

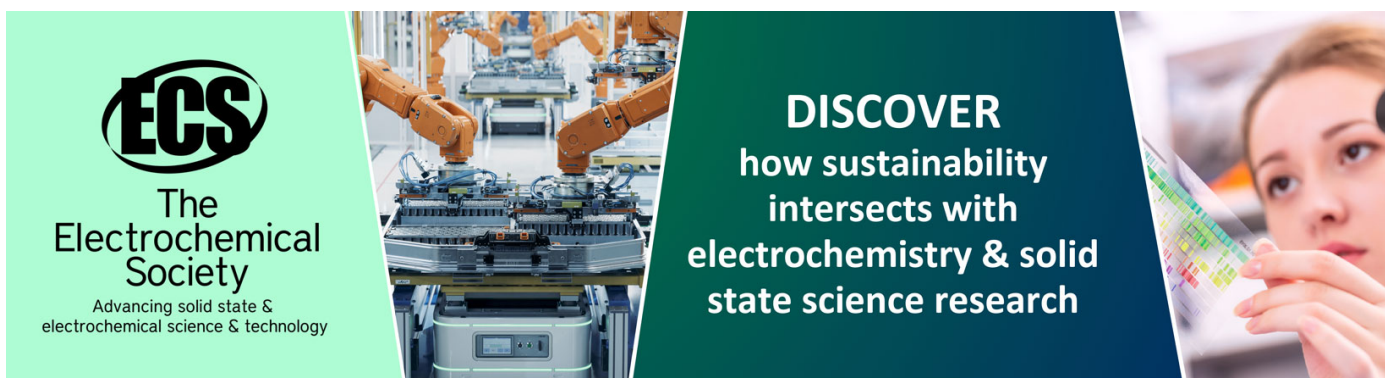
Adsorbate and defect effects on electronic and transport properties of gold nanotubes

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Adsorbate and defect effects on electronic and transport properties of gold nanotubes

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Abstract

First-principles calculations have been performed to study the effects of adsorbates (CO molecules and O atoms) and defects on electronic structures and transport properties of Au nanotubes (Au(5, 3) and Au(5, 5)). For CO adsorption, various adsorption sites of CO on the Au tubes were considered. The vibrational frequency of the CO molecule was found to be very different for two nearly degenerate stable adsorption configurations of Au(5, 3), implying the possibility of distinguishing these two configurations via measuring the vibrational frequency of CO in experiments. After CO adsorption, the conductance of Au(5, 3) decreases by $0.9G_0$ and the conductance of Au(5, 5) decreases by approximately $0.5G_0$. For O-adsorbed Au tubes, O atoms strongly interact with Au tubes, leading to around $2G_0$ of drop in conductance for both Au tubes. These results may have implications for Au-tube-based chemical sensing. When a monovacancy defect is present, we found that, for both tubes, the conductance decreases by around $1G_0$. Another type of defect arising from the adhesion of one Au atom is also considered. For this case, it is found that, for the Au(5, 3) tube, the defect decreases the conductance by nearly $1G_0$, whereas for Au(5, 5), the decrease in conductance is only $0.3G_0$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Gold quasi-one-dimensional (1d) nanostructures, such as nanowires and nanotubes, have attracted lots of attention due to their intriguing physical and chemical properties that are very different from bulk gold [1–4]. The recent rapid progress in experimental techniques enables us to fabricate these gold quasi-1d structures and measure their novel properties. Long gold monoatom chains have been produced in experiments by depositing single Au atoms onto a metallic NiAl(110) surface using a scanning tunneling microscopy (STM) tip [5, 6], and the unit conductance of such a gold chain was reported in another experiment [7]. Gold nanowires suspended between two bulk electrodes have been fabricated and intensively studied by either STM techniques [2] or the break junction method [3]. More recently, helical single-wall gold nanotubes were successfully synthesized in experiments [4]. Theoretical studies have shown that, among all freestanding gold tubes,

Au(5, 5) is the most stable one, and when suspended between two gold electrodes, the Au tube (5, 3) is the most energetically favored [8].

Owing to their helical structures, gold nanotubes have unique electronic and catalytic properties: it was predicted by a theoretical study that the chiral current flowing through gold tubes may induce a strong magnetic field [9, 10]. Both experimental and theoretical investigations have demonstrated excellent catalytic activity of gold nanotubes [11, 12]. These unique properties of gold nanotubes suggest the promise of gold tubes for future applications in nanoelectronics and nanocatalysis. In this paper, we shall discuss the effects of two important factors that may have major implications for real applications, chemical modifications and defects on the electronic and transport properties of gold tubes.

The chemical modification, in particular the adsorption or doping of small molecules, has been regarded as a very effective way to tune and control the electronic structure and

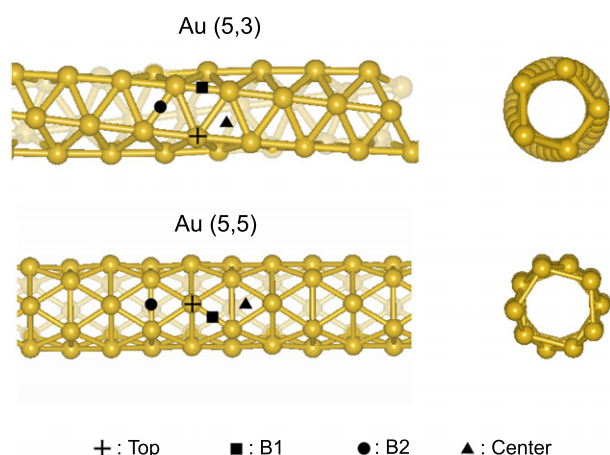


Figure 1. Geometric structures of (5, 3) and (5, 5) Au nanotubes and a schematic description of possible adsorbing sites for adsorption: top, B1 (bridge site 1) and B2 (bridge site 2), center.

conductance of quasi-1d nanostructures [13]. For instance, for In nanowires, both O and In adatoms can suppress the conductance of the wire by more than one-third [14], and the adsorption of a single CO atom on an Au nanochain turns the system from a metal to a semiconductor [6, 15]. Defects are important because, first, in the procedure of fabrication, in principle, defects are inevitable and, second, defects have been found to have significant effects on physical and chemical properties of nanosystems, which in many cases are essential for applications, for example, greatly defect-enhanced catalytic activity of gold nanoclusters on graphene [16]. In the present study, the adsorption of an CO molecule and O atom, and two types of defects, Au monovacancy and the defect arising from the adsorption of one extra Au atom on the tube, are considered.

2. Computational details

For structural optimization and electronic structure calculations, the first-principles method based on density functional theory (DFT) was employed via the computational package VASP [17, 18]. During calculations, a plane wave basis set with the cutoff energy 396 eV was used. The structures were relaxed until the force was less than $0.02 \text{ eV } \text{\AA}^{-1}$. The transport properties were calculated by ATK code within the nonequilibrium Green's function (NEGF) formalism [19–21]. Double- ζ -polarized basis and a cutoff energy of 150 Ryd for the grid integration were adopted in transport calculations. In all calculations, the Perdew–Burke–Ernzerhof (PBE) format of the GGA approximation was included [22]. Vibrational analysis was done by DMol₃ [23, 24]. In DMol calculations, the effective core potential (ECP) and a double numerical basis set including a d-polarization function (DND) were adopted.

3. Results and discussion

3.1. Adsorption configurations of CO, O and Au on Au(5, 3)/(5, 5) tubes

Figure 1 shows atomic structures of Au(5, 3)/(5, 5) tubes and possible adsorption sites (top, center and two inequivalent

Table 1. Energetics and structures of adsorbates (CO, O, Au) on Au(5, 3) and Au(5, 5) nanotubes. The adsorption energy ΔE is calculated by subtracting the energy of the total system from the sum of energies of the nanotubes and the adsorbates; d is the shortest length of the bonds formed by Au and adsorbates; δQ_x ($x = \text{CO}, \text{O}, \text{Au}$) and δQ_{Au} are the net partial charge transfers of the adsorbates and the Au atom with the shortest distance from the adsorbates.

Adsorbate	ΔE (eV) (site)	d (Å)	δQ_x	δQ_{Au}
Au(5, 3)				
CO	0.57(top)	1.99	0.389	−0.090
	0.54(B1)	2.12	0.399	−0.045
O	4.66(center)	2.12	−0.522	0.150
	4.65(B1)	2.03	−0.528	0.170
Au	2.28(center)	2.73	−0.060	0.028
	2.27(B2)	2.71	−0.048	0.009
Au(5, 5)				
CO	0.77(B1)	2.10	0.441	−0.050
O	5.13(center)	2.05	−0.507	0.139
Au	2.69(center)	2.74	−0.006	0.045

bridge sites, B1 and B2) of a CO molecule, O and Au atoms. In table 1, we list the adsorption energy, the bonding length defined as the shortest distance between the adsorbate (CO, O and Au) and the nearest Au atom, and the change in net charge of the adsorbates and the bonded Au atoms for the most stable adsorption configurations in different cases. In the case of Au(5, 3), for each adsorbate, we found that the difference between the binding energy of the lowest-energy configuration and that of the second-lowest one is around 0.03 eV. These two adsorption configurations are nearly degenerate and may coexist in experiments. We therefore show both of them in the table. Other adsorption configurations (not shown in the table) have binding energies at least 0.4 eV higher than the most stable one.

The side views of the optimized geometries of CO-or O-adsorbed Au(5, 3)/(5, 5) tubes are shown in figure 2. For the case of CO-adsorbed Au(5, 3), two nearly degenerate stable adsorption configurations are found as mentioned above: the top site adsorption (figure 2(a)), where the C atom directly binds to the Au atom, and the B1 adsorption (figure 2(b)), where the CO is on the bridge site of Au chains along the direction parallel to the tube axis. For the top site adsorption, the C–Au bonding length is 1.99 Å, comparable to that of CO adsorption on an Au chain (C–Au bond length 1.96 Å) on an NiAl surface [15]. As shown in figure 2(a), after the CO adsorbed on the top site, the Au(5, 3) tube undergoes a significant distortion, clearly suggesting the strong interaction between the CO molecule and the Au tube. For the B1 site adsorption (figure 2(b)), the distortion of the tube is much weaker although the adsorption energy in this case is almost the same as the top site adsorption. For the case of the Au(5, 5) tube, the lowest-energy state occurs when the CO molecule binds to the B1 site (figure 2(c)). The binding energy, 0.77 eV, is higher than in the case of Au(5, 3) by about 0.2 eV. In all cases, electron transfers from the CO molecule to the adjacent Au atom lead to a slightly positively charged CO molecule and negatively charged Au atoms (table 1).

Compared to CO, the binding of an O atom on Au tubes is much stronger (table 1). For the case of Au(5, 3), similarly,

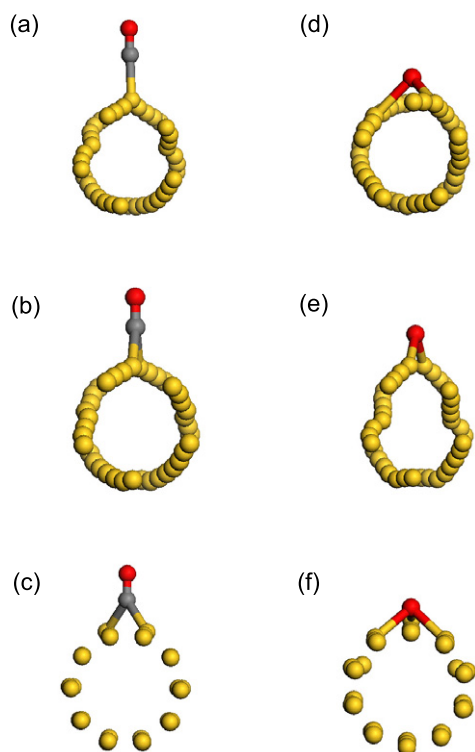


Figure 2. Adsorption geometries for CO adsorption on Au(5, 3) at top (a), B1 (b) and Au(5, 5) at B1 (c) sites, and oxygen adsorption on Au(5, 3) at center (d), B1 (e) and Au(5, 5) at center (f) sites, respectively. The C, O and Au atoms are depicted in gray, red and yellow, respectively.

there are two nearly degenerate adsorption configurations, the center (figure 2(d)) and the B1 site (figure 2(e)) adsorption, with the adsorption energy 4.66 and 4.65 eV, respectively. For Au(5, 5), the center site adsorption (figure 2(f)) is the most stable configuration with the adsorption energy of 5.13 eV. When bound on the B1 site of Au(5, 3), a significant distortion of the Au tube occurs. For all cases, electrons transfer from the Au tube to the O atom, causing the O atom to be negatively charged and the bound Au atoms positively charged, as shown in table 1.

The adsorption of one extra Au atom on Au tubes is also considered. For both Au tubes, the adsorption energy of the lowest-energy configuration is larger than 2.2 eV (table 1), suggesting that in the procedure of fabrication it is very possible to have Au adatoms on Au tubes. Later, we will show how the Au adatom affects electronic and transport properties of Au tubes.

3.2. Electronic structures of CO-and O-adsorbed Au(5, 3)/(5, 5) tubes

Here, we describe the electronic structures of CO/O-adsorbed Au(5, 3) and Au(5, 5) tubes. First, to understand the interaction between the CO molecule and Au tubes, we plot in figure 3 the local density of states (LDOS) projected on the CO molecule and bound Au atoms. Similar to the case of CO binding to Au nanoclusters [25], the highest occupied molecular orbital (HOMO) and the lowest unoccupied

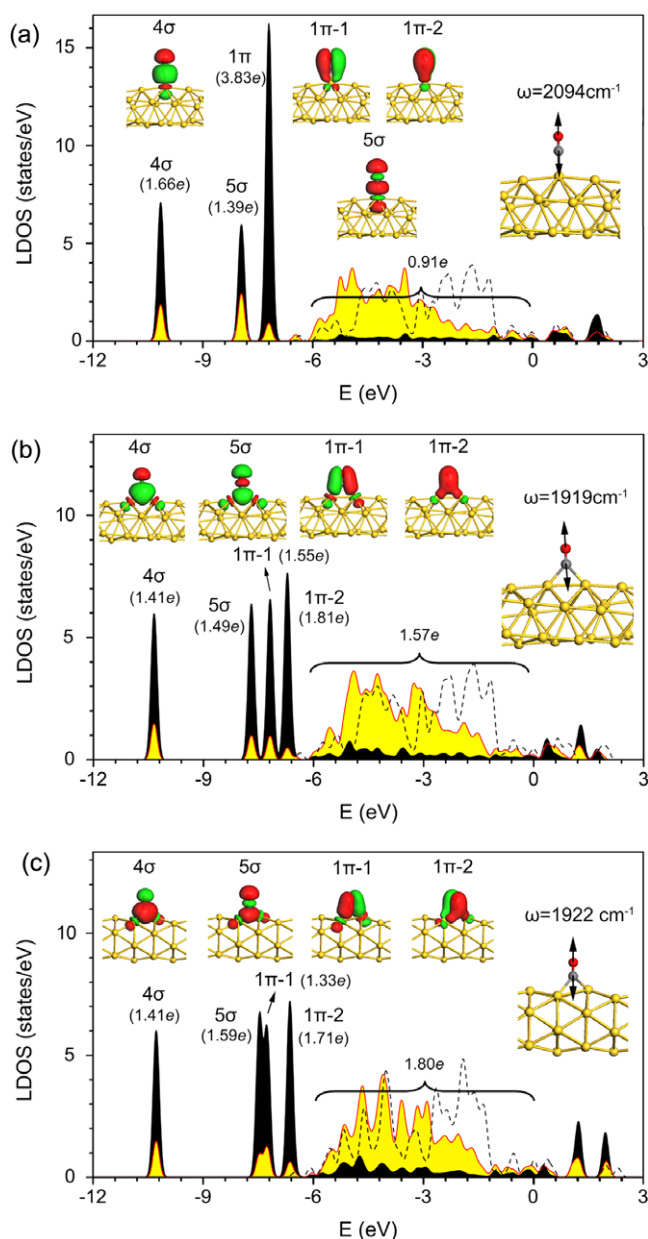


Figure 3. LDOS and orbitals of CO adsorbed on Au(5, 3) at top (a), B1 (b) sites and Au(5, 5) at B1 (c) sites. The LDOS projected on the CO molecule is shown in black and that projected on the gold atom with the shortest distance from the C atom is colored yellow. The populations of CO orbitals are calculated through integrating over the relevant peaks. Included also are the vibrational frequencies of the stretching mode for different adsorption configurations. The softening frequencies are evidence of the backdonation process during adsorption. Notice that the frequency of the free CO molecule is calculated as 2128 cm^{-1} .

molecular orbital (LUMO) of CO, 5σ and $2\pi^*$, have the biggest contribution to the chemisorption since the energy levels of these two states change significantly upon adsorption due to the hybridization with Au states. For top site adsorption on Au(5, 3) (figure 3(a)), the CO HOMO orbital 5σ is pushed below the 1π orbital whose energy level does not change much, and the LUMO orbital $2\pi^*$ is pushed below the Fermi energy and overlaps with the whole continuous d band of Au, leading

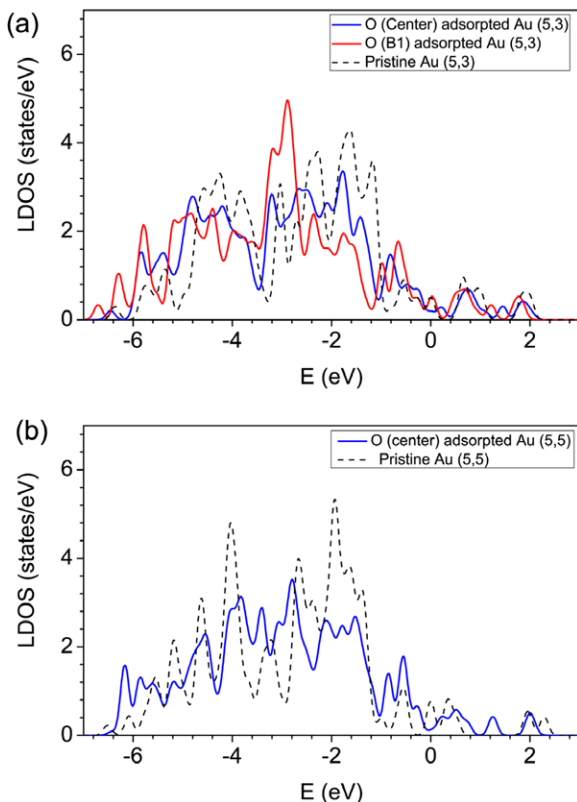


Figure 4. Comparison of Au states after O atomic adhesion with those of the pristine (5, 3) (a) and (5, 5) (b) Au tubes. For the adsorbed tubes, LDOS is projected onto the Au atom with the shortest distance from the O atom.

to the partial population of this orbital (the backdonation process [26, 27]). The amount of electrons backdonated to the $2\pi^*$ orbital can be roughly estimated by integrating the LDOS of CO within the energy range of the Au d band. In this case, about 0.9 electron is transferred from Au d bands to the CO anti-binding orbital $2\pi^*$. In the figure, we also plot the wavefunctions of several molecular orbitals of CO after adsorption, from which we can see that indeed the 5σ orbital strongly hybridizes with Au states, and 4σ as well as two degenerate 1π orbitals ($1\pi - 1$ and $1\pi - 2$) only weakly interact with the Au tube. When CO adsorbs on the B1 site of Au(5, 3) (figure 3(b)), different from top site adsorption, the 1π orbital also contributes to the chemisorption by significantly hybridizing with Au states and, as a result, the degeneracy between $1\pi - 1$ and $1\pi - 2$ is lifted. The amount of electrons backdonated to the $2\pi^*$ orbital in this case (1.57 electrons) is estimated to be larger than that of the top site adsorption.

The significantly different backdonation strength between the top site and B1 site adsorption implies a way to distinguish these two almost degenerate adsorption configurations of CO on Au(5, 3) in experiments. The more the CO anti-binding $2\pi^*$ orbital is backdonated, the weaker the CO bond will be. The strength of the CO bond can be seen from the bond length and also the vibrational frequency of the stretching mode of the molecule, the latter of which can be measured in experiments. Indeed, the CO bond length of the B1 adsorption, 1.165 Å, is larger than that of the top adsorption, 1.151 Å, due to the

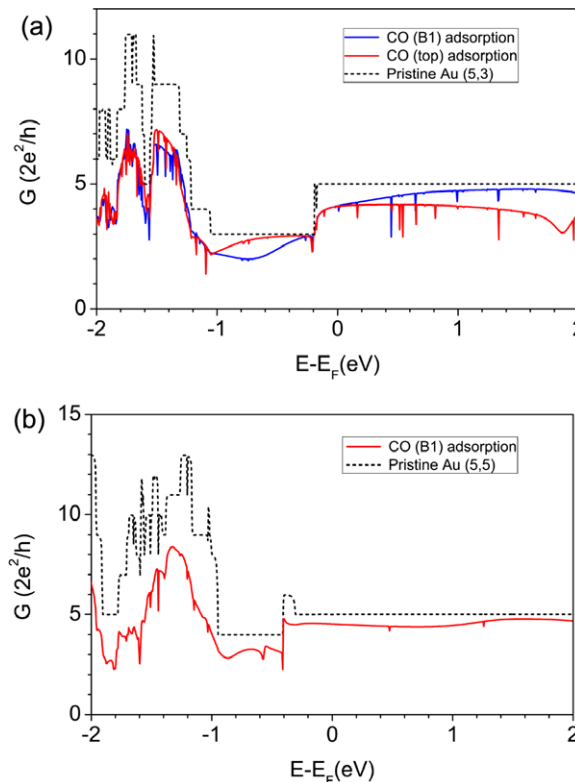


Figure 5. Quantum conductance spectrum for CO-adsorbed Au(5, 3) (a) and Au(5, 5) (b). The conductance spectra of pristine tubes (dashed lines) are also given for comparison.

stronger backdonation. Note that the calculated bond length of a free CO molecule is 1.146 Å, which is in good agreement with previous studies [12]. The vibrational frequency of the CO stretching mode is calculated to be 2094 cm^{-1} for top adsorption and 1919 cm^{-1} for B1 adsorption. The difference between these two vibrational frequencies should be able to be seen in experiments. As a test of the method of calculating vibrational spectra, for the same mode of the free CO molecule, our calculations give a frequency of 2128 cm^{-1} , which is in good agreement with the experimental value of 2140 cm^{-1} [28].

The backdonation of the $2\pi^*$ orbital, and the splitting of $1\pi - 1$ and $1\pi - 2$, are also observed for the lowest-energy adsorption of CO on Au(5, 5), the B1 adsorption (figure 3(c)). Here, the nearly 1 eV of the splitting between two 1π orbitals is much larger than that of the B1 adsorption of Au(5, 3) (about 0.5 eV). The CO bond length in this case is calculated to be 1.172 Å and the corresponding vibrational frequency of the CO stretching mode is 1922 cm^{-1} , about the same as that of the B1 adsorption on Au(5, 3).

In figure 4, we show the LDOS of the Au atom bound with the O before and after O adsorption. Again, for Au(5, 3), there are two nearly degenerate adsorption configurations, the center and the B1 adsorption, and for Au(5, 5) the most stable configuration occurs when the O atom binds to the center position. For all cases, the O adsorption causes large changes of the LDOS of the bound Au atom, indicating the strong interaction between the O and the Au tube.

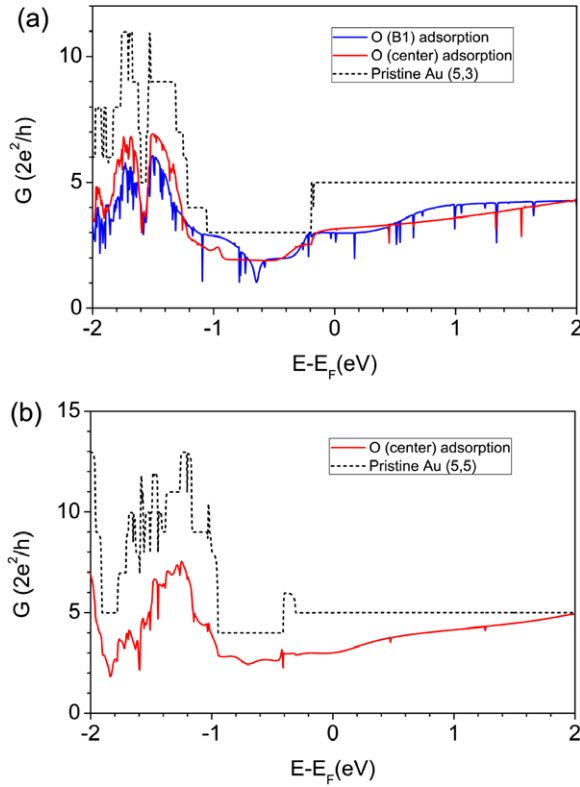


Figure 6. Quantum conductance spectrum for oxygen-adsorbed Au(5, 3) (a) and Au(5, 5) (b). The conductance spectra of pristine tubes (dashed lines) are also given for comparison.

3.3. Conductance of CO/O-adsorbed Au tubes

Now, we turn to the analysis of the conductance of chemically modified Au tubes. It has been reported that an Au monoatom chain has one unit of conductance, and the adsorption of a single CO molecule greatly decreases the conductance of the Au monochain from 1 to $0G_0$ [15]. It would be interesting to see how the adsorption of CO or O modifies the conductance of Au(5, 3)/(5, 5) tubes, which are essentially the aggregation of five strands of Au atoms.

The calculated conductance spectra of the pristine and CO-adsorbed Au(5, 3) and Au(5, 5) are shown in figure 5. The conductance of both pristine tubes at Fermi energy is $5G_0$, in agreement with previous studies [8]. For Au(5, 3), the CO adsorption decreases the conductance at the Fermi energy of the tube by $0.9G_0$ for both top and B1 adsorption, suggesting that Au(5, 3) may be used as a chemical sensor for CO molecules. For Au(5, 5), the lowest-energy configuration of CO adsorption decreases the conductance at the Fermi energy of the tube by $0.5G_0$. Compared to CO, the effects of an O atom on transport properties are much more pronounced due to the stronger interaction between the O atom and the Au tube (figure 6). For both tubes, the O adsorption causes the drop in the conductance at the Fermi energy by around $2G_0$.

3.4. Defect effect on conductance of Au tubes

Finally, we discuss the effects of two types of defects, the Au monovacancy and the defect arising from the adhesion

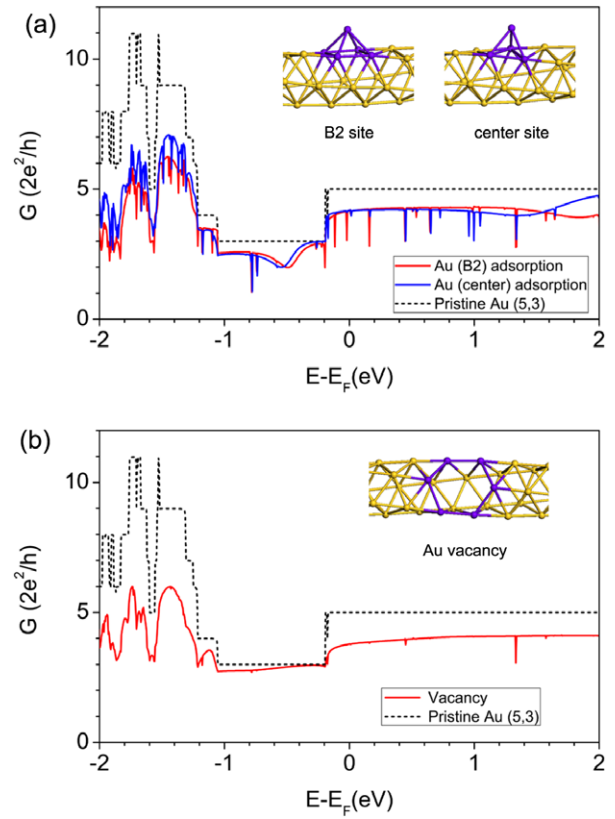


Figure 7. Conductance as a function of energy for defective Au(5, 3) tube with defects arising from Au adhesion (a) and monovacancy (b) on the tube. The relaxed defective structures are given as the insets, where the atoms around the defective site are highlighted by violet balls. It can be seen that the Au adatom distorts the tube differently at different adsorption sites.

of one extra Au atom, on the conductance of Au tubes. In table 1, we give the adsorption energies of a single Au atom on Au(5, 3) (2.28 eV@center and 2.27 eV@B2) and Au(5, 5) (2.69 eV@center). The formation energies of a monovacancy are calculated to be 3.32 and 3.52 eV for Au(5, 3) and Au(5, 5), respectively, which are rather small compared to those of CNTs (>10 eV) [29]. The high adsorption energies of one Au atom and relatively low formation energies of the monovacancy suggest that these two types of defects are likely to occur in the fabrication of Au tubes.

The conductance spectra and optimized structures of defective Au(5, 3) are given in figure 7. For cases of the extra Au atom adsorbed on the tube (B2 and center sites), after relaxation, pyramid-like structures are formed as shown in figure 7(a). The conductance spectra of both two adsorption configurations show very similar behaviors, and at the Fermi energy the conductance decreases by about $0.8G_0$ for both configurations. For the Au monovacancy, the defect decreases the conductance of the tube at the Fermi energy by about $1.2G_0$ (figure 7(b)). Similarly, the Au monovacancy on Au(5, 5) causes a $0.9G_0$ of drop in conductance at the Fermi energy (figure 8). The Au adatom on Au(5, 5) only leads to a decrease of $0.3G_0$ of the tube, as we can see from figure 8.

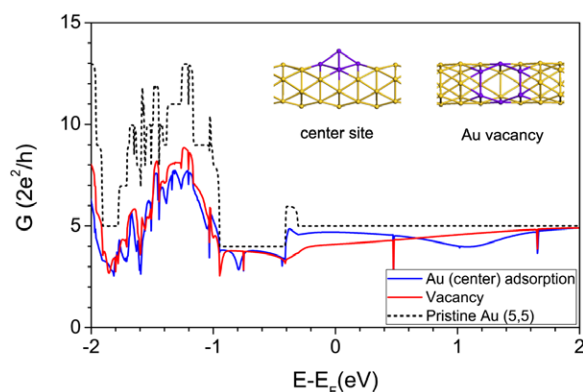


Figure 8. Conductance as a function of energy for defective Au(5, 5) tube with defects arising from Au adhesion (blue line) and monovacancy (red line) on the tube. The relaxed defective structures are given as the insets, where the atoms around the defective site are highlighted by violet balls.

4. Conclusions

We have investigated, via the first-principles method based on DFT, the influence of adsorbates (CO molecule and O atom) and defects on the electronic and transport properties of Au(5, 3) and Au(5, 5) nanotubes. For Au(5, 3), we found that there are two nearly degenerate stable adsorption configurations for both a CO molecule and O atom. For the case of CO, for both tubes, HOMO and LUMO states of CO contribute the most to the chemisorption. For one of these two degenerate configurations of Au(5, 3), the B1 site adsorption, and the stable adsorption configuration of Au(5, 5), the 1π orbital is also involved in the bonding between CO and the Au tube. The hybridization between the CO $2\pi^*$ and Au states is dominated by the so-called backdonation process in which the electrons are transferred from Au d bands to the CO anti-binding $2\pi^*$ orbital. We also predicted a significant difference between the vibrational frequencies of the CO molecule for two degenerate stable adsorption configurations of Au(5, 3), which may be used to distinguish these two configurations in experiments.

After CO adsorption, the conductance of Au(5, 3) decreases by $0.9G_0$ and the conductance of Au(5, 5) decreases by approximately $0.5G_0$. For O-adsorbed Au tubes, O atoms strongly interact with Au tubes, leading to around $2G_0$ of a drop in conductance for both Au tubes. These results may have implications for Au-tube-based chemical sensing. When a monovacancy defect is present, we found that, for both tubes, the conductance decreases by around $1G_0$. Another type of defect arising from the adhesion of one Au atom is also considered. For this case, it is found that the defect decreases the conductance by nearly $1G_0$ for the Au(5, 3) tube and the

decrease of the conductance is around $0.3G_0$ for the Au(5, 5) tube.

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