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# Molecular conformation changes in alkylthiols ligands as a function of size in gold nanoparticles.

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The bonding of hexanethiols to gold nanoparticles of 1.5, 2.0 and 3 nm was studied using X-ray Absorption Near Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine Structure (EXAFS). The XANES spectra revealed that a substantial fraction of hexanethiol molecules were weakly bound, in addition to the molecules forming covalent bonds with Au surface atoms. The weakly bound molecules could be easily removed by washing in dichloromethane. After removal of the weakly bound molecules the S K-edge XANES spectrum reveals peaks due to S-Au and S-C bonds with intensities that change as a function of particle size. We explain this as the result of distortions occurring in the molecules adsorbed on the smaller particles. The distortions arise from the poor packing due to the high curvature of the particles. In addition, EXAFS results show that the smaller particles bind more molecules per Au atom than the larger ones, which is again interpreted as a result of the curved nature of the surface.

One of the most interesting features of alkyl hydrocarbon chains is their flexibility that allows them to change conformation to maximize space filling. This is driven by minimization of van der Waals energy and facilitated by the easy formation of gauche distortions with 0.16 eV activation energy. Organic-thiolates in particular are extensively used as capping agents to prevent sintering and as ligands that can be functionalized to provide desirable chemical properties. On Au(111) alkylthiolates form self-assembled monolayers (SAM) that have been studied extensively [1]. The molecules form an ordered lattice with  $(\sqrt{3} \times \sqrt{3})R30^\circ$  periodicity [2] with one sulfur atom bound to three gold atoms. Since the gold spacing of  $\sim 5$  Å is slightly larger than the van der Waals diameter of the chains, the molecules tilt to an angle of  $\sim 30^\circ$  to maximize contact. The tendency of chain molecules to maximize packing is expected to lead to interesting effects when the surface of gold is not flat, as is the case of nanoparticles (NP), a system that is widely used in today nanotechnology applications [3].

A review by Whitesides [1] summarizes the state of the art on the structure of SAM on NP based on spectroscopic (IR and NMR) and chemical reactivity results. S-enrichment on the nanoparticles surface was proposed [4] based on thermal gravimetric analysis (TGA) of NP of  $\sim 4.4$  nm diameter. A higher ratio of alkanethiols per gold atom over that of the flat Au(111) crystal surface lead to the proposal that the S atoms in the thiol molecules occupies alternate binding sites (edges and corners).

X-ray absorption techniques are specially appropriated to study the interaction between metal and sulfur in alkanethiol-capped NP. Sham and coworkers made some of the first contributions [5–7], followed soon by further studies [8–10]. In a recent study Liu et al. [11] found that the alkyl chain length strongly affects the electronic in-

teractions between adjacent NP by tunneling effect when the alkyl chains contain less than six carbons. These results and the potential applications of thiol-capped Au NP to biology, nanoelectronics, etc. demand a thorough understanding of their geometric and electronic structure as a function of nanoparticle size and of the role of ligands and their bonding to the NP. We present here the results of a study using X-ray absorption techniques, in particular XANES S K-edge and EXAFS Au  $L_3$ -edge.

The gold NP used in this study had average core diameters of 1.5 nm, 2 nm, and 3 nm ( $\pm 0.3$  nm). They will be referred to in this paper as Au15, Au20 and Au30 respectively. The particle core size was controlled by the synthesis conditions [4] and measured by HRTEM [12]. Synthesis was performed following the Brust reaction [3], where  $AuCl^{-4}$  is transferred to toluene using tetraoctylammonium bromide as the phase-transfer reagent. Addition of hexanethiols followed by reduction with  $NaBH_4$  generated hexanethiol protected gold NP ( $C_6SH$ ). The core size of gold NP could be controlled by changing the thiol:gold mole ratio and reaction temperature [4]. Extraction and annealing of 1.8 nm gold NP (thiol:gold = 3:1, 0°C) resulted in the isolation of 1.5 nm gold NP [13]. The reactions with thiol:gold mole ratio of 2:1 and 1:2 at room temperature resulted in the formation of 2 and 3 nm gold NP, respectively.

X-ray absorption measurements were performed at the SXS and XAS beamlines of the Laboratorio Nacional de Luz Sincrotron (LNLS) in Campinas, Brazil. XANES spectra were obtained at the S K-edge (2472 eV) and EXAFS spectra were obtained at the Au  $L_3$ -edge (11919 eV). Details of the experimental setup of the SXS beamline have been published elsewhere [14]. The X-ray absorption spectra were recorded in total electron yield (TEY) mode by collecting the emitted current with an electrometer connected to the sample. The experiments were per-

formed in a vacuum of  $10^{-8}$  mbar, at room temperature. The energy scale was calibrated using the Mo  $L_3$ -edge, at 2520 eV. The XANES spectra were background subtracted and normalized to the post-edge intensity. EXAFS experiments at the Au  $L_3$ -edge were performed in transmission mode using a Si(220) monochromator and two ion chamber detectors. For EXAFS characterizations the NP were diluted in hexane. The effect of irradiation as a possible source of modification of the structure of the alkylthiol molecules was investigated by comparing x-ray absorption spectra acquired immediately after sample introduction with those after 30 minutes of irradiation. No changes were observed within the experimental error.

The first and unexpected finding of our studies is that the as-prepared, alkylthiol-capped nanoparticles contain a large amount of weakly bound molecules that contribute substantially to the x-ray absorption spectra. This is shown in Fig. 1 by the XANES spectra of Au15 before (a) and after (b) washing in dichloromethane. The spectrum before washing is identical to that of free alkylthiols reported in the literature, which shows only one peak corresponding to excitations into the S-C bond states [5, 6]. After washing, the spectrum shows two peaks separated by about 7 eV. The peak at lower energy has been assigned to excitations into S-Au bond states (peak "a"). The other corresponds to excitations into the S-C bond (peak "b"). The higher energy of this peak, relative to that in the unbound molecules, reflects the formation of the S-Au bond [5]. The presence of free molecules around the NP, never reported before, illustrates the importance of carefully controlling the preparation methods. We expect this phenomenon to be much more prevalent in small particles than in flat surfaces due to their high surface curvature. The high curvature should prevent close molecular packing of the covalently bound ligands, thus facilitating intercalation of other molecules bound by weaker van der Waals forces.

The second finding of our study is that the bonding structure of the covalently attached molecules is a strong function of the particle size. Fig. 2 shows XANES S K-edge spectra of the three nanoparticles sizes after the washing procedure. As can be seen the relative intensities of peaks *a* and *b* are different in each sample. The change affects the relative intensity of the peaks but not their energy. This immediately indicates that the bonds giving rise to these peaks (S-Au and S-C) are not significantly changed. Thus we can exclude rupture of S-C bonds, formation of S-S bonds (dimerization), or any other major modification of the chemical nature of the system.

We propose that the changes are due to the formation of distorted molecular conformations, by rotations around the S-C bond and by gauche defects in the alkyl chains. These deformations would change the relative orientations of the molecular orbitals in the final states relative to that in the undistorted molecules, thus changing the absorption amplitude  $A$  ( $A \propto \langle \Phi_{initial}^S | E \cdot x | \Phi_{final} \rangle$ ).

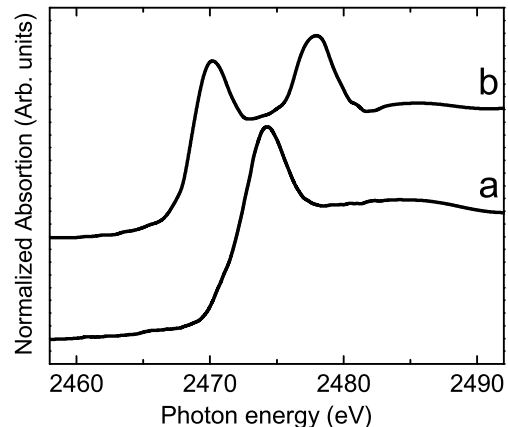


FIG. 1: Sulfur K-edge XANES spectra of 1.5 nm Au nanoparticles capped with hexanethiols. (a) Before and (b) after washing in dichloromethane. Weakly bound molecules dominating the spectrum in (a) are removed leaving only the covalently bound ones in (b).

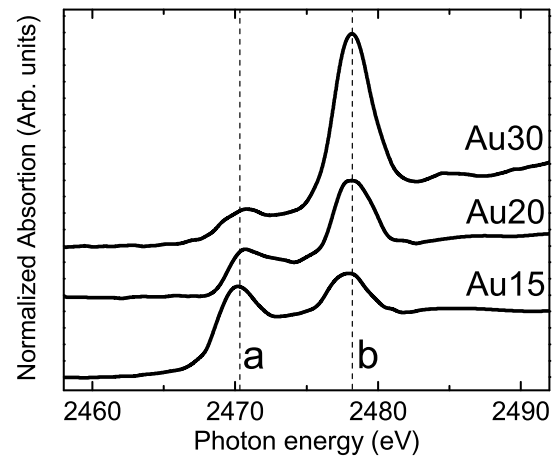


FIG. 2: Sulfur K-edge XANES spectra of hexanethiol capped Au nanoparticles as a function of particle size. Diameters are 3.0, 2.0 and 1.5 nm ( $\pm 0.3$  nm), for Au30, Au20 and Au15 respectively. Peaks *a* and *b* correspond to final states of S-Au and S-C bonds respectively. Notice that only the relative peak intensity changes, while the energy remains constant.

Such molecular distortions should be facilitated by poor packing due to the high curvature of the surface of small particles, an effect that should be less important as the particle size increases. The changes observed in Fig. 2 should reflect this change in curvature and packing. The driving force for distortions is the max-

imization of van der Waals energy, which is accomplished by filling space through bending of the molecules.

TABLE I: Fitted values for the mean coordination number  $N$ , energy shift  $E_0$ , Debye Waller factor  $\sigma$ , and interatomic distance  $R$  for first coordination shell around Au atoms. Errors are indicated in parenthesis.

Sample	Au30	Au20	Au15
$N_{Au-Au}$	9.4(8)	8.4(8)	7(1)
$E_{0Au-Au}$		2.2(2)	
$\sigma[\text{\AA}^{-2}]_{Au-Au} \times 10^3$	111(6)	104(6)	11(1)
$R[\text{\AA}]_{Au-Au}$	2.825(4)	2.826(4)	2.824(7)
$N_{Au-S}$	0.4(2)	0.5(2)	0.8(3)
$E_{0Au-S}$		6(1)	
$\sigma[\text{\AA}^{-2}]_{Au-S} \times 10^3$	4(3)	5(3)	6(4)
$R[\text{\AA}]_{Au-S}$	2.33(2)	2.34(2)	2.322(6)

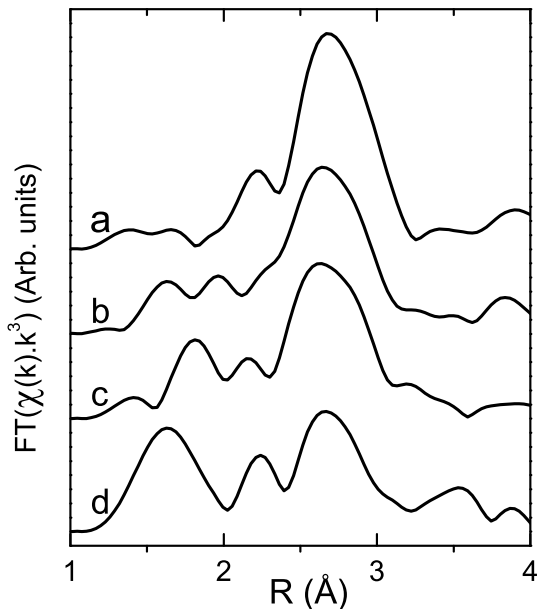


FIG. 3: Fourier transforms of the EXAFS oscillations after the Au  $L_3$ -edge of a) metallic Au (signal attenuated 60%), b) Au30, c) Au20 and d) Au15 samples.

The third finding of our work derives from EXAFS experiments at the Au  $L_3$ -edge. Fig. 3 shows the Fourier transforms of the EXAFS oscillations for the three NP (without phase correction). Two peaks are present for the three samples. The one at a shorter distance (around 1.8 Å) corresponds to a sulfur shell around the absorber while the one at 2.7 Å corresponds to a gold shell. EXAFS fits were performed in order to obtain the average

TABLE II: Average particle size, surface Au-atomic concentration, and S:Au atomic ratio derived from EXAFS fitting (Table I). Surface atom concentrations are determined assuming spherical NP. Errors are indicated in parenthesis.

Sample	Radii[Å]	EXAFS	
		Surface Atoms	$S : Au$
Au15	6(1)	0.80(2)	1.0(1)
Au20	7.0(5)	0.75(1)	0.67(2)
Au30	10.0(5)	0.61(1)	0.61(2)

coordination number  $N$  for each shell (Table I). From the Au-Au average coordination numbers, and assuming that the particles are spherical, the sizes of the NP were determined using a method already utilized for Pt NP [15]. The radii of the particles determined are shown in Table II as well as the percentage of atoms on the surface for each NP. From this number, and from the fitted Au-S coordination, the S:Au atomic ratio on the surface can be estimated [9]. The values obtained are all larger than 3:1, corresponding to the S:Au atomic ratio of alkylthiol monolayers on Au(111) single crystal surface (see Table II). This supports previous proposals of high S:Au ratios in NP and is another manifestation of the high surface curvature. Indeed a high curvature makes more Au surface atoms accessible for bonding with S of the alkylthiol molecules. To confirm this result the S K-edge XANES spectra in Fig. 2 were fitted with an arctan function and two Gaussians. Assuming as before that the S-Au bond has not changed substantially (as supported by its constant peak energy), the variation in the area of the fitted peak  $a$  (S-Au bond) for the different spectra is also related with the S:Au atomic ratio variation at the surface of the NP and it can be compared with the EXAFS results (Fig. 4). Although both XANES and EXAFS determinations are independent (the areas of the fitted Gaussian corresponding to the S-Au bond and the S:Au atomic ratio respectively), the good qualitative agreement between their trends with the particle size is a good confirmation that the above interpretation is correct. In summary, we have obtained new information about the structure of alkylthiol ligands on Au nanoparticles that derive from the nanoscale size of the Au particles. First we have found that the as-prepared samples can easily incorporate substantial numbers of alkylthiol molecules that are weakly bound to the particles in addition to the strongly bound ones that form covalent S-Au bonds. Both types of molecules produce distinctive X-ray absorption spectra. We have shown that the weakly bound molecules can be removed by washing in solvents. Our second observation is a substantial change in the conformation of the molecules with particle size, which is manifested in the relative intensities of the X-ray absorption cross sections for transitions from the initial

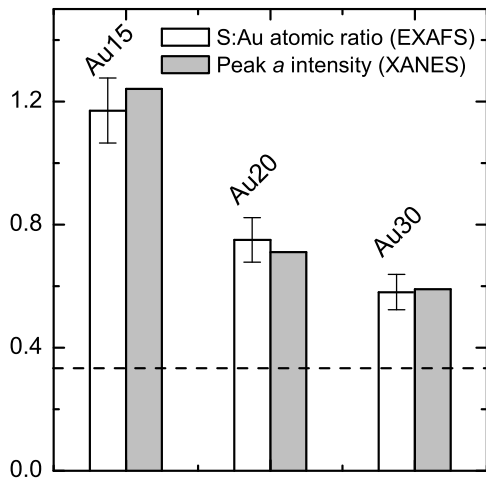


FIG. 4: S:Au atomic ratio obtained from EXAFS Au  $L_3$ -edge fits and area of the S-Au peak in the XANES S K-edge. Horizontal dashed line indicates the corresponding S:Au atomic ratio for hexanethiol monolayer on Au(111).

S K-orbital to the final state orbitals of S-Au and S-C bonds. We interpret this result as an effect of molecular distortions that change the orientation of the final state orbitals, particularly those deriving from S-C bonds. We propose that the effect of distortions is a more efficient space filling of the more open ligand shells of small particles and are driven by optimization of the van der Waals energy. A final and correlated effect, again related to the small size and high curvature of the Au particles is the higher atomic ratio of S to Au surface atoms revealed directly by EXAFS data and indirectly by XANES. All the observations are consistent with the enormous influence of particle size, through the high curvature of their surface, on the structure and conformation of the ligand molecules, an effect that should be of great importance in applications of chemically tagged nanoparticles.

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