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# DEFECT ENHANCED GAS ADSORPTION IN HEXAGONAL NANOSTRUCTURES FOR POTENTIAL APPLICATIONS

**N.R.Devi[1], V.Gayathri[2]**

[1,2]*Department of Physics, Thiagarajar College of Engineering, Madurai, (India)*

## ABSTRACT

*We present the first principle study of density functional hydrogen ($H_2$) and carbon dioxide($CO_2$) adsorption in the three different hexagonal nanotubes, such as, zinc oxide nanotube (ZnONT), silicon carbide nanotube (SiCNT) and carbon nanotubes (CNTs) for different chiral angles. Zigzag (9,0) zinc oxide nanotube gives high $H_2$ adsorption binding energy compare to other nanostructures.. We observed $CO_2$ molecule chemisorbed on ZnONT and SiCNT whereas the physisorption is predominant in CNT. We have also investigated the effect of defects in the nanotubes. We analyzed that defect enhances the gas adsorption binding energy. The results of ZnO and SiC nanotubes are compared with carbon nanotube. The results are analyzed for possible fuel cell and environmental applications.*

***Keywords*: *Carbon Nanotubes, Silicon Carbide Nanotube, Zinc Oxide Nanotubes, Hydrogen And Carbon Dioxide Adsorption.***

## I. INTRODUCTION

With their nano size, porous nature, unique physical, chemical and mechanical properties of nanostructure materials attract lot of interest among scientific community all over the world. Some of the potential applications include energy storage, field emission, smart fabrics, sensor and environmental etc. [1]. Among several factors various types of defects in nanostructures are observed to influence the basic properties. In this work some of the emerging nanostructures are investigated for gas adsorption phenomena.

Hydrogen is more efficient and less expensive and is a possible replacement for gasoline in terms of reducing greenhouse gases [2]. Hectic research is going on all over the world to store hydrogen in various carbon nanostructures [3, 4]. Equally important issue under investigation is to reduce green house effect through the capture of carbon dioxide. Carbon nanostructures for this application are recently developed technology [5]. It exists in gaseous state due to their large concentration in the atmosphere affect the greenhouse effect. Human life in the earth is in need of perfect storage system for hydrogen and membrane for carbon dioxide capture.

It is expected that high surface area, chemical inertness and stable solid-gas adsorption characteristics of CNTs provide good medium for hydrogen storage. In the current scenario there are lot of research papers devoted to the adsorption studies in CNTs for possible gas sensor, hydrogen storage and nanoelectronics application. Dillon *et al.* [3] have made significance contributions on the physisorption of hydrogen in carbon nanotubes and reported the storage ranges from 5-10wt%. Experimental investigation of hydrogen adsorption through the monolayer surface of carbon nanotubes was studied by Zuttel *et al.* [6]. Our recent study shows the strong role

of structural defects on $H_2$ adsorption in carbon nanostructures [7]. Similarly the CO2 adsorption in SWCNT was carried out by Cinke et al. [8]. Quinonero *et al.* [9] was performed the simulation studies of CNT in $CO_2$ atmosphere. Several authors have analyzed the SWNTs on this issue through molecular dynamics simulation.

ZnONTs are structurally related to CNTs and has attracted great interest in the last few years because it has been predicted to have unique optical, electrical and piezoelectric properties. Few hydrogen adsorption studies exist on ZnO nanowires. Storage capacity of 0.83wt% in ZnO nanowires has been reported by Q.Wan *et al.* [10] under pressure of value 3.03Mpa. Similar to zinc oxide nanostructures, SiCNT has great potential applications in optical and optoelectronics devices. Electrical property of this material is observed to vary as a function of length. Due to this chemical reactivity of the material becomes tunable. The energy band gap falls within the range of 2.39 - 3.3 eV for these nanostructures. Mpourmpakis *et al.* [11] carried the hydrogen adsorption studies on silicon carbide nanotubes and found that it is a novel material for hydrogen storage. Owing to this SiCNT becomes a good contender immaterial for hydrogen storage search. It is observed from the above literatures that there are only few studies on $CO_2$ adsorption in ZnONTs and SiCNT. In this context the present study is an interesting one for material research.

Here we are interested to study the $H_2$ storage and $CO_2$ capture in different novel structures with hexagonal network. In our work we have considered the three different types of nanotubes such as ZnONT, SiCNT and CNT. In each case we considered the three different chirality of nanotubes, such as, (5,5) armchair, (9,0) zigzag and (6,4) chiral, which has approximately same diameter. The adsorption of hydrogen and $CO_2$ through nanotube sidewall has been done for which the molecular axis positioned perpendicular and above the corresponding hexagonal ring. In order to study the role of structural defects we have introduced the defects like pentagon and heptagon in the hexagonal structures. They are one to one opposite to each other. The results are compared with CNTs are tabulated. The computational details are given in the next section.

## II. COMPUTATIONAL DETAILS

The first principle of density functional theoretical calculation is performed for estimating the adsorption binding energy ($E_{ads}$) of hydrogen molecule and $CO_2$ on outer surface of opened single-walled nanotubes. The total energy of the system was calculated using Kohn-Sham equation. In this work, we have included the generalized gradient approximation (GGA) for the electron exchange and correlation effects, which is very suitable for long-range van der Walls interaction [12]. We have used Perdew, Burke and Enzerhof (PBE) potential and the double numerical polarization (DNP) basis set for the present study as it is more suitable for adsorption energy calculation. The binding energy values are estimated form the well-known equation,

$$E_b = E(nanotube) + E(H_2) - E(nanotube + H_2)$$

where, $E$ (nanotube+$H_2$), $E$ (nanotube) and $E$ ($H_2$) are the total energy of the corresponding nanotubes with $H_2$ and $CO_2$ molecule, free nanotube, and the energy of hydrogen and $CO_2$ molecule respectively. The energy values are minimized by adjusting the separation between the molecule and adsorption site from the wall of the nanotubes. The interpretation of results in both defect and defect free cases are discussed in the next section.

## III. RESULTS AND DISCUSSION

We have performed the $H_2$ and $CO_2$ adsorption in the three different types of nanotubes ZnONT, SiCNT and CNT in both defect and defect free cases. The molecular simulation studies are carried out with three various chiral angles of 0°, 23.4° and 30° corresponding to (9,0), (6,4) and (5,5) nanotubes. The binding energy of the system was calculated for single $H_2$ and $CO_2$ molecule .The ZnONT and SiCNT have hexagonal structure as like in CNTs. They are constructed by replacing an alternative carbon atom in CNT by Zn and O in the case of ZnONT and Si and C in the case of SiCNT. We have considered the 40, 36 and 50 number of atoms corresponding to (5,5) (9,0) and (6,4) nanotubes.

### 3.1 $H_2$ Adsorption

The adsorption of gas molecule through nanotube sidewall has been carried out for the gas molecular axis positioned perpendicular and above hexagonal ring. There is van der Waals binding interactions taking place between hydrogen molecule and the exterior wall of nanotubes. The binding energy varies as a function of chiral angle and the zigzag (9,0) ZnONT tube carries the highest value of 0.087 eV. Our observed values are in agree with the study of An *et al.* [13] .Whereas in the case of polar SiCNTs, the value remains almost the same. It indicates the chirality has no role in SiCNT. For CNT, there is a small change in binding energy of the order of 0.005 eV between armchair and chiral tubes. For semiconducting zigzag CNT, there is a reduction of binding energy up to 10%. Our estimated values of binding energies of CNTs are coinciding with the existing literature Alonso *et al.* [14]. Fig. 1 Ball and stick model of $H_2$ adsorption in (5,5) ZnONT.

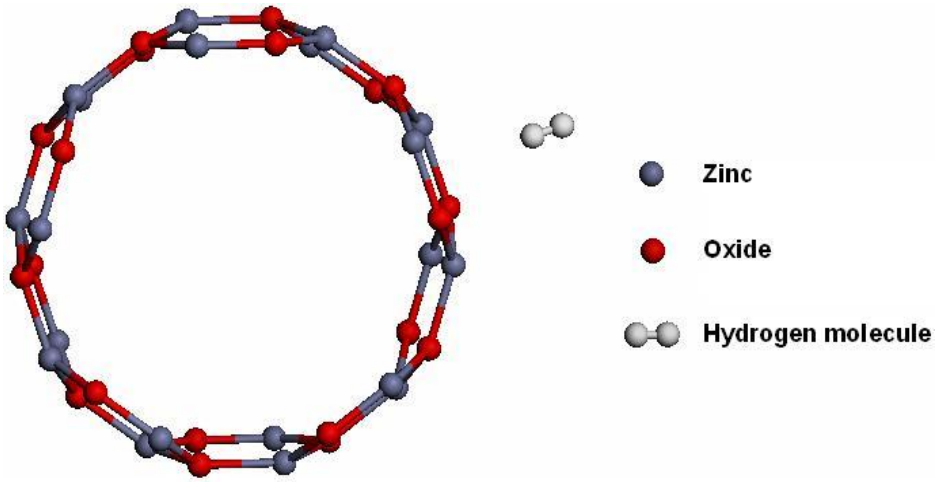


**Fig.1: Ball and Stick Model of $H_2$ Adsorption in (5,5) ZnONT**

The adsorption binding energy decreases in the defected nanotube compare to the defect free zinc oxide nanotube. The electro negativity of oxygen atom weakens the bonding between the adsorbent and adsorbate. Our present investigation indicates that the pentagon and heptagon defect further weakens this interaction that leads to decrease in binding energy values in ZnONT. As reported in our earlier work, the structural defects strongly influence the binding in CNTs. While comparing the $E_b$ values of chiral and achiral CNTs, chiral (6,4) tube give large value due to the strong electron coupling effect. Fig. 2 gives the physisorption of $H_2$ on defected (6,4) SiCNT. For SiCNT, the indirect band gap type (5,5) SiCNT tube gives high binding energy compare to direct band gap (6,4). We presume that the many valley effect on hydrogen interaction enhances the binding that

is unique to SiCNTs. The estimated values of binding energy are listed in TABLE 1. The binding energy changes as a function of chiral angle in nanotubes are given in Fig. 3.

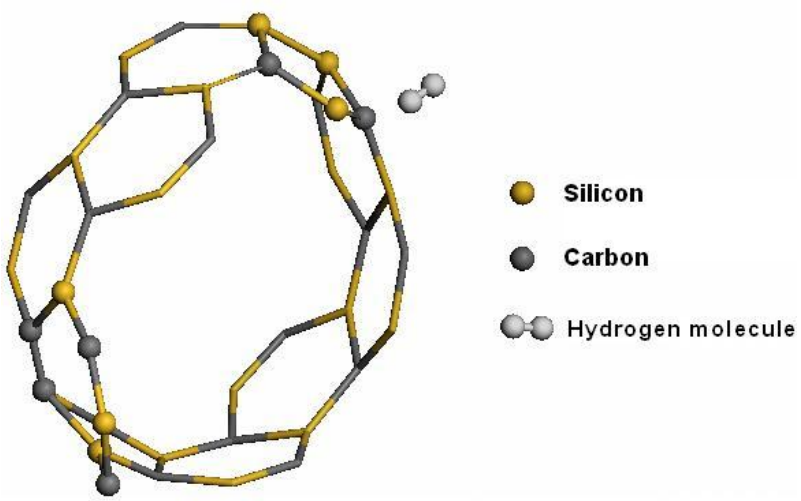


**Fig. 2 Ball and line model of $H_2$ adsorption in defected (6,4) SiCNT**

**Table. 1 The binding energies $E_b$ (eV) of $H_2$ molecule in defect free and defected nanotubes**

| Tube | (5,5) | | (9,0) | | (6,4) | |
|---|---|---|---|---|---|---|
| | Defect free | Defected | Defect free | Defected | Defect free | Defected |
| ZnONT | 0.062 | 0.048 | 0.087 | 0.075 | 0.065 | 0.048 |
| SiCNT | 0.071 | 0.132 | 0.070 | - | 0.060 | 0.066 |
| CNT | 0.072 | 0.075 | 0.065 | 0.069 | 0.077 | 0.133 |

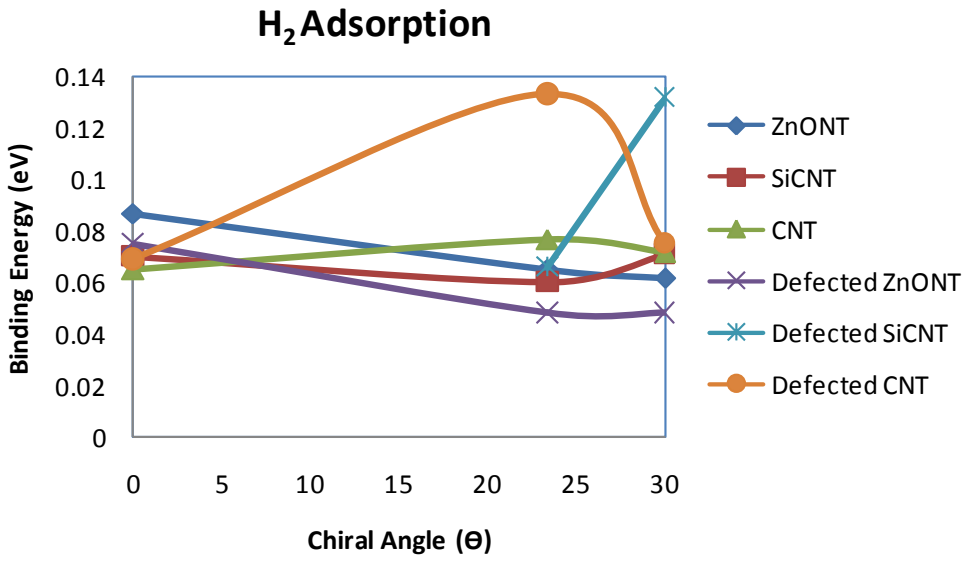


**Fig. 3 Binding Energy Changes as a Function of Chiral Angle (0°, 23.4° and 30° ) for $H_2$ Adsorption in Nanotubes.**

### 3.2 $CO_2$ Adsorption

The $CO_2$ molecule adsorbed on the outer surface of (5,5) defect free zinc oxide nanotube gives the binding energy of 1.136 eV. We could observe that there is an increment of binding energy of 0.853 eV in (9,0) ZnONT compared to (5,5) tube. The chiral (6,4) defect free ZnONT provides still higher binding energy of about 2.578 eV than these two types. This large value of binding energy indicates the $CO_2$ molecule is chemisorbed on the outer surface of ZnONT which implies that there is a strong hybridization takes place between ZnONT and $CO_2$ molecule. The interaction of $CO_2$ with one of the oxygen in ZnONT gives the stable carbonate structure leads to very high adsorption as expected. Our present results are in coincidence with the existing literature reported by Martins *et al.* [15]. In the case of SiCNT, the armchair (5,5) tube gives the large value of binding energy 1.859 eV. The zigzag (9,0) SiCNT gives the binding energy of 1.446 eV. Fig. 4 shows the $CO_2$ adsorption in (9,0) SiCNT. We obtained 0.319 eV decrement in binding energy in chiral (6,4) SiCNT. Similar to ZnONT, We could observe a strong formation of chemical bond between the surface of SiC nanotube and the $CO_2$ molecule. This may be due to sharing of electrons of oxygen in $CO_2$ with SiCNT [16]. Since carbon nanotube is one of the potential candidates for gas adsorption, we have investigated all kinds of CNTs with respect to $CO_2$ molecule. Binding energy for armchair, zigzag and chiral tubes are 0.570 eV, 0.1573 eV and 0.254 eV, respectively. This is due to van der Waals interaction between the tube wall and $CO_2$. Our results are in good agreement with the reported literature by Cinke *et al.* [8].

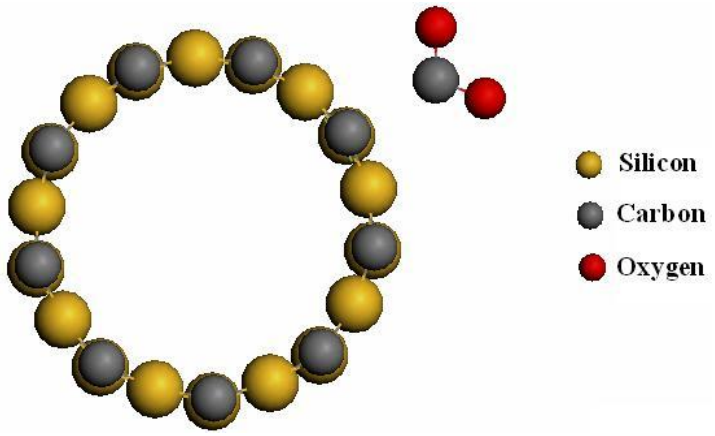


**Fig. 4 Schematic View of $CO_2$ Adsorption in (9,0) SiCNT**

The role of structural defects on $CO_2$ adsorption is presented in this section. The planar pentagon and the boat shaped heptagon are introduced oppositely which leads to negative curvature at the inner side of the tube that gives small bend in the walls. The excess of electrons on the pentagon and a deficiency on the heptagon tend to form a six-π-electron system. Electronically, it will modify the structure considerably and it leads to enhance the molecule adsorption binding energy in all types of tubes. The values are estimated to be 1.63 eV for the defected (5,5) ZnONT, which is higher than the defect free value. For the zigzag case we could observe an increment of 0.611 eV. Our results show a smaller increment in the energy value of chiral tube. Though the binding energy values are larger than zigzag and armchair type, it seems that the defect has lesser role in the chiral tubes. When we analyze the results of defected SiCNT armchair gives larger increment compared to defect free case. For both SiCNT and ZnONT effect of defect plays stronger role than the chiral. From the results we could observe the very strong chemisorptions will take place in defected nanotubes than free tubes.

It is interesting to note the behavior of CNTs slightly different than the ZnONT and SiCNT. We got the highest value of increment of 0.137eV binding in defected zigzag (9,0) CNT. Fig. 5 gives the schematic view of $CO_2$ adsorption in defected (9,0) ZnONT. The amchair and chiral defected CNTs provides the very less improvement with respect to defects. Our results are consistent with the Mackie *et al.* [17] had carried out the work on $CO_2$ adsorption by N-doped CNT. Fig. 6 represents the binding energy as a function of chiral angle for $CO_2$ adsorption on nanotubes. TABLE 2 gives the calculated binding energy value in all type of nanotubes.

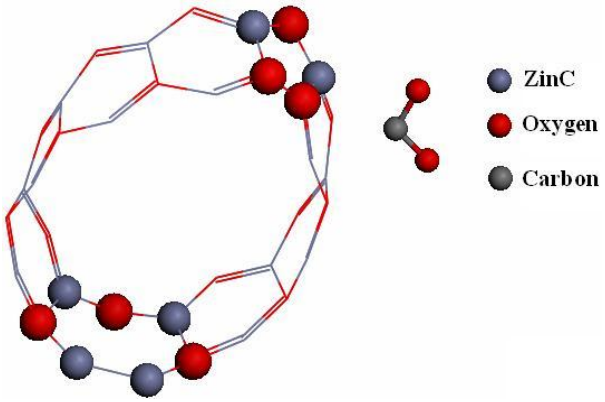


**Fig. 5 Side view of $CO_2$ adsorption in defected (9,0) ZnONT**

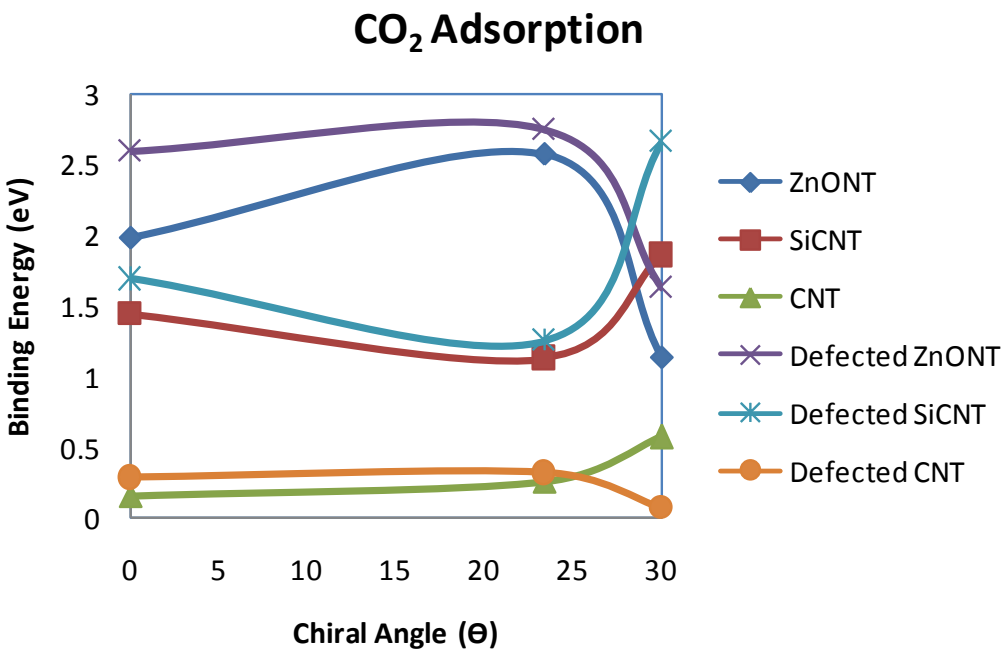


**Fig. 6 Binding Energy Changes as a Function of Chiral Angle (0°, 23.4° and 30° ) for $CO_2$ Adsorption in Nanotubes.**

**Table. 2 The binding energies $E_b$ (eV) of $CO_2$ molecule in defect free and defected nanotubes.**

| Types of tube | (5,5) | | (9,0) | | (6,4) | |
|---|---|---|---|---|---|---|
| | Defect free | Defected | Defect free | Defected | Defect free | Defected |
| **ZnONT** | 1.136 | 1.63 | 1.989 | 2.6 | 2.578 | 2.75 |
| **SiCNT** | 1.859 | 2.66 | 1.446 | 1.69 | 1.127 | 1.252 |
| **CNT** | 0.570 | 0.065 | 0.157 | 0.280 | 0.254 | 0.315 |

## IV. CONCLUSION

Doping in nanotubes, creating vacancies and functionalizing with N containing groups are sum of the techniques to improve the adsorption of gas molecule on the tube surfaces. We have compared our results corresponding to both defect free and defected cases are concluded that the structural defects influence the adsorption more than the above technique. This is an interesting result for the practical applications of nanostructures in fuel cell and environmental application.

## REFERENCES

[1]. V. N. Popov, Carbon nanotubes: properties and application, Materials Science and Engineering R, 43, 2004, 61–102.

[2]. T.N. Veziroglu and F. Barbir, Hydrogen: the wonder fuel, International Journal of Hydrogen Energy, 17(6), 1992, 391-404.

[3]. A.C. Dillon, T. Gennett, J.L. Alleman, K.M. Jones, P.A. Parilla and M.J. Heben, Carbon nanotube materials for hydrogen storage, Proceedings of U.S. DOE/NREL Hydrogen Program Review, 1999, NREL/CP-570-26938.

[4]. F.A. Vilaplana, Ab initio computational investigation of physisorption of molecular hydrogen on chiral single-walled carbon nanotubes', The Journal of Chemical Physics, 122(21), 2005, 214724.1-214724.7.

[5]. W.L. Yim, O. Byl, J.T. Yates Jr and K.J. Johnson, Vibrational behavior of adsorbed $CO_2$ on single-walled carbon nanotubes, The Journal of Chemical Physics, 120(11), 2004, 5377-5386.

[6]. A. Züttel, P. Sudan, P.H. Mauron, T. Kiyobayashi, C.H. Emmenegger, and L. Schlapbach, Hydrogen storage in carbon nanostructures, International Journal of Hydrogen Energy, 27(3), 2002, 203-212.

[7]. V.Gayathri and R.Geetha, Hydrogen adsorption in defected carbon nanotubes, Adsorption, 13(1), 2007, 53-59.

[8]. M. Cinke, J. Li, C.W. Bauschlicher, A. Ricca and M. Meyyappan, $CO_2$ adsorption in single-walled carbon nanotubes, Chemical Physics Letters, 376(5-6), 2003, 761-766.

[9]. D. Quinonero, A. Frontera and P.M. Deyà, Feasibility of single-walled carbon nanotubes as materials for $CO_2$ adsorption: A DFT study, Journal of Physical Chemistry C, 116(39), 2012, 21083-21092.

[10]. Q. Wan, C.L. Lin, X.B. Yu and T.H. Wang, Room-temperature hydrogen storage characteristics of ZnO nanowires, Applied Physics Letters, 84(1), 2004, 124-126.

[11]. G. Mpourmpakis, G.E. Froudakis, G.P. Lithoxoos and J. Samios, SiC nanotubes: a novel material for hydrogen storage, Nano Letters, 6(8), 2006, 1581-1583.

[12]. J.S. Arellano, L.M. Molina, A. Rubio, M.J. Lopez and J.A. Alonso, Interaction of molecular and atomic hydrogen with (5,5) and (6,6) single wall carbon nanotubes', The Journal of Chemical Physics, 117(5), 2002, 2281-2288.

[13]. W. An, X. Wu and X.C. Zeng, Adsorption of $O_2$, $H_2$, CO, $NH_3$ and $NO_2$ on ZnO Nanotube: a density functional theory study, Journal of Physical Chemistry C, 112(15), 2008, 5747-5755.

[14]. J.A. Alonso, J.S. Arellano, L.M. Molina, A. Rubio and M.J. Lopez, Interaction of molecular and atomic hydrogen with single-wall carbon Nanotubes, IEEE Transaction Nanotechnology, 3(2), 2004, 304-310.

[15]. J.B.L. Martins, E. Longo, O.D.R. Salmon, V.A.A. Espinoza and C.A. Taft, The interaction of $H_2$, CO, $CO_2$, $H_2O$ and $NH_3$ on ZnO surfaces: an Oniom study, Chemical Physics Letters, vol. 400(4-6), 2004, 481-486.

[16]. M.R. Sonawane, D. Habale, B.J. Nagare and R. Gharde, Interaction of $O_2$, $CO_2$, $NO_2$ and $SO_2$ on Si-doped carbon nanotube, International Journal of Applied Physics and Mathematics, 1(2), 2011, 138-143.

[17]. I.D. Mackie and A.G. Dilabio, $CO_2$ adsorption by nitrogen-doped carbon nanotubes predicted by density-functional theory with dispersion-correcting potentials, Physical Chemistry and Chemical Physics, 13(7), 2011, 2780-2787.