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Report:

Ensembles of well characterized nanometer sized clusters were investigated by small angle X-ray scattering (SAXS). The scattering data was evaluated by Guinier analysis providing the average radii of the embedded clusters. As samples, Pb, Au, Co, Er, and FePt clusters were generated by a laser vaporization source and embedded in MgO or Ge matrices grown on mica substrates (Inset Fig. 2) [1,2]. The size distribution of the clusters was measured before sample preparation by time-of-flight mass spectrometry and afterwards by transmission electron microscopy [3]. The radii determined by the different methods were compared and a good agreement of the results was found.

A representative mass distribution spectrum for lead clusters is depicted in Fig. 1. The cluster radii were calculated from the cluster masses by using the specific density and the molar volume of the corresponding bulk material. A Gaussian function was

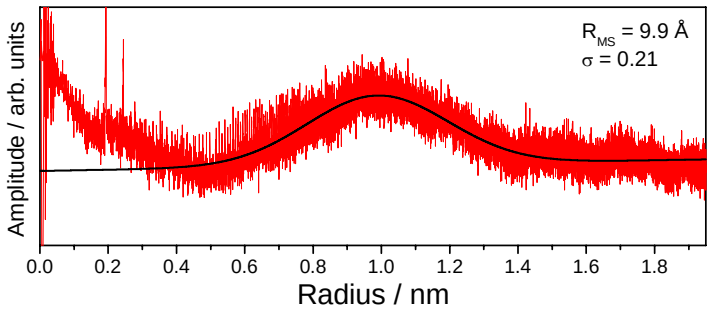

Fig. 1: Radius distribution of lead clusters before co-deposition determined from mass spectrometry. The solid line represents a Gaussian curve used to extract the particle radius given in the figure.

used to extract the particle radii and relative distribution widths σ (half width at half maximum). In the case of lead clusters a radius of 9.9 Å and a relative width of 0.22 was calculated (Fig. 1).

For Guinier analysis, one quadrant of the isotropic SAXS scattering pattern was radially integrated, so that a one-dimensional data set was obtained. In the low angle regime and for widely separated particles, the Guinier approximation of the scattering function [4]

$$I(q) \propto (\Delta n_e)^2 e^{-q^2 R_g^2/3} \qquad (1)$$

was used. Δn_e is the difference of the electronic densities of the participating materials and in the exponent, R_g is the radius of gyration which is, for spherical particles, related to the real particle radius by $R_g^2 = 3/5 R_{SAXS}^2$. By plotting the data in a $\ln(I(q))$ versus q^2 plot, the slope of the linear part can be used to calculate R_g. As example, the results are shown for lead clusters in Fig. 2. For particle ensembles with a size distribution, a further correction was necessary because the scattering cross-section is proportional to the cluster volume and therefore larger particles are overestimated in the Guinier-plots. This reduces the radii determined from SAXS by a factor of 1.13. In the case of lead clusters, a value of R_{SAXS} = (11.5 ± 0.3) nm is calculated.

The relationship between the radii determined by the different techniques, i.e. by SAXS and mass spectrometry, is depicted in Fig. 3, filled squares. A linear function, which was forced to go through the origin of the graph was used to fit the data of these samples,

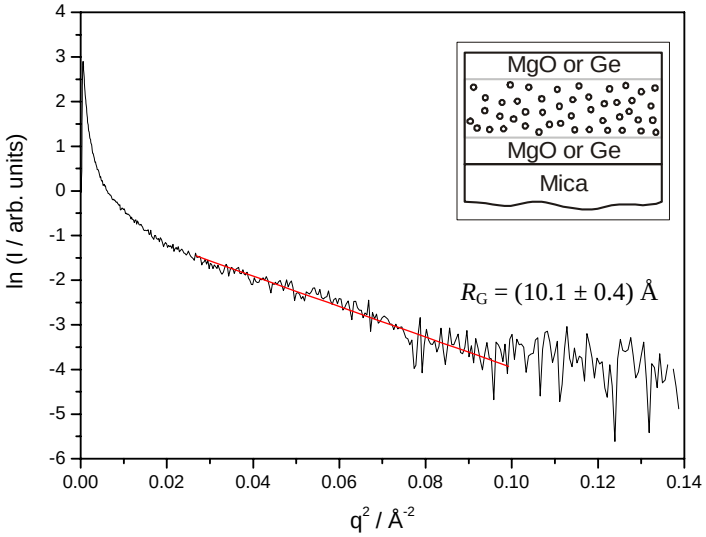

Fig. 2: Small angle scattering pattern from a sample containing Pb clusters in a Ge matrix. The solid straight line represents a linear fit employing Eq. 1. **Inset:** Schematic cross-section of the sample (not drawn to scale).

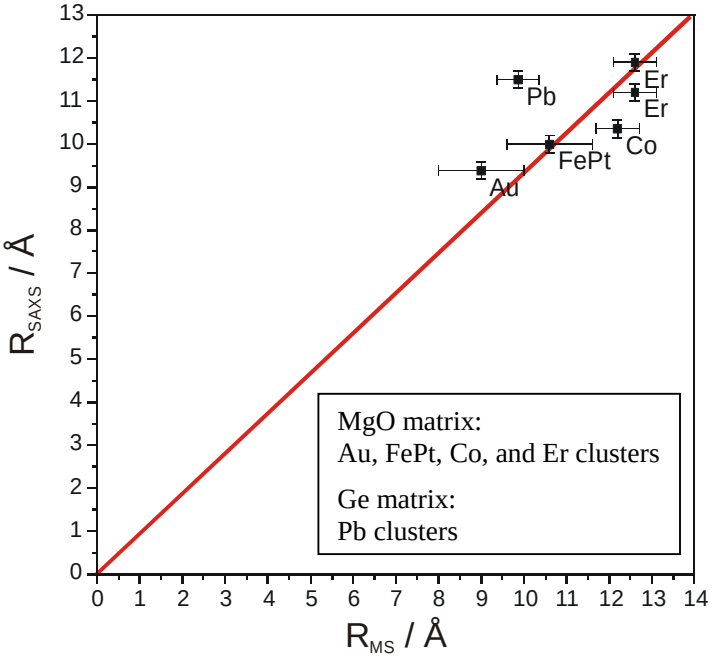

Fig. 3: Comparison of the cluster radii before (horizontal axis) and after (vertical axis) embedding the clusters in the matrix. The solid line is a linear fit through the origin. A slope of R_{SAXS}/R_{MS}(140°C) = 0.94 ± 0.05 has been extracted.

which were prepared at 140°C. A ratio of R_{SAXS}/R_{MS} = 0.94 ± 0.05 was determined. Under ideal circumstances, meaning that the data were perfectly in agreement, a value of 1 should have been obtained. The deviation of this value from 1 is possibly caused by the fact that the approximations made for the Guinier analysis or the size polydispersity are not fulfilled. For instance, the assumptions that the scattering entities would be spherical or the usage of a Gaussian particle size distribution. Nevertheless, this correlation between the radii determined by the two methods shows the capability of small angle X-ray scattering to determine an average particle radius which is in reasonable agreement with other experimental techniques which are more traditionally used in this field. Thus we conclude that transmission SAXS can be an adequate method to determine the dimensions of nanoparticles in a matrix even when the nanoparticle/matrix composite is deposited onto a relatively thick substrate.

Using this fundamental finding, we have investigated the influence of the substrate temperature during cluster co-deposition, i.e. during embedding the clusters in the matrix. Samples produced at an elevated substrate temperature of 500°C exhibited an increased average cluster radius in the SAXS measurements [3]. The radii of these clusters were significantly larger, by a factor of approximately 1.5. We attribute these increased dimensions to the incidence of coalescence and Ostwald ripening during the co-deposition of the clusters at elevated temperatures.

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