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Fundamentals and Applications of Solution Plasma

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Liquid-phase plasma is not well known compared with gas-phase plasma. We name the liquid-phase plasma "solution plasma" because of the generation of different plasmas by choosing the combinations of solvents and solutes in solutions. We can generate a glow discharge with a pulsed power generator by controlling several parameters for the ignition of the discharge. It is important to generate the glow discharge in solutions, which realizes the formation of a new reaction field at almost room temperature. We measured the basic physical and chemical properties of solution plasma by time-resolved optical spectroscopy and coherent ant-Stokes Raman spectroscopy (CARS). The solution plasma is applicable to nanomaterials synthesis, surface modifications, water treatment, sterilization, decomposition of cellulose and toxic compounds, and so far.
Keywords: solution plasma, liquid-phase plasma, nanomaterial syntheses, reaction field

1. Introduction

Gas-phase plasma is used widely in many industrial fields, such as electronic device manufacturing processes, hard coating processes, and surface treatment processes. 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 and electrical discharge machining. 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. Therefore the development of studies on the liquid-phase plasma is very important from the viewpoints of a scientist and an engineer.

Then we have named the liquid-phase plasma "solution plasma (SP)" because we can generate a variety of plasmas by choosing the combination of solvents and solutes in solutions. We can generate a glow discharge, a corona discharge and an arc discharge with a pulsed power generator by varying the several parameters related to the ignition of a discharge.

Especially it is important to generate the glow discharge in solutions, which realizes the formation of a new reaction field for material development at almost room temperature. We can make "cold plasma" in "cold solutions". Hence we use the name "solution plasma" as the glow discharge in solutions in this paper.

The objective of this paper is to report on the fundamentals and applications of solution plasma.

2. Model and Features of Solution Plasma (SP)

A model of the solution plasma is shown in Fig. 1. The plasma is located in the center and surrounded by gas phase which surrounded by liquid phase. There are two interfaces, plasma/gas interface and gas/liquid interface. The plasma is confined by a condensed phase, which produces unique features of the SP and realizes fast reaction. We need basic studies on the properties of SP and the novel reaction kinetics. We are studying the

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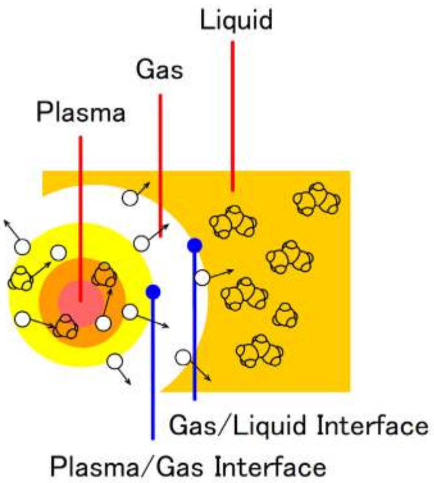

Fig. 1 A model of solution plasma.

detailed structure of the SP now. Thus, the solution plasma is interesting from the viewpoints of both physics and chemistry.

Solution plasma has advantages as a reaction field over conventional chemical reaction, reaction with arc discharge in liquid and plasma electrolysis as show in Fig. 2. And solution plasma chemistry is located at the interdisciplinary area among solution chemistry, electrochemistry and plasma chemistry as show in Fig. 3. Therefore solution plasma chemistry breaks ground for new plasma chemistry.

3. Generation of Solution Plasma

We have developed many types of the generation systems of solution plasma. There are

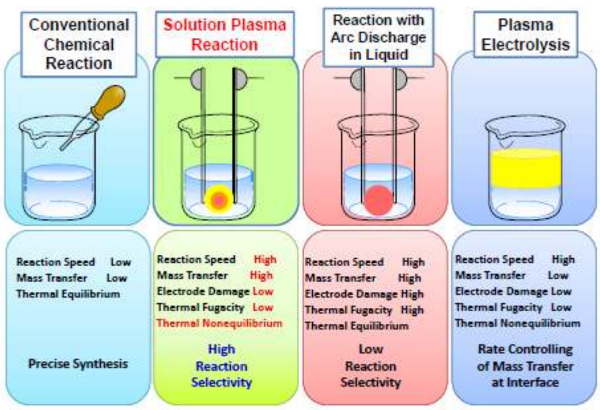

Fig. 2 Advantage of solution plasma as reaction field.

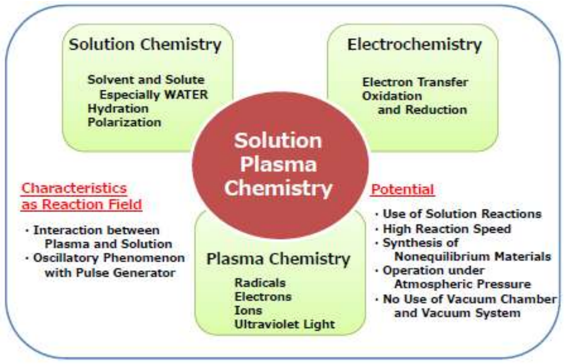

Fig. 3 Interdisciplinary nature of solution plasma chemistry.

many factors related to its generation such as pulsed power supplies (pulse width, frequency,waveform, stability, etc.), electrodes (material, shape, size, interelectrode distance, etc.), properties of solutions (solvent, solute, concentration, electric conductivity,temperature, etc.) and so on. A typical experimental settup using two wire-type electrodes of tungsten is shown in Fig. 4. At the shorter interelectrode distance such as 1 mm the continuous discharge was formed, but the longer distance such as 5 mm the two separated discharges at the electrodes were formed. The regions of three types of discharges are shown in Fig. 5. The property of plasma at each region is different, which is imporetant sonce we can modify the property of plasma by varying the interelectrode distance.

The window for the glow discharge in liquid is narrow compared to the discharge in gas as shown in Fig. 6. This is a reason why the formation of glow discharge in liquid was difficult. By using a

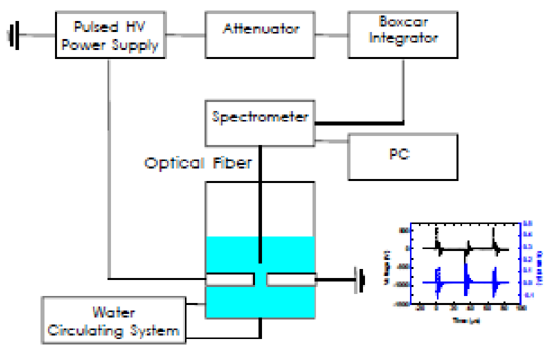

Fig. 4 Experimental setup for solution plasma.

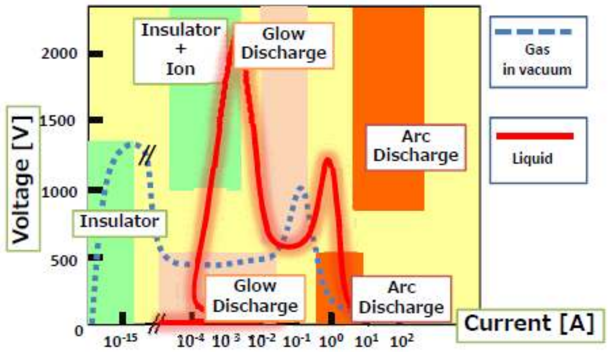

Fig. 5 Regions for three types of discharges.

newly developed power supply we can generate glow discharge in liquid, namely we can form cold plasma in cold water.

4. Physics of Solution Plasma

The time-resolved optical spectroscopy shown in Fig. 7 is used for the measurement of physical properties of plasma. The typical electron temperature is 7000-8000 K and electron density is 10^{6} cm^{-3}.

During one pulse (2 μs) the oscillation of emission was observed, and its cycle length was 100 ns and its frequency was 10 MHz. A very high frequency phenomenon is occurred and its elucidation is important. This oscillatory phenomenon relates to the formation mechanism of solution plasma and the possibility of shock wave or ultrasonic wave.

There are two important effects related to solution plasma; “cage effect” and “trapping effect”.

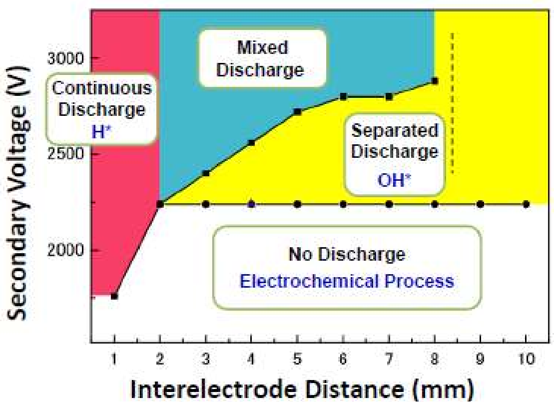

Fig. 6 Voltage-current curves for discharges.

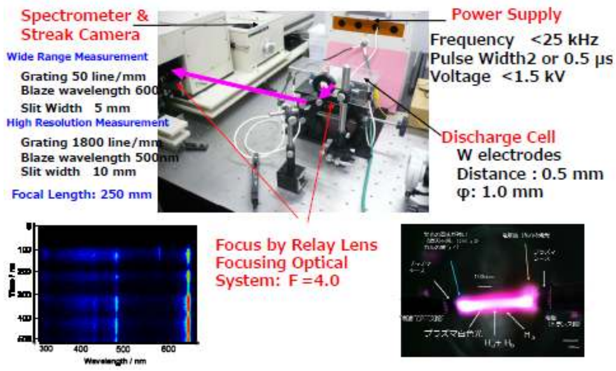

Fig. 7 Time-resolved optical spectroscopy at Yui Laboratory, Tokyo Univesity of Science.

Radicals formed by a discharge are surrounded by solvent molecules and easily quenched by the molecules, and the production of gas molecules is occurred by recombination. The gas molecules form bubbles. This is “cage effect”. Next radicals and ions in bubbles make solvation with solvent molecules after collision and deactivation with strong emission. This makes quenching of plasma. This is “trapping effect”. These two effects relate to the formation process of plasma.

5. Chemistry of Solution Plasma

The coherent anti-Stokes Raman spectroscopy (CARS) show in Fig. 8 is used for the measurement of chemical properties of plasma. One measuring result used p-benzoquinone is shown in Fig. 9. The resonance structure of p-benzo-quinon

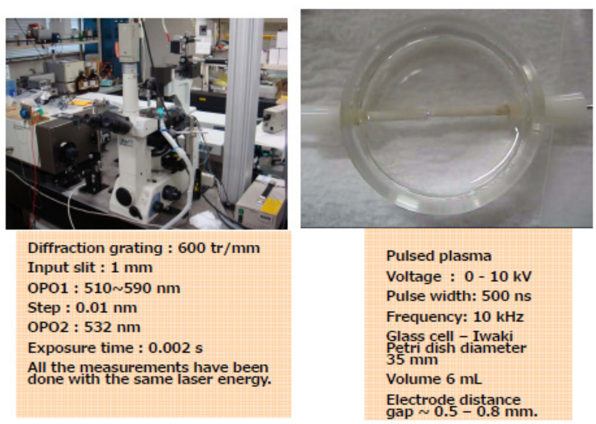

Fig. 8 Coherent anti-Stokes Raman spectroscopy (CARS).

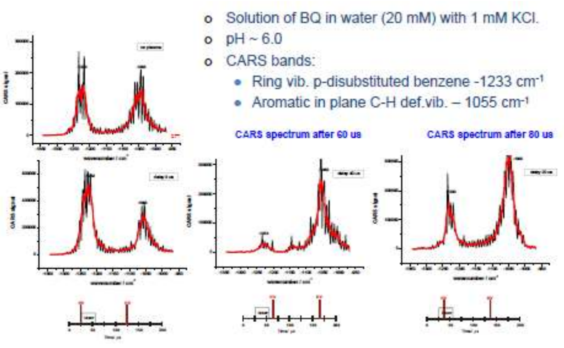

Fig. 9 CARS spectra for p-benzoquinone solution with incresing discharge time.

molecure is found during discharge and electrons are delocalized. By CARS the solvent information surrounded by plasma is obtained. CARS is effective to analyze the chemical properties of solution plasma.

6. Applications of Solution Plasma

Solution plasma has a much broader range of applications and we are developing solution plasma processing (SPP). We can use aqueous and nonaqueous solutions, liquid nitrogen, supercritical fluids, etc. for solution plasma processing 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 as shown in Fig. 10. Some results of materials processing by using solution plasma are shown in Fig. 11.

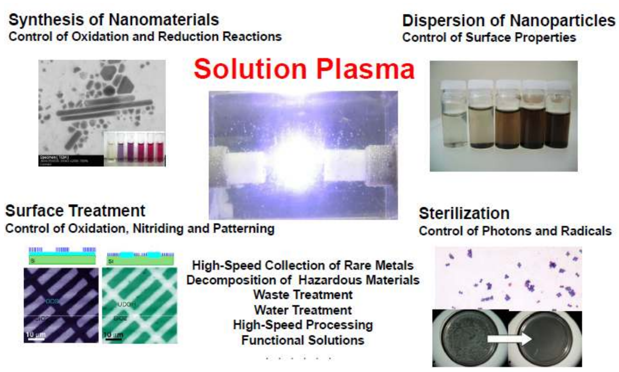

Fig. 10 Solution plasma processing for new technology.

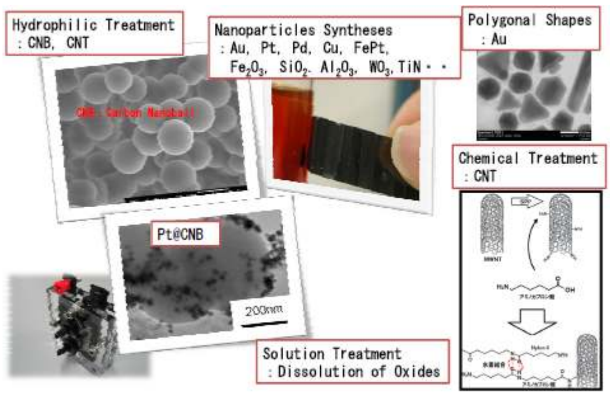

Fig. 11 Materials processing by solution plasma.

Nanoparticles of metal and alloys, oxides, and nitrides are synthesized in aqueous and nonaqueous solutions. The reduction of metal ions by hydrogen radicals is mainly occurred in the syntheses of metal nanoparticles. The size of the nanoparticles is 4-15 nm and the size distribution is narrow. The TEM images of gold nanoparticles synthesized are given in Fig. 12, and the formation of multiply twinned particles in solution plasma processing is distinguishing compared to the conventional chemical process. The syntheses of polygonal gold nanoparticles are possible.

The syntheses of nanoclusters less than 2 nm are also possible by solution plasma processing. Fig. 13 shows the TEM image of gold nanoclusters which size is around 1 nm. The mass production of nanoclusters becomes possible by using solution plasma. The nanoclusters show different characte-

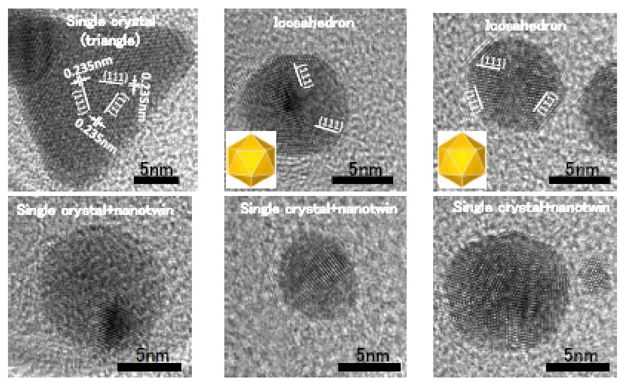

Fig. 12 TEM images of gold nanoparticles by solution plasma.

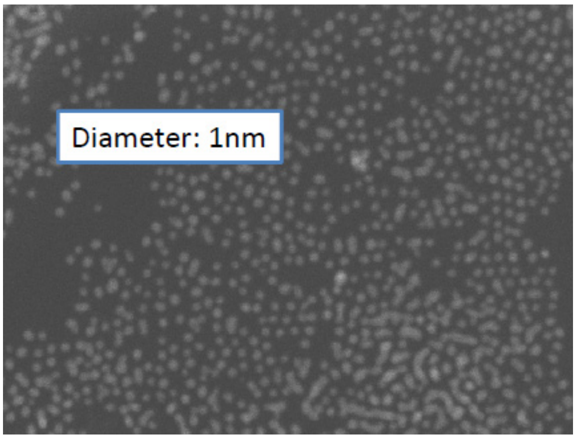

Fig. 13 TEM image of gold nanoclusters by solution plasma.

ristics from nanoparticles and develop new properties.

Solution plasma is effective for the hydrophilic treatment of particles. Carbon nanoballs and carbon nanotubes are easily dispersed in water. The surface modification of these materials is also possible. By using this technique we can make high-quality composites. Solution plasma is applicable to composition of cellulose and toxic compounds.

In conclusion solution plasma has wide applications in industries as shown in Fig. 14. We are developing the large vessel system using a number of electrodes, flow-type reactor system, flat electrode system, etc. for the industrial uses. A manufacturing system is shown in Fig. 15.

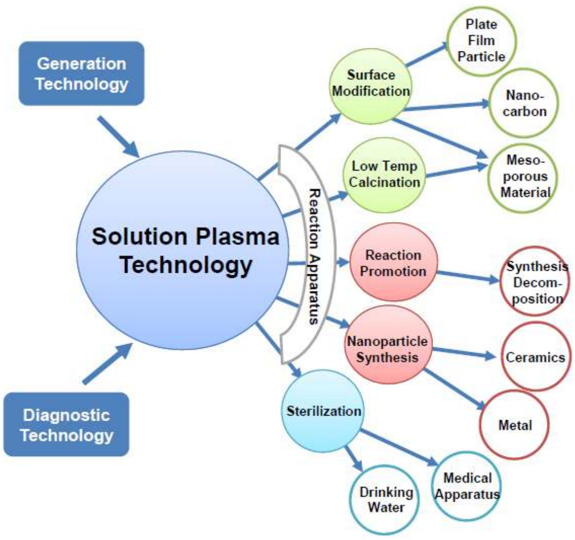

Fig. 14 Development of solution plasma technology.

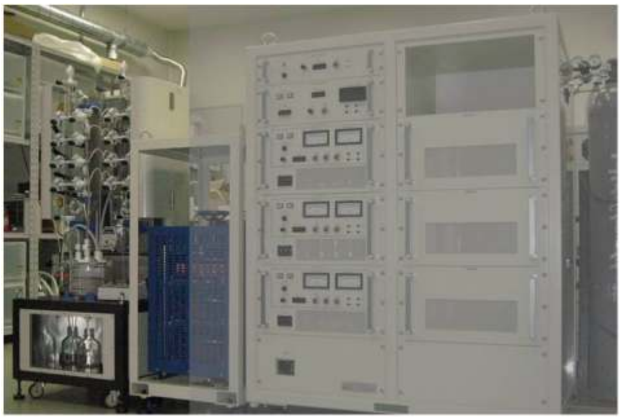

Fig. 15 A flow-type maufacturing system for syntheses of nanoparticles (co-work with Kurita Seisakusho).

7. Summary

Solution plasma is a promising new plasma and has a much broader range of applications. The physics and chemstry of solution plasma are developing now, but basic properties of solution plasma are unclear. We hope much more developmet of solution plasma and solution plasma processing.

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