

THEORETICAL INVESTIGATION OF TRANSITION METAL-INCORPORATED PORPHYRIN-INDUCED CARBON NANOTUBES: A POTENTIAL HYDROGEN STORAGE MATERIAL

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Abstract— *The systemic study of the chemical functionalization of (10,0) SWCNT doped with porphyrin-like nitrogen defects (4ND-CN_xNT) with 10 different transition metals (TMs-Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) defined as TM/4ND-CN_xNT was done with the aid of spin-unrestricted density functional theory (DFT). The composite material TM/4ND-CN_xNT shows very strong binding to hydrogen molecule and can act as a media for storing hydrogen. The electronic properties are also reported.*

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

1 INTRODUCTION

Hydrogen is the cleanest, sustainable and renewable energy carrier, Hydrogen is an ideal fuel has several advantages such as easy to produce, convenient fuel for transportation, versatile, converts easily to other energy forms at the user end, high utilization efficiency, and environmentally compatible (zero- or low-emission). Hydrogen energy system is expected to progressively replace the existing fossil fuels in the future; the latter are being depleted very fast and cause severe environmental problems. In particular, proton exchange membrane fuel cell is one potential use of hydrogen to reduce atmosphere pollution. To achieve this goal feasible onboard hydrogen storage systems have to be developed.

Carbon nanotubes (CNT) have attracted much interest due to their many exceptional properties [1-20, 24-26] for example the usage as hydrogen storage material [1-5]; there are nonetheless many areas to be considered in storing hydrogen wherein pristine tubes are not the most appropriate. This is because of their rather wide spread characteristic physical and chemical properties, high surface area and abundant pore volume porous carbon is considered as good adsorbent. For conventional porous carbon, the hydrogen uptake is proportional to its surface area and pore volume, while, regretfully, a high hydrogen adsorption capacity (4 wt %) can be only obtained at very low temperatures such consistent with theoretical calculations.

Doping of nanotubes is expected to provide solutions for these limitations. Indeed, the incorporation nitrogen atoms into the

honeycomb lattice leads to chemical activation of the rather passive surface of a carbon nanotube and adds additional electronic states around the Fermi level. It has to be stressed that the characterization of the effects doping has on a single nanotube is difficult to qualitatively and quantitatively determine. These problems arise mainly because of sample impurities; dopant concentrations; single tube measurements. The characterization comprises the direct probing of the dopants in the nanotube and the overall effect the dopants has on the nanotube properties. On the other hand, nitrogen-doped carbon nanotubes can be synthesized by pyrolyzing ferrocene/melamine mixtures at elevated temperatures [13]. Changes in the electronic structure of carbon nanotubes due to the introduction of nitrogen in the lattice have been identified using scanning tunneling spectroscopy [8, 9]. Nitrogen-doped tubes are metallic with no apparent band gap, in contrast to undoped tubes with varying electronic character. Nitrogen-doped carbon nanotubes with different nitrogen contents synthesized by chemical vapor deposition (CVD) with pyridine as the nitrogen source and acetylene as the carbon source contain pyridine-like and porphyrin-like structures [9, 10], as revealed by X-ray photoelectron spectroscopy (XPS). For the porphyrin-like, nitrogen substitution accompanied with vacancy (labeled as 4ND) is formed in the sidewall of single-walled carbon nanotube (SWCNT) is a four-nitrogen divacancy.

These 4ND defects in nitrogen-doped nanostructures may enhance reactivity and immobilize species such as transition metals [18, 20]; the incorporation of nitrogen atoms and transition metals into carbon nanotubes affords structures with the ability to participate in hydrogen bonding, US Department of Energy (DOE) Hydrogen Plan has set a standard for this discussion by providing a commercially significant benchmark for the amount of reversible hydrogen adsorption. The

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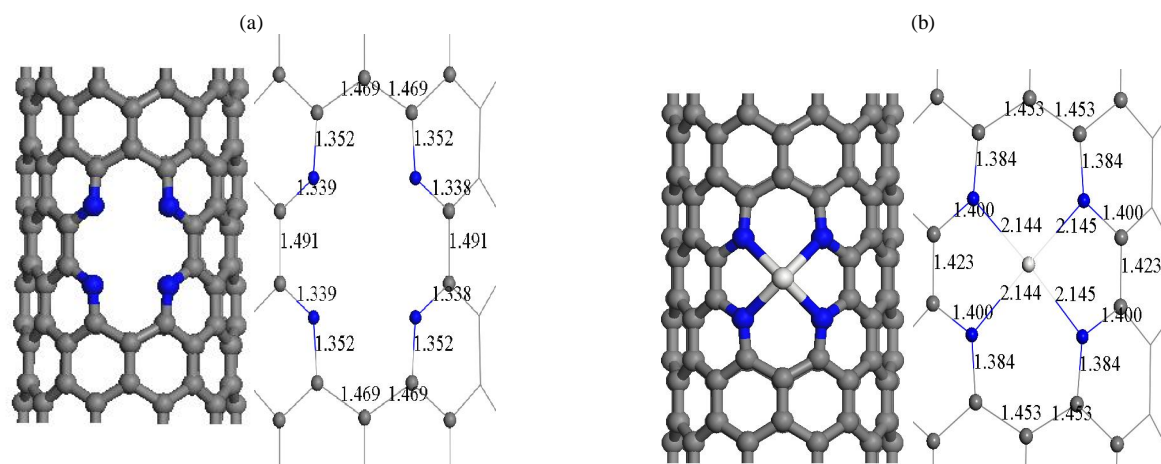


Fig.1. Optimized geometry of (a) the infinite (10,0) zigzag SWCNT with porphyrine defects (4ND-CN_xNT) and (b) 4ND-CN_xNT functionalized with TM. Gray color depicts Carbon atoms; blue is Nitrogen, and white is TM in this case Scandium.

benchmark requires system-weight efficiency (the ratio of stored hydrogen weight to system weight) of 6.5 wt% hydrogen and a volumetric density of 62 kg H₂ /m³.

Theoretical calculations revealed that the porphyrin defects in SWCNT resulted in a decreased value of band gaps and the electronic properties of SWCNT can be effectively modified, which are strongly dependent on the TMs absorbed [20]. Also the binding strengths of TMs with 4NV-CN_xNT are significantly enhanced when compared to the pure SWCNT such that binding is stable and favorable dictated by a strong binding energy that could improve transition metal dispersion over the metal decorated SWCNT [20]. 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].

Our aim in this work is to theoretically investigate the structural geometry, energetic stabilities, and electronic properties of hydrogen-chemisorptions for a (10, 0) carbon nanotubes functionalized with 10 different TMs (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) using the spin-polarized density-functional theory method. The final aim of this work is the evaluations of the possibility that these TM decorated nitrogen-containing carbon nanotubes behave as hydrogen-storage materials.

2 METHODOLOGY

Calculations have been performed with density functional theory implemented in *Dmol³* package [21]. The calculations were all-electron spin-unrestricted with double numerical plus polarization basis set (DNP) with atomic cutoff set at 4.6 Å. The generalized gradient approximation by Perdew, Burke, Ernzerhof (PBE) was employed for the exchange-correlation functional [22]. Calculations were performed with supercells of zigzag (10, 0) zigzag SWCNT with porphyrin defects (4ND-CN_xNT) (see Figure 1(a)). A triclinic supercell of 30 x 30 x 12.78 Å³ was used to simulate the nanotube with infinite length. The lattice parameter *c* equaled to fivefold of the periodicity of

(10,0) SWCNT and the lattice parameters *a* and *b* were large enough to ignore the effect of neighboring tubes. The Monkhorst-Pack scheme [23] was used in the Brillouin zone with 1 x 1 x 5 special K-points for all geometry optimizations that were carried out with the 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. The Fermi levels of the band structures and density of states (DOS) were reset at the 0 eV position.

Two types of modified nanotubes were considered: (i) Substitution of nitrogen dopants with vacancy formation, by removing two C atom among four hexagons and replacing the four surrounding C atoms with 4N atoms (4ND-CN_xNT) (Figure 1(a)) and (ii) Chemical functionalization of TM on 4ND-CN_xNT (see Figure 1(b)).

3 RESULTS AND DISCUSSIONS

3.1. 4ND Structure and electronic properties

The considered fully nitrogen-containing (10, 0) carbon nanotubes formed by C₁₇₄N₄ units are 7.83 Å in diameter and 12.78 Å in length. The interlayer bond lengths calculated by density-functional theory for, C–N and C–C bonds are ~1.338–1.352 Å (see Figures 1(b)), and ~1.425–1.429 Å, respectively. A typical (sp³)C–C(sp³) bond length is 1.54 Å. The C–N bond length for amines is 1.479 Å. Due to the two missing C atom, the C–N bond lengths of porphyrin-like doping are smaller. To analyze the bond lengths and bond angles, all nanotube geometries were optimized at the same level of theory, including porphyrin as a reference. Based on the comparison of the bond angles and bond lengths of porphyrin, the structure with porphyrin-like defect functionalized with TM can be observed as shown in figure 1(b) for Sc has an increase in the C–N bond lengths of nanotube which is ~1.384–1.400 Å although it has smaller bond lengths than amine. Impurities in CNTs produce their own local strains and deformation as was expected for these structures.

<i>TM</i>	D_{TM-N} (Å)	E_b-TM (eV)	C_{TM} (e)	$\mu_{total TM}$	D_{TM-H_2} (Å)	E_b-H_2GGA (eV)	C_{TM-H_2} (e)	$\mu_{total TM-H_2}$	D_{H_2} (Å)	C_{H_2} (e)
Sc	2.144	8.765	0.704	0	2.324	0.239	0.573	0	0.766	0.059
Ti	2.075	8.256	0.517	0.001	1.921	0.536	0.418	0	0.828	0.022
V	2.059	7.801	0.381	2.470	1.954	0.228	0.290	2.3641	0.786	0.482
Cr	2.054	5.945	0.470	0	1.866	0.238	0.430	0	0.808	0.012
Mn	1.991	6.353	0.294	2.915	2.179	0.105	0.243	2.824	0.764	0.034
Fe	1.967	7.397	0.231	1.911	1.630	0.311	0.142	0	0.837	0.044
Co	1.950	7.598	0.195	0.9694	1.885	0.198	0.150	0.917	0.778	0.037
Ni	1.923	7.089	0.127	0	3.143	0.013	0.131	0	0.750	0.004
Cu	2.030	8.212	0.360	0	2.075	0.067	0.346	0	0.764	0.138
Zn	2.056	7.105	0.472	0	2.212	0.119	0.442	0	0.759	0.037

Table 1. Average TM–N distances (D_{TM-N}) of TM/4ND-CN_xNT, binding energy (E_b) of an individual TM on the 4ND-CN_xNT, calculated charge transfer using Hirshfeld population analysis, the charges transferred from TMs to the (10,0) CN_xNT with 4ND defect (C_{TM}), and total magnetic moment ($\mu_{total TM}$). Average distance between the TM and H₂ (D_{TM-H_2}), average adsorption energies per H₂ on TM-decorated CN_x nanotube with porphyrine-like defects using GGA (E_b-H_2GGA), charge transferred from TMs to the (10,0) CN_xNT in the presence of H₂ (C_{TM-H_2}), total magnetic moment ($\mu_{total TM-H_2}$) in the presence of H₂, H–H distances (D_{H_2}), and charge transferred from H₂ to TM atom (C_{H_2}).

The formation energies of the nitrogen-containing carbon nanotubes pyridine-like and porphyrin-like vacancy were calculated previously by Mananghaya et al. [20] using the density-functional theory method at the GGA-PBE /DNP level and found out that for a (10,0) nitrogen-doped CNT with porphyrin-like the calculated formation energy is 3.10 eV while the pyridine-like vacancy is around 3.17 eV. The formation-energy values have a close relationship to the nanotube structures in this study. These indicates that formation of a divacancy is preferred over monovacancy and the dangling bonded carbon atoms near the divacancies would be replaced with four nitrogens from N₂ molecules in the gas phase in the presence of catalysts or iron oxides. Hirshfeld population analysis shows that charge of the order 0.116 e on each of the four nitrogen atoms of 4ND-CN_xNT, hence this site of the nanotube is very reactive as it can act as a strong oxidizing agent for transition metal atoms.

When a TM atom is adsorbed on the CN_xNT, two kinds of initial configurations were considered: (1) the TM is directly bound to the hollow site of 4ND; (2) the TM is attached to the sites near 4ND. The TM adsorptions on the defect sites are the most stable after optimization because of their higher reactivity than other sites [16, 20]. The most stable configurations of TMs adsorbed on 4ND-CN_xNT (labeled as TM/4ND-CN_xNT) is listed in table 1 and are characterized by forming multiple TM–N bonds at the hollow sites. All the TMs are projecting from the sidewall of the 4ND-CN_xNT in various ways. The average TM–N distances (D_{TM-N}) of TM/4ND-CN_xNT range from 1.923 (Ni) to 2.144 (Sc) Å. Thus it can be surmised that N and TM impurities in CNT produce their own local strains and results in the respective deformation. The binding energy (E_b) of an individual TM on the 4ND-CN_xNT was defined as:

$$E_b = E(4ND-CN_xNT) + E(TM) - E(TM/4ND-CN_xNT), \quad (1)$$

where E denotes the total energy of the optimized system in

the bracket. In table 1 all $E_b > 0$ corresponding to a stable optimized configuration and indicates bonding. Presence of porphyrin-like nitrogen defects is very crucial for enhancing the metal binding to the defects. The CN_xCNT with 4ND defects uses two valence electrons to form a lone pair. Strong interaction exists between p orbitals of N atoms and the d orbitals of various TMs due to their hybridization with each other. In Table 1: the calculated charge transfer using Hirshfeld population analysis is shown, the charges transferred from TMs to the (10,0) CN_xNT with 4ND defect range from 0.127 e (Ni) to 0.704 e (Sc). Partially cationic character of the TMs results due to the charge transfer, and thus facilitating the adsorption of foreign species such as hydrogen gas as discussed in the next section.

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

When one H₂ molecule is adsorbed on the TM/4ND-CN_xNT system the H–H bond length is elongated from 0.752 Å of a free H₂ to to as high as 0.828 Å (for Ti) as advertise in table 1. Optimized TM–H₂ is found to range from 1.630 (Fe) to 3.143 (Ni) Å. It is seen in the table depending on the TM incorporated that 0.004e (Ni) to 0.482e (V) electron are transferred from H₂ to TM atom and the entire TM atoms still carry a positive charge (manifested in C_{TM-H_2} column), indicating that more H₂ molecules can be absorbed.

Interestingly, Sc posses the maximum electron transferred of about 0.573 e and the maximum number of H₂ molecules that can be bound to the Sc/4ND-CN_xNT system was calculated, the GGA predicted that the Sc atom could absorb up to five H₂. Correspondingly, the average adsorption energies per H₂ based on PBE-GGA calculations is summarized in table 1. The predicted adsorption energy ranges from 0.013 to 0.536 eV. Adsorption energies per H₂ based on LDA-PWC ranging from 0.255 to 1.058 eV was obtained and the resulting calculation is in good agreement with the adsorption requirement of hydro-

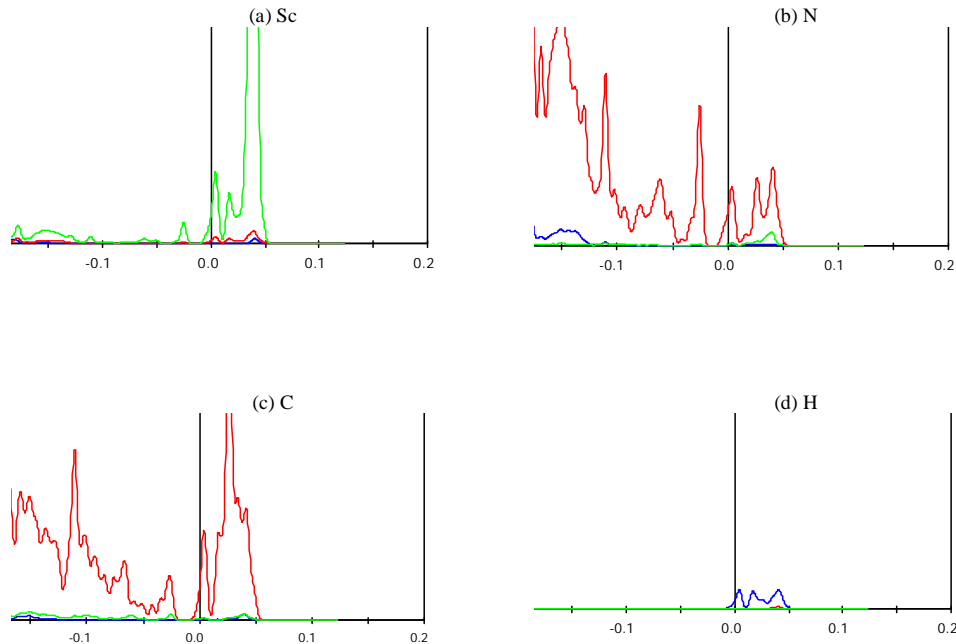


Fig.2. The PDOS of (a) Sc, (b) N, (c) C and (d) H in the adsorption system for the (10,0) CNT. A smearing of 0.002 eV was applied for all graphs. The blue, red and green plots denote s, p and d orbitals, respectively.

gen storage at room temperature [26]. Ti posses the highest average adsorption energy in GGA calculations. Most importantly, all the adsorbed H_2 remain molecular.

3.3 Nature of interaction between hydrogen and Transition metal atom

To understand the nature of binding between the metal atom and the hydrogen molecules, the partial density of states (PDOS) is calculated. The calculated PDOS for TM atom doped 4ND-CN_xNT and the hydrogen adsorbed are provided in Fig. 2a - 2d respectively. From the Fig. 2a and 2b it is visible that binding states just below the Fermi level $E-E_f$ is mainly attributed to the TM d orbital are hybridized with p of nitrogen atom. In the case of hydrogen adsorbed d orbital of the TM hybridized with the p orbital of nitrogen and simultaneously with the s orbital of hydrogen.

5 CONCLUSIONS

The electronic properties of single-walled carbon nanotubes in the presense of porphyrin defect and TM impurities were studied using density functional theory. Porphyrin defects in SWCNT caused an enhanced metal binding and the chemical functionalization of all TMs is thermodynamically stable 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 TM/4ND-CN_xCNT was observed which is within the adsorption re-

quirement of hydrogen storage at room temperature and these results all shows a potential media for storing hydrogen.

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