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On the evolution and electronic properties of self-assembled gold nanowires

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ABSTRACT

The crucial importance for implementing nanomaterials to nanotechnology applications is their characterization in terms of structure and properties. Here we present electronic and conductive properties of seven different gold nanowires (1. zigzag, 2. rhomboid, 3. ladder, 4. c-ribbon, 5. h-ribbon, 6. pentagonal pyramid and 7. capped pentagonal bipyramid) that can be formed due to self assembly from the linear atomic chain. From density functional calculations backed up with molecular dynamics, nudged elastic band and geometry optimizations, it was found that, by reducing the tension on the linear atomic chain of gold atoms, it spontaneously self-assembles into one of the observed, energetically more stable motifs. It is revealed that as self assembly progresses, the electronic property of the motifs undergo semi-metallic → semiconducting → metallic transformations. The observed electronic behavior is further supported by the current-voltage (I–V) characteristics. It is noticed that few selective structures exhibit perfect linear behavior of I–V curve whereas rest follow typical semiconductor curve. Interestingly, pentagonal pyramid displays perfect negative differential resistance with a high peak to valley ratio (PVR) of 17.25 which ensures its potential for oscillators application. Our findings include the possibility of tailoring the electronic properties of gold NW during their evolution in self assembling process.

1. Introduction

Nanowires (NW) are the typical 1-D structures which pledge to serve as building blocks in emerging nano-devices [1–4]. Their research is increasing continuously, covering wide areas, from basic properties to innovative applications [5–9]. It is known that the physical and electronic properties of NW are ruled by quantum-mechanical effects and are, therefore, highly dependent upon their diameter and shape [10]. Intensive research on NW has made it possible to synthesise them from different materials and on various substrates [11–13], however, obtaining a NW with desired electronic properties is yet a hard nut to crack. Owing to their unique 1-D confinement, attempts are being made to produce NW of controlled diameter, various shapes and surface orientations [11,14]. Also, efforts have been made to tailor their electronic properties via doping or adsorption of different atomic species [7,15,16]. Amongst all, metallic NW have attracted special attention of the research community due to potential for interconnections in upcoming nano-devices [17–20]. Their another advantage is that their diameter can be achieved up to mono atomic regime [21,18]. These mono atomic NW (also known as atomic chains) have been produced experimentally for a number of metals like Au, Co, Pt, Pd, etc. [18,19]. Coura et al. [19] reported the formation of linear atomic chains of gold resulting from stretching of gold NW. Hasmy et al. [22] studied the formation of suspended monoatomic chains of noble metals (Au, Ag, Cu) and revealed that Au is forming longer atomic chains than that of Ag and Cu. In an another study, Li chains exhibit potential to act as an atomic switch [23]. Fully spin polarized electrical transport was observed even at room temperature in the suspended chains of Co, Pd and Pt [18]. Besides these experimental reports, theoretical investigations have also been made to understand the evolution and potential applications of linear atomic chains. NW encapsulated in nanotube or absorbed on it has also been studied [24–26]. It is remarkable to note that previous studies are mainly focused on the linear atomic chains. On the other hand, the possibility of other deformed atomic chains are almost unexplored which can present interesting physics.

Motivated from this, in the present work, we have investigated the structural and electronic properties of Au atomic NW in various

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possible geometries evolving from the linear atomic chains. We simulated their self-assembly from the linear atomic chain and determined the mechanism and the energetics for each Au atomic NW in order to prove possibilities for their self-assembly. Our simulations of the self-assembly of a gold nanowire describe the reverse process, reported by Coura et al. [19]: instead of stretching of a NW to a linear atomic chain, we are letting a linear atomic chain to self-assemble by shrinking.

2. Computational method

Simulation of the self-assembly of gold nanowires was performed as a sequential series of geometry optimizations and molecular dynamics calculations. Geometry that was used in each step was created from the previous one in the sequence by contracting one dimension of the simulation cell by 5%. As an initial geometry, a single-atom thick gold nanowire (20 atoms long) was used with periodic boundary conditions applied. Tetragonal cell shape was used with the variable cell dimension parallel to the chain direction. Dimensions of the cell, perpendicular to the chain direction were fixed at 50 Å in order to prevent any significant interaction between chains from neighboring cells. General gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) [27] functional within the Density functional theory [28] was used in geometry optimization and molecular dynamics calculations. Siesta method, [29,30] implemented in the Siesta program package was used for calculations. Double ζ with polarization (DZP) basis set was used. The orbital cut-off radius was defined with the energy shift of 250 meV. Numeric evaluation of spatial properties, during DFT calculations were done on a grid whose size is determined by its plane-wave cutoff energy of 200 Ry. Geometry optimization was done with the conjugated gradient algorithm until forces were smaller than 0.03 eV/Å. MD calculations were done with Nose thermostat at constant temperature of 300 K and Nose mass of 50 Ry/fs, with time step of 1 fs. The simulated system with the size of 20 atoms is large enough to develop a great number of atomic configurations during the simulation procedure. That often created non-homogeneous systems, with more than one structural motif. The simulation of the self-assembly process can be seen as animation (Au_self_assembly.mp4) in supplementary material. In order to investigate the characteristics of self-assembled atomic motifs, the original system of 20 atoms was cut into smaller systems with less than 10 atoms, but with the more homogeneous atomic arrangement. Obtained systems were subjected to geometry optimization. For each optimized system, a trajectory with 11 successive geometries was created by the interpolation of atomic coordinates between the optimized Au nanowire motifs and the initial geometry of the same size (linear atomic chain), in order to gain insight into the mechanism of the self-assembly of gold nanowires. In-house implementation of the nudged elastic band (NEB) method [31] was used for the optimization of the reaction trajectories to the minimum energy path. The optimized initial trajectory with 11 geometries was used for creation of more detailed trajectory with 21 geometries. That, more detailed trajectory was created by inserting geometries between each neighboring pair of geometries in the initial trajectory with 11 geometries. Inserted geometries were created by interpolation of geometries of neighboring pairs. Siesta program was used for obtaining energies and energy gradients for all geometries during NEB optimizations.

For the computation of electronic structures, supercell models of self-assembled gold NW were used. The supercell was taken periodic in z-axis and confined with a vacuum region of 10 Å along x and y-axes. The Brillouin zone was sampled with 100 equispaced k point along the periodic direction. The transport properties were explored by incorporating density functional theory based nonequilibrium transport as implemented in Atomistix ToolKit Virtual Nanolab (ATK-VNL) [32]. ATK uses Landauer–Büttiker formalism $G = G_0 \sum_i T_i$ where G_0 $(= 2e^2/h)$ is the quantum of conductance and T_i is transmittance of the i^{th} channel at the Fermi level. First, the transmission spectra is calculated which accounts the total transmission across the Fermi level:

$$T(E, V) = T_r[\mathbf{t}^\dagger \mathbf{t}](\epsilon), \tag{1}$$

where $\mathbf{t}$ is the transmission amplitude matrix given by

$$\mathbf{t}(\epsilon) = [T_L(\epsilon)]^{1/2} \mathbf{G}(\epsilon) [T_R(\epsilon)]^{1/2}. \tag{2}$$

Once, transmission spectra has been calculated, the current is determined as:

$$I = G_0 \int_{-\infty}^{\infty} d\epsilon [n_F(\epsilon - \mu_L) - n_F(\epsilon - \mu_R)] T_r[\mathbf{t}^\dagger \mathbf{t}](\epsilon). \tag{3}$$

3. Results and discussion

3.1. Geometries

The self-assembly of gold nanowires is made under assumption of collapsing a nanowire in the form of the linear atomic chain of gold atoms (Fig. 1a). Although some of obtained geometries have the same number of atoms, they have different unit cell size (parallel to nanowires). Therefore these geometries correspond to nanowires with a different distensions. The first geometry that appears has the same bonding pattern as the linear atomic chain of gold atoms, but their atoms are arranged in the zigzag fashion (Fig. 1b and 01_zigzag.mp4 in supplementary materials). All atoms

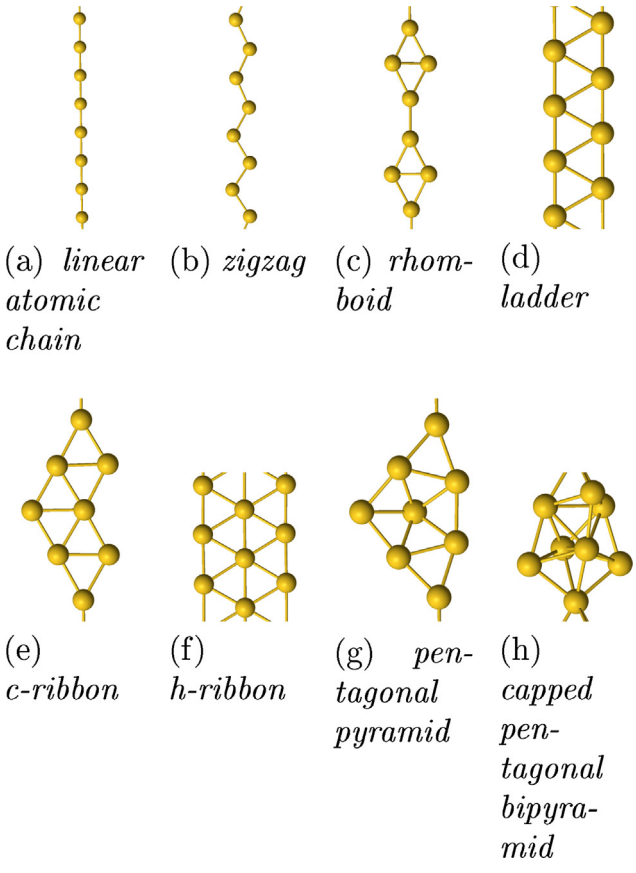

Fig. 1. Geometries of self-assembled gold nanowires.