



	Experiment title: Study of the atomic and electronic structure of Ag clusters in room temperature ionic liquids	Experiment number: MA-1973
Beamline: ID 26	Date of experiment: from: 02.10.2013, 8:00 to: 06.10.2013, 8:00	Date of report: 28.03.2014
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Report:

The purpose of the experiment MA-1973 was to study the electronic and atomic structure of Ag clusters deposited into the room temperature ionic liquid (RTIL) [1] 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆]. The investigation was carried out by measuring the x-ray absorption near edge structure (XANES) of the Ag L₂ absorption edge. Our experiments showed that no differences between bulk Ag and large Ag crystals formed in the RTIL could be observed. Further the spectrum of small aggregated clusters differs from the Ag bulk spectrum. And above all it could be observed that the exposition of small aggregated Ag clusters to x-ray radiation leads to fragmentation of the aggregates to small nanoclusters which seem to be stable over weeks.

Ag clusters with a mean diameter of about 2nm were produced in a thermal cluster source [2]. Here Ag was vaporised and then expanded with an Ar carrier gas through a supersonic nozzle into vacuum. The thus formed clusters were deposited into a volume of about 27 ml (*sample 1*) and 20 ml (*sample 2*) of [Bmim][PF₆]. The deposition amounts were m₁ = 4.8 mg for *sample 1* and m₂ = 0.7 mg for *sample 2*, controlled by a quartz crystal oscillator. It could be observed that the clusters in *sample 1* started to aggregate to large crystals. Because in sputter experiments [3] where ionised Ag atoms were sputtered into [Bmim][PF₆], the produced clusters seems to be stable, for preparation *sample 2* an electron emitting hot cathode was mounted next to the cluster beam and the RTIL surface to enable ionisation effects. After cluster deposition the samples were characterised by UV-Vis measurements of the cluster plasmon excitation [4]. Due to the higher viscosity at lower temperatures the samples were stored at 4-7 °C to prevent further aggregation.

The XANES measurements were performed at the Ag L₂ absorption edge in fluorescence mode in an energy range of 3.510 - 3.600 keV for *sample 1* and 3.515 - 3.556 keV for *sample 2*. The modification of the scan range for *sample 2* was necessary because the lower deposition amount in comparison to *sample 1* caused a much lower signal-to-noise-ratio so that scan range had to be decreased to enable an increase of the number of scans in the same time. The samples were installed in a custom build cool and heatable sample cell where temperature was controlled by a chiller.

XANES spectra recorded under the same conditions were summed up, the background was subtracted by a linear fit at the pre edge region and then normalised to the integral under each spectrum.

After measurements on crystals (*sample 1*) and clusters (*sample 2*) in pure [Bmim][PF₆], 1-Dodecanethiol was added to form ligand functionalized nanoparticles. Despite 1-Dodecanethiol is not soluble in [Bmim][PF₆] an interaction of the cluster with the thiol was expected by additional treatment in an ultrasonic bath, because sulphur is known as a good reactant for silver [5].

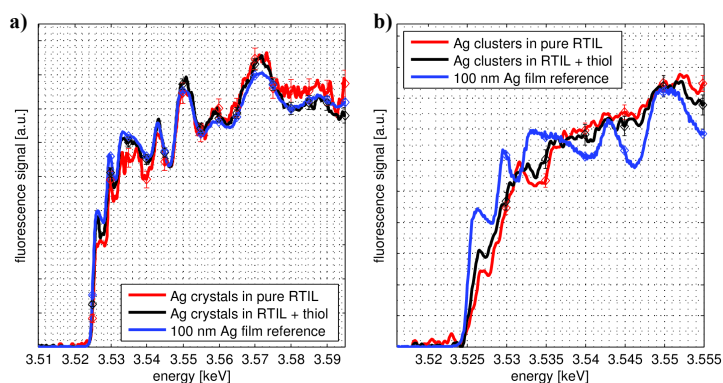


Figure 1: XANES spectra of a) Ag crystals (*sample 1*) and b) aggregated Ag clusters (*sample 2*) in [Bmim][PF₆] before and after adding 1-Dodecanethiol to the sample in comparison to Ag bulk.

The results of XANES measurements of *sample 1* with clusters which aggregated to large crystals are shown in Fig. 1a). The spectrum of Ag crystals in pure [Bmim][PF₆] is similar to the measured reference spectrum of a 100nm thick Ag film on SiO₂. Afterwards, 1-Dodecanethiol was added like explained before. The then recorded spectrum looks similar to the one in pure RTIL with the exception of a stronger peak at the absorption edge. Because the so called white line emerges due to free d-orbitals in case of an oxidation state it is possible that low amounts of the Ag atoms reacted with the sulphur headgroup to Ag₂S. The small effect can be a result of the low surface to volume ratio of the

crystals which prevents a strong influence of the chemisorbed sulphur atoms.

The spectrum of *sample 2* is shown in Fig. 1b). Clear differences in comparison with the reference spectrum and the spectra of *sample 1* are visible. This lead to the assumption that the aggregated clusters did not form a bulk like system. Additionally the spectra differ from the XANES spectra recorded from separated Ag clusters deposited into SiO₂ aerogel [5] but have similarities to deposited clusters in PDMS [6]. After adding 1-Dodecanethiol the height of the absorption edge increased. Above the absorption edge the spectrum change only marginally within the statistical error. Because of the higher surface-to-volume-ratio a stronger influence as at *sample 1* would be expected. Therefore the formation of ligand functionalized clusters could not be proved for sure.

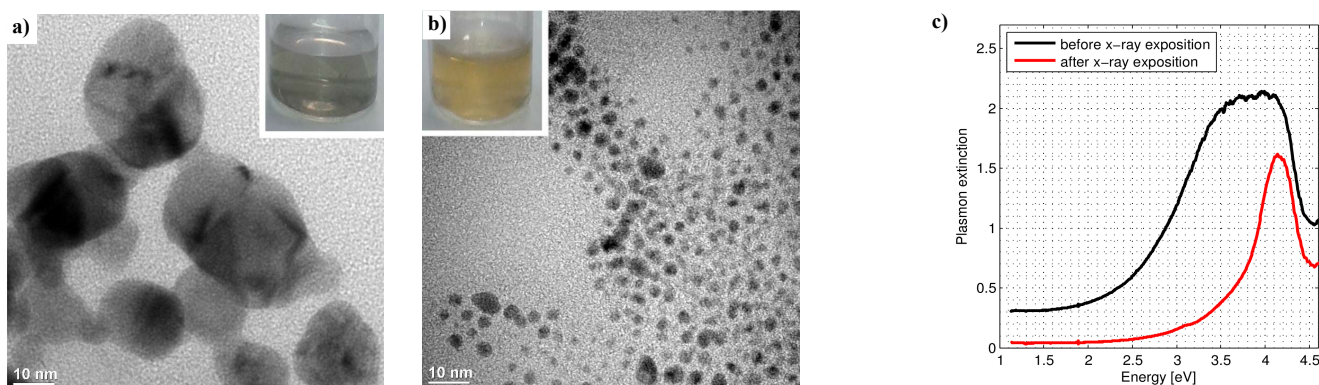


Figure 2: TEM [8] of aggregated clusters (*sample 2*) before XANES measurements a) and after XANES measurements b). UV-Vis measurements of *sample 2* before and after XANES experiment c).

It was observed that *sample 2* had changed their colour after the exposure to the x-ray beam from grey (Fig. 2a) inset) to yellow (Fig. 2b) inset).

The change in the colour can be explained by a fragmentation of the small aggregated clusters to nanoclusters with a mean diameter of about 2nm. Several weeks after beamtime non-irradiated and irradiated fractions of *sample2* were investigated with transmission electron microscopy TEM [8], shown in Fig. 2. It is remarkable that the small fragments seems to be stable for weeks.

UV-Vis measurements of the cluster plasmon excitation (Fig. 2c)) performed during the beamtime at the ESRF show a strong extinction a peak from about 3.5eV to 4eV before x-ray exposure. After x-ray exposure the extinction becomes a narrow peak at 4eV. The sample was diluted significantly with pure RTIL for this spectrum because otherwise the extinction in the peak exceed the range of the spectrometer. An excitation of the silver plasmon at an energy of about 4eV might be attributed to small nanoclusters consisting of about only 10 atoms [7] which can not be resolved by TEM measurements.

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