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Effect of structural defects on the hydrogen adsorption in promising nanostructures

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ABSTRACT

Hydrogen adsorption in various nanosystems is one of the well studied topics of interest, due to its significance for the automobile applications. Scientists are considering novel nanostructures to enhance the storage capacity of hydrogen through various mechanisms and adsorption is one of the important process for this purpose. Here, we are interested in the structural aspects of some of emerging and promising nanostructures like carbon nanotube (CNT), zinc oxide nanotube (ZnONT) and silicon carbide nanotube (SiCNT) for hydrogen adsorption and storage. A set of three nanotubes for the above materials are considered and each type consists of three tubes of same diameter but different chirality. Density functional theory (DFT) based calculations are performed in both defected and defect free tubes for complete analysis. We could observe a strong role of defect in SiC and CNT but less effect in ZnO for the hydrogen adsorption phenomena. We could observe the two fold binding energy in defected armchair SiC and chiral CNT than defect free materials. A considerable change in HOMO-LUMO band gap (E_g) is observed in three nanotubes.

1. Introduction

Thirst for energy generation is one of the sensitive issues in world over. All means of energy production like solar, tidal and wind are investigated vigorously to meet the demand for the society. Hydrogen energy is predicted to be best fuel for future energy applications since it is the most abundant element in the universe having lot of interesting properties like high-energy content, lightweight, richest in energy per unit mass and above all pollution free. Hydrogen can be separated from hydrocarbons through the application of heat (a process known as reforming) and also separated from water through the electric current (a process known as electrolysis). However due to the explosive nature and large volume, transportation and storage are the main hindrances faced by the hydrogen economy. Hydrogen storage is a crucial issue in fuel cell design and application – a safe, compact and inexpensive system that is capable of storing relatively large amount of hydrogen is highly desirable [1]. In this regard, the researchers in all over the world carrying out experimental and theoretical work, in order to probe the suitable method of storing and transporting hydrogen.

Due to high surface area, chemical inertness and stable solid-gas adsorption characteristics, carbon nanotube (CNTs) seems to be a good medium for hydrogen (H_2) storage. Physisorption and chemisorption techniques are widely used for storing hydrogen in carbon nanostructures in which physisorption provides safe and reliable method. Other applications of CNTs include energy storage, field emission, smart fabrics, environmental molecular electronics, etc. [2]. It is known that depending upon rolling axis relative to the hexagonal network of the graphene sheet, carbon nanotube (CNT) are classified as armchair, zigzag and chiral types. Most of the researchers are concentrated on the physisorption of hydrogen in carbon nanotubes [3–14]. Dillon et al. [3] reported the hydrogen storage capacity of single wall carbon nanotube (SWCNT) ranges from 5 to 10 wt%. Züttel et al. [4] experimentally investigated the hydrogen adsorption through the monolayer surface of carbon nanotubes. The SWCNTs functionalized with Ti atoms are observed to increase the storage capacity up to 8 wt% as reported by Yildirim and Ciraci [5]. Whereas functionalization with other transition metal atoms like Sc, V and doped with B, N, P and S increases the binding sites for H_2 on CNT surface [6,7]. In addition to the above materials TiO_2 nanotubes, Si atom decorated C_{60} and pillared graphene also attract researchers working on this issue [8–10]. Our recent study shows the strong role of structural defects on H_2 adsorption in various types of CNTs [11].

Research labs all over the world are investigating various mechanisms to reach target value of 6 wt% set by the US department of energy (DOE) for on board automobile applications. There are two

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important aspects to achieve the required level of storage for any practical applications. First task lies in selecting a suitable material, then finding the suitable storage methods. None of the existing methods ie, compression, liquefaction, storage in metal hydride and gas adsorption can meet the desirable kinetics that opens wide range of explorations of novel materials for high storage capacity. Study of hydrogen adsorption in hexagonal nano structures like zinc oxide nanotubes (ZnONTs) and silicon carbide nanotubes (SiCNTs) apart from CNTs becomes an important one. It is interesting to note that ZnONT and SiCNT are structurally related to carbon nanotubes. ZnO has hexagonal wurtzite nanostructures with direct wide bandgap of 3.37 eV and strong excitonic binding energy of 60 meV at room temperature, which makes it a promising material for high efficiency applications in optoelectronics, chemical sensors, surface acoustic wave transducers, optical wave guides, solar cells and spin electronics, etc. [15]. Several authors analyzed the adsorption and interaction of hydrogen in ZnO nanostructures both theoretically and experimentally [16–18]. The ZnO nanomaterials provide higher thermal stability and it is preferable for hydrogen storage applications. Moreover it has large surface to volume ratio, pore size and grain size. ZnO has oxygen vacancies on metal-oxide surfaces making them electrically and chemically active with the adsorbates that is another favorable point for hydrogen adsorption. Few studies exist on ZnO in the form of nanowires, nanobelts and nanospheres [19,20]. Mg doped ZnO nanowires is investigated by Pan et al. [21] who have reported the highest hydrogen intake of the order of 2.79 wt%.

Equally important silicon carbide nanotubes have proven applications in optical and optoelectronics devices. SiCNTs are direct or indirect bandgap semiconductors with bandgap falling in the range of 2.39 - 3.3 eV [22–24]. Surface area of the material is an important factor that decides the hydrogen storage capacity. Mpourmpakis et al. [25] reported the hydrogen adsorption in SiC nanotubes and interpreted an increase of 20% in binding energy compared to pure CNTs. The hydrogen storage in SiC nanotubes with lithium doping was investigated by Wang and Liew [26]. They observed an increase in binding due to the charge transfer from lithium. He et al. [27] carried out the work on synthesis and hydrogen storage capacity of SiC nanotube. It is observed that hydrogen storage capacities in silicon carbide nanotubes are better than multi wall carbon nanotubes. Hydrogen interaction with native defects in SiC nanotubes were studied by Baierle and Miwa [28].

In this study we have considered CNT, ZnO and SiC nanotubes with three different chirality's, such as, armchair (5,5), zigzag (9,0), and chiral (6,4) with having almost same diameter for hydrogen adsorption. The structural defect of one pentagon and one heptagon are deliberately created opposite to each other to study its effect on hydrogen adsorption. In the present work we have considered the stable molecular configuration in which the hydrogen molecular axis positioned perpendicular and above carbon ring [11]. The values of binding energy and HOMO-LUMO band gaps with and without defects are reported and analyzed. The system with full coverage is also studied when the nanotube surface is fully covered with one molecule per graphitic hexagon. The computational details are presented in the following section.

2. Computational details

First principles density functional theory based calculations are performed for evaluating the adsorption binding energy (E_{ads}) of hydrogen molecule on outer surface of opened single wall ZnONT, SiCNT and CNT. The total energy of the system was estimated through simulation by means of Kohn-Sham equation. We have carried out the DFT calculations using the generalized gradient approximation (GGA) with Perdew-Burke-Enzerhof (PBE) functional for the electron exchange correlation [29]. All-electron calculations were performed with the double numerical basis set plus polarization (DNP) function implemented in the Dmol3 simulation package. The binding energy values are estimated from the well-known equation,

$$E_b = E\,(\text{nanotube}) + E(H_2) - E\,(\text{nanotube} + H_2). \quad (1)$$

Table 1
The binding energy (eV), equilibrium nanotubewall-H_2 separation (Å) and storage capacity (S_c in wt%) for the physisorption of hydrogen molecule on defect free (5,5), (9,0) and (6,4) ZnONT, SiCNT and CNT.

Tube	ZnONT			SiCNT			CNT		
	E_b	D_{eq}	S_c	E_b	D_{eq}	S_c	E_b	D_{eq}	S_c
(5,5)	0.062	2.55	1.2	0.071	2.91	2.5	0.072	2.64	4
(9,0)	0.087	2.84	1.15	0.070	2.49	2.3	0.065	2.28	3.8
(6,4)	0.065	2.71	1.5	0.060	3.4	2.9	0.077	2.65	4.8

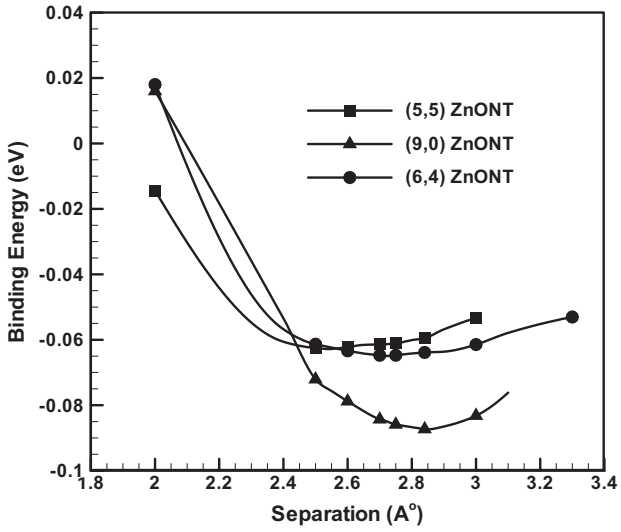

Fig. 1. Binding energy variation of H_2 as a function of separation for (5,5), (9,0) and (6,4) ZnONT.

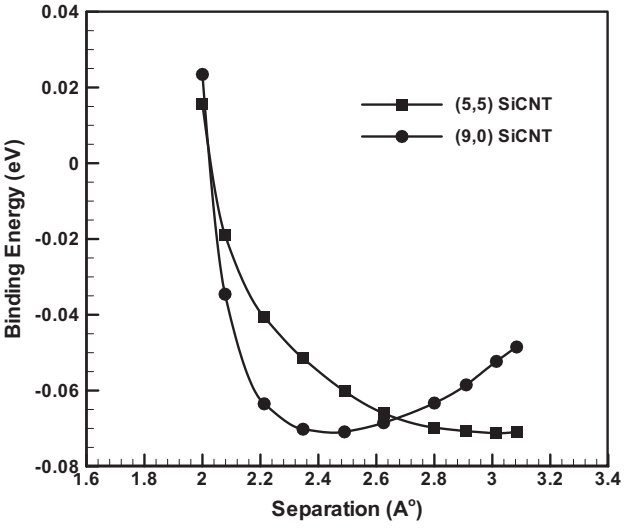

Fig. 2. Binding energy variation of H_2 as a function of separation for (5,5) and (9,0) SiCNT.