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Growth and properties of Au nanowires*

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Abstract

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 a Au₇₉ nanoparticle as building block. The density functional calculations show that the interaction of the Au nanoparticles takes place preferentially along the [111] direction, in agreement with 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.

* 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!

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 titanium dioxide (TiO_2), a compound largely used in heterogeneous catalysis, where these authors have been able to synthesize anatase nanoparticles with a large percentage of reactive facets. A particularly interesting form of nanostructure is that 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]. Au nanowires and other nanostructures [16-20] with special features such as conductance [21,22] and transport properties [23,24] have been reported and also been at the focus of several theoretical studies [17,25-33].

The synthesis of one-dimensional 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 stabilizing 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 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

1
2 (111) or (100) facets.
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4 **Computational models and methods**

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6 The Au nanowires have been studied using the strategy described in a previous work concerning
7 the self assembling mechanism of Pd nanoparticles [34]. This makes use of the advantages of periodic
8 approaches which allows one to model single molecules, clusters or periodic structures. Single particles
9 have been modelled by placing them into a large enough supercell, with a vacuum space of 1 nm in all
10 directions to avoid interactions between species in the neighbouring cells. Nanowires are modelled
11 simply by reducing one of the three directions of the supercell while maintaining the vacuum width in
12 the other two directions. The result is an infinite series of non-interacting nanowires all built from the
13 same structural. This array of infinite nanowires is, of course, an artificial construct resulting from the
14 three-dimensional imposed in the calculation which in turn is a necessary requirement when using a
15 plane wave basis set, which span the whole space with the periodicity imposed by the unit cell chosen.
16 This requirement can be removed by making use of a localized basis set although this is likely to
17 introduce other problems due to the need to use large basis sets. The use of periodic symmetry also
18 imposes the need to handle the necessary numerical integrations in the reciprocal space. However, the
19 supercells used are sufficiently large to allow one to obtain meaningful results by considering the Γ -
20 point only. The building blocks used to construct the nanowires are compact nanoparticles cut from the
21 *fcc* metal bulk containing 79 atoms. These structures exhibiting low-index planes provided initial
22 geometries for subsequent geometry optimisation [35-40]. For convenience, the centre of each particle
23 has been placed at the unit cell centre.
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27 The energy of the isolated particles and of the resulting nanowires has been obtained from
28 density functional theory (DFT) based calculations using a plane wave basis set. The optimum
29 structures have been obtained from total energy minimization. The geometry optimization and most of
30 the calculations were carried out using the Local Density Approach (LDA) form of the exchange-
31 correlation potential. (VWN) [41], and the final energy obtained from a single point calculation using
32 the Perdew-Wang (PW91) [42] implementation of the Generalized Gradient Approach (GGA) to the
33 exchange-correlation potential. For metals, this methodology provides structural results closer to
34 experiment and has been used extensively for structure properties determination [38-40]. The effect of
35 core electrons on the valence electron density was described by projector augmented wave (PAW)
36 method [43,44], and the cut off for the kinetic energy of the plane-wave basis set has been set to 315 eV
37 which has been shown to be sufficient for the present purposes. A Gaussian smearing technique, with a
38 0.2 eV width, has been applied to enhance convergence but all energies presented below have been
39 obtained by extrapolating to zero smearing (0 K). All minima on the potential energy surfaces were
40 determined by relaxing the structure until self-consistent forces are lower than 0.01 eV/Å. In the
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1 optimization geometry calculations all atoms were allowed to relax without imposing any constraint.
 2 This is at variance of previous work where some calculations were carried out by fixing the atoms in the
 3 particle core and relaxing only those in the interacting facets [34]. All calculations have been carried out
 4 using the VASP code [44-46].
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9 **Results and discussion**

10 The different nanostructures that can be formed by self-assembling nanoparticles are dictated by
 11 the possible surface connections between the nanoparticles. The nanoparticles described in the previous
 12 section expose only (111) or (111) and (001) facets depending on whether their shape is octahedral or
 13 cubo-octahedral. Consequently, the resulting superstructure, or in this case the resulting nanowire,
 14 grows along the [001] or [111] directions. In the first case, the particles assemble through the (001)
 15 particle facet [34] and, in the second case, the particles interact through (111) surfaces. From the
 16 existing literature concerning gold nanowires there are indications that the nanowire grow preferentially
 17 along the [111] direction [6,16,17]. In order to confirm this hypothesis, we study nanowires made by
 18 merging nanoparticles so as to contact their (001) facets either in a parallel way [34] or twisting one of
 19 the particles 45° along the axis perpendicular to (001) or by merging two parallel (111) facets. The
 20 resulting nanowires are labelled as NW-001, NW-tw-001 and NW-111, respectively (Figure 1). Note
 21 that in the case of the NW-tw-001 nanowire there are two Au₇₉ nanoparticles in the unit cell.
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33 The interaction between Au₇₉ nanoparticles leads to nanowires with a diameter of the order of
 34 1.5 nm which are similar to those obtained in experiments where the Au nanowires are grown in organic
 35 media [16]. This interaction is always attractive with a minimum in the total LDA energy with respect to
 36 the interparticle Au_n-Au_n separation. The equilibrium distance appears at distances between 0.22 and
 37 0.26 nm depending on the type of nanowire (Figure 1). This is within the LDA interlayer distance of
 38 0.25 nm meaning that the particles are in quite close contact. This is also in agreement with
 39 experimental results for the distance between atomic layers of a single crystalline nanowire grown in
 40 organic media along the [111] direction. These nanowires have a diameter of the order of 1.6-2 nm and
 41 the interatomic distances estimated from the transmission electron microscopy (TEM) images is of 0.23
 42 nm [16,17]. This is not surprising since it is well-known that GGA tends to overestimate intermetallic
 43 distances whereas LDA (VWN) reproduces the Au-Au distance surprisingly well [38]. Conversely, LDA
 44 is known to severely overestimate the interaction energies because of the self-interaction problem. This
 45 is, in part, remedied by the GGA functionals. Hence, we have estimated the interaction energies from
 46 single point PW91 calculations at the LDA optimized structure [38], this is indicated as GGA//LDA.
 47 The energy gain in forming the NW-001 nanowire is of 3.85 eV per Au₇₉ unit. For the NW-tw-001
 48 nanowire the interaction is considerably stronger 4.97 eV per Au₇₉ unit as it could be anticipated from
 49 the shorter equilibrium distance between the interacting units (0.22 nm). Finally, for the NW-111
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1 nanowire, which links the (111) surfaces of the interacting nanoparticles, the calculated interaction
2 energy is still larger reaching a value of 10.06 eV per Au₇₉ unit. The stabilization energy arises from the
3 increase in atomic coordination or, alternatively, from the **loss** of atoms with low coordination number.
4 This energy may be distributed between atoms in contact. For the NW-tw-001 nanowire, there are four
5 atoms interacting per each side but since the particle is also interacting with one particle per side the
6 stabilization comes from four atoms per particle. For the NW-tw-001, this leads to a stabilization of 1.26
7 eV per contact atom. For the NW-111 nanowire one has twelve atoms in contact and the stabilization
8 energy per atom is now 0.84 **eV per contact atom**. The lower value for the interaction energy per contact
9 atom in the NW-111 is easy to understand. Here, the surfaces in contact are the (111) which are the most
10 stable ones and involve atoms with larger coordination number which favour the [111] direction of
11 grow. **Note that from the stabilization energy per contact atom only one would tend to think that the**
12 **nanowire will grow through the (100) facets. However, proper consideration of the number of**
13 **interacting atoms in each facet clearly shows that growth through the [111] direction is preferred.**
14 Moreover, the fact that the interaction through (111) facets is considerably larger than the one through
15 (100) surfaces is in agreement with experimental evidence that the growth of Au nanowires takes place
16 preferentially along the [111] direction.
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30 Next, we comment on the electronic structure of the Au nanowires as emerging from the density
31 of states (DOS) plots. These are carried out at the GGA/LDA level. Nanoparticles made from metal
32 atoms exhibit a semiconductor state because they are usually too small to develop a band structure
33 similar to that of the bulk metal. Hence, Au nanoparticles exhibit a significant density of states near the
34 Fermi level but with a small band gap (0.13 eV) that disconnect electrons to conduction band. Figure 2
35 shows the evolution of the DOS plots from the isolated Au₇₉ nanoparticle to bulk Au passing through the
36 NW-tw-001 and NW-111 nanowires, which are the most stable ones. The DOS in Figure 2 show that the
37 number of states at the Fermi level decreases in going from the nanoparticle to the bulk with
38 intermediate values for the nanowires. The DOS plots also show that the center of the d-band; which is a
39 good descriptor of the reactivity of transition metal structures [47], becomes deeper when going from
40 the nanoparticle to the bulk. This is consistent with the fact that bulk Au is inert whereas Au
41 nanoparticles have a particular catalytic activity. From the DOS plots one can also predict that the
42 reactivity of the nanowires will be intermediate between isolated nanoparticles and bulk Au. This is also
43 consistent with previous work indicating extended Au surfaces with low coordinated Au atoms are able
44 to dissociate molecular hydrogen [48] but the same sites are not able to dissociate molecular oxygen
45 which requires really small particles [49]. Further information about the electronic structure of the Au
46 nanowires studied in the present work can be found from the Bader analysis of the electron density [50].
47 The Bader analysis has been carried out for the GGA density obtained at the LDA geometry
48 (GGA/LDA). The Bader analysis reveals several differences between NW-001 and NW-tw-001. In the
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2 first case, the connecting atoms have slightly less **negative** charges than the isolated particle whereas the
3 atoms in the free (001) and (111) facets essentially maintain the charge as in the isolated particle. For the
4 NW-tw-001 nanowire, the connecting atoms are more negatively charged than the corresponding ones in
5 the isolated particle whereas the atoms in the free (001) facets have a more negative charge than in the
6 isolated particle. Finally, for the NW-111 nanowire, the atoms in the (001) facets tend to be more
7 negatively charged than the equivalent ones in the isolated nanoparticle. This analysis shows that the
8 formation of the nanowire induces a significant electronic rearrangement although the charges in the
9 atoms are always rather small, never exceeding 0.15e.

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11 The discussion so far has been centered on Au nanowires built from Au₇₉ nanoparticles. At this
12 point it is interesting to explore the influence of the particle size on the self assembling mechanism and
13 structural properties of the resulting nanowire. Figure 3 compares the potential energy curve for the
14 formation of NW-tw-001 nanowires built from Au₃₈ and Au₇₉ both with cubo-octahedral shape. The
15 interaction energy per building block unit is 5.38 and 4.97 eV for the nanowires built from Au₃₈ and
16 Au₇₉ nanoparticles, respectively. Moreover, the minimum of the corresponding potential energy curves
17 also appears at comparable distances. The close similarity between these values strongly suggest that the
18 interaction is dominated by the atoms which are in close contact, four Au atoms in (001) facets in each
19 case. This results strongly suggest that possible differences in the self-assembling process are likely to
20 originate from structural differences between the building blocks, i.e. are of the interacting (001) facets
21 rather than size of the nanoparticle.

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23 Finally, we consider the effect of changing the metal atom while maintaining the structural unit.
24 To this end, Figure 4 reports the potential energy curves for NW-tw-001 nanowires built from Cu₃₈, Ag₃₈
25 and Au₃₈ nanoparticles. The three potential energy curves are also very similar and the main difference
26 is in the strength of the interaction, the largest value corresponding to the Au nanowire (5.34 eV per
27 Au₃₈ unit) and the smallest to the Ag nanowire (3.34 eV per Ag₃₈ unit) with the Cu one lying in between
28 (4.24 eV per Cu₃₈ unit). Hence, one expects that Au nanowires are formed easily and that Ag nanowires
29 are the most difficult to form. This is in agreement with experimental results indicating that Au
30 nanowires are obtained in a rather simple way [16, 17].

31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 **Conclusions**

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53 The self assembling of Au nanoparticles into nanowires of different structure has been
54 investigated by means of a periodic approach within density functional theory following the strategy of
55 previous work on Pd nanowires [34]. The results reported in the present work have been obtained using
56 a Au₇₉ nanoparticle as building block. However, calculations carried out using a smaller nanoparticle
57 (Au₃₈) as building block allows us to conclude that the self assembling mechanism is general and that
58 the process is dominated by the structural features of the interacting nanoparticles rather than by the
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2 particular size of the building block.

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4 The interaction of the Au nanoparticles takes place preferentially along the [111] direction, this is
5 through the (111) facets rather than through the (100) ones which dominate the formation of Pd
6 nanowires. This preference for the growth through the [111] direction is in agreement with experimental
7 observation and allows us to further validate this computational approach to the study of metallic
8 nanowires.
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12 The electronic structure of the different Au nanowires built from Au₇₉ is intermediate between
13 that of the isolated nanoparticle and that of the bulk metal. This is perhaps not surprising but has
14 important consequences for the chemistry of such nanostructures.
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18 Finally, calculations carried out for nanowires built from Cu, Ag and Au nanoparticles containing
19 38 atoms reveal that the self assembling mechanism is general but that the strength of the interaction is
20 dictated by the chemical nature of the metal with Au being the coinage metal leading to stronger
21 interaction between the nanoparticles.
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26 27 **Acknowledgements**

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Captions for figures

Figure 1: Potential energy curve for the interaction of an infinite chain of Au₇₉ nanoparticles as a function of the d(Au₇₉-Au₇₉) 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 optimized nanowires and isolates particles obtained at the GGA//LDA level.

Figure 2: DOS of Au₇₉ nanoparticle, NW-tw-001 and NW-111 nanowires and of bulk gold. Arrows indicate the center of d-band and the numbers near Fermi level are the number of states at this level.

Figure 3: Potential energy curve for the interaction of an infinite chain of Au₃₈ and Au₇₉ 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 Cu₃₈, Ag₃₈ and Au₃₈ 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.

Figure 1

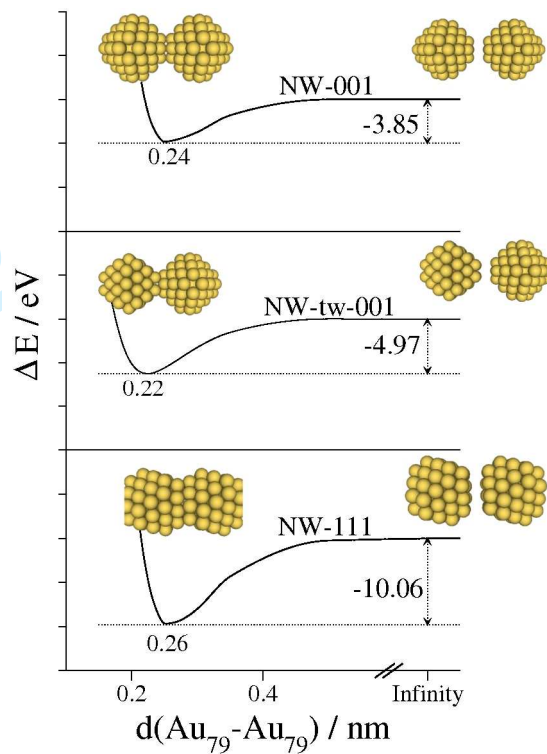


Figure 2

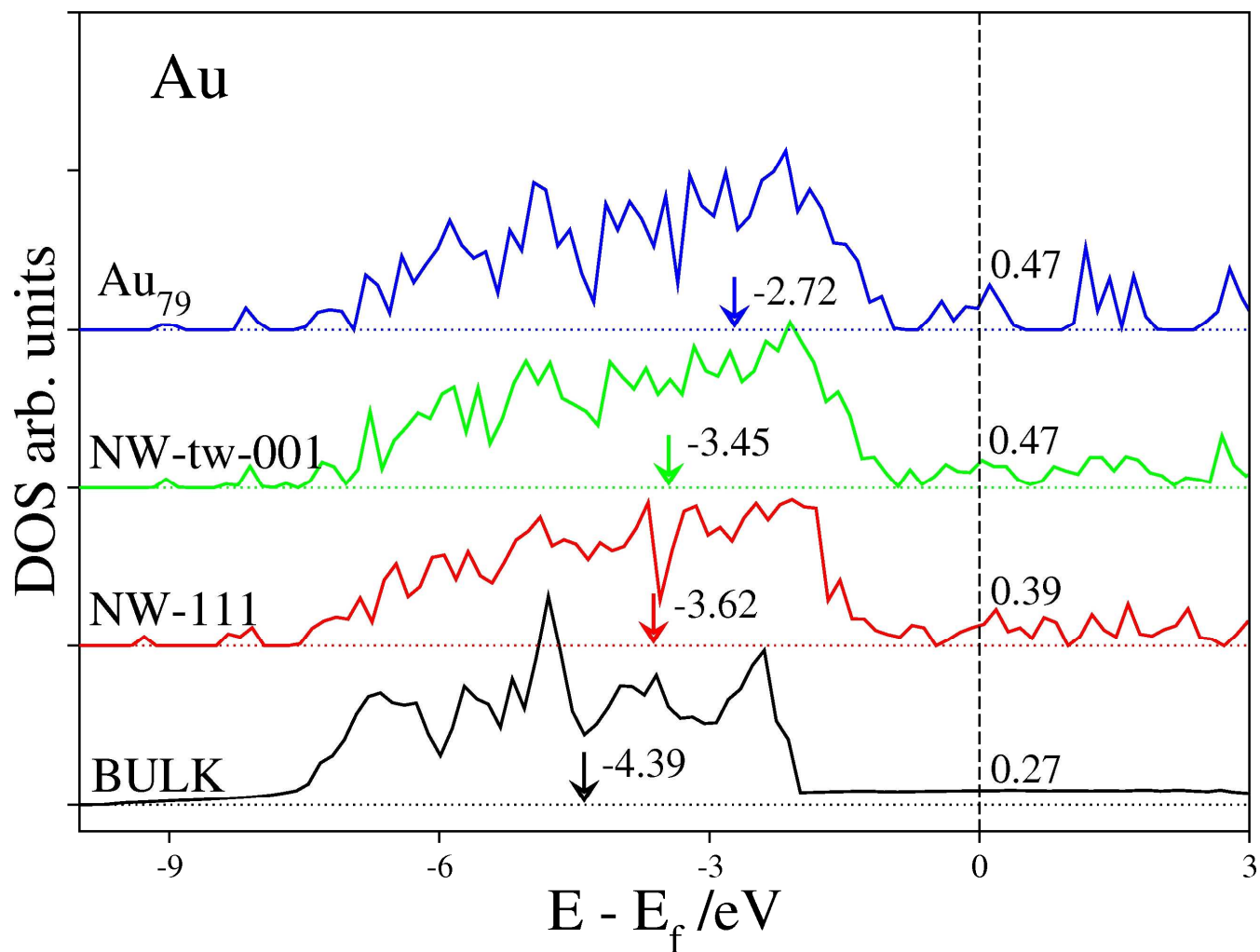


Figure 3

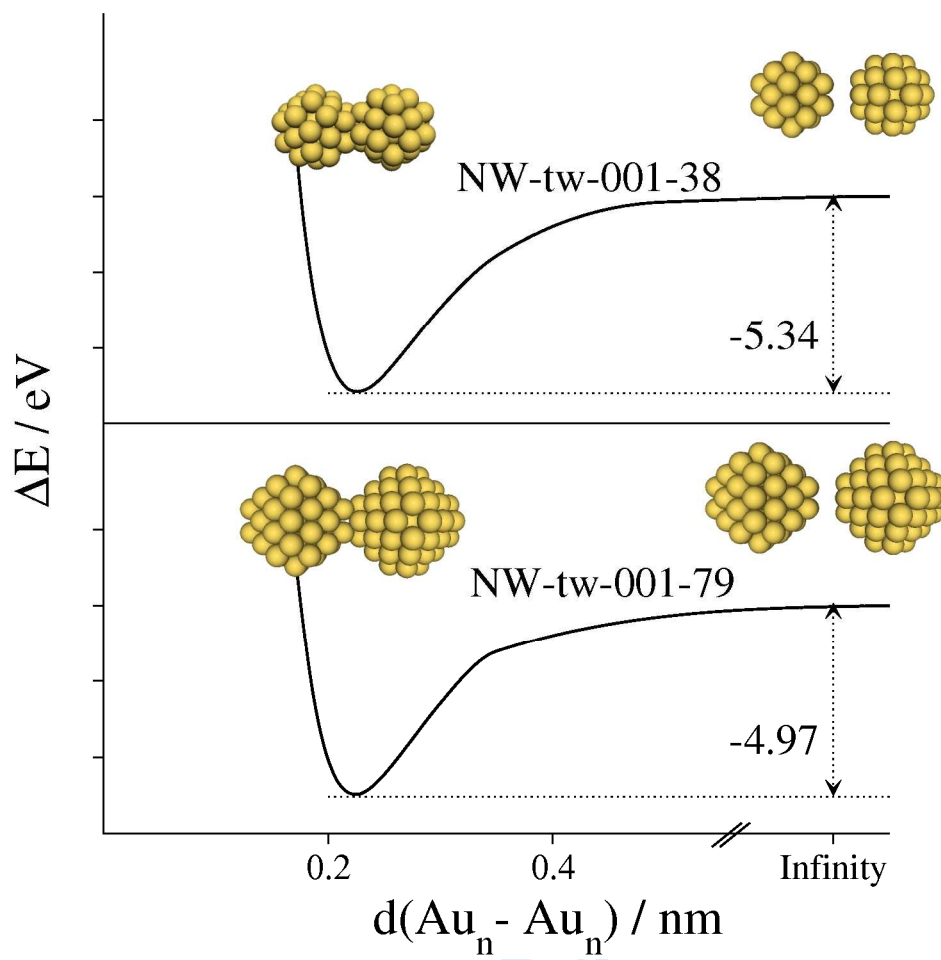
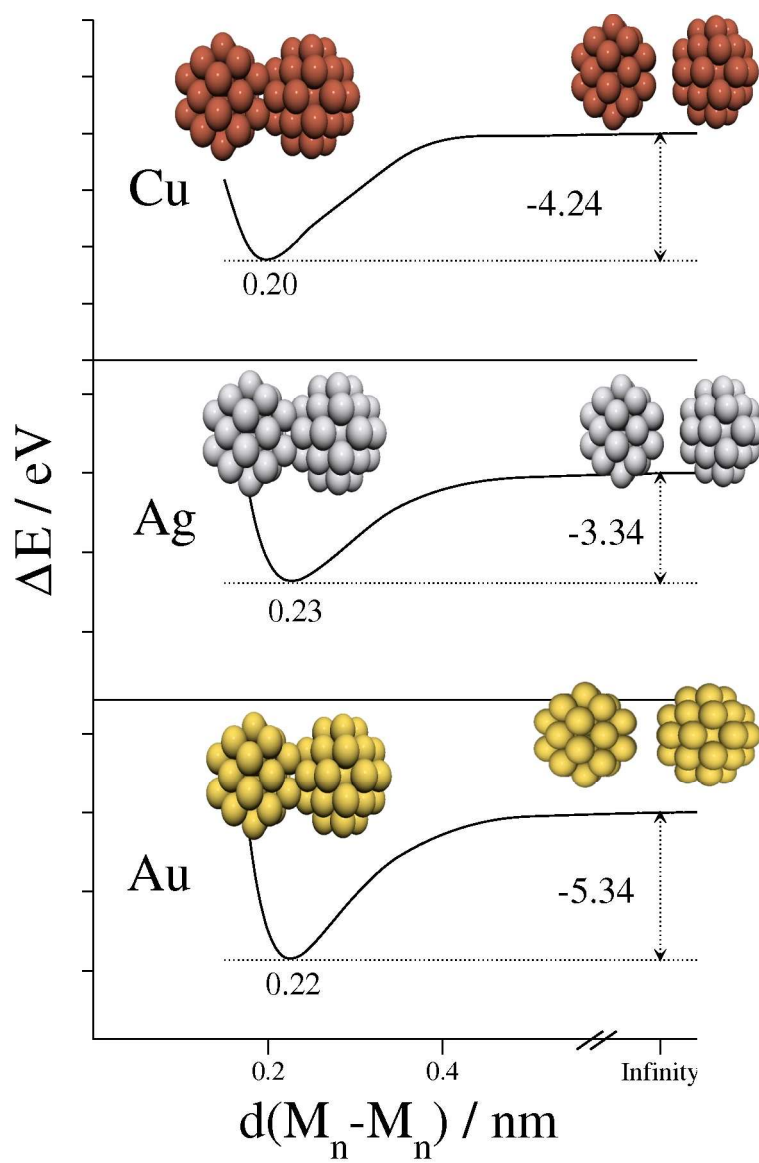


Figure 4



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