

Geometric structure and electronic behavior of Rh decorating effect on zigzag CNTs (n=7-12): A DFT study

Hao Cui¹, Xiaoxing Zhang^{1,2,*}, Yongjian Zhou¹, and Jun Zhang¹

¹State Key Laboratory of Power Transmission Equipment & System Security and New Technology, Chongqing University, Chongqing 400044, China.

²School of Electrical Engineering, Wuhan University, Wuhan 430072, China.

Article Info

Received 29 October 2017

Accepted 15 November 2017

*Corresponding Author

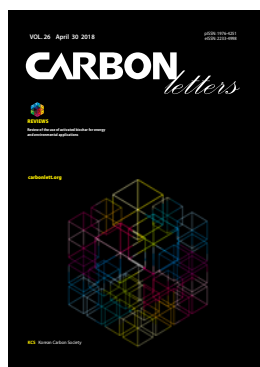
E-mail: xiaoxing.zhang@outlook.com

Tel: +86-136-2727-5072

Open Access

DOI: <http://dx.doi.org/10.5714/CL.2018.26.061>

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<http://carbonlett.org>

pISSN: 1976-4251

eISSN: 2233-4998

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Abstract

Comprehensive calculations of the Rh decoration effect on zigzag CNTs with n ranging from 7 to 12 were conducted in this work to understand the effect of Rh doping on geometric structures and electronic behaviors upon metallic and semiconducting CNTs. The obtained results indicated that Rh dopant not only contributes to the deformation of C-C bonds on the sidewall of CNTs, but also transforms the electron distribution of related complexes, thereby leading to a remarkable increase of the conductivity of pure CNTs given the emerged novel state within the energy gap for metallic CNTs and the narrowed energy gap for semiconducting CNTs. Our calculations will be meaningful for exploiting novel CNT-based materials with better sensitivity to electrons and higher electrical conductivity compared with pure CNTs.

Key words: Rh dopant, CNT, DFT

Introduction

Transition metal (TM) doped CNTs have been theoretically demonstrated to have superior physicochemical properties such as higher conductivity[1,2] and preferable electron accepting/withdrawal behavior[3] as well as stronger reactivity and catalytic properties, thus broadening their potential applications to gas adsorption[4,5] associated with gas sensing[6-8], compared with pure CNTs. This is attributed to the sidewall modification of metal atom(s), which takes advantage of the delocalized π -electron density along the backbone of the nanotube[9]. In these calculating researches, (5, 5) [10] and (8, 8)[11,12] metallic CNTs in parallel with (8, 0)[13,14] and (10, 0)[15] CNTs with semiconducting behaviors are usually employed to act as metal doping supports for further property research; meanwhile, for TMs, those with good catalytic properties such as Pd[16] and Pt[17], together with inexpensive ones as alternatives to noble metals (including Fe, Co, and Ni)[18]_ENREF_20 are regarded as excellent candidates for sidewall decoration of nano-supporters, in order to enhance related performance of insulated ones.

Meanwhile, there is a lack of comprehensive research in terms of geometric structure and electronic behavior of (n, 0) zigzag CNTs. This is important because it can systemically shed light on the physicochemical properties of zigzag CNTs, regardless of whether they are metallic ($n=3k$, k is integer) or semiconducting ($n=3k\pm 1$, k is integer). In addition, there have been few theoretical studies on the electronic characteristics of Rh decorated CNTs. As a stable metal in the Pt main group, Rh can lend CNTs good catalytic performance upon certain interactions[19]. Therefore, this material could also provide promising applications like Pt or Pd doped CNTs due to the combined strengths of CNTs and Rh. Prior to this, however, it is imperative to understand the properties of Rh decorated carbon nano-supporters.

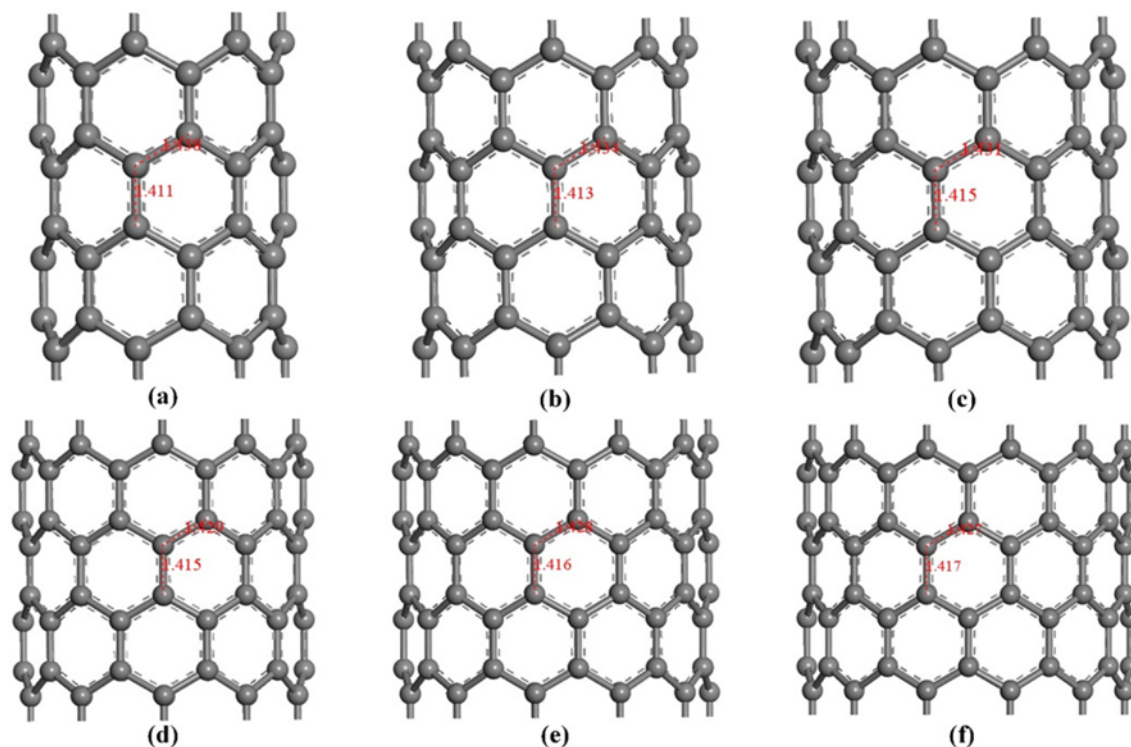


Fig. 1. Geometric structures of intrinsic zigzag CNTs. a) (7, 0) CNT; b) (8, 0) CNT; c) (9, 0) CNT; d) (10, 0) CNT; e) (11, 0) CNT; f) (12, 0) CNT. The red values represent the related bond length.

In the present work, theoretical calculations for Rh decorated zigzag CNTs (Rh-CNTs) with n ranging from 7 to 12 were conducted in order to expound the Rh decorating effect on semiconducting and metallic CNTs. Our calculation results not only provide a systematic analysis for functionalized CNTs by TM, revealing the detailed electronic properties of Rh-CNTs, but also suggest novel materials to researchers for further investigation of their potential applications.

2. Computational details

The double numerical plus polarization (DNP) basis sets were applied in the density functional theory (DFT) calculations in the Dmol[3] package[20]. The generalized-gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) and Spin-unrestricted DFT[21] is employed to obtain all the results analyzed below. In order to avoid interaction between adjacent cells, a single-walled CNT with a periodic boundary condition of $20 \text{ \AA} \times 20 \text{ \AA} \times 8.5 \text{ \AA}$ was defined[22]. The core treatment was set as semi-core pseudopotentials to manage the interaction between the nucleus and valence electron, whereas the Brillouin zone k -point sampling was performed in a $1 \times 1 \times 9$ Monkhorst-Pack mesh[23,24] which presents a good approximation for CNTs. The energy tolerance accuracy, maximum force, cut-off orbital, and displacement were set as 10^{-5} Ha , $2 \times 10^{-3} \text{ Ha/\AA}$, 3.7 \AA , and $5 \times 10^{-3} \text{ \AA}$, respectively[25].

3. Results and discussion

3.1 Analysis of geometry comparison between intrinsic and Rh decorated CNTs

The geometric structures for Rh-CNT after optimization are depicted in Fig. 1, where the ranking (a) to (f) refers to the zigzag CNTs with n separating from 7 to 12, respectively. There are two kinds of C-C bonds that we emphasized to illustrate the geometry of carbon tubes, namely the A bond in the axial direction of the tube and the Z bond in the zigzag direction of the tube. It is found that the A bond becomes gradually prolonged from 1.411 \AA to 1.417 \AA whereas the Z bond is shortened from 1.438 \AA to 1.427 \AA with increasing n of CNTs from 7 to 12. This phenomenon stems from the increasing curvature of the CNTs resulting from the augmented radius.

With regard to Rh decoration on the CNT sidewall, there are two categories of possible configurations, namely A and Z sites above the zigzag and axial C-C bonds. After the systems relaxed, we found that the adsorption of one Rh atom on the A site presents a much more stable structure with 0.12 eV lower energy than the Z site, which is consistent with a previous report³. Therefore, we adopted the A decorating site in the following calculations and analysis with the optimized geometries shown in Fig. 2, where the Rh atoms are described by blue-green balls. The Rh-C bond length is larger than that of the C-C bond because of the larger radius of the Rh atom compared with the C atom²⁶. In addition, the bond

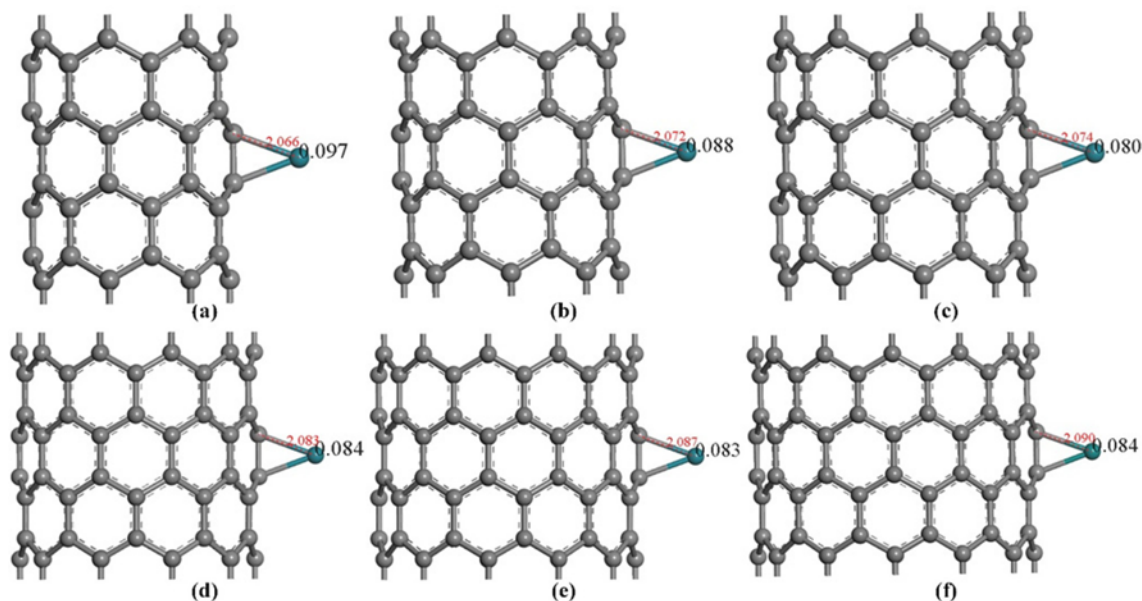


Fig. 2. Geometric structures of Rh decorated zigzag CNTs. a) Rh-(7, 0) CNT; b) Rh-(8, 0) CNT; c) Rh-(9, 0) CNT; d) Rh-(10, 0) CNT; e) Rh-(11, 0) CNT; f) Rh-(12, 0) CNT. The red values represent the bond lengths while black values represent the carried electron number of the Rh dopant.

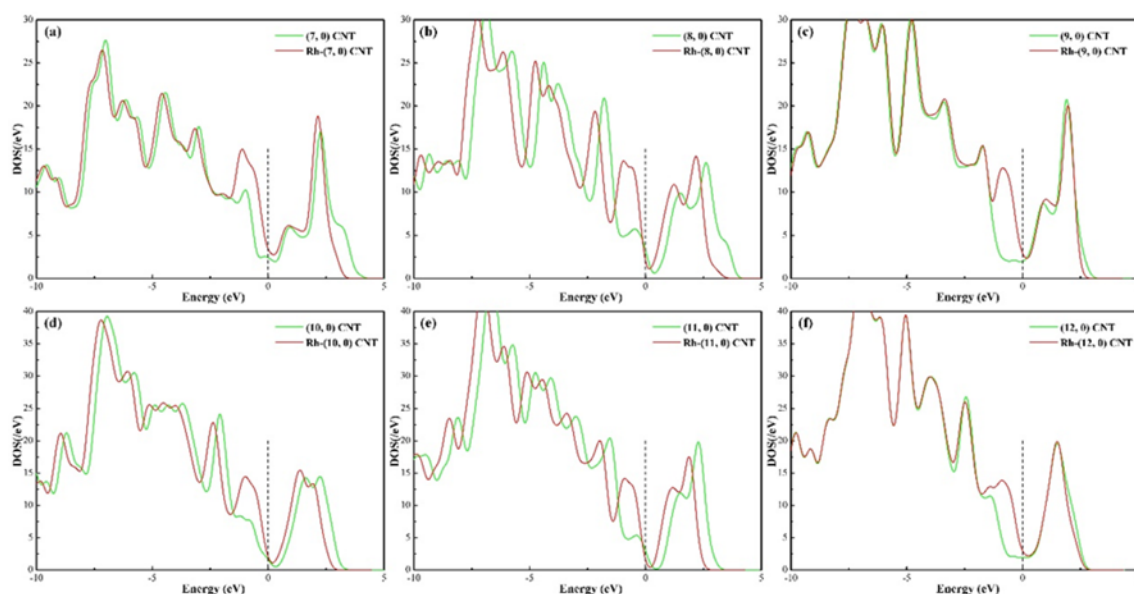


Fig. 3. Comparison of DOS distributions between intrinsic and Rh decorated CNTs. The dash line is the Fermi level.

length of Rh-C increases with increasing n of $(n, 0)$ CNTs as well, from 2.066 Å in the Rh-(7, 0) CNT system to 2.090 Å in the Rh-(12, 0) CNT system. The nature of Rh-C bonding is hybridization between d -states of Rh atoms and p -states of adjacent C atoms. Meanwhile, CNTs with high curvature promote overlap between p and d wavefunctions[27], thus making a stronger binding force of Rh-C bonds and further shortening the length of these bonds. The Mulliken population analysis show that all the Rh dopants possess a positive charge with an electron transfer value of around

0.09 ± 0.01 e, indicating that electrons transfer from the Rh dopant to the representative CNTs. This is in agreement with the electron withdrawing property of TMs.

3.2 Analysis of density of state comparison between intrinsic and Rh decorated CNTs

To distinctly expound the electronic behavior of the Rh decorating effect on the zigzag CNTs, density of state (DOS) calcula-

Table 1 E_v , E_c , E_g , and E_f of intrinsic and Rh decorated CNT.

Systems	E_v (eV)	E_c (eV)	E_g (eV)	E_f (eV)	
Intrinsic CNT	(7, 0)	-4.956	-4.334	0.622	-4.846
	(8, 0)	-5.067	-4.439	0.628	-4.688
	(9, 0)	—	—	0	-4.588
	(10, 0)	-4.881	-4.225	0.656	-4.607
	(11, 0)	-4.981	-4.003	0.978	-4.582
	(12, 0)	-4.594	-4.482	0.113	-4.581
Rh-CNT	(7, 0)	-5.034	-4.521	0.513	-4.869
	(8, 0)	-4.997	-4.462	0.535	-4.781
	(9, 0)	—	—	0	-4.716
	(10, 0)	-4.751	-4.336	0.415	-4.740
	(11, 0)	-4.965	-4.128	0.837	-4.737
	(12, 0)	—	—	0	-4.747

tions were conducted. The obtained distributions of intrinsic and Rh decorated CNTs are displayed together in Fig. 3 for better comparison whereas related parameters of the conduction band (E_c), value band (E_v), energy gap (E_g), and Fermi level (E_f) are listed in Table 1.

To the best of our knowledge, for a zigzag CNT, if n is a multiple of 3, it is a metallic tube; otherwise, it is a semiconductor. Among our representative CNTs, the (7, 0), (8, 0), (10, 0), and (11, 0) CNTs possess semiconducting properties while the (9, 0) and (12, 0) CNTs have metallic properties. From Table 1 it is seen that four kinds of semiconducting CNTs have relatively large E_g values: 0.622, 0.628, 0.656 and 0.978 eV respectively. Meanwhile, the (12, 0) CNT has a rather narrow gap with 0.113 eV and the (9, 0) CNT has a 0 gap between E_v and E_c . These results powerfully demonstrate and confirm the semiconducting and metallic characteristics for related (n , 0) zigzag CNTs. On the other hand, we can also find in Table 1 that after Rh doping on the sidewall of the proposed CNTs, the energy gaps of the semiconducting CNTs undergo a large shift to a smaller scale with a reduction of about 0.1 eV for each system, indicating the Rh doping effect on the electronic behaviors of the CNTs. That is, the chemisorption of an Rh atom induces a novel state within the band gap of CNTs, thereby leading to a reduction of the corresponding E_g . This result agrees well with that in the Pt decorating CNT system where the band gap narrowed to/by 0.284 eV after one Pt atom decorates on the sidewall of the (8, 0) CNT.

From the DOS distributions between intrinsic and Rh decorated CNTs shown in Fig. 3, some qualitative conclusions with respect to electronic performance can be drawn as well. Specifically, it could be found that the DOS curve near the Fermi level is dramatically affected by the decoration of one Rh atom, which is an indicator of the electronic behavior that transforms the electrical conductivity of this complex. Furthermore, the influence of the Rh dopant towards a semiconducting CNT would be even stronger than that towards the CNT with a metallic prop-

erty. In the Rh-(9, 0) CNT and Rh-(12, 0) CNT systems, the DOS peaks almost overlapped with those of intrinsic CNTs in bulk of area except for those areas surrounding the Fermi level surrounding the Fermi level, where extremely sharp peaks within the energy gap appear in the Rh decorated systems. Such conditions can also be seen in the Rh doped semiconducting systems and, furthermore, a more obvious phenomenon in these systems is the shift of the DOS peaks towards a lower region. This shift can be explained as a decrease in the effective Coulomb potential due to the accepting charge effect of the carbon nano-support, in good consensus with the decreased E_f for the whole systems along with the positive electron number carried by Rh atoms. In addition, we can find a narrowed gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, which leads to improved conductivity for Rh decorated configurations. All these conclusions are in line with previous analyses.

4. Conclusions

In this paper, we performed DFT calculations to investigate the Rh effect on the geometric structure and electronic behavior of zigzag (n , 0) CNTs with n ranging from 7 to 12. Results suggest that Rh decoration not only contributes to the deformation of C-C bonds on the sidewalls of CNTs, but also transforms the electron distribution of related complexes. The Rh decorated on the CNTs would be the most stable by the A site, namely above the C-C bond in the axial direction of the nanotube, and such decoration can remarkably increase the conductivity of pure CNTs owing to the emerged novel state within energy gap for metallic CNTs and the narrowed energy gap for semiconducting CNTs. All these changes give rise to the strong decoration effect of Rh on zigzag CNTs. Our calculations would be meaningful for exploiting novel CNT-based materials with better sensitivity

to electrons and higher electrical conductivity compared with pure CNTs.

Contributions and Competing interests: Xiaoxing Zhang guided this work, Hao Cui performed the research and wrote this manuscript while Yongjian Zhou and Jun Zhang modified the writing in order to improve its quality. All authors have no conflicts of interest about its submission.

Acknowledgment

We acknowledge financial support from the graduate research and innovation foundation of Chongqing, China (No. CYB17009) and Natural Science Foundation of China (No. 51537009).

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