

A DENSITY FUNCTIONAL THEORY-BASED INVESTIGATION OF SCANDIUM-INCORPORATED PORPHYRIN-INDUCED CARBON NANOTUBES: A POTENTIAL HYDROGEN STORAGE MATERIAL

Michael Mananghaya, Emmanuel Rodulfo, Gil Nonato Santos

Abstract—Functionalization is a technique used to improve the reactivity of single-walled carbon nanotubes (SWCNT). Functionalization of a (10, 0) zigzag nanotube segment containing 120 C atoms with porphyrin defects (4ND) was investigated with the aid of spin-unrestricted density functional theory (DFT). The nanotube with defect was functionalized with Scandium defined as Sc/4ND-CN_xCNT. It is found that the porphyrin defects characterized by four-nitrogen divacancies in SWCNT resulted in decreased band gaps. The stability of Sc functionalization is dictated by a strong binding energy, suggesting a reduction of clustering of metal atoms over the metal-decorated SWCNT. We likewise report the very strong binding to hydrogen molecule of the composite material Sc/4ND-CN_xCNT, which may be considered, for hydrogen storage. Finally, the formation energies and electronic properties are also reported.

Index Terms— Binding Energy, Density Functional Theory, Porphyrin Defects, Single-Walled Carbon Nanotubes.

1 INTRODUCTION

Single walled carbon nanotubes (SWCNT) have been investigated intensively both experimental and theoretically [1], [2], [3], [4], [5] for usage as hydrogen storage material. It was demonstrated hydrogen storage capacity of pure carbon nanotubes at ambient temperature is no more than 1 wt%. The interaction between hydrogen molecules and carbon nanotubes is van der Waals interaction in nature. Pure carbon nanotubes (CNT) are not proper material for hydrogen storage. Fortunately, different chemical and physical properties of CNT can be modified by the introduction of dopants and defects.

Nitrogen (N) has roughly the same atomic radius as carbon (C) atoms and the extra electrons from the nitrogen dopants are particularly attractive because semiconducting nanotubes are expected to become metallic upon N doping. Several groups [6], [7], [8], [9], [10], [11], [12], [13], [14] have been successful in synthesizing N-doped CNTs (CN_xNTs) in various approaches. Specifically, the synthesis of SWCNT bundles doped with N was reported [15] using aerosol-assisted chemical vapor deposition (CVD); N dopants are substituted into the C network with and without vacancy formation. Porphyrin-like (labeled as 4ND) formed by removing two central C atom among four hexagons and replacing the four surrounding C atoms with 4 N atoms and pyridine-like defects (labeled

as 3NV) which is formed by removing a central C atom among three hexagons and replacing the three surrounding C atoms with 3 N atoms [8], [9] are formed simultaneously in the side-walls of SWCNTs as verified through spectroscopic measurements [16], [17]. Coexistence of 3NV and 4ND indicates that the nanotubes reactivity compared with pure CNTs is increased [15].

Modification of CNTs electronic and magnetic properties can also be achieved through chemical functionalization of transition metals (TMs); TM-dispersed materials have been studied recently for large hydrogen storing capacity. With respect to release temperature The TM-H₂ binding energy and ratio look very promising [18]. However, TM atoms tend to easily aggregate instead of being atomistically dispersed due to strong metal cohesion and poor reversibility in TM dispersion has been a major concern [19]. It was suggested to increase the binding strength between metal and dispersant materials by chemical functionalization of TM with CN_xNTs with 4ND defects in order to overcome poor dispersion [18], [19], [20].

Pure carbon nanotubes are not proper for hydrogen storage. Remarkably large amount of hydrogen can be stored in functionalized nanotubes. In order to find how the N doping and TM functionalization in SWCNTs affects the binding energy of H₂, in this paper, we used first-principle spin-unrestricted density functional theory (DFT) to study the largest number of H₂ adsorption on Sc-doped SWCNTs with 4ND defects by gradually increasing the number of H₂ molecules to these Sc-doped SWCNTs with porphyrin deficiencies.

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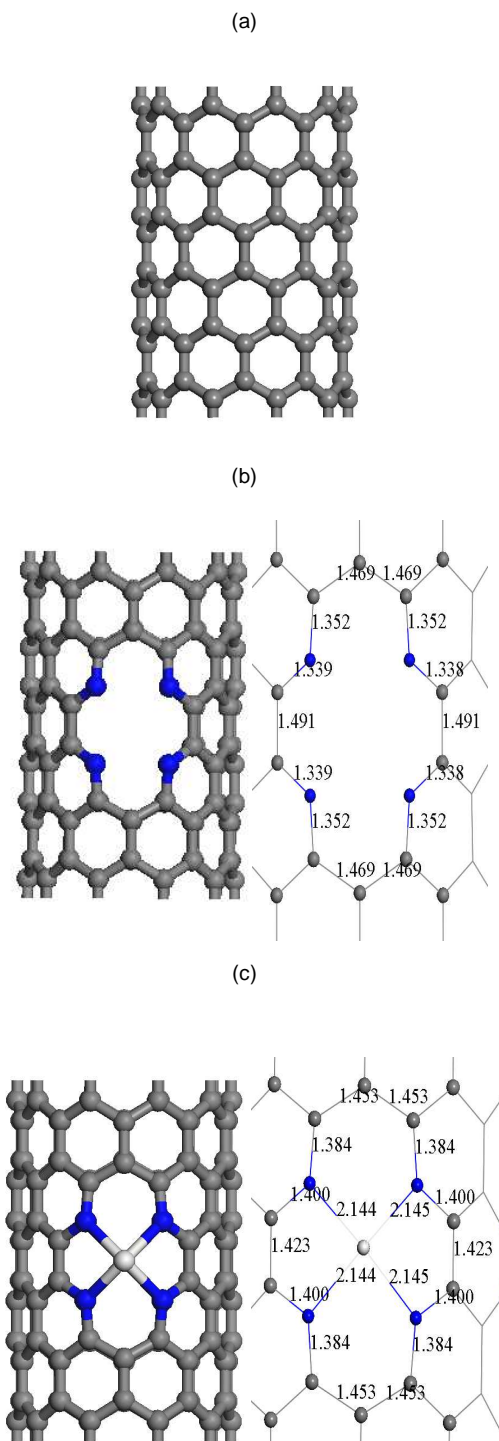


Fig.1. Optimized geometry of (a) the infinite (10,0) zigzag SWCNT, (b) SWCNT with porphyrine defects (4ND-CN_xNT), (c) 4ND-CN_xNT functionalized with Sc. Gray color depicts carbon atoms; blue is Nitrogen, and white is Scandium.

2 METHODOLOGY

The electronic properties were studied using first-principles density functional theory (DFT), via *Dmol³* code, available from Accelrys [21] with localized atom centered basis set defined numerically on a dense radial grid. Double numeric polarized (DNP) basis set with atomic cutoff set at 4.6 Å was used. Calculations were performed with supercells of zigzag (10, 0) CNT (see Fig. 1(a)) with length of $a = 12.78$ Å. For supercell geometries, all-electron spin-restricted calculations, along with gradient-corrected Perdew-Burke-Ernzerhof (PBE) functional [22] were carried out with a five Monkhorst-Pack k-points [23] set for the Brillouin zone integration. Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm with convergence criterion of 0.005 Å on displacement and 10^{-5} a.u. on the total energy and electron density were utilized to carry out the geometry optimizations. To simulate the SWCNTs, a hexagonal lattice was used with a wall-to-wall distance of at least 10 Å sufficient enough to avoid in-plane interactions between nanotubes in adjacent unit cells. Two types of modified nanotubes were considered: Substitution of nitrogen dopants with vacancy formation, by removing two C atom among four hexagons and replacing the four surrounding C atoms with 4 N atoms (4ND-CN_xNT) (see Fig. 1(b)) and chemical functionalization of Sc on 4ND-CN_xNT (see Fig. 1(c)). The Fermi levels of the band structures and density of states (DOS) were reset at the 0 eV position.

3 RESULTS AND DISCUSSIONS

3.1. Structure and electronic properties of CNT with 4ND defects.

The (10, 0) tube was chosen as a typical semiconducting tube for investigation. Fig. 1(a) show the relaxed geometries of (10, 0) nanotube. Pure (10,0) SWCNT with the diameter of 7.83 Å was chosen in the present work. Due to the two missing C atom, the C-N bond lengths of porphyrin-like doping are determined to be ~1.338-1.352 Å (see Fig. 1(b)), depending on the orientation, as compared to ~1.425-1.429 Å for the C-C bonds. Also an increase in the C-N bond lengths of nanotube with porphyrin-like defect functionalized with Sc can be observed as shown in Fig. 1(c) which is ~1.384-1.400 Å thus, N and TM impurities in CNTs produce their own local strains and deformation.

The formation energies (E_f) defined as:

$$E_f = E_{\text{tot}} - n_C \mu_C - n_N \mu_N, \quad (1)$$

where E_{tot} is the total energy of the (10, 0) and (5, 5) CN_xNT, n_C and n_N are the number of C and N atoms, respectively. μ_C is the chemical potential of C obtained from the corresponding pure CNT, and μ_N is the chemical potential of N obtained from nitrogen in gas phase. The calculated formation energy of the (10,0) CNT (C₁₁₄N₄) is on the average of 3.10 eV as in [20]. The synthesis of N-doped carbon nanotubes is usually carried out at 700-900°C using nitrogen-rich precursors for CVD processes [24], [25]. Spectroscopic analysis have revealed that C-N bonding of N-doped carbon nanotubes might be attributed to

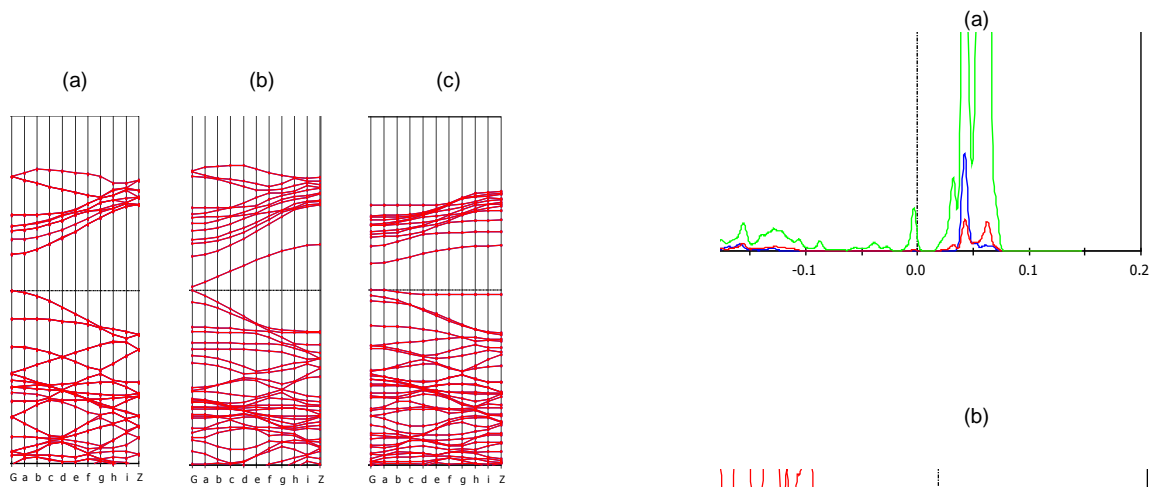


Fig.2. The band structures of (a) pure (10,0) CNT, (b) (10,0) CNT with porphyrin-like defect and (c) Sc adsorbed on (10,0) zigzag CN_xNT with porphyrin-like defect. The Fermi level is set as zero and plotted with a broken line. All system indicates that this is non-magnetic. Energies at the vertical axis are at arbitrary units.

sp²-substitution of C atom with a N atom, pyridine-like doping, porphyrin-like doping, and molecular N₂, respectively. Sufficient energies to form pyridine-like and porphyrin defects in N-doped carbon nanotubes are provided with relatively high synthesis temperature and use of catalysts, though the formation energies of pyridine-like defects are higher than sp²-substitution and porphyrin-like defects.

To clarify the issues on the effects of the formation of 4ND defects have on the electronic properties of CNT the band structures of the CN_xNT with 4ND defects are examined in Fig. 2. The band gap of (10,0) CNT is around 0.71 eV, which is greatly decreased to around 0.054 eV for the 4ND defect. This can be explained by examining the band structure; the four N atoms introduce a new energy level above the Fermi level. Mananghaya et al. [20] have shown that the formation energy of a pyridine-like vacancy is around 3.17 eV on the average can render the CNT to possess metallic features. The new energy level within the band gap that is closer to the Fermi level is due to the extra nitrogen atom present in the 4ND defect compared to the 3NV defect.

When Sc metal is adsorbed on the CN_xNT with 4ND deficiency, as initial guesses, we consider the TM is directly bound to the hollow site of 4ND and the TM is attached to the sites near 4ND and after full structural optimization it is found out that the Sc-adsorption on the hollow site is energetically favorable. Sc-adsorption on the hollow site leads to the formation of Sc-porphyrin-like structure in which the adsorbed Sc is protruded from the tube sidewall with an average Sc-TM bond length of 2.144 Å. The binding energy (E_b) of an individual Scandium metal on the 4ND-CN_xNT nanotube was defined as

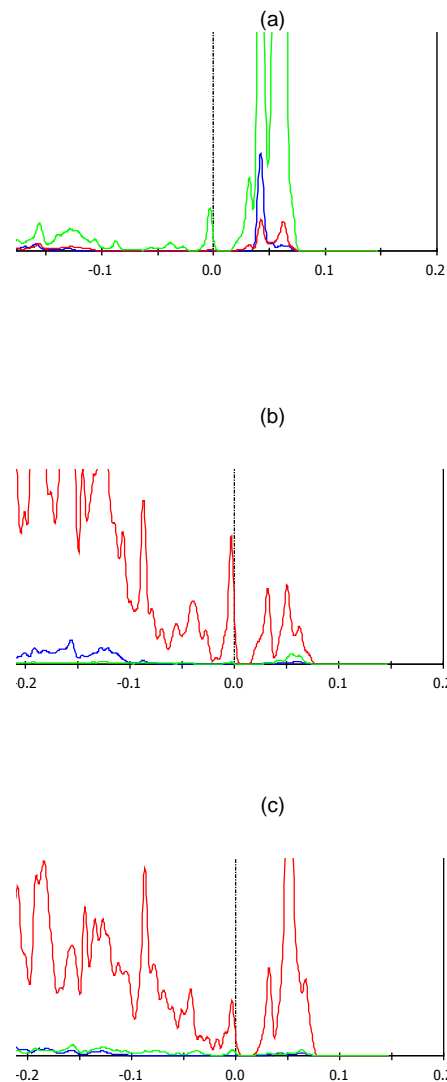


Fig.1. The PDOS of (b) Sc, (c) N and (d) C in the adsorption system for the (10,0) CNT. A smearing of 0.002 eV was applied for all graphs. The blue, red and green plots denote s, p and d orbitals, respectively.

$$E_b = E_{\text{tot}}(4\text{ND-CN}_x\text{NT}) + E_{\text{tot}}(\text{TM}) - E_{\text{tot}}(\text{TM}/4\text{ND-CN}_x\text{NT}), \quad (2)$$

where E_{tot} denotes the total energy of the optimized system in the bracket. $E_b > 0$ corresponds to a stable optimized configuration and indicates bonding with a binding energy of 9.12 eV. On the other hand, due to the N participation and the vacancy defect, the binding energy of Scandium on 4ND-CN_xNTs is larger than the pure CNTs [20].

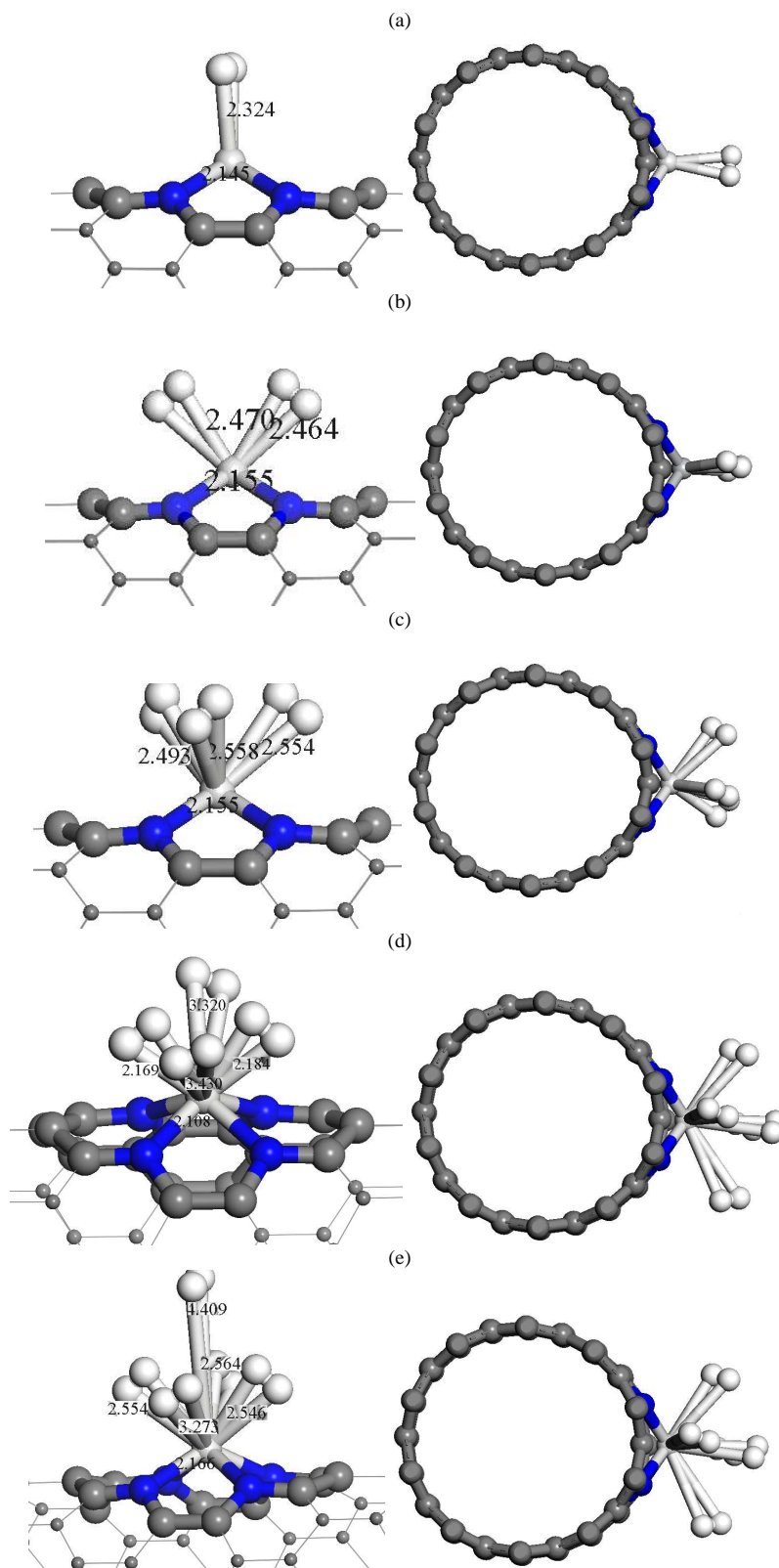


Fig.4. Optimized geometry of Sc-decorated (10,0) CNTs containing a porphyrine defect with one to five hydrogen molecules absorbed. Gray color depicts carbon atoms, blue is nitrogen, white is hydrogen and Sc.

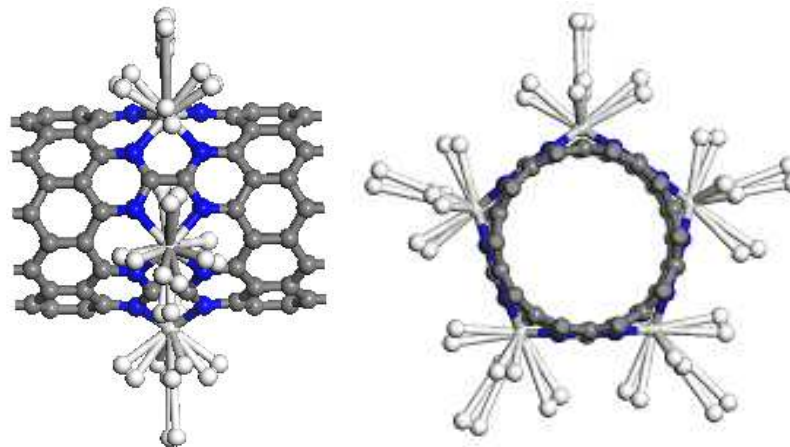


Fig.5. Optimized geometry of Sc-decorated (10,0) CNTs containing five porphyrin defect with twenty five hydrogen molecules absorbed. Five Sc atoms were used to decorate the tube. Gray color depicts carbon atoms, blue is nitrogen, white is hydrogen and Sc.

TABLE 1.
 Average adsorption energies per H₂ on Sc-decorated CN_x nanotube with porphyrin-like defects

System	Adsorption energies per H ₂ (eV)
1H ₂ -Sc/4ND-CN _x NT	0.23942
2H ₂ -Sc/4ND-CN _x NT	0.17816
3H ₂ -Sc/4ND-CN _x NT	0.15249
4H ₂ -Sc/4ND-CN _x NT	0.11401
5H ₂ -Sc/4ND-CN _x NT	0.09704

The formation of porphyrin-like nitrogen defects is very crucial for enhancing the metal binding to the defects. The strong interactions between these TMs and the 4ND-CN_xNT can be explained through partial densities of states (PDOS), that is, Sc adsorption on the 4ND-CN_xNT as shown in Figs. 3(a)–3(c) for the (10, 0) CNT. It is found that the d electrons of Sc and the p electrons of C and N atoms mainly contribute to the electronic states near Fermi level. In other words, strong interaction exists between the d orbitals of Sc and the p orbitals of N atoms due to their hybridization with each other. This is reasonable, because the CN_xCNT with 4ND defects uses two valence electrons to form a lone pair. The non-bonding lone pair of the nanotube is greatly enhanced compared with the case of the pure CNT. Moreover, the Hirshfeld charge analysis indicates that about 0.704 e electrons are transferred from the Sc atom to the 4ND-CN_xNT structures, leading to partially cationic Sc atom. We should point out as displayed in Fig. 2.c that this tube is semiconductor material after the adsorption of Sc atom with a band gap of 0.52 eV due to the charge transfer from the Sc atom to the tube. Partially cationic Sc can attract H₂ as discussed next.

3.2. Hydrogen Storage of Sc decorated CNT with 4ND defects.

The H-H bond length is elongated from 0.752 Å of a free H₂ to 0.766 Å when one H₂ molecule is adsorbed on the Sc/4ND-CN_xNT system. Optimized Sc-H and Sc-N distances are found to be 2.323 and 2.147 Å on the average, respectively. It is found that 0.118 e electrons are transferred from H₂ to Sc atom but the Sc atom still carries a positive charge of 0.573 e, indicating that more H₂ molecules can be absorbed on the Sc atom. The corresponding adsorption energy is 0.239 eV. The number of H₂ was gradually increased to address the maximum number of H₂ molecules that can be bound to the Sc/4ND-CN_xNT system and after full relaxation for every H₂ adsorption configuration, the GGA predicted that the Sc atom can absorb up to five H₂ as shown in Fig. 4. Correspondingly, based on GGA-PBE calculations the average adsorption energies per H₂ are summarized in table 1. The predicted adsorption energy ranges from 0.097 to 0.239 eV. Most importantly, the H-H distances are increased slightly from 0.752 Å to around 0.758 Å due to the charge transfer from the H₂ molecules to the Sc/4ND-CN_xNT yet all the adsorbed H₂ remain molecular.

The adsorption of H₂ molecules was studied further on a 5 Sc functionalized to a CN_xNT with 5 4ND defects, in this case each Sc atom carries a positive charge of 0.658 e. Five H₂ was placed on each Sc atom. A starting configuration for geometry optimization is taken by attaching 25 H₂ around the Sc atoms above the five defects. In the resulting optimized structure shown in Fig. 5, the hydrogen atoms remain molecular with an average bond length of around 0.755 Å. The average hydrogen adsorption energy is 0.092 eV per H₂ calculated using GGA-PBE functional. A calculation using LDA-PWC was also carried out and average hydrogen adsorption energy is 0.277

eV per H₂. The LDA calculation is in good agreement within the adsorption requirement of hydrogen storage at room temperature of 0.20 ~ 0.70 eV/H₂ [26].

4 CONCLUSIONS

The electronic properties of single-walled carbon nanotubes in the presence of N and Sc impurities were studied using Density Functional Theory. The calculated band structures and density of states denote that the impurities can impose a significant effect on the electronic properties of (10,0) CNTs. Porphyrin defects in SWCNT caused a great reduction in the value of band gaps. The chemical functionalization of Sc is thermodynamically stable and bonding is favorable dictated by a strong binding energy of 9.12 eV suggesting a considerable reduction of clustering of metal atoms over the metal decorated nanotube. Finally, very strong binding of hydrogen molecule to the composite material Sc/4ND-CN_xCNT was observed which is within the adsorption requirement of hydrogen storage at room temperature and shows a potential media for storing hydrogen.

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