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Interaction of Au nanowires with impurities

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Abstract. We report the results of our first-principles studies of the interaction between an infinite monoatomic gold nanowire and a carbon-monoxide molecule. We show that the gold monoatomic nanowire is capable of absorbing the CO molecule at the distances of about 1.8 Å and forms a bond with the carbon atom. Further, we find that dissociation of the CO molecule as the source of gold nanowire contamination with carbon, which is widely discussed in literature as the possible reason for the striking stability of gold nanowires under stretching, is thermodynamically unfavored.

PACS. 68.65.La Quantum wires – 73.20.Hb Impurity and defect levels; energy states of adsorbed species – 71.55.-i Impurity and defect levels

For the past decade gold monoatomic wires have been a subject of many experimental [1–3] and theoretical [4–8] studies. One of the most striking and attractive issue for researchers is the ability of a gold monoatomic nanowire to remain stable under stretching to interatomic distances much larger than the average interatomic distance in the bulk gold [1,2]. Stability of the gold nanowires can be influenced by different factors, and, in particular, by impurities [9]. Contamination with light elements, such as hydrogen, oxygen, and carbon may crucially affect stability and conductance of gold monoatomic nanowires but cannot be easily detected in regular experiments. However reactivity of gold nanostructures [10], particularly nanowires [11], with light elements is currently intensively discussed (see, for instance, Ref. [12,13]). Carbon has been pointed out as an element whose presence may explain in a reasonable way some specific properties of gold nanowires [14–17] such as extremely large interatomic distances, up to 3.6 Å and unusual transport properties [21]. Thus it appears to be of interest to study possible ways of formation of the carbon-doped monoatomic gold nanowires in more detail. A deeper understanding of the mechanisms of contamination of the gold nanowires may lead to a possibility to tune their properties by consistent doping of gold [4,5,14,18] and may serve as a tool for future design of nanodevices [19]. For instance, impurities of hydrogen and oxygen could be absorbed from the atmosphere (for instance, hydrogen is an element present even in very high vacuum [20]). Carbon, the most common impurity, can be possibly transfered into the nanowires from a substrate [16]. Another possibility of carbon transportation into the gold nanowires is the absorption of atoms of volatile carbon oxides, which are always present in the atmosphere and are likely to participate in contamination during formation of a a gold nanowire.

In the present work we study by means of first-principles calculations the behavior and thermodynamical stability of a CO molecule in the vicinity of an infinite gold monoatomic chain.

Total energy calculations were performed in the framework of the frozen core all-electron Projector Augmented Wave (PAW) method [22], as implemented in the program VASP [23]. It was shown that this method gives realistic results for different gold systems, such as bulk, surfaces and nanoparticles [4,24–26]. Exchange and correlation effects were treated in the framework of the generalized gradient approximation (GGA) [27].

The infinite monoatomic nanowire have modeled with a three-dimensional periodic tetragonal supercell with the linear chain placed along the c-axis [4]. The unit cell contains 4 atoms of Au and atoms of C and O. Periodic images in the x-y plane are separated by a large distance of 14 Å, making interaction between them and their periodic images negligible. The CO molecule is settled in the vicinity of the gold chain. All structural configurations of the CO-Au complex are relaxed. During the relaxation procedure Au atoms are shifted along the propogating c-axis, depending on the configuration and distance of the CO molecule from the gold chain, but the gold chain holds its linear form.

Integration other the Brillouin zone was performed on a $1\times1\times14$ k-point mesh. Plane wave cut-off of 500 eV was

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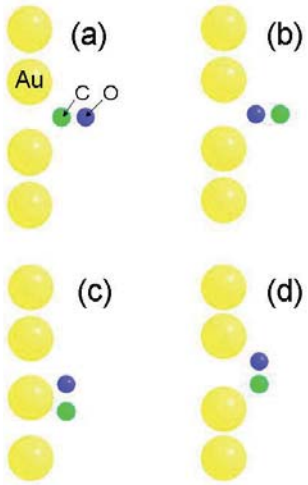

Fig. 1. Structural configurations of the CO-Au complex.

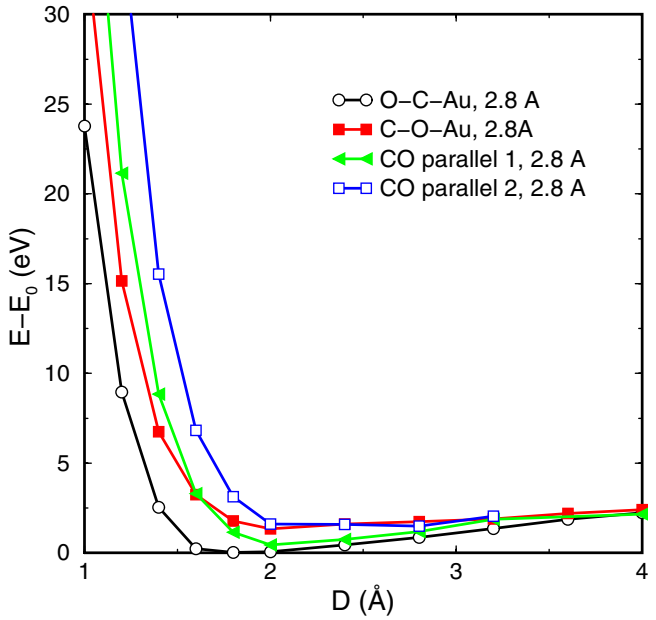

Fig. 2. (Color online) Energy curves for the CO molecule placed at different distances from gold nanowires. Total energies are given for four orientations: perpendicular to the main nanowire axis ((a) C close to the wire and (b) O close to the wire) and parallel ((c) Au atom between C and O and (d) CO molecule between two Au atoms). The average Au-Au distance is 2.8 Å. The total energy for the equilibrium average Au-Au distance of (a) O-C-O configurations (E_0) is taken as reference. D - the distance from the Au-chain to a closest atom of the CO molecule.

used. The relaxation procedure were carried out according to the Methfessel-Paxton scheme [28]. All necessary convergence tests were performed.

In order to find the equilibrium configuration of the gold monoatomic nanowire doped with a CO molecule, we considered configurations with different orientation of the CO molecule regarding the *c*-axis of the gold chain (see Fig. 1) and varied both the distance of the molecule from the gold chain and the average interatomic Au-Au distances in the chain. The first (a) and the second (b) cases describe the CO molecule perpendicular to the *c*-axis of the gold chain, in such a way that either carbon or oxygen atom is situated closer to the gold atoms. In the third and fourth cases the CO molecule is parallel to the main axis, C and O atoms are placed close to one Au atom (c) or to a pair of gold atoms (d) All considered configurations were subjected to structural relaxations leading to minimization of the Hellmann-Feynmann forces. When the CO molecule or separate C and O atoms are placed in the vicinity of the Au chain the adjacent Au atoms move aside along the *c*-axis of the Au chain. Herewith the Au chain keeps almost linear structure. The equilibrium average Au-Au interatomic distances found for all four orientations of the CO-Au complex are close to ∼2.8 Å. In Figure 2 we show energies of the CO-Au-nanowires as a function of the distance of the CO molecule from the Au chain whose average Au-Au interatomic distance corresponds to the equilibrium value ∼2.8 Å. Energy curves of all configurations have minima when the CO separation from the gold nanowire is of about 1.8 Å for the O-C-Au configuration and 2 Å for the C-O-Au configuration. Consequently the binding energy of the CO-Au complex is negative and there is a definite attraction of the CO molecules by the gold nanowire. Energy of the system is extremely sensitive to the position of the CO molecule regarding the gold chain. The most stable configuration corresponds to the case when the line connecting C and O atoms is perpendicular to the gold chain with the carbon atom staying closer to the gold chain. For this configuration the CO molecule is attracted by the gold chain to the closest distance. This configuration is energetically more favorable than a structure with the CO molecule rotated in such a way, that C and O atoms are exchanged, with the relative difference in total energy of ∼1.5 eV. It actually means that the carbon atoms form a bond with the gold chain and on the contrary, the oxygen atom is repelled by the gold chain. Stability of the particular orientation is conditioned by to the balance between the competitive tendencies of the gold chain to absorb the C atom and to repeal the O atom, which at the same time have a strong bond with carbon. The stable configuration of the gold chain is very similar to the configuration found very recently in the pure gold monoatomic nanowires doped with a single carbon atom [17]. The CO molecule has the C atom bonded with two Au atoms at nearly equal distances and the O atom, standing out of the gold nanowire (see Fig. 2).

In order to test whether dissociation of the CO molecule in the neighborhood of the gold chain is possible, we performed calculations of the O-C-Au configuration with continuous separation of the O from the C-Au complex. The Au-Au interatomic distances were also varied. Particularly, we selected for the analysis the interatomic Au-Au distances equal to 2.8 Å, 3.0 Å, and 3.2 Å,

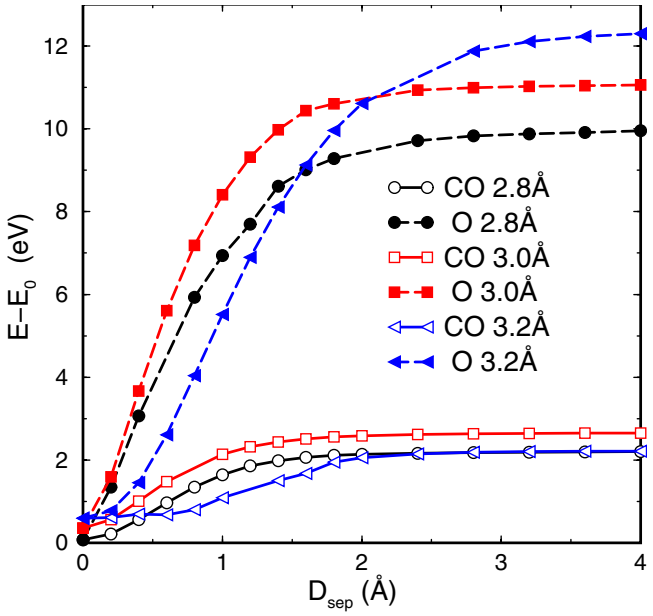

Fig. 3. (Color online) Energy curves for monoatomic Au wires doped with the CO molecule. Energies were calculated for different separation distance of the CO molecule from their equilibrium position in the CO-Au complex and for the oxygen atom extraction to different separations from its equilibrium position in the O-C-Au complex. Three sets are given for three different average Au-Au distances, 2.8 Å, 3.0 Å, and 3.2 Å, respectively. The energies for the equilibrium average Au-Au distance 2.8 Å (E_0) is taken as reference for each configuration.

corresponding to qualitatively different cases of stretching of the pure gold nanowire, namely to its nearly equilibrium, stretched, and disrupted (dimerized) configurations, respectively. In first two cases it was found that the molecule tended to make a bond with the nanowire, though the molecule tried to position itself in such a way that the oxygen atom is most distant from the gold atoms. The last case, 3.2 Å, corresponds to a stage of disrupting when the gold chain is already broken. In this case we observed a stable bond between gold and carbon atoms, while the next bond, between gold and oxygen atoms, was broken. In Figure 3 we compared energies of the continuous separation of the O atom with the energies of the separation of the whole CO molecule from the equilibrium position of the O-C-Au complex. When the whole CO molecule is separated (solid curves) the total energy increases until it reaches an energy plateau, when the Au chain and the CO molecule do not interact with each other. However the dissociation of only the O atom (long-dashed curves) is energetically much less favored (by about 7.5–10 eV depending on the average Au-Au interatomic distance). Therefore bonding between atoms in the CO molecule is much stronger than between the carbon atom and the gold nanowire.

In conclusion we have shown that a gold nanowire is able to absorb impurities of CO, based on the fact that the total energy of the Au-CO systems has minima when the CO molecule is placed at a distance of about 1.8 Å from the Au nanowire and the binding energy of the CO-molecule absorption by the gold nanowire is negative. Our results demonstrate that the gold nanowire attracts carbon atom, whereas the oxygen atom is repeled. Even though to draw a robust conclusion the effects of kinetics are to be taken into account, it is apparent that the dissociation of the CO molecule in the vicinity of the gold nanowire is not favored and, consequently, absorption of carbon from the carbon-monoxide present in the atmosphere as a source of impurities in the gold nanowire is hardly possible. So we suggest that it is most probable that the gold nanowires are obligated to carbon-containing substrates for the contamination.

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