XAFS studies of Au nanocrystals passivated by different surfactants

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Abstract. The electronic and atomic structures of Au nanocrystals affected by different surfactants (PPh₃, PVP, and dodecanethiol) capping were studied by X-ray absorption fine structure (XAFS) at Au L3-edge. For PPh₃, PVP, and dodecanethiol-capped Au nanocrystals, the surface Au atoms interact with P, O, and S atoms respectively; however, only for dodecanethiol-capped Au nanocrystals, a significant electron transfer between Au and S atoms is observed. The extend-XAFS results reveal that the atomic structure disorder of Au-Au shell gradually increases from 0.0095 to 0.0152 Å² when the surfactants goes from PPh₃ to dodecanethiol. These results suggest that the surfactants would change the electronic and atomic structures of Au nanocrystals rather than merely passivates on the surface of Au nanocrystals.

1. Introduction

Gold nanocrystals possess unique electronic, optic and surface properties, and have been widely used in fields such as catalysis, electronics, optics, biology and medicine [1-4]. For nanomaterials, surfactants are very important because they not only make the nanocrystals stabilized but also link nanocrystals with the outsides, enabling the particles to be applied in different environment. For example, in the field of biology and medicine, gold nanocrystals are usually covered with a modified thiolate ligands, the end of which are initially connected with nucleotides, proteins or antibodies [5,6]. Gold nanocrystals show high catalytic activities by covering with well-defined polymers known as dendrimers which does not fully passivate particles so that substrates can access the particle surface [7]. Besides, surfactants have great influence on the electronic and atomic structures of nanocrystals which can be used to modify the chemical and physical properties of gold nanocrystals [8,9]. Therefore, it is important to study the surfactant-effects on gold nanocrystals for fundamental research and for scientific applications.

Because different surfactant-effects on gold nanocrystals result in different properties of gold nanocrystals, understanding the interaction between surfactants and particles is essential and has been widely studied for decades. Since the interaction between surfactants and particles can directly cause the variation of electronic and atomic structures of gold nanocrystals, investigation on the electronic and atomic structures of gold nanocrystals passivated by different surfactants can give some hints to the surfactant-nanoparticle interaction.

In this work, x-ray absorption spectroscopy (XAFS) was employed to study the local atomic and electronic structures of gold nanocrystals covering with different surfactants (riphenylphosphine
(PPh3), polyvinylpyrrolidone (PVP), and dodecanethiol (C12H26S)). The samples were prepared by wet chemical method. The aim is to determine the effects of surfactants on the structures of gold nanocrystals.

2. Experimental

PPh3 covered gold nanocrystals [10]: 0.050g of AuClPPh3 and 0.088g of tert-butylamine-borane powder were mixed in 40 ml of benzene to form a clear solution. The mixture was kept stirring at room temperature for one day to complete the reaction.

PVP covered gold nanocrystals [11]: To the aqueous solution of HAuCl4 (1mM, 50ml) was added 555.5mg (0.0139mmol) PVP. The mixture was further stirred for 30 minutes under a bath of 0℃. Then, the aqueous solution of NaBH4 (0.1M, 5ml) was rapidly added into the mixture under vigorous stirring. The mixture was kept stirring at room temperature for one day to complete the reaction.

Dodecanethiol capped gold nanocrystals: 0.050g of AuClPPh3 and 0.088g of tert-butylamine-borane powder were mixed in 40 ml of benzene to form a clear solution. Then 0.4mmol dodecanethiol was added into the solution. The mixture was kept stirring at room temperature for one day to complete the reaction.

XAFS measurement: The Au L3-edge XAFS spectra were measured at the U7C beamline of the National Synchrotron Radiation Laboratory (NSRL), China. For XAFS measurements, the solutions were transferred to a 10-mm-thick Teflon cell to obtain optimized edge-jumps.

3. Results and discussion

The TEM images of Au nanocrystals covered by different kinds of surfactants are shown in fig.1. It can be observed that PPh3-Au nanocrystals tend to be polydisperse, however it turns much better when Au nanocrystals covered with PVP. For dodecanethiol-Au nanocrystals, the particles are evenly spaced and orderly arranged. The insets in fig.1 display the average sizes and corresponding size distributions of Au nanocrystals. By changing the passivated surfactants to PPh3, PVP, and dodecanethiol, the sizes of Au nanocrystals gradually vary to 7.2±0.4, 3.5±0.4, and 3.1±0.1 nm, respectively. From the above, it can be suggested that different surfactants have different effects on the size of Au particles and among these three surfactants, dodecanethiol shows the strongest ability in narrowing the size distribution of gold nanocrystals.

![Figure 1. TEM images of Au nanocrystals covered by (a) PPh3, (b) PVP, (c) dodecanethiol; the insets display corresponding size distributions](image1)

![Figure 2. The normalized XANES spectra of Au nanocrystals capped by PPh3, PVP and dodecanethiol. The spectrum of Au foil is displayed for comparison](image2)
Surfactant-induced electronic and atomic structure changes of Au nanocrystals could be obtained by means of x-ray absorption fine structure (XAFS, including XANES and EXAFS). The normalized Au L$_3$ edge XANES spectra of Au nanocrystals capped by PPh$_3$, PVP, and dodecanethiol are shown in fig.2. The XANES spectrum of Au foil is also displayed for comparison. The XANES spectra exhibit four characteristic peaks A-D locating at around 11915, 11924, 11937 and 11960 eV, respectively. When covered with dodecanethiol, Au nanocrystals exhibit much more intense white-line peak A (corresponding to the electronic transition from the 2p3/2 to the 5d5/2, 3/2 states), indicating an increase in d-hole population just above the Fermi level, in good agreement with electro-negativity considerations (S is slightly more electronegative than Au) [12]. As compared with Au foil, peak B, C and D of Au nanocrystals are shifted to higher energy and reduced in intensity. The peak B that is apparent for Au foil is absent for Au nanocrystals capped by dodecanethiol. The weakness of the intensity could be attributed to the increase of the structure disorder of Au nanocrystals.

![Figure 3.](image)

(a) $k^2\chi(k)$ and (b) Fourier transformed $k^2\chi(k)$ spectra of gold nanocrystals passivated by different surfactants.

Table 1. The fitting parameters and corresponding results

| Sample       | Bond       | $R$ (Å)       | $N$  | $\sigma^2 (10^{-3} \text{Å})$ | $\Delta E$ (eV) |
|--------------|------------|---------------|------|-----------------------------|-----------------|
| Au-foil      | Au-Au      | 2.88±0.01     | 12   | 8.4±0.4                     | 3.6±0.4         |
| PPh$_3$      | Au-Au      | 2.82±0.01     | 10.4±0.4 | 9.5±0.4                     | 4.1±0.4         |
| PVP          | Au-Au      | 2.81±0.01     | 10.2±0.4 | 12.9±0.6                     | 4.1±1.0         |
| dodecanethiol| Au-S       | 2.30±0.03     | 1.2±0.2 | 5.0±0.6                     | 2.7±0.5         |
|              | Au-Au      | 2.79±0.02     | 10.5±0.2 | 15.2±1.8                     | 0.5±0.3         |

The $k^2\chi(k)$ and Fourier transformed (FT) $k^2\chi(k)$ spectra of gold nanocrystals passivated by different surfactants are displayed in fig.3 (a) and (b). The spectra of Au foil are plotted for comparison. As shown in fig. 3 (a), the shape of the $k^2\chi(k)$ spectra of samples capped with PPh$_3$ and PVP are similar with that of Au foil. When Au nanocrystals are covered with dodecanethiol, the profile of the oscillation curve is quite different with that of Au foil especially in the range of 6-12 Å$^{-1}$. The local atomic structure of Au nanocrystals covered with different surfactants can be more explicitly manifested by Fourier transformed $k^2\chi(k)$ spectra. As shown in fig. 3 (b), the peaks in the range of 2.5-3 Å are the nearest Au-Au coordinations. When covered with PPh$_3$ and PVP molecules, the FT spectra of Au nanocrystals keep basic features of Au foil except for the reduced intensity. However, when covered with dodecanethiol, Au-S coordination appears in the low R-region and the intensities of Au-Au coordination are sharply decreased. For all samples, Au-Au coordinations move towards low R range comparing with that of Au foil. Quantitative least-squares curve-fitting (Tab.1) shows Au-Au bond length of thiol-capped particles is 2.79 Å while that of Au foil is 2.88 Å. From PPh$_3$, PVP,
dodecanamine to dodecanethiol, structural disorder degree of Au-Au increases from 0.0095, 0.0129, to 0.0152 Å². These results indicate that surfactants are not merely passivates the surface of Au nanocrystals and by forming chemical bonds like Au-S, the atomic structure of gold nanocrystals could also be greatly distorted [13].

Based on the above results, it can be suggested that different surfactants has different effects on Au nanocrystals. PPh₃ and PVP weakly cover the particle surface, and they stabilize the particles by physical adsorption. However, dodecanethiol stabilizes the nanocrystals by forming Au-S bond which may result in great structure distortion of the particles.

4. Conclusions

In summary, we prepared gold nanocrystals covered by different surfactants with wet chemical methods. By using XANES and EXAFS, we compared their local electronic and atomic structures. The XANES results show that the electron-transfer occurs when gold nanocrystals is passivated by dodecanethiol ligands, which results in the change of the electronic structure of gold nanocrystals. And based on the EXAFS results, the passivated surfactants cause distortion of atomic structure of gold nanocrystals. For PPh₃, PVP, and dodecanethiol covered Au nanocrystals, the atomic structure disorder of Au-Au shell was gradually increased from 0.0095 to 0.0152 Å. And dodecanethiol interacted with Au nanocrystals by forming strong Au-S bond, which may contribute to the greatly distorted structure.

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