Intrinsic Stability of the Smallest Possible Silver Nanotube

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Recently, Lagos *et al.* [Nature Nanotech. **4**, 149 (2009)] reported the discovery of the smallest possible Ag nanotube with a square cross section. *Ab initio* density functional theory calculations strongly support that the stability of these hollow structures is structurally intrinsic and not the result of contamination by light atoms. We also report the first experimental observation of the theoretically predicted corrugation of the hollow structure. Quantum conductance calculations predict a unique signature of $3.6G_0$ for this new family of nanotubes.

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In spite of many years of investigation, the study of stretched atomic size metal wires [nanowires (NWs)] continues to produce unexpected results, such as the existence of atomic chains [1–3], the unusual behavior of nanoalloys [4], and the discovery of the smallest possible nanotube with a square cross section [5] (Fig. 1), reported from *in situ* high resolution transmission electron microscopy (HRTEM) experiments. Even from a pure theoretical point of view, the existence of these Ag tubes has never be considered.

The precise origin of the stability of these nanostructures remains to be determined. It is possible that these nanotubes are not naturally hollow [5] but a direct consequence of impurity atoms (C, N, O, etc.), inside and/or outside the tubes or substitutionally replacing Ag atoms. From the experimental point of view it is very difficult to determine whether this in fact occurs because of the low contrast generated by light atoms in HRTEM images [6–8]. In order to address these issues we carried out *ab initio* calculations to determine whether the structural presence of impurities or contaminants is consistent with the available experimental HRTEM data [5].

We have carried out *ab initio* density functional theory using the well-known SIESTA code [9–11] in the framework of local density approximation [12]. In order to guarantee high precision results we have used double-basis set plus polarization function and norm-conserving pseudopotentials built on Troullier-Martins scheme [13] and considering scalar relativistic effects. We first tested the SIESTA parameters for Ag perfect crystalline bulk structures, relaxing both cell lattice vectors and atomic positions. The obtained values are in very good agreement with the available experimental values (4.014 and 4.087 Å, for theoretical and experimental [14] values, respectively).

We have considered tubes formed by 6 Ag lattice parameters (24.08 Å long) with two buffer frozen layers at both tube ends (see Fig. 2). In principle, any number of frozen layers can be used, but for [110] structures two has been proved sufficient. For more details about the choice and importance of frozen layers in NW simulations, see Refs. [15,16]. As these tubular structures can only exist due to high stress generated by the crystallographic apexes in the experiments, the use of buffer layer is necessary to mimic these conditions. If let to freely relax in the geometric optimization calculations, the tubular structures would collapse, evolving to a more (amorphous) globular configuration. In this work, the tubes were generated from an ideal fcc structure where one central atom is removed in alternating layers following the proposed model for their atomic arrangement [5]. This peculiar structure is formed by the stacking of 2 different layers containing 4 atoms each $(4_A/4_B)$, instead of a $(5_A/4_B)$ in an expected fcc square rod along the [001] direction (see Fig. 1 and supplementary materials [17]).

Many possible contaminant configurations have been considered (see Fig. 2). The cases of impurities occupying all removed Ag atoms from an ideal fcc arrangement, as well as cases of single impurities, inside and outside the tube were all taken into consideration. We have chosen as possible contaminants H, C, N, and O atoms, which are the most probable contaminants [6–8] considering the experimental conditions in the HRTEM experiments.

In Fig. 2 we show the schematic initial configurations and the obtained optimized geometries for the different contaminants. As we can see from Figs. 2(b)–2(e), for all the cases of multiple impurities inside the metal tube, the structures collapsed. For the cases of single impurities inside the tube, the presence of H and N atoms also leads to tube collapse, while C and O atoms produce a local structural rearrangement that would be possible to detect in the HRTEM experiments. Impurities located outside the tube [Figs. 2(l)–2(o)] generate significant structural distortions that would also be easily detectable in electron microscopy images. The case of a single O atom attachment

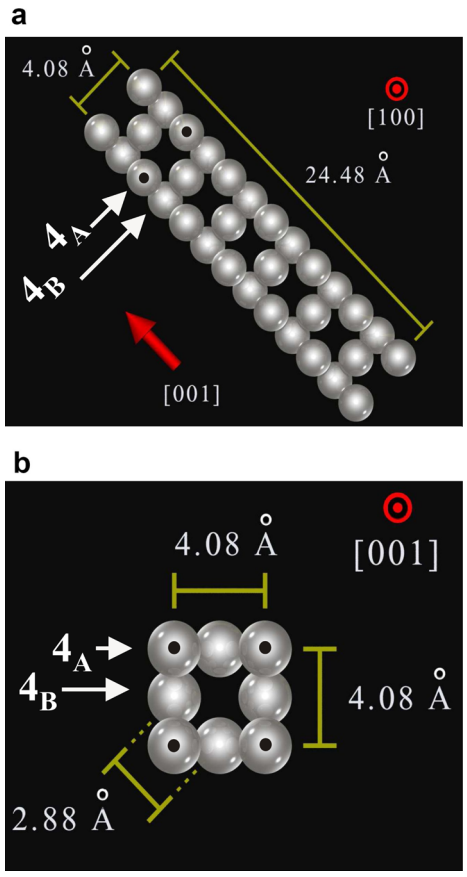

FIG. 1 (color online). Atomistic representation [shown along longitudinal (a) and perpendicular (b) views] of the smallest possible Ag tube with a square cross section [5]. The dark points on the silver atoms indicate atoms on the same plane. See text for discussions.

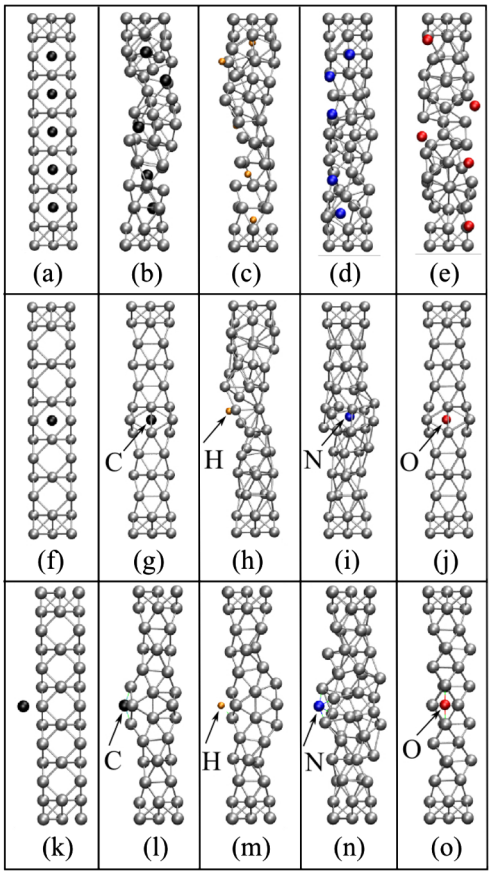

FIG. 2 (color online). Schematic initial configuration for multiple contaminants (a), single contaminant inside (f), and single contaminant outside (k). Their corresponding optimized geometries are presented in the second (carbon), third (hydrogen), fourth (nitrogen), and fifth (oxygen) columns, respectively.

on the Ag tube [Fig. 2(o)] is very interesting: the structure is completely reorganized along the whole tube length considered in our calculations. The new atomic arrangement [Figs. 3(a)–3(c)] is formed by the stacking of atomic planes containing 4 atoms, where one atomic plane having a square shape in the tubular structure [indicated as 4_A, Fig. 3(d)] has been reorganized into a triangular morphology. A more detailed analysis shows that this configuration can be misleading because its projection [Fig. 3(b)], when observed along the [010] direction [vertical direction in Figs. 3(c) and 3(d)], may erroneously suggest that the hollow structure has been preserved (see supplementary materials [17]).

In a strict sense, our theoretical calculations predict that pure Ag tubes besides being hollow should also exhibit a slight corrugation [see Fig. 4(a)] of lateral {010} facets due to the contraction of the atomic layers [indicated as 4_A, Fig. 3(d)], where a vacancy was generated [5]. The detection of this kind of relaxed tubular structure would represent an additional and convincing evidence for the stability of the hollow metal nanostructure.

In order to confirm this hypothesis, we have carried out further HRTEM analysis and experiments. We have generated silver NWs *in situ* in a HRTEM (JEM 3010-URP 300 kV, resolution of 1.7 Å) following the procedure developed by Takayanagi and co-workers [18,19]. Experiments were realized at room and liquid nitrogen

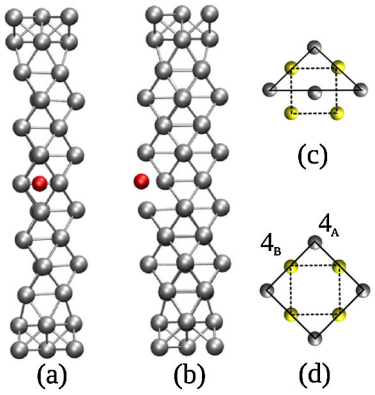

FIG. 3 (color online). (a) Frontal ([100]) and (b) 90° rotated ([010]) views of the structure shown in Fig. 2(o) (initial tubular axis along [001] direction). Its cross section (c) and the expected (d) cross section for the Ag tubular atomic arrangement [17].

temperature (300 and ~150 K) [20,21]. Images were acquired using a TV camera (Gatan 622SC, 30 frames/sec) and recorded by a DVD (detailed experimental procedures can be found in Ref. [4]. In order to measure distances with high precision (subpixel accuracy), atomic positions were determined using the center of mass approach by calculating the mass center coordinates of the intensity distribution of the region around each single or column atom. This approach allows us to determine Ag-Ag distances with small error bars (~ 0.02 Å) [22].

In Fig. 4 we present HRTEM results of the spontaneous formation of a Ag nanotube with a square cross section at ~150 K. It can be seen from Fig. 4(b) that the nanotube displays the typical bamboolike contrast pattern, generated by a supposed hollow structure. The dynamics of Ag tube formation and more detailed structural information can be obtained from video2 in the supplementary materials [17]. In Fig. 4(c) we present a zoomed view of the highlighted square region indicated in Fig. 4(b), where 4 atomic layers, perpendicular to the wire axis, are highlighted. We have measured the width of the planes from the atomic positions on the wire surface or facets (indicated by white dots). An alternating pattern of atoms up and down can be seen, indicated by the triangular arrows, which evidences the corrugation of lateral [010] NW facets. Notice that layers where vacancies were created (second and third layers from left to right) exhibit a distance contraction of ~0.1 Å with respect to first and third layers, respectively. The tube stability (at least as a metastable configuration) is a direct consequence of the Ag surface energy minimization. The square cross section, as a result of a loss of an inner tubular Ag atom, minimizes the surface energy because it maximizes the [100] Ag surfaces.

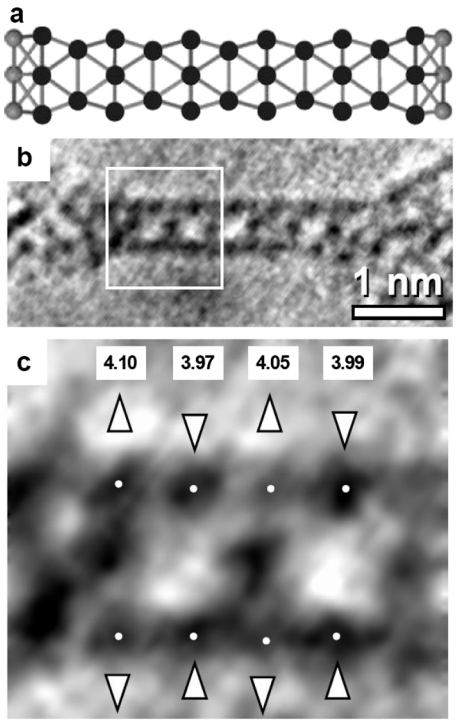

FIG. 4. (a) Predicted corrugated tubular structure from *ab initio* calculations. (b) High resolution transmission electron microscopy (HRTEM) image of the spontaneously formed smallest possible Ag nanotube with a square cross section (~ 4 Å wide). (c) Zoomed image of the square highlighted region indicated in Fig. 4(b). The atomic positions are indicated by white dots. The triangular arrows show the expanded (up) and contracted (down) interatomic distances.

In principle, it would also be possible to form these hollow tubes from mechanically controllable break junction (MCBJ) experiments (putting two clean silver surfaces into contact and pulling them apart) [1,23]. From MCBJ experiments it is possible to obtain data about quantum conductance. For completeness, we have also calculated the predicted quantum conductance for these tubes using the well-known Landauer scattering formalism [24]. We have performed the conductance calculations using extended Huckel theory. The molecular orbitals were calculated taking into account the *s*, *p*, and *d* Ag atomic orbitals, as well as, overlap and energy matrix elements extending beyond first-neighbor atoms [25]. More details about the formalism can be found in Refs. [25,26].

In our simulations, two semi-infinite silver bulk (leads) structures were coupled to the Ag nanotube (inset of Fig. 5). The tubular structure was generated using geometrical data from bulk lattice spacings [5]. In principle, we could have used the geometry obtained from the SIESTA calculations. However, the extended Huckel methodology used to calculate the conductance uses several approximations in such a way that the conductance absolute value can have an uncertainty in the 0.2–0.4 range. Considering these error bars, the use of an idealized geometry or the one obtained from the SIESTA calculations is not expected to produce significantly different results. For comparison purposes we have also carried out transport data calculations using the SIESTA geometry and different

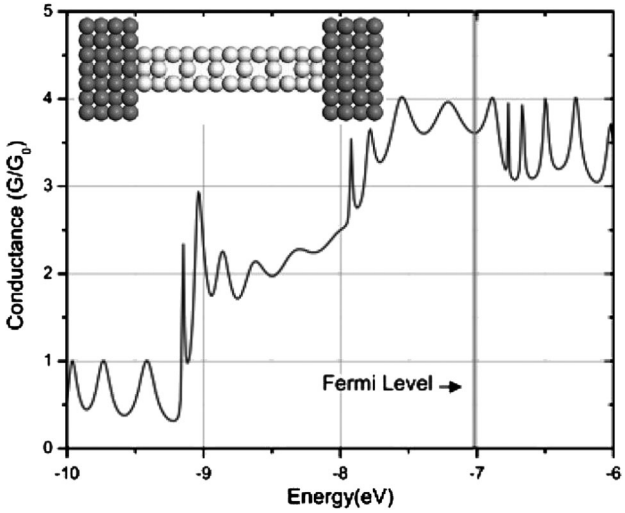

FIG. 5. Theoretical quantum conductance for the silver tube with square cross section. The inset shows the structural model used in the conductance calculations. See text for discussions.

leads. The obtained results are basically the same (see in Fig. 5).

In Fig. 5 we present the conductance results. The model predicts a conductance at the Fermi level of $\sim 3.6G_0$. This is a distinct ''signature,'' different from other values predicted and/or observed in other silver nanostructures [23]. This could provide valuable information to look for corrugated hollow tubes in MCBJ experiments. A natural question is how we can confidently identify the structures once we have intrinsic (and different) error bars in the calculations and in the MCBJ experiments. Our calculations suggest that conductance around $3.6G_0$ should be expected for tubular Ag structures. However, in principle, it must be accepted that several atomic arrangements may produce conductance plateaus with this particular value. From the experimental point of view, the conductance measurement is based on a two-contact approach. This approach does not allow performing the subtraction of the series resistance corresponding to the electrical contacts (or apexes for a nanowire system); as a consequence, the conductance plateau can be observed with a downward shift up to $0.4G_0$ value. It should be noticed that during the wire thinning the conductance evolution (usually called conductance curve in the literature) shows a series of conductance plateaus associated with the most favorable atomic structures. Here, we must emphasize that the appearance of a series of plateau values (or curve profiles) is not random at all; a careful analysis of several hundreds curves clearly shows that a few families ($\sim$ 3–4) of plateau sequences represent usually more than 95% of the measured conductance curves. These few statistically relevant conductance evolutions (which we call a ''signature'') are interpreted as a sequence of atomic structures, usually using information derived from atomic resolution HRTEM imaging. The calculated conductance of these atomic arrangements must explain the whole conductance curve (sequence of observed conductance plateaus). The important point to be noted is that we do analyze many possible structural evolutions, which must be reasonable from the point of view of HRTEM results and structural considerations (symmetry, surfaces energy, etc.). We do not use the calculated conductance of a single structure as proof of structural identification. The calculated transport values must form a sequence in agreement with the few signatures that are statistically relevant in the transport experiments. This methodology allows us to confidently associate a specific structure with the conductance plateaus of the sequence (or signature).

In summary, our results strongly support that the tubes are corrugated and their stability is structurally intrinsic. The completely unexpected discovery of this new family of noncrystallographic structures reinforces the importance of studying mechanically stressed nanostructures. The interplay between surface energies and elastic deformations allows their metastable existence. Their study is of fundamental importance to better understanding and applications in nanomechanics and nanotribology experiments, where contacts are formed and stretched.

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