Sulfur K-edge XANES study of dihydrolipoic acid capped gold nanoparticles: dihydrolipoic acid is bound by both sulfur ends†

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Received (in Cambridge, UK) 23rd July 2004, Accepted 12th October 2004
First published as an Advance Article on the web 30th November 2004
DOI: 10.1039/b411231h

Dihydrolipoic acid (DHLA) capped gold nanoparticles (Au@DHLA) are characterized in solid and liquid states by sulfur K-edge XANES spectroscopy; it clearly shows that DHLA is anchored to gold thanks to both sulfur ends.

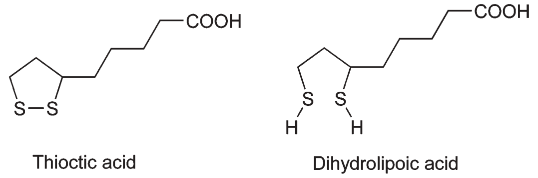
As demonstrated by Mirkin *et al.*, the use of multithiolated species improves the stability of gold nanoparticle colloids.[1] The increase of stability is intuitively attributed to the presence of at least two thiol groups per molecule which all interact with surface gold atoms. Up to now, this assumption has not been obviously confirmed by any spectroscopic characterization owing to the limited choice of efficient techniques for determining the chemical forms of sulfur atoms. Among them, X-ray photoelectron spectroscopy (XPS) is widely used to establish the atomic composition and to study the chemisorptive properties of some organosulfur species adsorbed on gold surfaces. The XPS investigations about the adsorption of dithiols and disulfides on gold plates showed that the number of sulfur atoms involved in the grafting was in fact dependent on the structure of the molecules.[2] However the application field of XPS is restricted to solid samples, excluding the colloidal solutions which is the form required for numerous applications (particularly for nanostructured coatings and for biological uses).

Since it was demonstrated that the spectra of thiols (R–S–H) and disulfides (R–S–S–R) exhibit characteristic feature differences,[3] X-ray absorption near edge structure (XANES) spectroscopy at the sulfur K-edge, which is a powerful tool to assess the electronic structure, coordination geometry and oxidation state of the absorbing atom, has been used extensively for characterizing sulfur oxidation states in biological samples.[4] Thanks to the large penetration depth of X-rays, the main advantage of XANES lies in the possibility to characterize samples in the liquid state. Recently, dodecanethiol coated gold or palladium nanoparticles were characterized by XANES spectroscopy at the gold or palladium $L_{3,2}$-edge[5,6] and at the sulfur K-edge for palladium particles.[6] These studies revealed a charge flow from the metallic core to the sulfur *via* the surface interaction between metal and sulfur atoms. However this technique has, to our best knowledge, never been applied to the characterization of gold nanoparticles covered by stabilizers containing several sulfur atoms.

We propose herein sulfur K-edge XANES spectroscopy as an attractive approach for characterizing multithiolated or disulfide species adsorbed on gold surface nanoparticles not only in the solid state but also in very dilute colloids. This study is focused on dihydrolipoic acid (DHLA) capped gold nanoparticles (Au@DHLA). DHLA is a dithiolated molecule terminated by a carboxylic acid easily obtained by the reduction of thioctic acid, TA (Scheme 1).[7]

The synthesis of Au@DHLA was similar to that reported by Brust *et al.* for the preparation of gold clusters protected with *p*-mercaptophenol monolayers.[8] The resulting black powder was easily redispersed in an aqueous 0.01 M sodium hydroxide solution and yielded a dark red to black colloid which can be stored for several weeks without particle growth or agglomeration. The diameter of the Au@DHLA nanoparticles was estimated to be 5.0 ± 0.8 nm from HRTEM and at least 75% of Au@DHLA particles have a hydrodynamic diameter, measured by photon correlation spectroscopy, of between 5.1 and 8.0 nm. XPS experiments performed on Au@DHLA revealed the presence of an organic layer around the nanoparticles whose atomic composition (C : S = 4.525 and O : S = 1.075) is close to the calculated composition for DHLA (C : S = 4.0 and O : S = 1.0).

The sulfur K-edge XANES spectra of Au@DHLA, in the solid state (*i.e.* dried Au@DHLA particle powder) or dispersed in aqueous sodium hydroxide (0.01 M) solution, are compared to the spectra of thioctic acid and pure DHLA (*i.e.* reduced thioctic acid in the absence of gold nanoparticles) (Figs. 1a–1d). Their study is based on a direct fingerprint approach: the information about the environment of the sulfur atoms is retrieved from the shape and the energy position of the white line (the most intense structure in the XANES spectrum). It has been verified that the energy position is not sensitive to the distortion induced by self-absorption which can occur for the samples containing a high sulfur content such as TA, DHLA (15% in weight) and Au@DHLA in the solid state (1.5%).† The white line of the XANES spectrum of thioctic acid exhibits two peaks (at 2472 and 2473.6 eV) (Fig. 1a) while the DHLA spectrum displays a single peak (at 2472.8 eV) (Fig. 1b). The relative positions of these peaks are in accordance with those



Scheme 1

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† Electronic supplementary information (ESI) available: synthesis protocol, hydrodynamic diameter measurements, HRTEM images, XPS data for Au@DHLA, XANES set-up description and data processing. See http://www.rsc.org/suppdata/cc/b4/b411231h/
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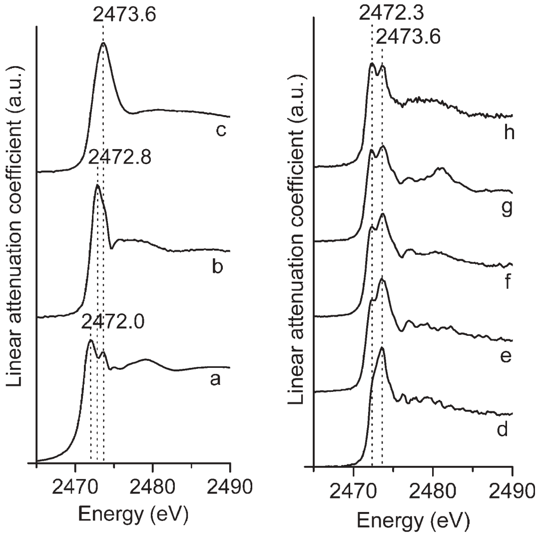

Fig. 1 Sulfur K-edge XANES spectra of (a) thioctic acid, (b) dihydrolipoic acid, (c) Au@DHLA (solid state), (d) Au@DHLA (liquid state) in the presence of (e) r = 5%, (f) 13%, (g) 33% and (h) 50% of free DHLA (with $r = [\mathrm{DHLA}]_{\mathrm{free}}/([\mathrm{DHLA}]_{\mathrm{free}} + [\mathrm{DHLA}]_{\mathrm{grafted}})$).

measured for cysteine (2473.2 eV) and cystine (2472.4 and 2474 eV), respectively, a thiolated amino acid (R–S–H) and its disulfide oxidized form (R–S–S–R).[9] Therefore, the first peak (at 2472 eV) of the thioctic acid spectrum can be attributed to the 1s transitions to the molecular orbitals of the S–S bond (S 1s → S–S transitions) and the second peak to the S 1s → S–C and S 1s → S–H transitions which are at similar energy positions. The single peak of DHLA (at 2472.8 eV) corresponds to the S 1s → S–C and S 1s → S–H transitions.

The XANES spectrum recorded for the Au@DHLA nanoparticle powder (Fig. 1c) obviously shows that the shape of the white line is different to that in the pure TA spectrum (Fig. 1a). The Au@DHLA powder spectrum exhibits indeed only one peak at 2473.6 eV. The absence of the 2472.0 eV peak assigned to S 1s → S–S transitions allows us to rule out the formation of a disulfide bond[10] when DHLA molecules are adsorbed on the gold surface. However pure DHLA and Au@DHLA powder spectra do not superimpose: the position of the peak (2473.6 eV) seen for Au@DHLA (Fig. 1c) is 0.8 eV higher in energy compared to the white line position of the pure DHLA spectrum (Fig. 1b). This shift towards high energy is attributed to the interaction between the sulfur atoms of adsorbed DHLA and the surface gold atoms since the energy position of the peak associated with S 1s → S–C transitions is greatly influenced by the sulfur atom environment. A similar shift has been observed in the case of dodecanethiol capped palladium nanoparticles.[6] Moreover the absence of an additional peak at 2472.8 eV (characteristic of free DHLA) in the spectrum of Au@DHLA (Fig. 1c) clearly shows that most sulfur atoms are consequently placed in the same surroundings: in the solid state, almost each DHLA molecule is anchored on the gold particles by both sulfur atoms.

As in the solid state, the white line of the XANES spectrum of the Au@DHLA colloid (Fig. 1d) is mainly characterized by one peak at 2473.6 eV. However, a shoulder is observed at 2472.3 eV. It is suspected to be related to a small amount of unbound sulfur atoms of the DHLA molecules which may have been partially (one sulfur atom out of two) or totally (both sulfur atoms) degrafted from the gold surface during the redispersion of the Au@DHLA nanoparticle powder in an alkaline solution.

To confirm that this desorption is very limited, a series of XANES spectra of the Au@DHLA colloid were recorded after the addition of known proportions of DHLA molecules and are reported in Figs. 1e–1h. They all display two peaks at 2472.3 and 2473.6 eV, which are respectively similar to the energies of the shoulder and the main peak of the colloid spectrum (Fig. 1d). The 2473.6 eV peak is also observed in the case of the Au@DHLA XANES spectrum performed in the solid state (Fig. 1c). Furthermore, neither its amplitude nor its position is affected by the addition of significant quantities of DHLA in the solution (Figs. 1e–1h). As a result, this peak (2473.6 eV) can be attributed to the sulfur atoms adsorbed on the gold surface.

On the contrary, the relative amplitude of the second peak at 2472.3 eV clearly increases as a function of the DHLA amount added to the colloid (Figs. 1e–1h). This peak is therefore attributed to free DHLA although it is shifted by 0.5 eV towards lower energy with respect to the white line of the pure DHLA spectrum (Fig. 1b). The unexpected 0.5 eV gap actually mirrors the effects of the DHLA dilution in the alkaline Au@DHLA colloidal solution. Indeed the XANES spectra from Figs. 1e–1h were recorded after the addition of pure DHLA in the alkaline solution which was required for dispersing Au@DHLA nanoparticles whereas Fig. 1b displays the spectrum of pure DHLA. A shift of the same order of magnitude was already observed in the case of cysteine when increasing the pH.[4] It was attributed to the deprotonation of the ionizable –SH groups.

Curve fitting of the spectra† using Voigt functions and an arctangent curve provided the area ratio of the 2472.3 and 2473.6 eV peaks. It was assessed that the shoulder observed at 2472.3 eV in the Au@DHLA colloid spectrum (Fig. 1d), which was attributed to free DHLA, corresponds to less than 5% of the totality of the sulfur atoms. If desorption occurred effectively after redispersion of the solid powder in the alkaline solution, the phenomenon is very restricted.

In conclusion, we demonstrated, thanks to the XANES experiments, that most DHLA molecules used as stabilizers during gold nanoparticle synthesis are anchored by both sulfur atoms. This efficient grafting seems to seriously limit the stabilizer desorption. These results are extremely important because the use of functionalized gold nanoparticles as biological probes could be disturbed by the desorption or by an undesirable exchange of the grafted molecules. Since this technique allows us to distinguish the different chemical forms of sulfur atoms, it opens a new way for monitoring the synthesis of organosulfur capped gold nanoparticles.

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