

First-Principles Studies of SnS₂ Nanotubes

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ABSTRACT

First principles calculations are used to predict the stability and electronic structures of SnS₂ nanotubes. Optimization of several structures and their corresponding strain energies confirms the stability of SnS₂ nanotube structures. Electronic structure calculations show that SnS₂ nanotubes could have moderate band gaps regardless of their chirality. It suggests that SnS₂ nanotubes would be well suited to use as semiconductor wires in nanoelectronic devices if they are synthesized. Adsorption of NH₃ onto SnS₂ is also investigated and discussed with regard to potential sensor application.

Keywords: SnS₂, metal-chalcogenide, nanotubes, first principles, gas sensors

1 INTRODUCTION

Since carbon nanotube(CNT) structure was found[1], there have been extensive investigations on applications of CNTs. CNTs are fascinating because of their diversities of electronic structure, from metal to semiconductor, depending on their chiralities. However, these diversities became a major disadvantage in CNT's real applications for electronic devices. Besides CNTs, syntheses of new nanotubes from various inorganic materials were reported recently. Especially inorganic nanotubes from metal chalcogenide, MoS₂ and WS₂, have received a great deal of attention, because they were found to be semiconductors regardless of their chiralities[2]. Since Tenne et al.[3] had found fullerene-like nanoparticles derived from a layered structure of WS₂, syntheses of nanotubes of WS₂ and MoS₂ were reported by the same group[2] and others[4]. Very recently, Tenne's group also reported synthesis of fullerene-like nanoparticles of SnS₂ [5]. SnS₂ is very similar to MoS₂ and WS₂, since it has a layered structure and it shows semiconductor properties. SnS₂ based materials show semiconducting properties, even when it has nanoporous structures [6]. Even though SnS₂ nanotubes are not synthesized experimentally yet, it is worthwhile to investigate them theoretically for future applications. In this paper, we report a possibility of SnS₂ nanotubes and their electronic structures investigated in the framework of density functional theory. The adsorption of NH₃ on SnS₂ nanotubes are also discussed for sensor application.

2 COMPUTATIONAL METHODOLOGY

The most stable structure of layered SnS₂ consists of a triple layer of S-Sn-S, similarity to MoS₂. These triple layers are stacked together by van der Waals interactions separated 5.94 Å. Since 2-D projected structure of the triple layers is similar to a graphene sheet, the SnS₂ nanotubes can be classified to "armchair" (n,n) nanotubes and "zig-zag" (n,0) nanotubes, depending on rolling directions, as in CNT's[7].

We have performed first-principles calculations of several hypothetical SnS₂ nanotubes using atomic orbital based density functional theory (DFT) with the generalized gradient approximation (GGA) of Perdew and Wang, implanted in Dmol³[8]. The details of calculations can be found in the previous report [9].

3 RESULTS AND DISCUSSIONS

The optimized structures of armchair and zigzag nanotubes are shown in Fig. 1, and the optimized radiuses are listed in Table 1. These optimization of the several nanotubes confirm the stability of nanotube (NT) structures of SnS₂. We have also calculated the strain energies of SnS₂ NTs. The strain energy per atom is defined as $E_S = E_{NT} - E_{Layer}$, where E_{NT} is the energy per atom of the SnS₂ NT and E_{Layer} is the energy per atom of the SnS₂ layer. The strain energies per atom increase with $1/R^2$ following the classical $1/R^2$ strain law, as shown in Fig. 2, albeit we have calculated only four different NTs. In Fig. 2, we have compared the calculated strain energies of SnS₂ NTs with the reported values of MoS₂ NTs and CNTs [11,12]. From the $1/R^2$ strain energy of SnS₂, one can expect very large strain energy for small diameter nanotubes, since SnS₂ NTs are constructed by rolling a triple layer of S-Sn-S.

Table 1. The radiuses and HOMO-LUMO gaps of optimized nanotube structure of SnS₂

		radius (Å)	HOMO-LUMO gap (eV)
zigzag	(10,0)	6.65	0.64
	(12,0)	7.75	0.84
armchair	(8,8)	8.80	0.85
	(10,10)	11.3	1.00

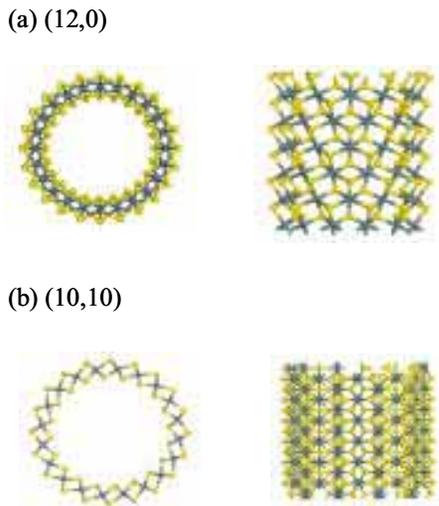


Fig. 1 Optimized nanotube structures; (a) (12,0) zigzag nanotube, (b) (10,10) armchair nanotube

It is reasonable for SnS₂ NTs to require much more energies than CNTs for narrow tubes. However, the strain energies of SnS₂ NTs are comparable to those of CNTs for larger diameter than 20 Å. It is noted that the strain energies of SnS₂ are much smaller than those of MoS₂, even both of them are constructed from triple layer of chalcogenides. It infers that SnS₂ NTs can be easily synthesized considering that MoS₂ NTs were already synthesized even though they require more strain energies than SnS₂ NTs. The calculated energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are listed in Table 1. The gap values are in the range from 0.6 eV to 1.0 eV regardless of chiralities of SnS₂ NTs, which are comparable to the band gaps of semiconducting CNTs.

In order to model NH₃ adsorption on the theoretically obtained SnS₂ NT, a NH₃ molecule is attached to a (10,0) NT unit cell as shown in Fig. 3. To find a bound configuration, we calculated binding energy as a function of the distance between N and the nearest S atom of the NT. The binding energy, E_b , is defined as $E_b = E_t(NT+NH_3) - E_t(NT) - E_t(NH_3)$, where $E_t(NT+NH_3)$ and $E_t(NT)$ are total energies of the NT with and without a NH₃ molecule, respectively, and $E_t(NH_3)$ is the total energy of an isolated NH₃ molecule. After finding the minimum E_b varying the N-S distance, the structure of NT with NH₃ are reoptimized allowing the atoms of NH₃ and nearby 4 S atoms and 3 Sn atoms to relax, while other atoms in the NT are constrained to their initial positions.

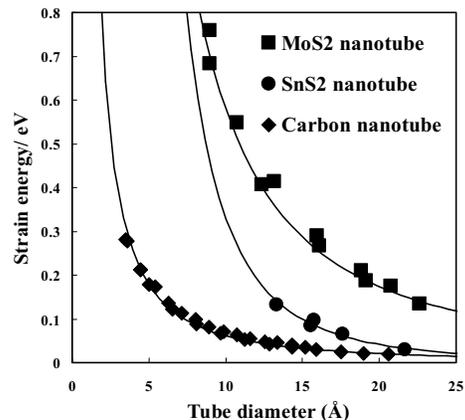


Fig. 2 Strain energies vs. tube diameters of SnS₂ nanotubes compared with those of MoS₂ nanotubes[11] and CNTs[12].

The calculated binding energy is -0.19 eV for NH₃ molecule on the SnS₂ NT. The charge transfer is found to be 0.04 electrons from a NH₃ to SnS₂ NT. These values are very close to those of CNT (-0.18 eV for binding energy and 0.04 e for charge transfer) in our previous calculations [13]. The adsorption seems physisorption rather than chemisorption, that is plausible for sensor application. The electron density of HOMO is shown in Fig. 3-b. The most of HOMO charge density is located near NH₃ molecule and some charges are on the SnS₂ NT which seems transferred from NH₃ molecule.

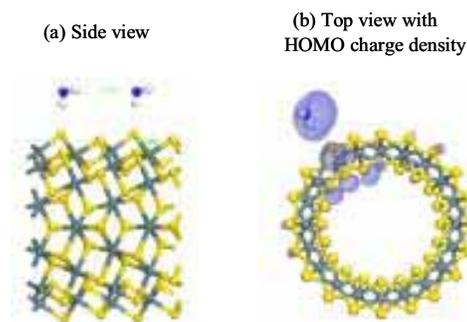


Fig. 3 Optimized structure of NH₃ molecules attached to (10,0) SnS₂ nanotube; (a) side view where NH₃ molecules are separated by 6.30 Å, (b) top view of the same system with HOMO charge density

4 CONCLUSION

In conclusion, optimizations of the several SnS₂ NTs and their strain energies confirm the stability of NT structures of SnS₂, even they are not experimentally synthesized yet. The calculated HOMO-LUMO gaps clearly show that SnS₂ NTs could be semiconductors with moderate band gaps regardless of their chiralities. It suggests that SnS₂ NTs can be easily used as semiconductor wires in nano-electronic devices, that is a great advantage in real applications, compared to CNTs and MoS₂ NTs. In order to see the possibility of gas sensor application of this hypothetical SnS₂ NT, we have shown that adsorption of NH₃ on SnS₂ NT is physisorption and charge transfer occurs from NH₃ to SnS₂ NT. If SnS₂ NTs is synthesized, semiconducting SnS₂ NTs could be a very plausible 1-dimensional sensor material for NH₃ detection.

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REFERENCES

- [1] S. Iijima, *Nature*, **354**, 56 (1991),
- [2] R. Tenne, *Colloids and Surfaces A*, **208**, 83 (2002)
- [3] R. Tenne, L. Margulis, M. Genut, and G. Hodes, *Nature*, **360**, 444 (1992).
- [4] M. Remskar et al., *Science*, **292**, 479 (2001)
- [5] S. Y. Hong, R. Popovitz-Biro, Y. Prior, and R. Tenne, *J. Am. Chem. Soc.*, **125**, 10470 (2003)
- [6] T. Jiang, G. A. Ozin, A. Verman and R. L. Bedard, *J. Mater. Chem.*, **8**(7), 1649 (1998)
- [7] M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, "Science of Fullerenes and Carbon Nanotubes", Academic, New York (1996)
- [8] G. Kresse, J. Hafner, *Phys. Rev. B* **47**, C558 (1993)
- [9] DMol³ is a registered software product of Accelrys Inc.; B. Delley, *J. Chem. Phys.*, **92**, 508 (1990)
- [10] H. Chang, E. In, K. Kong, J.-O Lee, Y. Choi, and B.-H. Ryu, *J. Chem. Phys. B*, **109**, 30 (2005)
- [11] G. Seifert, H. Terrones, M. Terrones, G. Jungnickel, and T. Frauenheim, *Phys. Rev. Lett.*, **85**, 146 (2000)
- [12] H. Hernández, C. Goze, P. Bernier, and A. Budio, *Phys. Rev. Lett.*, **80**, 4502 (1998)
- [13] H. Chang, J. D. Lee, S. M. Lee and Y. H. Lee, *App. Phys. Lett.*, **79**, 3863 (2001)