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Comparative Study of Hydrogen Adsorption on Alkali Metal Assisted Carbon-Nano Structured Materials

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Abstract: ***Using first-principles density functional theory, we have studied the hydrogen storage capacity of alkali metal decorated graphene and carbon nanotubes. Due to curve nature of nanotubes, it shows higher capacity of storing hydrogen than the graphene. We also found that the sodium decorated nano-structure adsorbs more hydrogen molecules than the lithium and potassium decorated systems. The charge transfer from metal to the nanotubes is responsible for the higher hydrogen uptake. The gravimetric density of hydrogen for the alkali metal assisted carbon nanotubes is calculated to be 9.2 wt% to 11.2 wt %.***

Keywords: density functional theory, hydrogen storage, carbon nanotubes, binding energy**.**

1. Introduction

Hydrogen is considered to be a promising alternative to the conventional energy sources. It is widely accepted as clean and renewable energy source. Because of its high abundance in nature it can form an ideal substitution of traditional carbon based fossil fuels. But the challenge to the hydrogen economy is the safe hydrogen storage and efficient hydrogen carriers (1-4). The carbon nanotubes and the graphene are considered to be hydrogen storage materials due to its unique electronic structure and excellent physical and chemical properties such as interstitial sites, diameter of nanometer scale, cylindrical shape, and porosity (5-7). The carbon nanotube was discovered by the IIjima (8). Dillon et al have performed first experiment of hydrogen storage on carbon nanotubes (9). After those different carbon nanomaterials such as carbon fullerene, carbon nanotubes and graphene were investigated for the hydrogen adsorption (10-12). The pure CNT or pure graphene were not suitable for the H_2 storage (13). Chandrakumar et al., studied hydrogen adsorption on alkali metal doped fullerene and found that Na doped fullerene gives 9.5 wt% of hydrogen storage capacity (14). C. Ataka and co worker investigated calcium adsorbed graphene for the hydrogen storage and predicted 8.4 wt% of hydrogen storage capacity (15). W. Liu et al., studied hydrogen storage on lithium attached carbon nanotubes and predicted 13.45 wt % of hydrogen storage capacity (16). Recently we studied the hydrogen adsorption capacity on sodium doped graphene and single walled carbon nanotube (17-18). U.S. Department of Energy (DOE) proposed goals, such that the H_2 storage capacity should exceed 6.0 wt % (19). We studied metal attached carbon nanotube and graphene for the hydrogen storage. In this study the hydrogen adsorption medium based on carbon nanostructures such as SWCNT and graphene doped with alkali metals has been designed. We started with adsorption site for the metal on graphene. The hollow site (above the carbon hexagon) is found to be most stable that means atom posses minimum energy at that position. The graphene with atom at hollow site was studied for the hydrogen storage. Similarly the lithium, sodium and potassium are strongly adsorbed on the SWCNTs at the hollow site. After metal doping the hydrogen allow to interact with the Metal-SWCNT. The hydrogen binding and its electronic properties were studied using density functional theory (DFT). The amount of hydrogen uptake has been measured. It was found that the 11.2 wt% of hydrogen storage capacity on the SWCNT and 9.2wt% capacity on graphene. Since the SWCNT has higher storage capacity than the graphene due to the curve nature of SWCNT.

2. Computational Methods

Our first principles calculations were carried out using the CASTEP code (20) within the Local Density Approximation (LDA) with Perdew–Zunger parameterization (21) of Ceperley–Alder data (22) as well as generalized gradient approximation (GGA) by Perdew–Burke–Ernzerhof (PBE) (23). Since van der Waals contributions and Coulomb interactions with metal-graphene were better accounted by LDA. In case of SWCNT the reciprocal space were represented by 1x1x7 Monkhorst and Pack grid. A vacuum width of 15 Å was fixed along the x-direction and y-direction that is perpendicular to the axis of SWCNT. All atoms were fully relaxed until the forces on each atom were less than 0.002 Hatree/Å. For graphene the reciprocal space were represented by 7x7x1 Monkhorst and Pack grid. In this study, we have

chosen a (8, 0) SWCNT which is zigzag type of nanotube having length of 6 Å. It has total 64 carbon atoms and is placed in a 24 Å × 27 Å × 8.58 Å tetragonal supercell. The atomic positions are relaxed using conjugate gradient method until the force on each atom becomes less than 0.002 Hatree/Å. Such relaxed SWCNT was used for adsorption of alkali metals and then successive adsorption of the hydrogen molecules. The multiple alkali metals were also studied for the verification of clustering effect of metals on SWCNT.

3. Results and discussion

The study begins with the adsorption of metals on SWCNT. The alkali metals Li, Na and K adsorbed on it having different binding energies. Here we report the first principles studies on the alkali metal doped SWCNT and predicted that it is one of the most suitable candidates for high capacity hydrogen storage medium. The results of SWCNT are compared with graphene. The sodium from all these alkali metals has large capacity for the hydrogen adsorption in the molecular form on SWCNT and the graphene.

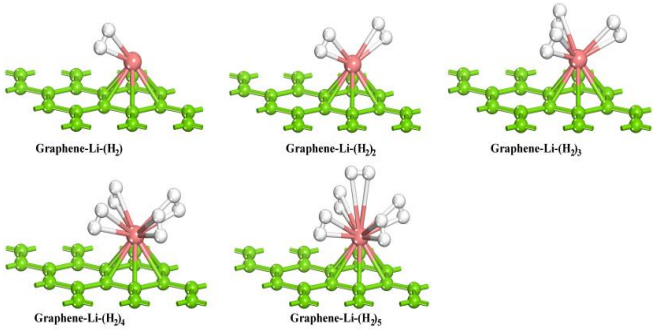

Figure 1: Adsorption of hydrogen molecules on Li-graphene structures.

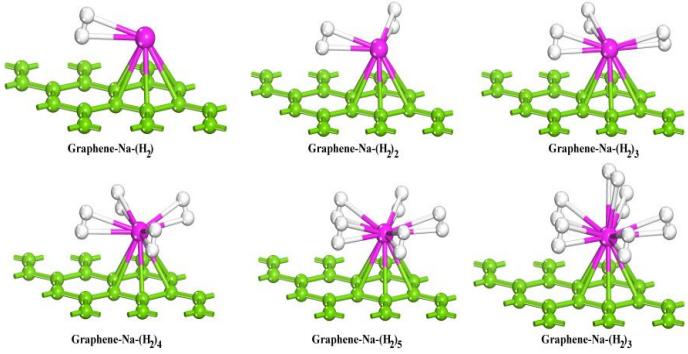

Figure 2: Adsorption of hydrogen molecules on Na-graphene structures.

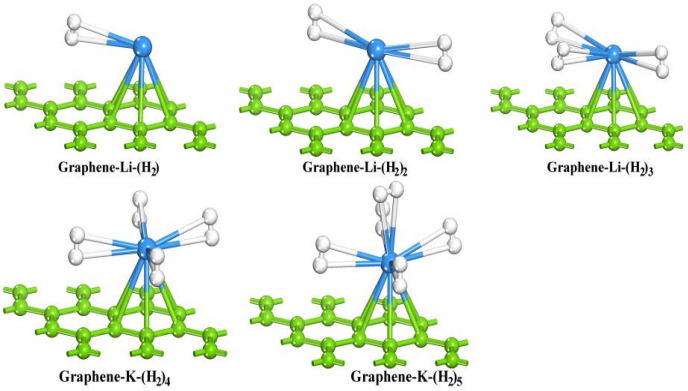

Figure 2: Adsorption of hydrogen molecules on Na-graphene structures.

We started with graphene a 2D carbon nanostructure. The graphene is substrate and the alkali metals such as lithium, potassium and sodium as adsorbate materials. The Li, K and Na adsorbed at hollow site on graphene with binding energy of -1.01 eV, -1.2 ev and -1.21 eV respectively.

Table 1: Binding energies of hydrogen molecules on alkali metal doped graphene.

No of H_2	Binding Energy (eV)					
	Li		Na		K	
	LDA	GGA	LDA	GGA	LDA	GGA
0	-1.01	-0.85	-1.21	-0.58	-1.2	-0.91
1	-0.26	-0.09	-0.16	-0.02	-0.08	-0.01
2	-0.26	-0.11	-0.20	-0.03	-0.11	-0.03
3	-0.24	-0.08	-0.22	-0.06	-0.12	-0.02
4	-0.21	-0.06	-0.22	-0.06	-0.16	-0.15
5	-0.19	-0.04	-0.22	-0.06	-0.16	-0.07
6	-	-	-0.20	-0.05	-	-

The Li-graphene bondlength is found to be 2.14 Å and Na-graphene bondlength is 2.7 Å, whereas the K-graphene bondlength is higher than other that is 3.0 Å. When the alkali metal adsorbed, the partial charge transfer takes place from metal to the graphene. The molecular hydrogen is allowed to interact with metal doped graphene. The first hydrogen molecule adsorbed on top of lithium atom with its molecular axis parallel to the plane of graphene. The H_2-Li distance is 1.8 Å and H_2-K bond distance is 2.9 Å whereas H_2-Na distance was 2.41 Å. The binding energies of first H_2 on Li-graphene, K-graphene and Na-graphene are calculated to be -0.08 eV, -0.09 eV and -0.16 eV respectively. For the remaining hydrogen binding energy is tabulate in Table. 1. As the gravimetric adsorption density of Na-graphene complex is higher than the other structures so we studied the density of states (DOS) of the same structure, it gives hydrogen adsorption characteristics. After studying hydrogen storage on plane 2D surface that is graphene we have also investigated the same on the curved 1D surface that is on SWCNTs. It began with the attaching of alkali metal atom on SWCNT. The lithium atom adsorbed at average distance of 2.2 Å where as Na-SWCNT and K-

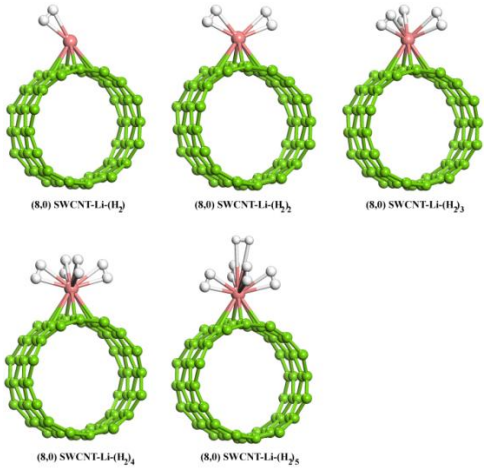

Figure4: Adsorption of hydrogen molecules on Li-SWCNT structure.

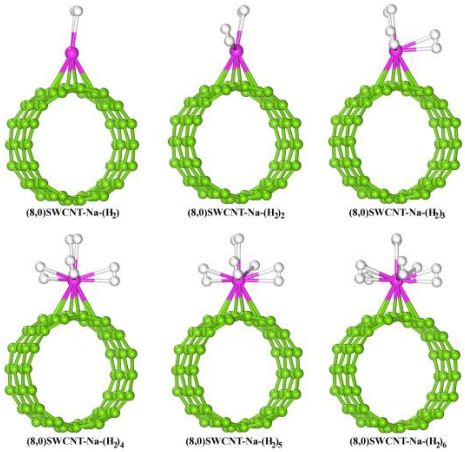

Figure4: Adsorption of hydrogen molecules on Na-SWCNT structure.

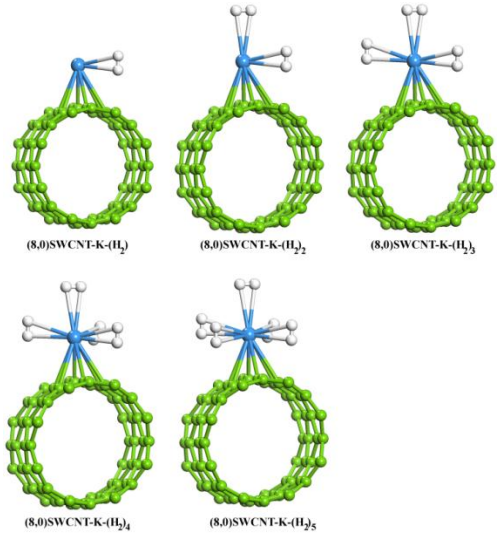

Figure4: Adsorption of hydrogen molecules on K-SWCNT structure.

SWCNT average bond distance is 2.3 Å and 2.7 Å respectively. The binding energies of Li, Na and K on SWCNT calculated with LDA functional are found to be -2.19 eV, -2.05 eV and -1.85 eV respectively. The binding energies of Li, Na and K on SWCNT calculated with GGA functional are found to be -0.85 eV, -0.58 eV and -0.91 eV respectively. The lithium strongly binds with SWCNT whereas sodium and potassium binds with moderate binding energy.

The hydrogen molecules adsorbed on every system with different bondlength and binding energy. In case of SWCNT both metal atoms and hydrogen molecules adsorbed strongly as binding energy is found to be higher than the graphene it is due to the curved nature of SWCNT. Li-SWCNT complex adsorbed five hydrogen molecules with average binding energy of -0.13 eV/ H_2 calculated with LDA. The average H_2-Li bondlength is calculated to be 2.24 Å. The sodium-SWCNT adsorbed maximum six hydrogen molecules with average binding energy of -0.26 eV/ H_2. The average H_2-Na bondlength is found to be 2.3 Å. The potassium-SWCNT adsorbs five hydrogen molecules with average binding energy of -0.14 eV/ H_2. The average H_2-K bondlength is calculated to be 2.65 Å. In both the cases alkali metal transfer partial electrons to carbon atoms which polarize H_2 molecules, such charge transfer is responsible for higher hydrogen storage capacity.

To calculate the wt% of the Na-SWCNT-complex, we adsorbed eight Na atoms on different hexagons with minimum distance between two Na atoms larger than 5 Å to avoid the clustering of Na atoms. On eight Na atoms 48 hydrogen molecules adsorbed easily which gives 12 wt% of gravimetric density for the hydrogen. Similarly in case of graphene we have attached two Na atoms on both sides of graphene and each Na adsorbs six H_2 molecules showing 9.2 wt % of storage. In similar way the gravimetric density for hydrogen of Li-SWCNT and K-SWCNT complex is found to be 9 wt % and 9wt % respectively.

No of H_2	Binding Energy (eV)					
	Li		Na		K	
	LDA	GGA	LDA	GGA	LDA	GGA
0	-2.19	-1.92	-2.05	-1.32	-1.85	-1.41
1	-0.17	-0.11	-0.18	-0.16	-0.19	-0.039
2	-0.11	-0.08	-0.27	-0.16	-0.12	-0.030
3	-0.14	-0.10	-0.26	-0.14	-0.13	-0.040
4	-0.16	-0.08	-0.26	-0.13	-0.15	-0.045
5	-0.13	-0.05	-0.26	-0.12	-0.16	-0.046
6	-	-	-0.26	-0.12	-	-

4. Summary and Conclusions

We have studied hydrogen storage capacity of metal assisted graphene and SWCNT. The pure graphene and SWCNT shows low hydrogen storage capacity. So the graphene and SWCNT are decorated with alkali metal which enhances the storage density for the hydrogen. As metal atom adsorbed on SWCNT the charge transfer takes place from metal to carbon atoms of SWCNT, induces dipole which is responsible for higher hydrogen adsorption. The alkali metal decorated graphene

shows gravimetric density maximum of 9.2 wt% and the SWCNT shows maximum of 11.2 wt%.

References

[1] B. Sakintuna, L. Farida, M. Hirscher, "Metal hydride materials, for solid hydroen storage: a review," Int J Hydrogen Energy, pp.321121, 2007.

[2] Z. Ao, F. Peeters, "High-capacity hydrogen storage in Al-adsorbed graphene," Phys Rev B, pp. 205406, vol 81, 2010.

[3] W. Liu, Y. H. Zhao, Y. Li, Q. Jiang, E. J. Lavernia, " Enhanced hydrogen storage on Li-dispersed carbon nanotubes," J. Phys Chem C, vol. 113, pp. 2028, 2009.

[4] Z. Ao, A. Hernandez-Nieves, F. Peeters, "The electric field as a novel switch for uptake/release of hydrogen for storage in nitrogen doped graphene," Phys Chem Chem Phys, vol. 14, pp. 14637, 2012.

[5] KS. Novoselov, AK. Geim, SV Morozov, D Jiang, SV Dubonos, AA. Firsov, "Electric field effect in atomically thin carbon films," Science, vol. 306 pp.5696, 2004.

[6] LA Ponomarenko, RV Gorbachev, GL Yu, DC Elias, "Cloning of dirac fermions in graphene superlattices," Naturevol. 497, pp. 7451, 2013.

[7] J.R. Cheng, X.H. Yuan, L. Zhao, D.C. Huang, M. Zhao, L. Dai, R. Ding, Carbon, vol. 42, pp. 2019, 2004.

[8] S. Iijima, "Helical microtubules of graphitic carbon," Nature, vol. 358, pp. 56-58, 1991.

[9] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Klang, D. S. Bethune, and M. J. Heben, Nature London vol. 386, pp. 377, 1997.

[10] M Yoon, S Yang, C Hicke, E Wang, D Geohegan and Z. Zhang, PRL, vol. 100, pp. 206806, 2008.

[11] C. Ataca, E. Akturk, S. Ciraci and H. Ustunel, Applied Physics Letters, vol. 93, pp. 043123, 2008.

[12] Y Li, G Zhou, J Li, BL Gu and W Duan, J. Phys. Chem. C vol. 112, pp. 19268–19271.

[13] I. Cabria, M. J. Lopez and J. A. Alonso, "Enhancement of hydrogen physisorption on graphene and carbon nanotubes by Li doping," The Journal of Chemical Physics vol. 123, pp. 204721, 2005.

[14] K. R. S. Chandrakumar and Swapan K. Ghosh, "Alkali-Metal-Induced Enhancement of Hydrogen Adsorption in C60 Fullerene: An ab Initio Study," Nanoletters, vol.8(1), pp. 13-19, 2008.

[15] C. Ataca, E. Akturk, and S. Ciraci, "Hydrogen storage of calcium atoms adsorbed on graphene: First-principles plane wave calculations," Physical Review B, vol. 79, pp. 041406, 2009.

[16] W. Liu, Y. H. Zhao, Y. Li, Q. Jiang, and E. J. Lavernia, "Enhanced Hydrogen Storage on Li-Dispersed Carbon Nanotubes," J. Phys. Chem. C, vol. 113,pp. 2028–2033,2009.

[17] B. J. Nagare, Darshan Habale, "Hydrogen adsorption on Na–SWCNT systems," J. Mater. Chem., vol. 22, pp. 22013, 2012.

[18] Darshan Habale, Rita A. Gharde, "Hydrogen Adsorption on Sodium-attached Graphene," Elixir Comp. Chem. Vol. 67, pp. 21452-21455, 2014.

[19] J. F. Stampfer, CE. Holley, JF. Suttle, J. Am. Chem. Soc., vol. 82, pp.3504, 1960.

[20] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson and M. C. Payne, Z. Kristallogr., vol. 220(5–6), pp. 567-570, 2005.

[21] J. P. Perdew and A. Zunger, Phys. Rev. B, vol. 23, pp. 5048, 2008.

[22] D. M. Ceperley, Phys. Rev. Lett., vol. 45, pp. 566, 1980.

[23] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., vol. 77, pp. 3865, 1996.