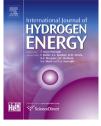Available online at www.sciencedirect.com

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Hydrogen adsorption by perforated graphene

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ABSTRACT

We performed a combined theoretical and experimental study of hydrogen adsorption in graphene systems with defect-induced additional porosity. It is demonstrated that perforation of graphene sheets results in increase of theoretically possible surface areas beyond the limits of ideal defect-free graphene (~2700 m^2/g) with the values approaching ~5000 m^2/g. This in turn implies promising hydrogen storage capacities up to 6.5 wt% at 77 K, estimated from classical Grand canonical Monte Carlo simulations. Hydrogen sorption was studied for the samples of defected graphene with surface area of ~2900 m^2/g prepared using exfoliation of graphite oxide followed by KOH activation. The BET surface area of studied samples thus exceeded the value of single-layered graphene. Hydrogen uptake measured at 77 K and 296 K amounts to 5.5 wt% (30 bar) and to 0.89 wt% (120 bar), respectively.

Introduction

Hydrogen storage by physisorption is an attractive alternative due to fast kinetics and full reversibility of adsorption/desorption cycles. Nanostructured carbon materials have been considered as promising candidates for hydrogen storage applications due to high surface areas and chemical stability [1,2]. Activated carbons [3,4], carbon nanotubes [5,6], graphite nanofibers [7] and carbide derived carbons [8] have been actively studied for hydrogen storage applications during last decades. It is known that hydrogen uptake correlates well with the BET surface area and micropore volume for most of the high surface area adsorbents including carbon materials [3,9–11]. Typical uptake observed for these materials at ambient temperature and 100 bar of H_2 pressure is about 0.3 wt% per 1000 m^2/g (maximal about 1 wt%). At liquid nitrogen temperature the maximal values reach about 4–6 wt% [12].

Recently, the family of nanostructured carbons has been expanded to include graphene-related materials which were initially reported to store hydrogen significantly better [13–15] compared to other nanostructured carbons with similar surface areas [3,16–18]. More recent studies revealed that hydrogen uptakes by graphene-related materials follow standard correlation between hydrogen adsorption and surface area both at room and liquid nitrogen temperatures [19].

However, most of the previously published studies have been performed only on reduced graphene oxide (r-GO)

samples [15,20–22] with surface areas far below (300–1200 m^2/g) theoretical values for pure graphene (2630 m^2/g) [23]. So far, hydrogen sorption properties were reported only for the samples with maximal surface area of about 2300 m^2/g [19]. Therefore, full potential of graphene-related materials for hydrogen storage applications still remains to be explored.

It is often assumed that maximal surface area which can be achieved for graphene is about 2630 m^2/g which is the value for single-layered graphene [23]. However, the surface area of exfoliated r-GO can be further increased using KOH-activation procedure [24,25] (widely used for preparation of activated carbons [26]) up to values as high as 3100 m^2/g. It is also known that BET surface areas in the range 3000–3500 m^2/g can be achieved for some activated carbons [16,17,27]. High surface area of KOH-activated samples has been attributed to the high density of holes in graphene sheets that was confirmed, among other methods, by direct electron microscopy observations [24,25].

These experimental results provide evidence that the surface area of perforated graphene-related materials can exceed the maximal theoretical value reported for defect-free graphene, thus providing promise for better hydrogen adsorption. However, it is unclear how much better surface areas and hydrogen uptakes can be achieved in graphene-related materials since no systematic theoretical studies have been performed so far to evaluate the influence of holes and other defects.

To address this problem, we first need to construct models of multilayered graphene structures modified by perforation and then to evaluate their hydrogen uptakes. The latter task can be accomplished using classical Grand canonical Monte Carlo simulations (GCMC) [28] which were shown to provide reliable estimations of hydrogen uptake for different porous materials [9]. To explicitly account for quantum effects, more sophisticated methods (for example, based on quantized liquid density functional theory) [29] were also proposed but their use in practice is much more limited due to large demand for computational time. Furthermore, quantum corrections are almost negligible for temperatures above ~50 K [30]. Active theoretical studies of hydrogen storage in carbon-based nanostructures (e.g. graphene, graphite intercalated with fullerenes, carbon foams, nanotube packings etc.) have been performed in recent years [29,31–33], in parallel to intensive research on hydrogen storage in other porous materials, such as metal–organic and covalent organic frameworks (MOFs and COFs) [34,35].

In this work we propose several simple models demonstrating that surface area of multilayered graphene materials can be further increased by introducing large number of specific defects (holes). Several types of idealized structures with different degrees of perforation were modelled for hydrogen adsorption with theoretical surface areas approaching about 5000 m^2/g and corresponding hydrogen uptake of ~6.5 wt% at 77 K estimated using classical GCMC simulations. Hydrogen adsorption was studied for the samples of activated r-GO with the BET surface area of about 2900 m^2/g (thus exceeding the surface area of defect-free graphene) at 77 K and at the room temperature, revealing that maximal hydrogen adsorption is in good agreement with perforated graphene models.

Experimental section

Samples with high surface area were prepared using two step procedure: 1) thermal exfoliation of graphite oxide which yields r-GO with typical BET surface area about 430–450 m^2/g [19] and 2) r-GO powder (400 mg) was stirred in methanol KOH solution (20 ml, K/C ratio 1.7), the resulting mixture dried under vacuum at 40 °C and annealed under argon flow at 800 °C for 1 h. This reaction yielded about 100 mg of powder. Nitrogen isotherm was recorded using Quantachrome Nova 1200e (Surface area & Pore size analyzer) apparatus at liquid nitrogen temperature after degassing at vacuum conditions at 150 °C for at least 12 h. The isotherm was re-measured after experiments with evaluation of H$_2$ uptakes. Prior to measurements of hydrogen uptakes the sample was annealed in H$_2$ gas (10–15 Bar) at 350–500 °C and vacuum degassed. Hydrogen isotherms at 77 K and 296 K were recorded using Hiden Isochema Intelligent Manometric Instrument (IMI) volumetric system [36,37]. At ambient temperature the uptake was also checked using Rubotherm gravimetric system, see details elsewhere [19,38].

Computational methodology

Hydrogen adsorption simulations were performed with the MUSIC code [28]. The H$_2$/H$_2$ and H$_2$/graphene interactions were described by the Lennard–Jones (LJ) potential. The H$_2$ molecule was modelled as a rigid diatomic molecule with a bond length 0.74 Å where each hydrogen atom represented LJ interaction site. The potential parameters for the hydrogen molecule (σ = 2.72 Å; ε = 10.0 K) were taken from Ref. [39]. The potential parameters for the carbon atoms in graphene were adopted from the DREIDING force field [40]. Lorentz–Berthelot mixing rules were applied to calculate H$_2$ – graphene LJ potential parameters. Hydrogen adsorption isotherms were modelled for two different temperatures (T = 77 K and T = 100 K) throughout a wide range of pressures (P = 0.01–100 bar). Fugacities needed to define the chemical potential in the GCMC simulations were derived from the Peng–Robinson equation of state. The available free volume was calculated using a non-adsorbing species (He) as a probe [41]. The surface area was estimated by "rolling" a probe molecule with a van der Waals diameter of N$_2$ (3.68 Å) over the surface of graphene sheets as described in Ref. [34].

Results and discussion

To estimate the influence of defects on hydrogen storage properties, we designed several model structures made of graphene sheets perforated by holes of variable size and relative area. The porosity of model structures was selected to be close to the one achieved in experiments [4] (around 1.1 cm^3 g^{-1}). Examples of studied model systems I–IV are shown in Fig. 1 and consist of infinite parallel graphene layers (separated by 7 Å – the optimal distance as was shown in Ref. [29]) with holes of different sizes (~6–30 Å).