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Generation of Plasmas in Porous Materials with A Gas-Liquid Mixed Phase Medium

気液混合媒質を用いた多孔質体中のプラズマ生成

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Generation of plasmas in porous materials with a gas-liquid mixed phase medium has been performed, where the liquid and gaseous medium is conductivity-controlled water and nitrogen gas. In comparison to conventional one-point electrical discharge between two stylus electrodes, this technique enables us to treat large volume liquid medium flowing in a fluid channel. The generation of plasmas in the porous materials has been confirmed by observing optical emission. Application capability of this technique has been demonstrated by performing synthesis of Au nano-particles.

1. Introduction

In contrast to the conventional solution chemistry, the solution plasma processing (SPP), which has been invented by O. Takai and N. Saito [1,2], involves accelerated electrons which contribute to generate active chemical species, such as radicals, ions, UV photons and metastable excited atoms. Such active species are expected to enhance through-put of the solution chemistry and to promote the reactions which do not proceed without catalysts.

In our previous work, we have successfully obtained glow discharges in water, and applied this technique to modify the surface of nano-materials [3]. Since our solution plasma is ignited in a small volume between two stylus electrodes, actual treatment area or volume should be enlarged for practical industrial application. In the case of gas phase processes, large area processing is realized by producing large area plasmas. In the case of SPP, however, large volume plasmas in liquid are meaningless, because the most important region is gas-liquid interface. Thus, preparation of large number of tiny plasmas (microplasmas) is rather important in the case of SPP. This should be named as “integrated micro solution plasma”.

In order to realize the integrated micro-solution plasmas, we have recently utilized interfaces between a plane dielectric plate and porous dielectric material, and successfully obtained large area integrated micro solution plasma [4]. In this work, we report that 3-dimensionally integrated plasmas can be obtained in a porous dielectric material, and demonstrate that Au nano-particles can be synthesized by using this technique.

2. Experimental

Figure 1 shows schematic illustration of the experimental setup for generating 3D integrated micro solution plasmas. The reactor is constructed with the EVAC glass components. The main porous material, in which the plasma is generated, is porous SiO_2 (pumice) containing random pores. Most of the pores are connected topologically, although some of them are isolated. Averaged size of the pores is approximately 0.5 mm (diameter). The second small-size porous material is used for supplying gas (N_2, 2 L/min) from the bottom side of the main porous material. In future, both of the gas and liquid will be fed through the electrode in order to have gas-liquid mixed phase medium efficiently.

A metal electrode, where the high voltage pulse is applied, is inserted in the center axis of the porous material. The grounded electrode is attached on the outer surface of the glass components as shown in Fig.1. The liquid medium employed in this work is water with NaCl (16 mS/m) for observation of plasma. The liquid used for Au

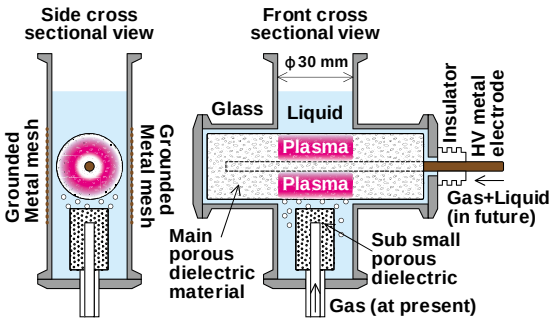

Fig.1 Schematic illustration of the experimental setup for generating 3D integrated micro solution plasmas.

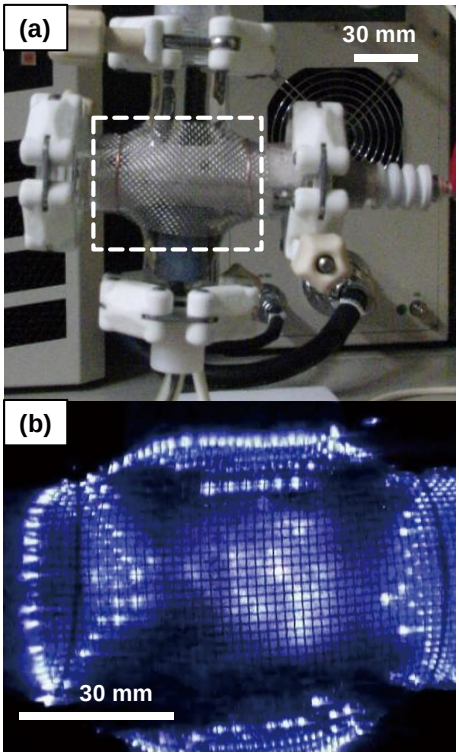

Fig.2 (a) Photograph of the experimental setup without discharge, and (b) observed optical emission from the plasma generated in the porous material.

nano-particle synthesis is 0.15-mM $H(AuCl_4)$-$4H_2O$ (hydrogen tetrachloro- aurate (III) tetrahydrate) aqueous solution (150 uS/cm) with 10 wt.% gelatin. In both cases, voltage is supplied from a bipolar high voltage power source (Haiden, SBP-5K-HF2), from which square-wave pulse voltage with 5-kV amplitude is supplied. Pulse frequency is 20 kHz and pulse width is 20 us.

3. Results and Discussion

Figure 2(a) shows actual experimental setup corresponding to the Fig.1. Figure 2(b) shows optical emission from inside of the porous materials. We can see volume-plasma generation in the porous material, although its size is not distributed uniformly. The parasitic discharges are also observed at the edges of metal mesh, but they can be avoided by utilizing conductive thin films (ITO, for example) evaporated on the outer surface of the glass component. This result indicates that our concept is appropriate for obtaining volume 3D integrated micro solution plasmas.

In order to confirm capability of material processing by using this technique, we have performed Au nano particle synthesis using $H(AuCl_4)$ aqueous solution. Only the liquid material has been replaced form water to the $H(AuCl_4)$ aqueous solution for this experiment.

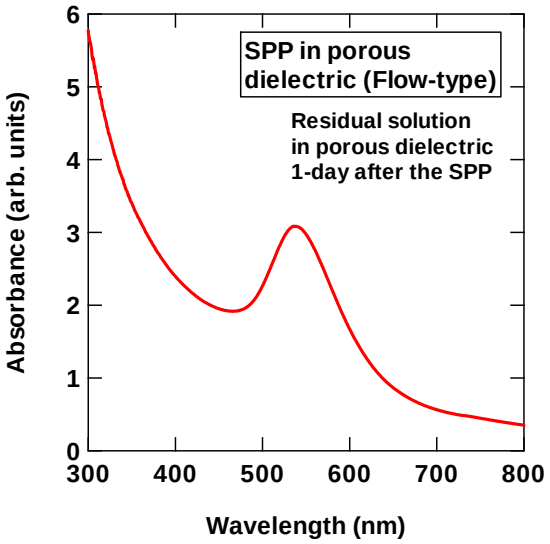

Fig.3 Absorbance spectrum of the residual wine-red colored liquid substance after the 3D integrated micro solution plasma process (10 min.) of the $H(AuCl_4)$ aqueous solution.

Figure 3 shows optical absorbance spectrum of the residual wine-red colored liquid substance in the reactor after 10-min treatment with the 3D integrated micro solution plasmas. We can see a broad absorption peak around the 550 nm, which corresponds to plasmon resonance absorption by Au nano particles [1,2]. This result indicates that our 3D integrated micro solution plasma has capability of Au nano particle synthesis.

Because of the basic concept of this technique, we can expect that this technique can be applied to continuous large volume processing for synthesizing Au nano particles by appropriately designing the process reactor.

Acknowledgments

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