

X-Ray Studies of the Structure and Electronic Behavior of Alkanethiolate-Capped Gold Nanoparticles: The Interplay of Size and Surface Effects

Peng Zhang and T. K. Sham

Department of Chemistry, the University of Western Ontario, London N6A 5B7 Canada

(Received 3 February 2003; published 19 June 2003)

We report a study of the structure and electronic properties of a series of thiol-capped Au nanoparticles (NP) of nominal sizes of 1.6, 2.4, and 4.0 nm. Transmission electron microscopy, x-ray powder diffraction, x-ray absorption fine structure, and x-ray photoemission spectroscopy have been used to investigate the size-dependent systematics of lattice contraction and charge redistribution of these NPs. It is found that the lattice contracts and the d charge at the Au atom site depletes relative to bulk Au as the size of the NP decreases. The implication of these observations is discussed in terms of the interplay of quantum-size and surface effect.

DOI: 10.1103/PhysRevLett.90.245502

PACS numbers: 61.46.+w, 61.10.Ht, 73.22.-f, 79.60.Jv

The interplay of structure and electronic properties of nanostructures is of paramount importance to the advancement of nanoscience and nanotechnology [1–3]. In the nanoregime, two important factors come into play. One is the quantum confinement of the electrons, the size effect [4]; the other is the increasing contribution of surface atoms, the surface effect. The surface atom to bulk atom ratio increases dramatically as the particles size decreases (e.g., in a 2.5 nm particle, ~25% of all the atoms are on the surface). Both the quantum-size and the surface effects result in the electron redistribution (e.g., s - d rehybridization in d -band metals) of all NP atoms. Since NP minimizes its surface energy, this behavior leads to stability issues that are critical to the controlled fabrication of monodispersed NPs.

The tendency of nanocrystallites to nucleate and aggregate provides a challenge to the experimental investigations of the size dependence of the structural and electronic properties of NPs since these studies require nearly monodispersed particles. Two approaches have been employed to achieve this goal. One is to synthesize a well-defined molecular cluster, such as the chloride of triphenyl-phosphine capped Au₅₅ cluster [5–7]. The other is to cap the NPs with molecular species that interact with the surface, preventing the NP from further nucleation/aggregation [8–15]. The latter strategy has been quite successful in stabilizing and controlling the NP size of metal and semiconductors [8,9]. Capping molecules usually contain functional groups such as amine, alcohol, thiol, and phosphine, providing a wide range of interaction strength. For example, dendrimers with amine and alcohol groups interact weakly with Au NPs and preserve the electronic properties of a “naked” NP. On the other hand, thiols interact strongly with an Au surface and induce significant charge redistribution. Incidentally, thiol-Au interaction also exhibits the interesting property of self-assembly [10]. Thus, by changing the nature of the capping molecule while maintaining the size of the NP

[11], or by changing the size of the NP using the same capping molecule [12–14], we can study the systematic of the interplay of size and surface effect on the structure and electronic properties of NPs. Here we report a study of Au NPs using the latter scheme.

Au NP was selected for this study not only because there are established methods for the preparation of nearly monodispersed Au NPs, but also because there are many powerful probes: Electron microscopy (TEM and SEM), x-ray powder diffraction (XRD), Mössbauer spectroscopy [15], x-ray absorption fine structures (XAFS), and x-ray photoemission spectroscopy (XPS). In this study, in addition to conventional TEM, XRD, and UV-visible spectroscopy, we used XAFS [including x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structures (EXAFS)] and XPS to reveal the local structure and bonding. What emerges from this study is that there is a significant interplay between the size and the surface effects that determines the structure and the electronic properties of the nanoparticle.

A series of n -dodecanethiol-capped Au NPs prepared by colloidal synthesis techniques [8,13] in the presence of the thiol was investigated. The ratio of the Au salt, HAuCl₄ (0.03M) and the thiol determines the size of the thiol-capped NPs. We used ratios (Au:S) of 1:3, 1:1, and 6:1 (at 0 °C, 3.5 h) yielding NPs of 1.6, 2.4, and 4.0 nm, respectively, as revealed by the TEM in Fig. 1 (obtained using a Philips CM20 TEM operated at 200 keV). Figure 1 also shows the UV-visible spectra, XRD, and the Fourier transform (FT) and back-transform of the Au L_3 -edge EXAFS of these NPs and bulk Au. The XRD results were obtained with a Rigaku RTP 300R x-ray diffractometer. Au L_3 -edge, and S K - and $L_{3,2}$ -edge spectra were obtained at the PNC-CAT of the Advanced Photon Source (APS) at Argonne National Laboratory and at the Canadian Synchrotron Radiation Facility (CSRF) at the Synchrotron Radiation Center

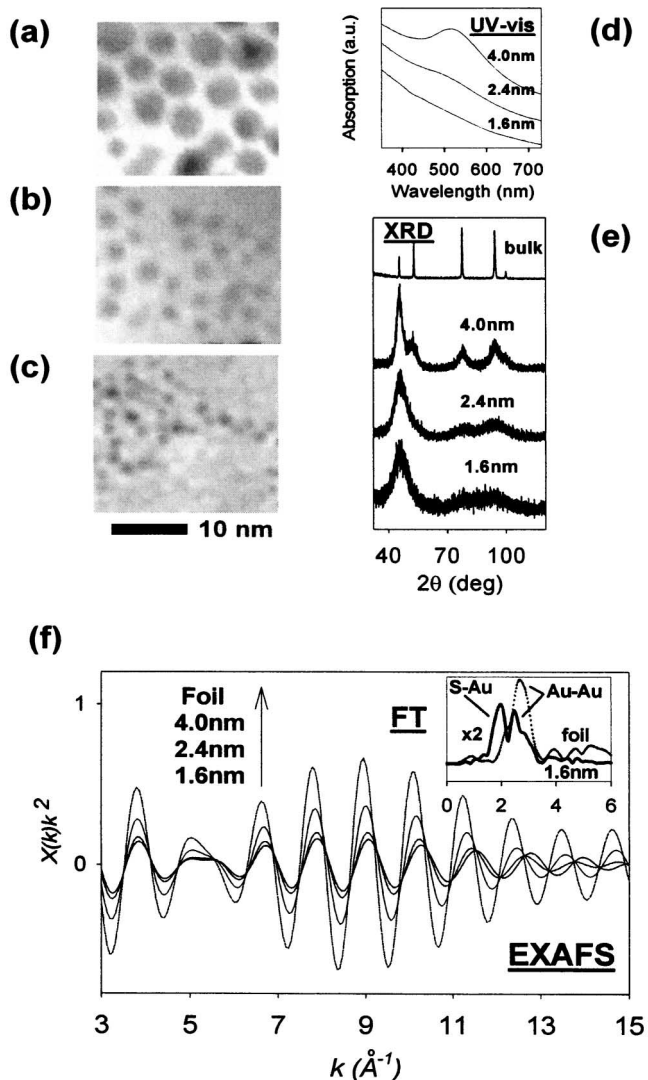


FIG. 1. (a)–(c): TEM images of the NPs of 4.0, 2.4, and 1.6 nm; (d): UV-visible absorption spectra of the NP samples; (e): XRD of the NP samples and bulk Au; (f): Fourier back-transform of the 1st Au-Au shell in R space of the three NPs and the bulk (gold foil). Inset: the FT-EXAFS (k^2 weighting, k -range 3–15 \AA^{-1}) of the 1.6 nm NPs compared with Au metal.

(SRC), University of Wisconsin-Madison, respectively. XPS results were obtained using a Kratos XPS spectrometer at Surface Science Western.

The TEM images in Figs. 1(a)–1(c) clearly show that the size of the NPs studied is distinctly different (the size distribution is $\sim \pm 15\%$ of the nominal size for 100 particles). The decrease in size is also borne out in the increasing broadening of the peaks in the XRD, Fig. 1(e), which shows that the Au NPs exhibit diffraction patterns identical to fcc Au. A close examination reveals that the 2θ shifts slightly to a larger value as the NP size decreases. This indicates a lattice contraction in the thiol-capped NPs, in good agreement with recent observations [13,14]. EXAFS analysis for the 4.0, 2.4, and 1.6 nm NPs

shows a lattice contraction of 0.7%, 1.1%, and 1.4%, respectively, relative to the bulk. The observation of a size-dependent lattice contraction is most apparent in the back-transform of the radial distribution of the first Au-Au shell in k space, Fig. 1(f). It clearly shows a shorter Au-Au distance (the oscillation becomes progressively farther apart in k space as the NP size decreases) and a reduction in coordination number and increasing disorder (less intense and broad oscillations). In the 1.6 nm NPs, the presence of capping thiols (Au-S bond) can be clearly identified in the inset of Fig. 1(f).

Figure 2 shows the normalized Au L_3 -edge XANES of the three NPs and Au metal (bulk). A couple of features are worth noting. First, all NP spectra exhibit the same resonance pattern as that of Au metal albeit with a significant broadening, indicating that they all have Au-like environment but with a significant disorder as revealed in the EXAFS. Second, the perhaps more significant observation is the intensity systematic of the resonance at the threshold (whiteline) associated with a $2p_{3/2}$ to $5d_{5/2,3/2}$ dipole transition probing the unoccupied densities of d states at the Fermi level. Figure 2 shows that the whiteline intensity increases in the order of bulk < 4.0 nm NP < 2.4 nm NP < 1.6 nm NP. A more intense whiteline relative to that of Au metal indicates an increase in d -hole population (d charge depletion in the NP) just above the Fermi level, in good agreement with electronegativity considerations (S is slightly more electronegative than Au). Using an established procedure [11,16–18], we estimated that there is an increase of 11.2%, 9.0%, and 7.2% in the d -hole count for the NPs of 1.6, 2.4, and 4.0 nm, respectively, relative to the Au metal where the d -hole population (~ 0.40 from band structure calculation) above the Fermi level in Au arises from s - d hybridization.

The effect of charge redistribution upon thiol-capped Au NP formation and its size dependence were examined with XPS. The Au $4f$ core level and the valence band of the NPs on a carbon substrate, together with relevant parameters are shown in Figs. 3 and 4, respectively. Two features are apparent in Fig. 3. First, the Au $4f_{7/2}$ of the NP shifts to higher binding energy for small NP

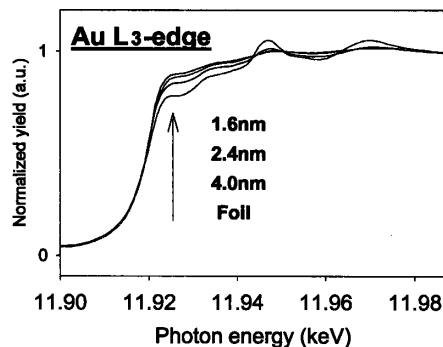


FIG. 2. Au L_3 -edge XANES of the NP samples and gold foil.

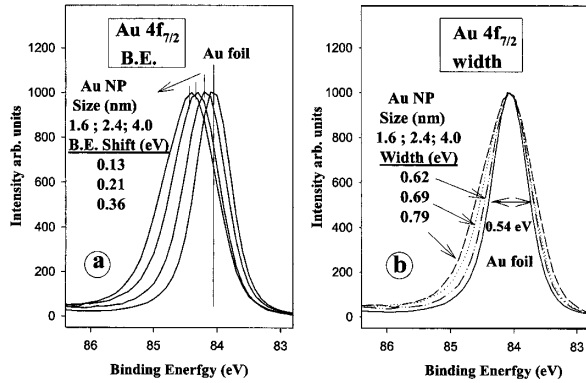


FIG. 3. (a): Au $4f$ XPS spectra of the three NP samples and bulk gold (b): same as (a) except that the $4f$ peaks of the NP samples were aligned with that of bulk gold. The binding energy shifts and the linewidths are also shown.

size [Fig. 3(a)]. This indicates that the d charge at the Au site of the NPs is depleted relative to the bulk since the binding energy shift depends on the charge redistribution and the Coulomb integrals $F_{4f,6s}$ and $F_{4f,5d}$ of which the latter is significantly larger than the former [18]. Second, there exhibits a linewidth broadening [Fig. 3(b)] as the NP size decreases. This broadening is accompanied by a systematic increase in the asymmetry at the higher binding energy side of the Au $4f$ peak. This observation can be attributed to both the increasing inhomogeneity of the Au atoms in the smaller clusters (increasing surface/bulk atom ratio) and the presence of more localized unoccupied d states at the Fermi level, enhancing a many-body effect known as the Doniach-Sunjic line shape [19]. These observations are consistent with the Au L_3 -edge XANES result that Au in these NPs depletes d charge.

The valence band spectra probe the electron distribution of the occupied densities of states of both s and d character. The Au d -band is below (~ 2 eV) the Fermi level and dominates because of its high population and cross section while the s character appears as a Fermi edge at zero binding energy. It has been established that Au-Au d - d interaction is very strong and the Au d -band width and apparent spin-orbit splitting become narrower as the coordination number of the nearest Au atom decreases [20,21]. The d -band width W , and the apparent spin-orbit splitting, Δ_{5d} , are marked in Fig. 4. The latter can be expressed as the quadrature of the effect of band formation, A_{band} , and the atomic spin-orbit splitting $\Delta_{s.o.}$ (1.5 eV) in Au atom,

$$\Delta_{5d} = (\Delta_{\text{band}}^2 + \Delta_{s.o.}^2)^{1/2}.$$

The band term decreases with the number of nearest Au neighbors. Thus the surface d band and apparent spin-orbit splitting are narrower than the bulk counterpart [22]. It is established that when Au is diluted in a metal matrix in alloy formation [20,21], both W and Δ_{band}

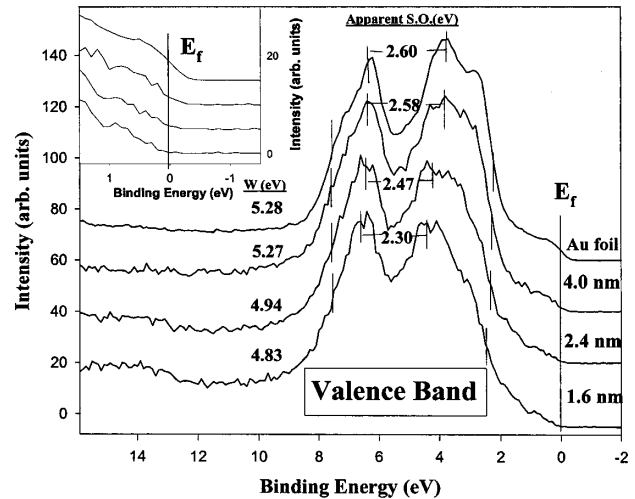


FIG. 4. Valence band XPS spectra of the NP samples and bulk gold. The d -band widths (between the point of inflection of the top and the bottom of the d band) and apparent spin orbit splitting as marked are also shown. Inset: zoomed spectra near the Fermi level.

become narrower upon the reduction in the coordination number of nearest Au neighbors. We can see from Fig. 4 that the top of the d band moves away from the Fermi level as the NP size decreases. This is accompanied by a bandwidth narrowing, a reduction in apparent spin-orbit splitting, and a centroid shift in the same direction as Au $4f$ (5.14 eV in bulk Au, 4.97 eV in 4.0 nm NP, 4.86 eV in 2.4 nm NP, and 4.57 eV in 1.6 nm NP). This is expected since the fraction of surface Au atom increases (the nearest Au coordination number decreases on average).

It is interesting to note that there is a clearly identifiable Fermi edge in the valence band of Au metal at zero binding energy. The edge diminishes somewhat in the spectrum of the 4.0 and 2.4 nm NPs. It is not noticeable in the 1.6 nm NP. This observation is in accord with the behavior of the plasmon peak in the UV-visible spectra [Fig. 1(d)]. We attribute this lack of Fermi edge to a significant reduction of conducting s character at the Fermi level. Thus the 1.6 nm is on the verge of a metal to insulator transition. It has been reported that such a transition takes place in the x-ray induced decomposition of an Au_{55} cluster [7].

We now examine the correlation of the electronic properties with the structure of the NPs in terms of the effect of size and surface chemistry (the role of the capping molecule). It is generally recognized that the naked or the weakly capped Au NPs contract noticeably relative to the bulk as revealed by XAFS [11,23,24]. In the presence of capping thiol molecules, the NP still contracts but the contraction is reduced somewhat depending on the NP size. The lattice contraction of noncapped Au NPs is $\sim 2\%$ for NPs of ~ 2 nm [23,24], and $< 1.5\%$ for the thiol-capped NPs [11,13,14]. It should be noted that the naked

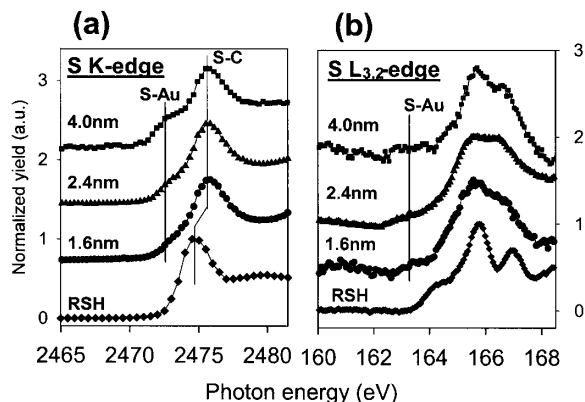


FIG. 5. (a) S K-edge and (b) S $L_{3,2}$ -edge XANES of the three NP samples and the free thiol. The peaks corresponding to the S-Au and S-C states are marked.

NP minimizes its surface energy through rehybridization of both the surface and the core Au atoms enhancing d - d interaction in the core while in thiol-capped NPs, surface energy minimization is facilitated by Au-S interaction. It has been observed that in weakly dendrimer-capped Au NPs, the Au L_3 whiteline is slightly less intense than that of the bulk [11]. This is in contrast to an increase in whiteline intensity in the thiol-capped NP (Fig. 2). We propose that for the thiol-capped NPs, there is a strong covalent interaction involving some charge transfer (including d charge) from the NP to the thiol in agreement with electronegativity consideration. This leaves the Au atoms in the NP with depleted d charge at the Au site. The Au L_3 -edge XANES and the Au XPS support this notion. Since d - d interaction determines the strength of the Au-Au interaction, a reduction in d charge will slightly weaken this interaction resulting in a slightly relaxed lattice in thiol-capped NPs relative to the weakly capped and naked NPs [11,14,23,24].

Finally, we want to report the Au-S interaction from the S perspective. The discussion above implies that Au-S interaction is not very sensitive to NP the size (e.g., S occupying a Au surface threefold hollow site). Figure 5(a) shows the S K-edge XANES of the NPs and the free thiol. The S K-edge of the NPs exhibits a pre-edge shoulder that is at about the same energy for all NPs although the intensity decreases somewhat at the 1.6 nm NP and is absent in the free ligand. A similar shoulder is also observed in the $L_{3,2}$ edge [Fig. 5(b)]. This shoulder is attributed to the antibonding state of Au-S interaction involving both s and p character of S. Its decrease in intensity for the 1.6 nm NP at the S K-edge is more noticeable than at the $L_{3,2}$ edge and is attributed to the increasing presence of Au-S sites of symmetry less than threefold. Overall, the Au-S interaction is indeed less

sensitive than Au-Au interaction to the NP size for the thiol-capped NPs in this study.

We have presented a systematic study of the structural and electronic property in a series of thiol-capped Au NPs. It appears that some degree of tuning of the size and electronic properties of Au NPs can be achieved by controlling the balance of the size and the nature of the capping molecules.

Research at the University of Western Ontario and CSRF is supported by NSERC of Canada. XAFS were obtained at the PNC-CAT at APS at Argonne National Laboratory (supported by U.S. DOE under Contract No. DE-AC02-98CH10886) and at SRC, University of Wisconsin-Madison (supported by U.S. NSF, Grant No. DMR-0084402). We thank S. M. Heald, R. Gordon, K. H. Tan, Y.-F. Hu, X. H. Sun, and Surface Science Western Staff for their technical assistance at various stages of this work.

- [1] G. Schmid, in *Nanoscale Materials in Chemistry*, edited by K. J. Klabunde (Wiley, New York, 2001).
- [2] A. P. Alivisatos, *J. Phys. Chem.* **100**, 13 226 (1996).
- [3] G. Schmid, *Clusters and Colloids* (VCH, Weinheim, 1994).
- [4] M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.* **23**, 183 (1990).
- [5] G. Schmid, *Inorg. Synth.* **7**, 214 (1990).
- [6] M. A. Marcus *et al.*, *Phys. Rev. B* **42**, 3312 (1990).
- [7] H. Boyen *et al.*, *Phys. Rev. Lett.* **87**, 276401 (2001).
- [8] M. Brust *et al.*, *J. Chem. Soc. Chem. Commun.* **1994**, 801 (1994).
- [9] C. B. Murray, D. B. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).
- [10] A. Ulman, *Chem. Rev.* **96**, 1533 (1996).
- [11] P. Zhang and T. K. Sham, *Appl. Phys. Lett.* **81**, 736 (2002).
- [12] M. J. Hostetler *et al.*, *Langmuir* **14**, 17 (1998).
- [13] P. Zhang and T. K. Sham, *Mater. Res. Soc. Symp. Proc.* **738**, 351 (2003).
- [14] D. Zanchet *et al.*, *Chem. Phys. Lett.* **323**, 167 (2000).
- [15] F. M. Mulder *et al.*, *Nanostruct. Mater.* **7**, 269 (1996).
- [16] A. Mansour, J. Cook, and D. Sayers, *J. Phys. Chem.* **88**, 2330 (1984).
- [17] C. Tyson *et al.*, *Phys. Rev. B* **45**, 8924 (1992).
- [18] T. K. Sham, M. L. Perlman, and R. E. Watson, *Phys. Rev. B* **19**, 539 (1979).
- [19] S. Doniach and M. Sunjic, *J. Phys. C* **3**, 285 (1970).
- [20] T. K. Sham *et al.*, *Phys. Rev. B* **41**, 11 881 (1990).
- [21] A. Bzowski *et al.*, *Phys. Rev. B* **51**, 9979 (1995).
- [22] P. H. Citrin and G. K. Wertheim, *Phys. Rev. B* **41**, 11 881 (1990).
- [23] A. Balema *et al.*, *Surf. Sci.* **156**, 206 (1985).
- [24] A. Pinto *et al.*, *Phys. Rev. B* **51**, 5315 (1995).