Analytical Study on Structural, Electronic and Elastic Property of ZnS Nanotube

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Abstract: The structural, electronic and elastic property of single-walled ZnS nanotubes (SW-ZnS NTs) with armchair and zigzag structures were investigated. The stability and elastic modulus in SW-ZnS NTs were also investigated. A study was also carried out to determine the band gap energy of the nanocrystalline ZnS. We have seen that by increasing the diameter and proportional to the Zn-S bond length, both the stability and Young’s modulus were decreased. The stable structures were obtained by density functional calculations. The obtained results suggest this material for nano-electronic devices and applications.

Key words: density functional theory, nanotube, stability, elastic modulus.

I. INTRODUCTION

In recent years, semiconductor nanocrystals (NCs) have emphasized big concern due to their unique structural, electronic, and optical properties initiating from their large surface-to-volume (S/V) ratio and quantum confinement effect and the surface effect. Zinc Sulfide (ZnS) is an II-VI group semiconductor with band gap energy of 3.7 eV at room temperature and it has received a lot of devotion due to its prominent applications in many fields. It has potential applications in electronics and optoelectronics because of its wide direct band gap [1]. ZnS shows various luminescence properties such as photoluminescence, electroluminescence. The combined optical and structural studies have offered essential perceptions into the relevant electronic energy levels and their correlation with the optical and structural properties of ZnS. This provided a lot of applications of this phosphor material for solid-state lighting, imaging, and other photonic devices. These ZnS semiconductor nanomaterials have many applications in electroluminescence devices, phosphors, light emitting displays, optical sensors etc. One-dimensional (1D) ZnS nanostructures have attracted increasing applications because they possess unique properties compared to the bulk crystal due to the quantum confinement effect and the surface effect [2]. Over the past few years, major attempts have been done on the synthesis of ZnS tubular structures [3]. The synthesized nanotubes mainly have a hexagonal cross-section (HCS) with widths of hundreds nanometers and lengths of up to a few millimeters. Theoretically, Pal et al. first studied arm-chair and zigzag SW-ZnS NTs using density functional tight-binding method [4]. They found that the energy gaps of the SW-ZnS NTs depend on their helicity and are always smaller for zigzag (n, 0) nanotubes than armchair (n, n) ones. Then, Zhao et al. studied SW-ZnS NTs with HCS using interatomic potential calculations [5]. They concluded that the formation energies of the multiwalled nanotubes decrease with increasing wall thickness, irrespective of the diameter of the tube. Recently, ZnS nanostructures have shown a great assurance as functional and structural nano building blocks in nanoelectronics, nanooptoelectronics, and nanolasers [6]. Although the mechanical properties are crucial for designing such device, the elasticity of 1D nanostructure is attaining a much more attention. The elastic properties of ZnS nanowires revealed that Young’s modulus was decreased with increasing diameters [7]. It has been shown in the previous researches on SW ZnO nanotubes that Young’s modulus was increased dramatically with the increased diameters and inversely proportional to the Zn-O bond length [8]. Many research works have been done on ZnS NTs, but to the best of our knowledge, only very limited experimental information is currently available on their mechanical properties. In the absence of definitive experimental results, the first-principles calculations can provide vital calculations of SW-ZnS NTs mechanical properties. However, to our knowledge, there were no the reported mechanical results on ab initio calculations of SW-ZnS NTs.

The stability and elastic modulus in SW-ZnS NTs were investigated by a computational study. We have seen that by increasing the diameter and proportional to the Zn-S bond length, both the stability and Young’s modulus were decreased. The stable structures were obtained by density functional calculations.

II. THEORETICAL METHODS AND COMPUTATIONAL TECHNIQUES

Single-walled carbon NTs, which can be viewed as a graphene sheet rolled into tubes, are usually indexed by a pair of integers (n, m) to represent their helicities [9]. In this paper, we have considered two types of SW-ZnS NTs, namely, armchair and zigzag. The original structures of armchair (m, m) and zigzag (n, 0). Single Wall ZnS NTs are constructed by rolling up a ZnS graphitic sheet. We have...
varied the index m from 5 to 12, and n from 7 to 14, respectively. Using periodic boundary conditions, SW-ZnS NTs are modeled in a tetragonal supercell and are infinitely long along the z-axis. We used framework of density functional theory (DFT) with Perdew-Burke-Ernzerhof correction (PBE) and generalized- gradient approximation (GGA) for the calculations [10]. SCF calculations are performed with a convergence criterion of $10^{-6}$ Hartree on the total energy. We have used convergence criterion of 0.002 Hartree/Å$^2$ for the forces and 0.005 Å$^2$ for the displacement for the full optimization.

### III. RESULTS AND DISCUSSIONS

#### STRUCTURAL PROPERTIES AND STABILITY

We have taken a pair of (6, 6) as an armchair and (8, 0) as Zigzag for making the optimized geometry of SW-ZnS NTs. It has been shown in Fig 1. Apart from the fact that in SW- CNTs, all of the carbon atoms lie on a cylindrical surface, after geometry optimization, Zn atoms move inward whereas S atoms move outward, with respect to their initial position. Thus total energy of the system got reduced since the electron-electron repulsion was lowered. Table 1 shows the average diameters of Zn atom ($d_{z}$), S atoms ($d_{s}$) at two different coaxial cylindrical surfaces, and the radial buckling $\delta$. It can be seen that the buckling decreases with increasing tube diameter. This feature is the same as those observed in ZnS quantum dots [11], ZnS nanotubes, and ZnS nanowires [12].

To analyze the stability of the pair atom of SW-ZnS NTs, the binding energy of ZnS atom, $E_b$, is defined as:

$$E_b = (E_{ZnS}) / N - E_{Z} - E_{S}$$

where $E_{ZnS}$ is the total energy of the ZnS atoms in a nanotube and N is the number of the pair Zn and S atoms. $E_{Z}$ and $E_{S}$ is the energy of the single Zn and S atom respectively. The binding energy as a function of diameter is shown in figure 2. In figure 2, the comparison of binding energies of the armchair and zigzag types of NTs are shown. The graph shows that armchair is found to be more stable than those of zigzag.

#### Table 1: The average diameters, $d_{z}$ and $d_{s}$ of S and Zn atoms and the radial buckling $\delta$ of the armchair and zigzag ZnS NTs with their common diameters d.

<table>
<thead>
<tr>
<th>Zigzag</th>
<th>$d_{z}$ (nm)</th>
<th>$d_{s}$ (nm)</th>
<th>$\delta$ (nm)</th>
<th>d (nm)</th>
<th>$d_{z}$ (nm)</th>
<th>$d_{s}$ (nm)</th>
<th>$\delta$ (nm)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7, 0)</td>
<td>0.95</td>
<td>0.85</td>
<td>0.10</td>
<td>0.90</td>
<td>5.5</td>
<td>1.30</td>
<td>1.05</td>
<td>0.99</td>
</tr>
<tr>
<td>(8, 0)</td>
<td>1.05</td>
<td>0.97</td>
<td>0.11</td>
<td>1.01</td>
<td>6.6</td>
<td>1.34</td>
<td>1.26</td>
<td>0.09</td>
</tr>
<tr>
<td>(9, 0)</td>
<td>1.14</td>
<td>1.09</td>
<td>0.13</td>
<td>1.13</td>
<td>7.7</td>
<td>1.42</td>
<td>1.49</td>
<td>0.09</td>
</tr>
<tr>
<td>(10, 0)</td>
<td>1.17</td>
<td>1.22</td>
<td>0.16</td>
<td>1.26</td>
<td>8.8</td>
<td>1.54</td>
<td>1.69</td>
<td>0.07</td>
</tr>
<tr>
<td>(11, 0)</td>
<td>1.30</td>
<td>1.34</td>
<td>0.18</td>
<td>1.38</td>
<td>9.9</td>
<td>1.57</td>
<td>1.91</td>
<td>0.07</td>
</tr>
<tr>
<td>(12, 0)</td>
<td>1.34</td>
<td>1.47</td>
<td>0.20</td>
<td>1.51</td>
<td>10.10</td>
<td>1.76</td>
<td>2.14</td>
<td>0.07</td>
</tr>
<tr>
<td>(13, 0)</td>
<td>1.42</td>
<td>1.55</td>
<td>0.22</td>
<td>1.64</td>
<td>11.11</td>
<td>1.98</td>
<td>2.37</td>
<td>0.06</td>
</tr>
<tr>
<td>(14, 0)</td>
<td>1.54</td>
<td>1.59</td>
<td>0.24</td>
<td>1.78</td>
<td>12.12</td>
<td>2.21</td>
<td>2.60</td>
<td>0.06</td>
</tr>
</tbody>
</table>

![Figure 1: The top-view and side-view of the relaxed structures of the armchair (6, 6) (a) and zigzag (8,0) (b) SW-ZnS NTs. The gray (small) and yellow (big) balls represent Zn and S atoms.](image)

![Figure 2: The binding energy of SW-ZnS NTs as a function of diameter.](image)

The binding energies of both NTs increase with increasing diameter, which indicates their less stability with increased diameter. On the other hand, single-walled ZnO NTs have more stability with increased diameter [8]. It suggests that we can obtain stable SW-ZnS NTs with a small diameter.

### ELECTRONIC PROPERTIES

Figure 3 shows the graphical relationship between energy gap and diameter of ZnS NT. It has been shown that the energy...
In summary, we have investigated the structural, stability and elasticity of SW-ZnS NTs using Density Functional Theory. We consider two types of tubes, namely armchair, and zigzag forms. It is demonstrated that the stability and Young’s modulus of both types of SW-ZnS NTs are decreased with increasing tube diameter and proportional to the Zn-S bond length.

IV. CONCLUSION

In summary, we have investigated the structural, stability and elasticity of SW-ZnS NTs using Density Functional Theory. We consider two types of tubes, namely armchair, and zigzag forms. It is demonstrated that the stability and Young’s modulus of both types of SW-ZnS NTs are decreased with increasing tube diameter and proportional to the Zn-S bond length.

REFERENCES


Figure 3: Energy Gap of SW-ZnS NTs as a function of diameter.

\[ Y = V_0 \left( \frac{1}{\epsilon} \right)^{2} E / |\epsilon|^{2} \]

where \( V_0 \) is the equilibrium volume, \( E \) is the total energy, and \( \epsilon \) is the strain.

Figure 5 shows the bond length as a function of diameter. The graph shows that bond length of zigzag NTs is more than armchair NTs at small diameters. With the increase in diameter, the bond length of armchairs decreases more.

ELASTIC PROPERTIES

Figure 4 shows the relationship between Young’s modulus and diameter of both types of ZnS NTs. The graph shows that the elasticity of armchair and zigzag NTs decrease monotonically with increased diameter. The elasticity of zigzag NTs is larger than those of armchair NTs at small diameters. To characterize the elastic properties of SW-ZnS NTs, we investigate Young’s modulus of two types of SW-ZnS NTs. The Young’s modulus is calculated as the second derivative of the total energy with respect to the strain at the equilibrium, i.e.

\[ Y = \frac{1}{V_0} \left( \frac{1}{\epsilon} \right)^{2} E / |\epsilon|^{2} \]