Study of CO\textsubscript{2} Adsorption in Low Cost Graphite Nanoplatelets

Ashish Kumar Mishra and Sundara Ramaprabhu

Abstract—The growing needs of fossil fuel energy pose a great challenge in the control of CO\textsubscript{2} emissions in our atmosphere. Adsorption can be considered to be one of the more promising methods for CO\textsubscript{2} capture. In the present work, graphite nanoplatelets were prepared by acid intercalation followed by exfoliation technique. These graphite nanoplatelets were further functionalized and characterized by different characterization techniques. The CO\textsubscript{2} adsorption capacity was measured by high pressure Sieverts’ apparatus using vander Waals equation. Maximum adsorption capacity of 0.0036, 0.004 and 0.0049 mol/g was observed at 12 bar equilibrium pressure and at 100, 50 and 25 ºC temperature respectively. Isotherm deviates largely from Dubinin - Radushkevitch equation and hence suggests the adsorption via interaction with functional groups and gas condensation rather than micropore filling.

Index Terms—Adsorption, Exfoliation, Functionalization, Graphite nanoplatelets, Sieverts’ apparatus,

I. INTRODUCTION

Emissions from the combustion of fossil fuels are contributing to an increase in the concentration of CO\textsubscript{2} in the atmosphere. The use of fossil fuels accounts for about 75% of the current anthropogenic CO\textsubscript{2} emissions. It is generally accepted that this increase in atmospheric CO\textsubscript{2} may be resulting in a global climate change. It has been a long demanding task to counteract the greater level of greenhouse gases including carbon dioxide (CO\textsubscript{2}) to render eco friendly environment. The current world research is focused on the investigation of materials and techniques, which can capture large amount of CO\textsubscript{2}. As an alternative method for CO\textsubscript{2} capture, adsorption can be considered to be one of the more promising methods, offering potential energy savings compared to absorbtion systems, especially with respect to compression costs. Previously, pressure swing adsorption (PSA) using solid sorbents has gained interest due to its low energy and capital investment costs [1]-[4].

In terms of achieving high adsorption capacities, activated carbons (ACs) and zeolite-based molecular sieves have shown much promise. ACs generally give higher additional capacity at pressures greater than atmospheric compared to zeolites. CO\textsubscript{2} adsorption capacities of activated carbons depend on their pore structure but also on the surface chemistry properties [5], [6]. Along with ACs, one dimensional carbon based nanostructures like single walled and multi walled carbon nanotubes also provide a good alternative for CO\textsubscript{2} adsorption due to their large surface area and high porosity [7].

In the present work we have synthesized functionalized graphite nanoplatelets with acid intercalation of graphite followed by thermal exfoliation and functionalization. Carbon dioxide adsorption capacity of functionalized graphite nanoplatelets was studied using Sieverts’ apparatus at three different temperatures (25, 50 and 100ºC). Further adsorption behavior of CO\textsubscript{2} was tested with Dubinin - Radushkevitch equation.

II. EXPERIMENTAL SECTION

A. Preparation of functionalized graphite nanoplatelets

Graphite was vigorously stirred with conc. HNO\textsubscript{3} and conc. H\textsubscript{2}SO\textsubscript{4} in 1:3 ratios for three days. Vigorous stirring of graphite under strong acidic medium may cause the formation of acid intercalated graphite and hence partial oxidation of graphite. This intercalated graphite further thermally exfoliated at 1000 ºC [8]. This large amount of heat supplied to the sample increase the entropy and hence may lead to the destacking of the graphite plates. This destacking leads to the formation of graphite nanoplatelets (GNP). These GNP were further treated with conc. HNO\textsubscript{3}, which introduces hydrophilic functional groups (-COOH, -C=O, and -OH) at the surface of GNP [9]. These functionalized graphite nanoplatelets (f-GNP) were further washed several times with water to achieve pH=7 followed by drying.

B. Characterization

Surface morphology of f-GNP was characterized by JEOL 3010 High resolution transmission electron microscope. X-ray powder diffraction analysis was performed by X’ Pert Pro PANalytical X-ray diffractometer. FTIR study was performed by using PERKIN ELMER Spectrum One FT-IR spectrometer. Adsorption studied was performed with indigenously designed Seiverts’ apparatus.

C. Adsorption Studies

Adsorption studies were carried out using indigenously designed high pressure Seiverts’ apparatus, which has been well used for high pressure hydrogen sorption studies [10]. The experimental setup consists of stainless tubes, tees, elbow joints and needle valves procured from NOVA, Switzerland. They can withstand up to 1000 bar pressure. The pressure transducers procured from Burster, Germany are used to monitor the gas pressure in the range 0-50 bar.
Numbers of cycles were performed to recheck the adsorption capacity and the values were found to be almost consistent. Samples were degassed at 150°C under high vacuum ($10^{-9}$ Torr) to regain their adsorptive sites for CO$_2$ and the same sample again used for adsorption study and adsorption capacity was found to be repeatable.

III. RESULTS AND DISCUSSION

A. Morphological and structural Study

TEM (fig. 1a) image of f-GNP reveal its morphological structure. TEM image clearly suggest the induced disorderness in graphite structure due to acid intercalation followed by exfoliation. Different groups of graphite layers can be seen in the TEM image, suggesting the destacking of ordered graphitic structure.

X-ray diffractogram of pure graphite and f-GNP is shown in fig. 1b. X-ray pattern clearly shows less number of counts for f-GNP compared to pure graphite. This may be attributed to the short range order in f-GNP compared to the pure graphite suggesting the destacking of ordered graphitic structure.

![Figure 1a. TEM image of functionalized graphite nanoplatelets](image)

![Figure 1b. X-ray diffractogram of pure graphite and functionalized graphite nanoplatelets](image)

B. Raman spectra analysis

Raman spectroscopy has been used to investigate the vibrational characteristics of carbon samples. Fig. 2 shows the Raman spectra of pure graphite and f-GNP. Raman spectra for each carbon sample show the presence of D-band (around 1345 cm$^{-1}$) and G-band (around 1575 cm$^{-1}$). D-band corresponds to the defect or disorderness in the graphitic structure and it is activated by disorder in sp$^2$ carbon network. G-band corresponds to the tangential mode of vibrations related to the graphitic structure [11]. Ratio of intensity of D-band to G-band ($I_d/I_g$) was found to be different for each sample. Additionally, a small shift to higher frequency region was observed for D and G-band in case of f-GNP compared to the pure graphite. This shift can be attributed to the functional groups attached to the surface of f-GNP. Attachment of functional groups at the surface of f-GNP may increase the energy necessary for vibrations to occur (due to change in the reduce mass of harmonic oscillator), which is reflected in the higher frequency of Raman peaks.

In addition, the crystallite size ($L_a$) depends on the value of $I_d/I_g$ by following equation-

$$L_a = \frac{C(\lambda)}{I_d/I_g}$$  \hspace{1cm} (I)

Where $C(\lambda)$ is the constant depending on the wavelength of the laser light used in Raman spectroscopy [12], [13]. Equation-1 clearly suggests that with the increasing value of $I_d/I_g$, the crystallite size decreases and hence the number of layers in graphite structure decreases.

The higher value of $I_d/I_g$ suggests the increased disorderness in the corresponding carbon sample. Lowest value of $I_d/I_g$ for pure graphite suggests the high orderness in pure graphite. A Raman spectrum of GNP exhibits the higher value of $I_d/I_g$, suggesting the introduction of defects in f-GNP caused by acid intercalation and thermal exfoliation.

C. Fourier transform infrared spectrogram analysis

Fig. 3 shows the FTIR spectrum of f-GNP and CO$_2$ adsorbed f-GNP. FTIR study of f-GNP confirms the defective sites at the surface of graphite nanoplatelets and the presence of >C=O (1632 cm$^{-1}$), >C=O (1022,1106 cm$^{-1}$), =CH$_2$ (2850,
2924 cm$^{-1}$) and –OH (3436 cm$^{-1}$) functional groups at the surface of graphite nanoplatelets, while peak at 1385 cm$^{-1}$ may be due to the carboxylic group (-COO) attached to the f-GNP [8].

In the case of CO$_2$ adsorbed f-GNP an addition peaks was noticed at 2319 cm$^{-1}$ which corresponds to the asymmetric stretching of CO$_2$ molecules. Along with asymmetric stretching, shift was observed in most of the peaks which may be due to the adsorbed CO$_2$ in the pores of nanotubes and interaction of CO$_2$ with the functional groups (like carbonyl etc.) attached to the surface of f-GNP [14], [15].

$$\Delta n_{\text{adsorbed}} = n_1 - (n' + n'')$$

Where `n_1` is the number of mole of CO$_2$ in the initial volume `V_o` at the known initial pressure `P_i`. `n'` is the number of moles in `V_o` at equilibrium pressure `P_{eq}` and `n''` is the number of moles in cell volume `V_c` at equilibrium pressure `P_{eq}`. Where `n_1`, `n'` and `n''` can be calculated by using following equations:

$$abn_1^i + aV_n^i = (RT + P_b)V_i^i$$

$$abn_1'' + aV_n'' = (RT + P_b)V_{i'}$$

$$abn_1''' + aV_n''' = (RT + P_b)V_{i''}$$

Where `T` is the cell temperature and `R` is the universal gas constant. 'a' and 'b' are the vander waals coefficient for gas.

Fig. 4 shows the CO$_2$ adsorption behavior of f-GNP at three different temperatures (25, 50 and 100 ºC). It clearly shows that with increase in pressure adsorption capacity increases at all temperature, which may be attributed to the condensation of gas in pores at high pressure. Maximum adsorption capacity of 0.0036, 0.004 and 0.0049 mol/g was observed at 12 bar equilibrium pressure and at 100, 50 and 25 ºC temperature respectively.

Increase in adsorption capacity at higher pressures may be attributed to the more interaction of CO$_2$ gas molecules with the functional groups and the pores at the surface of f-GNP. In addition, due to high pressure condensation of CO$_2$ gas may take place and hence results in more adsorption capacity.

$$E = n'P_{eq}^2/n''P_{eq}'^2$$

Where `E` is given by-

$$W = \Delta n * M / \rho$$

Where `\Delta n` is the amount of CO$_2$ adsorbed in mol/g, ‘M’ is the molecular weight (M=44g) and ‘\rho’ is the density of the CO$_2$ adsorbate at the temperature T (\(\rho=0.85g/cc\) at 298K).

E. Temperature Dependence

Fig. 5 clearly shows the CO$_2$ adsorption dependence on temperature for f-GNP. This suggests that with increase in temperature the adsorption capacity of f-GNP decreases, which may be attributed to the higher kinetic energy of CO$_2$ gas molecules at higher temperatures. At lower temperatures, the CO$_2$ molecules possess lower kinetic energies and therefore a good interaction between CO$_2$ molecules and f-GNP increases the adsorption capacity. At low pressures CO$_2$ adsorption capacity increase linearly with decrease in temperature, while at higher pressures it does not follow linear behavior. This may be attributed to the large condensation of gas at high pressure and low temperature due to the interaction between the gas molecules themselves.

**Dubinin-Radushkevitch (D.R.) Equation**

The CO$_2$ adsorption isotherm at room temperature for f-GNP was treated by the Dubinin-Radushkevitch (D.R.) equation [16], [17]. D.R. equation can be represented as follows:

$$\ln W = \ln W_0 + (R/E)^2[T \ln (P_0/P)]$$

Where ‘W’ is the amount of adsorbed CO$_2$, ‘W_0’ is the microporous volume and ‘E’ is the characteristic adsorption energy. ‘W’ is given by-

$$W = \Delta n * M / \rho$$
in the mesopores and interaction of CO₂ with functional groups at the surface of graphite nanoplatelets.

![Graph showing adsorption capacity vs temperature]

Figure 5. Variation of adsorption capacity of functionalized graphite nanoplatelets with temperature at different pressures

IV. CONCLUSION

The present work described the cost effective preparation and functionalization of graphite nanoplatelets and study of its CO₂ adsorption capacity at high pressures. FTIR study confirms the adsorbed CO₂ in the pores of functionalized graphite nanoplatelets. The present work demonstrates that f-GNP can be used as CO₂ adsorbent under high pressure conditions like exhaust of thermal power plants and cement industries and hence can reduce the amount of CO₂ in atmosphere. Desorption of adsorbed CO₂ at 150°C in vacuum suggests the reuses of adsorbent and hence more commercial advantage. Additionally this desorbed CO₂ can be used for packaging in food industries.

REFERENCES


Ashish Kumar Mishra is a Research scholar at the Department of Physics, Indian Institute of Technology Madras, India.

S. Ramaprabhav is a professor at the department of Physics, Indian Institute of Technology, Madras, India. He received his PhD in 1984, from Indian Institute of Technology, Madras. His current areas of research include synthesis and applications of carbon based nanomaterials and other nanotubular structures.