sub>2</sub> purging system for CO<sub>2</sub> and moisture and a wide-range mercury cadmium telluride (MCT) detector cooled by liquid N<sub>2</sub>. XRD patterns were collected by a Rigaku R-AXIS IV imaging plate detector mounted on a Rigaku RU-H3R rotating copper (Cu) anode X-ray generator (λ = 1.54 Å). The Origin Lab-9 software was used for the deconvolution of the diffractogram in the 2θ region 0–62° and the detailed analysis of the structural features.

N<sub>2</sub> and H<sub>2</sub> adsorption/desorption isotherms at 77 K were recorded up to 1 bar using an Autosorb 1-MP (Quantachrome) volumetric gas sorption analyzer. Ultra-pure N<sub>2</sub> (99.999%) and H<sub>2</sub> (99.9999%) gases were used. Prior to measurement, the samples (~40 mg) were degassed under high vacuum (10<sup>-6</sup> mbar) at 250 °C for approximately 12 h. Porous properties were determined by analyzing the N<sub>2</sub> adsorption/desorption data using Quantachrome's ASIWin software. Total specific surface area (SSA) was calculated by the multi-point Brunauer–Emmett–Teller (BET) method in the relative pressure range 0.05 < P/P<sub>0</sub> < 0.20. Micropore volume and micropore SSA were both calculated by the Carbon Black statistical thickness equation (t-plot). Pore size distribution (PSD) was estimated by the Quenched Solid Density Functional Theory (QSDFT) using the nitrogen-carbon equilibrium transition kernel at 77.4 K for slit-shaped pores.

CO<sub>2</sub> and CH<sub>4</sub> adsorption/desorption isothermal curves were recorded both at 273 K and 298 K and up to 1 bar using a Micromeritics 3Flex volumetric gas sorption analyzer along with a PolyScience circulating bath (50:50 vol.% water:ethylene glycol mixture) for maintaining constant temperature during experiment. Same degassing conditions were applied to the samples (~50 mg) as previously described (10<sup>-6</sup> mbar and 250 °C for 24 h), while both carbon dioxide and methane gas of ultra-high purity (99.9999%) was used. The isosteric enthalpies of adsorption (ΔH), towards both CO<sub>2</sub> and CH<sub>4</sub>, at a constant surface coverage (θ) were extracted using the Clausius–Clapeyron equation [52] for the two operating temperatures (i.e. 273 and 298 K):

$$\Delta H = -R \left[ \frac{\partial \ln(P)}{\partial (1/T)} \right]_{\theta} \quad (1)$$

where,  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $P$  is the pressure in mbar and  $T$  is the temperature in K. The adsorption selectivity of CO<sub>2</sub> over CH<sub>4</sub> was calculated using the Ideal Adsorbed Solution Theory (IAST) approach [53,60]. The single component adsorption isotherms were described by fitting the data with the following virial-type equation:

$$P = \frac{v}{K} \exp(C_1 v + C_2 v^2 + C_3 v^3 + C_4 v^4) \quad (2)$$

where,  $P$  is the pressure in mbar,  $v$  is the amount adsorbed in mmol g<sup>-1</sup>,  $K$  is the Henry constant in mmol g<sup>-1</sup> mbar<sup>-1</sup> and  $C_i$  are the constants of the virial equation. The free energy of desorption at a given value of

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