Materials processing by efficient utilization of plasma-liquid interface

T. Shirafuji

Department of Physical Electronics and Informatics, Osaka City University, Osaka, Japan

Abstract: Plasma in contact with liquid can be used for various materials processing such as nanomaterials synthesis and water purification. In most cases, however, direct effects from plasma are localized at plasma/liquid interface and do not reach deep inside the liquid. For efficient utilization of the effects from plasma, two types of schemes are proposed. One is multiple-bubble plasma in which we can expect larger plasma/liquid interface. Another is thin film formation at the interface in which only the interface processes are utilized.

Keywords: plasma, liquid, interface bubble, processing, thin film, nanomaterials

1. Introduction

Researches on plasma in or in contact with liquid have a long history since Michael Faraday examined electrical discharges in various liquids on July 4, 1836 [1]. His major interests were simple physical phenomena such as sparks. At present, we know that plasma in or in contact with liquid involves much more complex physical and chemical phenomena, which can be used for various materials processes. Among them, synthesis or treatment of nanoparticles using plasma in liquid has been extensively studied up to now. However, we should ask ourselves whether we are really utilizing the "only plasma" features.

Figure 1 shows penetration depth of several effects which are available when the liquid surface is in contact with plasma. Although this figure is drawn as plasma on the planar liquid surface, it can be applied also to plasma in liquid and liquid in plasma. As can be understood from this figure, the direct effects provided from plasma do not reach deep inside liquid phase and are localized at the plasma/liquid interface. In the liquid phase far from the plasma/liquid interface, reactions proceed their own solution chemistries although the very first triggering reactions are provided by plasma at the interface.

To utilize direct effects of plasma more efficiently, we should design the process which preferentially use interface reactions. We have proposed two types of schemes for this purpose as described below.

2. Multiple-bubble plasma

Conventional plasma in liquid mostly use the scheme shown in Fig. 2(a), in which small plasma in a bubble is surrounded by large volume liquid. In this system, only the limited part of liquid near the bubble is treated by the plasma. A favourable scheme should be multi-bubble plasma as shown in Fig. 2(b), in which much more plasma/liquid interface are formed. However, it is known that discharge ignition in floating bubble shown in Fig. 2(c) is very difficult owing to less primary electrons from liquid surface.

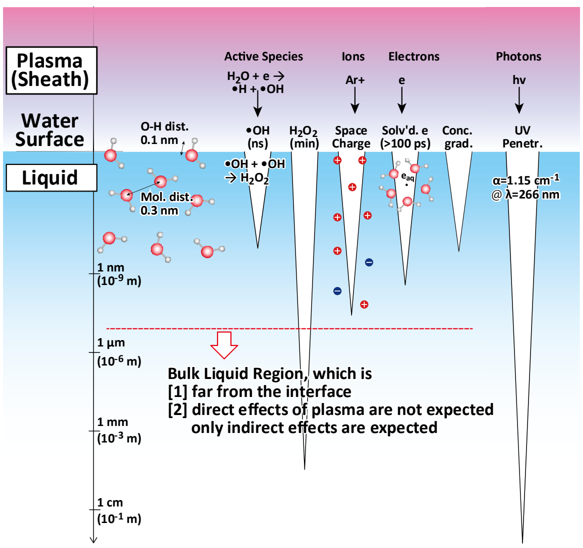

Fig. 1 Schematic illustration of a water interface together with indication of the penetration depth of direct effects provided by plasma.

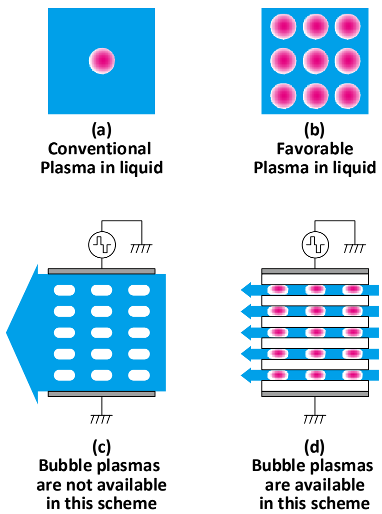

Fig. 2 (a) Conventional plasma in liquid, (b) Favourable plasma in liquid, (c) Simple idea which does not work, (d) practical approach for realizing (c).

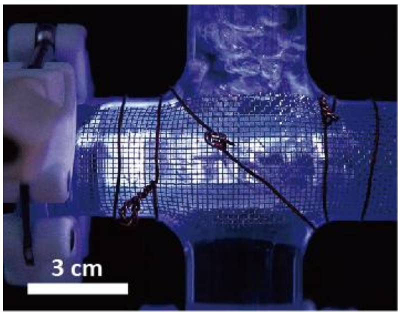

Fig. 3 Overview of a 3D integrated micro solution plasma reactor constructed on the basis of concept (d) in Fig. 2.

For overcoming this difficulty, we have proposed to use porous dielectric material, in which gas bubbles and liquid flow all together as shown in Fig. 2(d). In this case, bubbles are partially in contact with solid surface which supply primary electrons. Fig. 3 shows an image of the discharge obtained on the basis of this concept. The reactor shown in this figure have shown 16-fold efficiency in methylene-blue decomposition in comparison to the conventional reactor based on the concept of Fig. 2(a). Details are described in our previous reports [2].

3. Thin film formation at the interface

Plasma has been utilized for fabricating various functional thin films using plasma-enhanced chemical vapor deposition or plasma polymerization. Most of the thin films are fabricated on solid substrates from gas-phase species. Recently, plasma in contact with liquid has been intended for various applications including nanomaterials synthesis. However, there are no reports on the formation of functional films (or membranes) to the best of my knowledge.

Although Gubkin had already fabricated thin films of Ag, Pt, and ZnO at a plasma/liquid interface in 1887 [3], these films were formed through simple reduction or oxidation reactions at a plasma/liquid interface. Recently, the author has fabricated free-standing thin films composed of cross-linked gelatine with embedded gold nanoparticles (GNPs) at a plasma/liquid interface [4]. Formation of a free-standing functional film (or membrane) has a great benefit when we use the film as it is, because we do not need to peel the film off the substrate.

The experimental setup for this work was very simple. The plasma in contact with the aqueous solution was generated by dielectric barrier discharge (DBD) of Ar gas in a gas gap between the surface of the aqueous solution and the top dielectric electrode. The initial aqueous solution to be exposed to plasma was held on the bottom glass plate and was prepared from aqueous solutions of 75 mL of 0.3 mM HAuCl4 and 2 mL of 10 wt % gelatine. Details are described in elsewhere [4].

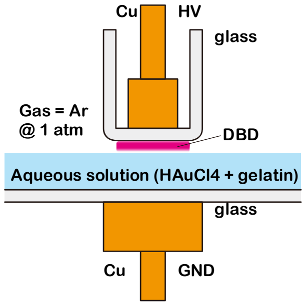

Fig. 4 Schematic illustration of the experimental setup for thin film formation on liquid surface.

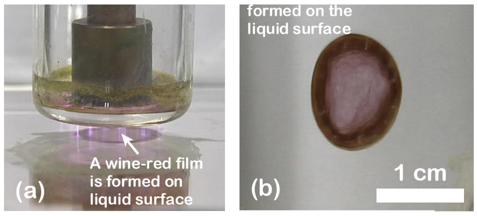

Fig. 5 DBD on aqueous solution of $HAuCl_4$ and gelatine can create free-standing thin film composed of GNP and cross-linked gelatine.

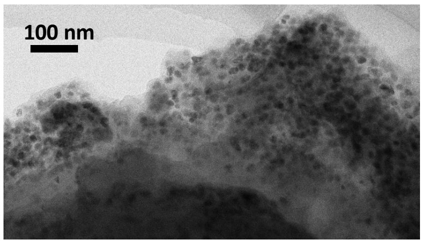

Fig. 6 TEM bright field image of the GNP-embedded cross-linked gelatine thin film.

Fig. 5(a) and 5(b) show snap shots of thin film formation at a plasma/liquid interface during and after discharge, respectively. A wine-red thin film is formed on the liquid surface in contact with plasma. Detailed analysis of the film has revealed that it is composed of cross-linked gelatine and embedded GNPs. The left-over liquid kept its transparency, which means that all the plasma assisted processes are confined at the localized plasma/liquid interface. If we change the composition of the film and nanoparticles, we can explore various possibilities to prepare functional free-standing thin films.

References

[1] M. Faraday, Faraday's Diary. Vol. III (HR Direct, Riverton, UT, 2008) p.54.
[2] T. Shirafuji, A. Nomura, and Y. Himeno, Plasma Chem. Plasma Process. **34**, 523-534 (2014).
[3] J. Gubkin : Ann. Phys. **268**, 114 (1887).
[4] T. Shirafuji, Y. Nakamura, S. Azuma, N. Sotoda, and T. Isshiki, Jpn. J. Appl. Phys. **57**, 0102BE (2018).