First-Principles Study of Helical Silver Single-Wall Nanotubes and Nanowires

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ABSTRACT

We investigate the electronic structures of extended helical silver single-wall nanotubes (AgSWNTs). Because these helical nanotubes are essentially comprised of \( n \)-atom strands winding about the nanotube’s axis, we systematically examine, strand by strand, the electronic properties and the number of conduction channels associated with these structures. Herein, we study a special case of high-symmetry nanotubes. Nanotubes with sufficiently large radii were also calculated with a silver atomic chain inserted along the nanotube’s axis. The analysis is carried out within a first-principles, all-electron self-consistent local density functional approach (LDF) adapted for helical symmetry. Modeling helical silver (or gold) single-wall nanotubes entails rolling up a sheet of atoms and mapping the atoms onto the surface of a cylinder, comparable to rolling up a graphite sheet for a carbon nanotube. It is well known that controlling the size and shape of silver and gold nanostructures results in the ability to tailor the optical and catalytic properties of these materials. In this preliminary study, we consider changes in the electronic structures of these materials as each nanotube is built strand by strand.

INTRODUCTION

Although a range of procedures are available for constructing gold and silver nanowires, only one method has produced gold nanowires with helical periodicity. [1,2] This method utilizes high-resolution transmission electron microscopy (HRTEM) to irradiate a gold thin film until holes form, creating a bridge between two holes. As this bridge thins, it undergoes a surface reconstruction, forming a helical nanowire or nanotube. It is essentially a top-down approach relying on the surface reconstruction properties present in gold, which are not as dominant in silver. [3] Nonetheless, another method, one that does not rely on surface reconstruction, may produce similar helical silver nanowires. For example, Hong et al., synthesized silver nanowires, with 0.40 nm diameters, in an ambient solution phase. [4] Although not immediately apparent, these ultra-thin silver nanowires do exhibit helical periodicity.

The gold nanowires reported experimentally [1,2] have been studied theoretically by others. [5-9] In a recent first-principles study, the authors show that current flows helically about the nanowire axis, indicating that helical gold nanowires are good candidates for nanometer-scale solenoids. [9] Because changes in electronic structure and conductance are related to the nanowire geometry, these systems may also prove useful in sensing applications. As a starting point, we decided to model these helical systems using silver, a simpler system to treat.
COMPUTATIONAL METHOD AND MODELS

We investigate the electronic structures of silver nanotubes and nanowires using a first-principles, all-electron self-consistent LDF approach adapted for helical symmetry. A 3-21G basis set was used, along with 512 points in the first Brillouin zone. The first-principles approach used here has been discussed in detail elsewhere. [10,11] Modeling the silver nanotubes involves “rolling up” a triangular sheet of silver atoms and mapping the atoms onto the surface of a cylinder, comparable to rolling up a graphite sheet for a carbon nanotube. For the triangular sheet depicted in Fig. 1, each Bravais lattice vector, $R$, is defined by two primitive lattice vectors $a_1$ and $a_2$ and the pair of integers $(n_1, n_2)$, so that the lattice vector

$$ R = n_1 a_1 + n_2 a_2. $$

The radius for an $(n_1, n_2)$ nanotube is given by

$$ \rho = \frac{|R|}{2\pi} = \frac{d}{2\pi} \sqrt{n_1^2 + n_2^2 - n_1 n_2}, $$

where $d$ is the Ag-Ag bond length from the triangular sheet, prior to rolling up the tube. The notation chosen here is consistent with the notation used elsewhere [1,2,6-8,12] and is related to the convention used for carbon nanotubes. As shown in Fig. 1, a line of symmetry extends through the triangular lattice for $n_1 = n_2$, and another line of symmetry is present for $n_1 = 2n_2$. All possible AgSWNTs can be reduced by symmetry to an irreducible wedge formed between the two lines of symmetry. Herein, we will focus on five specific $n_1 = n_2$ type single-wall nanotubes: the (4,4), (5,5), (6,6), (7,7), and (8,8). The (6,6), (7,7), and (8,8), having sufficiently large radii, were also calculated with an inserted silver atomic chain along their axis. A larger assortment of nanotubes is considered in other work. [13]

Figure 1. Triangular network of silver (or gold) atoms. Basis vectors are designated as $a_1$ and $a_2$. Each tube is labeled by two integers, $(n_1,n_2)$, defined by the rollup vector $R$. The dashed lines represent lines of symmetry; an irreducible wedge is formed between the lines $n_1 = n_2$ and $n_1 = 2n_2$. 
CONDUCTION CHANNELS

The conductivity of these systems is of interest because of the observation of quantized conductance in gold and silver nanowires. [5,14] The conductivities of the related gold nanowires [7-9] and very thin silver nanowires [15,16] have been addressed in other theoretical studies. The number of conduction channels, or the number of bands crossing the Fermi level, do not always correspond to the number of atom rows in the helical gold nanowires. [7-9,12] Takayanagi et al., observed quantized conductance through individual strands of tip-suspended gold atoms. [14] The conductance was observed in units of $G_0 = 2e^2 / h$, where $e$ is the electron charge and $h$ is Planck’s constant. With each gold atomic chain contributing one channel of conductance, the quantized conductance for an $N$-channel system is expressed as $N G_0$, meaning that the conductance is quantized such that it increases by $2e^2 / h$ whenever a band crosses the Fermi level. [17,18] Additional methods can further determine if these channels are completely open. In the present study, we are only interested in the number of available conduction channels.

Within the $(n_1,n_2)$ notation scheme chosen here, $n_1$ is equal to the number of helical strands comprising the tube. One important question is whether quantized conductance is observed in increments of $n_1 G_0$ in the helical AgSWNTs. Specifically, are $n_1$ conduction channels present for a given $(n_1,n_2)$ silver nanotube? To examine this possibility, we calculate the band structures of these AgSWNTs, by “building” these structures strand by strand. Figure 2 (a-f) illustrates this concept for a (6,6) AgSWNT, and Figure 2 (g) shows the insertion of the atomic chain along the axis of the nanotube.

For each individual configuration shown in Fig. 2, the corresponding band structure is given in Fig. 3. While the structures with one or two strands supply one or two channels of conductance, respectively, this trend begins to decline with the addition of the third strand. Upon adding the sixth strand, thus completing the (6,6) AgSWNT, there are only five channels of conductance present. The addition of the seventh strand, along the axis of the nanotube, contributes one additional conduction channel; there are now six channels of conductance available for the seven-stranded composite system.

Figure 2. (a-f) The (6,6) AgSWNT assembled strand by strand. (g) The (6,6) AgSWNT with an inserted silver chain along the axis of the nanotube. The nanotube is tilted at a slight angle to aid in visualization.
Figure 3. (a-f) Band structures for the (6,6) AgSWNT, assembled strand by strand, corresponding to the respective structures in Figure 3. (g) Band structure for the (6,6) AgSWNT with the inserted silver chain along the axis of the nanotube.

The number of conduction channels does not always correspond to the number of atomic strands comprising the structure. By calculating the band structures for the AgSWNTs considered here, we observe the following: the (4,4) AgSWNT has three conduction channels, the (5,5), (6,6), and (7,7) AgSWNTs have five conduction channels, and the (8,8) AgSWNT has seven conduction channels. The addition of the central chain to the (6,6), (7,7), and (8,8) AgSWNTs contributes one additional channel of conductance. We also note that the Fermi level rises with the addition of each strand, while decreasing upon inserting the axial chain.
ENERGETIC RESULTS

The total energy versus the number of strands is shown in Fig. 4. The (6,6) AgSWNT with the inserted chain has the lowest total energy, therefore it is set to zero and all other energies are plotted with respect to zero. With the addition of each strand, from 1 to \( n - 1 \), the total energy falls off inversely proportional to the number of strands. Upon adding the \( n^{th} \) chain, there is an abrupt lowering of the total energy, and the energy drops even further upon inserting the axial chain into the (6,6), (7,7), and (8,8) AgSWNTs. Preliminary results indicate a similar smooth trend for \( n_2 = 1 \) type AgSWNTs. While for other \( (n_1,n_2) \)-type AgSWNTs, the total energies decrease with the addition of each strand, this trend is not always as smooth as is the case for \( n_1 = n_2 \) and \( n_2 = 1 \) type AgSWNTs.

![Figure 4](image.png)

**Figure 4.** Total energy versus the number of strands for \( n_1 = n_2 \) type structures. x’s represent the (4,4) AgSWNT, *’s represent the (5,5) AgSWNT, \( \Delta \)’s represent the (6,6) AgSWNT, □’s represent the (7,7) AgSWNT, and ○’s represent the (8,8) AgSWNT. Solid markers, ▲, ■, and ●, represent the (6,6), (7,7), and (8,8) AgSWNTs with inserted chains along their axis.
CONCLUSIONS

Changes in the electronic structures and conduction channels of extended helical AgSWNTs were investigated as a function of the number of strands in the structure. While the number of conduction channels in a AgSWNT does not always coincide with the number of atom strands comprising the nanotube, the addition of an atomic chain along the axis of the nanotube always contributed one additional channel of conductance. The total energies of the AgSWNTs studied here decreased smoothly, with the successive addition of each strand. Because such changes in the electronic structure and conductance vary according to geometry, these helical structures may potentially be useful in sensing and other applications.

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REFERENCES

15. J. Zhao, C. Buia, J. Han, and J. P. Lu, Nanotechnology 14, 501 (2003).