Observation of Single Atoms and Nano Structures in Liquid using Scanning Transmission Electron Microscopy

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Use of liquid is indispensable in our activities for substance transportation and chemical reaction. Because such liquid properties are dominated by the atomic/molecular configurations and motions, local area analysis in liquid is crucial for further development of liquid applications. However, the existing liquid analysis methods, such as x-ray diffraction and optical spectroscopy, are not good for local area investigation; therefore, more advanced methods with high spatial resolution have been strongly desired. Here, we have applied atomic resolution scanning transmission electron microscopy (STEM) to the liquid analysis, and then addressed observations of single atoms and nano inhomogeneous structures in liquid.

Contrary to our purpose, the general method that seals liquid with two solid films is unsuitable for the observation of single atoms in liquid and liquid nano structures because of the sample thickness [1,2]. In order to keep the atomic resolution, a thin liquid sample without the solid films should be prepared. Therefore, ionic liquid, which has almost no vapor pressure, was selected as the observed liquid, and then it was dropped on a holey solid film to form liquid films in the holes by surface tension. FIG.1 illustrates the fabrication process. The thickness of the liquid film was measured at about 10 ~ 50 nm [3,4]. Because this value is much less than the mean free path length, this liquid sample can provide the observation with the original atomic resolution.

We selected 1-octyl-3-methylimidazolium chloride (C₈mim-Cl) as a measured ionic liquid. C₈mim-Cl has high viscosity, which helps to observe the atomic/molecular movement, and clear nano inhomogeneous structures composed of polar/non-polar domains [5,6]. This means that C₈mim-Cl is a suitable object for our purpose. Next, we added gold complex ions (AuCl₄⁻) into C₈mim-Cl and observed it with high angle annular dark field STEM (HAADF-STEM). Because the HAADF-STEM intensity is approximately proportional to the square of atomic number Z, the gold atoms (Z = 79) in C₈mim-Cl, composed of light elements (Z ≦ 17), would be observed very bright. FIG.2 shows the HAADF-STEM image of C₈mim-Cl with gold atoms. In this image, many bright spots considered as the gold atoms are observed. The inset in FIG.2 shows the histogram of the spot size. The peak of the fitted gauss function appears at about 0.0085 nm², converted into a 0.10 nm circle. This value is close to the electron probe diameter of about 0.08 nm, concluding that almost all of the bright spots correspond to single gold atoms. In addition, we analyzed the behavior of the atoms by obtaining the continuous images. Nano inhomogeneous structures in ionic liquid C₈mim-Cl was also investigated from the coordination of the gold atoms. We will report the detailed results in our presentation with movies of the atomic movement.

References


**FIG. 1.** Illustration of the fabrication method of the liquid sample.

**FIG. 2.** HAADF-STEM image of C₈mim-Cl with 0.1M AuCl₄⁻, (inset) histogram of the bright spot size.