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In situ TEM observation of dynamic behavior of metal-based nanoparticles in ionic liquid

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Abstract

We performed *in situ* observation of gold nanoparticles in ionic liquid with atomic resolution transmission electron microscope (AR-TEM) and researched particle's moving and connecting under electron beam irradiation in several ionic liquids. From this study, we confirmed wide ranging applicability to observe microscopic phenomena in liquid at atomic resolution by the usage of ionic liquid and TEM.

1. Introduction

For controlling the structure of nano-devices made by self-organized or crystal growth, observation of them under liquid or gas situation is necessary for analyzing and controlling their material property. Thus it is very important to apply the liquid to transmission electron microscope (TEM) observations with atomic resolution for analyzing the mechanism of crystal growth processes and chemical reaction generally occurring in liquid. For observing the phenomena in liquid with electron microscope, it is necessary to prevent liquid from evaporating and diffusing in the sample space. As the most promising method, the environmental cells are employed. The environmental cell is a thin container having two windows for transmittance of electron beams [1]. Gas or liquid state reactants are inserted environmental cell and chemical reaction or crystal growth are occurred at liquid or vapor phase. In this manner, phenomena in the liquid is able to be observed by TEM. In recent years, metallic nanoparticles were floating and coupling each other in the liquid cell was observed [2]. But observation with this method has some difficulty because its experimental instruments are very complicated and expensive to operate.

On the other hand, the use of ionic liquid can be employed as another method of observing the phenomenon in the liquid. Because of extremely low vapor pressure, the sample with the liquid can maintain the vacuum in the TEM for observations. Furthermore, there is few risk of sample's charge-up because ionic liquid has electrical conductivity derived from an electrolyte [3]. For wider applicability and easier TEM observation with liquid environment, it is very important to develop the method.

In this work, the purpose of this study is to observe a phenomenon involving a structural change of the metal-based nanoparticles in the liquid with atomic resolution. And to evaluate whether ionic liquid is worth to using for observing the phenomena in liquid with TEM and getting the same images as the environmental cell.

2. Methods

The gold nanoparticles were produced by glow discharge in aqueous solution. A schematic picture of the experimental setup of generation of metal nanoparticles is shown in Fig. 1. Pt anode mesh and Au cathode is set in the electrolytic solution K_2CO_3 (0.1 mol/L) and applied a voltage between the electrodes at 140 V for one hour. The generated Nanoparticles were condensed and cleaned in ultrapure water by using centrifuge. Gold nanoparticles were set on the carbon mesh on the TEM grid, and ionic liquid (1-ethyl-3-methyl imidazolium tetrafluoroborate: $EMImBF_4$) was dropped on it. Ionic liquid was removed to reduce the thickness so that electron beam can transmit the sample of thickness.

This sample was observed by high resolution TEM with spherical aberration corrector (JEOL JEM-ARM200F). Accelerating voltage is 200 kV. During electron beam irradiation, beam current density of electron beam is 150 pA/cm^2 on the screen. And each TEM images were captured at the current density of 10 ~ 20 pA/cm^2. Also we performed video image capturing under constant current density which is smaller than 150 pA/cm^2.

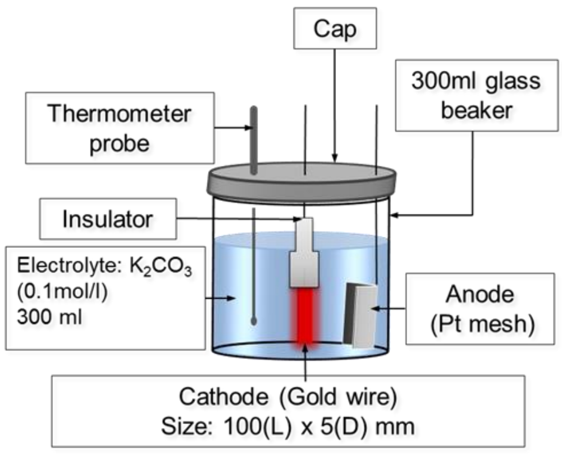

Fig.1 Picture of experimental setup of the system to produce gold nanoparticles [4, 5].

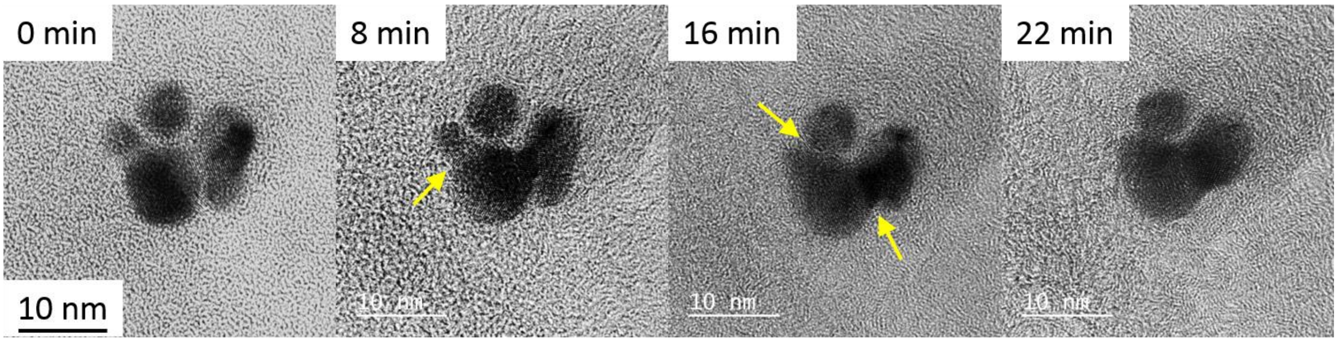

Fig. 2 Sequence of 35 nm ×35 nm images of changing of gold nanoparticles in ionic liquid by electron beam irradiation. Starting electron beam irradiation, gold nanoparticles are closed each other and connected. Connected area of gold nanoparticles became thick and four nanoparticles are united finally.

3. Results and discussion

Figure 2 and figure 3 show a series of TEM images which is the change of gold nanoparticles in ionic liquid membrane. In the figure, dark gray contrast parts are gold nanoparticles and the light gray parts are ionic liquid. At first, gold nanoparticles moved. And then, particles are attached and connected area between the particles got thick. We also observed contrast changing of united nanoparticle through the morphology changing. As the result of the electron beam irradiation, nanoparticle grows larger and includes multiple twinned structure. Electron beam irradiation at small current density did not induce those migration and combination. Therefore, electron beam irradiation caused these phenomena including crystal growth or particle motion in the liquid.

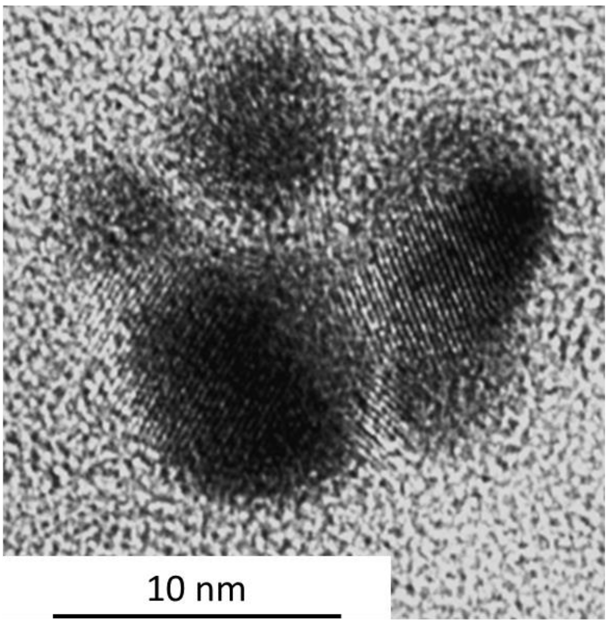

Fig. 3 Enlarged image of left panel of figure 2.

4. Conclusion

Using the ionic liquid for TEM observation, it is developed that ionic liquid could keep the characteristics of liquid because gold nanoparticles are moved and connected under the liquid condition in the TEM. In this experiment, the nanoparticles connect each other and the process speed depends on the electron density. The motion of the gold nanoparticles would be very slow compared to the nanoparticles in the aqueous solution of environmental cells because almost all ionic liquid has the high viscosity compared to aqueous solution. This property is useful to analyze motion of nanomaterials in the liquid. We confirmed that ionic liquid can be applicable enough to observe phenomena in the liquid with atomic resolution by TEM.

5. Future works

Not only the crystal growth by electron beam irradiation, the application of photon irradiation for the nanodevice is proposed. By changing the energy or wavelength of LASER, appearance of properties or controlling the sample structure is possible. Observing the photon irradiation by AR-TEM, in situ observation of photocatalytic effects or crystal growth becomes available.

Acknowledgements

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