Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(5):2069-2072

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

First-principles study of the (n, m) chiral ZnO nanotubes

Fuchun Zhang, Hongwei Cui, Xingxiang Ruan and Weihu Zhang

College of Physics and Electronic Information, Yan an University, Yan an, China

---

ABSTRACT

The geometric structure and electronic structure of (n, m) chiral singled walled ZnO nanotubes (NTs) have been calculated adopting first-principles calculation methods based on density function theory. The energy calculated results show that the binding energies of (n, m) chiral ZnO NTs are negative values, indicating (n, m) chiral ZnO NT is able to exist steadily. With the increase of pipe diameter for ZnO NTs, the total energy decreased and band gap increased gradually, and the system tends to more stable. The calculated results of electronic structure show that (n, m) chiral ZnO NTs are a direct wide band gap semiconductor, with valence band top mainly composed of O 2p states and conduction band bottom mainly composed of Zn 4s states. Moreover, intense interaction between Zn 3d and O 2p appears in energy zone from -6.3 eV to 0.0 eV, characterized by apparent hybridization of sp3 and sp2, which plays a key role in ZnO NTs with stable configuration.

Keywords: ZnO, nanotubes, first-principles, electronic structure.

INTRODUCTION

Since the carbon NT was discovered by Iijima [1] in 1991, theoretic and experimental researches prove that C NT is peculiar and abundant in performance. One-dimensional (1-D) nanomaterials including NTs, nanowires, and nanorods have been attracting great interest due to their unique electronic, mechanical properties and great potentials for nanotechnology applications compared to corresponding bulk materials. These research findings greatly arouse enthusiasm of research on NTs [2-4]. In recent years, the researchers have carried out other types of NTs insensitive to chirality in structure, such as TiO_2 [5], SiC [6], BN [7], ZnS [8] and ZnO [9-11]. In particular, ZnO is characterized by wider band gap (3.37 eV) and larger exciton binding energy (60 meV), being an important material with photovoltaic conversion function, and the field emission characteristic of its nano structure shows potential application value in vacuum microelectronic device such as field emission flat panel display, X ray source and microwave device. Compared with other optoelectronic material such as GaN, it is characterized by low dielectric constant, large photoelectric coupling coefficient, high chemical stability and excellent piezoelectricity and photo-electricity, what is more important is that ZnO as wide band gap semiconductor shows band bending and negative electronic affinity in high field density, thus, it is considered one of the most promising field-emissive cathode material [12]. At present, the research on ZnO nanostructure has made substantial progress. Scientific research groups in the world have successfully synthesized ZnO nanomaterials with different structures, such as low dimension ZnO nanorod, nanowire, nanobelt, and some nanomaterials with special structure, for example, ZnO nano-comb, and nano-disc. The above mentioned research of ZnO material show potential application in catalysis, gas sensor, optoelectronic memory, optical-electrical converter, nanometer optoelectronic system, field effect transistor, laser and transparent conductive film. The paper will make systematic theoretical study on the structures and properties of (n, m) chiral ZnO NT based on density functional theory (DFT) so as to reveal the structure characters and electronic property change of the ZnO NTs. These results may be provided theoretical basis for preparing single-walled ZnO NTs and developing the optoelectronic devices based on ZnO NTs.

EXPERIMENTAL SECTION

Theoretical model and calculation method

As for the theoretical model of ZnO NTs, we adopt the construction method the same to CNT. Lamellar structure through ZnO NT curls into columnar (n, m) chiral ZnO NT along axial direction, an (n, m) chiral ZnO NT is formed. The (4, 2) and (6, 3) ZnO NT are as shown in Fig.1 (a) and (b).

In this study, all the structural optimizations and electronic properties are calculated by adopting first-principles calculation method based on DFT [13], The 1.2 nm vacuum space is used to minimize the interaction effects of neighboring supercells that result from the finite supercell. First, the ZnO NTs are subjected to geometric structure optimization and obtain the stable ZnO NTs models. Second, the optimized ZnO NTs are subjected to calculations of electronic structures and basic properties. The exchange-correlation functions are handled with generalized gradient approximation (GGA), and the ultra-soft pseudo potentials are used for Zn and O to represent interaction potential between ion core and valence electrons; Zn and O valence-electron configurations are $3d^{10}4s^2$, $3s^22p^4$ respectively. In reciprocal space, plane wave cut-off energy E_{out}=360 eV, convergence precision in iteration process is 1×10^{-5}eV, with residual forces on every atom no more than 0.05 eV/ Å, and the internal stress is no more than 0.1 GPa, and a 1×1×16 Monkhorst- Pack K-point sampling is used for Brillouin zone integration for NTs.

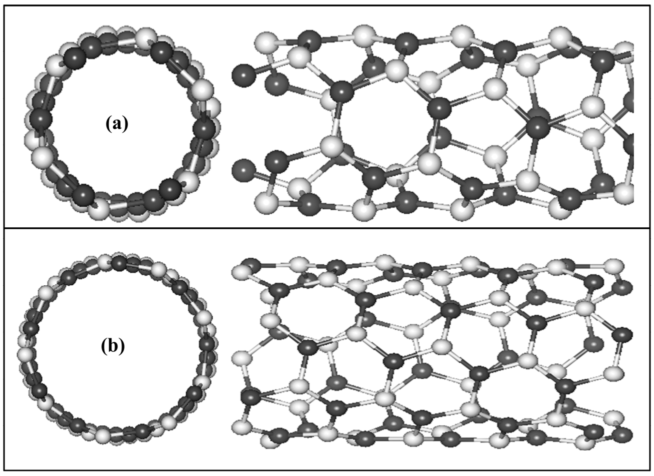

Fig.1 The (n, m) chiral ZnO NT (the red and grey balls represent oxygen and zinc atoms, respectively) (the black and grey balls are Zn atom and O atoms, respectively)

RESULTS AND DISCUSSION

First, the ZnO NT is subject to analysis the geometric structure and stability, we adopt total relaxation to optimize the structure of (n, m) chiral ZnO NT with NTs rolled up from a graphitic ZnO single layer, the optimized results show that ZnO NT with curled structure becomes cylindrical tube-like structures similar to the C NT (see Fig.1), and the calculated results are negative values and similar for all investigated NTs, indicating that ZnO NT may exist steadily. In addition, Zn and O atoms show relaxation along tube wall inward and outward to a certain extent, and every Zn (O) atom in optimized ZnO NT is subject to bonding with three nearest O (Zn) atoms, the above results are consistent with experimental and theoretical findings [14-17]. Table 1 gives geometry parameter of chiral ZnO NT after relaxation, it is observed from table 1 that binding energy gradually decreases with the increase of diameters of the ZnO NTs, which indicates that the larger the diameters of the ZnO NTs are more stable. But the band gaps are increases with the increase of diameters due to obvious quantum size effect, In addition, with the increase of diameter, the $r_{\text{zn-o}}$ bond length along axis C is on gradual decrease. The variation range of Zn-O we calculated is from 1.908Å to 1.926 Å.

Table 1 Calculated Bind Energy (eV), band gap E_g(eV), bond lengths($r_{\text{zn-o}}$) and Diameters(nm)

	(n, m)	Diameters (Å)	E_g (eV)	$r_{\text{zn-o}}$ (Å)	Bind Energy (eV)
Structure	(4,2)	5.510	1.728	1.926	-13.45728
	(4.3)	6.218	1.739	1.920	-13.47882
	(5,3)	7.213	1.754	1.908	-13.49217
	(6,3)	8.125	1.763	1.914	-13.49783
	(7,3)	9.183	1.759	1.917	-13.50034

The band structures and density of state (DOS) of chiral (n, m) ZnO NT are as shown in Fig.2 and Fig.3. It is observed from Fig.2 that the ZnO NT is a direct band gap semiconductor along high symmetry point Γ(0,0,0)→ Z(0.5,0.5,0.5) in brillouin zone, The bottom of the conduction band and the top of the valence band are located at Γ Point, in which the lowest unoccupied states show large dispersion due to the large surface/bulk ratio along point Γ (0,0,0)→Z (0,0,0.5), and the dispersion of the highest occupied states start to weaken, the locality states starts to strengthen with increasing of ZnO NTs diameter. The calculated band gap (1.728 eV-1.763 eV) is much more than ZnO bulk material (0.92eV) obviously. The band gap broadening effect is as a result of radial restriction effect. It is observed from the PDOS of O and Zn atoms in Fig.3 that the valence bands show three energy zones, the low energy zone (19.0 eV～-17.0 eV) is mainly formed by O 2s orbital electrons, the bottom valence band zone (-6.3 eV～-4.0 eV) is mainly formed by Zn 3d and O 2p orbital electrons, which means that there is a larger hybridization between Zn 3d and O 2p orbital in valence band, the top valence band zone (-4.0 eV～0.0 eV) is mainly formed by O 2p orbital electrons. For conduction band, it is observed from Fig.3 that the conduction band bottom is as a result of Zn 4s orbital electrons, is similar to ZnO bulk mateial, and takes on certain dispersion character. In particular, the conduction band bottom and valence band top are primarily composed of O 2p and Zn 4s states, namely chiral (n,m) ZnO NT band gap is mainly dependent on O 2p and Zn 4s states.

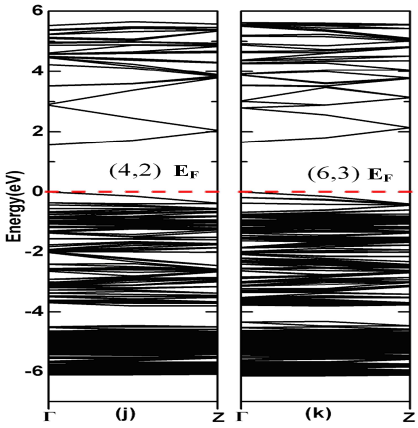

Fig.2 Calculated energy band of (n, m) ZnO NTs

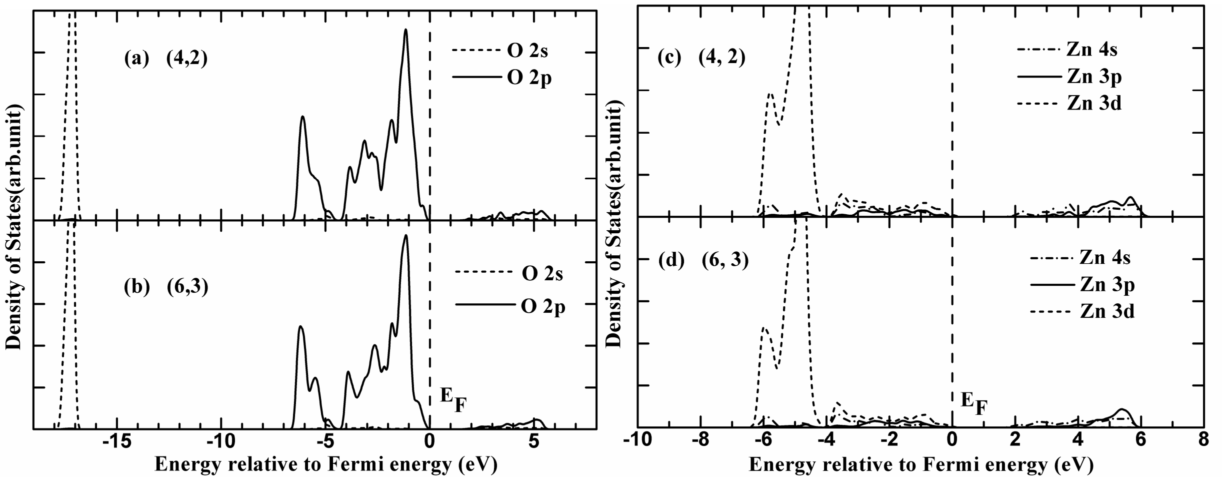

Fig.3 Calculated DOS of ZnO NTs (a) TDOS; (b) PDOS of ZnO, (c) PDOS of Zn and (d) PDOS of O

Fig.4 shows the calculated chiral (6, 3) ZnO NT on lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) at Γ point. It is observed from Fig.3 (a) that the LUMO is mainly located on O atoms characterized by O 2p like dangling bonds and interaction, and form bond and weak anti-bond state interactions around adjacent Zn atoms. For the HOMO, the Fig.3 (b) shows that it is mainly situated on O orbital, and the HOMO is mainly form the π orbital attribute, being consistent with molecular orbital of C NT. In addition, the partial HOMO orbital are on the surrounding Zn atoms, which means that it is t form the sp^3 and sp^2 hybrid orbital on the Zn and O ion due π bonds of a grapheme-like planar sheet, diminishing the energy and overall gap broadening effects. These above results are very important for forming ZnO NTs with steady structures.

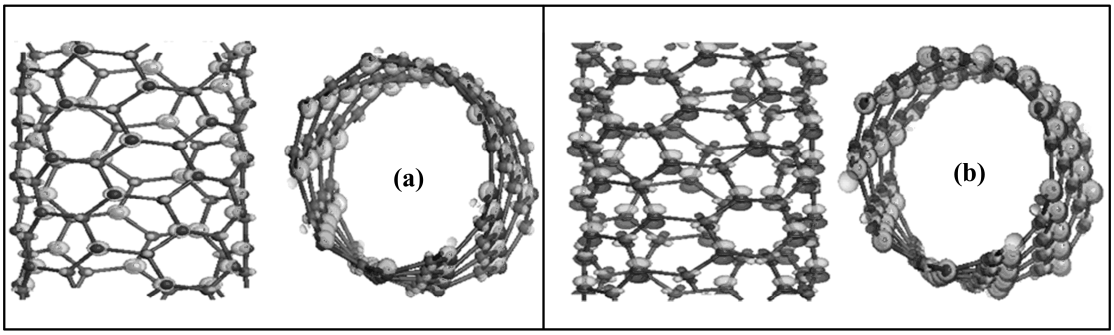

Fig.4 The LUMO and HOMO states for the (6,3) ZnO NT (a) the charge density of the LUMO states at Γ, (b) the charge density of the HOMO states at Γ

CONCLUSION

In conclusion, we have studied the electronic structures and basic properties of the chiral (n, m) ZnO NT using the first-principles based on DFT. The paper mainly studies the band structure, density of states and occupied molecular orbital. The results show that (n, m) chiral ZnO NTs have columnar tubular structure identical with that of C NT and exists steadily. The results of electronic structure show that the chiral (n, m) ZnO NT is direct wide band gap semiconductor by theoretical prediction, with conduction band bottom and valence band top on point Γ in the brillouin zone Γ point and the band gap much higher than that of ZnO bulk material. With the increase of diameter of the chiral (n, m) ZnO NTs, the valence band is obviously broaden and shifts to low-energy direction. Moreover, the band gap increases with the increase of diameter, which shows the significant quantum size effect.

Acknowledgements
This work was supported by the Scientific Research Program of the Educational Committee of Shanxi Province, China (No.2013JK0917), the Scientific Research Program of Yan'an, China (No.2013-KG03), the Scientific Research Foundation of Yan'an University (No.YDZD2011-03), the National Undergraduate Training Programs for Innovation and Entrepreneurship National Training Programs of Innovation and Entrepreneurship for Undergraduates (201210719024) and Industry-study-research of YuLin city.

REFERENCES

[1]S Iijima. *Nature*, **1991**(7), 354: 56-58.
[2]P Ball. *Nature*, **2001**, 414(6860): 142-144.
[3]R H Baughman; A A Zakhidov; A Walt. *Science*, **2002**, 297(5582): 787-792.
[4]R H Baughman. *Science*, **2003**, 300(5617): 268-269.
[5]R Poulomi; B Steffen; S Patrik. *Angew. Chem. Int. Ed.* **2011**, 50(13), 2904-2939.
[6]L Z Pei; Y H Tang; Y W Chen, et al. *J.Appl. Phys.*, **2006**, 99(11): 114306.
[7]L Wirtz; A Marini; A Rubio. *Phys. Rev. Lett.*, **2006**, 96 (12): 126104.
[8]P Sougata; G Biplab; S Pranab, *J. Phys. Chem. C*, **2007**, 111(4); 1556-1559.
[9]J P Cheng; R Y Guo; Q M Wang. *Appl. Phys. Lett.*, **2004**, 85 (22): 5140-5142.
[10] H D Yu; Z P Zhang; M Y Han; et al. *J. Am. Chem. Soc.*, **2005**, 12798(8): 2378-2379.
[11] B L Wang; S Nagase; J J Zhao; et al. *Nanotechnology*, **2007**, 18(34): 345706.
[12] R Z Wang; B Wang; H Wang; et al. *Appl. Phys. Lett.*, **2002**, 81(15): 2782-2784.
[13] S J Clark; M D Segall; C J Pickard; et al. *Z. Kristallogr*, **2005**, 220(5-6): 567-570.
[14] W Z Xu; Z Z Ye; D W Ma; et al. *Appl. Phys. Lett.*, **2005**, 87(9): 093110.
[15] Y J Xing; Z H Xi; Z Q Xue; et al. *Appl. Phys. Lett.*, **2003**, 83(9): 1689-1691.
[16] A Wei; X W Sun; C X Xu. *Appl. Phys. Lett.*, **2006**, 88(21): 213102-213105.
[17] C X Xu; G P Zhu; X Li; et al. *J. Appl. Phys.*, **2008**, 103(9): 094303.
[18] Z C Tu; X Hu. *Phys. Rev. B.*, **2006**, 74(3): 035434.
[19] Sakir Erkoc, Hatice Kökten. *Physica E*, **2005**, 28: 162-165.