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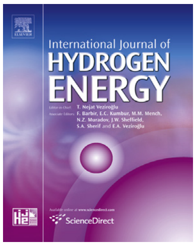

Doping effects of Co on exo-hydrogenated narrow single-walled carbon nanotubes

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ABSTRACT

Density functional theory (DFT) calculations with the generalized gradient approximation (GGA) were employed for a systematic study of electronic structure and morphologic characteristics of bare and exo-hydrogenated Co-doped single walled carbon nanotubes (CNTs). Two internally and one externally doping configurations for the cobalt adatoms were investigated. Binding energies, bond lengths and angles, under full and half converge of the adsorbed hydrogen atoms were calculated for both cases. Effect of hybridization between the Co-3d and the H-s orbitals showed that the exo-hydrogenated CNTs with full and half coverage cases would be stable in the internally doped Co atom systems; whereas, the stability of the hydrogenated systems under externally doped Co adatom was not trivial. In general, for the externally Co-doping, the Co atoms can act as additional adsorbents so the amount of total adsorbed hydrogens could be varied substantially; whereas, for the internally Co-doping the nature of the exo-hydrogenation (being atomic or molecular) shows nanotube's chirality dependent.

1. Introduction

Materials with low weight and large specific area that could store a large amount of hydrogen would make the hydrogen fuel feasible for clean energy production. One of the actively explored lines is to adsorb hydrogen on various carbonaceous materials such as activated carbons, carbon-derived materials and carbon nanotubes (CNTs). Orinakava et al. (2011) have reviewed a considerable set of 224 experimental and theoretical articles on the issue of hydrogen storage in carbon nanotubes which in general, it has been accepted that the pristine CNTs are not proper materials for hydrogen storage (Hydrogen adsorption is below 1 wt.%) [1]. Although, the US Department of Energy (DOE) has targeted about 9 wt.% for molecular hydrogen gravimetric storage capacity by the year 2015 [2], but because of very weak interaction between the H_2 molecules and the pristine CNTs (~0.04 eV), a noticeable hydrogen storage capacity solely through molecular adsorption is improbable [3]. Moreover, we have already shown in our recent paper that the interaction would be enough strong just for very narrow nanotubes with diameters less than 4 Å [4], but nowadays unfortunately, there is no a systematic control on diameters of the synthesized CNTs.

Alternatively, the atomic adsorption seems not to be a suitable storage method due to its very high stability with energy range of 2–4 eV. In fact, some researchers have been focusing on how to weaken the atomic adsorption energy or strengthen the molecular adsorption energy to improve the storage applications [5]. In this regard, functionalizing of the CNTs by transition metal (TM) elements, potentially gives

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them ability to store remarkable amounts of hydrogen via hybridization between the TM-d states and the H_2 states with binding energies of 0.2–0.6 eV [3,6–8].

Besides that the molecular hydrogenation of the CNTs has been a noticeable issue but a number of common features exist in all the experimental reports that make the atomic adsorption/desorption process inevitable, 1 – the stored hydrogen could not be desorbed completely at ambient temperature in vacuum (existence of hysteresis in the sorption isotherms and substantially rising in desorption at noticeable higher temperatures [9]); 2 – The H_2 molecules can be detached in vicinity of the CNT surface through spill over mechanism [10]; 3 – carbonaceous coated surfaces have a promising industrial applications [11]; 4 – metallic nano-particle catalysts (Fe, Co, Ni,…) have often been used in the synthesis of the CNTs and their residual particles may influence the hydrogen storage capacity via their catalytic role for hydrogen dissociation, at temperatures near room temperature [12,13]; 5 – in electrochemical applications such as rechargeable hydrogen batteries, the hydrogen ions in the electrolyte are chemisorbed into carbonaceous electrodes [14,15].

According to the above reasons and because of lacking theoretical studies, the intention of this work is to study the influence of chirality as well as of curvature on the exo-hydrogenation of the narrow Co-CNT systems. In this regard, we have chosen the cobalt doped (9,0), (5,5) CNTs with very close diameters in one hand and the very narrow (5,0) CNT on the other hand. The morphological and electronic structural studies of the narrow Co-CNTs systems before and after the exo-hydrogenation were performed, consistently.

2. Computational and structural model

Density functional theory (DFT) “Quantum ESPRESSO” package [16] with Perdew–Burke–Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) for the exchange correlation energy [17,18] were employed in the calculations. To observe the effects of internal core electrons on valence electronic states, we used ultrasoft pseudopotentials [19] and also, the Brillouin zone integration was carried out using the Monkhorst–Pack scheme with 1*1*12 k-points. To consider an isolated CNT, we chose a hexagonal super cell whose side was 18 Å, so that the coupling of neighboring tubes would be certainly eliminated. Finally, all systems were fully relaxed to minimize the total energy down to 10^{-4} eV accuracy. To search for high-capacity hydrogen-storage nanostructures consisting of a combination of carbon nanotubes and cobalt, we first considered (5,5) &(9,0) CNTs with roughly the same diameters ($d \approx 6.79$ Å) and also the narrow (5,0) CNT ($d \approx 3.92$Å). Three distinct configurations were considered for Co atom which had these conditions: the Co atom was put at the center of the CNTs (CET); the Co atom was put inside and near the wall of the CNTs (NER) and finally the Co atom was put at the center of hexagon on the wall of the CNTs (HEX). In this study, exo-hydrogenation occurred fully and halfway covering the outer surface of the CNTs by forming external C–H bonds.

3. Results and discussion

3.1. Co/CNT systems

After structural relaxation of the (5,0), (9,0) and (5,5) Co-CNTs systems the most structural variations on the CNTs occurred for the HEX configuration. For the HEX configuration the doped Co atom was pushed out from the wall of the CNTs; whereas, for the CET and NER configurations the tube's deformations were very small. Incidentally, to find out stability of the configurations, the bonding energy (E_{bind}) for the HEX, NER and CET configurations was calculated. The results are summarized in Table 1, as can be seen all of these configurations are stable.

Lowdin charge analysis shows changes of charge distribution on the atomic orbitals of Co and C atoms before and after doping. The charge around Co clearly shows incomplete charge transfer from Co to CNT, implying the presence of the hybridization between Co and CNT. The interaction between Co and CNT is primarily ionic due to the charge transfer from Co to C orbitals. The hybridization essentially occurs among Co-3d and C-2p orbitals, indicating that Co atom is ionized and suggesting a possibility for H adsorption due to the polarization mechanism (Fig. 1).

3.2. H/CNT systems

In the electrochemical process of hydrogen adsorption, the ambient species of hydrogens in an electrolyte are hydrogen ions. These will exothermally adsorb at the top sites of carbon atoms on the tube wall, forming an arch-type tube. Hydrogen with up to a coverage $\Theta = 1$ or equivalent to 7.7 wt.% can be stored in an *arch-type* tube.

At first, hydrogen atoms were initially placed about 1.1 Å away from the top of the carbon atoms on the tubes wall along the tube axis and relaxed fully with carbon atoms at the tube. Fig. 2 for example shows the cross sections of the fully relaxed geometry of the hydrogenated (5,0) CNT at $\Theta = 1$.

In the $\Theta = 1$ coverage, the circular cross section was still retained (Fig. 2a). The C–C back-bond lengths were extended (average of the all bonds extended from about 1.43 Å to 1.53 Å). The diameter was expanded from that of the ideal CNT. The repulsive energies between H atoms and those between H atoms and the tube wall expanded the diameter, similar to the lattice expansion of the *c*-axis in the graphite during the

Table 1 – Bonding energy of Co doped (9, 0), (5,5)&(5-0) CNTs with different configurations.

CNT	Configuration	E_{bind} (eV)
(5–0)	(CNT-Co)HEX	−4.08
	(CNT-Co)NER	−4.08
	(CNT-Co)CET	−3.67
(9–0)	(CNT-Co)HEX	−2.86
	(CNT-Co)NER	−2.99
	(CNT-Co)CET	−2.18
(5–5)	(CNT-Co)HEX	−3.94
	(CNT-Co)NER	−3.54
	(CNT-Co)CET	−2.72