

プラズマ気液界面における物理・化学現象と新規ナノバイオ物質創製
**Physical and Chemical Phenomena on Plasma Gas-Liquid Interface and
 Synthesis of Novel Nano-Bio Materials**

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1. Introduction

Plasmas generated in contact with liquid [1] have attracted much attention as a novel reactive field in creation of functional nanoparticles [2] because the brand-new chemical reactions are yielded at the gas-liquid interface, which are induced by the physical actions of the non-equilibrium plasmas. Especially, the patterned gold nanoparticle (AuNP) structure can be synthesized by the gas-liquid interfacial plasma and is expected to be applied to novel bio-imaging device, optoelectronic device, photoelectric device, and so on, using a principle of the surface plasmon resonance of the AuNPs.

To realize the periodic structure of the nanoparticles, we adopt a novel plasma technique combined with introduction of ionic liquids under strong magnetic fields up to 4 tesla (T) [3]. 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.

2. Experimental Apparatus

Figure 1(a) shows the schematic of an experimental setup for nanoparticle structure formation using a gas-liquid interfacial discharge plasma (GLIDP) under strong magnetic fields, which has a glass cell with 15 mm inner diameter and 10 mm depth in a cylindrical glass chamber with 75 mm diameter and 200 mm length. A DC voltage V_D is supplied to an upper cathode electrode composed of a stainless steel (SUS) plate and a SUS mesh grid is used as an anode electrode to promote a spatial diffusion of the plasma. Typical discharge current is $I_D=1\sim 3$ mA. Nitrogen gas is adopted as a discharge gas in view of its reactivity, and the gas pressure P_{gas} is varied from 20 to 100 Pa.

The new kind of the ionic liquid (N.N.N.-Trimethyl-N-propyl-ammonium Bis (trifluoro methane sulfonyl) imide) put in the glass cell is placed on a peltier element which is located at a distance of 50 mm from the anode electrode. Since this ionic liquid does not become supercooled state, we can make the ionic liquid solid state by cooling the ionic liquid using the peltier element located under the glass cell. When the strong magnetic fields are applied along the machine axis, the generated plasma is strongly magnetized, and then, the periodic plasma structure formed by the mesh anode is maintained just above the ionic liquid as shown in Fig. 1(b). Typical plasma parameters for $I_D=3$ mA, $P_{\text{gas}}=30$ Pa, $z=10$ mm are as follows: electron density $n_e\sim 10^{10}$ cm⁻³, electron temperature $T_e\sim 0.35$ eV, plasma space potential $\phi\sim 1$ V.

The AuNPs are synthesized in the ionic liquid by the plasma reduction of Au chloride (HAuCl₄). The ionic liquid can be cooled by the peltier element and becomes the solid state as mentioned above, with keeping the AuNP structure formed by the plasma irradiation at the liquid interface.

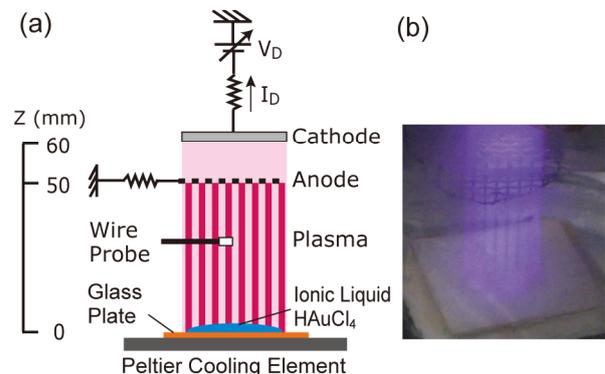


Fig. 1. (a) Schematic of experimental setup for nanoparticle structure formation and (b) photo of the formed periodic plasma structure. $P_{\text{gas}}=30$ Pa, $I_D=3$ mA, $B=1$ T.

3. Experimental Results

Figure 2 shows photos of the temporal evolution of the periodic AuNP structure which is formed at the gas-liquid interface in accordance with the periodic plasma structure under the condition of the strong magnetic field of $B = 1$ T for (a) $I_D = 3$ mA and (b) $I_D = 1$ mA. The density of the periodic structured AuNPs increases with plasma irradiation time t_{pi} , and the obvious structure is formed typically within $t_{pi} = 2$ min. Surprisingly, the synthesized AuNPs have the mesh shape for $I_D = 3$ mA, namely, the AuNPs are synthesized in the shadow region of the wire of the mesh anode electrode as shown in Fig. 2(a). For $I_D = 1$ mA, on the other hand, the AuNPs are oppositely synthesized in the hole regions of the mesh anode electrode.

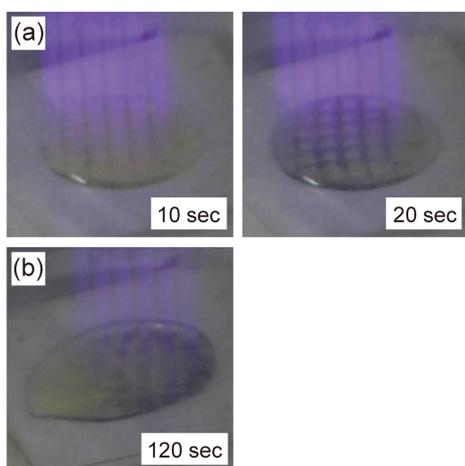


Fig. 2. Temporal evolution of the periodic nanoparticle structure formed by controlled gas-liquid interfacial plasmas for (a) $I_D = 3$ mA and (b) $I_D = 1$ mA. $P_{gas} = 30$ Pa, $B = 1$ T..

To explain the phenomena, we use the model of the AuNP synthesis as shown in Fig. 3(a). As mentioned above, the charged particles such as the electrons and the positive ions cannot reach to the shadow region of the ring electrode, namely, only neutral radicals can arrive at the shadow region. The ionic liquid used in this experiment is described in Fig. 3(b), which has C-H bond in cation (positive ion) and C-F bond in anion (negative ion). When the radicals in the plasma are irradiated to the ionic liquid, the C-H bond of the ionic liquid is considered to be dissociated, and the generated hydrogen radicals reduce the Au ions [3], resulting in the synthesis of AuNPs in the shadow region of the ring electrode. On the other hand, in the plasma irradiation region, relatively high-energy ions are irradiated to the ionic liquid, and the C-F bond whose dissociation energy ($D = 5.07$ eV) is

larger than that of the C-H bond ($D = 4.29$ eV), can be dissociated by the high-energy ions. Therefore, the AuNPs are destroyed by the oxidation effect of the fluorine radicals which come from the dissociation of the ionic liquid by the collision with the high energy charged particle. Here, Larmor radius of the nitrogen molecular ion is calculated to be about 0.1 mm based on the assumption that the ion temperature is room temperature and $B = 1$ T. Since the wire diameter of the ring electrode is 0.6 mm, the ring shaped AuNP structure can remain even if the ions slightly irradiate inside the shadow region of the wire due to the Larmor motion.

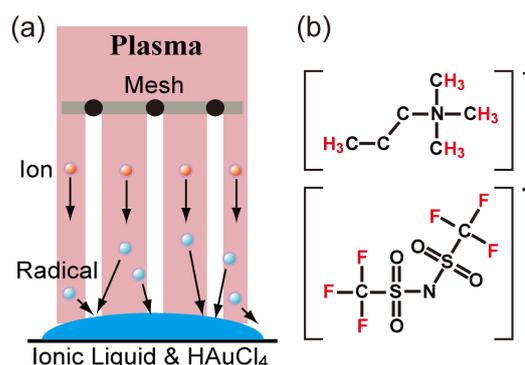


Fig. 3. (a) Model of the synthesis mechanism of the ring shaped Au nanoparticles and (b) chemical formula of the ionic liquid used in this experiment.

4. Conclusions

The periodic AuNP structures are formed, which correspond to the shape of the strongly-magnetized plasmas generated using the mesh electrode on the ionic liquid. It is interesting that the structure of the AuNPs depends on the discharge current, namely, the AuNPs are synthesized in the plasma ion irradiation region for small discharge current, while the AuNPs are synthesized in the shadow region of the mesh for relatively large discharge current. These phenomena are well explained by the reduction and oxidation effects of the radicals which are generated by the plasma irradiation to the ionic liquid and resultant dissociation of the ionic liquid.

References

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