PDMS embedded Ag clusters: Coalescence and cluster-matrix interaction

S Roese, D Engemann, S Hoffmann, K Latussek, C Sternemann and H Hövel
Fakultät Physik / DELTA, Technische Universität Dortmund, 44221 Dortmund, Germany
E-mail: stefanie.roese@tu-dortmund.de

Abstract. Polydimethylsiloxane (PDMS) has proven to be a suitable embedding medium for silver clusters to prevent aggregation. In order to investigate the influence of the PDMS on the electronic and local atomic structure of the clusters the measurement of x-ray absorption near edge structure (XANES) spectra for different coverages of silver clusters in PDMS and calculations of corresponding XANES spectra have been performed. The coalescence process and the cluster-PDMS interaction were investigated with XANES.

1. Motivation
Due to their optical activity [1] and their anti-microbial behavior [2] silver nanoparticles are a recent field of research, which has lately become more and more application-oriented. For the preservation of the size-selective cluster properties the clusters have to be embedded into a medium to prevent them from aggregation. A suitable medium is PDMS, a polymeric substrate, which enables a penetration of clusters with velocities of about 10³ ms⁻¹ into the PDMS surface [3], where they stay separated up to a certain amount of cluster material. Separating clusters with ligands always has the consequence that the atoms at the cluster surface are in contact with the ligand material, possibly affecting the electronic and structural characteristics of the clusters. The influence of PDMS on the properties of the embedded Ag clusters can be examined with XANES.

2. Experimental
2.1. Cluster production and sample characterisation
The Ag clusters with a diameter of 2.0 ± 0.6 nm (determined by transmission electron microscopy (TEM) measurements), corresponding to a mean cluster size of 250 atoms, are produced in a supersonic nozzle expansion with a source temperature T = 2300 K, resulting in a cluster velocity of about 1.5·10³ ms⁻¹ [4]. The source chamber is connected to the deposition chamber by a heated skimmer. The produced clusters hit a PDMS film of 1.2 ± 0.2 µm thickness prepared on a SiO₂ silica glass substrate, which is mounted on a manipulator inside the deposition chamber. The cluster coverage was measured with a quartz crystal balance and found to be between 0.09 and 2 ML (cluster-monolayer), where one ML corresponds to a closed packed ML of clusters. UV/Vis transmission measurements on the deposited Ag clusters have been performed in-situ and ex-situ for additional sample characterization [5].
2.2. XANES measurements

XANES with fluorescence detection [6] is a suitable method to investigate the electronic and structural properties of clusters since a high signal to noise ratio is needed due to the low amount of cluster material in the PDMS sample. Changes in the oxidation state or sulfidation are detectable [7]. The experiments were performed at beamline ID26 [8] of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. A Si(111) monochromator (intrinsic resolution of $1.4 \times 10^{-4}$) was used and the x-ray beam was focused on the sample with a size of approx. $0.1 \times 0.6 \text{mm}^2$ at an angle of incidence of $45^\circ$ with respect to the beam axis. In order to measure XANES spectra in partial fluorescence yield (PFY) an x-ray emission spectrometer with four Ge(220) analyser-crystals was used. Thus, the signal to noise ratio in the XANES measurement was significantly improved and relatively low coverages of matrix embedded Ag clusters could be studied. The analyser energy was set to 3.1505 keV employing the Ge(220) Bragg reflection. Hence, we focused on the Ag L$_2$ edge (3.524 keV) by scanning the incident energy between 3.510 and 3.600 keV. A total energy resolution of 0.4 eV was obtained. Several spectra were recorded at each coverage. No radiation damage was observed. The single spectra were summed up and normalized to the intensity of the impinging beam. After background subtraction the spectra were normalized to their area below the entire spectrum.

3. FEFF calculations

The measured XANES spectra are compared to theoretical calculations performed with FEFF9 [9]. The FEFF parameters were adjusted, so that the calculated fcc Ag bulk spectrum fits to the measurement of the Ag reference. A full multiple scattering radius of 8 Å, the Hedin-Lundqvist self-energy, a 4 eV shift of the entire spectrum and a reduction of the lifetime broadening by 1 eV was used. The construction of coordinate sets describing the atomic structure of the clusters was necessary to calculate the FEFF spectra of separated clusters. It is known, that small free silver metal clusters use to exhibit an icosahedral structure [10, 11]. Clusters with ligand shells (e.g. Au$_{55}$) often are identified with a cuboctahedral structure [12], which is basically a segment of the fcc crystal structure, even if recent studies showed that the geometries might be more complicated [13]. For the FEFF calculation shown here, corresponding to the mean cluster size of 250 atoms, cuboctahedra with 147 or 309 Ag atoms with bulk next neighbor distances (2.89 Å) are chosen. These numbers are geometrically magic and due to their closed shells they are considered to be distinctly stable [14].

4. Results

4.1. XANES measurements of samples with different cluster coverages

The measured XANES spectra for different Ag cluster coverages in PDMS and an Ag reference are shown in fig. 1. All error bars for $\geq 0.20 \text{ML}$ are within the line thickness. The UV/Vis transmission measurements revealed that for the lowest coverage separated cluster with a mean size of 250 atoms can be assumed [5]. Here, about half of the atoms are located at the cluster surface and are therefore in contact with the PDMS. The general structure of the spectra particularly for higher energies hardly varies, but for low coverages (0.09 ML and 0.20 ML) a significant change of the spectra in the energy range of 3.53 - 3.55 keV is observed. With increasing coverage...
the spectra approximate progressively the Ag bulk spectrum, which is indicative of cluster coalescence to larger silver islands in agreement with results of UV/Vis spectroscopy [5].

Fixed cross-over points in all spectra indicate that the spectra for cluster coverages of 0.20, 0.63, 1.20 and 2.00 ML might be modeled by a superposition of the absorption spectrum of the silver reference sample (100 nm Ag film) and the XANES signal measured for the separated clusters (lowest coverage of 0.09 ML).

Hence, we modeled the spectra of intermediate coverages by linear combinations of the XANES spectrum of the bulk measurement and that of the separated clusters via a least squares fit as shown in fig. 2. Obviously, the change of the XANES spectra due to cluster coalescence at higher coverage can be described by a decrease of the surface-to-volume ratio of clusters due to their larger mean size. However, superposition also leads to structural features, that do not occur in the measured spectra (see region around 3.53 - 3.55 keV). This leads to the assumption, that these features might be a fingerprint of the PDMS-cluster interaction, which only becomes visible at low coverages as in this case 50% of all atoms within the clusters are in contact with the PDMS. To distinguish between the effect of coalescence and cluster matrix interaction FEFF calculations will be discussed as follows.

4.2. Comparison to FEFF calculation

Fig. 3 shows the comparison of the measured spectra to the results of the FEFF calculations. The comparison of the measured 100 nm Ag film and the corresponding FEFF calculations shows a good overall agreement. This is valid also with respect to the FEFF calculation of the 309 atoms Ag cluster which is compared to an intermediate coverage (0.63 ML).

The smearing out of features for energies smaller than 3.55 keV by going from bulk to smaller cluster is clearly visible, even if at this coverage already particles larger than the mean size of 250 atoms are formed, as UV/Vis spectroscopy indicates [5].

However, the measured spectra for coverages below 0.63 ML are not resembled by the FEFF calculation neither of the 309 nor the 147 atoms cluster. This is indicative for a strong interaction between the surface atoms of the cluster and the embedding PDMS matrix, strongly affecting the local geometric and electronic structure. This interaction will have to be characterized in a next step using structural models of embedded clusters, i.e. considering the local environment due to the PDMS matrix.
5. Summary
In the present study the influence of PDMS on embedded silver clusters was examined with Ag L₂ edge XANES and complementary FEFF calculations. Silver clusters with a mean size of 2 nm deposited and embedded into PDMS were investigated with XANES. The XANES spectra of different cluster coverages vary significantly from each other and from the corresponding Ag bulk measurement in the near edge region. With a linear superposition of the XANES spectra of bulk and the lowest coverage it is possible to reproduce the structural features in the spectra of already aggregated clusters slightly larger than the original 2 nm size. Appropriate FEFF calculations for cuboctahedra consisting of 147 and 309 atoms also describe spectra for this intermediate coverage, but do not resemble some of the structural features, which can be found in the XANES spectrum for the lowest coverage, i.e. for separated matrix embedded Ag clusters. Therefore we draw the conclusion, that these features are tentatively attributed to the interaction between the PDMS and the surface atoms of the well separated clusters. In a next step this effect will be examined for different cluster embedding media.

Acknowledgments
We are grateful to Kristina Kvashnina and Pieter Glatzel at ESRF for providing assistance in using beamline ID26 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France for the Ag L₂ XANES measurements. Samples were precharacterized by XANES measurements at the Ag L₃ edge that were previously performed at BL8, DELTA, Dortmund, Germany. The help of Ralph Wagner is gratefully acknowledged. We thank ESRF and DELTA for providing synchrotron radiation and NRW Forschungsschule for financial support.

References
[1] Kreibig U and Vollmer M 1995 Optical Properties of Metal Clusters (Berlin: Springer)
[2] Kim J S et al. 2007 Nanomedicine 3 95-101
[3] Corbelli G, Ghisleri C, Marelli M, Milani P and Ravagnan L 2011 Adv. Mater. 23 4504-08
[4] Hövel H, Fritz S, Hilger A, Kreibig U and Vollmer M 1993 Phys. Rev. B 48 18178-188
[5] Hoffmann S 2012 Dissertation TU Dortmund
[6] Bunker G 2010 Introduction to XAFS (Cambridge: University Press)
[7] Behrens P 1992 Solid State Commun. 81 235-239
[8] Gauthier C, Sole V A, Signorato R, Goulon J and Moguiline E 1999 J. Synchrotron Radiat. 6, 164-166
[9] Rehr J, Kas J, Vila F D, Prange M P and Jorissen K 2010 Phys. Chem. Chem. Phys. 12, 5503-13
[10] Häkkinen H and Moseler M 2004 Phys. Rev. Lett. 93 093401
[11] Blom M N, Schooss D, Stairs J and Kappes M M 2006 J. Chem. Phys. 124 244308
[12] Wilson N and Johnston R 2002 Phys. Chem. Chem. Phys. 4 4168-71
[13] Walter M, Moseler M, Whetten R L and Häkkinen H 2011 Chem. Sci. 2 1583-87
[14] de Heer W 1993 Rev. Mod. Phys. 65 611-676