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Hydrogen adsorption by perforated graphene

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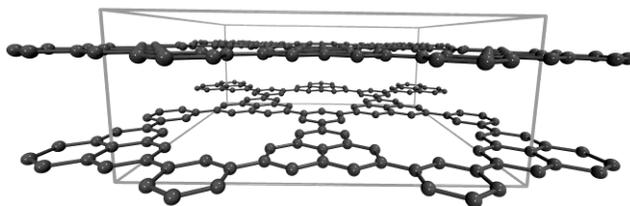
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Abstract

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 ($\sim 2700 \text{ m}^2/\text{g}$) with the values approaching $\sim 5000 \text{ m}^2/\text{g}$. 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 $\sim 2900 \text{ m}^2/\text{g}$ 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.



Keywords: *graphene-based nanostructures, hydrogen storage, high surface area, porous materials*

Highlights:

- Model structures of multilayered perforated graphene with surface areas up to $\sim 5000 \text{ m}^2/\text{g}$ were proposed
- Hydrogen uptake for model structures was estimated to be at most 6.5 wt% at 77 K
- The samples of perforated graphene with surface area of $\sim 2900 \text{ m}^2/\text{g}$ were synthesized
- Hydrogen uptake of perforated graphene was measured to be 5.5 wt% (77 K) and 0.89 wt% (296 K)

1. 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 H₂ pressure is about 0.3 wt% per 1000 m²/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, 17] [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 m²/g) theoretical values for pure graphene (2630 m²/g).[23] So far, hydrogen sorption properties were reported only for the samples with maximal surface area of about 2300 m²/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 m²/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 m²/g. It is also known that BET surface areas in the range 3000-3500 m²/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 $5000 \text{ m}^2/\text{g}$ and corresponding hydrogen uptake of $\sim 6.5 \text{ wt\%}$ 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 $2900 \text{ m}^2/\text{g}$ (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.

2. 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 m²/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 40⁰C and annealed under argon flow at 800⁰C for one hour. 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 150⁰C for at least 12h. The isotherm was re-measured after experiments with evaluation of H₂ uptakes. Prior to measurements of hydrogen uptakes the sample was annealed in H₂ gas (10-15 Bar) at 350-500⁰C 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]

3. Computational methodology

Hydrogen adsorption simulations were performed with the MUSIC code²⁸. The H₂/H₂ and H₂/graphene interactions were described by the Lennard–Jones (LJ) potential. The H₂ 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 ($\sigma = 2.72$ Å; $\epsilon = 10.0$ K) were taken from.[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 H₂ – 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 \AA) over the surface of graphene sheets as described in Ref. 34.

4. 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 experiments⁴ (around $1.1 \text{ cm}^3/\text{g}$). Examples of studied model systems **I–IV** are shown in **Figure 1** and consist of infinite parallel graphene layers (separated by 7 \AA – the optimal distance as was shown in Ref. 29) with holes of different sizes ($\sim 6\text{--}30 \text{ \AA}$).

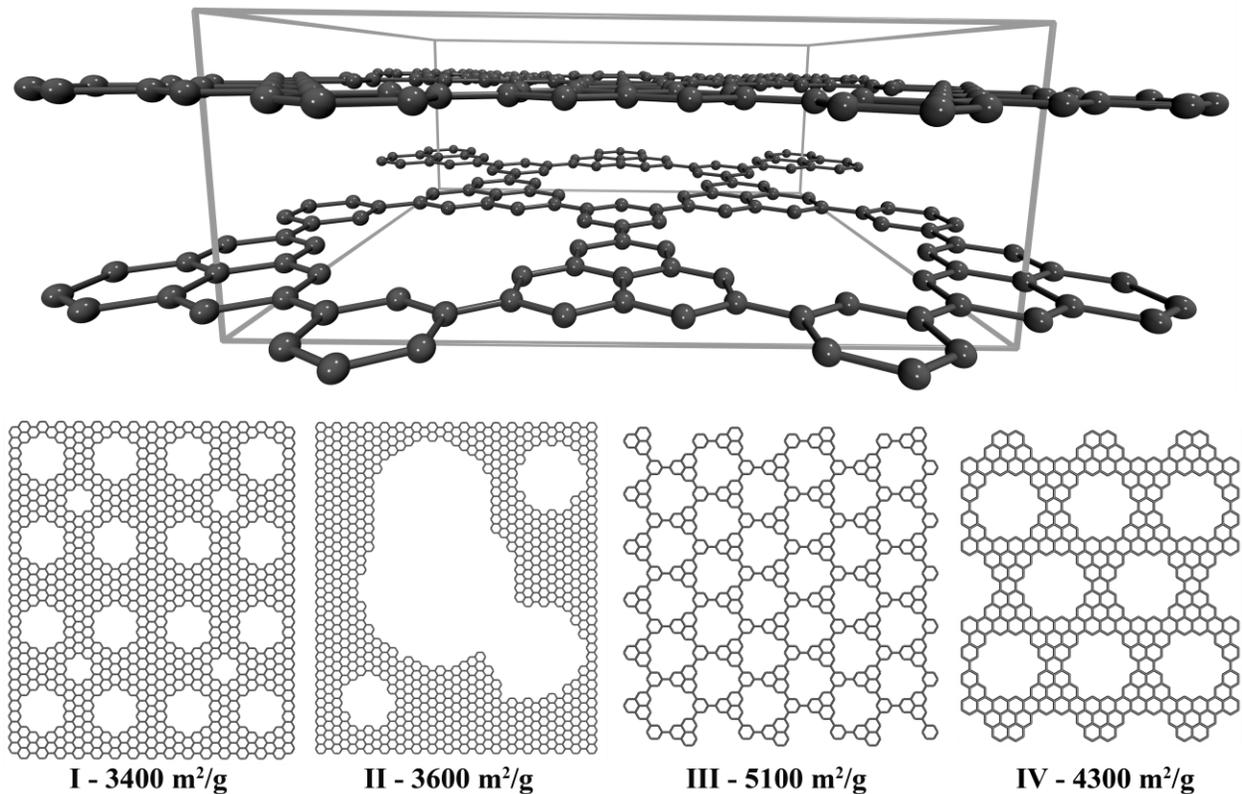


Figure 1. Structural models of perforated graphene. Top: an example of a 3D stacking of perforated graphene sheets (a perspective view). Bottom: different patterns of defects within graphene sheets considered in this work.

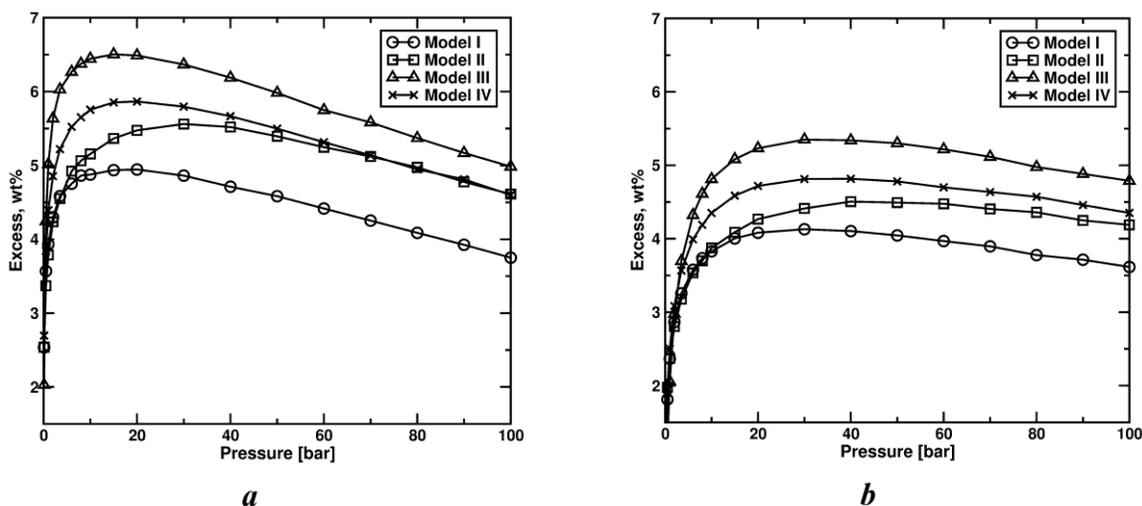


Figure 2. Simulated adsorption isotherms at $T=77$ K (a) and $T=100$ K (b) for the models of perforated multilayered graphene with the following surface areas and pore volumes: $3400 \text{ m}^2/\text{g}$ and $0.80 \text{ cm}^3/\text{g}$ (model I); (II) $3600 \text{ m}^2/\text{g}$ and $1.10 \text{ cm}^3/\text{g}$ (model II); $5100 \text{ m}^2/\text{g}$ and $0.95 \text{ cm}^3/\text{g}$ (model III); $4300 \text{ m}^2/\text{g}$ and $0.90 \text{ cm}^3/\text{g}$ (model IV).

Structures of type I and II can possibly be prepared experimentally starting from ideal graphene by removing part of carbon atoms. The structures similar to type III could be synthesized using bottom-to-top approach starting from molecular precursors following polymerization and polycondensation reactions.[42] Another example of hypothetical highly perforated structure shown in **Figure 1** is Model IV constructed by connecting coronene molecules into 2D sheets. This structure can be proposed as feasible for experimental realization since it is known that coronene can be easily converted into dimeric, chain-like and bulk polymeric forms.[43, 44]

While the design of 2D sheets shown in **Figure 1** seems to be feasible, the main experimental problem would be to separate perforated graphene layers by the distance sufficient for the penetration of molecular hydrogen. One of the possible solutions could be to use certain molecular pillars. However, in practice it is difficult to achieve a uniform distribution of pillars in between the graphene-oxide sheets. As a result, the surface area of pillared graphene-oxide normally does not exceed $\sim 800 \text{ m}^2/\text{g}$.[45]

Calculations of adsorption isotherms demonstrate that by introducing holes within graphene layers it is possible to increase hydrogen uptake due to higher porosity and higher

surface areas (**Figure 2**). Note that a somewhat similar idea to increase the surface area of graphene by creating defects was already mentioned in the literature[46] but was not validated yet for hydrogen storage applications.

From the general point of view, taking some carbon atoms out of the graphene sheets creates additional pores but also decreases the surface available for the hydrogen adsorption. The balance between these two parameters can be varied by changing the size and proportion of the area occupied by the holes, as illustrated in **Figure 1**.

Analysis of simulation results shows that the optimal strategy to achieve higher surface areas is to introduce regular arrays of small holes (6–7 Å in diameter, especially as in the model III, *cf.* Fig. 2) rather than to create larger ones (25–30 Å). Using small holes (model III), it is possible to achieve surface areas of up to ~5100 m²/g. Structural models with larger holes (up to 30 Å) results in essentially the same theoretical density (~1.1 cm³/g) but the maximal surface area is decreasing to ~3600 m²/g. Simulations of hydrogen adsorption performed on models shown in **Figure 1** demonstrate, that, indeed, the uptake can be increased proportionally to the change of surface area.

For example, the model II shows saturation uptake of 5.5 wt% at 77 K and 30 bar, *cf.* Fig. 2). Maximal storage capacity (6.5 wt% at 15 bar, 77 K) was found for the model III (Fig. 2) with the pore volume ~0.95 g/cm³ and surface area of nearly 5100 m²/g. Upon increasing the temperature from 77 K to 100 K, the uptake lowers by at most 1.5 wt% (Fig. 2). Incorporating more defects does not yield higher storage capacities because of the significant reduction in the number of adsorption sites. The perforated structure with very high proportion of holes relative to remaining graphene skeleton can be considered as variant of covalent organic frameworks (COFs).[47]

The maximal predicted uptake for perforated structures is in good agreement with experimental results obtained for carbon-based materials with similar surface areas. For example, porous aromatic frameworks (PAFs) with the BET surface area of 5600 m²/g can adsorb *ca.* 7.0 wt% at 77 K.[48]

The structures suggested above are, of course, idealized models. For example, experimentally characterized defected graphene materials consist of irregularly perforated sheets with essentially non-planar shape. This type of strongly defected graphene sheets packed into multilayered assemblies would be separated by the distance variable in the nanometer scale due

to curvature geometries. However, it was shown that the curvature of graphene sheets has only minor effect (within ~0.5 wt% or less) on hydrogen physisorption.[49] Therefore, we believe that our models provide useful insight into trends and limitations for the design of perforated graphene structures.

Theoretical modelling presented above provides strong promise for the design of new type of high surface area graphene materials with improved hydrogen storage parameters. However, making structures with precisely defined size of holes, their density and the distance between graphene sheets is a rather challenging task for experimental realization.

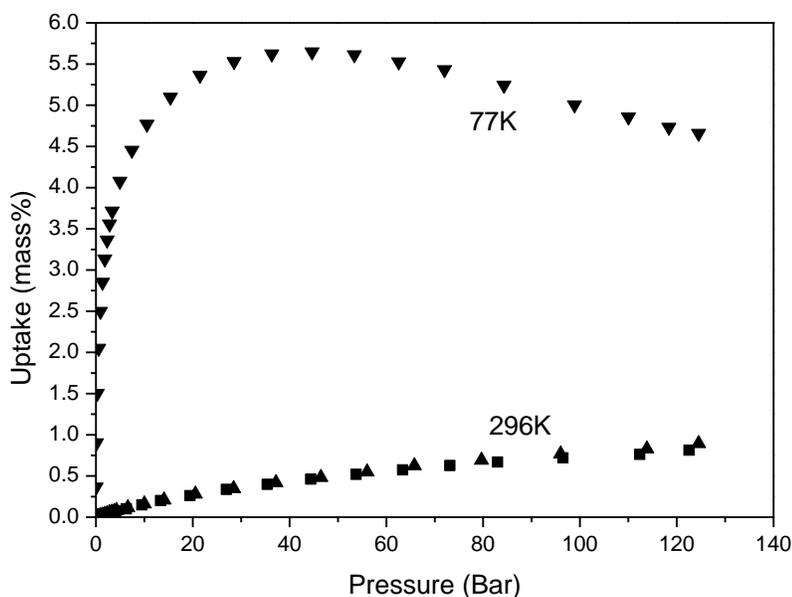


Figure 3. Hydrogen isotherms recorded from a-r-GO sample with 2900 m²/g BET surface area at 77K (▼) and at 296K (▲, ■).

Activation of r-GO powder using annealing with KOH is so far the only method which allows to achieve surface areas exceeding theoretical value for the defect-free graphene. The materials are not ordered in 3D and the exact size of the holes induced by activation is difficult to evaluate precisely. Nevertheless, we suggest that detailed characterization of hydrogen uptakes for these materials provides a reasonable opportunity to verify some of the theoretical conclusions presented above. Therefore, we prepared a sample with surface area of ~2900 m²/g and measured hydrogen uptakes at 77 K and 296 K (**Figure 3**) using volumetric method. The hydrogen uptake at 296 K was also verified using Rubotherm gravimetric system. The surface

area of the studied sample ($2900 \text{ m}^2/\text{g}$) was estimated using nitrogen adsorption (detailed analysis of N_2 isotherm is provided in supporting information). Pore size distribution evaluated using slit pore QSDFT model showed two major peaks centered around 0.8 nm and 1.8 nm with cumulative pore volume of $1.4 \text{ cm}^3/\text{g}$, in a good agreement with the data provided for similarly prepared samples in ref.[24]

Hydrogen isotherms at 77 K and 296 K are shown in **Figure 3**. The isotherm recorded at liquid nitrogen temperature shows saturation at around 30 bar ($\sim 5.5 \text{ wt}\%$) while at ambient temperature the uptake is not saturated at maximal pressure of 120 bar (0.89 wt%). Hydrogen uptake at ambient temperature was also verified using gravimetric method which showed reasonable agreement (0.83 wt%) with volumetric data.

Isotherms experimentally measured for a-r-GO sample show maximal uptakes at somewhat higher pressures compared to isotherms simulated for theoretical models (**Figure 2**) while the maximal uptakes are in reasonably good agreement. The a-r-GO sample and theoretical models are similar in two parameters: surface areas exceeding theoretical maximum for the defect-free graphene and relatively narrow pore size distribution. The main difference between experimental samples and model systems is the absence of precisely defined distance between perforated 2D sheets essential for the structures shown in Figure 1. The pore size distribution evaluated using nitrogen isotherms shows one peak at 0.8 nm, very close to theoretically required optimal distance between graphene sheets.²⁹ However, broader peak in the pore size distribution is found at $\sim 1.7 \text{ nm}$ which is above the optimal value. Therefore, perforated graphene materials with a well-defined pore size can be expected to show even higher hydrogen storage capacity exceeding the one achieved in our experiments (5.5 wt% at 77 K, 30 bar).

Considering reversible nature of physisorption, high stability of graphene-related materials at ambient conditions (compared to *e.g.* MOFs) and theoretically predicted possibilities of further increasing hydrogen uptakes by *e.g.* doping with boron, calcium or transition metal adatoms,[50-52] graphene can be suggested as a rather promising material for hydrogen storage applications.[1, 2]

5. Conclusions

In conclusion, theoretical modelling demonstrates that introducing defects (holes) allows to increase the surface area of carbon materials over the limit of defect-free graphene

(2630 m²/g). The surface areas of perforated multilayered graphene structures can be tuned in the range ~3000-5000 m²/g with corresponding hydrogen uptakes up to ~6.5 wt% predicted at 77 K. Strongly perforated structures are possibly more easy to synthesize using bottom-to-top approach, *e.g.* by molecular assembly of polycyclic aromatic hydrocarbons. Hydrogen isotherms predicted for idealized perforated structures are in fair agreement with the hydrogen uptake (5.5 wt%, 77 K) measured for highly defected graphene material produced using KOH activation of r-GO powder.

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Supporting information

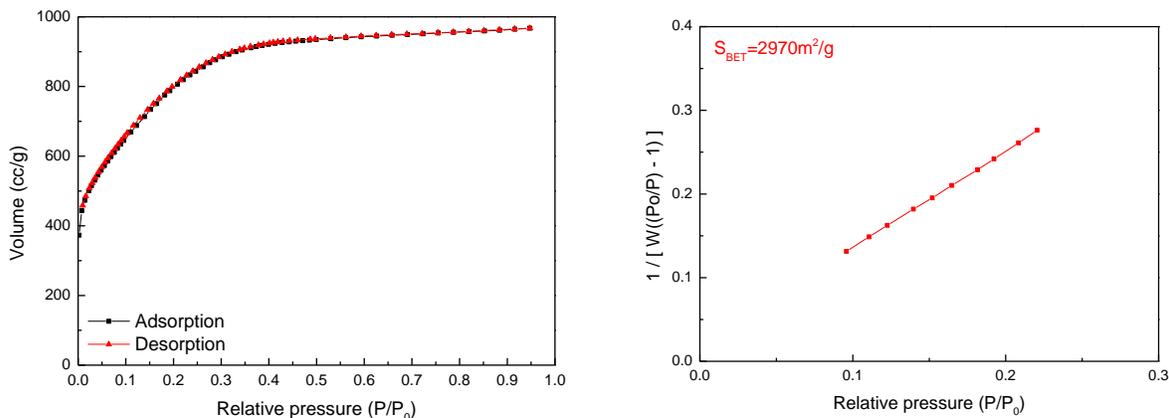


Figure 1S N₂ adsorption/desorption analysis of a-r-GO (2970 m²/g) performed after hydrogen annealing and H₂ uptake tests. The interval of P/P₀ for Bet plot was selected using procedure by J. Rouquerol (J. Rouquerol, P. Llewellyn and F. Rouquerol, Studies in Surface Science and Catalysis, 2007; 160:49-56). Simple fitting between 0.1 and 0.3 values yields 2800 m²/g value.

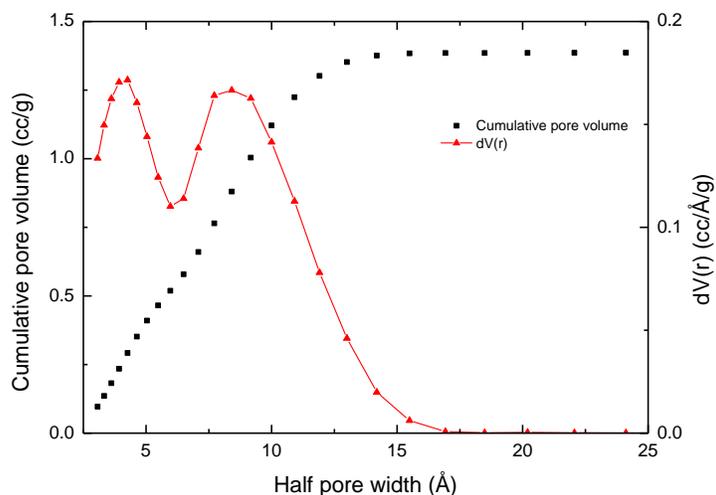
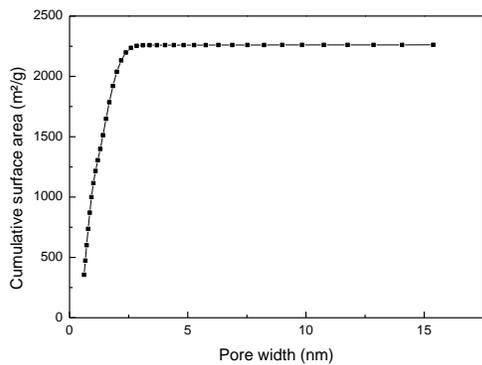
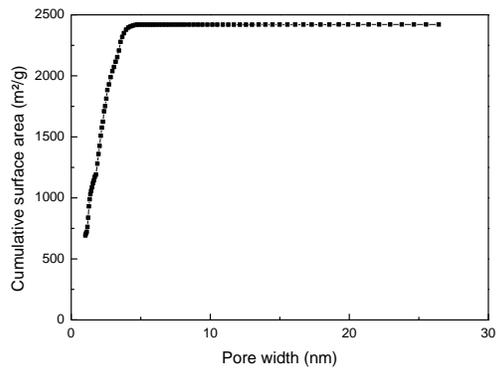


Figure 2S 'Quenched solid density functional theory' (QSDFT) pore size distribution and cumulative pore volume for a-r-GO.



a)



b)

Figure S3. Cumulative surface area of a-r-GO sample calculated according to a) QSDFT slit pore model and b) NLDFT slit-cylindrical pore model.