（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

CROSS TOKAI **Experimental Report** J-PARC	承認日Date of Approval 2017/9/16 承認者Approver Jun-ichi Suzuki 提出日 Date of Report 2017/08/19
課題番号 Project No. 2017A0007 実験課題名 Title of experiment Structural Analysis of Silver Nanoparticles in Emulsions Composed of Ionic Liquid/Water/Surfactant Systems. 実験責任者名 Name of principal investigator Masafumi Harada 所属 Affiliation Nara Women's University	装置責任者 Name of responsible person Hiroki Iwase 装置名 Name of Instrument/（BL No.） BL15 実施日 Date of Experiment 2017/06/19～2017/06/21

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

1. D_2O(100μL)/[OMIm][PF_6](2mL)/Tween20(80μL)
2. D_2O solution of $AgNO_3$(100μL)/[OMIm][PF_6](2mL)/Tween20(80μL)/Benzoin(10mg) before photoirradiation.
3. D_2O solution of $AgNO_3$(100μL)/[OMIm][PF_6](2mL)/Tween20(80μL)/Benzoin(10mg) after photoirradiation.

[OMIm][PF_6]: 1-octyl-3-methylimidazolium hexafluorophosphate, Tween20: $C_{12}H_{23}F_6N_2P$,
Benzoin: $C_{14}H_{12}O_2$

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Experimental

Preparation of the Ag particles in D_2O-in-[OMIm][PF_6] microemulsions.

Colloidal dispersions of Ag particles were synthesized by the photoreduction of $AgNO_3$ in the presence of Tween20 in D_2O-in-[OMIm][PF_6] microemulsions. The concentration of Ag^+ ion in the D_2O-in-[OMIm][PF_6] microemulsions were 60.3mM. The weight fraction of Tween20 ($W_{Tween20}$(wt%)), the [OMIm][PF_6]-to-Tween20 molar ratio (R) and the weight fraction of D_2O (W_{D2O}(wt%)) was adjusted to 3.3 (%), 102, and 4.1 (%), respectively. Here the value of $W_{Tween20}$ and W_{D2O} is a fraction of surfactant and D_2O, respectively, relative to the sum of weight of [OMIm][PF_6], Tween20, D_2O and benzoin. Briefly, 80μL of Tween20 was added to 2 mL of [OMIm][PF_6] followed by the addition of 10 mg benzoin powder and the mixture was then stirred vigorously. Prior to the UV-light irradiation of a 500W super-high-pressure mercury lamp, 100μL of D_2O solution of $AgNO_3$ (1.32 M) was added to the mixed solution with the simultaneous ultrasonication. Subsequently, the obtained Ag^+-containing D_2O-in-[OMIm][PF_6] microemulsions were poured into a quartz cell and irradiation by UV-light was started with continuous stirring using a magnetic stirrer.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

SANS experiments of the Ag particles in D_2O-in-[OMIm][PF_6] microemulsions.

SANS experiments were performed using a time-of-flight diffractometer, on the BL15 (TAIKAN) at J-PARC, Japan, in the q range of 0.07-14 nm^{-1} at room temperature with neutron wavelengths between 0.1 and 0.7 nm. All data were normalized to an absolute intensity by the coherent scattering of a glassy carbon as a reference sample after the necessary data corrections such as air scattering, empty-cell scattering, and the transmission factor. A sample changer was mounted on the goniometer. The solution samples were placed into a quartz cell. The thickness of the cell was 1.0 mm for all the samples. For the contrast variation (CV) SANS measurements, the scattering length density (SLD) of Ag atom is 3.47 (10^{-6}/Å^2). Here the SLDs of H_2O and D_2O are -0.561 (10^{-6}/Å^2) and 6.402 (10^{-6}/Å^2), respectively. Hence, since the SLD of the Ag particles is matched to that of the mixture for H_2O/D_2O=42/58, we can estimate the average size of the water droplets that consisted of aggregates of ionic precursors of $AgNO_3$ before photoreduction and Ag particles after photoreduction.

Results and discussion

Figure 1 shows SANS patterns (log $I(q)$ vs. log q) of the colloidal dispersions of Ag particles in D_2O-in-[OMIm][PF_6] microemulsions during photoreduction in the presence of Tween20. A comparison with the D_2O-in-[OMIm][PF_6] microemulsions without ionic precursors of $AgNO_3$ is also performed. The scattering patterns do not change at larger q range ($q \geq 1.5$ nm^{-1}), and the broad scattering peaks (centered around 3.0 nm^{-1}) of each sample do not shift at all. This might suggest that the production of Ag particles does not so much affect the morphology of high degree of self-organization in [OMIm][PF_6]. However, the peak intensity of Ag^+-containing D_2O-in-[OMIm][PF_6] microemulsions decreases in intermediate q range of 0.4 – 1.5 nm^{-1} when compared to pure D_2O-in-[OMIm][PF_6] microemulsions, although no peak shift is observed in this range. It reveals that D_2O droplets are formed in [OMIm][PF_6], and Ag^+ ions are dissolved in the D_2O droplets. Furthermore, the peak intensity of D_2O-in-[OMIm][PF_6] microemulsions containing Ag particles after photoreduction decreases much more in this q range. The decrease in the intensity can be attributed to the decrease in the total contrast factor resulting in reduction in scattering intensity of the samples containing Ag^+ ions and Ag particles. On the other hand, there is no significant difference in intensity at low q region ($q \leq$ 0.2 nm^{-1}). This strongly indicates that fractal structure of aggregates consisting of many droplets in the microemulsions is generated. To estimate the fractal structure, CV SANS measurements should be done in future work after the incoherent scattering subtraction of [OMIm][PF_6].

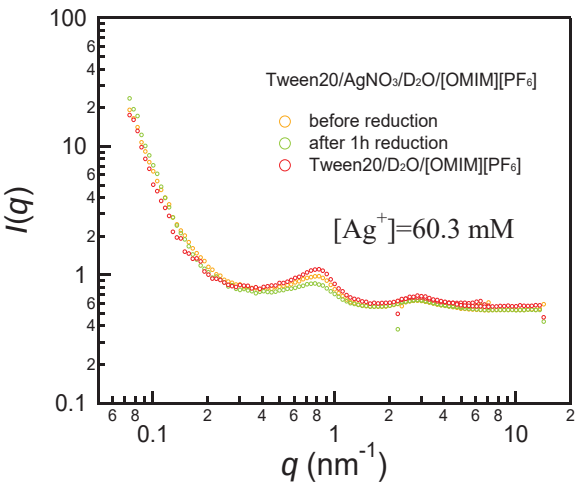

Fig. 1. SANS profiles of the Ag colloidal solutions prepared in Tween20/D_2O/[OMIm][PF_6] before and after the photoirradiation.

References

[1] M. Harada et al., *J. Colloid Interface Sci.*, 339 (2009) 373-381.
[2] M. Harada et al., *J. Colloid Interface Sci.*, 406 (2013) 94-104.