Solution plasma processing (SPP)*

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Abstract: Liquid-phase plasma is not well known, although it has been used sparingly in water treatments and electrical discharge machining. We have named the liquid-phase plasma "solution plasma" and developed solution plasma processing (SPP). This paper reports the applications of SPP to syntheses of nanoparticles, surface modification of metals, and sterilization of water.

Keywords: solution plasma; nanoparticles; surface modification; sterilization.

INTRODUCTION

Gas-phase plasma is used widely in many industrial fields, such as electronic device manufacturing processes (plasma etching, sputtering, plasma-enhanced chemical vapor deposition, etc.), hard coating processes (ion plating, sputtering, etc.), and surface treatment processes (low- or atmospheric-pressure plasma treatments, sputtering, plasma etching, etc.). Solid-phase plasma has been used for surface plasmon resonance (SPR) spectroscopy, nanoparticles, etc., and plasmonics is developing as a new research field.

On the other hand, liquid-phase plasma is not well known, although it has been used sparingly in water treatment [1] and electrical discharge machining [2]. The fundamental properties of liquid-phase plasma have not been determined, including its generation techniques, its state, and activated chemical species in it. However, it would be reasonable to expect a higher reaction rate under lower-temperature conditions with greater chemical reaction variability, since the molecular density of the liquid phase is much higher than that of the gas phase.

Figure 1 shows three categories of plasma corresponding to the pressure–temperature relationship of three phases. This figure summarizes the present status of plasma research.

We have named the liquid-phase plasma "solution plasma" because we can generate a variety of plasmas by choosing the combinations of solvents and solutes in solutions. We are currently developing solution plasma processing (SPP). We can use aqueous and nonaqueous solutions, liquid nitrogen, supercritical fluids, etc. for SPP.

This paper reports the applications of SPP to nanoparticle synthesis, surface modification of metals, and sterilization of water.
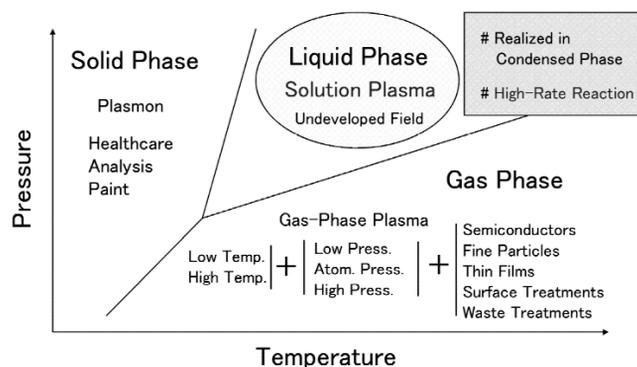

Fig. 1 Three categories of plasma corresponding to the pressure–temperature relationship of three phases.

SOLUTION PLASMA PROCESSING

The study of the solution plasma is less advanced than that of the low-pressure plasma. Figure 2 summarizes the chronological development of both the low-pressure and solution plasmas. SPP has several advantages over low-pressure plasma processing (LPPP). Studies of solution plasma and SPP should therefore be expedited, since it is expected that technological advances will result in the development of numerous industrial applications, and will complement parallel developments in LPPP.
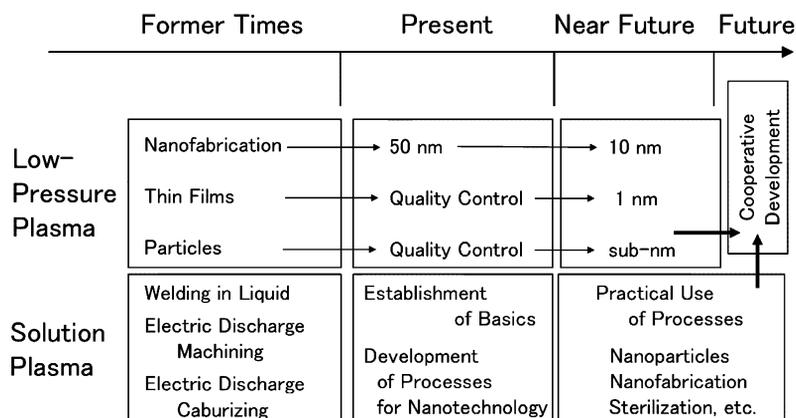

Fig. 2 Chronological development of both low-pressure and solution plasmas.

The detailed structure of the solution plasma is unclear at present. A model of the solution plasma is shown in Fig. 3. The plasma is located at the center and surrounded by a gas phase, which is surrounded by a liquid phase. There are two interfaces: plasma/gas and gas/liquid. Since the solution plasma is confined by its condensed state, it displays unique properties and can promote fast reactions. These properties and novel reaction kinetics offer a scope for basic studies on the solution plasma, from the viewpoints of both physics and chemistry.

The solution plasma has many potential application fields such as nanomaterial synthesis, surface modifications, water treatment, sterilization, recycling of rare metals, and decomposition of toxic compounds.

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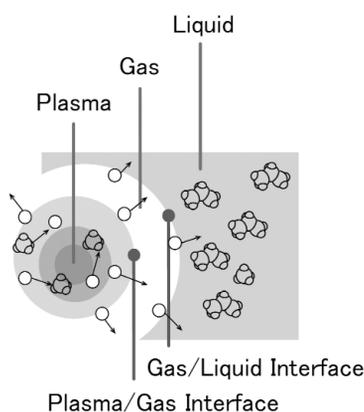
Fig. 3 Model of the solution plasma.

NANOPARTICLE SYNTHESIS BY SOLUTION PLASMA PROCESSING

Few studies have been reported on materials processing in the solution plasma although this reaction field is promising. Recently, the synthesis of carbon nanotubes in the solution plasma has been the subject of vigorous investigation [3–7]. Nomura et al. demonstrated the synthesis of carbon-related materials with a microwave-generated plasma in a hydrocarbon liquid under evacuation [6]. The evacuation prevents the oxidation of products such as graphite, silicon carbide, diamond-like carbon, and carbon nanotubes. The most attractive feature of this process is that the liquid phase plays an important role as a plasma reactor. However, this method is limited to nonpolar solvents such as hydrocarbons, because polar solvents adsorb microwaves and prevent plasma formation.

We synthesized nanocolloidal particles by a spark discharge in aqueous and nonaqueous solutions under an open environment, and determined the fundamental characteristics of the synthesized nanocolloidal particles. The experimental set-up of the discharge system is shown in Fig. 4, and the photograph of one type of solution plasma is shown in Fig. 5. Two metal wire electrodes were placed in an acrylate vessel. A bipolar direct current (DC) pulsed power supply was used to generate the spark discharge in the solutions.
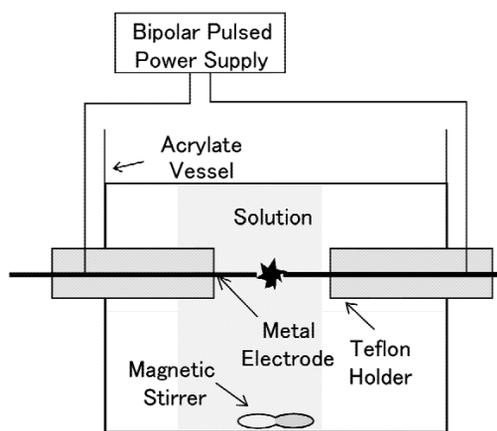
Fig. 4 Experimental set-up of the discharge system.
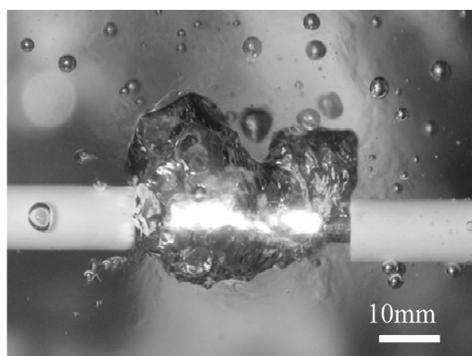
**Fig. 5** Photograph of one type of solution plasma.

For the synthesis of colloidal gold nanoparticles, the aqueous and nonaqueous solutions of $HAuCl_4$ were used. We varied the concentration of solutions and additives for the solutions, and electrode distances and electric conditions for the generation of plasma.

First, we determined the physical and chemical properties of the solution plasma, such as I–V characteristic and plasma density. Second, we synthesized various types of gold nanoparticles with high production rates by varying the preparation conditions.

The typical preparation conditions used were as follows: electrolyte, aqueous $HAuCl_4$ solution; additives, KCl and gelatin; electrode material, tungsten; interelectrode gap, 0.3 mm; reaction volume, 150 mL; voltage, 2.5 kV; and pulse width, 2 μs. KCl was used for adjusting the electric conductivity of solutions, and gelatin was used to avoid aggregation of particles.

The color of the solution containing colloidal gold nanoparticles varied with discharge time. The color was light yellow initially and changed to dark red with increasing discharge time. This color change is due to the plasmon absorption of gold nanoparticles.

The typical shape of the nanoparticles was spherical. Figure 6 shows a transmission electron microscopy (TEM) image of the nanoparticles, and Fig. 7 shows the size distribution of the nanoparticles measured from the TEM image obtained at the aqueous $HAuCl_4$ solution concentration of 0.60 mM. The average diameter was 10.5 ± 3.6 nm. This average diameter varied with preparation conditions. The result of the energy-dispersive X-ray (EDX) analysis indicated that the nanoparticles were composed of gold. The IR adsorption spectra revealed that the height of the gold-plasmon peak at 540 nm increased with the discharge time. This also confirmed the synthesis of gold nanoparticles by SPP.
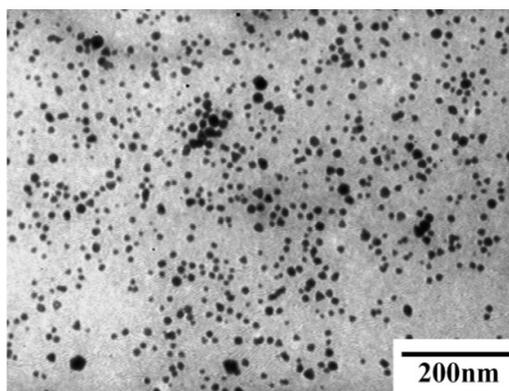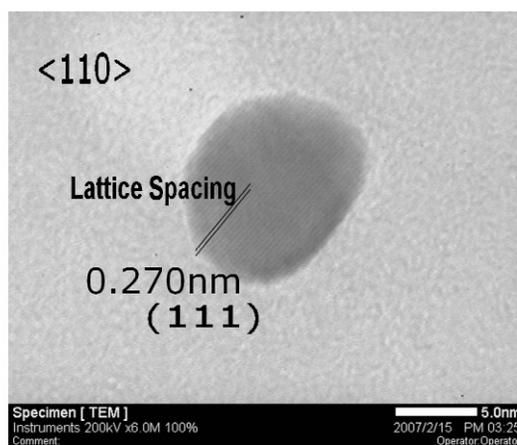

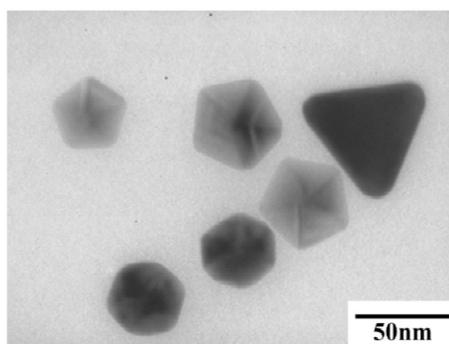**Fig. 6** TEM image of gold nanoparticles synthesized in a 0.60 mM $HAuCl_4$ aqueous solution by SPP.
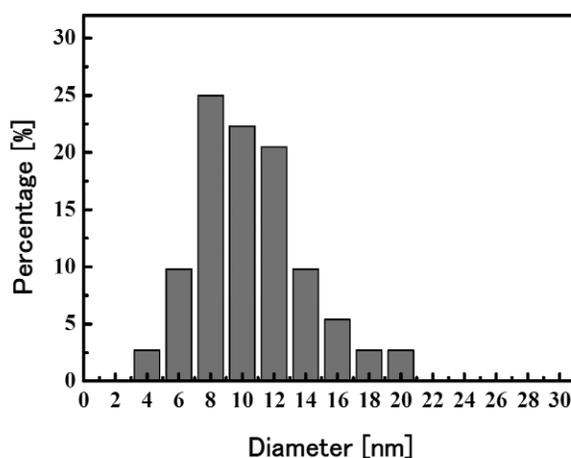
Fig. 7 Size distribution of gold nanoparticles synthesized in a 0.60 mM HAuCl$_4$ aqueous solution by SPP.

Figure 8 shows a high-resolution (HR) TEM image of a gold nanoparticle. The lattice spacing is 0.270 nm for the (111) plane, which is slightly larger than that of bulk gold.

Fig. 8 Spherical gold nanoparticle synthesized by SPP.

The synthesis of topological gold nanoparticles is possible via the aqueous solution plasma, as shown in Fig. 9. In this figure, we can see trigonal, pentagonal, and hexagonal gold nanoparticles. The formation mechanism of the exotic nanoparticles is under investigation. SPP is a very promising technique for the formation of gold nanoparticles of different shapes. Therefore, it can be used to synthesize novel nanoparticles.

Fig. 9 Polygonal gold nanoparticles synthesized by SPP.

SURFACE MODIFICATION OF METALS BY SOLUTION PLASMA PROCESSING

Surface modifications such as oxidation, nitriding, and carburizing have been investigated mainly with the gas-phase plasma. Recently, SPP has been used for surface modification of metals [8–10]. Thick oxide films were grown rapidly on aluminum, titanium, and magnesium.

We studied the electrical properties of solution plasma modification of titanium and aluminum substrates using the I–V characteristics and evaluated the properties of the modified surfaces [10].

The experimental set-up for surface modification was similar to the system shown in Fig. 4, which consisted of an electrolytic cell with a magnetic stirrer and a high-power unipolar pulsed DC voltage source with a frequency of 60 Hz. The temperature of the electrolyte was maintained at 20 °C with an immersed coiled stainless steel tube connected to a thermostatted bath using a recirculation pump.

An aluminum or a titanium plate with 0.8 cm^2 area was used as an anode, and a stainless steel plate with a much larger area (40 cm^2) was used as a cathode. Sodium hydroxide and trisodium phosphate with different concentrations in deionized water were used as electrolytes. The pH of solutions was maintained between 8 and 12.

Current–voltage characteristics revealed three regions of the modification process, as shown in Fig. 10, for aluminum as the substrate and 2 g/L NaOH in deionized water as the electrolyte. Figure 10 also shows images of the sample surfaces at various discharge states. For low input voltages, between 0 and 150 V, the current intensity was low, and only oxygen evolution at the anode and hydrogen evolution at the cathode surfaces were observed (region I with a slope of 0.5 mA/V). When the applied voltage was increased, the current intensity increased rapidly (region II with a high slope of 7.5 mA/V) and the quantity of evolved gases increased. When the applied voltage exceeded a threshold value of 175 V, microarcs began to develop on the surface of the anode. The threshold voltage value was dependent on the electrolyte concentration. This process was accompanied by visible light emission and a high-frequency noise. The microarc discharges were short-lived and moved randomly on the modified surface. After the entire anode surface was covered with microarcs (end of region II, at 200 V), when the applied voltage was increased further, the slope changed to a lower value (region III with a slope of 2.7 mA/V), and the intensity of light and sound emitted by arcs developed on the modified surface increased.

The growth rates of aluminum and titanium oxide films increased with discharge current densities. A high growth rate of 1.7 μm/min was obtained for both substrates. The aluminum oxide film consisted of two layers, as revealed by SEM observation of the cross-section of an aluminum substrate after modification. The external layer had low strength and high porosity, and could be removed easily. The internal layer was hard and adhered well to the substrate, because locally developed transient high temperature melted the growing oxide layer on the substrate and improved the adherence.
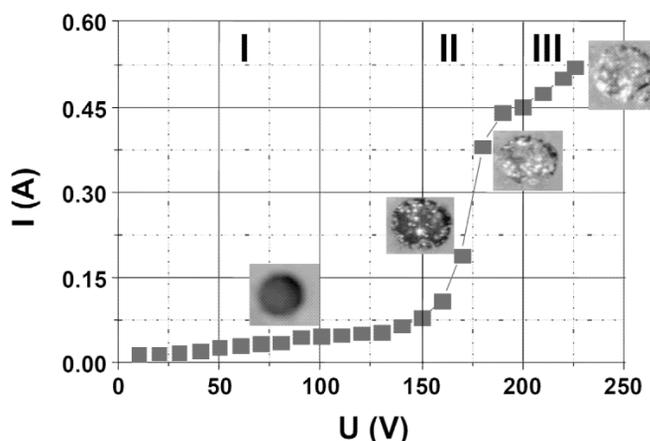
Fig. 10 Current–voltage characteristics for surface modification of aluminum by SPP.

Nanoindentation measurements revealed also this layered structure by two slopes of force–displacement curves. The hardness of the external loose layer was ~6 GPa, whereas that of the internal dense layer was ~33 GPa. The harder aluminum oxide film was formed near the substrate by SPP. Therefore, as an alternative to conventional anodization, SPP is a promising method for the formation of thick oxide films on metal substrates with high growth rates.

STERILIZATION OF WATER BY SOLUTION PLASMA PROCESSING

Chlorine, ozone, and UV light are currently the most commonly used agents for sterilization of water. However, methods using these agents have problems regarding the safety of humans, efficiency, and cost. Therefore, an advanced sterilization method with high safety and high performance is required. We evaluated the use of SPP for sterilization of water.

The survival rates of bacteria were examined with and without solution plasma. The experimental set-up used was similar to that shown in Fig. 4. The voltage used was 800 V, and the pulse on/off time was 40 s. Four electrolytes, KCl, NaCl, Na_2SO_4, and CH_3COONa, were used. Na_2SO_4 and CH_3COONa solutions were found to be effective for solution plasma sterilization because KCl and NaCl solutions produced ClO^- ions, which killed bacteria without the solution plasma. For the Na_2SO_4 and CH_3COONa solutions, bacteria were killed only with the solution plasma.

Two types of bacteria were used: *E. coli* uc4100 (a representative gram-negative bacterium) and staphylococcus aureus (a representative gram-positive bacterium). If we will find the effect on these two bacteria, we will get the similar effect on other bacteria. We varied the concentration of bacteria in electrolytes and discharge time. The experimental result is shown in Fig. 11 for *E. coli*. A similar result was also obtained for *Staphylococcus aureus*. After a 20 s discharge, almost all bacteria were killed and after a 30 s discharge, all bacteria were killed. The numbers of both bacteria decreased quickly with increasing discharge time. Therefore, SPP is very effective in killing bacteria in water.
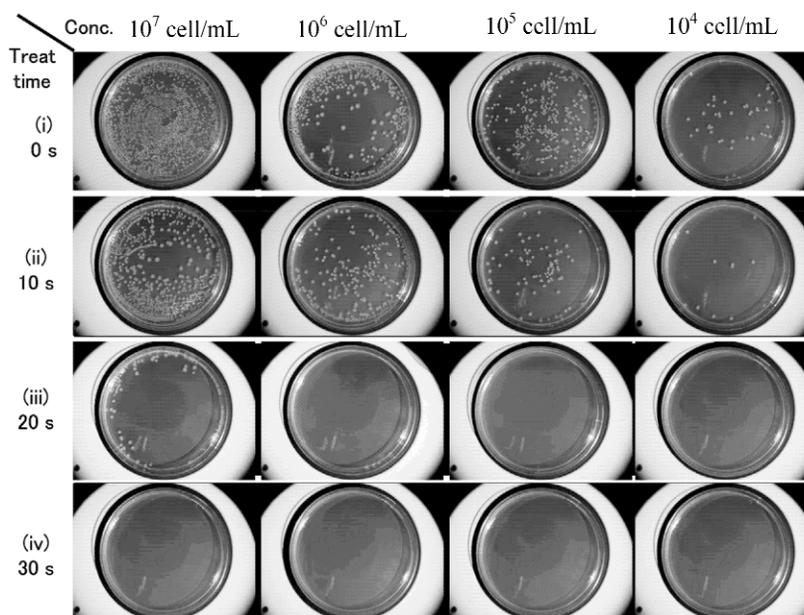
Fig. 11 Culture of *E. coli* after the solution plasma treatment. The concentration of *E. coli* and discharge time were varied.

CONCLUSION

Basic study on the solution plasma from the viewpoints of fundamental physics, chemistry, and application-oriented engineering is initiated. This will contribute a great deal to the development of new plasma fields for SPP. SPP is promising in industrial applications.

ACKNOWLEDGMENTS

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