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Chapter 5

Application of Doped-Graphene in Adsorption of Small Molecules: A Review

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5.1 Introduction:

Graphene is basically a two dimensional sheet of carbon atoms possessing sp^2 hybridization arranged in a honeycomb like structure (Figure 5.1). The excellent physicochemical properties of graphene like electrical, thermal, optical and mechanical features are due to extended π-electronic conjugation in long order. Graphene finds applications in solar cells, fuel cells, super capacitors and batteries. Both experimental and theoretical studies have shown that the electronic structure of graphene can be tuned by doping it with foreign atoms (non-metallic). Due to doping, the catalytic activity of graphene increases because of augment of active sites in it. Theoretical calculations have revealed that B/N co-doping of graphene results in alteration of its optical properties, so that it is reflected in the visible region [1].

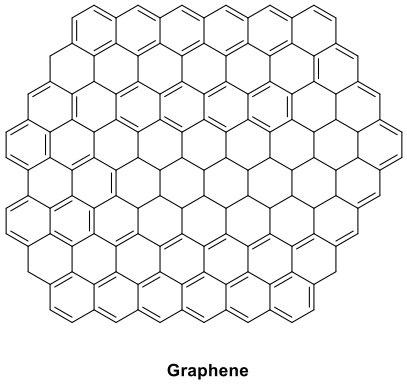

Figure 5.1- Honeycomb like structure of graphene

DFT has now turned into a popular tool for analyzing properties of substances at molecular level. The parameters like binding energy, adsorption energy, density of states, partial density of states, electronic charge density etc. are quite essential in understanding interaction of molecules on a surface. Hence, theoretical studies are considered fruitful to explore chemical reactivity in several cases.

5.2 Recent Works:

In the present article, some recent theoretical works on adsorption of small molecules on surface of pure and doped graphene have been briefly highlighted.

Ling Ma et al. [2] have performed DFT study on sensing of small gas molecules viz. CO, NH_3, O_2 and NO_2 by pristine graphene and Palladium-doped graphene. Their study has revealed that the adsorption of these gas molecules on pristine graphene is weak (physical interaction). However, the adsorption takes place much effectively on Pd-doped graphene.

Introduction of foreign atoms can tune the interaction of graphene sheets with hydrogen molecules. According to DFT calculations [3], the trend of interaction energy is Ti-doped graphene > Zn-doped graphene > Al-doped graphene sheet. An important conclusion was drawn that doping with an atom does not improve interaction of graphene with hydrogen molecules.

Wu et al. [4] have studied doped graphene as anode materials in lithium-ion batteries with the help of DFT computations. The adsorption of lithium is enhanced by doping B atom. Diffusion and desorption barrier is low in case of N doping. Their study has implied that N-doped graphene is very important in Li-ion batteries.

Al-doped graphene is considered as a nanostructure adsorbent for adsorption of NO_2 and N_2O [5]. DFT calculations have shown that the adsorption of these two

molecules on pristine graphene is weak i.e. physisorption. Doping of Al increases the extent of adsorption by changing the electronic structure of pure graphene.

Beside these, Al-doped graphene is considered as a powerful tool for adsorption of small molecules like CO, H_2O and CO_2. Rad et al. [6] have studied adsorption of these molecules in pure and Al-doped graphene with the help of DFT. Their study comes out with the conclusion that pristine graphene is not a good adsorbent for the mentioned molecules.

The adsorption of SO_2 and SO_3 molecules on pure and doped graphene sheets have also been studied by Rad and co-workers [7]. It was found that the adsorption of these molecules on N-doped graphene is accompanied by high adsorption energy and high net charge transfer as compared to pure graphene. It was confirmed from density of states (DOS) study that there orbital hybridization between the above mentioned molecules and N-doped graphene. But, orbital hybridization is absent in case of pristine graphene. Thus, N-doped graphene is considered as a sensor or adsorbent for SO_2 and SO_3.

Doping of fourth group elements in graphene lattice have been studied with the help of quantum and molecular dynamics calculations [8]. Doping of fourth group elements in graphene lattice causes pyramid-shaped roughness in the graphene. Van der Waals radius of the doping element influences the amount of roughness. The simulation of water droplets on graphene surface has suggested that graphene is a weak hydrophobic material.

Phosphorus-doped graphene is regarded as an appropriate sensor for NH_3 and H_2S molecules. On the other hand, silicon-doped graphene is a suitable sensor of H_2S. DFT calculations have suggested that Si-doped graphene is a semiconductor and P-doped graphene exhibits metallic behavior. The interaction of Si-doped graphene with NH_3 does not cause any change in electronic and chemical

properties in doped-graphene sheet and hence Si-doped graphene is not a good sensor for NH_3 molecule [9].

Hassani et al. [10] have studied the adsorption of methane on boron, nitrogen and lithium doped graphene sheet with the help of DFT. Their study has suggested that Li-doped graphene is a suitable tool for adsorption of methane and thus can act as methane storage device.

The interaction of some biologically important molecules (hypoxanthine, xanthine and uric acid) with graphene has been studied by Yang et al. [11]. It was concluded that the interaction of the above mentioned molecules with graphene is stable.

The adsorption of p-Nitrophenol on graphene is enhanced by doping it with Pt-clusters [12]. Due to this doping, the substrates exhibit magnetic character and the band gap of the surface gets decreased.

Au-doped graphene has been identified as a sensor for cysteine. Zhang et al. [13] have studied that the binding energy in adsorption of cysteine on Au-doped graphene is high as compare to pristine graphene. Doping of graphene with Au leads to transfer of charge between graphene sheet and cysteine. As a result of charge transfer, there is a significant change in the electrical conductance of graphene.

Petrushenko et al. [14] have studied the physisorption of N-containing heterocycles on graphene-like boron nitride-carbon heterostructures. The selected molecules in their study were pyridine, pyrazine, pyrimidine, pyridazine and 1, 3, 5- triazine. The results were compared with benzene. The adsorption energy was maximum for pyridazine.

Wang et al. [15] have explored the performance of seven well-liked density functional (namely ωB97X-D, B97-D, B-LYP-D3, M05-2X, M06-2X, M11-L and N12) for depicting adsorption of small molecules on graphene. B97-D, B-LYP-D3 and ωB97X-D perform good and M05-2X, M06-2X, M11-L underestimate adsorption strengths. The functional N12 fails in this respect. It was concluded that small basis like 6-31G (d) and jun-cc-pVDZ are not good for studying adsorption of small molecules on graphene correctly.

The interaction of doxorubicin (a well-known drug used for treatment of cancer) with graphene has been studied recently by Tonal and co-workers [16]. DFT computations have the interaction of doxorubicin with graphene does not make any major changes in the electronic properties of graphene.

The binding energy of interaction is approximately 0.5 eV. It has been shown by molecular dynamics that there is a weak interaction between drug and graphene even at room temperature (300 K).

Researchers have also studied the adsorption of manganese atom on graphene [17]. DFT calculations have shown that adsorption energy is high in case of defected graphene with higher number of carbon atoms. However, adsorption energy is low in case of pure graphene.

Jia et al. [18] have performed extensive study on oxidation of palladium cluster on single vacancy graphene. In Pd clusters, point defects act as a potential binding trap for adsorption of oxygen molecule.

With increase in the size of cluster, binding energy also increases. It was found that there is shift in electron density from Pd cluster to graphene. The support of graphene to Pd clusters plays more crucial role in adsorption of oxygen molecule as compared to bare Pd clusters.

5.3 Conclusion:

The geometrical and electronic properties of graphene can be tuned by doping of various elements in the sheet. This is done by using different precursors depending upon applications needed. The chemical activity of pure graphene is low. This is due to the reason that the electronic structure of pristine graphene is symmetric and uniform. Due to introduction of heteroatoms in graphene, electronegativity difference is created and hence, the chemical reactivity increases.

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