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## XANES Study of the Radiation Damage on Alkanethiolates-Capped Au Nanoparticles

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**Abstract.** The radiation damage during XANES experiments on alkanethiols capped gold nanoparticles has been investigated. Different carbon length chains and nanoparticle sizes have been studied. Changes in the spectra after 45 minutes of irradiation, using a bend magnet, were observed for chains with more than 6 carbon atoms and are associated with the cleavage of S-C bonds and formation of atomic sulphur on the nanoparticle surface.

### 1. Introduction

Self-assembled monolayers (SAM) of *n*-alkanethiolates on Au(111) have been extensively studied [1]. However the nature of the metal-sulfur bond and the spatial arrangements of sulfur groups on the gold surface are still controversial. It is now accepted the formation of an ordered sulfur lattice based on a  $(\sqrt{3}\times\sqrt{3})R30^\circ$  overlayer [2-6]. This structure corresponds to a molecule-molecule spacing of  $\sim 5 \text{ \AA}$  and an area per molecule of  $\sim 21.6 \text{ \AA}^2$ . In this full-coverage phase, which corresponds to the highest possible packing of the molecules, S: Au ratio is 3:1. In contrast, the structure of *n*-alkanethiolates on the surface of Au nanoparticles (NPs) is not so well understood, although the thiol-capping strategy is widely used to fabricate highly stable NPs [2]. In the last years many works have dedicated to understand the SAM of alkanethiols on the surface of gold NPs [8]. Hostetler et al. suggested from thermal gravimetric analysis (TGA) results that small Au NPs (<4.4 nm) have a higher density of alkanethiols per gold atom than an ideal, perfectly flat single crystal Au(111) surface [9]. Authors have attributed this higher coverage to the occupancy of alternate binding sites (edges and corners). We have found similar results and attributed this higher coverage to higher accessibility of S atoms due to the high curvature of the NPs [10]. Jadzinsky et al. have also found a higher sulfur coverage on thiol-capped gold NPs [11].

X-ray based techniques as X-ray Photoemission Spectroscopy (XPS) is nowadays a common technique used to the study of thiol-capped gold NPs and lots of works have been made to establish the radiation damage produced during experiments on thiols although discrepancies on which is the effect of irradiation on thiols and which are the sulfur species produced because of the irradiation still exist [8, 12]. On the other hand, X-ray absorption spectroscopies, like XANES, have been only used more recently to study the state of the sulfur on the surface of the NPs [13, 14] and because of this,

very little information exist on how the X-ray beam affect the structure of the thiols. As X-ray absorption spectroscopies studies can be very time consuming, exposing the sample to high doses of X-rays, and changes on the state of the absorber can be produced during the experiments. This exposure has the consequence that the final spectrum represents an average over the different states of the absorbing atoms during the time of the experiment. In this work we study the radiation damage produced by X-rays coming from synchrotron light during XANES experiments on S-Au and S-C bonds in alkanethiolates-capped gold NPs.

## 2. Experimental

The gold NPs used in this study have average core diameters of 1.5 nm, and 2.2 nm, and are stabilized by butanethiol, hexanethiol and nonanethiol. The particle core size is related to the synthesis conditions [9] and it was already determined in all samples by HRTEM [15]. The synthesis of gold NPs with different core dimensions in toluene/*H*<sub>2</sub>O from alkanethiols was analogous to the Brust reaction [7] and was reported previously [10].

X-ray absorption fine structure measurements with soft and hard X-rays were obtained at the SXS and XAS beamlines respectively at the Laboratorio Nacional de Luz Sincrotron (LNLS), Campinas, Brazil. XANES spectra were obtained at the *S K*-edge (2472 eV) and EXAFS and XANES spectra were obtained at the *Au L*<sub>3</sub>- edge (11919 eV). For XANES experiments at the *S K*-edge, all samples were carefully washed to evaporate all free thiols from the solution. NPs diluted in dichloromethane and the solvent was completely evaporated in vacuum in order to lower the boiling point of the solvent. This cycle was repeated until all free thiols were completely removed for each sample. In order to obtain the desired high resolution of about 0.5 eV a *Si* (111) double-crystal monochromator with a slit aperture of 1.0 mm was used. Details of the experimental setup of the SXS beam line have been published elsewhere [16]. The X-ray absorption spectra were recorded in total electron yield (TEY) mode, collecting the emitted current for each photon-energy with an electrometer connected to the sample. Experiments were performed in a vacuum of 10<sup>-8</sup> mbar at room temperature. The energy scale was calibrated setting the *Mo L*<sub>3</sub>-edge, defined by the first inflection point of the X-ray absorption spectrum of *Mo* metallic foil sample to 2520 eV. The final TEY XANES spectra were obtained after background subtraction and normalization to the post-edge intensity. XANES spectra were taken in quick scans to avoid as much as possible radiation damage during each scan. This resulted in statistically poor spectra, but important features were strong enough as to be evaluated and compared. In all cases two spectra were taken, being the second one taken after 45 minutes of constant irradiation. XANES spectra at the *Au L*<sub>3</sub> edge were taken in transmission mode.

## 3. Results

Figure 1 shows the XANES spectra at the sulfur K-edge of NPs with two different sizes capped with hexanethiols after washing in dichloromethane. Figure 2 shows the XANES spectra for a set of three NPs with the same size (1.5 nm) and different thiol lengths: (a) butanethiol, (b) hexanethiol and (c) nonanethiol. Two spectra are shown for each sample: the first one obtained after putting the samples in the chamber and a final one taken 45 minutes after first acquisition with continuous exposure of the sample to the X-ray beam.

The two peaks at 2470 eV and 2478 eV present in the spectra of all samples corresponds to the S-Au and S-C bonds as has been shown previously [13, 14]. Changes in the relative intensity of the two peaks between samples with different size (Figure 1) are evident and have been already discussed [10]. We interpreted the different intensity of the peaks as an effect of molecular distortions that change the orientation of the final state orbital, particularly those deriving from S-C bonds. We proposed 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 second effect that would be modifying these peaks intensities is the existence of a sulfur-enrichment at the NPs surface as the nanoparticle is smaller. Differences between the intensities of the peaks for the samples with the same

size and different capping lengths are not so clear. Now, apart from these sources of changes in the NPs spectra, differences in the relative intensities of the two peaks are observed for almost all samples after 45 minutes of exposure to the X-rays. These changes are evidencing modifications in the nature of the S-C and S-Au bond and thus changes in the sulfur state during the experiments which are produced by radiation damage of the thiols due to the X-ray beam.

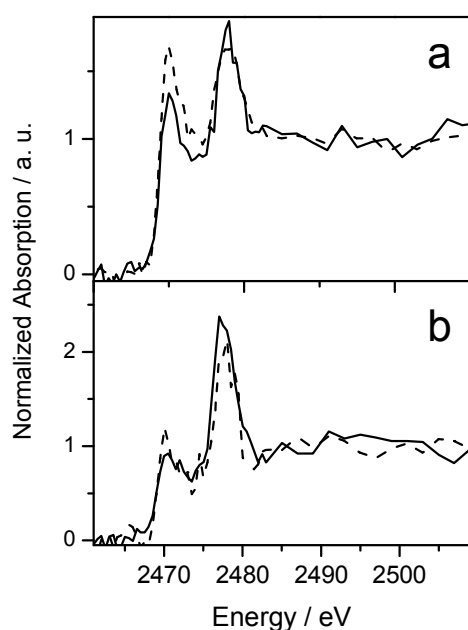


Figure 1. XANES spectra at the sulfur K-edge of 1.5 nm (a) and 2.2 nm (b) hexanethiol capped gold nanoparticles. Solid lines show the first spectra and dashed line a spectra taken after 45 minutes of irradiation.

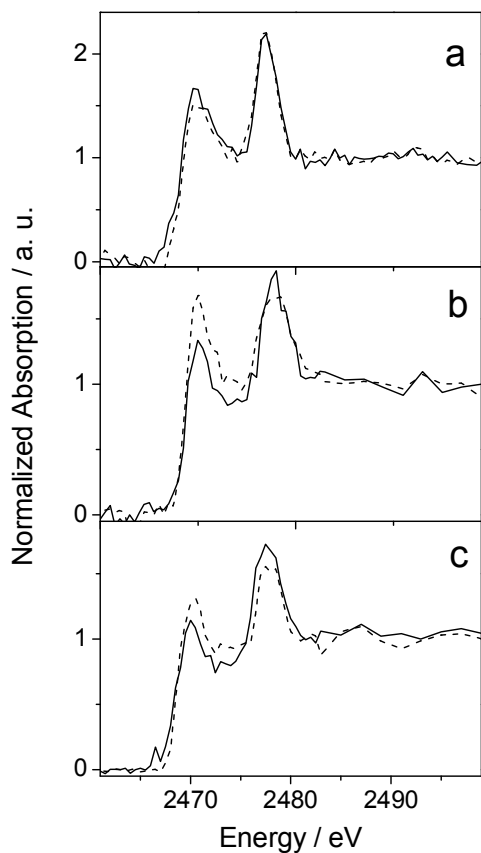


Figure 2. XANES spectra at the sulfur K-edge of 1.5 nm gold nanoparticles capped with (a) butanethiol, (b) hexanethiol and (c) nonanethiol. Solid lines show the first spectra and dashed line a spectra taken after 45 minutes of irradiation.

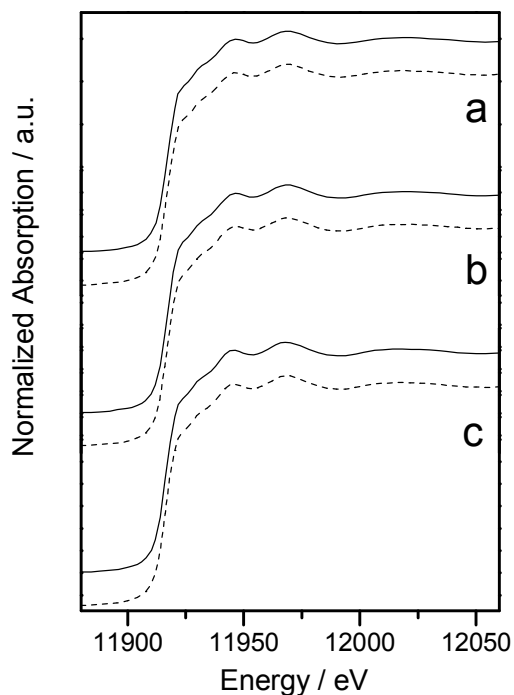


Figure 3. XANES spectra at the Au  $L_3$  edge of 1.5 nm gold nanoparticles capped with (a) butanethiol, (b) hexanethiol and (c) nonanethiol. Solid lines show the first spectra and dashed line a spectra taken after 45 minutes of irradiation. The spectra are vertically displaced for comparison purposes.

#### 4. Discussion

The effect of X-ray irradiation on thiols self assembled monolayers have been extensively studied in the last years [17-19]. However, discrepancies on which is the effect of irradiation on thiols and which are the sulfur species produced because of the irradiation still exist [12]. Lamont et al. suggested that the new sulfur structures observed by XPS are due to atomic sulfur on gold, resulting from the fission of the C-S bond and desorption of the hydrocarbon chain fragment [20]. Kondoh and Nozoye studied the effect of electron irradiation of (CH<sub>3</sub>S) self-assembled monolayers on Au(111) and found that the methyl moiety desorbs via S-C bond cleavage, leaving a sulfur adatom on the surface [21]. They observed the existence of sulfur atoms or sulfur island on Au(111) with STM. Zharnikov et al. proposed that there is an incorporation of sulfur into the alkyl chains via bonding to irradiation-induced carbon radicals in the adjacent aliphatic chains [22]. Zubregel et al. [23] proposed the existence of dialkyl disulfide species, where one S atom interacts with the Au substrate and the other one is slightly higher. The desorption of the alkanethiol chain has also been observed [24].

The trend observed in the XANES spectra at the sulfur K-edge for the two NPs after 45 minutes of exposure to the X-ray beam is very similar both samples (see figure 1): an apparent increase of the intensity of the S-Au peak and a decrease of the intensity of the S-C peak. In addition, a decrease in the minimum between both peaks is observed which could be related to a change in the edge position. The effect on each peak and in the edge position will be discussed later. This tendency is more evident for smaller NPs while is weak for the biggest ones. When the length of the carbon chain is changed, similar results are obtained (figure 2). However for the NPs capped with butanethiols, differences between the two spectra are not so clear and considering the noise level of the spectra they can be considered as identical. It is possible that, because a lower stability of the short carbon chain of butanethiol, damages are so fast that cannot be followed by our experiments. Theoretical calculations indicate that the Au-S binding energy does not depend on the carbon chain length [25]. However, our results may be indicating that different radiation induced reactions may be taken place for short and long thiol chains. In addition, it has been reported that butanethiols SAMS on Au(111) can desorb just because of ultra high vacuum conditions [26] so this possibility should not be ruled out.

No radiation damage effect is observed in the Au L<sub>3</sub> XANES spectra of the 1.5 nm nanoparticles capped with different alkanethiols. As it can be seen from figure 3, the initial spectrum and the last one taken after 45 minutes of irradiation show no differences. Although the spectra represent the average over all Au atoms present in the NPs, almost one half of all Au atoms are placed at the nanoparticle surface so, if electronic changes are due to the different species produced by irradiation on the NPs on the surface, we expected to be able to observe these changes. However, it has already been shown that changes in the Au 5d electron density because of the alkanethiol adsorption is difficult to quantify from XANES spectroscopy at the Au L<sub>3</sub> edge. The absence of any change in the spectra shows that the Au L<sub>3</sub> edge is not as sensible as the sulfur K-edge to the radiation damage.

To evaluate quantitatively these changes in the K-edge XANES profiles, a simple curve fitting analysis was carried out by using a set of two Gaussians and an arctangent function as shown in figure 3. The simulated curves fit the experimental spectra very well in the whole region. Note that this simulation method was employed not for a strict determination of the electronic transitions but simply for evaluation of the peaks intensity and position in each spectrum. Changes in both peaks intensities are observed, however, the S-Au peak at 2470 eV decreases its intensity after irradiation, contrary to what was supposed previously from the visual inspection of the spectra. This is a consequence of the shift in the edge position to lower energy, indicating the reduction of the average oxidation state of sulfur. A decrease of the S-C peak at 2478 eV is also observed. Considering the proposed models for the sulfur species formed after irradiation with X-rays, our results are consistent with the cleavage of some C-S bonds, and the consequent appearance of atomic sulfur on the nanoparticle surface as has already been reported for XPS radiation damage [27]. Being XANES an average technique, the cleavage of some S-C bonds would result in a decrease of this interaction in the

total XANES spectrum as it is observed. In addition, the appearance of atomic sulfur on the surface would result in a reduction of the average oxidation state of sulfur, shifting the edge position to lower energies. Also, the S-Au interaction would be reduced and thus the intensity of the peak assigned to this bond will decrease as observed. In the same direction, as the van der Waals forces that limit the sulfur density would be reduced because of the smaller density of carbon chains in this new configuration produced by the S-C cleavage, a less compact SAM arrangement could be formed on the nanoparticle surface which could also lead to a decrease of the S-Au interaction.

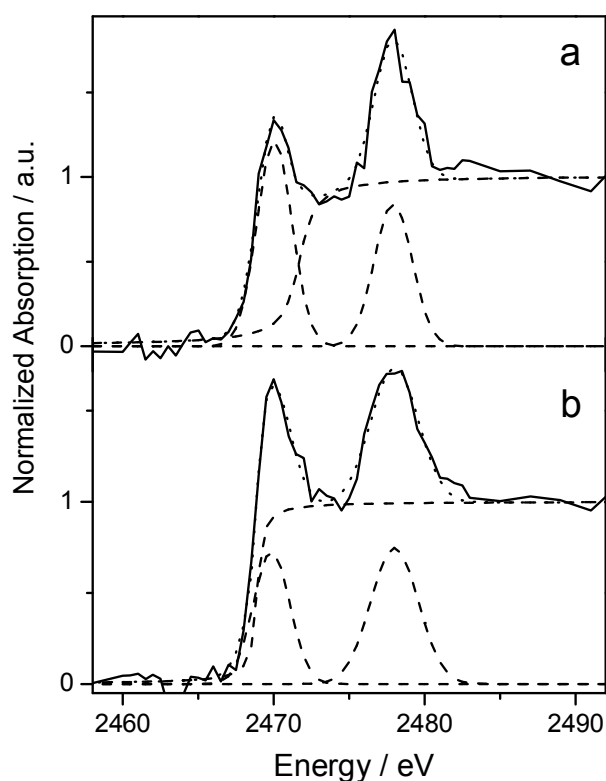


Figure 4. Linear combination fit of the initial (a) and final (b) XANES spectra at the sulfur K-edge of 1.5 nm gold nanoparticles capped with hexanethiol using 2 Gaussians and one arctangent functions. Solid line: experimental data, dashed line: individual functions, pointed line: total fitted function.

An important remark is that, even though, the irradiation with X-rays leads to a change in the intensity of both characteristic peaks of the XANES spectrum at the sulphur K-edge, this effect is small compared with the intrinsic effect due to the particle size. As it can be seen from figure 1, the difference of the relative intensities of these peaks in each sample is smaller than the differences from one sample to the other. As a consequence, the use of XANES to study the S-Au interaction in thiol-capped nanoparticles could still be valid, but short time acquisition would be desired in order to minimize the radiation damage during the experiment. However, some concerns have to be made when trying to evaluate in a quantitative manner the intensities of the peaks appearing in the XANES spectrum, as changes in their intensities are expected during the acquisition due to radiation damage as has been shown. It would be more convenient to perform a bigger number of fast scans even if the statistics is poor than to perform smoother scans with long acquisition time at each energy. Because of this, only qualitative analysis of the XANES spectra should be made when the samples are exposed for long periods of time to the X-ray beam or even in cases where fast spectra are taken as in dispersive XAS but there is no control of the radiation damage.

## 5. Conclusions

Radiation damage on alkanethiol-capped Au NPs was observed during the acquisition of XANES spectra at the sulfur K-edge in ultra high vacuum conditions. Changes in the S-Au and S-C peak intensities of the XANES spectra are observed, indicating changes in the sulfur species adsorbed on the nanoparticle surface probably due to cleavage of the carbon chains and the appearance of atomic sulfur on the nanoparticle surface. Because of this, fast scan experiments should contribute to minimize radiation damage and improve quantitative analysis of XANES spectra of alkanethiol capped Au nanoparticles at the sulfur K edge.

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