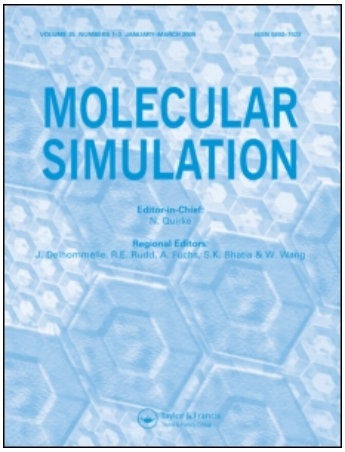

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Growth and properties of Au nanowires

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Growth and properties of Au nanowires[†]

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The self-assembling of Au nanoparticles into nanowires of different structure has been investigated by means of a periodic approach within density functional theory using an Au_{79} nanoparticle as a building block. The density functional calculations show that the interaction of the Au nanoparticles takes place preferentially along the [111] direction, in agreement with the experimental. The electronic structure of the different Au nanowires studied is found to be intermediate between that of the isolated nanoparticle and that of the bulk metal. This is perhaps not surprising but has important consequences for the chemistry of such nanostructures. Finally, calculations carried out for nanowires built from Cu, Ag and Au nanoparticles containing 38 atoms reveal that the self-assembling mechanism is general but that the strength of the interaction is dictated by the chemical nature of the metal with Au being the coinage metal leading to stronger interaction between the nanoparticles.

Keywords: nanowires; density functional theory; self assembling

1. Introduction

The study of materials at the nanoscale is believed to open new fascinating applications and technology and it is generally motivated by the change in physical and chemical properties of these systems compared to their bulk counterpart [1]. For instance, by proper understanding of chemical processes taking place at the nanoscale it is possible to produce crystals with the desired shape and crystalline structure, as recently shown by Yang et al. [2] in the case of titanium dioxide (TiO_2), a compound largely used in heterogeneous catalysis. These authors were able to synthesise anatase nanoparticles with a large percentage of reactive facets. A particularly interesting form of nanostructure is the one that is composed of one dimensional (1D) chains, carbon nanotubes being probably the best known example [3,4] with practical applications already at hand [5]. These 1D nanostructures provide important building blocks for bottom-up approaches because of the multitude of interesting properties that they exhibit, such as their large anisotropy, which makes them ideal candidates for many applications, such as biosensors, logic circuits, field-effect transistors and non-volatile memory elements [6–10]. The discovery of carbon nanotubes had a tremendous impact on the field with new materials being discovered almost weekly. Many of the known 1D nanostructures involve semiconducting materials such as oxides [11] or phosphides [12] but metals have also attracted attention. In particular, noble metals such as Au have been the focus of intense research since they possess a lattice configuration comprising a single element, with a simple face-centred cubic (fcc) crystalline structure. Also Au nanowires promise applications in nanoelectronics, biomedicine, sensing and catalysis [13,14], especially after the discovery of quantum conductance through individual rows of suspended gold atoms [15]. The Au nanowires and other nanostructures [16–20] with special features such as conductance [21,22] and transport properties [23,24] have been reported and have also been the focus of several theoretical studies [17,25–33].

The synthesis of 1D Au nanostructures without the help of *ex situ* techniques, such as chemical etching, is desirable not only for fundamental research purposes but also for future nanodevice design and fabrication. For instance, it is likely that Au nanowires will be obtained through a self-assembly oriented attachment growth of suitable nanoparticles. This follows from the fact that nanoparticles may have a large surface-to-volume ratio and self-assembling reduces the surface energy thus stabilising the system [6]. Nevertheless, a precise knowledge of the formation mechanism at a microscopic level cannot be achieved easily without the help of theoretical analysis. Recently, the mechanism of Pd nanowires growth by a self-assembling process of nanoparticles of different

[†]This work is dedicated to the memory of José Antonio Mejias who left us without his company too early. Some of us had the privilege to share time with him, to discuss science and to walk through the streets of his beloved Sevilla. We miss your smile José Antonio but we keep your vital attitude towards life, never giving up!

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size has been reported [34]. In the present paper we extend the previous work to study structural and several relevant properties of 1D Au nanostructures built from Au_{79} building block, a cubo-octahedral nanoparticle of ~ 1.5 nm width exhibiting (111) and (100) facets. In particular, we report results for the self-assembly mechanism of Au nanowires grown by interconnecting Au_{79} particles either through the (111) or (100) facets.

2. Computational models and methods

The Au nanowires have been studied using the strategy described in a previous work concerning the self-assembling mechanism of Pd nanoparticles [34]. This makes use of the advantages of periodic approaches which allow one to model single molecules, clusters or periodic structures. Single particles have been modelled by placing them into a large enough supercell, with a vacuum space of 1 nm in all directions to avoid interactions between species in the neighbouring cells. Nanowires are modelled simply by reducing one of the three directions of the supercell while maintaining the vacuum width in the other two directions. The result is an infinite series on non-interacting nanowires all built from the same structure. This array of infinite nanowires is, of course, an artificial construct resulting from the 3D imposed in the calculation which in turn is a necessary requirement when using a plane wave basis set, which span the whole space with the periodicity imposed by the unit cell chosen. This requirement can be removed by making use of a localised basis set, although this is likely to introduce other problems due to the need to use large basis sets. The use of periodic symmetry also imposes the need to handle the necessary numerical integrations in the reciprocal space. However, the supercells used are sufficiently large to allow one to obtain meaningful results by considering the Γ-point only. The building blocks used to construct the nanowires are compact nanoparticles cut from the fcc metal bulk containing 79 atoms. These structures, exhibiting low-index planes, provided initial geometries for subsequent geometry optimisation [35–40]. For convenience, the centre of each particle has been placed at the unit cell centre.

The energy of the isolated particles and of the resulting nanowires has been obtained from density functional theory (DFT) based calculations using a plane wave basis set. The optimum structures have been obtained from total energy minimisation. The geometry optimisation and most of the calculations were carried out using the local density approach (LDA) form of the Voskow, Wilk and Nusair exchange-correlation potential [41], and the final energy obtained from a single point calculation using the Perdew–Wang (PW91) [42] implementation of the generalised gradient approach (GGA) to the exchange-correlation potential. For metals, this methodology provides structural results closer to the experiment and has been used extensively for determination of structural properties [38–40]. The effect of core electrons on the valence electron density was described by projector augmented wave (PAW) method [43,44], and the cut-off for the kinetic energy of the plane-wave basis set has been set to 315 eV which has been shown to be sufficient for the present purposes. A Gaussian smearing technique, with a 0.2 eV width, has been applied to enhance convergence but all energies presented below have been obtained by extrapolating to zero smearing (0 K). All minima on the potential energy surfaces were determined by relaxing the structure until self-consistent forces are lower than 0.01 eV/Å. In the optimisation geometry calculations all atoms were allowed to relax without imposing any constraint. This is at variance with the previous work where some calculations were carried out by fixing the atoms in the particle core and relaxing only those in the interacting facets [34]. All calculations have been carried out using the VASP code [44–46].

3. Results and discussion

The different nanostructures that can be formed by self-assembling nanoparticles are dictated by the possible surface connections between the nanoparticles. The nanoparticles described in the previous section expose only (111) or (111) and (001) facets depending on whether their shape is octahedral or cubo-octahedral. Consequently, the resulting superstructure, or in this case the resulting nanowire, grows along the [001] or [111] directions. In the first case, the particles assemble through the (001) particle facet [34] and, in the second case, the particles interact through (111) surfaces. From the existing literature concerning gold nanowires there are indications that the nanowire grows preferentially along the [111] direction [6,16,17]. In order to confirm this hypothesis, we study nanowires made by merging nanoparticles so as to contact their (001) facets either in a parallel way [34] or twisting one of the particles 45° along the axis perpendicular to (001) or by merging two parallel (111) facets. The resulting nanowires are labelled as NW-001, NW-tw-001 and NW-111, respectively (Figure 1). Note that in the case of the NW-tw-001 nanowire there are two Au_{79} nanoparticles in the unit cell.

The interaction between Au_{79} nanoparticles leads to nanowires with a diameter of the order of 1.5 nm which are similar to those obtained in experiments where the Au nanowires are grown in organic media [16]. This interaction is always attractive with a minimum in the total LDA energy with respect to the interparticle Au_n–Au_n separation. The equilibrium distance appears at distances between 0.22 and 0.26 nm depending on the type of nanowire (Figure 1). This is within the LDA interlayer distance of 0.25 nm meaning that the particles are in quite close contact. This is also in agreement with experimental results for the distance between atomic layers of a single crystalline nanowire grown in organic media along the [111]

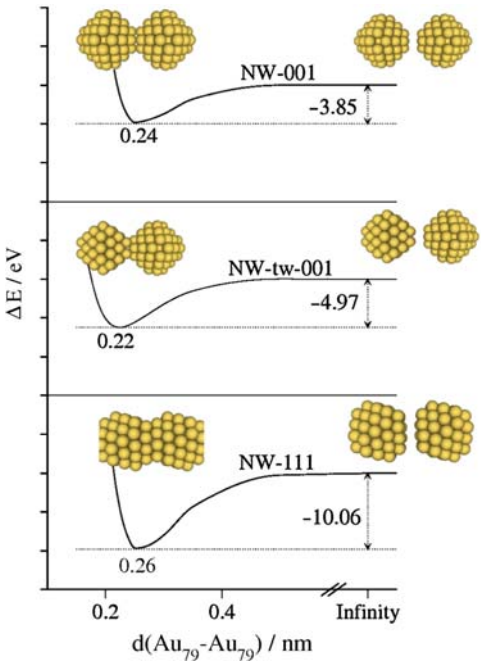

Figure 1. Potential energy curve for the interaction of an infinite chain of Au_{79} nanoparticles as a function of the d(Au_{79}–Au_{79}) distance, the minimum in the curve corresponds to the stable NW-100, NW-tw-100 and NW-111 (see text) nanowire formed. Numbers near arrows stand for the energy difference between optimised nanowires and isolates particles obtained at the GGA//LDA level.

direction. These nanowires have a diameter of the order of 1.6–2 nm and the interatomic distances estimated from the transmission electron miscroscopy (TEM) images is of the order of 0.23 nm [16,17]. This is not surprising, since it is well-known that GGA tends to overestimate intermetallic distances whereas LDA (VWN) reproduces the Au–Au distance surprisingly well [38]. Conversely, LDA is known to severely overestimate the interaction energies because of the self-interaction problem. This is, in part, rectified by the GGA functionals. Hence, we have estimated the interaction energies from single point PW91 calculations at the LDA optimised structure [38]: this is indicated as GGA//LDA. The energy gain in forming the NW-001 nanowire is of 3.85 eV per Au_{79} unit. For the NW-tw-001 nanowire the interaction is considerably stronger by 4.97 eV per Au_{79} unit as it could be anticipated from the shorter equilibrium distance between the interacting units (0.22 nm). Finally, for the NW-111 nanowire, which links the (111) surfaces of the interacting nanoparticles, the calculated interaction energy is still larger reaching a value of 10.06 eV per Au_{79} unit. The stabilisation energy arises from the increase in the atomic coordination or, alternatively, from the loss of atoms with low-coordination number. This energy may be distributed between the atoms in contact. For the NW-tw-001 nanowire, there are four atoms interacting per side but since the particle is also interacting with one particle per side the stabilisation comes from four atoms per particle. For the NW-tw-001, this leads to a stabilisation of 1.26 eV per contact atom. For the NW-111 nanowire one has 12 atoms in contact and the stabilisation energy per atom is now 0.84 eV per contact atom. The lower value for the interaction energy per contact atom in the NW-111 is easy to understand. Here, the surfaces in contact are the (111) which are the most stable ones and involve atoms with larger coordination number which favour the [111] direction of growth. Note that from the stabilisation energy per contact atom only one would tend to think that the nanowire will grow through the (100) facets. However, proper consideration of the number of interacting atoms in each facet clearly shows that growth through the [111] direction is preferred. Moreover, the fact that the interaction through (111) facets is considerably larger than the one through (100) surfaces is in agreement with experimental evidence that the growth of Au nanowires takes place preferentially along the [111] direction.

Next, we comment on the electronic structure of the Au nanowires as emerging from the density of states (DOS) plots. These are carried out at the GGA//LDA level. Nanoparticles made from metal atoms exhibit a semiconductor state because they are usually too small to develop a band structure similar to that of the bulk metal. Hence, Au nanoparticles exhibit a significant DOS near the Fermi level but with a small band gap (0.13 eV) that disconnects electrons to conduction band. Figure 2 shows the evolution of the DOS plots from the isolated Au_{79} nanoparticle to bulk Au passing through the NW-tw-001 and NW-111 nanowires, which are the most stable ones. The DOS in Figure 2 show that the number of states at the Fermi level decreases in going from the nanoparticle to the bulk with intermediate values for the nanowires. The DOS plots also show that the centre of the d-band, which is a good descriptor of the reactivity of transition metal structures

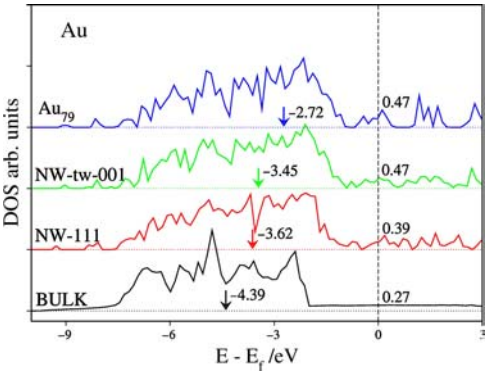

Figure 2. DOS of Au_{79} nanoparticle, NW-tw-001 and NW-111 nanowires and of bulk gold. Arrows indicate the centre of d-band and the numbers near Fermi level are the number of states at this level.

[47], becomes deeper when going from the nanoparticle to the bulk. This is consistent with the fact that the bulk Au is inert whereas Au nanoparticles have a particular catalytic activity. From the DOS plots one can also predict that the reactivity of the nanowires will be intermediate between the isolated nanoparticles and the bulk Au. This is also consistent with the previous work indicating that the extended Au surfaces with less-coordinated Au atoms are able to dissociate molecular hydrogen [48] but the same sites are not able to dissociate molecular oxygen which requires really small particles [49]. Further information about the electronic structure of the Au nanowires studied in the present work can be found from the Bader analysis of the electron density [50]. The Bader analysis has been carried out for the GGA density obtained at the LDA geometry (GGA//LDA) and it reveals several differences between NW-001 and NW-tw-001. In the first case, the connecting atoms have slightly less negative charges than the isolated particle whereas the atoms in the free (001) and (111) facets essentially maintain the charge as in the isolated particle. For the NW-tw-001 nanowire, the connecting atoms are more negatively charged than the corresponding ones in the isolated particle whereas the atoms in the free (001) facets have a more negative charge than in the isolated particle. Finally, for the NW-111 nanowire, the atoms in the (001) facets tend to be more negatively charged than the equivalent ones in the isolated nanoparticle. This analysis shows that the formation of the nanowire induces a significant electronic rearrangement, although the charges in the atoms are always rather small, never exceeding 0.15 eV.

The discussion so far has been centred on Au nanowires built from Au_{79} nanoparticles. At this point it is interesting to explore the influence of the particle size on the self-assembling mechanism and structural properties of the resulting nanowire. Figure 3 compares the potential energy curve for the formation of NW-tw-001 nanowires built from Au_{38} and Au_{79} both with cubo-octahedral shape. The interaction energy per building block unit is 5.38 and 4.97 eV for the nanowires built from Au_{38} and Au_{79} nanoparticles, respectively. Moreover, the minimum of the corresponding potential energy curves also appears at comparable distances. The close similarity between these values strongly suggests that the interaction is dominated by the atoms which are in close contact, four Au atoms in (001) facets in each case. These results strongly suggest that possible differences in the self-assembling process are likely to originate from structural differences between the building blocks, i.e. are of the interacting (001) facets rather than the size of the nanoparticles.

Finally, we consider the effect of changing the metal atom while maintaining the structural unit. To this end, Figure 4 reports the potential energy curves for NW-tw-001 nanowires built from Cu_{38}, Ag_{38} and Au_{38} nanoparticles. The three potential energy curves are also

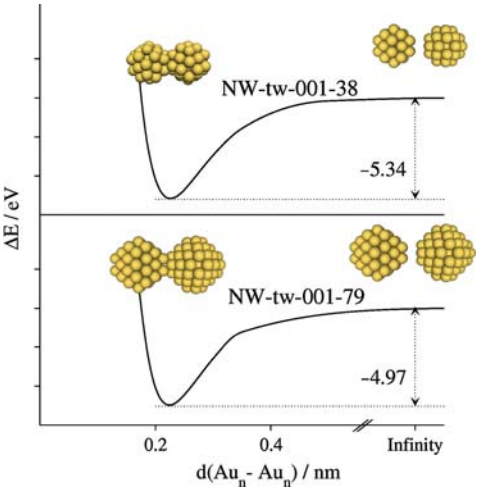

Figure 3. Potential energy curve for the interaction of an infinite chain of Au_{38} and Au_{79} nanoparticles resulting in NW-tw-001 nanowires as a function of the distance between the interacting particles. Numbers near arrows stand for the interaction energy per Au_n unit obtained at the GGA//LDA level. The optimum distance (in nm) is given by the numbers below the dotted line.

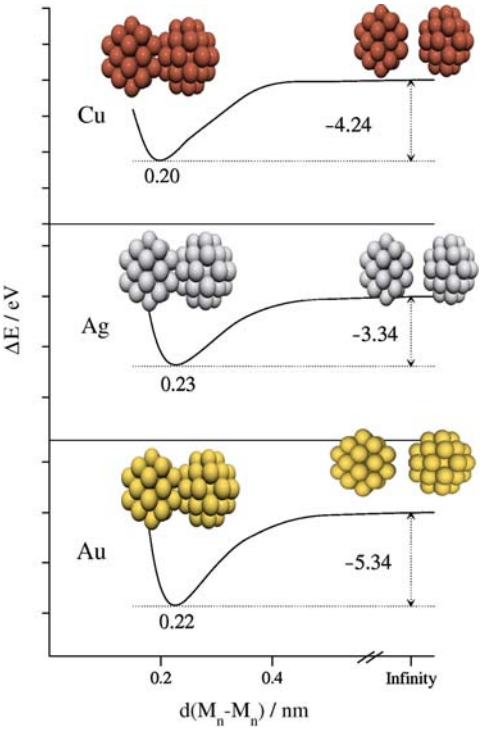

Figure 4. Potential energy curve for the interaction of an infinite chain of Cu_{38}, Ag_{38} and Au_{38} nanoparticles resulting in NW-tw-001 nanowires as a function of the distance between the interacting particles. Numbers near arrows stand for the interaction energy per unit obtained at the GGA//LDA level. The optimum distance (in nm) is given by the numbers below the dotted line.

very similar and the main difference is in the strength of the interaction, the largest value corresponding to the Au nanowire (5.34 eV per Au_{38} unit) and the smallest to the Ag nanowire (3.34 eV per Ag_{38} unit) with the Cu one lying in between (4.24 eV per Cu_{38} unit). Hence, one expects that Au nanowires are formed easily and that Ag nanowires are the most difficult to form. This is in agreement with the experimental results, indicating that Au nanowires are obtained in a rather simple way [16,17].

4. Conclusions

The self-assembling of Au nanoparticles into nanowires of different structure has been investigated by means of a periodic approach within DFT following the strategy of previous works on Pd nanowires [34]. The results reported in the present work have been obtained using a Au_{79} nanoparticle as building blocks. However, calculations carried out using a smaller nanoparticle (Au_{38}) as building blocks allow us to conclude that the self-assembling mechanism is general and that the process is dominated by the structural features of the interacting nanoparticles rather than by the particular size of the building block.

The interaction of the Au nanoparticles takes place preferentially along the [111] direction, this is through the (111) facets rather than through the (100) ones which dominate the formation of Pd nanowires. This preference for the growth through the [111] direction is in agreement with the experimental observation and allows us to further validate this computational approach to the study of metallic nanowires.

The electronic structure of the different Au nanowires built from Au_{79} is intermediate between that of the isolated nanoparticle and that of the bulk metal. This is perhaps not surprising but has important consequences for the chemistry of such nanostructures.

Finally, calculations carried out for nanowires built from Cu, Ag and Au nanoparticles containing 38 atoms reveal that the self-assembling mechanism is general but that the strength of the interaction is dictated by the chemical nature of the metal with Au being the coinage metal leading to stronger interactions between the nanoparticles.

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