20PA-010

Control of plasma-liquid interaction of atmospheric-pressure glow discharge using liquid electrode

液体電極を用いた大気圧グロー放電の気液界面での反応の制御

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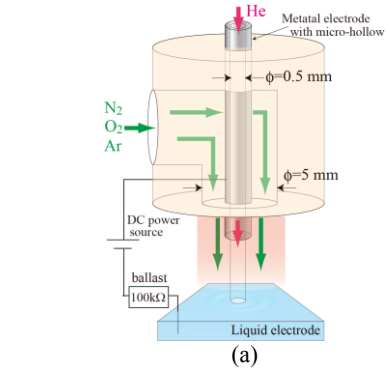
To control the plasma-liquid interaction, we use sheath flow system which can control the gas species around the discharge space. Using this system, plasma emission and reaction in liquid of atmospheric DC glow discharge using liquid electrode can be controlled. For the synthesis of metal nanoparticles in aqueous solution, we propose dual plasma electrolysis, which consists of a Hoffman electrolysis apparatus with two atmospheric glow discharge plasmas as electrodes instead of conventional metal electrodes immersed in a liquid. Size and shape of nanoparticles also can be controlled by using sheath flow system.

1. Introduction

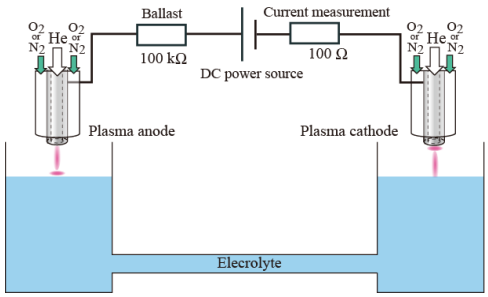
Atmospheric non-thermal plasma in and in contact with liquids has attracted considerable interest in view of its potential use in a wide range of applications [1]. Previously we investigated the fundamental characteristics of atmospheric DC glow discharge using liquid electrode [2,3] and synthesis of NPs (nanoparticles) by electrolysis with atmospheric plasma [4]. To control the discharge characteristics including reaction in liquid is important for to extend the application. In this study, we propose the method for the control of the discharge by using sheath flow system. Using this system, the gas species in the electrode gap can be controlled. We investigate the influence of sheath flow gas species on the synthesis of NPs and the characteristics of the discharge.

2. Experimental procedure

Fig. 1(a) shows experimental setup for atmospheric DC glow discharge using liquid electrode. The details of the experimental setup for the generation of liquid electrode is described in Ref.[2]. The discharge is generated between metal nozzle electrode and liquid electrode. The metal nozzle electrode is made of stainless steel with inner diameter of 500 μm diameter. To generate stable discharge, helium is fed through the hollow of the nozzle electrode to the outside, and a discharge is generated in the gap in ambient air. When helium is fed to the ambient air, the surrounding air is entrained into the helium flow. The surrounding air affects the discharge characteristics. To avoid the effect of air, we use the



(a)



(b)

Fig. 1: Experimental setup (a). atmospheric DC glow discharge using liquid electrode (b) plasma electrolysis system for synthesis of NPs.

sheath flow system. The sheath gas (N_2 or O_2) flows around the helium gas flow. Using this system, the gas species in the electrode gap can be controlled. Fig. 1(b) shows the experimental setup of dual plasma electrolysis for synthesis of metal NPs. In order to divide the anodic and cathodic reactions, we used an H-shaped glass vessel reactor known as the Hoffman electrolysis apparatus. The reactor is filled with an electrolyte of $HAuCl_4$ aq. (0.3mmol/l) or $FeCl_2$ aq. (0.1 mol/l). To avoid influence of air

existence, we use sheath flow system. For the mass synthesis, For the mass synthesis and the better control of interaction between plasma and liquid surface, we also developed the continuous liquid-flowing electrode system and try the nanoparticle synthesis with the flowing system.

3. Synthesis of metal nanoparticles

When plasma electrolysis with $HAuCl_4$ using N_2 sheath flow occur, the color of the liquid on both the plasma anode and cathode sides becomes red, as shown in Fig. 2. This red color results from the surface plasmon resonance of Au nanoparticles, and it indicates the generation of Au nanoparticles. In the case of without sheath flow, liquid color becomes red same as the case of N_2 sheath flow. However, in the case of using O_2 sheath flow, liquid color does not become red. Fig. 3 shows the TEM image of NPs synthesized by plasma electrolysis with N_2 sheath flow. The NPs synthesized positive-ion irradiation at the plasma anode have triangular structures and their size is about 100 nm, as shown in Fig. 3(a). The NPs synthesized by electron irradiation at the plasma cathode side have many dendrite structures and their size is about 50 nm, as shown in Fig. 3(b). The selectivity of the size and shape is good. In the case of without sheath flow, the selectivity of NPs's size and structures are not so good. Although the reason is not clear, we confirmed that size and shape can be controlled by using sheath flow system.

We also confirmed that the Au NPs can be synthesized using the continuous liquid-flowing electrode system. The continuous flowing system enables us to control the processing time duration which is the interaction time between plasma and local liquid surface and to make large amount of NPs by long-time operation without exchanging liquid in the vessel. From these reasons, we are now trying to apply this system to the mass synthesis of Au NPs with a good selectivity.

We try to synthesize not only Au NPs but also Fe_3O_4 NPs. Fig. 4 shows the images of plasma electrolysis with $FeCl_2$ aq. for synthesis of Fe_3O_4. To avoid oxidation in liquid, ethanol with 10ml is added to the $FeCl_2$ aq. with 50ml. In the case of using O_2 sheath flow and without sheath flow, liquid color becomes yellow, as shown in Fig. 4(a)(b). It indicates oxidation reaction such as $Fe^{2+} \rightarrow Fe^{3+}$ occur because Fe^{3+} indicates yellow in general. In the case of using N_2 sheath flow, black materials are synthesized in liquid, as shown in Fig. 4(c). We confirmed that these black materials can be collected by neodymium magnet and it has magnetization. In $FeCl_2$ aq., metal

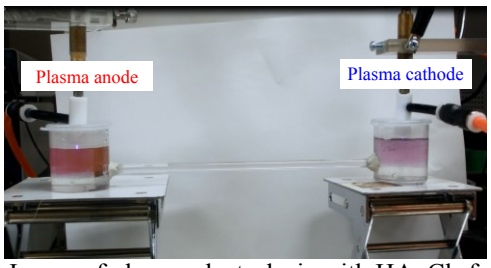
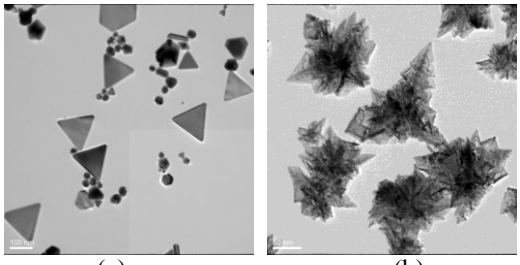
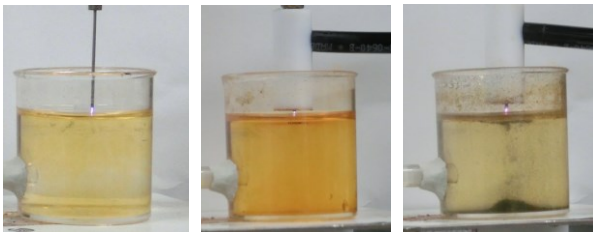


Fig. 2 Image of plasma electrolysis with $HAuCl_4$ for synthesis of Au NPs using N_2 sheath flow for. (After 5min. Current 3 mA.)



(a) (b)

Fig. 3 Au NPs synthesized by plasma electrolysis with N_2 sheath flow. (a) plasma anode(b) plasma cathode.



(a) (b) (c)

Fig. 4 Image of plasma electrolysis with $FeCl_2$. for synthesis of Fe_3O_4. (After 5min. Current 3 mA.) (a)w/o sheath flow, (b) O_2 sheath flow (c) N_2 sheath flow. (Photos are taken after 10 min. Current 3 mA.)

cation is only $Fe2^+$. The reaction such as $Fe^{2+} \rightarrow Fe^{3+}$ occurs easily. For synthesis of Fe_3O_4, both Fe^{2+} and Fe^{3+} are needed. In the case of using, O_2 sheath flow and without sheath flow, only oxidation reaction occur at the plasma-liquid interface. Although the details are not clear, using N_2 sheath flow, the oxidation reaction can be controlled and therefore, Fe_3O_4 is synthesized.

Acknowledgments

This work was supported financially in part by a Grant-in-Aid for Scientific Research on Innovative Areas (No 21110007) from Ministry of Education, Culture, Sports, Science and Technology, Japan.

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