

Electronic Structure and Bonding of Au on a SiO₂ Cluster: A Nanobullet for Tumors

Q. Sun, Q. Wang, B. K. Rao,* and P. Jena[†]

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284, USA

(Received 23 March 2004; published 28 October 2004)

The binding of gold atoms to a small silica cluster has been studied by using density functional theory with generalized gradient approximation for exchange and correlation. It is shown that gold atoms bind to silicon atoms with dangling bonds and serve as seeds for the growth of Au islands. The large electron affinity of gold causes a significant change in the electronic structure of silica resulting in a substantial reduction in the highest occupied and the lowest unoccupied molecular orbital and the optical gap, thus allowing it to absorb near infrared radiation. This suggests that a small cluster can have a similar functionality in the treatment of cancer as the large size nanoshell, but for a different mechanism.

DOI: 10.1103/PhysRevLett.93.186803

PACS numbers: 73.22.-f, 71.15.Nc, 31.15.Ar, 87.54.Br

Silica, one of the most abundant materials on Earth, has a wide range of applications in microelectronics, optical communications, and thin-film technology [1–4]. Gold, on the other hand, is the noblest of all metals, but at nanosize range gold clusters exhibit unusual catalytic behavior [5]. Recently an exciting new application of gold-coated silica nanoshells has been found in treating tumors and cancer [6–8]. The nanoshell consists of a silica (SiO₂) core of order 100 nm coated with about 20 nm of gold. It absorbs near infrared light (NIR) and converts that light to heat, causing irreversible thermal cellular destruction. When the nanoshells were incorporated into human breast cancer cells in a test tube, and then exposed to NIR, 100% of the cancer cells were killed. Similarly, the nanoshells injected directly into the tumors of living mice and subjected to NIR have been found to destroy tumors within days. The advantages of gold-coated silica nanoshells in the treatment of cancer are (i) the process is noninvasive and (ii) both gold and silica are harmless to the human body. Besides the promising applications in cancer, nanoshells can also be incorporated into temperature-sensitive hydrogels to synthesize a new type of composite material that collapses on laser irradiation.

Recently attempts have been made to understand the optical properties of gold-coated silica nanoshells using a simple model and electromagnetic theory. It has been shown that the optical response is due to the hybridization of the surface plasmons of the inner and outer shells [9]. Motivated by these results we have investigated the coating of a small silica cluster (of the order of a few nanometers) with Au to understand (i) if such a small cluster can absorb infrared radiation and (ii) if so, does the mechanism for such absorption have an electronic origin? While a lot of work has been carried out on silica clusters, no work is available to our knowledge on the interaction of gold with a silica cluster. For example, it is not known how Au atoms attach to a SiO₂ cluster? What role do the defects in nanosilica play on the binding of Au? What effect does Au have on the electronic structure of SiO₂?

In this Letter we have addressed these issues for the first time by concentrating on a (SiO₂)₃ cluster, which has been synthesized in experiment [10]. This cluster is the smallest nanosilica that contains Si atoms with both four-fold coordination and dangling bonds; therefore, it can be used to shed light on the role of defects on the binding of Au by a nanosilica system. We want to see if a small gold-coated silica cluster can exhibit similar optical properties as observed in 100 nm size nanoshells. We have examined the binding site of Au, the growth of Au islands on a silica nanocluster as Au concentration is increased, and the effect of gold coating on the electronic structure of silica.

We have used the self-consistent linear combination of atomic orbital molecular orbital approach. The total energies are calculated using density functional theory (DFT) and generalized gradient approximation for exchange-correlation potential [Perdew-Wang 1991 (PW91)]. The atomic orbitals are represented by a Gaussian basis. We have used the 6-311 + +G (3df, 3pd) basis set for oxygen and silicon, and the Stuttgart relativistic effective core potential basis set for gold [11]. The structures were optimized without a symmetry constraint using the GAUSSIAN 98 code [12]. The convergence for energy and force are 0.00001 eV and 0.001 eV/Å, respectively. To check the accuracy of exchange-correlation potential and the basis set, we calculated the bond length for dimers of O₂, Si₂, Si-O, AuSi, and Au₂. They are found to be 1.220, 2.245, 1.570, 2.350, and 2.560 Å, respectively, in good agreement with the experimental values of 1.210, 2.246, 1.510, 2.260 [13], and 2.50 Å [14]. For Au-O, no experimental bond length is available to compare, but the binding energy of 2.47 eV is very close to the experimental value of 2.30 ± 0.2 eV [13].

It is well established that the geometries of (SiO₂)_n clusters in the small size range ($n < 12$) are chainlike [10,15–17]. Thus these structures consist of some Si atoms that do not have the full fourfold coordination. It is expected that in a silica nanoshell dangling bonds will exist as they do in SiO₂ clusters and that the sites with dangling bonds may play a role in the binding of Au

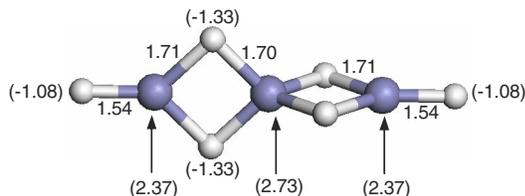


FIG. 1 (color online). Geometry and charge distribution of $(\text{SiO}_2)_3$. The numbers in parentheses refer to charges, while other numbers refer to bond lengths in Å. The balls with light color are for O atoms. The arrows specify the charges on Si atoms.

atoms. Figure 1 shows the structure of $(\text{SiO}_2)_3$. Recently, rodlike nanosilica on the order of 100 nm have been synthesized in experiments [18,19].

To determine the equilibrium structure of the $\text{Au}(\text{SiO}_2)_3$ cluster, we have used six different initial configurations for optimizing the geometry. These are shown in Fig. 2(a) where the Au atom was allowed to bond to different Si and O atoms in the $(\text{SiO}_2)_3$ cluster. After full optimization, these six structures converged to the same one as shown in Fig. 2(b). Here the Au atom binds to one of the Si atoms at the end site. This is because in Si_3O_6 , the middle Si atom is fully coordinated, while the two end Si atoms are threefold coordinated. The resulting dangling bonds provide the preferable sites for the adsorption of the Au atom. The adsorption energy is found to be 1.14 eV, suggesting that the binding is strong. This is consistent with the recent finding that the Au atom and the Au magic cluster can strongly interact with the Si cluster [20,21].

The adsorption of Au causes redistribution of charges throughout the cluster. In Si_3O_6 , the two O atoms at the end sites get about one electron, while each of the double

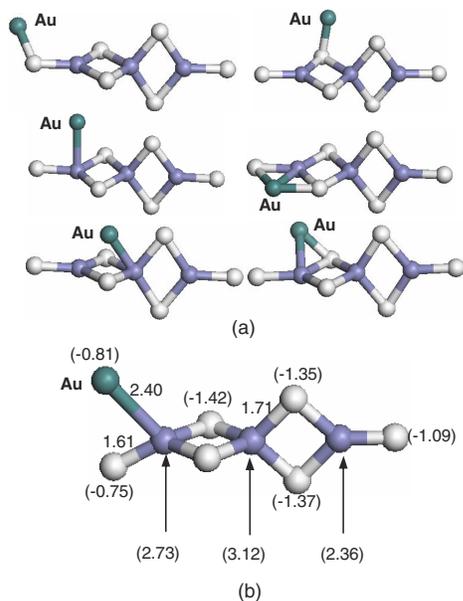


FIG. 2 (color online). (a) Six initial structures of $\text{Au}(\text{SiO}_2)_3$ used for geometry optimization. (b) Final optimized geometry.

bridged O atoms gets 1.33 electrons. Si atoms at the end lose 2.37 electrons, while the middle one loses 2.73 electrons. It is interesting to note that Au is the most electronegative metal, comparable to selenium, and only slightly more electropositive than sulfur and iodine. Therefore, it can form ionic compounds such as Au^-Cs^+ [22]. A similar thing also happens when Au is adsorbed on Si_3O_6 , where the Au atom gets 0.81 electron [see Fig. 2(b)], while its neighboring end O atom gets only 0.75 electron. Consequently, the corresponding Si-O bond length is increased.

When the second Au atom was added, it was found to bind to the Si site at the other end with the remaining one dangling bond, making all the silicon atoms fully coordinated. Figure 3 gives the equilibrium geometry of the $\text{Au}_2(\text{SiO}_2)_3$ cluster along with the various bond distances and charge distribution. Each of the two Au atoms once again gets about 0.82 electron. The cluster gains an additional 1.24 eV energy as the second Au atom is attached to $\text{Au}(\text{SiO}_2)_3$.

Study of the structure of $\text{Au}_3(\text{SiO}_2)_3$ is more revealing as the location of the third Au can illustrate if Au has a tendency to cluster. Three different initial configurations were tried by attaching the third Au atom to the end Si sites, the middle Si site, and to one of the Au atoms. These are shown in Figs. 4(a)–4(c). The geometry optimization resulted in two isomers as shown in Figs. 5(a) and 5(b). When the third Au atom was placed near the Si sites, the Au atom could not be adsorbed on these sites because of the full coordination of Si. Au atom automatically moved to the O site at the end of the chain [Fig. 5(a)]. The Au-O bond length is 2.03 Å, and the third Au atom gets very little charge. However, we found that this configuration is 0.22 eV higher in energy than another structure shown in Fig. 5(b), where the third Au atom binds to another Au atom forming a cluster. In this configuration, the Au dimer has a bond length of 2.55 Å, and each Au atom gets about 0.4 electron. Si atoms on the average lose about three electrons. The binding energy of $\text{Au}_3(\text{SiO}_2)_3$, defined as the energy gained by dissociating the cluster into $(\text{SiO}_2)_3$ and three Au atoms, is 4.57 eV. This amounts to 1.52 eV/Au atom, which is larger than the binding energy of Au in $\text{Au}(\text{SiO}_2)_3$ and $\text{Au}_2(\text{SiO}_2)_3$. This clearly establishes the fact that Au atoms would tend to cluster on the SiO_2 cluster. We further emphasize the fact that dangling bonds or defects on SiO_2 play an important role in the binding of Au atoms.

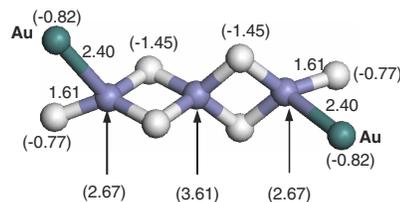


FIG. 3 (color online). Geometry and charge distributions in $\text{Au}_2(\text{SiO}_2)_3$.

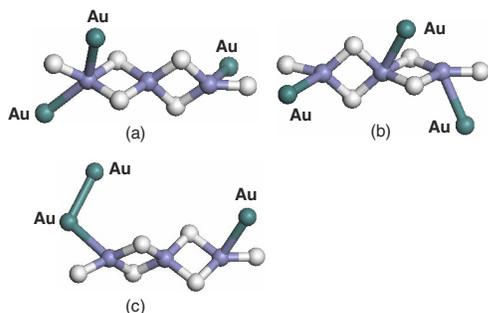


FIG. 4 (color online). Three different initial configurations for $\text{Au}_3\text{-Si}_3\text{O}_6$.

The electronic structure of the Au coated silica nanocluster can be analyzed by studying the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The HOMO and LUMO orbitals are plotted in Fig. 6. We see that the main contributions to these two frontier orbitals come from the Au cluster and its neighboring atoms, which suggests that in the next growth stage the incoming Au atoms will preferably bind with an existing Au cluster and/or with its neighboring atoms. In this way an Au island will be formed. This is what indeed happens in experiments, where Au atoms form islands or dots on the silica particle surface [23–27].

An analysis of the energy eigenvalues can also reveal the effect of Au coating on the electronic structure of the silica nanocluster. In Fig. 7 we show 20 energy eigenvalues around the Fermi level for $(\text{SiO}_2)_3$ and $\text{Au}_3\text{-(SiO}_2)_3$ clusters, respectively. Without Au coating, the energy level distribution for $(\text{SiO}_2)_3$ is marked by a larger energy gap. As three Au atoms are coated, the gap is not only reduced considerably, but the interaction with gold atoms also changes the energy level distribution.

The most fascinating application of the nanobullet is in killing cancer and tumor cells by using optical absorption.

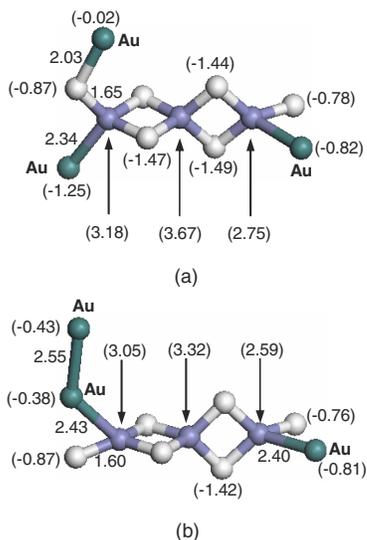


FIG. 5 (color online). Two low energy isomers of $\text{Au}_3\text{-Si}_3\text{O}_6$.

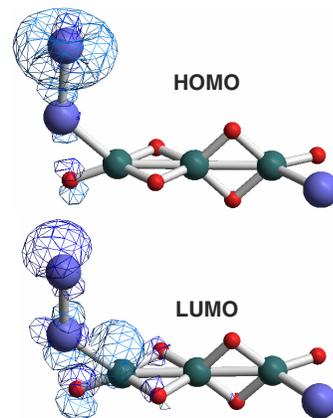


FIG. 6 (color online). HOMO and LUMO orbitals for $\text{Au}_3\text{-(SiO}_2)_3$.

Therefore, we have studied the effect of gold coating on the optical properties of the nanosilica cluster. To this end, we performed time-dependent density functional (TD-DFT) calculations [28] with the same basis set used in the preceding calculations. In TD-DFT, the time-dependent analog of the exchange-correlation functional, E_{xc} , is a functional of the time-dependent electron density $\rho(\mathbf{r}, t)$. We used the PW91 form as that used in structure optimization. Table I lists our results. For $(\text{SiO}_2)_3$, the optical gap is found to be 4.16 eV. When one Au atom is attached to this cluster, the optical gap reduces to 1.66 eV. No further change occurs in the gap when the second Au atom is attached as it binds to the remaining threefold coordinated Si atom. However, when the third Au atom is attached, the optical gap is again reduced to 0.52 eV, which corresponds to the wavelength of 645 nm. The optical absorption in $\text{Au}_3\text{-(SiO}_2)_3$ is thus close to the NIR region. It has been found experimentally that the absorption wavelength for gold-coated silica nanowires is in the region of 550–600 nm [18]. When a 22 nm thick gold shell was coated on a 96 nm diameter silica core, the absorption wavelength was found to be 700 nm [7].

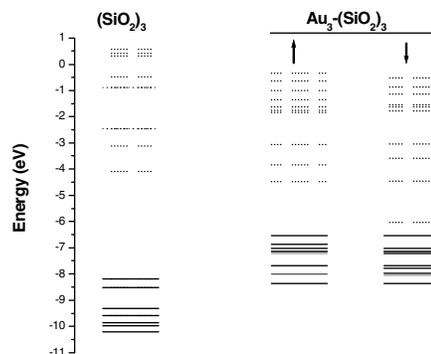


FIG. 7. Energy eigenvalues for $(\text{SiO}_2)_3$ and $\text{Au}_3\text{-(SiO}_2)_3$. The solid lines refer to occupied states, and the dotted lines for unoccupied levels. Because of the multiplicity of two for $\text{Au}_3\text{-(SiO}_2)_3$, spin-up and spin-down states are drawn separately.

TABLE I. Binding energy (ΔE , eV) per Au atom, average charge (Δq) per Au atom, optical gap (E_{OG} , eV), and oscillator strength (f).

Cluster	ΔE	Δq	E_{OG}	f^*100
(SiO ₂) ₃	4.16	0.67
Au-(SiO ₂) ₃	1.14	-0.81	1.66	0.12
Au ₂ -(SiO ₂) ₃	1.19	-0.82	1.65	0.10
Au ₃ -(SiO ₂) ₃	1.52	-0.53	0.52	0.06

Although our calculated optical response of the Au-(SiO₂)₃ cluster is similar to that of the large nanoparticle, the mechanisms are entirely different. In small clusters, the optical response is due to the Au induced levels at the gap, while in 100 nm size particles the optical response is due to the plasmon interaction [9]. The advantage of having a small cluster with similar functionality as the large particle is that it can easily penetrate the crowded environments such as the biological milieu of cells and live tissues for effective drug delivery.

We should point out that the (SiO₂)₃ cluster studied here represents a 1D SiO₂ based nanorod, whereas the real nanosilica are three dimensional. To see what role the dimensionality can play on the HOMO-LUMO gap we calculated the equilibrium geometry and electronic structure of the Au coated (SiO₂)₁₂ cluster which has a three dimensional structure [17]. We have confirmed [29] that it is the formation of Au islands and not the dimensionality of the system that plays a dominant role in the optical properties. We should also point out that the density functional theory usually underestimates the energy gap. Since our calculated optical gap in Au₃(SiO₂)₃ is 0.52 eV (645 nm), an increase in this gap will bring it closer to the NIR region seen experimentally.

In summary, we studied the interaction and growth of Au atoms on a silica nanocluster by using density functional theory. We found that the adsorption of the Au atom on the Si site is difficult if it is fully coordinated. However, the existence of defects and dangling bonds on Si atoms leads to potential adsorption sites. The adsorbed Au atoms in turn act as seeds in the further growth of gold islands. Since Au atoms are electron acceptors, the coating of Au on silica not only changes the local atomic environment but also changes its charge distribution and electronic structure. Especially the optical gap is greatly reduced upon Au coating. This reduction in the optical gap makes it possible to absorb near infrared light. Since recently there has been great progress [10,20,31] in the synthesis of multicomponent clusters using dual targets and dual-laser vaporization source in helium atmosphere,

it is hoped that our work will stimulate the synthesis of Au coated silica clusters.

*Deceased.

†Corresponding author.

Electronic address: pjena@vcu.edu

- [1] *The Physics and Chemistry of SiO₂ and the Si-SiO₂ Interface*, edited by C.R. Helms and B.E. Deal (Plenum, New York, 1988).
- [2] A. Salleo *et al.*, Nature Materials **2**, 796 (2003).
- [3] S. Che *et al.*, Nature Materials **2**, 801 (2003).
- [4] K. Suzuki *et al.*, J. Am. Chem. Soc. **126**, 462 (2004).
- [5] Q. Sun *et al.*, J. Chem. Phys. **120**, 6510 (2004).
- [6] L. R. Hirsch *et al.*, Proc. Natl. Acad. Sci. U.S.A. **100**, 13 549 (2003).
- [7] L. R. Hirsch *et al.*, Anal. Chem. **75**, 2377 (2003).
- [8] M. Brongersma, Nature Materials **2**, 296 (2003).
- [9] E. Prodan *et al.*, Science **302**, 419 (2003).
- [10] L. S. Wang *et al.*, Z. Phys. D **40**, 36 (1997).
- [11] D. Andrae *et al.*, Theor. Chim. Acta **77**, 123 (1990).
- [12] M. J. Frisch *et al.*, 1998 GAUSSIAN 98 (Gaussian, Pittsburgh, PA, 1998).
- [13] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC Press, Boca Raton, FL, 2000).
- [14] B. Douglas, *Concepts and Models of Inorganic Chemistry* (Wiley, New York, 1983), 2nd ed.
- [15] S. K. Nayak *et al.*, J. Chem. Phys. **109**, 1245 (1998).
- [16] S. T. Bromley *et al.*, Phys. Rev. Lett. **90**, 035502 (2003).
- [17] Q. Sun *et al.*, Phys. Rev. Lett. **92**, 039601 (2004).
- [18] S. J. Limmer *et al.*, J. Phys. Chem. B **107**, 13313 (2003).
- [19] M. Paulose *et al.*, J. Nanosci. Nanotech. **3**, 341 (2003).
- [20] B. Kiran *et al.*, Angew. Chem., Int. Ed. **43**, 2125 (2004).
- [21] Q. Sun *et al.*, Eur. Phys. J. D **29**, 231 (2004).
- [22] G. C. Bond, Catalysis Today **72**, 5 (2002).
- [23] S. J. Oldenburg *et al.*, Chem. Phys. Lett. **288**, 243 (1998).
- [24] Y. Lu *et al.*, J. Am. Chem. Soc. **125**, 12 724 (2003).
- [25] L. Nagle *et al.*, Nano Lett. **3**, 51 (2003).
- [26] V. G. Pol *et al.*, Chem. Mater. **15**, 1111 (2003).
- [27] L. Petit *et al.*, Mater. Lett. **51**, 478 (2001).
- [28] R. E. Stratmann *et al.*, J. Chem. Phys. **109**, 8218 (1998).
- [29] The lowest energy structure of (SiO₂)₁₂ has four Si atoms with dangling bonds [17]. We coated this cluster with five Au atoms. Four of these atoms were found to saturate the dangling bonds, while the fifth was found to bond to one of the Au atoms similar that seen in the Au₃(SiO₂)₃ cluster. The calculations were performed using the VASP code with the projector augmented wave method [30] since it was computationally not possible to use the same level of theory used here for this large cluster. The details will be published elsewhere. The calculated gap was found to be 0.62 eV, which is nearly identical to that of Au₃(SiO₂)₃, namely, 0.60 eV.
- [30] G. Kresse *et al.*, Phys. Rev. B **54**, 11169 (1996).
- [31] S. Neukermans *et al.*, Phys. Rev. Lett. **90**, 033401 (2003).