



Experiment title: Study of Aggregation Behaviour and Interaction in Palladium Colloids by X-Ray Photon Correlation Spectroscopy	Experiment number: SC-238	
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Report:

We have studied the low frequency dynamics of colloidal palladium and platinum aggregates by x-ray photon correlation spectroscopy (XPCS) using a wide bandpath (1%) coherent x-ray beam from the ID10A undulator source at ESRF. Metallic nanoparticles are of interest for potential use in catalysis and electrocatalysis and a structural and dynamic characterization of these systems in solution at reasonably high concentrations is beyond the capability of conventional light scattering. We had shown in a precursor study [1] that photon correlation spectroscopy with coherent x-rays is capable of tracing colloidal dynamics in the q-range up to $6 \times 10^{-3} \text{ \AA}^{-1}$ over a wide time range (10^{-4} to 100 s).

We were able in the present study to improve the coherence parameters of the x-ray beam and we have verified and completed the data set on colloidal palladium aggregates (0.3vol%, dissolved in glycerol). The data confirmed the observation of translational diffusion with relaxation rates proportional to q^2 and inversely proportional to viscosity for $1.5 \times 10^{-3} \text{ \AA}^{-1} < q < 6 \times 10^{-3} \text{ \AA}^{-1}$ and $279 \text{ K} < T < 293 \text{ K}$. This work is the first quantitative XPCS study performed and the result has been published in Physical Review Letters [2].

We have extended the XPCS studies by investigating also colloidal Pt aggregates. Both Pd as well as Pt were stabilized with the zwitterionic surfactant dimethyldodecylammoniopropansulfonate. The concentration dependence as well as the role of the solvent was studied. Data analysis is under progress revealing the following preliminary observations:

A series of measurements on colloidal Pd and Pt materials in both water and glycerol showed that the relaxation rates in water are roughly 3 orders of magnitude higher than in glycerol. It could be demonstrated that the time range from 10^{-5} to 10^{-4} s is experimentally accessible by XPCS.

The concentration range from about 0.1 to 10% metal weight, corresponding to a volume fraction of up to a few % in Pd and up to about 0.2% in Pt was explored. This is the concentration range in which one would expect interactions due to overlap for fractal aggregates. Large aggregates

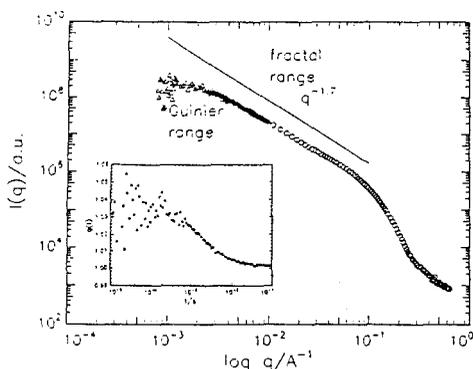


Fig:
Static scattering intensity $I(q)$ versus q on a logarithmic scale. At high concentration the fractal range is extended and the Guinier range cannot be resolved anymore at ID10. In the inset the corresponding correlation function for $q=0.002 \text{ \AA}^{-1}$ is shown.

were observed in all samples. In some cases (at intermediate concentrations) Guinier behavior was observed allowing an independent size determination from the static scattering. The fractal dimensions were similar in water and glycerol. The size of the aggregates is different (larger in glycerol). The fractal dimension is about 1.7 for Pt, which is close to the value expected for diffusion limited aggregation. Figure 1 shows an example for static data and a correlation function taken at $q=0.002 \text{ \AA}^{-1}$. For Pd a value of 2.8 was found which is not predicted by any model. The concentration range covered up to now seems not to strongly influence the observed diffusion constants, although there are apparent differences between Pd and Pt even for aggregates with comparable size as determined by static scattering. The concentration range covered might not yet be sufficient to experience interactions due to overlap effects. It appears mandatory to extend the studies to higher concentrations and to combine static and dynamic measurements.

- [1] T. Thum-Albrecht et al., ESRF Experimental Report SC106,1996
- [2] T. Thum-Albrecht, W. Steffen, A. Patkowski, G. Meier, E.W. Fischer, G. Grubel, D.L. Abernathy
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