



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# First-principles study of single atom adsorption on capped single-walled carbon nanotubes

Xiji Shao, Haijun Luo, Jianqiu Cai, Changkun Dong\*

Institute of Micro-nano Structures & Optoelectronics, Wenzhou University, Chashan University Town, Wenzhou, Zhejiang 325035, People's Republic of China

## ARTICLE INFO

### Article history:

Received 31 January 2014

Received in revised form

19 April 2014

Accepted 22 April 2014

Available online 17 May 2014

### Keywords:

First-principles

Carbon nanotube

Gas atom

Chemisorption

Fuel cell

## ABSTRACT

The effects of hydrogen, oxygen, and nitrogen atomic chemisorption on capped armchair (5, 5) single-walled carbon nanotubes (SWCNT) are investigated by first-principles calculations based on the density functional theory aimed at the CNT based fuel cell applications. O or N chemisorption could break C–C bond to form doping type structure. C–C bonds are weakened from H chemisorption, favoring hydrogen storage. Both C–adatom and related C–C bond lengths fluctuate from the cap top to the tube for each type of adsorbate. There is a total amount of about 1.0 e charge transfer between N or O atom and the carbon atoms, and the catalytic activity is expected to be higher with N adsorption around the cap top. The adsorption energies and work functions also vary with the adsorption at different sites. Atomic chemisorptions are more stable on the cap than on the tube due to smaller local curvature radius. The work functions increase to above 5.0 eV with the adsorption of N and O, and drop below 4.8 eV for H adsorption, comparing with 4.89 eV for the clean tube. DOS study reveals orbital information for electrons of adatom contributed to the valence bands and the conduction bands.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Carbon nanotubes (CNTs) possess unique geometrical structures, robust mechanical strengths, as well as superior physical and chemical properties [1–6], and have shown great potentials in various aspects of fuel cell applications, including hydrogen storage [7–10], electrode catalysis [11–13], and gas sensing [14,15]. Gas adsorption and related effects are important issues and have been investigated experimentally and theoretically in these fields. Meanwhile, atomic chemisorptions of gas species, particularly H, N, and O, which may occur from processes like molecular dissociations and the

plasma treatment, are playing more and more important roles.

Adsorption of hydrogen on the surface of porous CNT materials is promising for hydrogen storage, but the reliable method of hydrogen storage in CNTs is still far from being established. Reported hydrogen uptake capacities were remarkably scattered [16,17], leaving the hydrogen uptake mechanism uncertain. Most studies focused on the adsorption of hydrogen molecule in/on CNTs. However, experimental and theoretical investigations suggested the involvement of dissociated hydrogen atom adsorption for experimental data with significant amounts of hydrogen storage [18,19]. The investigation of the H chemisorption

\* Corresponding author. Tel.: +86 577 86689067.

E-mail addresses: [dck@wzu.edu.cn](mailto:dck@wzu.edu.cn), [changkun\\_dong@yahoo.com](mailto:changkun_dong@yahoo.com) (C. Dong).  
<http://dx.doi.org/10.1016/j.ijhydene.2014.04.157>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

properties is fundamental for the understanding and manipulating of the hydrogen storage.

For both the cathodic oxygen reduction reaction (ORR) and anodic hydrogen oxidation reaction, conventional catalysts are platinum and its alloys. However, drawbacks including slow reduction kinetics and high cost with Pt electrode limit the large-scale applications of the fuel cell technology. Among tremendous efforts on searching high active, inexpensive, and durable new electrocatalysts, developments of carbon nanostructure based materials are arousing more and more attention. Metal catalysts supported on CNTs have shown encouraging results in terms of activity and long-term stability [20,21]. To overcome the weak interaction between noble metals and CNTs, the functionalization of the CNT surface by the oxygen plasma is effective to improve the catalyst system performance [22,23]. XPS analysis implies that O atoms & O atom containing groups are grafted into the CNT surface after oxygen plasma to form metal–O–C bonds, inducing uniform dispersion of catalyst clusters at the CNT surface [24]. Recently, metal free nitrogen-doped carbon nanotube and graphene electrodes are being extensively studied for very encouraging ORR electrocatalytic activity and long-term operation stability in alkaline fuel cells and batteries [12,25–27]. However, reaction mechanism is considerable ambiguous. Chen et al. showed that higher nitrogen content in CNT leads to better ORR performance, attributed to the increase of ORR active surface defects due to the nitrogen doping [25]. Dai et al. reported the catalytic currents at the metal-free N-doped CNT or graphene electrode are 3 times higher than that at the Pt/C electrode [12,26], and believed that the nitrogen-induced charge delocalization changes the chemisorption mode of  $O_2$  from the usual end-on adsorption to a side-on adsorption, effectively weakening the O–O bonding to facilitate the oxygen reduction. Studies of the atomic O and N chemisorptions on the CNTs, especially on the structural and charge distribution performance, are important for the exploration of the reaction mechanism to promote the developments of CNT based catalyst techniques.

Hydrogen and oxygen sensing is an important aspect in the fuel cell system to make the operation safe. Among various CNT based sensing techniques, field effect transistor (FET) sensors show excellent properties due to large surface area and charge-sensitive conductance, especially to oxygen and oxygen-containing gaseous species [28,29]. The CNT work function, which is apt to change upon gas adsorption, is a key property to influence the Schottky barrier performance of the FET. The modification of material work function by hydrogen showed significant improvement of sensing property [30]. The investigation of the behavior of the work function under various gas ambiances benefits the development of sensing technique.

Most studies on atomic chemisorptions were conducted for non-capped tubes, and there is a lack on the comprehensive understanding of the effects for single atom chemisorptions on different sites of the capped SWCNTs. In this work, the structural and electronic properties of the capped (5, 5) SWCNT, including the bond structure, adsorption energy, work function, charge density distribution, and density of state (DOS), are investigated for the chemisorptions of H, O, and N atoms at various CNT sites based on the density functional theory (DFT).

## Theoretical methods

In this work, all the density functional theory calculations are performed using the Vienna ab initio simulation package (VASP) [31–33] with the projector augmented wave (PAW) method [34,35]. The generalized gradient approximation (GGA) in the version of Perdew–Burke–Ernzerh of (PBE) [36] is used for the electron exchange and correlation. A plane-wave basis set with a cut-off energy of 360 eV is used for the wave function expansion, and  $1 \times 10^{-4}$  eV convergence criterion is applied for total energy in super cells. A  $k$ -point mesh grid of  $(2 \times 2 \times 1)$  is used for structure optimization and  $(5 \times 5 \times 1)$  is used for the DOS calculation. Those values are taken as a compromise to ensure energy convergence and to reduce the computational time and memory requirements.

A Methfessel–Paxton [37] electronic energy smearing of  $\sim 0.15$  eV has been used to improve the convergences. The capped armchair (5, 5) carbon nanotube with 90 carbon atoms is selected for study. To avoid the interaction between two adjacent nanotubes, the supercell was placed in a box with dimensions of  $18 \times 18 \times 27$  Å during all the CNT calculations. Thus a vacuum separation of 12 Å is adopted for each direction. All the atoms are fully relaxed until the force on each atom is less than 0.01 eV/Å. The semi-spherical cap of the CNT is divided into four layers, as shown in Fig. 1. There are 10 dangling bonds at the other end. The optimized geometry of the SWCNT shows an average C–C bond length of 1.42 Å for the top pentagon structure and 1.43 Å for the rest of the nanotube.

The work function is defined as  $W_F = \phi - E_F$ , where  $\phi$  is the vacuum level and  $E_F$  is the Fermi level of the system. Adsorption energy is a key characteristic parameter for describing the adsorption behavior, which can be calculated from the following expression:

$$E_{\text{ads}} = (E_{\text{SWCNT}} + E_{\text{atom}}) - E_{\text{SWCNT+atom}} \quad (1)$$

where  $E_{\text{SWCNT+atom}}$  is the total energy of the SWCNT–adatom system,  $E_{\text{SWCNT}}$  and  $E_{\text{atom}}$  are the energies of the two isolated systems, respectively.

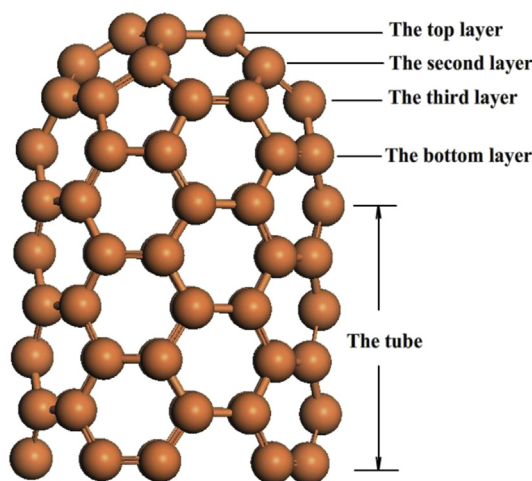


Fig. 1 – Illustration of the capped armchair (5, 5) SWCNT.

Download English Version:

<https://daneshyari.com/en/article/1270368>

Download Persian Version:

<https://daneshyari.com/article/1270368>

[Daneshyari.com](https://daneshyari.com)