Operando Observation of Vacuum and Liquid Interface while Conducting Gold Sputtering onto Ionic Liquid for Preparation of Au Nanoparticles

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ABSTRACT
In order to clarify the nanoparticles formation process of the metal sputtering onto ionic liquid, which is the facile method to prepare metal nanoparticles, the vacuum-liquid interface was captured by a camcorder while conducting gold sputtering. Because of intense color of Au clusters, move of Au clusters by convection of ionic liquid was clearly observed. The convection is a dominant factor in a transport of the resulting Au nanoparticles from the surface to interior of the ionic liquid.

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1. Introduction
Metal nanoparticles have attracted much attention as functional materials used in optical devices, catalysts, and sensors because of their unique properties. It is quite important to reveal the nanoparticle formation mechanism in order to control size and shape of the resulting metal nanoparticles. Recently preparation of metal nanoparticles using ionic liquid (IL), which is a kind of salt staying in liquid even at room temperature, is becoming popular because the preparation can be done without addition of any surface stabilizer. In addition to chemical and electrochemical preparation, by taking advantage of extremely low vapor pressure of IL, we have developed a clean method to prepare metal nanoparticles that is metal sputtering onto IL under vacuum conditions. This enables facile preparation of various kinds of nanoparticles, such as metal, alloy, metal oxide, and core-shell nanoparticles. The prepared nanoparticles exhibit several functions including electrocatalysis with high activity and good durability.

Based on the investigations focusing on relationship between the size distributions of the prepared nanoparticles and the sputtering conditions, we proposed that metal atoms and clusters generated by bombardment of the metal target due to energetic gas ions are aggregated on the IL surface before their sinking in the IL. It is, however, very hard to observe process of such the events by a microscope in a constrained sputtering chamber.

Although metal clusters and nanoparticles are inherently invisible by naked eyes, gold is exception because Au clusters (<2–3 nm) exhibit dark color due to quantized electronic energy structure and plasmon absorption of Au nanoparticles (>4 nm) gives vivid colors depending on their sizes. As a matter of fact, when gold sputtering on an IL was conducted, appearance and move of colored patterns were realized on the IL surface through a glass window, letting us notice a possibility to acquire information from the vacuum-IL interface without any specific microscopic devises. It was then attempted to capture the IL surface during sputtering by a camcorder, as a main object in the present study.

2. Experimental

1-Butyl-3-methylimidazolium chloride ([BMI]Cl; Kanto Chemical Co., Ltd.) and lithium bis(trifluoromethanesulfonyl)amide (Li[TfSA]; Morita chemicals Co., Ltd.) were mixed thoroughly in ultrapure water at ambient temperature, then [BMI][TfSA] was extracted by dichloromethane, followed by purification with ultrapure water several times.

Figure 1 shows a schematic illustration of an apparatus for capturing gold sputtering onto ionic liquid in a transparent glass cup.
3. Results and Discussion

Figure 2 shows frames picked from movies taken by the way shown in Fig. 1 while conducting Au sputtering onto [BMI][TFSA]. The side view of the cup and the surface of IL were taken. When Au sputtering began, powder-like brown materials homogeneously appeared on the entire surface of IL and they radiated outward. The observed tiny materials were confirmed to be Au clusters by spectroscopy and TEM observation (see Fig. 4) of the IL after the Au sputtering. In order to show more clearly the move of the Au clusters on IL with time, magnified pictures of the IL surface are given in Fig. 3. The contrast of each picture was increased by an imaging software to make spots formed by Au clusters be clearly recognized. Dashed line circles and scale bars are given in each picture to indicate how two spots moved with time. As these pictures show, two spots moved ca. 3 mm for 10 sec, giving its velocity of \(0.3 \text{ mm s}^{-1}\). The diffusion coefficient \((D)\) of [BMI][TFSA] having 50 cP of viscosity is estimated to be \(2.91 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}\) by the Stokes-Einstein relation with the Stokes radius of 1.5 nm that is a half of the average diameter (ca. 3 nm) of Au clusters estimated from a TEM image given in Fig. 4. If it is assumed that a concentration gradient is as high as 1 mol L\(^{-1}\)/cm (\(= 1 \times 10^6 \text{ mol m}^{-3}\)), the Fick’s laws of diffusion gives a flux \((f)\) of \(2.91 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}\). When a substance with a concentration of \(c \text{ [mol m}^{-3}\]) moves in a certain direction at a velocity of \(v \text{ [m s}^{-1}\]), the flux is defined as \(f = cv\). Then, \(c = 1000 \text{ mol m}^{-3}\) and \(f = 2.91 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}\) give \(v = 2.91 \times 10^{-7} \text{ mm s}^{-1}\). Apparently this value is much smaller than the velocity of the spot of Au clusters estimated from pictures given in Fig. 3.

It is then quite natural to ascribe the move of Au clusters with very high speed at vacuum-liquid interface to occurrence of convection of IL during sputtering. Thermal convection of liquid, which is called the Rayleigh-Bénard convection,\(^{113}\) is well known and its driving force is change in the liquid density by heating, generating convection in a vertical direction. The difference in temperature also causes change in surface tension. Increase in temperature lessens surface tension, producing a driving force for convection in a horizontal direction at the liquid surface from hot area to cold area. This is called the Marangoni convection. Therefore, the move of Au clusters observed at the surface of IL must indicate occurrence of the Marangoni convection during Au

Figure 2. Frames picked from movies of (a) the side view of a cup and (b) the surface of IL taken while conducting Au sputtering, and (c) schematic illustration of convections of ionic liquid caused by the Au sputtering. The arrows given in the figure show directions of the convections.

Figure 3. Frames picked from movie after 60 seconds, and expanded four pictures taken at 5 seconds interval. Two dashed line circles track the same spots of brown materials derived from Au clusters.

Figure 4. TEM image and their size distribution histogram of Au nanoparticles prepared by sputtering onto [BMI][TFSA] in glass cup (613.5 mm, depth 8.0 mm) for 5 min.

sputtering. In general, magnitude of plasma energy in a magnetron sputtering instrument is highest at the center of a target and it decreases toward the periphery. This might make the temperature gradient on the IL surface, inducing the observed convection.

When the Au clusters reached to the wall of the grass cup, they changed their direction toward the center of the cup and moved ca. 5 mm beneath the IL surface. The side view and the surface pictures taken at 45 sec in Fig. 2 show the first reaching of the Au clusters to the wall. Then, their returning to the center may be recognized by comparing the pictures taken at 45, 90, and 150 sec. Based on the observed fact, the convection flow routes depicted by white arrows in Fig. 2(c) seem to be appropriate. Such the behavior is very interesting because the Au clusters arriving at the wall of the cup can take other directions like downward convection but they took the horizontal movement with the opposite direction. Although further investigation is needed to clarify occurrence of the observed convection, it may be one of the reasons that the viscosity of IL at around surface could be decreased by the aforementioned increment of temperature during the sputtering.

Continuous supply of Au clusters and their moving due to the circular convection gathered Au clusters at the center where the liquid density should increase. As a result, downward move occurred as recognized from the side view pictures taken at 90 and 150 sec in Fig. 2(a). This could indicate generation of another convection but our measurement was unfortunately too short to know the whole aspect of the convection. However, according to the well-known fact that a convection takes circular flow, the black solid and broken arrows given in Fig. 2(c) can be speculated as the lower convection.

As already mentioned, Au clusters formed spots, which made patchy pattern as recognized from Fig. 3. The obtained patterns resemble the spinodal decomposition patterns caused by biphasic segregation reaction. In this sputtering method, the IL surface keeps high concentration of Au clusters because it is always supplied with gold clusters during sputtering. It is known that colloid solution undergoes phase separation when the particle volume fraction becomes very high. The same reason seems to be responsible for the formation of the patchy pattern, but the detailed origin is unknown at present.

4. Conclusion

We had speculated that the nanoparticles prepared by the metal sputtering on IL simply proceeded in the following steps; generation of Au species by sputtering and their falling onto IL; aggregation of Au clusters at the IL surface; sedimentation of the grown Au nanoparticles. On the other hand, only move of Au clusters in a vertical direction was considered. Surprisingly, however, the operando observation of the vacuum-IL interface while conducting sputtering has revealed that Au clusters on the IL surface are horizontally moved by the Marangoni convection with very high velocity. After one round trip from the center and glass wall and its reverse direction, Au clusters are gathered at the center, followed by their moving toward the bottom. It is then speculated that such the move of Au clusters influences physically property of the resulting Au nanoparticles. In order to clarify how the convection relates to the Au nanoparticles formation, we already began to the next investigation using several cups having different dimensions.

References