

First-Principles Studies of SnS₂ Nanotubes: A Potential Semiconductor Nanowire

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First principles calculations are used to predict the stability and electronic structures of SnS₂ nanotubes. Optimization of several structures and their corresponding strain energies confirm the stability of SnS₂ nanotube structures. Band 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.

Since the first findings on carbon nanotubes (CNTs),¹ there have been extensive investigations on the applications of CNTs. CNTs are fascinating because of their diversity of electronic structure, from metal to semiconductor, depending on their chirality. However, this diversity becomes a major disadvantage in applications of CNTs for real electronic devices. Nanotubes (NTs) prepared from various inorganic materials besides carbon have been reported recently; in particular, inorganic metal–chalcogenide (MoS₂, WS₂) NTs have received a great deal of attention because they were found to be semiconductors regardless of their chirality.² Since Tenne et al.³ found fullerene-like nanoparticles derived from a layered structure of WS₂, syntheses of WS₂ and MoS₂ NTs were reported by the same group² and others.⁴ Very recently, Tenne's group also reported the synthesis of fullerene-like nanoparticles of SnS₂.⁵ SnS₂ is very similar to MoS₂ and WS₂ in that it has a layered structure and SnS₂-based materials seem to always show semiconductor properties. Although SnS₂ NTs have not yet been synthesized, it is nonetheless worthwhile to investigate the possibility of SnS₂ NTs theoretically. WS₂ and MoS₂ NTs were successfully prepared after synthesis of their fullerene-like nanostructures.^{2–4} Considering that SnS₂ fullerene-like particles have been synthesized, SnS₂ NTs are very likely to be synthesized soon. Moreover, Ozin's group reported that nanoporous SnS₂ materials showed excellent sensor properties upon absorption of NH₃, H₂S, or alcohols.⁶ If SnS₂ NTs are synthesized, applications as nanosized sensors are likely. In this letter, we report on the possibility of SnS₂ NTs and their electronic structures investigated within the framework of density functional theory (DFT). The adsorption of NH₃ onto SnS₂ NTs is also discussed.

The most stable structure of layered SnS₂ consists of a triple layer of S–Sn–S, which is a CdI₂-type structure, with lattice parameters $a = 3.74$ Å and $c = 5.94$ Å, as shown in Figure 1. These triple layers are stacked, held together by van der Waals interactions, at a separation of 5.94 Å. As shown in Figure 1b, the two-dimensional projected structure of the triple layers is

similar to that of a graphene sheet, and, therefore, the SnS₂ NTs can be classified as “armchair” (n, n) or “zigzag” ($n, 0$) NTs depending, as in CNTs, on the rolling direction.⁷

We built two zigzag NTs, (10, 0) and (12, 0), and two armchair NTs, (8, 8) and (10, 10). For the zigzag NTs, 60 and 72 atoms were included in the unit cells of (10, 0) and (12, 0), respectively, and the periodicity along the tube axis was 6.30 Å. For the armchair NTs, 72 and 120 atoms were included in the unit cells of (8, 8) and (10, 10), respectively, and the periodicity along the tube axis was 3.64 Å.

The first principles calculations were performed using the DMol³ code,⁸ in which Kohn–Sham orbitals are expanded with a local atomic orbital basis. All calculations employed the double-numerical polarized basis set including the scalar relativistic effect for Sn. The gradient-corrected functional suggested by Perdew and Wang was used for the calculations.⁹

The optimized structures of armchair and zigzag NTs are shown in Figure 1c and 1d, and the optimized diameters are listed in Table 1. These optimizations confirm the stability of the 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 $1/D^2$, following the classical $1/D^2$ strain law where D is the diameter of the NT. In Figure 2, we compare the calculated strain energies of four calculated SnS₂ NTs with the reported values of MoS₂ NTs and CNTs.^{10,11} From the $1/D^2$ strain energy relation, we expect a very large strain energy for the small diameter SnS₂ NTs because they are constructed by rolling a triple (S–Sn–S) layer. It is reasonable for SnS₂ NTs to require much higher energies than CNTs for narrow tubes. However, the strain energies of SnS₂ NTs are comparable to those of CNTs for diameters larger than 20 Å. Note that the strain energies of SnS₂ are much smaller than those of MoS₂, even though both are constructed from a triple layer of chalcogenides. This implies that SnS₂ NTs can be easily synthesized, considering that MoS₂ NTs have already been synthesized yet possess a greater strain energy.

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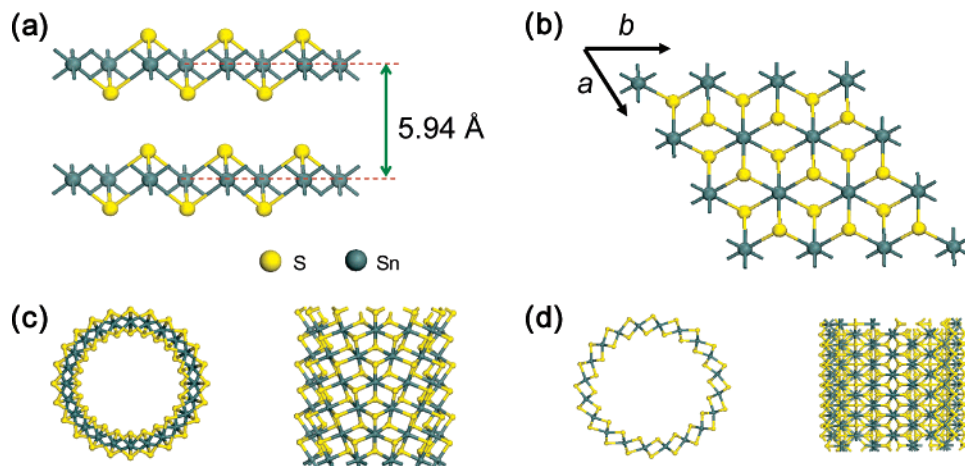


Figure 1. Layered structure and optimized NT structures of SnS_2 : (a) side view of S–Sn–S layers separated by 5.94 Å, (b) top view of SnS_2 where Sn and S atoms form a honeycomb network with an Sn atom located at the center of each honeycomb, (c) optimized structure of the zigzag (12, 0) NT, and (d) optimized structure of the armchair (10, 10) NT.

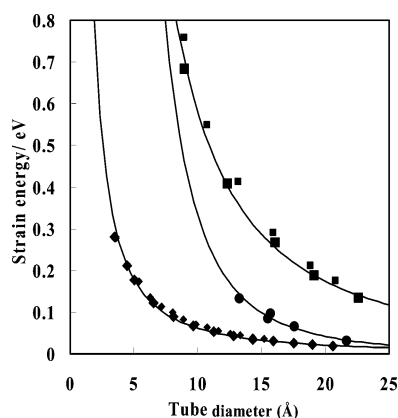


Figure 2. Strain energy versus tube diameter for SnS_2 NTs and, for comparison, MoS_2 NTs¹⁰ and CNTs.¹¹ The strain energies for SnS_2 NTs, MoS_2 NTs, and CNTs are represented by circles, squares, and diamonds, respectively. Solid lines are fits with the $1/D^2$ law.

TABLE 1: Calculated Diameters and HOMO–LUMO Gaps for Several SnS_2 NTs

NT	(<i>n</i> , <i>m</i>)	diameter (Å)	HOMO–LUMO gap (eV)
zigzag	(10,0)	13.3	0.64
	(12,0)	15.5	0.84
armchair	(8,8)	17.6	0.85
	(10,10)	22.6	1.00

The gap values between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the NTs were calculated and are listed at Table 1. The gap values are in the range from 0.6 to 1.0 eV regardless of chirality, values comparable to the band gaps of semiconducting CNTs. Note that the value of the HOMO–LUMO gap increases as the tube diameter increases within the same chirality, even though the gaps of the armchair NTs seem to be smaller than those of zigzag NTs for a given diameter. The similar trend was also found in MoS_2 NTs by electronic structure calculations.¹⁰ However, this behavior differs from that of CNTs, for which the band gap monotonically decreases as the tube diameter increases.¹²

To see the detailed band structures of SnS_2 NTs along the tube axis, the band structures were calculated using plane-wave basis DFT implanted in the Vienna ab initio simulation package^{13,14} within the generalized gradient approximation. We used ultrasoft pseudopotentials¹⁵ and expanded the valence orbitals on a plane-wave basis up to a kinetic energy cutoff of

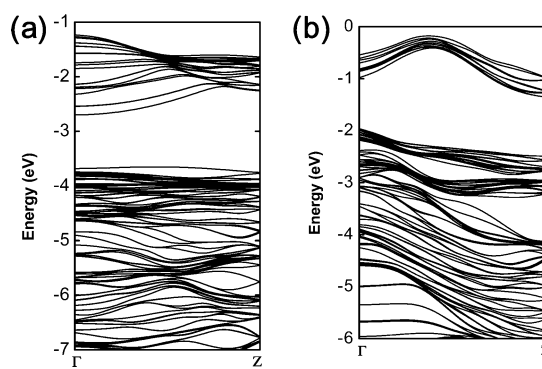


Figure 3. Band structures of the (a) zigzag (12, 0) NT and (b) armchair (10, 10) NT.

198 eV. The calculated band structures along the tube axis for SnS_2 NTs are shown in Figure 3. The band structures clearly show that SnS_2 NTs are semiconductors with moderate band gaps of 0.95 and 0.60 eV for (12, 0) and (10, 10) NTs, respectively. The band gap value for each tube is very close to the HOMO–LUMO gap reported in Table 1. This implies that the HOMO–LUMO gaps obtained from atomic orbital basis DFT can be directly used for the band gaps of SnS_2 NTs. As shown in Figure 3, the zigzag (12, 0) NT has a direct band gap, while the armchair (10, 10) NT has an indirect band gap; this is similar to the band structures of MoS_2 and WS_2 NTs. However, SnS_2 NTs have moderate band gaps regardless of their chiralities, while MoS_2 and WS_2 show very narrow band gaps for small diameter zigzag tubes.^{10,16}

To model NH_3 adsorption on the theoretical SnS_2 NTs, a NH_3 molecule is attached to a (10, 0) NT unit cell as shown in Figure 4. In this calculation, the atomic orbital basis density functional method implanted in DMol³ is used. As mentioned above, the unit cell of the (10, 0) NT has a *z*-axis periodicity of 6.30 Å; thus, NH_3 molecules are separated from each other by 6.30 Å, which is sufficient to neglect interactions between NH_3 molecules. To find a bound configuration, we calculated binding energies as a function of the distance between the N atom of NH_3 and the nearest S atom of the NT. The binding energy, E_b , is defined as $E_b = E_t(\text{NT} + \text{NH}_3) - E_t(\text{NT}) - E_t(\text{NH}_3)$, where $E_t(\text{NT} + \text{NH}_3)$ and $E_t(\text{NT})$ are the total energies of the NT with and without a NH_3 molecule, respectively, and $E_t(\text{NH}_3)$ is the total energy of an isolated NH_3 molecule. After finding the minimum E_b through varying the N–S distance, the structure of the NT with NH_3 was reoptimized, allowing the NH_3 atoms,

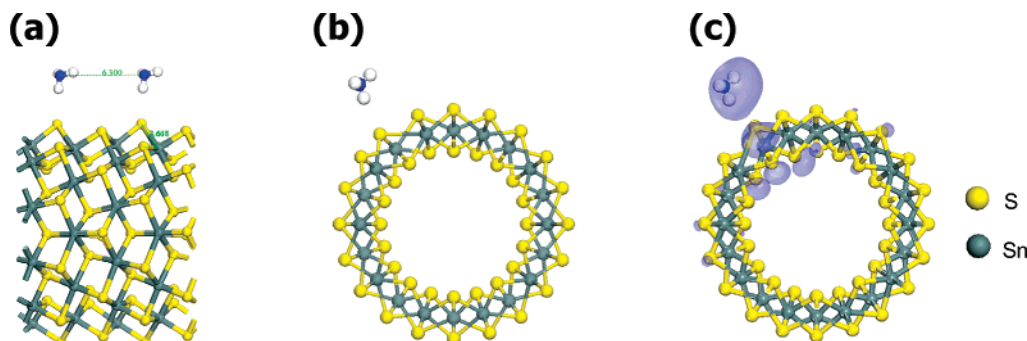


Figure 4. Optimized structure of NH_3 molecules attached to a SnS_2 (10, 0) NT: (a) side view, where NH_3 molecules are separated by 6.30 Å, (b) top view of a SnS_2 NT with a NH_3 molecule, and (c) HOMO charge density of the top view structure

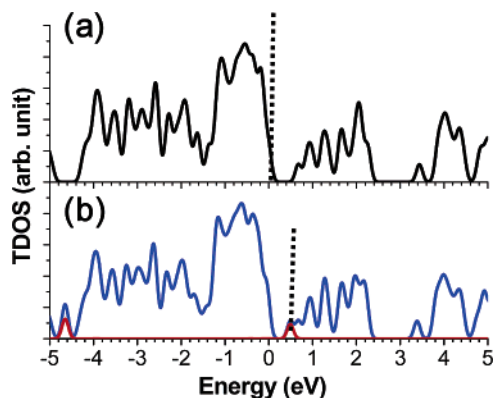


Figure 5. TDOS of a SnS_2 (10, 0) NT (a) without and (b) with a NH_3 molecule, where N(2p) PDOS is represented by a red line; the HOMO levels are marked with dashed lines for both cases.

nearby four S atoms, and three Sn atoms to relax while other atoms in the NT were constrained to their initial positions.

The calculated binding energy is -0.19 eV for a NH_3 molecule on the SnS_2 NT. The charge transfer is found to be 0.04 electrons from the NH_3 to the SnS_2 NT. These values are very close to those obtained previously in calculations of NH_3 adsorption onto a CNT (-0.18 eV for binding energy and 0.04 eV for charge transfer).¹⁷ The nature of the adsorption seems to be physisorption rather than chemisorption, indicating that SnS_2 NTs may be suitable for NH_3 sensor applications. The HOMO electron density is shown in Figure 4c. The greater part of the HOMO's charge density is located near the NH_3 , and some charge on the SnS_2 NT is apparently transferred from the NH_3 .

We have also calculated the total density of states (TDOS) and partial density of states (PDOS) for the (10, 0) NT with and without NH_3 . The density of states is calculated using Löwdin populations analysis with Gaussian broadening.⁸ Figure 5 shows the TDOS of SnS_2 with and without NH_3 . The Fermi level was taken as the HOMO energy level and marked with a dashed line in Figure 5. From the analysis of PDOS of NT without NH_3 at the valence band, we found that the first broad peak, in the 0 to -1 eV range, consists of a dominant contribution from S(p) with some Sn(d) contribution, while the other broad peak, in the -2 to -5 eV range, consists of S(p) and Sn(p) contributions. The conduction band consists of Sn(s) and S(p) contributions. This is similar to the previously reported TDOS of SnS_2 bulk.¹⁸ As shown in Figure 5b the additional peaks appear in the TDOS of SnS_2 with NH_3 . From the analysis of the PDOS, the additional peaks consist of a dominant contribution from N(2p) PDOS, marked as a red line in Figure

5b. Moreover, the HOMO level is moved to the additional peak immediately below the conduction band. This implies that adsorption of NH_3 generates a donor level originating from an occupied N(2p) orbital, where charge transfer seems to occur.

In conclusion, optimization of several SnS_2 NTs and their strain energies confirm the stability of NT structures of SnS_2 . The calculated HOMO–LUMO gaps and band structures clearly show that SnS_2 NTs will likely be semiconductors with moderate band gaps regardless of their chirality. This finding suggests that SnS_2 NTs would be well-suited to use as semiconductor wires in nanoelectronic devices, a great advantage in real applications compared to CNTs and MoS_2 NTs. In addition, we have shown that NH_3 is physisorbed on SnS_2 NTs and that charge transfer occurs from NH_3 to the SnS_2 NT, indicating that this hypothetical NT is suitable for gas sensor applications. We have also found a donor level generated on adsorption of NH_3 , which could be a major route for charge transfer. If SnS_2 NTs are synthesized, semiconducting SnS_2 NTs could be a feasible one-dimensional sensor material for NH_3 detection.

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