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Uptake of H₂ and CO₂ by Graphene

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Graphene samples prepared by the exfoliation of graphitic oxide and conversion of nanodiamond exhibit good hydrogen uptake at 1 atm, 77 K, the uptake going up to 1.7 wt %. The hydrogen uptake varies linearly with the surface area, and the extrapolated value of hydrogen uptake by single-layer graphene works out to be just above 3 wt %. The H₂ uptake at 100 atm and 298 K is found to be 3 wt % or more, suggesting thereby the single-layer graphene would exhibit much higher uptakes. Equally interestingly, the graphene samples prepared by us show high uptake of CO₂, the value reaching up to 35 wt % at 1 atm and 195 K. The first-principles calculations show that hydrogen molecules sit alternately in parallel and perpendicular orientation on the six-membered rings of the graphene. Up to 7.7 wt % of hydrogen can be accommodated on single-layered graphene. CO₂ molecules sit alternatively in a parallel fashion on the rings, giving use to a maximum uptake of 37.93 wt % in single-layer graphene. The presence of more than one layer of graphene in our samples causes a decrease in the H₂ uptake.

Introduction

Graphene has emerged to become an exciting new nanomaterial of carbon with many novel properties.^{1,2} Besides its fascinating electronic properties such as the fractional quantum Hall effect at room temperature, graphene has several other features of great interest. Many of the physical measurements on graphene have been made with samples prepared by the scotch-tape technique and there has been some recent effort to synthesize graphene samples on a larger scale. Such synthesis generally yields samples which are not single-layered and contain a few graphene layers.^{3–5} Studies of graphene prepared by such methods have revealed certain unexpected properties.⁵ Preliminary experiments indicate that graphene may have good sorption characteristics for hydrogen and carbon dioxide. We have, therefore, investigated the uptake of hydrogen and carbon dioxide by graphene samples obtained by exfoliation of graphitic oxide³ and conversion of nanodiamond.⁴ We have prepared samples possessing a wide range of surface areas and found them to exhibit relatively high uptakes of H₂ and CO₂, properties of potential interest in hydrogen storage and gas separation processes. To understand these properties we have carried out detailed first-principles calculations on the interaction of H₂ and CO₂ with single- and multilayered graphene. Physical adsorption of gases on some carbon nanostructures has been modeled earlier,^{5,6} but the present study provides greater insight on the origin of sorption of H₂ and CO₂ by graphene.

Experimental Section

We have prepared several graphene samples (EG 1, EG 2, EG 3, EG 4) by the exfoliation of graphitic oxide by following

the literature procedure^{3,7} and characterized the samples by X-ray crystallography, transmission electron microscopy, and other techniques. These samples contain 3–4 graphene layers as indicated by the analysis of the (002) reflection.⁷ Brunauer–Emmett–Teller (BET) surface areas were measured with a Quantachrome Autosorb-1 instrument. The surface areas were measured at 77 K with N₂ as the adsorbate. Analysis of (002) reflections in the X-ray diffraction patterns shows that they possess between 4 and 7 graphene layers. We have also prepared five samples of graphene DG 1, DG 2, DG 3, DG 4, and DG 5 by the transformation of nanodiamond.^{4,7} These samples contain 8–10 graphene layers as indicated by the analysis of the (002) reflection. The surface areas of the graphene samples also depend on the number of layers.⁸ We have treated the graphene sample, EG 3, with hydrogen at 1000 °C for 4 h to obtain EG 3-H₂, and with a 1:1 mixture of concentrated nitric and sulfuric acids at 100 °C under hydrothermal conditions to obtain EG 3-COOH. One sample of graphene, EG 5, was prepared by mechanical exfoliation of graphitic oxide in water, followed by treatment with hydrazine.⁹ Adsorption of hydrogen and CO₂ on the various graphene samples was measured at 77 and 195 K, respectively, using the Quantachrome instrument. High-pressure H₂ adsorption measurements was carried out at room temperature with a home-built apparatus.¹⁰

Results and Discussion

The BET surface areas of the graphene samples, obtained from exfoliation of graphitic oxide, EG 1, EG 2, EG 3, and EG 4, were in the range 639–1550 m²/g. The DG 1, DG 2, DG 3, DG 4, and DG 5 samples prepared from nanodiamond have surface areas in the range 280–1013 m²/g. The surface area of single-layer graphene is predicted to be 2600 m²/g.⁸ The surface areas of the samples prepared by us are lower because of the presence of more than one graphene layer. It must also be noted that the BET surface areas given here do not count for the pore effect.¹¹

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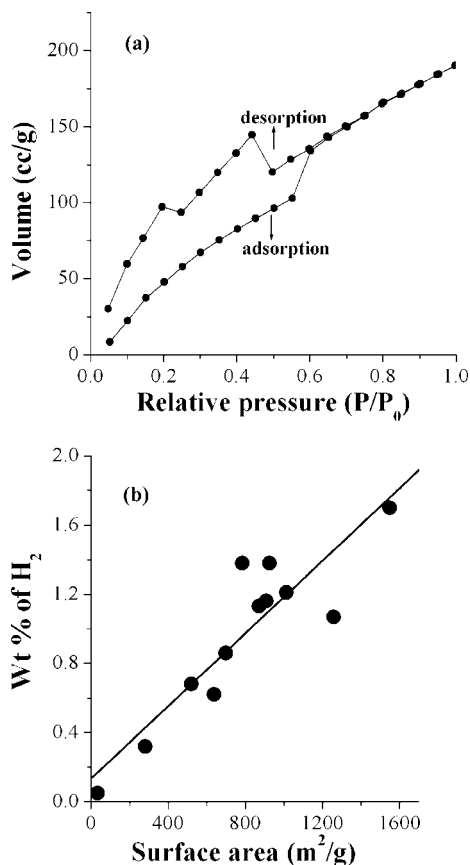


Figure 1. (a) Hydrogen adsorption and desorption isotherms of EG 1 at 1 atm of pressure and 77 K. (b) Linear relationship between the BET surface area and the weight percentage of hydrogen uptake at 1 atm of pressure and 77 K.

In Figure 1a we show typical adsorption and desorption curves for hydrogen in the case of EG 1 with a surface area of 1550 m²/g. This sample shows 1.7 wt % of H₂ uptake. Hysteresis can occur due to the weak interaction between the H₂ and the graphene sample or due to surface heterogeneity. It is more likely due to the presence of different sizes and shapes of pores. Such effects are also seen with nitrogen adsorption. The values of H₂ uptake by the various graphene samples prepared by us vary linearly with the surface area as shown by Figure 1b. By extrapolation of the plot in Figure 1b to the surface area of single-layer graphene, we estimate its hydrogen uptake at 1 atm and 77 K to be around 3 wt %, which is impressive. Typical high-pressure hydrogen adsorption isotherms are shown in Figure 2. We find EG 4 (with 1.4 wt % uptake at 1 atm and 77 K) exhibits a hydrogen uptake of 3.1 wt % at 100 bar of pressure and 298 K. One of the DG samples is found to exhibit an uptake of 2.5 wt % at 100 atm and 298 K. These values of the H₂ uptake at high pressure are comparable to those of single-walled nanotubes.⁸ It is possible that single-layer graphene will exhibit 5–6 wt % of H₂ uptake at 100 atm and 298 K. Following the DOE guidelines wherein 6 wt % H₂ uptake is required for automobiles, the present results are encouraging.¹²

We have studied the uptake of CO₂ at 1 atm and 195 K by several samples of graphene prepared by us. Figure 3 shows CO₂ adsorption and desorption curves of two samples. The EG samples show CO₂ uptake in the range of 21–34 wt %. The DG samples show somewhat variable values of CO₂ uptake in the range 10–38 wt %. It is possible that the small values of CO₂ uptake can occur in graphene samples containing large size particulates.

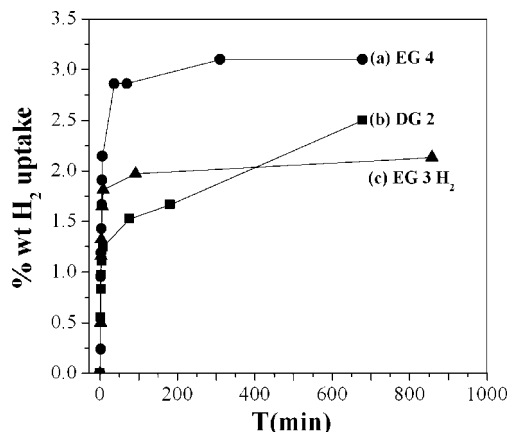


Figure 2. High-pressure hydrogen adsorption showing the variation of the weight percentage of hydrogen uptake at 100 atm and 298 K with time.

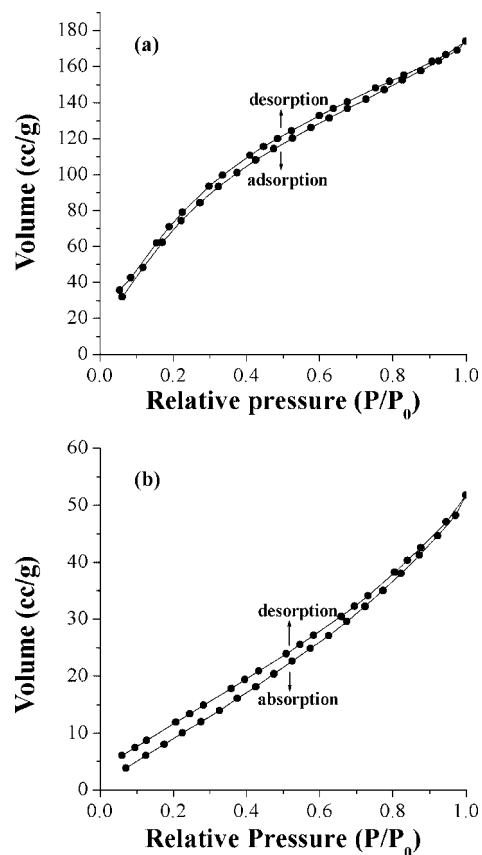


Figure 3. Carbon dioxide adsorption and desorption isotherms of (a) EG 1 and (b) DG 1 at 1 atm of pressure and 195 K.

A few workers have examined the adsorption of H₂, CO₂, and such gases on carbonaceous surfaces, but they generally consider bonding at edges.^{5,6} To explore the hydrogen and carbon dioxide uptake ability of graphene, we consider the 2D periodic graphene system with hydrogen and carbon dioxide using an *ab initio* density functional package, SIESTA.¹³ We have performed calculations within the generalized gradient approximation (GGA), considering Perdew–Burke–Ernzerhof (PBE) exchange and correlation functionals¹⁴ with the double- ζ polarized (DZP) basis set. The GGA approximation takes into account the semilocal exchange–correlations which have significant impact on low-dimensional systems like graphene. We place the 2D graphene in the *xy*-plane and assume the translation vector along the *z*-axis as 20 Å to create sufficient vacuum and

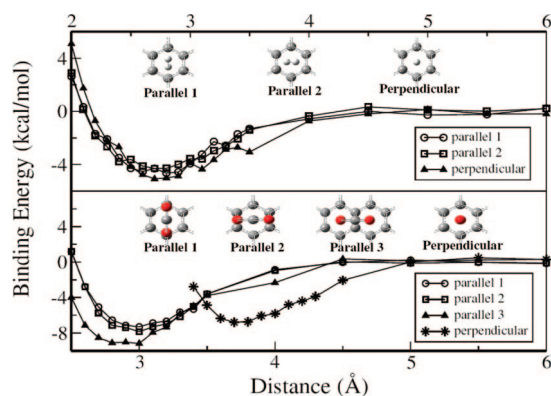


Figure 4. Binding energies of a single molecule on a graphene supercell as a function of distance with different adsorption orientations (shown in insets) for hydrogen (upper panel) and carbon dioxide (lower panel).

ensure that no interaction occurs between the adjacent layers. We have considered 400 Rydberg energy cutoff for a real space mesh size and a k -point sampling of 15 k -points, uniformly positioned along the 2D Brillouin zone. We first relax the structures of the graphene supercell, consisting of 72 carbon atoms, and the H_2 and CO_2 molecules separately at the same level of calculation. We vary the positions and distances of a single H_2 and CO_2 molecules separately on the relaxed structure of graphene to determine the most stable position with equilibrium distance for adsorption. We then gradually increase the density of H_2 and CO_2 molecules on the graphene sheet to determine the maximum weight percentage of uptake. To check the consistency of our calculations, we vary the graphene supercell size and perform the calculations. We have carried out similar calculations for graphenes with three and four graphene layers as well to determine the weight percentage with the knowledge of the adsorption conformation and equilibrium distances obtained from our single-layer calculations. We consider the distance between two adjacent layers in graphite as 3.35 Å, as observed experimentally, and the translation vector along the z -axis as 30 Å to create sufficient vacuum.

On the basis of the relaxed geometries, we consider three different orientations of hydrogen molecule on the graphene surface, namely parallel 1, parallel 2, and perpendicular as shown in the upper panel of Figure 4. The plot of binding energy with varying distance shows that the perpendicular orientation on the center of mass of a benzene ring gives the most stable structure at an equilibrium distance (r_{eq}) of 2.7 Å from the single-layer graphene with a binding energy of -5.073 kcal/mol. Parallel 1 and parallel 2 orientations also show stabilization around the same r_{eq} with binding energies of -4.612 and -4.382 kcal/mol, respectively. A similar r_{eq} value has been observed earlier.^{15–17} Although the binding energy differences among the different orientations arise from the nonsphericity of the H_2 molecule, the differences are negligibly small. Thus, all three orientations become almost equally significant.

In the case of carbon dioxide, we consider three different positions of parallel orientations, namely parallel 1, 2, and 3 and one perpendicular orientation as depicted in the lower panel of Figure 4. The binding energy values show that the parallel 3 structure is the most stable structure at $r_{eq} = 3.0$ Å from the graphene layer with a binding energy of -9.224 kcal/mol. The other two parallel orientations, namely 1 and 2, give binding energies of -7.295 and -7.848 kcal/mol at the same $r_{eq} = 3.0$ Å. For the perpendicular orientation, the binding energy is -6.785 kcal/mol at $r_{eq} = 3.7$ Å.

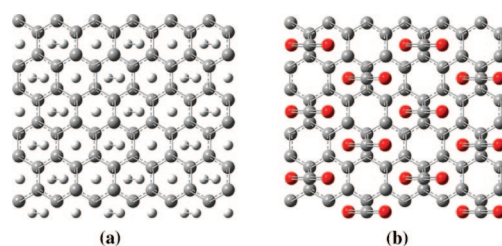


Figure 5. Graphene supercell with a maximum number of molecules of adsorbed hydrogen (a) and carbon dioxide (b).

With the knowledge of most stable position, orientation, and equilibrium distance of hydrogen as well as carbon dioxide, we gradually increase their density on one side of the graphene surface to estimate the maximum weight percentage of sorption. To start with, we consider the equilibrium distance for adsorption, as obtained from potential energy analysis in Figure 4, and relax the positions of H_2 and CO_2 , freezing the graphene supercell coordinates, to obtain the final preferred sorption geometry. Successive increase in H_2 density shows a small reduction in the binding energy per H_2 molecule, suggesting very weak repulsive interaction within the sorbed molecules. For perpendicular orientation of H_2 molecules, we find that each ring in the graphene plane can stabilize one hydrogen molecule at a distance of 2.89 Å from its center with a binding energy of -3.069 kcal/mol per hydrogen molecule. This leads to 7.69 wt % of hydrogen uptake by a single-layer graphene. Because of the small difference in binding energies, we have considered the parallel orientation as well (Figure 5a) and obtained a similar weight percentage of hydrogen uptake with a binding energy of -2.767 kcal/mol, with an equilibrium distance of 2.83 Å from the graphene plane. We too have considered a mixture of different orientations because of the small equilibrium conformational energy barrier within them. Both parallel 2 and perpendicular orientations on alternative benzene rings of the graphene supercell (Figure 5a) show the highest binding energy of -3.68 kcal/mol. However, in the optimized structure, the parallel 2 and perpendicular H_2 molecules are positioned at distances of 2.83 and 3.00 Å, respectively, from the graphene layer. The completely random mixture of all three orientations gains stability on optimization at the expense of diminished H_2 uptake. In this case, some of the H_2 molecules move away from the graphene supercell surface upon optimization, reducing the density of the adsorbate. The system, however, becomes stabilized primarily because of the lack of repulsion between the sorbed molecules as the distance becomes large. This observation suggests that the random adsorption of H_2 molecules on the graphene surface in reality will reduce the theoretically predicted maximum uptake of 7.69 wt %.

The values of binding energies indicate a lower energy of activation for desorption, suggesting graphene to be a satisfactory hydrogen storage material. However, keeping in mind that one may have a few-layer thick graphene instead of a single-layer graphene, we estimate the weight percentage of H_2 in graphenes with three layers and four layers as well. We obtain 2.70 and 2.04 wt % in the case of the three- and four-layer graphenes, respectively, with similar binding energies as in the case of single-layer graphene. Thus, from the van't Hoff equation, considering the entropy of vaporization of hydrogen as the entropy change in adsorption,¹⁸ we obtain a desorption temperature of 203 K for hydrogen at 1 bar of pressure.

For carbon dioxide uptake, we consider the parallel 3 conformation and obtain an adsorption of a maximum 12 molecules on one side of the graphene supercell with 72 carbon

atoms (Figure 5b), with a binding energy of -14.112 kcal/mol. This suggests maximum carbon dioxide uptake of 37.93 wt % on a single-layer graphene. In this case also the binding energy indicates a lower energy of activation for desorption. The relaxed distance of the CO₂ molecules from the graphene plane turns out to be 2.91 Å upon optimization. At this density, the binding energy per CO₂ molecule becomes higher than the binding energy of a single CO₂ molecule on the graphene supercell, suggesting a synergic stabilization. We have considered other CO₂ orientations including a mixture of more than one orientation, but failed to reach the value of 37.93 wt %. Three- and four-layer graphenes show maximum uptake of 16.92 and 13.25 wt %, respectively, for the geometry and density depicted in Figure 5b, with similar binding energies. We obtain the desorption temperature of carbon dioxide to be 657 K at 1 bar of pressure using the van't Hoff equation for the estimation of the entropy of vaporization of carbon dioxide.

We have obtained similar results in the case of different choices of supercells, which unambiguously prove that the theoretical estimates of the binding energy and the desorption temperature are hardly affected by the supercell size. It is known that density functional theory poorly describes dispersion forces. The dispersion forces become nontrivial in the case of interactions within dipolar or π -conjugated systems. However, for physisorption of gas molecules, the dispersion forces are less important. Although the dispersion corrections or second-order Møller–Plesset perturbation calculations (MP2)^{16,17} can improve the quantitative estimation of binding energies, the qualitative estimations would not change. This is evident from the large number of studies involving the same method for gas molecule adsorption in the literature.^{15–19} Moreover, the Lennard-Jones type of potential surface in Figure 4, particularly the well-rounded minima in the potential energy, supports our calculations.

Conclusions

In conclusion, the present study demonstrates that graphene samples prepared by exfoliation of graphitic oxide or conversion of nanodiamond exhibit significant uptake of H₂ and CO₂. While the maximum H₂ uptake found by us at 100 atm and 298 K is 3.1 wt %, it should be possible to increase it by preparing better samples and by reducing the average number of graphene layers. The high CO₂ uptake found by us can be of value for storage and separation. Our theoretical calculations also suggest graphene

to be satisfactory for H₂ and CO₂ storage. Interestingly, the H₂–graphene interaction energies obtained by us satisfy the optimum conditions for adsorptive storage of hydrogen.²⁰ Considering the DOE guidelines¹² and the known properties of materials for hydrogen storage,²¹ it appears that graphene is reasonably comparable to other porous carbon materials.^{22,23}

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