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Adsorption of carbon dioxide and carbon monoxide on the modified graphene surfaces

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Abstract
This paper presents the function and application of graphene and its derivatives in the field of adsorption. Graphene applications in toxic gases sensor and adsorption is major field of research. Structural properties of graphene make it a useful material for all of the above applications. The adsorption properties of graphene make it a commendable material in surface chemistry. Thus, graphene-based materials provide a huge thrust to the pollutant absorbent industry. Based on the application of graphene in controlling different pollutants by utilizing its adsorbent properties, this work stresses upon the useful applications of graphene in the context of adsorption of toxic gases. It is observed that PG surface is unfavourable for CO2/CO adsorption because of positive value of adsorption energies. After the doping of Li-atom this PG becomes suitable candidate for adsorption. Physisorption of both the gases is observed over Li-PG.

Keywords: graphene, toxic gases, doped graphene, adsorption, Li-PG

Introduction
World civilization leads to major changes in lifestyle and livelihood; at the same time, it also brings many issues which cause health problems and environmental concerns. In the present scenario, the major factors responsible for pollution worldwide are the industrial revolution, urbanization and population expansion. All these contribute in the pollution to water, soil and air. Industries are causing release of different pollutants, which are organic as well as inorganic. Eco-environments and the human health are affected by the major pollutants, including toxic gases (NO_x, SO_x, CO, NH_3), heavy metals, organics and bio-toxics. Some of the pollutants are biodegradable and some are not. The removal of non-biodegradable pollutants becomes a burden on our environment and is a major health concern.
Many gases are present in our surrounding. The main gases are Nitrogen (78%), oxygen (21%) and argon (0.9%) and carbon dioxide, methane, nitrous oxide and various synthetic chemicals make up remaining 0.1%. Most of the gases in the atmosphere are nitrogen and oxygen as they form the 99 % of the atmosphere. The rest 1 % of the atmosphere is made up of the remaining gases and these gases are called trace gases because they are present in very less quantity. Some of these gases are useful and some are harmful. The oxygen gas is essential for our life. There are also some other traces of gases which are useful for us. The dangerous gases for us is nitrous oxide, sulphur dioxide, methane, ozone, ammonia, hydrogen sulphide, carbon monoxide and carbon dioxide etc [1, 2]. Especially in surface chemistry, various contaminants can be removed from air and water systems.
Exposure of CO_2 and CO Effects our health. These effects include headache, restlessness, dizziness, difficulty in breathing, increasing heartbeat, sweating, coma, blood pressure etc [3-5]. The CO gas is odourless, tasteless and colourless. The exposure of CO at low concentration may result in dizziness and headache and exposure to higher concentration of CO would even lead to death. As the earth's temperature increasing, it is known as Global warming. The main cause of global warming is carbon dioxide gas. The exposure of higher concentration of carbon oxide is also harmful to human health. In this study will discuss the adsorption of CO2 and CO and graphene-based surfaces.

Graphene and its properties
It is a combination of graphite and suffix – ene. It is an allotrope of carbon as such as the graphite is an allotrope of carbon [6, 7]. It looks like a two-Dimensional honeycomb lattice nanostructure. Every atom in graphene, is connected to three neighbour atoms by sigma bond. The bonding seen in these are same as that of bonding in fullerenes and glassy carbon. The optimized structure of graphene is shown in figure 1.

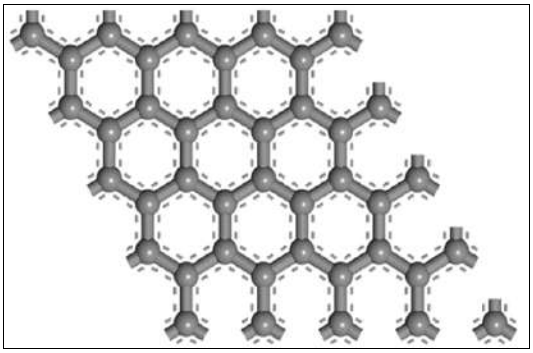

Fig 1: Optimized Graphene structure

The properties of graphene: Graphene surfaces has unique properties [8-13]

- High thermal conductivity
- High electrical conductivity
- High elasticity and flexibility
- High hardness and high resistance.
- It is 200 times stronger than steel but much lighter.
- It is able to generate electricity by exposure to sunlight.
- It is Transparent material.
- It has antibacterial effect because bacteria are not able to grow in it.
- It has high mechanical strength and high surface area.

Result and Discussion

In this study, we discussed the adsorption of CO_2 and CO on pristine and Li-doped graphene. First, to study the electronic structure of carbon dioxide and carbon mono-oxide, we optimize these structures to global minima. The optimized structure of CO_2 and CO are shown in figure 2.

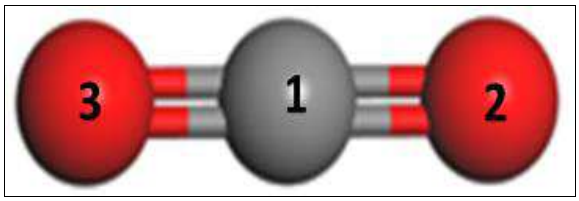

Fig 2: Optimized structure of CO_2 (Color codes: Gray: Carbon; Red: Oxygen)

In the optimized structure, the carbon is positively charged and both the oxygen atoms consist negative charge. Oxygen is more electronegative as compare to carbon atom, so it bears negative charge and carbon atom consist positive charge. In the adsorption process the chemical reactivity of adsorbent plays an important role and their chemical reactivity depends on the energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

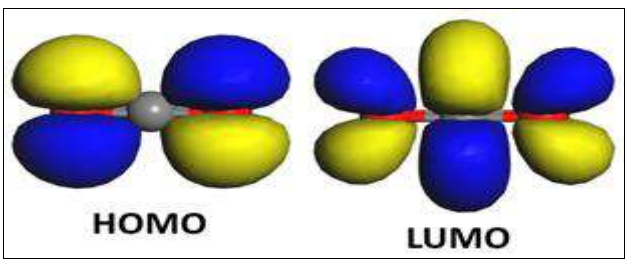

Fig 3: HOMO-LUMO plots of CO_2

HOMO-LUMO plots of CO_2 are shown in figure 3. HOMO plot mainly lies on electron rich oxygen atoms. LUMO plot lies on electron deficient carbon atom and anti-bonding orbital of oxygen atom. The HOMO-LUMO gap is calculated as 8.51 eV. The negative value of LUMO revels that the molecule is an electron good acceptor.

In case of carbon monoxide, the carbon has positive hirshfeld charge and oxygen is negatively charge (-0.072) due to its high electronegativity [14] as shown in figure 4.

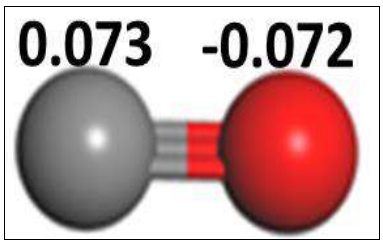

Fig 4: Optimized structure of CO (Color codes: Gray: Carbon; Red: Oxygen)

The HOMO-LUMO energy gap is observed 6.99 eV. The HOMO-LUMO plots are shown in figure 5.

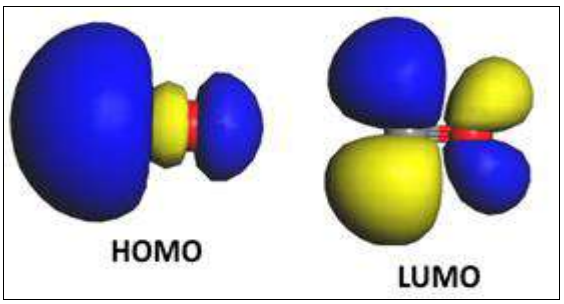

Fig 5: HOMO-LUMO plots of CO

Structure of Pristine and Li-doped Graphene

The optimized structure of Pristine Graphene (PG) and Lithium (Li) doped graphene are shown in figure 6. PG is planner with bond length of C-C (1.42 Å). The Li doped graphene also consist same C-C bond length as of pristine graphene, 1.42 Å. The distance between graphene sheet and Li atom is calculated 1.67 Å as shown in figure 6.

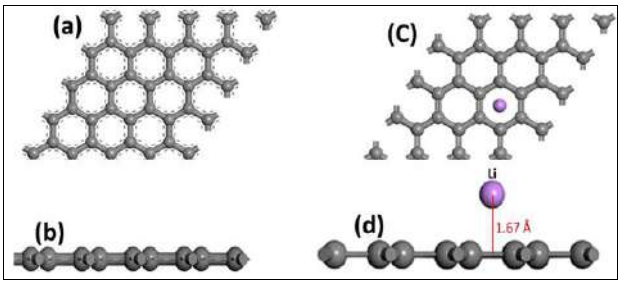

Fig 6: Top and side view of the PG and Li-PG surfaces; (a) top view PG, (b) side view PG, (c) top view Li-PG (d) side view Li-PG

Interaction of CO_2/CO with PG and Li-PG

For the adsorption of CO_2 gas and CO gas on pristine graphene, these gases are placed on vicinity of graphene surface. It is found that before adsorption and after adsorption, negligible changes are observed in adsorbent and adsorbate structures. The adsorption energy values of

CO2 and CO over PG are shown in table 1. The positive value of adsorption energy shows that adsorbent is an unfavourable surface for given adsorbate. Adsorption of carbon dioxide and carbon mono-oxide over pristine graphene is shown in figure 7.

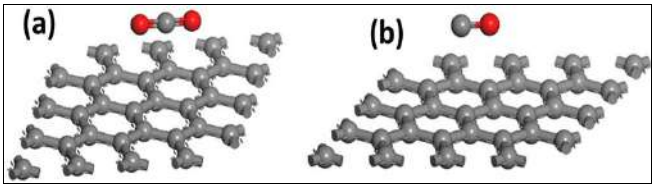

Fig 7: Adsorption of (a) CO_2 on PG and (b) adsorption of CO on PG

Table 1: Adsorption energies of CO2/CO over PG and Li-PG surfaces

Surface (Adsorbent)	Gases (Adsorbate)	Adsorption Energy (eV)
Pristine Graphene (PG)	CO_2	0.052 eV
Pristine Graphene (PG)	CO	0.054 eV
Li-Doped PG	CO_2	-0.230 eV
Li-Doped PG	CO	-0.191 eV

In case of Li-PG, some structural changes in adsorbate take place. In the adsorption of CO_2 over Li-PG, the structure of CO_2 changed from liner to V-shape as shown in figure 8. After adsorption, the distance between graphene sheet and Li atom change from 1.67 Å to 1.92 Å. CO_2/Li-PG adsorption energy is found -0.23 eV. There is a physisorption between adsorbate and adsorbent.

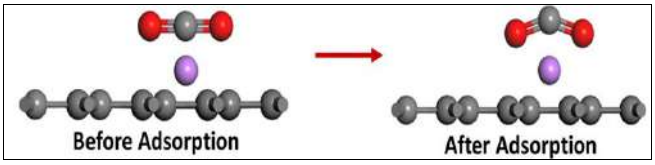

Fig 8: Adsorption of CO_2 on Li-PG

In case of CO on Li-PG, the distance between Li and graphene sheet change from 1.70 Å to 1.80 Å. The orientation of CO change from parallel to perpendicular, in which oxygen atom directed towards Li atom as shown in figure 9. There also physisorption with adsorption energy -0.19 eV.

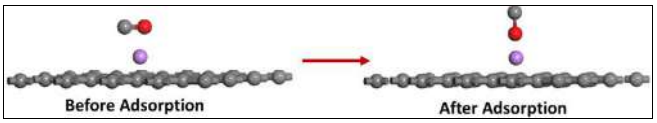

Fig 9: Adsorption of CO on Li-PG

Conclusion

From the graphene-based study, it has been concluded that the adsorbent properties of graphene can be exploited for the controlling of different pollutants, which cannot be controlled by different controlling agents. Its special properties will help in control of secondary pollutants which are non-degradable. Graphene and its derivatives can be further modified by use of different synthetic methods for control of various pollutants. A large number of transition metal doped graphene surfaces are found suitable candidates for adsorption of CO2/CO. In this work, we study the electronic structure of CO2/CO with their charges and HOMO-LUMO energies. We also studied the lithium doped graphene surface. It is observed that PG surface is unfavourable for CO2/CO adsorption because of positive value of adsorption energies. After the doping of Li-atom this PG becomes suitable candidate for adsorption. Physisorption of both the gases is observed over Li-PG.

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