The electronic structure and optical properties of Lu-doped 
ZnO nanotubes

Y Wu and S K Zheng
College of Electronic and Informational Engineering, Hebei University, 071002, 
Baoding, China

E-mail: zhshk@126.com

Abstract. The electronic band structures, density of states, and optical properties of pure and 
Lu-doped zigzag single-walled (6, 0) ZnO nanotubes (SWZONT) were studied using the 
density functional method within generalized gradient approximation. For the pure SWZONT 
system, the Fermi level locates at the valence band maxmum, while it deviates to the 
conduction band, and exhibits metal-like charicteristics after the Lu atom is introduced into the 
system. The Lu-doped SWZONT system is stable, and the semiconductor type (N type) is 
enhanced. Additionally, the catalytic oxidation activity was improved. The optical properties 
indicate that the Lu-doped SWZONT materials can be applied to UV optoelectronic devices.

1. Introduction
Nano-materials (particularly the low-dimensional semiconductor materials) are booming in nanosenser, 
electrochemical capacitance storage, luminescent devices and many other fields [1-3]. After Iijima 
found Carbon nanotubes in 1991, research regarding nanotubes became competitive. In addition to 
Carbon nanotubes, ZnO nanotubes also have attracted the attention of scientific reports [4, 5]. 
Compared to other low-dimensional nanostructures of ZnO in the form of nanocrystalline, nanowire, 
nano-film and so on, ZnO nanotubes have a unique quantum structure and novel optoelectronic 
properties. Specifically, ZnO nanotubes possess the necessary porosity and high surface-to-volume 
ratio. These qualities make ZnO nanotubes the best choice for hydrogen storage devices, photovoltaic 
cells, electrochemical supercapacitors, and many other applications.

ZnO nanotubes that were initially reported are polycrystalline, or boast an amorphous structure. In 
recent years, more methods have been used for synthesizing ZnO nanotubes. Wu [6] synthesized ZnO 
nanotubes with the pyrolysis of zinc acetylacetonate method. Zhang [7] prepared aligned ZnO 
nanotubes by means of metal organic deposition, using a sapphire substrate. In his study, they found 
that only by changing the growth pressure (from 10 Torr down to 0.06 Torr), at low temperature (350-
500°C) and under the condition without catalyst, could they secure modulate nanostructures forms, 
such as nano rods, nanotubes, or nano walls. These nanostructures are epitaxial growth, and have the 
same epitaxial growth connection with basement. The growth pressure of the nanotubes is described as 
P_v = 1-0.3Torr. Respectively, diameter and wall thickness of nanotube are about 500 nm and 100 nm.

Additionally, many methods regarding the preparation of ZnO nanotubes have been attempted, 
including thermal reduction [8], vapor phase growth [9], hydrothermal growth [10], gas-solid

1 Address for correspondence: S K Zheng, College of Electronic and Informational Engineering, Hebei 
University, 071002, Baoding, China. E-mail: zhshk@126.com.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution 
of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd
processes [11], sol-gel processes [12], Plasma aided molecular beam epitaxy growth [13], Zn(NH$_3$)$_4^{2+}$ precursor body heat decomposition [14], etc. All of the ZnO nanotubes gain a large value in regards to both diameter and thickness. Until now, a vast amount of effort was focused on the ultra-thin size of ZnO nanotubes. As for the rationality of their existence, and the possibility of the manufacturing of ZnO single-walled nanotubes, many theoretical explorations have been tested.

Single-walled ZnO nanotubes (SWZONTs) have not been experimentally reported, making theoretical analysis necessary. A vast number of theoretical simulation studies have predicted the feasibility of synthesis SWZONTs. Shen [15] calculated the energy of minute ZnO nanowires and single-walled nanotubes with the same number of atoms, using the first principles method. With the same size, the author discovered that a ZnO single wall nanotube is more stable than nanowires. Tu [16] introduced several characteristic vectors similar to single-walled carbon nanotubes. Chiral vector, C, is defined as two corresponding positions, with a pair of parameters (n, m), known as the index. However, the quantum size effect of SWZONTs [17] limits the energy band structure of ZnO nanotubes, and it is difficult to determine their exact potential optical and electrical properties.

Additionally, doping can alter the band structure and properties of the materials. This became a controversal issue in the field of materials research, and provides a new, effective way for the potential performance of SWZONTs’ development. It is reported that rare earth elements are widely used as dopant because of their 4f shell [18-19].

Pan [20] and An [21] calculated the electronic structure of ZnO nanotubes (6, 0) using first principles of the generalized gradient approximation. Although they gained different energy gaps, ZnO nanotubes were confirmed as a direct band gap semiconductor material. This finding was considered a big breakthrough. Combined, rare earth ions and semiconductor nanocrystals, and efficient light-emitting devices were formed in 2011 [22]. However, related theoretical research regarding doped SWZONTs is remains relatively small, and the rare earth element doped zigzag single-walled ZnO nanotubes of theoretical research has never been reported.

So, for this paper, we calculated the band structures, density of states, and optical absorption spectra of Lu doped SWZONTs and pure SWZONTs using first-principles based on density functional theory (DFT). By comparing the electronic structures’ differences between the pure and doped system, we bring forward instructional advice about SWZONTs.

2. Material and methods

Firstly, we created an infinite zigzag single-walled (6, 0) C nanotube. Then, the C elements were replaced with Zn and O side-by-side. The bond length was set as 0.190 nm. Finally, the model of single-walled (6, 0) ZnO nanotube was formed. All of the theoretical calculations were completed at the a×a×c orthogonal supercell zone, which leads to the extension of the nanotubes along the direction of c. The pure SWZONT is generated from a Carbon nanotube crystal structure, which has the lattice parameters, as a=1.926 nm, c =1.710 nm, α=β=90°, γ=120°. In order to have a significant understanding regarding the influences with Lu doped, one Zn atom is replaced by Lu. The zigzag single-walled (6, 0) ZnO nanotube is shown in figure 1.

![Figure 1](image_url)

**Figure 1.** The Model of Pure Single-Walled (6, 0) ZnO Nanotube

The calculations are performed according to the density function theory (DFT), which is based on pseudo-potential technology. The interaction between ion core and valence electrons is described by
ultrasoft pseudopotential. The Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA) is employed to depict the exchange-correlation energy for valence electrons. The cutoff energy of plane-wave is determined to be 380 eV. The maximum root-mean-square convergent tolerance is less than $1 \times 10^{-5}$ eV/atom, that is, the force imposed on each atom is not greater than 0.1 eV, and 0.1 GPa for stress. The Brillouin Zone’s integration is approximated using the special $k$-points sampling scheme of Monkhorst-Pack, and the $1 \times 1 \times 4$ $k$-points grid is used for the Brillouin zone integration along the nanotube axis. The valence electron configurations for Zn, O, Lu atoms are selected as: $3d^{10}4s^2$, $2s^22p^4$ and $4f^{14}5p^65d^16s^2$, respectively. All calculations are performed in reciprocal space.

3. Results and discussion

3.1. Band structure and density of states of SWZONT

The study of the electronic composition of the pure SWZONT system is essential to understand the influence caused by the dopant-Lu. For this reason, we calculated the band structure and the destiny of state of pure SWZONT, as shown below in figure 2.

![Figure 2. The Electronic Structure of the SWZONT. (a) Band structure; (b) Partial density of states.](image)

It can be seen from the band structure that the valence band’s top and the conduction band’s bottom are at the same $k$ point-$\Gamma$, which indicates that the SWZONT is a direct-gap semiconductor. Moreover, the energy band gap of SWZONT is approximately 1.75 eV, more approaching to Chen’s experimental data 3.24 eV [23] than He’s theoretical data 1.66 eV [24]. The most important reason for this is that the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) to electronics and electronic exchange correlation function between the defect treatments [5]. The valence band structure of the SWZONT can be separated into three sections: the lower valence band from -6.10 \sim -4.00 eV, the higher valence band from -4.00 \sim 0eV and the valence band at -17 eV with a width about 0.5 eV. The conduction band structure of the SWZONT was mainly located in 1.75\sim 4.33 eV.

From the figure 2(b), the lower valence band is primarily contributed by Zn-3d states, while the higher valence band mainly is contributed by O-2p, valence band at -17 eV mainly contributed by Zn-4s; the conduction band is composed of the hybridize influence caused by Zn-4s and O-2p. The conduction band minimum (CBM) and the valence band maximum (VBM) are composed of Zn-4s and O-2p, respectively.

3.2. The atomic structure of lu doped SWZONT

In order to examine the relationship between the dopant and the atomic structure directly, a model build is neutrally doped. The valence states of the dopant were not considered in the neutral doped
model. Only substituted doping or vacancy doping was used, which means no consideration about the inherent oxygen vacancy or anion hole.

The Lu doped SWZONT’s structure after geometry optimization was conducted, and is depicted above in figure 3. It can be seen that the introduction of the impurity element, Lu, results in greater structural distortion of the doped model. In the intrinsic SWZONT, the bond length of Zn-O was set as 1.900 Å, but in figure 3, the Zn-O length round impurity element, Lu, is longer (at an average of 1.953 Å). Additionally, the length of Lu-O (2.103 Å) is much longer than that of the Zn-O. The phenomenon occurs due to the associated quantum chemistry; because of the bigger atomic radius of Lu (217 pm) than Zn (142 pm), the length of Lu-O is longer than that of Zn-O. But, as the distance of Zn-O and Lu grow farther, the length of Zn-O’s gradual recovery proceeds to 1.900 Å. The change of the system’s structure greatly encourages the formation of oxygen vacancy near the impurity element Lu, which improves the system’s redox potential. Therefore, the catalytic ability has been improved as the introduction of Lu.

The Lu doped SWZONT’s structure after geometry optimization was conducted, and is depicted above in figure 3. It can be seen that the introduction of the impurity element, Lu, results in greater structural distortion of the doped model. In the intrinsic SWZONT, the bond length of Zn-O was set as 1.900 Å, but in figure 3, the Zn-O length round impurity element, Lu, is longer (at an average of 1.953 Å). Additionally, the length of Lu-O (2.103 Å) is much longer than that of the Zn-O. The phenomenon occurs due to the associated quantum chemistry; because of the bigger atomic radius of Lu (217 pm) than Zn (142 pm), the length of Lu-O is longer than that of Zn-O. But, as the distance of Zn-O and Lu grow farther, the length of Zn-O’s gradual recovery proceeds to 1.900 Å. The change of the system’s structure greatly encourages the formation of oxygen vacancy near the impurity element Lu, which improves the system’s redox potential. Therefore, the catalytic ability has been improved as the introduction of Lu.

![Figure 3: Atomic Structure of Lu Doped SWZONT](image)

**Figure 3.** Atomic Structure of Lu Doped SWZONT

The Lu doped SWZONT’s structure after geometry optimization was conducted, and is depicted above in figure 3. It can be seen that the introduction of the impurity element, Lu, results in greater structural distortion of the doped model. In the intrinsic SWZONT, the bond length of Zn-O was set as 1.900 Å, but in figure 3, the Zn-O length round impurity element, Lu, is longer (at an average of 1.953 Å). Additionally, the length of Lu-O (2.103 Å) is much longer than that of the Zn-O. The phenomenon occurs due to the associated quantum chemistry; because of the bigger atomic radius of Lu (217 pm) than Zn (142 pm), the length of Lu-O is longer than that of Zn-O. But, as the distance of Zn-O and Lu grow farther, the length of Zn-O’s gradual recovery proceeds to 1.900 Å. The change of the system’s structure greatly encourages the formation of oxygen vacancy near the impurity element Lu, which improves the system’s redox potential. Therefore, the catalytic ability has been improved as the introduction of Lu.

![Figure 4: The Electronic Structure of the Lu-SWZONT](image)

**Figure 4.** The Electronic Structure of the Lu-SWZONT. (a) Band Structure and DOS of Lu; (b) Partial Density of States.

3.3. Band structure and density of states of lu doped SWZONT

In order to analyze the influence of the impurity element, Lu, the band structure, and the partial density of states (PDOS) of Lu-SWZONT were plotted, which is shown in figure 4. Due to of the
minute effect the semiconductor material made by the valence band at \(-17\) eV, the graph’s range is near the Fermi level. It is apparent that the conduction band minimum of Lu-SWZONT is at the Fermi level, which means that the strengthening of the semiconductor type (N type). The conduction band and valence band were both moving towards low energy end and the energy of the doped system diminishes, which indicates that the system becomes more stable. Based on that factor, we noticed that the distance of the conduction band minimum (CBM) movement was longer than that of valence band maximum (VBM), therefore the width of band gap decreases, which results in the enhancement of the metallicity and electrical conductivity of the Lu-SWZONT system. This predicts the red shift of the absorption spectrum.

We analysed the cause of the CBM failure from figure 4. The main reason was that the Lu-6s states’ control of the CBM. In the case of pure SWZONT, Zn-4s states and O-2p states interact with each other to form the s-like anti-bonding and p-like bonding, and then form the energy gap. After Lu doping, Lu-6s states process the lower energy than Zn-4s states. Consequently, the s-like anti-bonding formed by Lu-6s and O-2p states in the Lu-SWZONT system contain low-energy than that formed by Zn-4s states and O-2p states in the intrinsic system. Thus, the CBM moved down. Simultaneously, the energy level between Lu-5d states and O-2p states is phenomenal; Compared to the Lu-SWZONT system, the p-d repulsion effect in the intrinsic system is much stronger when counteracting the p-p repercussion effect, which causes the VBM moved toward low energy end. Therefore, the p-p repercussion effect is stronger than the p-d repulsion effect, which results in the VBM moved toward low energy end at the Lu-SWZONT system.

Meanwhile, the conduction band is obviously broadening and becoming higher in destiny. Due to the repercussion effect from Lu-6s states and Lu-5d states, the conduction band grew corrugation fluctuation degree. This phenomenon reveals that the electron effective mass in conduction band digressed; and the non-local degree grew. There was an acceptor level intruded by Lu-5d states which decreased the necessary energy needed for electron transition. In total, Lu-4f leads to the separation of lower valence band and higher valence band obviously.

### 3.4. Optical properties
In regards to the zigzag single-walled (6, 0) ZnO nanotubes, optical properties are related to the electronic structure. So, the optical properties, dielectric function, absorption factors, and some other parameters can be deduced from the electronic composition. In the linear response range, the nanotubes macroscopic optical response characteristic can be described by the frequency dependent dielectric function [25]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

Specifically, $\varepsilon_1 = n^2 - k^2$, $\varepsilon_2 = 2nk$. From the momentum matrix elements between the occupied and unoccupied electronic states, and the Kramers–Kronig transformation, the real part $\varepsilon_1$, the imaginary part $\varepsilon_2$, absorption coefficient, energy loss spectrum and others optical constants can be calculated. The real part $\varepsilon_1$, the imaginary part $\varepsilon_2$ and the absorption coefficient can be represented as follows:

$$\varepsilon_1(\omega) = 1 + \frac{8\pi^2 \varepsilon^2}{m^2} \sum_{v,c, k\ell} d^3 K \frac{2}{(2\pi)} \times \frac{|e \cdot M_{cv}(K)|^2}{[E_c(K) - E_v(K)]}$$

$$\varepsilon_2(\omega) = \frac{4}{m^2 \omega^2} \sum_{v,c, k\ell} d^3 K \frac{2}{(2\pi)} \times |e \cdot M_{cv}(K)|^2 \times \delta [E_c(K) - E_v(K) - \hbar \omega]$$

$$\alpha = \sqrt{2\omega \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)\right]^{1/2}}$$
In this equation, $\hbar$ is Planck constant, $\omega$ is angular frequency, $k$ is extinction coefficient, and $K$ is reciprocal lattice vector. Subscripts $C$ and $V$ represent the conduction and valence bands of SWZONT, respectively. $BZ$ is first Brillouin zone, while $E_C(K)$ and $E_V(K)$ express the intrinsic level of the conduction and valence bands, respectively. We can deduce from (1)-(4) that the macro optical constants are closely related in microelectronic structure. The electronic structure is the theoretical foundation to analyse the optical properties.

![Figure 5.](image)

**Figure 5.** (a) Imaginary part of dielectric functions $\alpha_2$; (b) Absorption coefficient.

The optical characteristics of the Lu-doped SWZONT are systematically discussed on the basis of the calculated dielectric functions and the absorption coefficient. Figure 5 displays the dielectric functions ($\varepsilon_2$), which are the pandect of the optical properties for the two different configurations of the SWZONT systems. At the low energy region of figure 5(a), there are no differences between the Lu-doped and intrinsic system; however there was an occurrence at the high energy area, when the peak of the $\varepsilon_2$ increased. At this point, the value of Lu-doped system becomes twice as much as the pure system at 6 eV, which conform to in figure 4 that the energy band gap depress to 1.67 eV. This data indicates the introduction of the impurity element Lu would decrease the energy band gap effectively and improve the electrical conductivity simultaneously. On the other hand, we found that the area under the curve of Lu-doped is larger than that of the intrinsic, which suggests the width of dielectric functions are magnified. It also indicates that the introduction of the impurity element Lu would improve the dielectric functions width effectively.

Figure 5(b) presents the absorption coefficient of the SWZONT systems with two different configurations. It is clear that the absorption region is quite wide, and that the main absorption region still resides in the UV region. When compared with pure SWZONT, the additional absorption is observed at UV region for Lu-doped system, which is due to the decrease of energy band gap. More electrons in the valence band can be excited by the UV light to overcome the smaller energy. This declares that the doped materials can be used for UV optoelectronic devices.

### 4. Conclusions

The electronic structure and the optical properties of the Lu-doped zigzag single-walled (6, 0) ZnO nanotubes were studied by first-principles calculations, which are as follows:

- The Lu-doped SWZONT is still a direct-gap semiconductor; the introduction of Lu results in the decrease of the energy band gap and the improvement of the electrical conductivity.
- Lattice distortion was obvious in the Lu-doped system; the distortion encourages the formation of oxygen vacancy around the impurity Lu, which improves the system’s redox potential. The catalytic oxidation activity of the Lu-doped SWZONT was therefore improved.
The Lu-doped SWZONT system is stabilized because of the introduction of Lu, and the semiconductor type (N type) is enhanced in the Lu-doped system.

Lu-doped SWZONT materials can be applied to UV optoelectronic devices.

Acknowledgments
This work was financially supported by National Students’ Innovation and Entrepreneurship Training Program (201410075002) and CSC fellowship (2014-3012).

References
[1] Cui Y, Wei Q, Park H, et al. 2001 Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species Science 293 1289-92
[2] Cao L, Kong L B, Liang Y Y, et al. 2004 Preparation of novel nano-composite Ni (OH) 2/USY material and its application for electrochemical capacitance storage Chem. Commun. 14 1646-7
[3] Xin H, Liu X, Shi X, et al. 2005 High efficiency light emitting device U.S. Patent Application 11/196,856
[4] Xing Y J, Xi Z H, Xue Z Q, et al. 2003 Optical properties of the ZnO nanotubes synthesized via vapor phase growth Applied Physics Letters 83 1689-91
[5] Wu Y, Huang J C, Cui Y C, et al. 2014 First-principles study on optical properties of Cd-doped single-walled (8, 0) ZnO nanotube Applied Mechanics and Materials 668 27-30
[6] Wu J J, Liu S C, Wu C T, Chen K H, Chen L C 2002 Heterostructures of ZnO-Zn coaxial nanocables and ZnO nanotubes Applied Physics Letters 81 1312-4
[7] Zhang B P, Binh N T, Wakatsuki K, Segawa Y, Yamada Y, Usami N, Kawasaki M and Koinuma H 2004 Formation of highly-aligned ZnO tubes on sapphire (0001)substrates Applied Physics Letters 84 4098-100
[8] Hu J Q, Li Q, Meng X M, Lee C S and Lee S T 2003 Thermal reduction route to the fabrication of coaxial Zn/ZnO nanocables and ZnO nanotubes Chemistry Materials 15 305-8
[9] Xing Y J, Xi Z H, Xue Z Q, Zhang X D, Song J H, Wang R M, Xu J, Song Y, Zhang S L and Yu D P 2003 Optical properties of the ZnO nanotubes synthesized via vaporphase growth Applied Physics Letters 83 1689-91
[10] Sun Y, Fuge G M, Fox N A, et al. 2005 Synthesis of aligned arrays of ultrathin ZnO nanotubes on a Si wafer coated with a thin ZnO film Advanced Materials 17 2477-81
[11] Kong X Y, Ding Y and Wang Z L 2004 Metal-semiconductor Zn-ZnO core-shell nanobelts and nanotubes Journal of the Physics Chemicals B 108 570-4
[12] Wu G S, Xie T, Yuan X Y, Li Y, Yang L, Xiao Y H and Zhang L D 2005 Controlled synthesis of ZnO nanowires or nanotubes via sol-gel template process Solid State Communications 134 485-9
[13] Yan J F, Lu Y M, Liang H W, Liu Y C, Li B H, Fan X W and Zhou J M 2005 Growth and properties of ZnO nanotubes grown on Si (111) substrate by plasma-assisted molecular beam epitaxy Journal of Crystal Growth 280 206-11
[14] Zhang J, Sun L D, Liao C S and Yan C H 2002 A simple route towards tubular ZnO Chemical Communications 3 262-3
[15] Shen X, Allen P B, Muckrman J T, Davenport J W and Zheng J C 2007 Wire versus tube: Stability of small one-dimensional ZnO nanostructures Nano Letters 7 2267-71
[16] Tu Z C and Hu X 2006 Elasticity and piezoelectricity of zinc oxide crystals, single layers, and possible singlewalled nanotubes Physicals Review B 74 035434-40
[17] Mclaren A, Valdes-Solis T, Li G, et al. 2009 Shape and size effects of ZnO nanocrystals on photocatalytic activity Journal of the American Chemical Society 131 12540-1
[18] Pan H and Feng Y P 2008 Semiconductor nanowires and nanotubes: Effects of size and surface-to-volume ratio ACS Nano 2 2410-4
[19] An W, Wu X and Zeng X C 2008 Adsorption of O2, H2, CO, NH3, and NO2 on ZnO nanotube: A density functional theory study The Journal of Physical Chemistry C 112 5747-55
[20] Minami T, Yamamoto T and Miyata T 2000 Highly transparent and conductive rare earth-doped ZnO thin films prepared by magnetron sputtering Thin Solid Films 366 63-8

[21] Zhang Y G, Zhang G B and Wang Y X 2011 First-principles study of the electronic structure and optical properties of Ce-doped ZnO Journal of Applied Physics 109 063510

[22] Luo W, Fu C, Li R, et al. 2011 Er³⁺-doped anatase TiO₂ nanocrystals: Crystal-field levels, excited-state dynamics, upconversion, and defect luminescence Small 7 3046-56

[23] Chen S J, Liu Y C, Shao C L, et al. 2006 Photoluminescence study of ZnO nanotubes under hydrostatic pressure Applied Physics Letters 88 133127

[24] He A L, Wang X Q, Fan Y Q, et al. 2010 Electronic structure and magnetic properties of Mn-doped ZnO nanotubes: An ab initio study Journal of Applied Physics 108 084308

[25] Shen X C 1992 The Spectrum and Optical Property of Semiconductor (Beijing: Science Press) p 76 (in Chinese)