

## In-situ observation of formation of metal nanoparticles and nanocomposites

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### Introduction

There has been considerable interest in studies on preparation of metal nanoparticles in last decade. We focus our attention on the formation of metal nanoparticles that is stabilized by polymers, because such polymer-stabilized metal nanoparticles offers the possibilities of controlling spatial arrangements of the metal nanoparticles by use of various designs of polymers: For example, the morphologies of diblock copolymers enable us to make highly ordered patterns of metal nanoparticles[1]. There are thus many studies on chemical synthesis of polymer-metal nanocomposites. In our study, we focus on the formation process of metal nanoparticles to clarify the particle growth law. In this report, we restrict ourselves to present the results of palladium nanoparticles stabilized by polystyrene.

### Experimental

Time-resolved SAXS measurements were performed at the BL-15A, installed at Photon Factory, KEK, Tsukuba, Japan. The formation of palladium nanoparticles was induced by temperature jump from room temperature to around 180C.

### Results

Figure 1 shows typical results of time evolution of SAXS profiles after a temperature jump. One can see that the maxima and the minima around  $2.0\text{nm}^{-1}$  for (a) and  $1.0\text{nm}^{-1}$  for (b) progressively shift toward lower- $q$  region, showing the growth of the metal particles. Figure 2 shows a comparison of the scattering profile with a model fitting. Here, we adopted a spherical form factor with a size distribution of a Gaussian. The time evolution of the particle size and its standard deviation were thus determined from the SAXS profiles. Figure 3 shows a typical electron micrograph of the samples after the SAXS measurements and we confirmed our analysis of SAXS profiles by these images of the real space.

From the time dependence of the particle size, we found that the growth of the metal nanoparticles are mainly governed by the diffusion-limited aggregation process. We also found that the particle size can mainly controlled by the concentration of stabilizing polymer and that the size distribution is narrower at lower temperature, i.e., around 150C, than higher temperature, i.e., 180C. This is attributed to the higher diffusibility of reduced atoms at higher temperature. That is, the rate-determining step at 180C would be the reduction process, and, as a result, the particle size widely distributes from small (i.e.,

new) ones to large (old) ones at 180C. Further analysis are currently in progress.

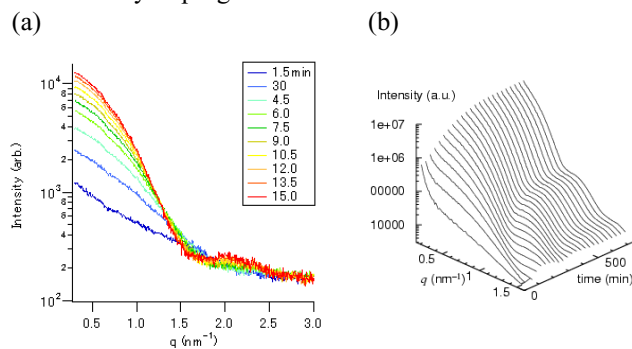


Fig.1: Time evolution of SAXS profiles after a temperature jump to (a) 180C and (b) 150C.

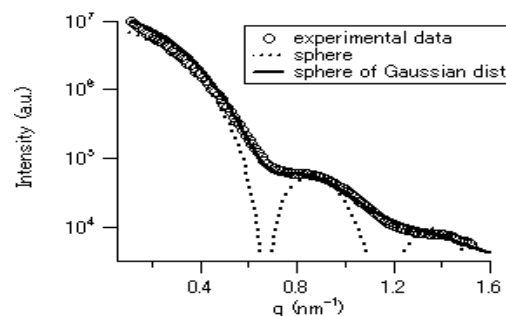


Fig.2: Comparison of the scattering profile (denoted by circles) and model fittings. The dotted line is the curve for isolated spheres of identical radius, and the solid line is obtained by the best fit of a model with a Gaussian distribution for the size of spheres.

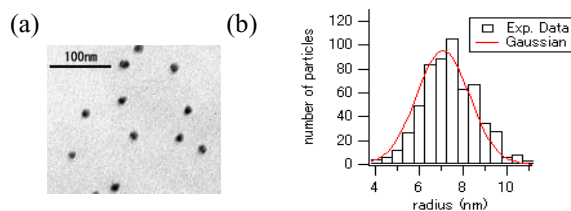


Fig.3: (a) Transmission electron micrograph of the sample which have been measured by use of SAXS. (b) A histogram for the sample in (a).

### References

[1] See, for e.g., T. Hashimoto, *Bul. Chem. Soc. Jpn.* 78 (2005) 1.

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