22G10

Structure-Controlled Synthesis of Gold-Nanoparticles Using Strongly-Magnetized Gas-Liquid Interfacial Plasma

気液界面強磁化プラズマによる金ナノ粒子の構造制御合成

Toshiro Kaneko and Rikizo Hatakeyma
金子 俊郎, 畠山 力三

Department of Electronic Engineering, Tohoku University
6-6-05 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
東北大学 大学院工学研究科 電子工学専攻 〒980-8579 仙台市青葉区荒巻字青葉6-6-05

A periodic structure of gold nanoparticles is formed by reducing an aqueous solution of gold chloride using a spatio-periodically generated plasma under the strong magnetic field. In addition, it is found that a ring-shaped nanoparticle structure is formed corresponding to the shape of a ring electrode inserted into the plasma, where the nanoparticles are synthesized at the position without plasma irradiation due to the shielding by the ring electrode.

1. Introduction

Recently, highly-ordered periodic structures of metal nanoparticles have attracted much attention due to their high catalytic activity, unique photosensitive reactivity, and so on. Especially, the synthesis of various kinds of nanoparticles using the plasma-liquid interfaces [1] 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 [2] under strong magnetic fields up to 4 tesla (T).

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.

This method could contribute to supplying a considerable amount of spatially-periodic nanoparticles available for the development of unique optoelectronic devices.

2. Experimental Apparatus

Figure 1(a) shows the schematic of an experimental setup for the discharge plasma in contact with an ionic liquid, 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.

The ionic liquid (N.N.N.-Trimethyl-N-propyl-ammonium Bis(trifluoromethanesulfonyl) 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. When the strong magnetic field is 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).

Gold nanoparticles (AuNPs) are synthesized in the ionic liquid by the plasma reduction of Au chloride such as $HAuCl_4 \cdot 3H_2O$ [3,4].

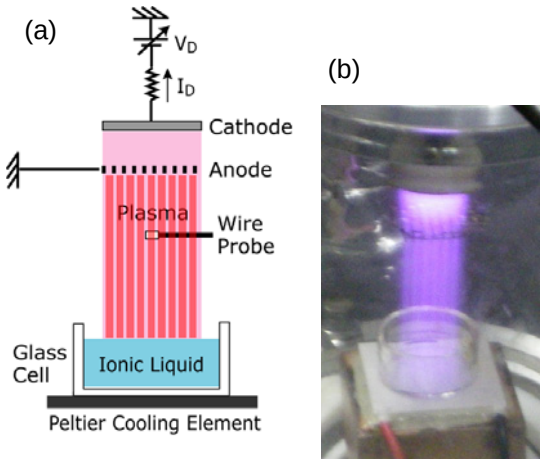

Fig. 1. (a) Schematic of the experimental setup, and (b) photo of the synthesized periodic plasma structure.

The ionic liquid can be cooled by the peltier element and becomes a solid state, with keeping the nanoparticle structure formed by the plasma irradiation at the liquid interface.

3. Results and Discussion

Figure 2 shows pictures of the temporal evolution of the periodic nanoparticle structure which is formed at the gas-liquid interface in accordance with the plasma structure under the condition of a strong magnetic field of B = 1 T. The density of the periodic structured nanoparticles increases with time, and the obvious structure is formed typically within 5 min. When the plasma is irradiated for longer than 5 min, the nanoparticles diffuse and the structure is broadened.

In order to suppress the diffusion of the nanoparticles, the temperature of the ionic liquid is reduced using the peltier element, resulting in the increase in viscosity of the ionic liquid. Although the diffusion of the nanoparticles is suppressed, the nanoparticle synthesis rate becomes low. Therefore, it is necessary to precisely control the temperature of the ionic liquid for the fine periodic nanoparticle structure.

As the next step, we attempt to form more finely periodic structures of the nanoparticles based on the self-organizing behavior of turbulent plasmas generated by the nonlinear development of plasma fluctuations. For this purpose, a ring electrode is inserted in the plasma column as shown in Fig. 3(a), and a positive DC bias voltage V_C is applied to the electrode. It is found that the high frequency fluctuation is excited by the positive bias voltage, however the self-organized plasma structure is not observed at present.

Using this configuration, the nanoparticles are

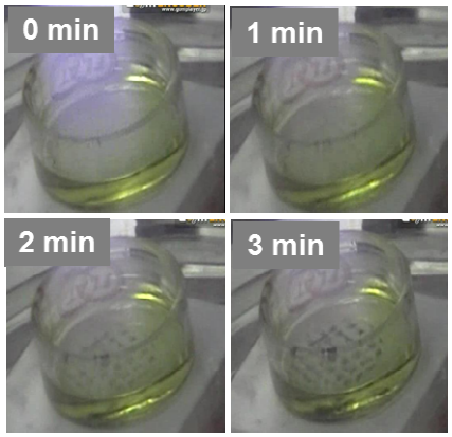

Fig. 2. Temporal evolution of the periodic nanoparticle structure formed by controlled gas-liquid interfacial plasmas.

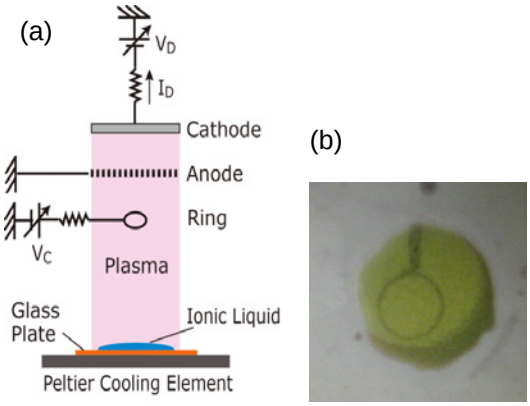

Fig. 3. (a) Experimental apparatus and (b) the ring shaped nanoparticle structure. B=1 T.

synthesized by reducing the Au chloride as shown in Fig. 3(b). It is found that the ring shaped nanoparticle structure is formed corresponding to the shape of the inserted ring electrode. This result means that the nanoparticles are synthesized at the position without plasma irradiation due to the shielding by the ring electrode.

Since the gold nanoparticles are usually synthesized by the reduction effect of the hydrogen radical in the plasma, the charged particles (positive ions or electrons) are considered to inhibit the synthesis of the nanoparticles in the plasma irradiation region.

4. Conclusions

Gold nanoparticles with periodic structure or ring shaped structure are synthesized using the strongly magnetized plasmas. The ring shaped nanoparticle structure is corresponding to the shape of the ring electrode inserted in the plasma.

These results imply that the pattered nanoparticle structure can be freely formed and is expected to be applied to the wavelength-selective wave guide using a principle of the surface plasmon resonance of the nanoparticles.

Acknowledgments

This work is supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] T. Kaneko, Q. Chen, T. Harada, and R. Hatakeyama: Plasma Sources Sci. Technol. **20** (2011) 034014.

[2] T. Kaneko, K. Baba, and R. Hatakeyama: J. Appl. Phys. **105** (2009) 103306.

[3] T. Kaneko, K. Baba, T. Harada, and R. Hatakeyama: Plasma Proc. Polym. **6** (2009) 713.

[4] Y. B. Xie and C. J. Liu: Plasma Proc. Polym. **5** (2008) 239.