Tuning the electronic behavior of Au nanoparticles with capping molecules

P. Zhang and T. K. Sham

Tuning the electronic behavior of Au nanoparticles with capping molecules

P. Zhang and T. K. Sham[a)]

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

The electronic behavior of gold nanoparticles (NPs) of ~ 2 nm capped with dendrimer and thiol molecules was studied with Au $L_{3,2}$-edge x-ray absorption near-edge structure (XANES). The results reveal the tunability of the d-electron distribution in the Au NPs by selective capping. That is, that the Au atoms in the NPs gain $5d$ electrons (relative to the bulk) when capped with weakly interacting dendrimers and lose $5d$ electrons when capped with strongly interacting thiol molecules. A semiquantitative analysis of the d-charge (holes) distribution is presented. This work demonstrates the important role of the capping molecules in the d-charge distribution of Au NPs and the usefulness of XANES in probing the electronic behavior of transition metal NPs. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1494120]

The d electrons play an important role in determining the electronic, optical, magnetic and catalytic behavior of transition metals.[1] When metal atoms are confined in a nanoscale space, factors affecting the electronic structure will become more complex. For example, the "nanosize effect" may result in stronger d-d interaction in gold nanoparticles (NPs) so that the d charge will increase at the Au site relative to the bulk.[2] Further, when the size of NPs decreases, a larger fraction of metal atoms will be located on the surface. As a result, the optimization of surface energy (reduced coordination number) and the metal-substrate or metal-adsorbate[3] interaction will influence the electronic structure of the transition metal NPs. Thus one can modify the electronic behavior of NPs by carefully controlling their surface environments. Here, we report that the d electron (or hole) distribution of ~ 2 nm Au NPs can be tuned by selective capping, that is, that the NPs gain d electrons when capped with the weakly interacting dendrimers but lose d electrons when capped with the strongly interacting thiols. The electronic behavior of the capped Au NPs were monitored by x-ray absorption near-edge structure (XANES), a technique that is very sensitive to the d-charge redistribution of transition metals induced by the change of local environments.[4] A semiquantitative result of the effect of capping on the Au d-charge (hole) distribution has been obtained.

Thiol and dendrimer-capped Au NPs were prepared according to the literature.[5,6] Briefly, gold salt ($HAuCl_4$ or $KAuCl_4$) solutions were reduced by $NaBH_4$ in the presence of the capping molecules, starburt poly(amidoamine) dendrimer of generation 4 with 64 hydroxyl end groups (Aldrich) and dodecanethiol (Aldrich). By controlling the ratio of gold and capping molecules, desired particle sizes can be achieved. Here we employed dendrimer-capped Au of ~ 2 nm diameter (dendrimer:Au$=1:40$, prepared at room temperature, denoted nano-Au1) and thiol-capped Au of ~ 2.1 nm diameter (thiol:Au$=1:1$, prepared at 0 °C, denoted nano-Au2).[7] The Au $L_{3,2}$-edge x-ray absorption measurements were made at the PNC-CAT BM beamline of the Advanced Photon Source at Argonne National Laboratory. The

XANES spectra of the thiol-capped NPs powder specimen (on aluminum substrate) were collected in fluorescence yield (FLY) at glancing angle (to enhance signal to background ratio) and the dendrimer-capped sample was measured in FLY in a H_2O solution in a polymer liquid cell. The XANES spectra analysis was performed by a pre-edge background subtraction followed by a normalization procedure described in the literature.[4(a,b)] The edge thresholds (E_0) of the NP samples were aligned to the Fermi levels of bulk Au.

Figure 1 shows the x-ray diffraction (XRD) patterns of the two NP samples and an Au foil. Both NP samples exhibit a broad diffraction peak corresponding to the (111) diffraction peak in bulk Au. A closer examination of the peak positions reveals that the lattice constants (d values) are 2.35 Å for bulk, 2.30 Å for nano-Au1 (2.13% contraction relative to bulk) and 2.33 Å for nano-Au2 (0.85% contraction), respectively. It should be noted that the lattice constants obtained from XRD results are average, however these results are semiquantitatively in good accord with the reported XRD[2a] and extended x-ray absorption fine structure (EXAFS) results.[8] The noticeable decrease in lattice constants in Au-nano1 can be understood in terms of a simple liquid drop model[9] where enhanced surface energy is a main reason for the contracted lattice (nanosize effect). In Au-nano2, however, the lattice contraction due to nanosize effect is largely compensated by the metal-capping molecule interaction.[8] These results point out, as expected, that the metal-capping molecule interaction in nano-Au1 is much weaker than in nano-Au2. Therefore, nano-Au1 can be considered as pure Au NPs,[10] whereas nano-Au2 as NPs capped with tightly binding ligands.[11]

Figure 2 shows the XANES spectra of the dendrimer-capped Au at the L_3 and L_2 edges. We have obtained XANES from both colloidal suspension (in liquid) and solid state specimen (thin film on silicon wafer) of nano-Au1 and the XANES in both cases are identical under the same experimental conditions. Since the liquid sample is more uniform and shows better signal-to-noise ratio in the x-ray absorption data, we employ the liquid XANES results in the following discussion. The XANES spectra of both nano-Au1 and bulk Au exhibit similar three peak patterns within the
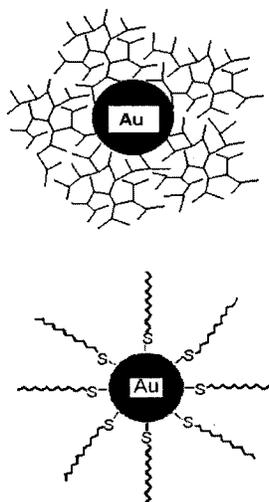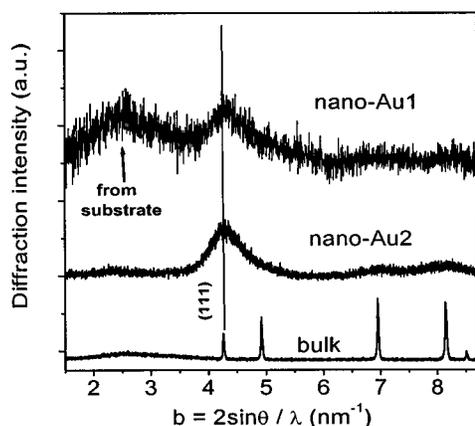
[a)]Electronic mail: tsham@uwo.ca

FIG. 1. Powder XRD patterns of the two NP samples and bulk Au. The different capping structures of the NPs are also illustrated (right).

first 40 eV above the edge, which is evidence for the existence of a fcc structure in the NPs. The first resonance at the edge is often known as white line, arising from $2p_{3/2,1/2} \rightarrow 5d$ dipole transitions, the intensity of which is very strong for most transition metals with a partially filled d band and is related to the unoccupied densities of d states (d-hole counts). Although the $5d$ orbitals in Au atoms are nominally full, due to s-p-d hybridization, small white line can still be detected in the XANES of bulk Au.[12] The area under the white line can thus be utilized to study the d-charge (hole) redistributions in various gold samples.[12] It is evident in Fig. 2 that the drendrimer-capped NPs exhibit a noticeable decrease in the white line intensity. Keeping in mind that Au $L_{3,2}$ XANES probes the electronic transition of $2p \rightarrow 5d_{5/2,3/2}$ orbitals and the relativistic effect is significant for $5d$ metals like Au and Pt, one can deduce from the above observation that Au atoms in nano-Au1 gain $5d$ electrons, or lose $5d$ holes, relative to the bulk sample. Such d-charge-redistribution behavior has also been found in the XANES of porous-silicon-supported Au NPs.[2a] In the Au NPs reported here, the nano-size effect plays a predominant role in modifying their electronic behavior. Stronger Au d-d interaction favors $s \rightarrow d$ rehybridization, increasing the d-electron count at the Au site in the NPs.[2]

The Au L_3, and L_2-edge XANES together with the Fourier transform (FT) of the L_3-edge extended x-ray absorption fine structure (EXAFS) are shown in Fig. 3 and the inset,

respectively. In contrast to nano-Au1, both the L_3 and L_2 spectrum of nano-Au2 exhibit a small but noticeable increase in the white line area (20 eV above the threshold[4(a)]) compared to the bulk. Unlike nano-Au1, the strong metal-capping molecule interaction has resulted in considerable change in the local environment of Au atoms in the NPs, as is clearly seen in the FT-EXAFS result which shows both Au–S and Au–Au bonds [Fig. 3(a)] inset). It should be noted that such an Au-ligand EXAFS peak does not exist in either the nano-Au1 sample or other weakly capped Au NPs. In fact, there is an interesting interplay between the strong Au-capping molecule interaction which modifies the surface of NPs, and the nanosize effect which leads to lattice contraction. It has been calculated that charge transfer (negative) from gold to sulfur in the ligand will modify the electronic behavior of thiol-capped Au clusters.[13] The increased white line intensity in the XANES in nano-Au2 yields a d-charge loss of ~ 0.07 e/atom (relative to bulk, see Table I), in good agreement with a recent calculated result of ~ 0.05 e/atom charge transfer in $Au_{38}(SCH_3)_{24}$.[13] Therefore, the d-charge redistribution of thiol-capped Au results in lattice relaxation which is a balance of the nanosize effect (contraction) and, as importantly, interfacial charge transfer through the Au–S bonding. We have also measured a series of thiol-capped Au NPs with sizes from 1.7 to 4.5 nm. The XANES of all these
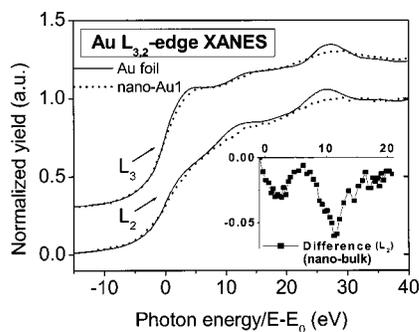

FIG. 2. Au $L_{3,2}$-edge XANES spectra of dendrimer-capped nanoparticles, nano-Au1, compared with bulk Au. The L_3-edge spectra were aligned with those of L_2 and shifted vertically for clarity. The inset shows the difference of the two spectra (nano-bulk) at L_2 edge.
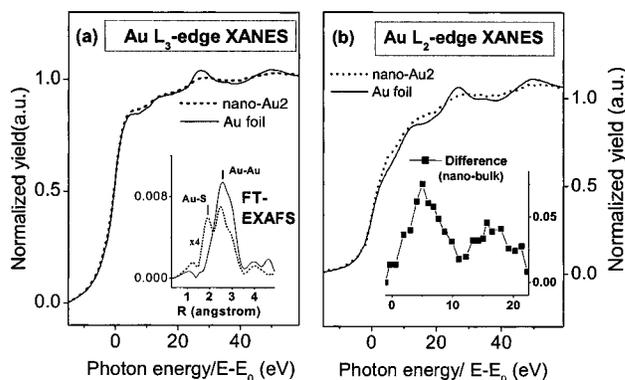

FIG. 3. (a) Au L_3-edge XANES and k^2-weighted FT-EXAFS (inset, the ordinate is the magnitude of the FT) of thiol-capped Au, nano-Au2, and bulk from the k-space range of $3.1–12.5$ Å^{-1} without phase correction. (b) Au L_2-edge XANES and difference spectrum (inset) of the same samples.

TABLE I. The d-holes distribution[a] of Au NPs calculated from XANES data.

	ΔA_3	ΔA_2 [b]	$h_{5/2}$	$\Delta h_{5/2}$ [c] (%)	$h_{3/2}$	$\Delta h_{3/2}$ [c] (%)	$h_{5/2}/h_{3/2}$	h_t	Δh_t [c] (%)
	eV/cm								
nano-Au1	-475	-333	0.271	-4.2	0.105	-11.0	2.6	0.305	-6.2
Au foil[d]	⋯	⋯	0.283	⋯	0.118	⋯	2.4	0.401	⋯
nano-Au2	522	581	0.296	4.6	0.141	19.5	2.1	0.473	9.0

[a]With ~10% uncertainty.
[b]Integrated from 10 eV below the edge to 15 eV above.
[c]Percentage relative to the values of bulk gold.
[d]Values taken from Ref. 12(b).

samples exhibit increased white line intensity relative to the bulk Au, in good accord with the observation of white line intensity discussed above. The details of these results will be published elsewhere.

Finally, we obtained the d-holes redistribution in the two Au NPs relative to bulk Au using established expressions[4(a),12,14]

$$\Delta h_{5/2} = (2.25\Delta A_3 - 0.5\Delta A_2)/C, \qquad (1)$$

$$\Delta h_{3/2} = 3\Delta A_2/C, \qquad (2)$$

where $\Delta h_{5/2}$ and $\Delta h_{5/2}$ are the change of d-hole counts in the $d_{5/2}$ and $d_{3/2}$ orbitals, ΔA_3 and ΔA_2 the difference in the area under the L_3 and L_2 white line between NPs and bulk Au, and C is constant characteristic of the absorption ($C = 75213$ eV/cm).[4(a)] The results are summarized in Table I. As seen from Table I, although the percentage change of total amount of $5d$ holes in the NPs Au is a few % ($<10\%$), the change in the direction of d-electron transfer depending on capping is significant. Interestingly, the holes in the $5d_{3/2}$ orbitals show a more significant change than that of the $5d_{5/2}$ in nano-Au2, indicating that the $d_{3/2}$ orbital is more sensitive to metal-ligand binding ($j = 5/2$, 3/2 are reasonably good quantum numbers in Pt and Au where the relativistic effect is important.). A systematic study of thiol-capped Au with varied sizes is under way to provide further quantitative analysis of the phenomenon.

In summary, we have shown that the electronic behavior of Au NPs can be tailored through selective capping. In addition, it is demonstrated that XANES can be an effective tool to evaluate the d-charge distribution in the Au NPs. This method can also be applied to the study of other transition metal NPs.

[1] A. Cottrell, *Introduction to the Modern Theory of Metals* (Institute of Metals, London, 1988).

[2] (a) I. Coulthard, I. S. Degen, Y. Zhu, and T. K. Sham, Can. J. Phys. **76**, 1707 (1998); (b) R. Benfield, D. Grandjean, M. Kroll, R. Pugin, T. Sawitowski, and G. Schmid, J. Phys. Chem. **105**, 1961 (2001).

[3] (a) M. Cini, M. Crescenzi, F. Patella, N. Motta, M. Sastry, F. Rochet, R. Pasquali, A. Balzarotti, and C. Verdozzi, Phys. Rev. B **41**, 5685 (1990); (b) K. Ohtani, T. Fujikawa, T. Kubota, K. Asakura, and Y. Iwasawa, Jpn. J. Appl. Phys., Part 1 **37**, 4134 (1998).

[4] (a) C. Tyson, A. Bzowski, P. Kristof, M. Kuhn, R. Sammynaiken, and T. K. Sham, Phys. Rev. B **45**, 8924 (1992); (b) I. Coulthard and T. K. Sham, Phys. Rev. Lett. **77**, 4824 (1996).

[5] M. Brust, M. M. Walker, D. Bethell, D. Schiffrin, and R. Whyman, J. Chem. Soc. Chem. Commun., 801 (1994).

[6] M. Garcia, L. Baker, and R. Crooks, Anal. Chem. **71**, 256 (1999).

[7] The average particle size of thiol-capped Au NPs is estimated from the Debye–Sherrer equation and fit well with the results of UV-vis, nuclear magnetic resonance and reported data (see M. Hostetler, J. Wingate, C. Zhong, J. Harris, R. Vachet, M. Clark, J. Londono, S. Green, J. Stokes, G. Wignall, G. Glish, M. Porter, N. Evans, and R. Murray, Langmuir **14**, 17 (1998). Due to the existence of the broad diffraction band centered around $b = 2.5$ nm-1 (Fig. 1) probably originated from dendrimer; the average size of the **nano-Au1** sample is estimated to be ~2 nm.

[8] D. Zanchet, H. Tolentino, M. Martins Alves, O. Alves, and D. Ugarte, Chem. Phys. Lett. **323**, 167 (2000).

[9] A. Balerna and S. Mobilio, Phys. Rev. B **34**, 2293 (1986).

[10] This is also supported by the fact that G4-dendrimer capped Au is not very stable and tends to aggregate after a period of time. See also F. Grohn, B. Bauer, Y. Akpalu, C. Jackson, and E. Amis, Macromolecules **33**, 6042 (2000).

[11] A. Templeton, W. Wuelfing, and R. Murray, Acc. Chem. Res. **33**, 27 (2000).

[12] (a) F. Lytle, Ber. Bunsenges. Phys. Chem. **91**, 1251 (1987). (b) L. Matheiss and R. Dietz, Phys. Rev. B **22**, 1663 (1980).

[13] H. Hakkinen, R. Barnett, and U. Landman, Phys. Rev. Lett. **82**, 3264 (1999).

[14] A. Mansour, J. Cook, and D. Sayers, J. Phys. Chem. **88**, 2330 (1984).