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Hydrogen Adsorption on Sodium-attached Graphene

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ABSTRACT

First principles calculations based on Density Functional Theory were carried out to study hydrogen storage capacity of sodium doped graphene. The pure graphene exhibits low hydrogen storage capacity hence we modified graphene by doping of sodium. Sodium occupies the empty (hollow) position on graphene with average carbon sodium bond-length of 2.64 Å. This investigation predicts that positively charged sodium atom on graphene physisorbed maximum six hydrogen molecules with the average adsorption energy 0.20 eV/H_2 amounting gravimetric density of 9.2 wt%. Mulliken population analysis shows that the charge transfer from sodium to graphene is responsible for higher hydrogen uptake than the pure graphene sheet.

Introduction

Primary sources of energy for various industrial, vehicular applications are fossils fuels such as coal, oil, natural gas. These are non-renewable sources of energy and readily available in nature. Use of these sources in large extent is hazardous to the environment, as it emits toxic gases such as carbon dioxide, sulphur dioxide, carbon monoxide etc. Fossil fuels are limited in nature and depleted rapidly. Researchers are trying to find out the alternative clean and renewable source of energy such as solar energy, hydrogen fuel etc. Hydrogen is one of the most promising alternative energy source and carrier as it is light weight and abundant in nature. [1] It has high energy mass density than other fuel and environmental friendly as it does not emit toxic gases. [2] It can be use for the development of fuel cell powered vehicles. [3] But the major challenge to the hydrogen economy is safe and efficient storage and transport of hydrogen. U.S. department of energy have set the target of hydrogen storage 9wt% (by 2015) for the practical application. Hydrogen can be stored by using various methods like compressed gas, liquefied hydrogen with different storage capacity. The materials such as metal hydrides, metal organic frameworks small organic molecules and carbon based nano-materials (nanotubes, fullerenes, graphene) etc. can be used for hydrogen storage. [4-8] There are many reports which demonstrate the carbon-based nano-materials can be used to store hydrogen safely. [9-11] Graphene a (2D) planer material which is single-layered honey-comb lattice nano-structure of carbon atoms. [12-13] It can be used to store hydrogen due to its light weight and large surface area.

Park and co workers have demonstrated that Li atoms dispersed on both sides of boron substituted graphene can adsorbs 8 hydrogen molecules giving 13.2 wt% storage capacity. [14] Chu et al., have shown that the gravimetric density for hydrogen on Titanium atom embedded on double vacant graphene is 6.3 wt%. [15] Ataca et al., proposed that Lithium covered graphene have hydrogen storage capacity of 12.8 wt%. [16] The gravimetric density of transition metal doped graphene for molecular hydrogen is found to be (4-5) wt% predicted by Kim et al. [17] Lee and co-workers shown that Calcium decorated zigzag graphene nano-ribbon can adsorbs 5 wt% of hydrogen. [18] Z M Ao and co-workers proposed 13.79 wt% of hydrogen storage capacity for the Aluminium adsorbed graphene. [19] Y S. Wang and co-workers predicted 7.44-8.96 wt% of gravimetric capacity for the hydrogen on calcium decorated graphyne nanotubes. [20] Wang et al reported 11.7 wt% of hydrogen storage capacity by boron substituted graphene decorated uniformly by Sodium. [21] We demonstrate theoretical study of hydrogen storage capacity of sodium attached graphene sheet due to following reasons,

Recently we have studied hydrogen adsorption on Na attached single walled carbon nanotubes showing high gravimetric density which is found to be nearly 11.2 wt%. [22-23]

Chandrakumar et al., proposed that alkali metal (Na, Li) attached benzene ring and curve induced graphene sheet enhances molecular hydrogen adsorption. [24]

Srinivasu et al., studied alkali metal (Na, Li) attached six member carbon ring (C6H6) to store hydrogen, there is improvement in the hydrogen adsorption due alkali metal. [25]

There is no report on hydrogen storage on Na doped graphene sheet.

We have investigated hydrogen adsorption capacity and various properties of sodium doped graphene by using Density Functional Theory calculations. Initially adsorption of sodium on pure graphene and its electronic properties were studied. The adsorption of hydrogen molecules on Na-graphene system and their bonding and energies were calculated. Next we evaluated their electronic properties such as partial density of states, Mulliken population analysis gravimetric density of Na doped graphene. The binding energy of Na and hydrogen molecules matches with results reported by Srinivasu et al. [25]

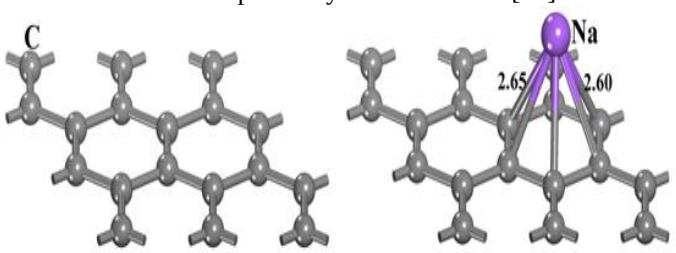

Fig. 1. A graphene and Na doped grapheme bond-lengths are expressed in Å

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Computational Methods

All structural optimizations and total energy calculations are performed using first principles method based on Density Functional Theory (DFT) implemented in CASTEP code. [26] Both generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) [27] and local density approximation (LDA) by Perdew-Zunger-Parametrization [28] of Ceperley Alder data [29] are used for exchange correlation energy. 380 eV cut-off energy with ultrasoft pseudo-potential was chosen for the plane wave basis. The Monkhorst-Pack scheme with 18x18x1 special K-points is used for Brillouin zone sampling for all the systems. All the structures are optimized using the conjugate gradient method. Convergence is achieved when the difference of the total energies of last two consecutive steps is less than $2x10^{-5}$ eV and the maximum force allowed on each atom is less than $5x10^{-2}$ eV/Å. In order to minimize interactions between periodical repeating structures we choose a simple cubic supercell of dimensions (7.38x7.38x20) $Å^3$.

Graphene is single layer carbon sheet of the graphite. Graphene can be metalized by adsorption of Na atom. Na-attached graphene sheet was used as model structure for the hydrogen adsorption. Initially sodium can adsorbs on different sites by which three possibilities have considered namely a top, axial, and hollow (Top site is Na atom adsorbed exactly on a top of carbon atom, in case axial site Na adsorbed on bridge over the C-C bond and the hollow site means Na adsorbs on hexagon of carbon-ring). With different Na adsorption site the hollow site has lowest energy is found to be most stable so this structure is used for the further calculation of molecular hydrogen adsorption.

The binding energy of Na atom is given by,

$BE_{Na} = E_{Na-graphene} - E_{graphene} - E_{Na}$

where $E_{Na-graphene}$, $E_{graphene}$ and E_{Na} are the total energies of Na-doped graphene, graphene and isolated Na atom respectively. Next, we used lowest energy structure of Na-graphene for H_2 adsorption.

The binding energy of H_2 molecule is given by,

$BE_{H2} = [E_{(H2)n+Na-graphene} - E_{Na-graphene} - nE_{H2}]/n$

where n indicates the number of H_2 molecules, $E_{(H2)n+Na-graphene}$, $E_{Na-graphene}$ and E_{H2} are the total energy of H_2-Na-graphene complex, Na-doped graphene and H_2 molecule respectively.

Results and Discussion

We have used graphene sheet of 18 carbon atoms as model structure. Sodium atom attached on three possible adsorption sites for sodium on the graphene namely 'T', 'A' and 'H'. Sodium was found to be most stable on hollow (H) because the binding energy of sodium on H site is lower than the other sites. Fig 1 shows pure graphene and the adsorption sites for sodium. Na binds strongly on the graphene with the LDA binding energy of -1.21 eV and C-Na bond-length of 2.45 Å which is consistence with the binding energy reported by Ataca et al. [11] Such a hollow site of sodium used for the further calculations.

The interaction of hydrogen molecules on Na-graphene system was investigated. The hollow site was the most stable site for sodium on graphene and used for the interaction of hydrogen. First hydrogen molecule adsorbed at the distance of 2.41 Å on Na atom having the binding energy -0.16 eV. Its position is perpendicular to graphene sheet as shown in fig.2. No change in l_{c-c} bond-length upon H_2 adsorption but decrease in average l_{c-Na} bond-length by 2.2% from 2.65Å to 2.59 Å. In similar way second molecule attached to Na near to first molecule at distance of 2.34 Å and having same position.

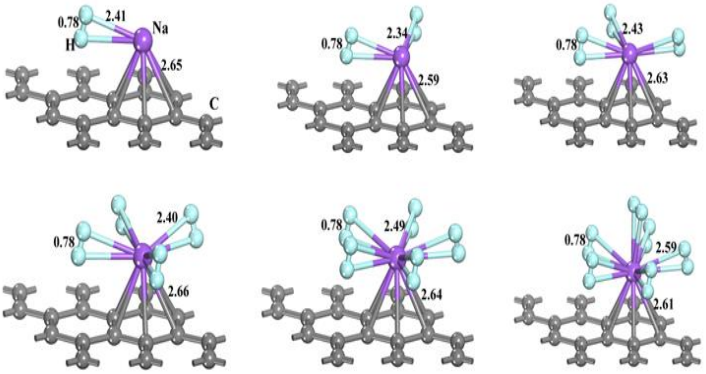

Fig. 2. Molecular hydrogen adsorption on sodium doped graphene, bond-lengths are expressed in Å.

The binding energy and Na-H bond-length was found to be -0.22 eV/H_2 and 2.5 Å respectively. Then third, fourth, fifth hydrogen molecules surrounds the sodium atom with nearly same Na-H bond-length and same binding energy. Sixth hydrogen molecule adsorbed on a top of sodium atom at a distance of 2.4 Å. It's was parallel with plane of graphene forming T shape as shown in fig.2. Maximum six molecules of hydrogen get adsorbed on Na-graphene system. All molecules surrounds Na atom at average distance of 2.4 Å except sixth molecule which sits on a top of Na atom. The average bond-length l_{H-H} have increased by 3% from 0.75Å to 0.78Å. The sodium and hydrogen binding energy and bond length are tabulated in table 1. The electronic properties were analysed by calculating the total density of states (DOS) for pure graphene sheet and partial density of states (PDOS) of sodium doped graphene system and of single hydrogen molecule adsorbed on Na-graphene system. As sodium adsorbed on graphene the total density of states of Na-graphene system changed by 2eV. Peak of Na 3s orbital near the Fermi energy matches with the peak of C 2p orbital showing strong bonding between sodium and graphene. (shown in fig. 3). Similarly as hydrogen molecule attached on Na-graphene system H 1s orbital shows weak bonding with Na 3s orbital.

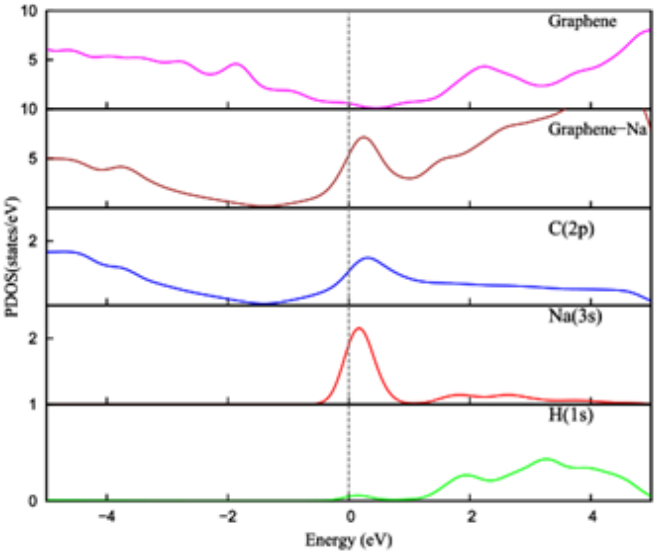

Fig. 3. The density of states of graphene and graphene-Na are shown. The partial density of states of carbon (2p) and sodium (3s) atoms of graphene-Na system. The Fermi level is set to zero and indicated by the dotted line.

Table 1: The bond length and binding energy (eV) of Na nad H_2 on graphene-Na.

No. of H_2 molecules	C-Na Bond length Å		Na-H Bond length Å		Sodium sites	B. E. (eV)	
	Maximum	Minimum	Maximum	Minimum		LDA	GGA
0	2.81	2.72	-	-	hollow	-1.21	-0.58
0	2.69	2.67	-	-	axial	-1.08	-0.46
0	2.60	2.60	-	-	top	-1.08	-0.44
0	2.67	2.61	-	-	-	-1.21	-0.58
1	2.57	2.65	2.41	2.47	-	-0.16	-0.02
2	2.53	2.64	2.34	2.43	-	-0.20	-0.03
3	2.55	2.66	2.41	2.45	-	-0.22	-0.06
4	2.56	2.67	2.40	2.52	-	-0.22	-0.06
5	2.63	2.67	2.43	2.59	-	-0.22	-0.06
6	2.60	2.64	2.44	2.57	-	-0.20	-0.05

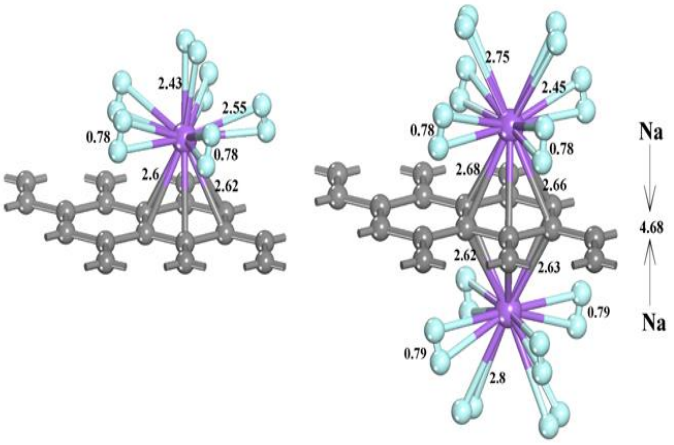

Fig. 4. The Coverage of H_2 molecules on sodium doped graphene bond-lengths are expressed in Å.

We also investigated adsorption of second sodium atom on graphene. It adsorbed on opposite side of first sodium atom at hollow position of carbon hexagon. After the geometry optimization distance between two sodium atoms was 4.68 Å with binding energy -0.85 eV/atom. Then we studied the molecular hydrogen adsorption on second Na atom. It also adsorbs maximum six molecules as shown in fig. 2. All molecules surround Na atom same as first. The binding energies of hydrogen molecules from one to six are -0.1, -0.15, -0.19, -0.2, -0.18, -0.16 eV respectively.

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Conclusions

In summary, the adsorption of hydrogen molecules on sodium doped graphene was studied using Density functional Theory. We have initiated by adsorption of sodium atom on pure graphene, Na prefers to adsorb on hollow site of carbon hexagon of graphene. The binding energy of sodium was found to be -1.074 eV and it binds maximum six hydrogen molecules with average binding energy -0.20 eV/H_2. Sodium atoms adsorbed on both sides of graphene showing 9.2 wt % of gravimetric density for the hydrogen.

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