

Carbon dioxide adsorption in graphene sheets

Cite as: AIP Advances 1, 032152 (2011); <https://doi.org/10.1063/1.3638178>

Submitted: 20 July 2011 . Accepted: 12 August 2011 . Published Online: 01 September 2011

Ashish Kumar Mishra, and Sundara Ramaprabhu

COLLECTIONS

Paper published as part of the special topic on [Chemical Physics](#), [Energy, Fluids and Plasmas](#), [Materials Science](#) and [Mathematical Physics](#)



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Adsorption of CO molecules on doped graphene: A first-principles study](#)

AIP Advances **6**, 025317 (2016); <https://doi.org/10.1063/1.4942491>

[Gas adsorption on graphene doped with B, N, Al, and S: A theoretical study](#)

Applied Physics Letters **95**, 232105 (2009); <https://doi.org/10.1063/1.3272008>

[Methane and carbon dioxide adsorption on edge-functionalized graphene: A comparative DFT study](#)

The Journal of Chemical Physics **137**, 054702 (2012); <https://doi.org/10.1063/1.4736568>



NEW: TOPIC ALERTS

Explore the latest discoveries in your field of research

SIGN UP TODAY!

Carbon dioxide adsorption in graphene sheets

Ashish Kumar Mishra and Sundara Ramaprabhu^a

Alternative Energy and Nanotechnology Laboratory (AENL), Nano Functional Materials Technology Centre (NFMTC), Department of Physics, Indian Institute of Technology Madras, Chennai – 600036, India

(Received 20 July 2011; accepted 12 August 2011; published online 1 September 2011)

Control over the CO₂ emission via automobiles and industrial exhaust in atmosphere, is one of the major concerns to render environmental friendly milieu. Adsorption can be considered to be one of the more promising methods, offering potential energy savings compared to absorbent systems. Different carbon nanostructures (activated carbon and carbon nanotubes) have attracted attention as CO₂ adsorbents due to their unique surface morphology. In the present work, we have demonstrated the CO₂ adsorption capacity of graphene, prepared via hydrogen induced exfoliation of graphitic oxide at moderate temperatures. The CO₂ adsorption study was performed using high pressure Sieverts apparatus and capacity was calculated by gas equation using van der Waals corrections. Physical adsorption of CO₂ molecules in graphene was confirmed by FTIR study. Synthesis of graphene sheets via hydrogen exfoliation is possible at large scale and lower cost and higher adsorption capacity of as prepared graphene compared to other carbon nanostructures suggests its possible use as CO₂ adsorbent for industrial application. Maximum adsorption capacity of 21.6 mmole/g was observed at 11 bar pressure and room temperature (25 °C). *Copyright 2011 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [doi:10.1063/1.3638178]

I. INTRODUCTION

Increasing emission of green house gases due to industrialization is one of the major concerns faced by our generation in the second decade of this new millennium. CO₂ is considered as a major anthropogenic contribution to climate change. Cement, steel and automobile industries are responsible for the increasing concentration of CO₂ in our milieu. As the development of any country largely depends on its industrial growth, it has been a long demanding task to control the CO₂ emission in atmosphere. The CO₂ capture and storage (CCS) technologies from flue gas are considered to be cost-effective means for reducing the CO₂ content in the environment. Various CO₂ capture technologies, including absorption, adsorption, cryogenics and membranes etc. are under study. Among those alternatives, the technology considered nowadays as mature is CO₂ scrubbing using amine solutions. However, high energy requirements for solvent regeneration, extensive corrosion of the equipment and the impact of the amine solutions life cycle on the surrounding ecosystems are being of major concern for the continuous use of this technology.¹⁻³

Adsorption is known to be an alternative solution of the above problems associated with CO₂ absorption in amine based solutions. The ability to regenerate an adsorbent and the ease of its regeneration are also important consideration. Different porous materials like zeolite-based molecular sieves, activated carbons (ACs), carbon nanotubes (CNTs) have attracted the attention of researchers for gas adsorption. ACs generally give higher additional capacity at pressures greater than atmospheric compared to Zeolites. Further, ACs are often preferred over Zeolites because of their relatively moderate strengths of adsorption for gases, which facilitates easier desorption.⁴⁻⁶

^aEmail:- ramp@iitm.ac.in



CNTs have been also investigated as alternative for CO₂ adsorption due to their large surface area and high porosity.⁷⁻⁹ However the cost of CNTs is of still a concern. Graphene, as new class of carbon nanomaterials, is found to be economical and has novel properties similar to CNTs. Use of graphene in different applications like supercapacitor, fuel cells and photovoltaic is of immense interest to the current scientific research.¹⁰ Storage capacity of graphene for different gases has been suggested in theoretical studies and CO₂ adsorption capacity is demonstrated at very low temperature (195 K), which has not much practical implication.¹¹ Therefore, there is need to investigate the CO₂ adsorption capacity of graphene at room temperature and moderate pressure for practical application of graphene in CCS technology.

In the present work, graphene sheets were synthesized by hydrogen induced thermal exfoliation of graphitic oxide at 200 °C, a technique developed by our group for possible large scale production of graphene.¹² Adsorption capacity of HEG for CO₂, was studied by high pressure Sieverts apparatus at three different temperatures (25, 50 and 100 °C) using pressure reduction technique. Physical adsorption of CO₂ in graphene sheets was confirmed using FTIR spectroscopy.

II. EXPERIMENTS

Graphene sheets were synthesized by exfoliation technique. To prepare graphene sheets, graphitic oxide was prepared first by oxidation of pure graphite using Hummers' method. In this method, the oxidation of graphite to graphitic oxide is accomplished by treating graphite with essentially a water-free mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate.¹³ This graphitic oxide was further thermally exfoliated at 200 °C under hydrogen atmosphere. This thermal shock under the presence of hydrogen gas leads to formation of graphene sheets.¹² As prepared graphene sheets were named as hydrogen exfoliated graphene (HEG) due to use of hydrogen in the exfoliation process. As prepared graphene sheets were further characterized by X-ray diffraction, Transmission electron microscopy, Raman spectroscopy and surface area analysis. Adsorption studies for CO₂ gas were carried out using high pressure Sieverts apparatus. Schematic description of Sieverts apparatus is given elsewhere.⁹ Adsorption capacity was calculated by incorporating van der Waals corrections in gas equation. Desorption of CO₂ was performed at 150 °C under high vacuum ($\sim 10^{-9}$ bar) after each cycle of adsorption. Adsorption capacity was found almost repeatable in the next cycle of adsorption, suggesting the regeneration of HEG for further use.

III. RESULTS AND DISCUSSION

Figure-1 shows the XRD pattern of pure graphite, graphite oxide and HEG. XRD pattern of pure graphite shows a high intensity peak around 26.7° corresponding to the graphitic structure (002). After oxidation, the (002) peak of graphite powder disappears and an additional peak at 10.6° is observed, which is corresponding to the (001) diffraction peak of graphite oxide.

Oxidation of graphite leads to the increase in d-spacing, which can be attributed to the oxide induced oxygen containing functional groups and inserted water molecules. XRD pattern of HEG shows very less intense peak around 24.4°, indicates the distorted graphite structure and hence suggests the formation of graphene sheets.¹² TEM image (Figure-2(a)) shows the morphological structure of HEG. The rapid removal of intercalated oxygen atoms and other functional groups in graphitic oxide, during exfoliation results in a wrinkled structure of graphene sheets. Figure-2(b) shows the Raman spectrum of HEG. It shows two peaks corresponding to D-band (1346.5cm⁻¹) and G-band (1575.3cm⁻¹) for HEG. D-band corresponds to the defects induced in the graphitic structure, while G-band corresponds to the in-plane vibrations of the graphitic structure. Almost equal intensity of G-band and D-band suggests small crystalline size and hence very few numbers of layers.¹²

BET surface area measurement of HEG (Figure-3) asserts the large hysteresis area of N₂ adsorption-desorption isotherm suggesting the wide distributions of pores. The specific surface area of HEG calculated using BET equation was found to be 442.87m²/g. Large hysteresis area indicates a near uniform distribution of pores and large surface area of HEG, suggesting the high quality of synthesized graphene sheets. As synthesized graphene sheets possess much larger special surface

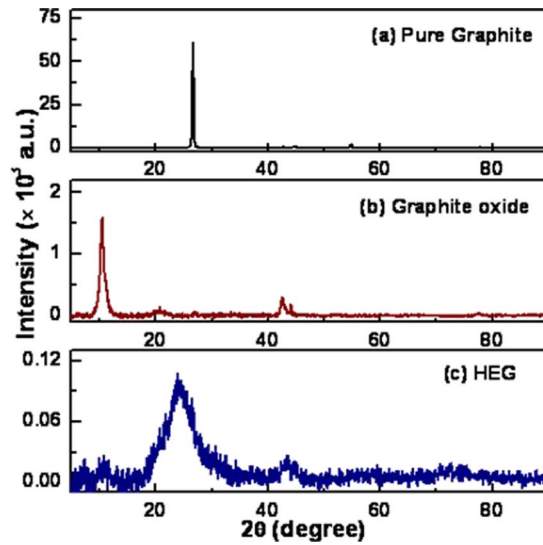


FIG. 1. XRD pattern of pure graphite (a), graphite oxide (b) and HEG (c)

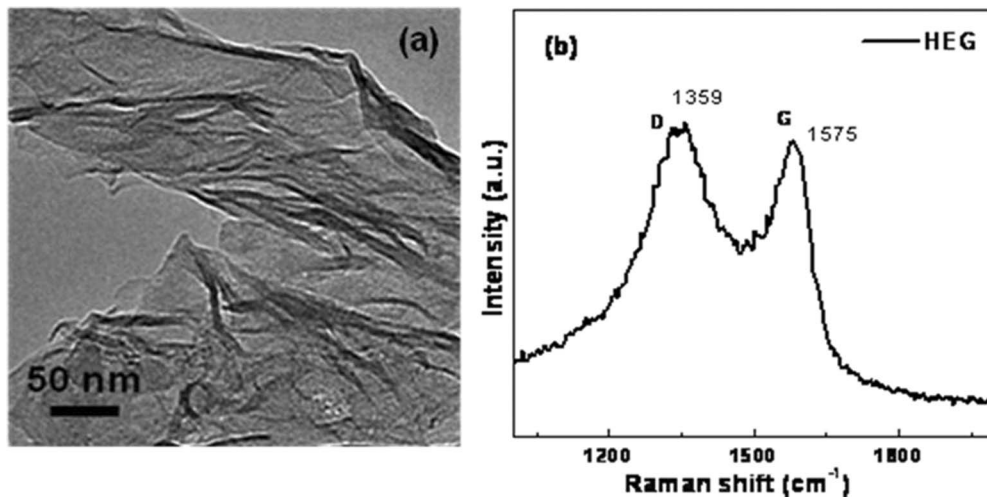


FIG. 2. TEM image (a) and Raman spectrum (b) of HEG

area, which indicates that the average particle size of graphite has been decreased during oxidation and rapid heating process under hydrogen atmosphere.

Amount of CO_2 adsorbed in mole was measured by calculating the number of moles of gas in the system before and after adsorption process. Number of moles of gas in the system can be calculated by following equation-

$$abn^3 + aVn^2 + (RT + Pb)V^2n - PV^3 = 0 \quad (1)$$

Where 'n' is the number of moles of gas present in volume 'V' of the system at pressure 'P' and Temperature 'T'. Constants 'a' and 'b' are the van der Waals constants for CO_2 gas.⁹

Figure-4(a) shows the adsorption isotherms of CO_2 for HEG at three different temperatures. Adsorption capacities of 21.6, 18 and 12 mmole/g were observed at 11 bar pressure and 25, 50 and 100 $^\circ\text{C}$ temperatures, respectively. It is evident from the isotherms that at each temperature the adsorption capacity increases with the increase in equilibrium pressure. This is attributed to the possible multilayer adsorption of CO_2 molecules in pores at high pressures.

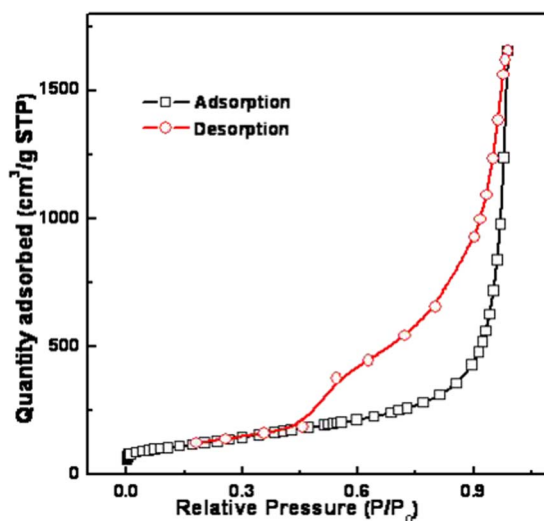


FIG. 3. Nitrogen adsorption-desorption isotherm of HEG

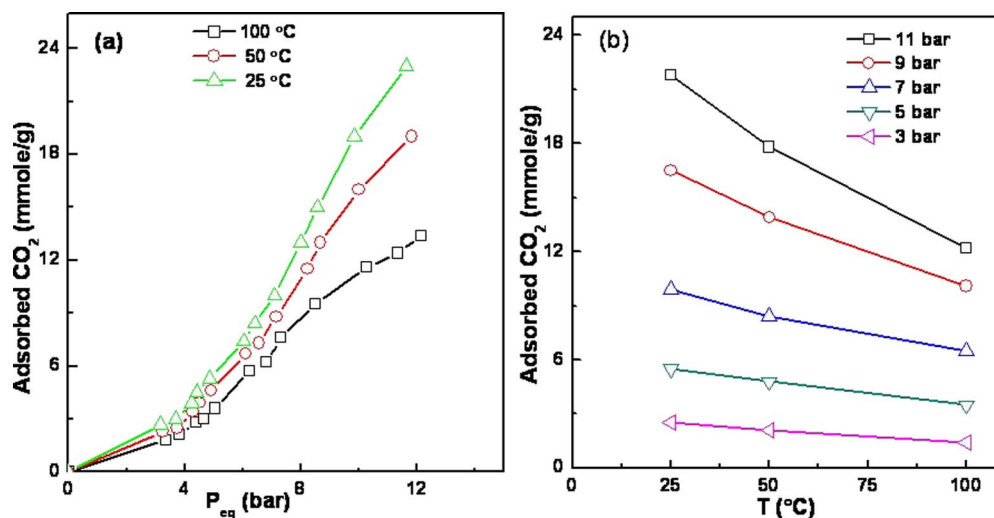
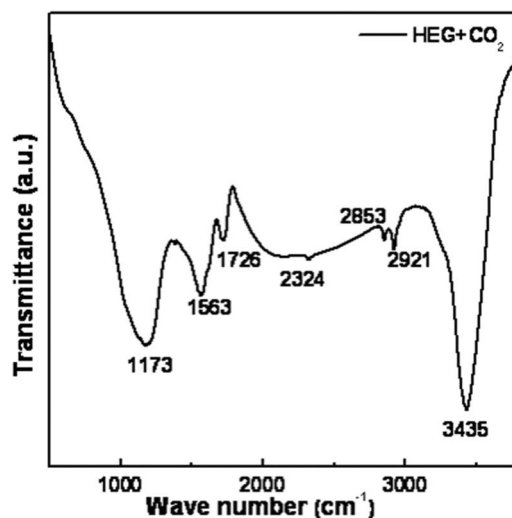
FIG. 4. CO₂ adsorption isotherms (a) and temperature variation of adsorption capacity (b) for HEG

Figure-4(b) shows dependence of CO₂ adsorption capacity on temperature for HEG and suggests decrease in capacity with increase in temperature. At higher temperatures CO₂ gas molecules possess high kinetic energy and hence higher desorption rate of CO₂ is possible. This results in lower adsorption capacity of HEG at higher temperatures. At lower temperatures, the CO₂ molecules possess lower kinetic energies and therefore possible condensation of gas takes place. Molecular adsorption of CO₂ in HEG was confirmed using FTIR study. Figure-5 shows the FTIR spectrum of CO₂ adsorbed HEG. The band corresponding to hydroxyl group (-OH stretching, 3435 cm^{-1}) is quite prominent as compared to the insignificant ratios of anti-symmetric and symmetric =CH_2 vibrations (2921 and 2853 cm^{-1}) for HEG. Intense peaks corresponding to the carboxylic and carbonyl groups were observed at 1726 ($>\text{C}=\text{C}$), 1563 ($=\text{CH}-$) and 1173 cm^{-1} ($>\text{C}=\text{O}$).¹² An additional peak was observed at 2324 cm^{-1} . This peak corresponds to the adsorbed molecular CO₂ in HEG and suggests the physical adsorption of CO₂.^{9,14,15}

Adsorption capacity of HEG for CO₂ was found higher to other carbon nanostructures (like ACs, CNTs) and zeolites at same pressure and temperature. Siriwardane *et al.* have reported ~ 7 mmole/g of CO₂ adsorption in AC.⁵ Gensterblum *et al.* reported nearly 6 mmole/g of CO₂ adsorption in AC

FIG. 5. FTIR spectrum of CO₂ adsorbed HEG

at 45 °C and 11 bar pressure.¹⁶ Zhang *et al.* have reported around 20% enhancement in CO₂ uptake by modifying the AC with nitrogen at room temperature and shown around 16 mmole/g adsorption capacity at 11 bar.¹⁷ In our earlier study on MWNTs adsorption capacity was observed 11.7, 8.3 and 7 mmole/g at 11 bar pressure and 25, 50 and 100 °C temperatures, respectively.⁹ Cavenati *et al.* have reported ~3.2 mmole/g of CO₂ adsorption in 13X zeolite at 12 bar pressure and room temperature.¹⁸ High pressure CO₂ adsorption study on different metal organic frameworks by Millward and Yaghi exhibits CO₂ adsorption capacity ranging from 2-8 mmole/g under similar conditions.¹⁹

IV. CONCLUSION

In summary, HEG shows higher adsorption capacity for CO₂ compared to other carbon nanostructures and zeolites, which may be directly attributed to the higher surface area of HEG. Regeneration property and high adsorption capacity of HEG make it suitable candidate for CCS technology. Additionally, cost effective production of HEG opens the wide area of research for the investigation of HEG based nanocomposites to achieve even higher CO₂ capture capacity to compete with commercial requirements.

ACKNOWLEDGMENTS

The authors acknowledge the supports of Office of Alumni Affairs, IITM and DST, India. The authors acknowledge SAIF and Department of Chemistry, IIT Madras for their support in FTIR and surface area analysis. One of the authors (Ashish) is thankful to DST India for providing the financial support.

¹D. Aaron and C. Tsouris, *Sep. Sci. Technol.* **40**, 321 (2005).

²H. L. Bai and A. C. Yeh, *Ind. Eng. Chem. Res.* **36**, 2490 (1997).

³A. B. Rao and E. S. Rubin, *Environ. Sci. Technol.* **36**, 4467 (2002).

⁴S. Sircar, T. C. Golden and M. B. Rao, *Carbon* **34**, 1 (1996).

⁵R. V. Siriwardane, M. Shen, E. P. Fisher and J. Poston, *Energy Fuels* **15**, 279 (2001).

⁶T. D. Burchell, R. R. Judkins, M. R. Rogers and A. M. Williams, *Carbon* **35**, 1279 (1997).

⁷M. Cinke, J. Li, C. W. Bauschlicher Jr., A. Ricca, and M. Meyyappan, *Chem. Phys. Lett.* **376**, 761 (2003).

⁸S. C. Hsu, C. S. Lu, F. S. Su, W. Zeng and W. Chen, *Chem. Eng. Sci.* **65**, 1354 (2010).

⁹A. K. Mishra and S. Ramaprabhu, *Energy Environ. Sci.* **4**, 889 (2011).

¹⁰A. K. Geim and K. S. Novoselov, *Nat. Mater.* **6**, 183 (2006).

¹¹A. Ghosh, K. S. Subrahmanyam, K. S. Krishna, S. Datta, A. Govindaraj, S. K. Pati and C. N. R. Rao, *J. Phys. Chem. C* **112**, 15704 (2008).

¹²A. Kaniyoor, T. T. Baby and S. Ramaprabhu, *J. Mater. Chem.* **20**, 8467 (2010).

- ¹³ W. Hummers Jr. and R. E. Offeman, *J. Am. Chem. Soc.* **80**, 1339 (1958).
- ¹⁴ W. M. Hlaing Oo and M. D. McCluskey, *Appl. Phys. Lett.* **86**, 073111 (2005).
- ¹⁵ W. L. Yim, O. Byl and J. T. Yates Jr. and J. K. Johnson, *J. Chem. Phys.* **120**, 5377 (2004).
- ¹⁶ Y. Gensterbluma, P. van Hemert, P. Billefont, A. Busch, D. Charrière, D. Lia, B. M. Krooss, G. de Weireld, D. Prinza and K. H. A. A. Wolf, *Carbon* **47**, 2958 (2009).
- ¹⁷ Z. Zhang, M. Xu, H. Wang and Z. Li, *Chem. Eng. J.* **160**, 571 (2010).
- ¹⁸ S. Cavenati, C. A. Grande and A. E. Rodrigues, *J. Chem. Eng. Data* **49**, 1095 (2004).
- ¹⁹ A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.* **127**, 17998 (2005).