

In Situ Quick-XAFS Study of the Growth of Pt Particles during Photoreduction

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The study of growth mechanism and formation kinetics of metal particles has a long tradition in colloid chemistry, and more recently nanoparticles become of great interest for the detailed understanding of the growth mechanism in liquid phase. The reduction-nucleation and the growth processes of Pt nanoparticles have been quantitatively investigated during the photoreduction by means of in situ Quick XAFS (QXAFS) technique. Here we report an in situ QXAFS technique with an atomic scale sensitivity to monitor the initial nucleation and growth kinetics of Pt nanoparticles with the size smaller than 2 nm.

Experimental

Colloidal dispersions of Pt nanoparticles ($[Pt]=24.4$ mM) were prepared by the photoreduction of the ionic precursor ($H_2PtCl_6 \cdot 6H_2O$) in the absence and presence of photo-activators, such as benzoin, benzophenone and acetophenone. In a typical procedure, 2.23 g of PVP (20.1 mmol of monomeric unit) and 0.156 g of benzoin was added to the 10 mL of ethanol solution, and stirred to dissolve PVP and benzoin completely. 10 mL of aqueous solution containing 0.488 mmol of $H_2PtCl_6 \cdot 6H_2O$ was subsequently added and mixed for 1 min. The mixed solution was then photoirradiated by a 500 W super-high-pressure mercury lamp with continuous stirring using a magnetic stirrer. In situ QXAFS measurements at Pt L_3 -edge were performed at room temperature in a transmission mode at BL-9C and 12C station. Data analysis was performed by REX2000 (Rigaku Co.).

Results and Discussion

The evolution of the Pt L_3 -edge XANES spectra of the colloidal Pt dispersions produced from $H_2PtCl_6 \cdot 6H_2O$ (i.e., ionic precursor of Pt^{4+}) in the presence of benzoin exhibits the white line intensity (11563 eV attributed to Pt-Cl bond) decreases in course of reduction time, as shown in Fig. 1(a). The isosbestic point shifts from 11569 eV to 11568 eV, especially in the reduction time between 10 min and 40 min, indicating the stepwise transformation of one species to another ($Pt^{4+} \rightarrow Pt^{2+} \rightarrow Pt^0$) [1]. The intrinsic peak intensity (11590 eV attributed to metallic Pt-Pt bond) increases with an increase of reduction time, suggesting the accumulation of small Pt nanoparticles. In order to clarify the kinetics of the Pt nanoparticle formation by means of the quantitative estimation of X-ray absorbance, we demonstrate the time evolution of the intensity of white line and intrinsic peak. The experimental data of $[Pt^{n+}]_t/[Pt^{4+}]_0$ and $[(Pt^0)_m]_t/[(Pt^0)_m]_{9000}$ as a function of t is shown in Fig. 1(b).

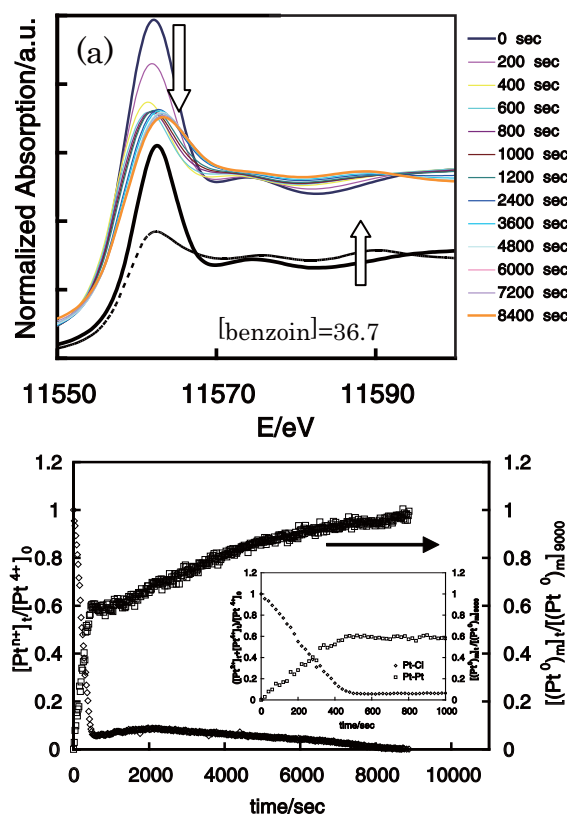


Fig. 1. (a) Pt L_3 -edge XANES spectra and (b) Plots of $[Pt^{n+}]_t/[Pt^{4+}]_0$ and $[(Pt^0)_m]_t/[(Pt^0)_m]_{9000}$ as a function of the reduction time (t) on the basis of the change in $\mu(E)$. The inset displays the corresponding enlarged plots during the first 1000 sec.

During the first 500-600 sec, as shown in the inset, kinetic data for $[Pt^{n+}]_t/[Pt^{4+}]_0$ shows a sigmoidal-like kinetics for the reduction of Pt^{4+} to Pt^{2+} ionic species. After the photoirradiation of 600 sec, its change slows down and gradually decreases in course of irradiation time with the consumption of Pt^{2+} ions. To the contrary, kinetic data for $[(Pt^0)_m]_t/[(Pt^0)_m]_{9000}$ has an approximately linear increase until the irradiation time of 500 sec. And it remains almost unchanged between 500 and 1000 sec, and then increases with a sigmoidal profile beyond 1000 sec [2], suggesting that the aggregative particle growth of nucleates occurs. The effect of the addition of the photo-activator is also examined.

References

[1] M. Harada et al., *Langmuir* **2006**, *22*, 2371. [2] V. N. Richards et al., *Chem. Mater.* **2010**, *22*, 3556.

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