XAFS ON CTAB-STABILIZED GOLD NANOPARTICLES

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The modifications of the electronic structure and the structural order with decreasing particles size are of great interest for the explanation of catalytic properties of gold nanoparticles. One of the issues is the predicted Au-Au bond contraction with particle size decrease. For the purpose of the study, x-ray absorption spectroscopy (XAFS) has been chosen as a probe, since it provides information about both, the local coordination and the electronic structure of the absorbing element. There were several studies on deposited gold nanoparticles employing XAFS [1, 2]. However, reports on experiments on free gold nanoparticles are scarce.

The study presented has been carried out on free gold nanoparticles (AuNP) in liquid cetrimonium bromide (CTAB) solution, and on freeze-dried CTAB/AuNP solutions. The gold nanoparticles were prepared by seeding growth according to the method reported by N.R. Nikhil *et al*. [3]. Samples of 3.2, 9.0, 13.4 and 28.0 nm diameter were received with a gold concentration of 2.5×10^{-4} mol/L. The average particle sizes were determined on a different lot of samples in a small angle x-ray scattering (SAXS) experiment. One lot was freeze-dried overnight immediately after preparation in a FINN-AQUA LYOVAC GT2 freeze-dryer in order to obtain powder samples of higher Au concentration. However, during the freezing process a change of the color of the substance from red to violet occurred during the transition from the intermediate gel phase to solid. Such a change of color indicates usually a coagulation of gold nanoparticles. A behavior like this has not been observed on a control sample with colloidal gold nanopaticles produced by standard citrate synthesis. The other lot was measured as cast shortly after preparation. The XAFS measurements were conducted in the fluorescence mode at the BAM*line* and µ-Spot beamlines at BESSY II, Berlin. Together with the samples a gold leaf reference of 200 nm thickness has been measured, too.

The obtained XAFS spectra did not show any significant differences in the near absorption edge region (XANES) indicating that the gold nanoparticles maintained the electronic structure of bulk gold in all the cases. The EXAFS spectra of the nanoparticles and the gold reference were almost identical, showing that there was no change in the local order of the nanoparticles with decreasing size. In order to estimate the Au-Au bond length parameter, *ab-inito* calculations using FEFF 8.40 have been employed. A first shell theory fit was performed of the experimental data sets using IFFEFIT 1.2.11c software.

The Au-Au bond length of the coagulated particles due to freeze-drying was the almost same for all four samples as that of bulk gold, 2.889 Å compared to 2.883 Å. The free gold nanoparticles in liquid CTAB solution have a slightly larger Au-Au bond length than bulk gold, by 4.2 pm; and no size depended behavior has been observed. This stays in contrast to standard citrate synthesized gold nanoparticles, where an increasing Au-Au bond length contraction of the same order of magnitude with decreasing particle size has been observed by our group on standard NIST gold nanoparticles [4] and has also been reported for deposited nanoclusters [1,2].

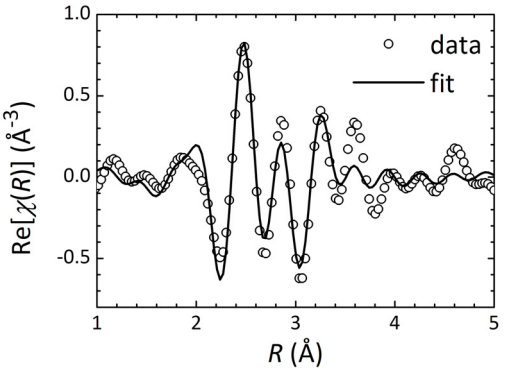

Figure 1. First shell fit of the FEFF generated model spectrum to the EXAFS spectrum of the smallest AuNP sample (3.2 nm) in liquid.

References

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