Effects of the electron irradiation energy on synthesis of gold nanoparticles using gas-liquid interfacial plasma

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Abstract. Structure controlled gold nanoparticles (AuNPs) are synthesized at the surface of the ionic liquid by the plasma irradiation under the strong magnetic field. The AuNPs are easily synthesized in the region where the edge of the plasma is irradiated, while hardly synthesized in the region where the core plasma is irradiated. In the plasma edge region, high energy electrons collide with neutral gas and the diffused low energy electrons generate the AuNPs by reducing Au ions of the gold chloride. On the other hand, in the core plasma region, the irradiated high energy electrons can dissociate the ionic liquid and generate the new compounds with oxidation effect, which inhibit the synthesis of the AuNPs.

1. Introduction

Recently, highly-ordered periodic structures of metal nanoparticles have attracted much attention due to their high catalytic activity [1], unique photosensitive reactivity [2], and so on. Especially, the synthesis of various kinds of nanoparticles using the plasma-liquid interfaces [3-6] is advantageous in that a reducing agent is the plasma itself, and then, the synthesis is continuous during the plasma irradiation. To realize the periodic structure of the nanoparticles, we adopt a novel plasma technique combined with introduction of ionic liquids [7-9] under strong magnetic fields up to tesla. Since the plasma generated under the strong magnetic field keeps its structure due to confinement along the magnetic field lines, the plasma structure can be transcribed to the liquid surface, resulting in the synthesis of the structured nanoparticles at the gas-liquid interface when the plasma reduces the metal chlorides in the liquid.

When the mesh anode is used to generate the plasma, the shadow region is made which have the shape of the wire of the mesh. Surprisingly, the nanoparticles are synthesized selectively in the shadow region [10]. However, the mechanism of the nanoparticle synthesis in the shadow region has not clarified.

In this paper, we focus on the effects of the electron irradiation energy to clarify the synthesis mechanism of the structure controlled nanoparticles. For that purpose, the difference of the gold nanoparticles (AuNPs) synthesis is measured by changing the discharge voltage ($V_{DC}$) which can control the electron irradiation energy. In addition, the relationship between the electron irradiation energy and the dissociation of the ionic liquid to generate the oxidizing agent is discussed.

2. Experimental setup

Figure 1 shows the schematic of an experimental setup for the discharge plasma in contact with the ionic liquid [11] containing a gold chloride (HAuCl$_4$), where the nitrogen plasma is generated between
a disk cathode (ϕ15 mm in diameter) and a mesh anode (ϕ20 mm in diameter), and is irradiated to the ionic liquid on the teflon plate (30 mm × 30 mm). Figure 2 shows the picture of the teflon plate for explaining the positional relationships between the plasma and the ionic liquid. The ionic liquid is placed in small holes (1) - (5) formed on the teflon plate at a distance of 45 mm from the anode electrode. When the strong magnetic field is applied along the machine axis, the generated plasma is strongly magnetized. The AuNPs are synthesized in the ionic liquid by the plasma reduction of HAuCl$_4$.

The experimental conditions are as follow: gas pressure $P_{\text{gas}}=30$ Pa, gas flow is 1.6 sccm, magnetic field $B=0.1$ T.

A kind of the ionic liquid is N, N, N – Trimethyl – N – propylammonium Bis (trifluoromethanesulfonyl) imide, and compositional formula is $C_8H_{16}F_6N_2O_4S_2$. The concentration of the HAuCl$_4$ is 20 mg/ml.

3. Results and Discussion

Figure 3 shows the pictures of the AuNPs which are formed at the gas-liquid interface under the condition that the discharge voltage and irradiation time are (a) $V_{\text{DC}} = 0.9$ kV, $t_i = 20$ s and (b) $V_{\text{DC}} = 0.9$ kV, $t_i = 40$ s, respectively, where the small holes on the teflon plate are not prepared. The AuNPs are easily synthesized in the region where the edge of the plasma is irradiated. However, the synthesized AuNPs quickly diffuse radially, and therefore the exact synthesized region cannot be identified. To investigate the relationship between the region where the AuNPs are easily synthesized and the region where the edge of the plasma is irradiated in detail, the ionic liquid is separately placed in each hole as shown in Figure 2.

Figure 4 shows the pictures of the ionic liquid, to which the plasma is irradiated under the condition that the discharge voltage and the irradiation time are (a) $V_{\text{DC}} = 0.8$ kV, $t_i = 120$ s and (b) $V_{\text{DC}} = 1.1$ kV, $t_i = 120$ s. A tiny amount of the ionic liquid is sputtered and dissociated by the plasma irradiation. The region where the blown materials are deposited on the teflon plate indicates the plasma irradiation region. In both cases, the AuNPs are synthesized in the holes (2), (4) where the sharp density and potential gradient are generated. However, at the hole (3), synthesis of the AuNPs depends on $V_{\text{DC}}$. 

Figure 1. Schematic of the experimental setup.

Figure 2. The picture of the teflon plate for explaining the positional relationships between the plasma and the ionic liquid.

Figure 3. The pictures of the AuNPs which are formed at the gas-liquid interface under the condition that the discharge voltage and irradiation time are (a) $V_{\text{DC}} = 0.9$ kV, $t_i = 20$ s and (b) $V_{\text{DC}} = 0.9$ kV, $t_i = 40$ s, respectively, where the small holes on the teflon plate are not prepared. The AuNPs are easily synthesized in the region where the edge of the plasma is irradiated. However, the synthesized AuNPs quickly diffuse radially, and therefore the exact synthesized region cannot be identified. To investigate the relationship between the region where the AuNPs are easily synthesized and the region where the edge of the plasma is irradiated in detail, the ionic liquid is separately placed in each hole as shown in Figure 2.

Figure 4 shows the pictures of the ionic liquid, to which the plasma is irradiated under the condition that the discharge voltage and the irradiation time are (a) $V_{\text{DC}} = 0.8$ kV, $t_i = 120$ s and (b) $V_{\text{DC}} = 1.1$ kV, $t_i = 120$ s. A tiny amount of the ionic liquid is sputtered and dissociated by the plasma irradiation. The region where the blown materials are deposited on the teflon plate indicates the plasma irradiation region. In both cases, the AuNPs are synthesized in the holes (2), (4) where the sharp density and potential gradient are generated. However, at the hole (3), synthesis of the AuNPs depends on $V_{\text{DC}}$. 

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namely, the AuNPs are synthesized for $V_{DC} = 0.8$ kV, while the AuNPs are not synthesized for $V_{DC} = 1.1$ kV.

The difference in the AuNPs synthesis at the hole (3) is attributed to the difference in the electron irradiation energy. For $V_{DC} = 0.8$ kV, the low energy electrons are irradiated to the ionic liquid, and generate the AuNPs by reducing Au$^{3+}$ of the gold chloride. For $V_{DC} = 1.1$ kV, on the other hand, the electron irradiation energy is higher than that for $V_{DC} = 0.8$ kV. The high energy electrons can dissociate the ionic liquid and generate the new compounds which are considered to affect the synthesis of the AuNPs. Here, optical emission spectra in the plasma region shows the H$_a$ peak derived from H atom, which is dissociated from the ionic liquid.

![Figure 3](image)

**Figure 3.** The pictures of the AuNPs synthesis which are formed at the gas-liquid interface under the condition (a) $V_{DC} = 0.9$ kV, $t_i = 20$ s and (b) $V_{DC} = 0.9$ kV, $t_i = 40$ s.

![Figure 4](image)

**Figure 4.** The pictures of the ionic liquid, to which the plasma is irradiated, (a) $V_{DC} = 0.8$ kV, $t_i = 120$ s and (b) $V_{DC} = 1.1$ kV, $t_i = 120$ s.

Figure 5 shows the Fourier transform infrared spectrophotometer (FT-IR) spectra of the new compounds in the ionic liquid for $V_{DC}=0.7$ -1.1 kV and $t_i=120$ s. The samples are made by the plasma irradiation to the ionic liquid on the glass plate as shown in Figure 3. The peaks around 3250 and 3350 cm$^{-1}$ gradually increase by increasing $V_{DC}$. The peaks are identified to be N-H bond, and therefore, the candidate of the new compounds consisting of N-H bond and derived from the used ionic liquid is determined to be Trifluoromethanesulfonamide (TFMS).

![Figure 5](image)

**Figure 5.** The FT-IR spectra of the new compounds.
Figure 6 shows the relative production rate of AuNPs and TFMS as a function of the discharge voltage $V_{\text{DC}}$ which corresponds to the electron irradiation energy. Here, the production rates of AuNPs and TFMS are evaluated by the peaks of UV-Vis spectra (550 nm) and FT-IR spectra ($3350 \text{ cm}^{-1}$), respectively. As the electron irradiation energy becomes higher, the production rate of TFMS monotonically increases. By contrast, the production rate of AuNPs is decreased when the production rate of TFMS is over a threshold. Therefore, the production of TFMS caused by the high energy electron irradiation affects the AuNPs synthesis.

Figure 6. The relative production rate of AuNPs and TFMS as a function of the discharge voltage.

Figure 7 shows the structures of (a) the ionic liquid used in this experiment and (b) TFMS. TFMS could be generated by dissociating the N-S bond of the ionic liquid and combining with H, and the acidity of TFMS is reported to be very strong. Hence, the TFMS shows the oxidative effect and inhibits the AuNPs synthesis when the electron irradiation energy is high. In the edge region, on the other hand, even high energy electrons collide with neutral gas and become low energy electron. Therefore, the AuNPs can be synthesized in the plasma edge region even for $V_{\text{DC}}=1.1 \text{ kV}$.

![Figure 7. The structures of (a) the ionic liquid and (b) TFMS.](image)

Figure 7. The structures of (a) the ionic liquid and (b) TFMS.

Figure 8 shows the plasma-irradiated ionic liquid ($V_{\text{DC}}=0.8 \text{ kV}$) (a) without additional TFMS and (b) with additional TFMS. The concentration of additional TFMS is TFMS/IL=50 mg/ml and the plasma irradiation time is 120s. In the case of the ionic liquid with additional TFMS, it is found that AuNPs are not synthesized. It indicates that TFMS has the inhibitory effect on the AuNPs synthesis.
4. Conclusion
We focus on the effects of the electron irradiation energy to clarify the synthesis mechanism of the structure controlled nanoparticles. We clarify the low energy electrons generate the AuNPs by reducing Au$^{3+}$ of the gold chloride, however, the high energy electrons can dissociate the ionic liquid and generate the new compounds which are considered to affect the synthesis of the AuNPs. The new compounds are determined to be TFMS, whose acidity is reported to be very strong. Hence, the TFMS shows the oxidative effect and inhibits the AuNPs synthesis when the electron irradiation energy is high.

These results are the first step of elucidating the mechanism of AuNPs synthesis. Furthermore, using this mechanism, we can freely form the patterned AuNP structure, which is expected to be applied to the biosensors and the bioimaging devices using a principle of the surface plasmon resonance of the AuNPs.

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