Adsorption-induced restructuring of gold nanochains

S. R. Bahn, N. Lopez, J. K. Nørskov, and K. W. Jacobsen

Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark,
DK-2800 Kongens Lyngby, Denmark

The chemical properties of single-atomic chains of gold atoms are investigated using density functional calculations. The nanochains are shown to be unusually chemically active with strong chemisorption of oxygen atoms and carbon monoxide. The chemisorption energies vary significantly with the strain/stress conditions for the chain. Oxygen atoms are found to energetically prefer to get incorporated into a chain forming a new type of gold-oxygen nanochain with a conductance of one quantum unit. We suggest that the long bond lengths observed in electron microscopy investigations of gold chains can be due to oxygen incorporation.

PACS number(s): 68.65.La, 61.46.+w, 62.25.+g

It has recently been shown that it is possible to form metallic wires consisting of a single-atom chain of gold atoms. This was first seen in molecular dynamics simulations[1,2] and subsequently found using different experimental approaches.[3,4] Several aspects of the mechanical, electrical, and chemical properties of such chains have been addressed both experimentally[3–6] and theoretically[2,6–12] and some of their properties are now well understood. However, one puzzle remains: the gold-gold bond lengths observed by electron microscopy[4,5] can be as long as 4 Å and are therefore in a regime where electronic structure calculations indicate the bonds to be unstable.[10] For comparison a bulk equilibrium gold-gold bond is only 2.9 Å. Initially the experiments using mechanically controllable break junctions seemed also to indicate very long gold-gold bonds[3] but later recalibrations of the distance measurements have brought the measurements in better agreement with theoretical expectations.[13]

Several possible explanations for the observed long bond lengths have been discussed including peculiar electronic correlation effects,[10] large van der Waals forces in the chains,[10] or special spinning zigzag chain geometries which in some cases could effectively render some of the gold atoms "invisible" in electron microscopy.[8]

In the following we discuss another possibility. On the basis of extensive density-functional calculations, we show that the bonding of carbon monoxide and oxygen to gold chains is unusually strong. In the case of oxygen, very stable oxygen-gold chains can be formed, and we suggest that these may give the long gold-gold distances observed experimentally. The calculations suggest that this may even happen without a change in the conductance of the chain: the resulting gold-oxygen chain is found to have a single band crossing the Fermi level indicating a conductance of one quantum unit, $2e^2/h$. A side result of these calculations is that gold chains are much more chemically active than other gold structures, suggesting that the chains may constitute a new kind of chemically active gold.

Gold is usually considered very "noble," i.e., chemically inert.[14] It is, for example, not energetically favorable for oxygen molecules to adsorb dissociatively on a gold surface.[15–17] However, it has become clear over the last years that the situation is very different for small particles of gold which cannot only be chemically active, but are even considered catalytic materials.[18,19] Several factors may play a role for the increased reactivity of small gold clusters. Small clusters have a large number of defects like steps and kinks which are more reactive than terrace atoms.[16] Furthermore the presence of a tensile strain—which in the case of the gold clusters could come from the interface between the clusters and a supporting material—is also known to increase the chemical activity.[16] Finally, for very small particles it is possible that direct quantum size effects could play a role for the reactivity.[19] All of these ingredients (low-coordinated atoms, strain, and quantum size effects) can be expected to be present to an even larger extent in gold chains: the coordination number in a perfect chain is as low as two, the chains are produced by mechanical stretching with significant strains as a result, and the observed quantized conductance is a clear demonstration of a quantum size effect. Gold chains can therefore be expected to have radically different chemical properties from that of flat gold surfaces.

The chemical properties of gold nanowires have been investigated by Hakkinen *et al.*[7] in a density functional study of a suspended four-atom gold chain interacting with a methylthiol molecule. The chain is initially in a stretched configuration where the two central atoms have dimerized and where the conductance is significantly below one quantum unit. The methylthiol is found to chemisorb on the chain and raise the conductance. Experimentally, the effect of adsorbates on the conductance quantization has been investigated for gold nanocontacts.[20]

In Fig. 1 we show the results of self-consistent density-functional theory (DFT) calculations on a gold chain with and without interaction with oxygen atoms and carbon monoxide molecules. The calculations have been performed with a DFT code[21] utilizing nonlocal ultrasoft pseudopotentials[22] and an expansion of the wave functions in plane waves up to a kinetic energy of 340 eV (400 eV, where oxygen is considered).[23] The PW91-GGA approximation to the exchange-correlation energy[24] is used. Periodic boundary conditions are employed and unless otherwise stated the unit cell contains two gold atoms with a sampling of the first Brillouin zone in eight **k**-points along the chain. With two atoms in the unit cell possible Peierl's distortions are allowed. The distance between neighboring chains is 11.7 Å.
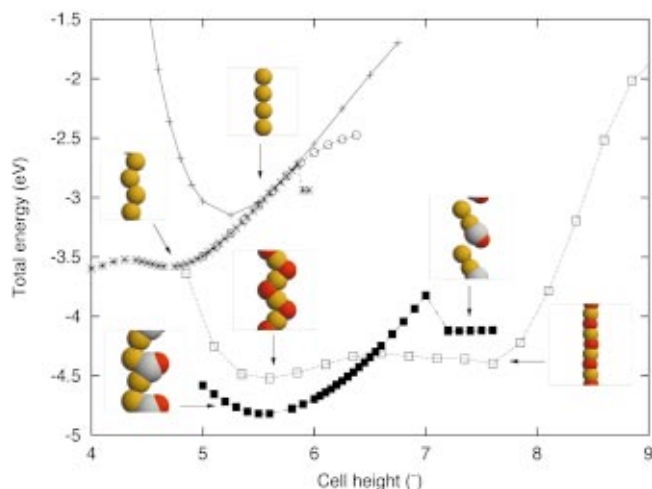
FIG. 1. (Color) Calculated binding energy curves for different chain structures as a function of unit cell height. The zero point of the energy is chosen corresponding to free, atomic gold atoms and the free molecules. The crosses are for a straight gold chain with atoms positioned equidistantly. The circles are for a chain with two gold atoms in the unit cell. The stars indicate a four-atom unit cell (with the length of the cell normalized to a two-atom cell). The filled squares are for a chain with CO coverage of 1/2 and the open squares for an O coverage of one. Selected atomic chain structures with gold (yellow), oxygen (red), and carbon (white) are shown as insets.

The binding energy curves shown in Fig. 1 are obtained by varying the height of the unit cell and relaxing all atomic positions until the forces vanish.

We have studied a number of different chain structures in Fig. 1. Focusing first on the case of pure gold, we have considered a chain which is constrained to be in a linear configuration with the atoms equidistantly spaced. The value of the cell height at the minimum point thus corresponds to an equilibrium nearest-neighbor-bond length of 2.6 Å in agreement with earlier calculations.[10,6] The inflection point of the binding energy curve appears at a bond length of 3.1 Å. This is an important length for chain stability. In a classical nearest-neighbor model for the bonding, a chain which is stretched beyond the inflection point will dimerize or break.

Next we consider a pure gold chain without any restrictions on the geometry (beyond the one imposed by a two-atom unit cell with periodic boundary conditions). At the minimum point for a cell height of 4.7 Å the chain exhibits a zigzag geometry,[8] and close to the inflection point of the straight-chain curve the zigzag chain is straightened out and a dimerization sets in. At the same time the energy curve begins to deviate from the equidistant chain. The result of a calculation with a four-atom unit cell closely follows the two-atom calculation until close to the inflection point where the four-atom chain breaks discontinuously.

Turning to the chemical properties, carbon monoxide readily chemisorbs on the chain. The chemisorption energy ΔE_{chem} depends on how much the chain is stretched and can therefore be defined as a function of the height d of a unit cell containing two gold atoms. In terms of the total energies
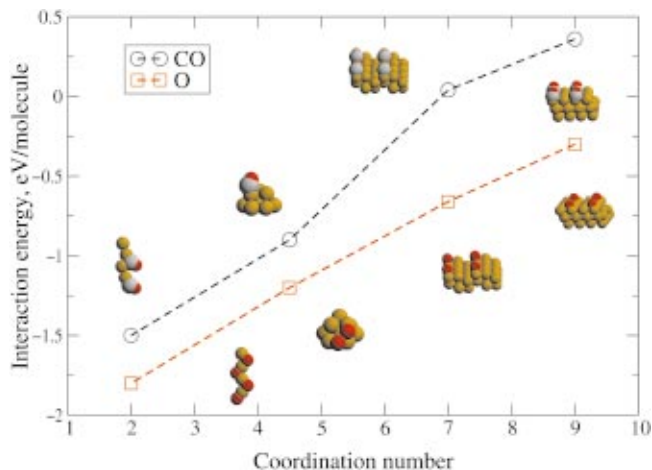

FIG. 2. (Color) Interaction energy in eV per molecule versus coordination number for gold atoms in different systems. Energies have been calculated with respect to the substrate and the gas phase molecule. Systems considered, ordered from higher to lower coordination number, are plain (111) and stepped (211) surfaces, aggregates containing ten gold atoms in two layers, and gold chains. For the chains a unit cell contains two gold atoms and one CO molecule or two O atoms. The height of the unit cell is 5.6 Å corresponding to the strongest binding configuration with CO or O chemisorbed. The calculated relaxed atomic structures are shown as insets with gold atoms in yellow, oxygen atoms in red, and carbon atoms in white.

of the chain with adsorbate and the pure chain and isolated adsorbate molecule, it is

$$\Delta E_{chem} = E_{chain+adsorbate}(d) - E_{chain}(d) - E_{adsorbate}. \tag{1}$$

The chemisorption energy of CO varies between -1 and -2 eV, depending on how much the chain is stretched. Au surfaces only bind CO very weakly,[16] and the strong bonding we find for the chains is typical of surfaces of much more reactive metals like Pt or Ni.[25] The chemisorption energy strongly depends on the height of the unit cell d: for a unit cell height given by the equilibrium zigzag structure of the pure gold chain the chemisorption energy is of the order -1
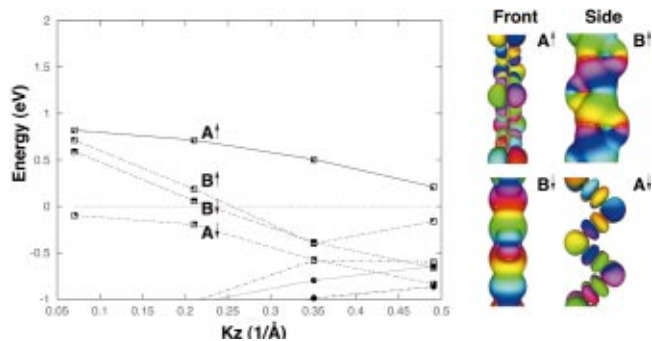

FIG. 3. (Color) Band structure diagram for the gold-oxygen chain at a cell height of 5.6 Å. The wave functions corresponding to the four bands indicated in the figure are shown to the right as iso-surfaces with the color indicating the phase of the wave function.

eV. However, as the chain is stretched the chemisorption energy increases significantly. At a cell height of 5.6 Å the chemisorption energy is almost −2 eV. Futhermore, the presence of CO leads to a longer equilibrium length and also an increased range of stability: in the presence of CO the chain can be stretched up to a length of 7 Å (per two gold atoms) before the breaking sets in. The chemisorption of CO leads to an opening of a gap in the electronic spectrum and the conductance is therefore expected to be much reduced.

The adsorption of atomic oxygen is even more peculiar, c.f. Fig. 1. The chemisorption energy is of the order −1.5 eV per two oxygen atoms relative to the energy of the free molecule, and the resulting structure can best be described as a gold-oxygen chain (see insets in Fig. 1) with the oxygen atoms in alternating positions on both sides of a straight string of gold atoms. Again the adsorption is much stronger than found previously for chemisorption on flat and stepped surfaces and for an 18-atom cluster.[16]

We suggest that the large reactivity of the gold chains is related to the fact that the gold atoms in the chain have a metal coordination number of two. In Fig. 2, we show the adsorption energy of atomic oxygen and of CO on different gold structures as a function of the gold coordination number N_{coor}. We include here gold surfaces ($N_{coor}=9$) and stepped gold surfaces ($N_{coor}=7$) from the calculations of Mavrikakis *et al.*[16] together with our calculated adsorption energies on the Au wires ($N_{coor}=2$). We have also included results for a Au$_{10}$ cluster ($N_{coor}=4$ or 5) to show results for an intermediate coordination number. There is a clear correlation with the coordination number such that the lower N_{coor} is, the stronger the bond. Such correlations are related to changes in the electronic structure, particularly the energy of the metal d-states.[25]

The gold-oxygen chain is very flexible over a large range of cell heights (from 5–8 Å) in which the chain can adjust the gold-oxygen-gold bonding angle with only a small change in energy, and it is clear that the chains are perfectly stable for gold-gold distances of more than 3.8 Å. The force constant of the chain at the minimum energy point is for a unit cell with two gold atoms determined to 1.3 eV/Å^2. Beyond a cell height of 8 Å the energy curve rises steeply indicating that significantly larger forces are needed to break a gold-oxygen chain than a pure gold chain. Also the absolute value of the binding energy shows the gold-oxygen chain to be more stable towards breaking because of thermal fluctuations than a pure gold chain.

To gain more insight into the character of the gold-oxygen chain, we show in Fig. 3 the one-dimensional band structure around the Fermi level together with a few representative wave functions. The magnetic moment is close to 1 bohr magneton and comes about because the band indicated "A"

splits up in a completely filled spin-down band and a completely empty spin-up band.[26] As can be seen from the wave functions the states in the "A" bands are mainly composed of gold d-orbitals and oxygen p-orbitals perpendicular to the gold-oxygen plane. The band indicated "B" splits up to a much lesser extent and both the resulting spin-up and spin-down bands cross the Fermi level. From the wave functions the "B" band is seen to involve a much larger component of the gold s-orbital together with the in-plane oxygen p-orbitals. The crossing of the Fermi level of the two partial bands shows the structure to be metallic with a conductance of one quantum unit $2e^2/h$. The conductance is thus the same as for a pure gold chain. It should be noted, however, that quite generally a detailed description of the hybridization between oxygen p-states and transition or noble metal d-states in metal oxides requires the inclusion of self-energy corrections not taken into account here.[27]

We conclude that the incorporation of oxygen into gold chains is very exothermic. We have also shown that the oxygen-gold chains are conducting, and that they have gold-gold distances in the same range as the long chain lengths observed in some experiments.[4,5] On this basis we suggest that what are observed in these experiments are in fact oxygen-gold chains. While oxygen atoms should not be observable in the experiments; it is only very recently that whole columns of oxygen atoms have been observed using high-resolution transmission electron microscopy (HRTEM).[28]

The formation of the oxygen-gold chains will clearly be a function of the experimental conditions and the pretreatment of the sample. This we suggest is the reason why the long gold-gold distances are only observed in some experiments and not in others.

The dissociation path for the oxygen molecules is still an open question. Our calculations show that the barrier for a direct, simple dissociation on a pure gold wire can be quite high (of the order 2 eV) making this path rather improbable at ambient temperatures. The dissociation may therefore require special geometries or perhaps the presence of particular impurities.

We also conclude that gold nanochains may be the most reactive condensed form of gold in existence. The gold in the chains has a coordination number of two, and is even more reactive than the small gold clusters that have recently been shown to be unusually chemically active.[18,19]

---

[1] G.M. Finbow, R.M. Lynden-Bell, and I.R. McDonald, Mol. Phys. **92**, 705 (1997).

[2] M.R. Sørensen, M. Brandbyge, and K.W. Jacobsen, Phys. Rev. B **57**, 3283 (1998).

[3] A.I. Yanson, G. Rubio-Bollinger, H.E. van den Brom, N. Agraït, and J.M. van Ruitenbeek, Nature (London) **395**, 783 (1998).

[4] H. Ohnishi, Y. Kondo, and K. Takayanagi, Nature (London) **395**, 780 (1998).

[5] V. Rodrigues, T. Fuhrer, and D. Ugarte, Phys. Rev. Lett. **85**, 4124 (2000); V. Rodrigues and D. Ugarte, Phys. Rev. B **63**, 073405 (2001).

[6] G. Rubio-Bollinger, S.R. Bahn, N. Agraït, K.W. Jacobsen, and S. Vieira, Phys. Rev. Lett. **87**, 026101 (2001).

[7] H. Hakkinen, R.N. Barnett, and U. Landman, J. Phys. Chem. B **103**, 8814 (1999).

[8] D. Sánchez-Portal *et al.*, Phys. Rev. Lett. **83**, 3884 (1999).

[9] L. De Maria and M. Springborg, Chem. Phys. Lett. **323**, 293 (2000).

[10] J.A. Torres *et al.*, Surf. Sci. **426**, 441 (1999).

[11] M. Okamoto and K. Takayanagi, Phys. Rev. B **60**, 7808 (1999).

[12] S.R. Bahn and K.W. Jacobsen, Phys. Rev. Lett. **87**, 266101 (2001).

[13] A. I. Yanson, University of Leiden, Ph.D. thesis (2001).

[14] B. Hammer and J.K. Nørskov, Nature (London) **376**, 238 (1995).

[15] N.D.S. Canning, D. Outka, and R.J. Madix, Surf. Sci. **141**, 240 (1984).

[16] M. Mavrikakis, P. Stoltze, and J.K. Nørskov, Catal. Lett. **64**, 101 (2000).

[17] H. Strømsnes, S. Jusuf, A. Bagatur'yants, O. Gropen, and U. Wahlgren, Theor. Chem. Acc. **106**, 329 (2001).

[18] M. Haruta, Catal. Today **36**, 153 (1997).

[19] M. Valden, X. Lai, and D.W. Goodman, Science **281**, 1647 (1998).

[20] C.Z. Li, H. Sha, and N.J. Tao, Phys. Rev. B **58**, 6775 (1998).

[21] Our DFT code "DACAPO" is publicly available at http://www.fysik.dtu.dk/campos

[22] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[23] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[24] J.P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).

[25] B. Hammer and J.K. Nørskov, Adv. Catal. **45**, 71 (2000).

[26] The energy associated with the magnetization is very small of the order 0.02 eV. The calculations shown in Fig. 1 are therefore performed nonspinpolarized.

[27] W.E. Pickett, Rev. Mod. Phys. **61**, 433 (1989).

[28] C. Kisielowski *et al.*, Ultramicroscopy **89**, 243 (2001).