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Synthesis and Structural Analysis of Metal Particles in Ionic Liquids

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Introduction

Room-temperature ionic liquids (RTILs) are regarded as an interesting class of tunable reaction solvents with essentially low volatility, wide electrochemical window, non-flammability and high thermal stability [1]. Recently we have synthesized Ag particles by the photoreduction of silver perchlorate ($AgClO_4$) in water-in-[OMIm][BF_4] microemulsions in the presence of Tween 20, and elucidated the formation mechanisms of Ag particles [2, 3]. In this study we have investigated the size and polydispersity of Pd particles synthesized by the decomposition of organometallic Pd precursors in the mixture of nonionic surfactant and RTILs, such as Tween 20 (or Triton X-100) and OMImCl (or DMImCl), by means of *in-situ* SAXS measurements.

Experimental

Colloidal dispersions of Pd particles were synthesized by the decomposition of palladium acetylacetonate, $Pd(acac)_2$, in the mixture of Tween 20 (or Triton X-100) and 1-octyl-3-methylimidazolium chloride (OMImCl) (or 1-dodecyl-3-methylimidazolium chloride (DMImCl)). For example, 0.5 mL of Tween 20 was added to 2 mL of OMImCl, followed by the addition of 11 mg $Pd(acac)_2$ and mixed vigorously. In this case, the weight fraction (wt%) of Tween20 ($W_{Tween20}$) and $Pd(acac)_2$ ($W_{Pd(acac)2}$) was 21.35 and 0.42, respectively. OMImCl to Tween20 molar ratio (R) was 19.5. Subsequently, the mixture solution was poured into a cell (optical path length 1 mm), and the sample was stepwise heated to 333, 353, 373, 393, 413, 433, and 453 K. The in-situ SAXS measurements were performed at each temperature at BL-6A or 15A. The scattering data was detected by a CCD camera with an X-ray image intensifier or PILATUS.

Results and Discussion

Fig. 1 shows the SAXS profiles of the colloidal dispersions of Pd particles at various temperatures (up to 453 K) in the presence of Tween 20 mixed with OMImCl or DMImCl. These SAXS profiles show that all the samples have a broad peak (centered around 2.6-2.7 nm^{-1} for OMImCl [2] and 2.1-2.3 nm^{-1} for DMImCl) observed in a q range larger than 1.5 nm^{-1} and a second inner peak in a q range ($0.3 < q < 1.4$ nm^{-1}). The former is characteristic of the interference peak due to the existence of ordering for ILs, and the latter is related to an

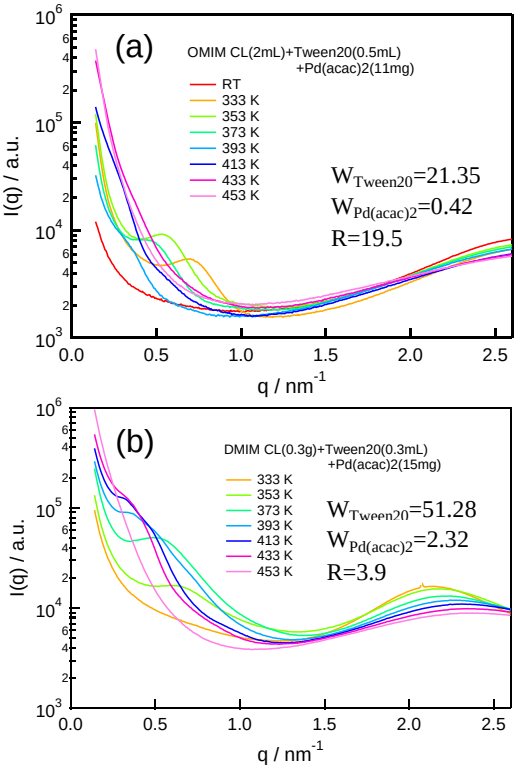

Fig. 1. SAXS profiles of the Pd colloidal solutions synthesized during raising the reaction temperature in the mixture of (a) Tween20/OMImCl and (b) Tween20/DMImCl.

interference due to the interaction between two neighboring Pd particles. Initially, the scattering profile has no second peak. The intensity of the second peak increases and its position shifts to lower q with increasing temperature. This indicates the growth of Pd particles in size during the temperature raising. From their Guinier plots, the average diameter of the aggregates, which consisted of ionic precursors of $Pd(acac)_2$ and Pd particles, is estimated to be about 30-40 nm. During the Pd particle formation process, aggregation of Pd atoms rapidly occurs in the micelles of Tween 20 in OMImCl rather than in DMImCl, indicating the dependence of the rate of particle formation on the alkyl chain lengths of ILs.

References

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