

## Photochemical Synthesis of Ag Particles in Water-in-Ionic Liquid Microemulsions

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### Introduction

Imidazolium-based ionic liquids (ILs) have often been used as a medium for the formation and stabilization of metal nanoparticles [1]. Recently we synthesized Ag particles by the photoreduction of silver perchlorate ( $\text{AgClO}_4$ ) in water-in-[OMIm][ $\text{BF}_4$ ] microemulsions in the presence of Tween 20 and investigated the formation mechanisms of Ag particles [2, 3]. In this study we have performed *in-situ* fluorescence EXAFS measurements to compare the size of Ag particles obtained in the biphasic systems of water-in-[OMIm][ $\text{PF}_6$ ] microemulsions in the presence of Triton X-100 (TX-100) or Tween 20 under high pressure  $\text{CO}_2$  system with those under ambient air.

### Experimental

Colloidal dispersions of Ag particles were synthesized in a high-pressure SUS 316 cell (inner volume of ca. 10 mL) by the photoreduction of the  $\text{Ag}^+$ -containing water-in-[OMIm][ $\text{PF}_6$ ] microemulsions in the presence of TX-100 or Tween 20 under the high-pressure  $\text{CO}_2$ . The high-pressure cell had four optical windows: two of them were CVD diamond windows for *in-situ* EXAFS measurements and the other two were quartz windows for the UV-irradiation from mercury lamp. For example, TX-100/water/[OMIm][ $\text{PF}_6$ ] microemulsions containing  $\text{AgClO}_4$  were prepared by adding  $\text{CO}_2$  into the cell which contained a mixture of  $\text{AgClO}_4$  aqueous solution, TX-100, [OMIm][ $\text{PF}_6$ ], and benzoin for photoreduction. The weight fraction ( $W_{\text{TX-100}}$ ) of TX-100 was varied from 0.30 to 0.63, and the [OMIm][ $\text{PF}_6$ ]-to-TX-100 molar ratio (R) and the water-to-TX-100 molar ratio (w) was changed accordingly as shown in Fig. 1. The concentration of [ $\text{Ag}^+$ ] in the system was 4.4 mM. The cell was kept at 35°C and 25 MPa for 1 h with continuous stirring to form microemulsions. After stirring, the microemulsion was photo-irradiated for 5 h to investigate the reduction of  $\text{Ag}^+$  and the formation of Ag particles. The *in-situ* EXAFS measurements were carried out in a fluorescence mode at NW10A. EXAFS spectra at Ag-K edge were collected by a 19-element Ge solid-state detector. Data analysis was performed by REX2000 (Rigaku Co.).

### Results and Discussion

Fig. 1 shows the Fourier transforms of colloidal Ag particles at the high-pressure  $\text{CO}_2$ . The peak observed around 0.26 nm is assigned to an Ag-Ag metallic bond of 0.287 nm, and the height of these peaks is less than that

Table 1. Structural parameters from EXAFS analysis for the colloidal dispersions of Ag particles prepared in the presence of surfactants (Tween 20 and TX-100) under  $\text{CO}_2$  pressure of 25 MPa in water-in-[OMIm][ $\text{PF}_6$ ] microemulsions.

Sample	bond	C.N.	$r / \text{\AA}$
$W_{\text{Tween20}}=0.31$ , in-situ	Ag-Ag	10.9	2.89
	collected <sup>a</sup>	Ag-Ag	9.6
$W_{\text{Tween20}}=0.64$ , in-situ	Ag-Ag	11.3	2.88
	collected <sup>a</sup>	Ag-Ag	11.3
$W_{\text{TX-100}}=0.30$ , in-situ	Ag-Ag	8.6	2.87
	collected <sup>a</sup>	Ag-Ag	7.3
$W_{\text{TX-100}}=0.63$ , in-situ	Ag-Ag	9.1	2.89
	collected <sup>a</sup>	Ag-Ag	8.5

<sup>a</sup> Collected samples are released to the ambient air after *in-situ* measurements.

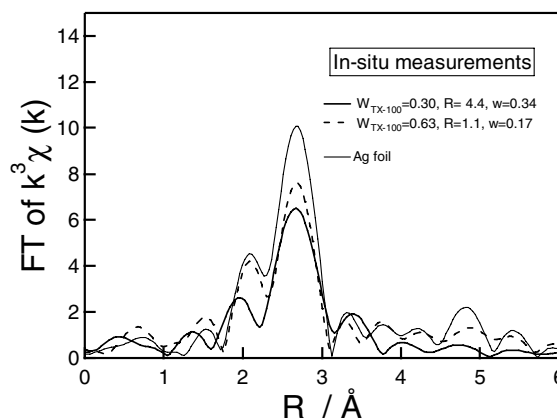


Fig. 1. Fourier transforms of the Ag-K edge *in-situ* EXAFS spectra for the colloidal Ag particles with different  $W_{\text{TX-100}}$ , prepared under high-pressure  $\text{CO}_2$ .

for Ag foil. The structural parameters for the Ag particles prepared with different W values are listed in Table 1. It is found that C.N. of Ag particles prepared with Tween 20 is larger than those with TX-100, and C.N. tends to become smaller after the Ag particles are released to the ambient air. The detailed analysis is in progress.

### References

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