

## Electronic structure of silver subnanowires in self-assembled organic nanotubes: Density functional calculations

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We use first principles calculations to investigate the structure and electronic properties of ultrathin silver (Ag) nanowires self-synthesized in organic calix[4]hydroquinone (CHQ) nanotubes. The insulating CHQ nanotubes get transformed to semiconducting calix[4]diquinone-dihydroquinone (CQHQ) tubes in the presence of Ag. These encapsulated nanowires have linear crystalline structure. The electron density around the Fermi level is localized on the Ag nanowire. This indicates that the organic tubes act as shields between Ag nanowires, and the quantum confinement is possible in the encapsulated Ag nanowires like in quantum dots.

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There is a lot of demand for fabricating metallic nanowires with specific electronic properties.<sup>1-9</sup> However the process is difficult because miniscule changes in the structure can lead to drastic effects on the electronic properties. In this context, the modulation of the properties of the nanowire as a result of its adsorption on a template is an attractive alternative.<sup>10</sup> Studies on Au metallic chains adsorbed on single-walled carbon nanotubes have revealed that the interaction between the nanotube and the Au chain is small.<sup>11</sup> However, considerable differences in the electronic characteristics of the adsorbed Au chain have been noted. The above observations indicate that one can implant suitable electronic characteristics on a metallic nanowire by tweaking the nature of the substance on which it is adsorbed. Until very recently such an idea seemed farfetched because there was no simple means of templating metallic nanowires on suitable substrates. However, a recent report elaborated on synthesis and characterization of ultrathin silver nanowires on an organic (calix[4]hydroquinone) substrate.<sup>12</sup> In the present report, we investigate the electronic characteristics of this system in detail using first principles calculations. Our aims are twofold. First, we examine the modulation of the electronic characteristics of the Ag nanowire as a result of its adsorption on the organic substrate, and second, we try to explain the origin of the modulation. Apart from possible applications in the design of futuristic electronic devices, the present study would also aid the understanding of the electronic characteristics of metallic systems adsorbed on organic templates. Density functional electronic structure calculations using ultrasoft pseudopotential plane-wave method were employed in the investigations of the CHQ nanotubes and the encapsulated Ag nanowires. The local density approximation (LDA) of Ceperley and Alder and Vanderbilt pseudopotential<sup>13</sup> were employed and the cutoff energy of the plane-wave basis set was 20 Ry. Full-potential linearized augmented plane-wave method<sup>14</sup> calculations were also carried out on the isolated Ag nanowire, which confirmed the reliability of the results. We initially carried out electronic structure calculations on the isolated CHQ nanotubes to highlight their distinct electronic characteristics as compared to other systems like carbon nanotubes or DNA wires. The x-ray structure,<sup>12</sup> with the hydrogens added, was used as the

starting structure for the calculations. All the optimizations were carried out in a crystal box with periodic boundary conditions without imposing symmetry constraints. Unlike the carbon nanotubes, which are held by covalent C-C bonds, these organic CHQ nanotubes are composed of infinitely long one-dimensional hydrogen bond arrays (four arrays per nanotube) and well-ordered inter-tubular p-p stacking pairs. The hydrogen bonds in these arrays are characterized by short O-O distances ( $\sim 2.58$  Å in agreement with the experimental value  $\sim 2.65$  Å, in contrast to the normal hydrogen bond length of 2.8–2.9 Å),<sup>15</sup> which indicates that the hydrogen bond relay effect in single dimensions would be quite significant.<sup>16</sup> The calculated p-p stacking distance between two adjacent hydroquinone moieties is 3.4 Å, which apart from being in good agreement with experiment, is similar to the stacking distance observed in double-stranded DNA strands.<sup>17</sup> The stacking structures show displaced p-p stacks.<sup>18</sup> An analysis of the electronic structure of the CHQ nanotubes reveals a band gap of 2.9 eV. The insulating nanotubes are contrasted with the conducting/semiconducting single-walled nanotubes and the semiconducting DNA wires.<sup>19</sup> Upon reduction with silver nitrate, there are significant changes in the chemical nature of the CHQ nanotubes which have a bearing on the eventual electronic characteristics. Thus the CHQ nanotubes get transformed to the corresponding calix[4]quinone-hydroquinone (CQHQ) nanotubes, whose band gaps of 0.3 eV indicate that they are semiconducting in nature. The gross structural feature of CHQ nanotubes is similar to that of CQHQ nanotubes, with well-ordered hydrogen bond arrays and inter-tubular p-p stacking pairs (Fig. 1). In the CQHQ nanotubes, there are only two infinitely long one-dimensional hydrogen bond arrays per nanotube because two –OH groups have been changed to =O groups by the reduction arisen from the self-synthesis process of Ag<sup>+</sup> into Ag. In the hydrogen bond arrays, the calculated O-O distances are again  $\sim 2.58$  Å, and the calculated stacking distance is also 3.4 Å.

In the reduction process, the Ag atoms can be located within the reduced CQHQ nanotube. Interestingly, it has been shown previously that there is an enormous enhancement of van der Waals forces between silver particles possessing nanodimensions.<sup>20</sup> Furthermore, it has also been

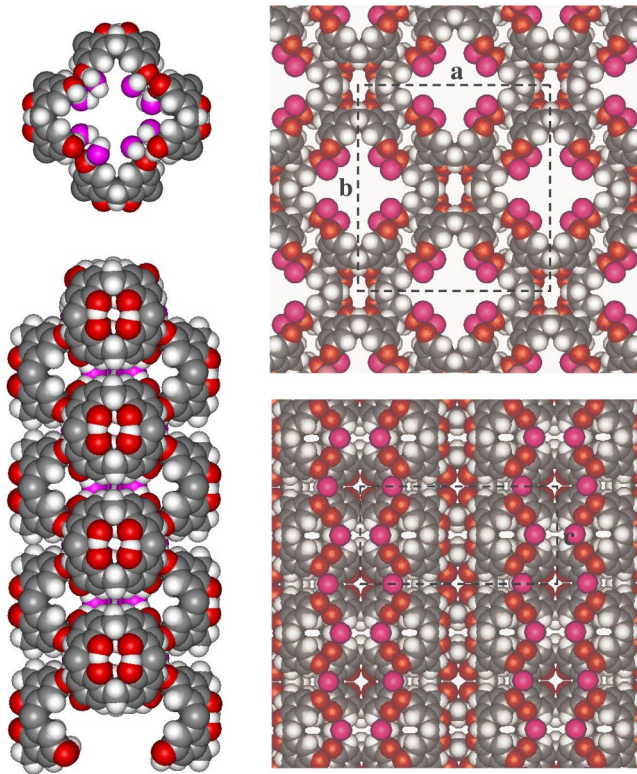


FIG. 1. (Color online) Top and side views of the calculated atomic structures of a single CQHQ nanotube (left) and CQHQ nanotube bundles (right); (O in quinone/hydroquinone: red, O in bridging water molecules between adjacent CQHQ monomers: purple, C: gray, H: white); ( $a=23.3$  Å,  $b=25.0$  Å,  $c=11.6$  Å). The inner and outer cross sections of a nanotube are  $8 \times 8$  and  $17 \times 17$  Å<sup>2</sup>, respectively. The one-dimensional short hydrogen bond arrays are shown with the wavy lines (right, bottom) comprised of the sequence of two red balls and one purple ball.

noted that the presence of similar argentophilic interactions led to systems with interesting physical properties.<sup>21</sup> The nearly cylindrical CQHQ nanotube possesses enough area to enclose the Ag wires (2/2 even up to 4/3) along the [110] axis. The notation  $n1/n2$  denotes the numbers of Ag atoms in the two neighboring [110] planes, and thus it has  $n1+n2$  Ag atoms in a unit cell. Charge balancing together with the structure of the CQHQ nanotube indicates the presence of eight Ag atoms in a unit cell. This unit cell is akin to four dumbbells, each of which contains two Ag atoms, superimposed on one another, and crisscrossed in their length. We have used a supercell geometry to simulate the Ag nanowires because the neighboring nanowires are sufficiently separated by five times the wire width along the [110] and [001] directions. The predicted equilibrium properties of the 2/2 [110] Ag nanowire are compared with those of the bulk fcc Ag in Table I.

The bulk Ag has an fcc structure with a lattice constant of 4.09 Å. The optimized lattice constant at the pseudopotential (LDA) level is predicted to be 4.07 Å. The calculated equilibrium lattice constant is in good agreement with the experimental one within 0.5% error. The lattice constants of the 2/2 nanowire along [001], [110], and [110] directions are 4.01,

TABLE I. Lattice parameters, modulus constants, and cohesive energies of the Ag bulk and [110] 2/2 Ag nanowire predicted by pseudo-potential LDA method.

		expt.	LDA
Ag bulk			
lattice constant	$a(\text{Å})[001]$	4.09	4.07
	$b,c(\text{Å})[\bar{1}10][110]$	2.89	2.88
modulus const. $B$ (Mbar)	1.007	1.164	
cohesive energy (eV/atom)	2.95	3.33	
[110] 2/2 Ag nanowire			
wire width	$a(\text{Å})[001]$	4.0	4.01
	$b(\text{Å})[\bar{1}10]$	-	2.79
lattice constant	$c(\text{Å})[110]$	2.75	2.78
	cohesive energy (eV/atom)	-	2.39

<sup>a</sup>The experimental values are from Ref. 12. Refer to the previous calculated values for Ag bulk ( $a=4.5$  Å,  $B=1.28$  Mbar).<sup>22</sup>

2.79, and 2.78 Å (Fig. 2). These are in good agreement with the experimental values (4.0 Å along the [110] direction and 2.75 Å along the [110] direction).<sup>12</sup> The calculated atomic layer spacing along the [110] wire axis (2.78 Å) is decreased by 4% relative to the corresponding calculated bulk value (2.88 Å), in good agreement with the experimental value (2.75 Å) which is reduced by 4% relative to the x-ray diffraction result of the bulk (2.89 Å). This compression is due to the reduced interaction from the outside of the surface, resulting in increased interaction toward inner atoms inside the surface, which can be seen in silver nanoclusters.<sup>23</sup> The interatomic spacing along [001] direction is predicted to be 4.01 Å, which is 2% smaller than the corresponding bulk value (4.09 Å). Results carried out using the full-potential linearized augmented plane-wave method are consistent with

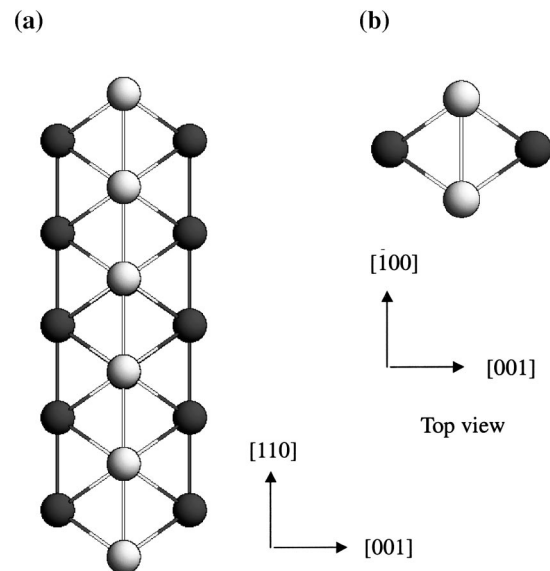


FIG. 2. Calculated structure of [110] 2/2 Ag nanowire. The black and gray spheres represent the Ag atoms along [001] and [110] directions, respectively (wire width:  $a=4.01$  Å,  $b=2.79$  Å, lattice constant  $c=2.78$  Å).

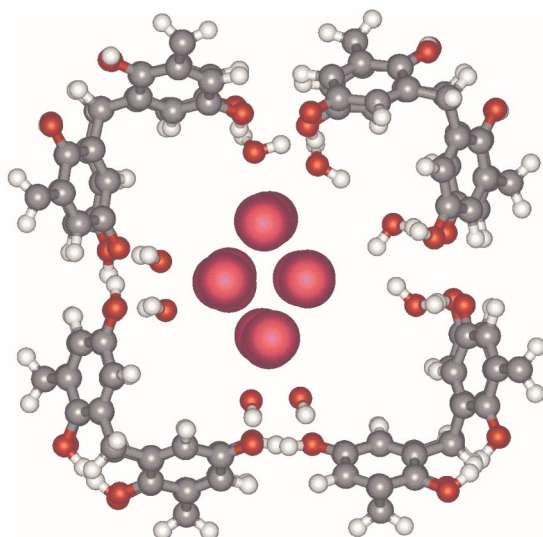


FIG. 3. (Color online) Top view of Ag nanowire inside a CQHQ organic nanotube (Ag: purple, O: red, C: gray, H: white).

the pseudopotential LDA results. Thus, here we report only the results based on the pseudopotential LDA results. The pseudopotential(LDA)-predicted bulk modulus is 1.16 Mbar, in good agreement with the experimental value of 1.01 Mbar. The predicted cohesive energy of the bulk is 3.3 eV/atom, in reasonable agreement with experimental value 2.95 eV/atom. In the case of the 2/2 nanowire, the predicted cohesive energy is 2.4 eV, which is 0.9 eV smaller than the bulk value. This indicates that the 2/2 nanowire alone might not be so stable. Although the interactions between nanotubes and nanowires should not be significant, the nanowires can be stabilized without deformation and chemical reaction in the presence of the organic support. Since the size of the 4/3 nanowire can (barely) fit inside the organic nanotubes, we have also investigated the 4/3 nanowire. The cohesive energy of the 4/3 nanowire is 2.6 eV, and so the gain of the 4/3 nanowire over the 2/2 nanowire is only 0.2 eV, which is not significant in spite of a three times increase in the number of atoms.

To study the electronic properties of Ag nanowire in the CQHQ nanotube, we calculated three band structures. The optimized structure of the CQHQ nanotube with Ag nanowire is shown in Fig. 3. In Fig. 4, the electronic band structure for the CQHQ nanotube with Ag nanowire is presented, in comparison with the band structures of the CQHQ nano-

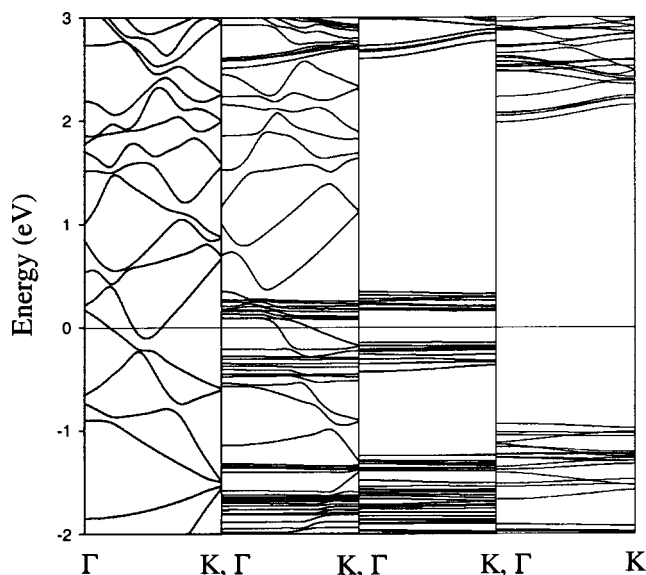


FIG. 4. Band structure for Ag nanowire (first from left), CQHQ nanotube with Ag nanowire (second), CQHQ nanotube (third), and CHQ nanotube (last).

wire and the Ag nanowire. The CQHQ tube is a semiconductor with small gap (0.3 eV). The CQHQ nanotube with Ag nanowire, however, creates several additional states in the band gap region. The band structure of the Ag nanowire within the organic nanotube is somewhat different from that of the pure Ag nanowire. The bands of Ag nanowire in the CQHQ nanotube near Fermi energy are shifted up relative to the bands of isolated Ag nanowire. This indicates that there is electron transfer from the Ag nanowire to the CQHQ nanotube, similar to the electron transfer phenomena observed in the interfacial reaction of C60 with silver.<sup>24</sup> Figure 4 shows the metallic character of the Ag nanowire in CQHQ as well as the metallic character of the Ag nanowire, in comparison with the semiconducting character of the CQHQ nanotube (which is contrasted with the insulating character of the CHQ nanotube).

Figure 5 shows the isosurface of the electron density of two bands close to the Fermi level. We find that the electrons in these bands are delocalized around the Ag nanowire. Thus, the Ag nanowire within the CQHQ nanotube still shows conducting behavior, and in particular, it shows quantum conductance since the two s channels cross the Fermi energy level. This is contrasted to the pure Ag nanotube for which

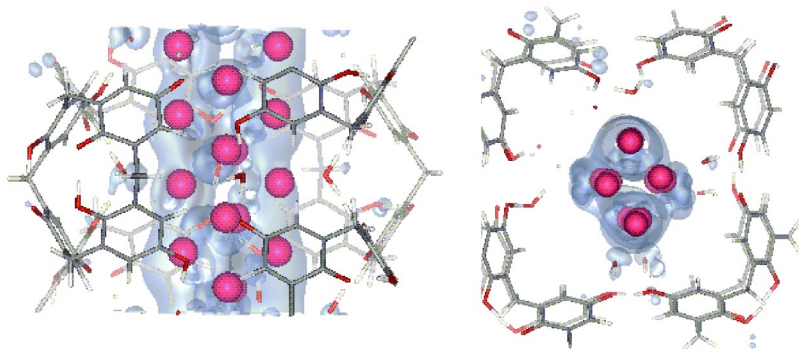


FIG. 5. Isosurfaces for the electron density near the Fermi energy level between the conduction and valence bands for the CQHQ tube with Ag nanowire (side and top views). It clearly shows that the electrons near the Fermi energy level are delocalized on the Ag nanowire.

three *s* channels cross the Fermi energy level. In the presence of an excess electron in a unit cell, we find that the charge density is still retained in the Ag nanowire inside the CQHQ nanotube (but not in the CQHQ nanotube). This could indicate that during the conduction along the Ag nanowire by an excess electron, the charge density is in the Ag nanowire so that the quantum confinement would be possible.

In summary, we have studied the electronic structure of silver nanowire and the surrounding nanotube using ultrasoft pseudopotentials and full-potential linearized augmented plane-wave methods. The Ag nanowire has the primitive fcc crystalline structure inside the organic nanotube. Compared

with the bulk lattice constants, the Ag nanowires have slightly smaller width and lattice constants (by 2–4% only). Two *s* bands cross the Fermi level suggesting the existence of two conducting channels for electronic transport as a quantum wire, resulting in the quantum conductance behavior. These nanowire arrays in the CQHQ organic nanotubes could find useful application for measurement of various electronic and optical properties of ultrathin nanowires, which should lead to useful applications to quantum electronic and optical devices.

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