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In-liquid plasma: a novel tool in the fabrication of nanomaterials and in the treatment of wastewaters

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Attempts to generate plasma in liquids have been successful and various devices have been proposed. Many reports have described the optimal conditions needed to generate plasma, and mechanisms have been inferred, together with the composition of the plasma. Elucidation of a stable method (and mechanism) to generate plasma in liquids has led to various active investigations into applications of this new energy source. This review article describes the generator and the generation mechanism of in-liquid plasma, and pays attention to the evolving technology. The characteristics of submerged plasma are summarized and examples of nanomaterials syntheses and wastewater treatment are given, both of which have attracted significant attention. Extreme reaction fields can be produced conveniently using electrical power even without the use of chemical substances and high-temperature high-pressure vessels. Chemical reactions can be carried out and environmental remediation processes achieved with high efficiency and operability with the use of in-liquid plasma. Suggestions for introducing in-liquid plasma to chemical processes are discussed.

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1. Introduction

1.1 In-liquid plasma: a novel energy source for chemical reactions

Many chemists think it is strange that as much as or more than 99% of the substances present in the Universe exist as plasma, whereas the typical gas, solid and liquid states of matter tend to be rather rare in that environment. Compared to the vast scale of the Universe, chemists manufacture products in these states



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(gas, solid, liquid) with very limited materials. Human beings have used plasmas (e.g., the sun and fire) as energy sources for millennia. These classical energy sources have been used in early chemical syntheses and chemical analyses, even though they are difficult to control in the manufacturing process. Accordingly, electrically powered heaters and steam have been used in carrying out chemical reactions. More recently, microwave chemistry has developed significantly in the use of microwaves as the energy source.¹ After World War II, the science behind changing substances artificially into plasma and then using this energy source in chemical reactions has been explored actively. However, combinations of plasma and chemical reactions have been limited to solid-phase reactions. Since ordinary plasma mimics a gas, its utilization in the liquid phase has only been possible in irradiating the liquid surface of a sample. Even with strong stirring, the effect of plasma on a liquid sample is not so pronounced. Nonetheless, chemists have considered using plasma as the energy source to activate chemical reactions, even though its use is difficult from the productivity viewpoint.

Recent years have also witnessed the successful generation of stable plasma in solution (referred to as in-liquid plasma); its application in various fields is currently being investigated. Use of in-liquid plasma has attracted significant attention as being a hot research topic. The state of new substances generated in liquids is expected to be a new tool in solution chemistry fostered by a combination of innovative ideas and the promise of novel materials synthesis. For instance, in-liquid plasma could be applied to fuel (hydrogen) recovery from a methane hydrate layer existing in Japanese waters; the method used is detailed in Fig. 1.² It involves irradiating a methane hydrate layer with in-liquid plasma to achieve dehydrogenation reaction

and recover hydrogen energy from bubbles deep in oceanic waters. In the existing method, the methane hydrate is recovered using a pump; however, it is possible to recover the required amount of hydrogen from the seabed without the use of pumps. Depending on conditions, in-liquid plasma can drive various chemical processes.

1.2 Plasma

Although plasma is an emerging technology in many fields of application, the history of plasma technology goes as far back as the 18th century. Georg Christoph Lichtenberg (1742–1799), a professor of mathematics in Göttingen (Germany), produced brush discharges by spreading fern spores between two electrodes.³

Michael Faraday (1791–1867), discoverer of electromagnetism in 1821, was the first to provide an explanation for Lichtenberg's observations. His countryman, Sir William Crookes (1832–1919), later discovered the fourth state of matter as radiating matter in discharge tubes,⁴ which he correctly assumed to consist of electrically charged gas molecules in the tubes: *de facto*, plasma was born. He later defined it in his lecture titled "On Radiant Matter" delivered before the British Association for the Advancement of Science, on 22 August 1879 at Sheffield (D. Appleton, The Popular Science Monthly, 1880, Volume 16, pp 157–167). Crookes discovery was followed nearly two decades later (1897) by Sir Joseph John Thomson's (1856–1940) postulation that atoms consist of positively charged electrons that possess a mass.⁵ This was also confirmed by the German chemist Eugen Goldstein, who discovered that the so-called canal rays consisted of positively charged particles with missing electrons (H^+ ions from hydrogen gas). Thus, plasma had been identified as a mixture of electrons and ions. The term plasma was finally defined by the American chemist Irving Langmuir (1881–1957) who in 1923 observed specific oscillations in an ionized gas that he referred to as plasma oscillations generated from an inhomogeneous charge distribution and to the natural tendency of the charge to redistribute uniformly inside the plasma.⁶ The first comprehensive published report on gas discharges was by the German physicist Johannes Stark (Die Elektrizität in Gasen), then Director of the Institute of Physics of the University of Greifswald. Stark was awarded the 1919 Nobel Prize for the discovery of the Doppler Effect in canal rays and for the splitting of the spectral lines in electric fields (the Stark Effect). At the end of 1918, Stark invited Rudolf Seeliger to the University of Greifswald who remained until 1955. Seeliger is one of the pioneers of modern plasma and gas-discharge physics. The fundamental physical properties of plasma were clarified in the first half of the 20th century by Seeliger and others, which led to rapid advances in the engineering applications of plasmas,⁷ as exemplified by the inventions of the mercury discharge lamp (Cooper Hewitt light: 1902), the mercury arc lamp (1905), and the high-pressure mercury lamp (1906) among others.

Coupling theory and technological innovations in plasma applications also advanced noticeably. In the second half of the 20th century, plasmas were used increasingly for a variety of

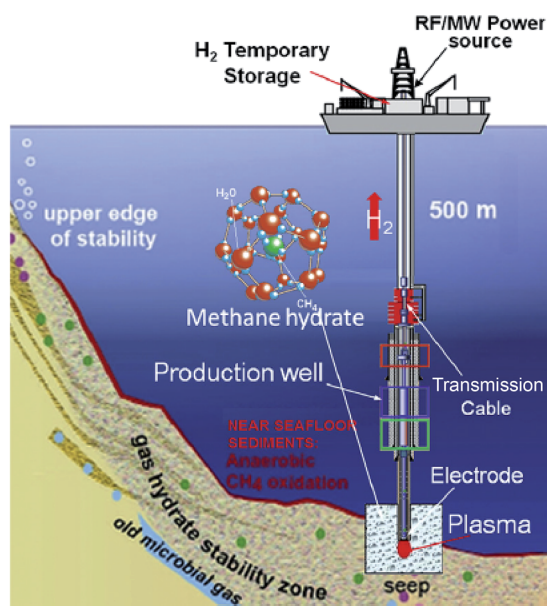


Fig. 1 Process for hydrogen production from hydrate fields in subsea sites using the plasma from the in-liquid method. Reproduced from Rahim and coworkers.² Copyright 2015 by Elsevier.



purposes, such as in neon tubes (vacuum) and in etching processes (hot). Technological progress in the mid-1990s also led plasmas to be generated non-thermally under atmospheric pressure, which opened loads of new possibilities since expensive and complex vacuum systems were no longer needed; processes could now be run continuously without putting stress on materials being treated. As a result, plasma-induced processes could then be applied in, for instance, the medical sector for the gentle sterilization of medical equipment and catheters. In 1996, Laroussi⁸ was one of the first to describe a novel sterilization method that used uniform glow discharge plasma generated at atmospheric pressure. He examined the inactivation of *Pseudomonas fluorescens* bacteria in yeast extract in a polypeptone glucose solution.

Starting with a handful of publications in the mid-1990s, the number of publications that dealt with applications of plasmas increased rapidly at the turn of the 21st century. Indeed, the total number of publications dealing with cold plasma has increased significantly in the past 20 years, attesting to the importance of this emerging technology. As we speak, various engineering application advances are being made. This indispensable technology has developed and currently used extensively in metal welding, in surface treatments, in the processing of materials and electronic components, in the fabrication of nanomaterials, and in wastewater treatment (among others).⁶

Plasma is classified as (i) high-temperature plasma (thermal equilibrium plasma), and (ii) as low-temperature plasma (non-thermal equilibrium plasma). Thermal equilibrium plasma is plasma generated by applying electrical power for a long time under conditions that the gas pressure is 5 kPa or more, and that the electron and gas temperatures are nearly equal. Since the ionization energy of atoms and molecules necessitates several eV or more (tens of thousands of degrees Celsius), some of the electrons and ions become high-energy particles. In general, the materials temperature in thermal equilibrium plasma reaches as much as several thousand degrees Celsius or more; this plasma is casually used as a heat source and light source for welding and lamps. By comparison, the electron temperature is higher than the gas temperature in non-thermal equilibrium plasma. For example, to convert a gas molecule into non-thermal equilibrium plasma, heat transfer to ions and molecules can be restricted by setting gas molecules to a reduced pressure state and by lowering the frequency of collision of electrons with ions or molecules. A characteristic of non-thermal equilibrium plasma is that its gas temperature is low and electrons are in a high-energy state, and as such it is used in the manufacturing of semiconductors and films through chemical reactions. Since non-thermal equilibrium plasma must maintain reduced pressure conditions, facilities such as a vacuum chamber and a vacuum evacuation device are required, even if plasma were generated by a short pulse discharge under atmospheric pressure conditions. This is often referred to as atmospheric pressure non-thermal equilibrium plasma because it has different properties from the plasma in vacuum.

2. In-liquid plasma

2.1 Why plasma can be generated in a liquid (and in a solid)

Since plasma is a state of matter generated by a destabilizing gas, one must ask whether plasma can also form in solids and liquids. Some people are still sceptical about this.

2.1.1 Solid plasma. Regardless of such scepticism, an electron in a metal (solid) contains free electrons that can move around a lattice point; collectively, these are oscillating electrons. When an external electric field is applied to a free electron, it acts as if it were an electron in gas plasma. Although the plasma defined by Langmuir is referred to as gas plasma,⁹ when applied to a solid it can be regarded as a solid plasma even for a solid (metals, semiconductors) that possesses free electrons.¹⁰ The collective oscillation of these free charges (mainly electrons) is known as plasma oscillation; quantizing this oscillation leads to formation of a Plasmon. When metallic nanoparticles are irradiated with specific light, a resonant luminescence appears caused by Plasmon absorption; applications of such nanoparticles in paints, in medical treatment, in measurements, and in microfabrication have been reported.¹¹

2.1.2 In-liquid plasma. For years, some techniques have made use of in-liquid plasma to perform electrical discharge machining, welding, and carburizing (and others) in liquids. Yet, only but a few research studies have taken the trouble to explore and exploit in-liquid plasma, so that its use has been rather limited. The report published by Clements in 1987 (ref. 12) on plasma generation by a high-voltage pulse discharge in water (material changed to a plasma state) was a leading research study of the 1980s. Since then, various studies of the physical elucidation of in-liquid plasma have been carried out from many research quarters, which reported that plasma generated in the liquid phase is a phenomenon greatly different from plasma in the gas phase and suggested the use of in-liquid plasma to wastewater treatment as one of several possible applications. Following these reports, researchers worldwide have optimized in-liquid plasmas with regard to such factors as pressure, temperature, density, viscosity, composition, and conductivity¹³ that have led to an accelerated development of in-liquid plasma generators. In addition to gas-phase plasma used in academia, the bases of plasma in the solid phase and in the liquid phase are now also academically established; systematization of plasma in each state of matter is progressing (Fig. 2). Research into practical applications is also on the increase.

There are two key methods of generating in-liquid plasma. The first key method is an underwater streamer discharge that produces linear plasma in the liquid; the dielectric breakdown of the liquid turns into a type of corona discharge considering the classification of general plasma. During the dielectric breakdown of water, micro-bubbles are formed near the electrode by cavitation produced either by a high electric field or by heating from a conductive current; the plasma is generated in the micro-bubble.¹² To generate an underwater streamer discharge, even in an aqueous solution, an electrical power of 50 to 400 kV and a current of 100 A or more are required. Industrially, it is difficult to achieve and maintain a steady-state



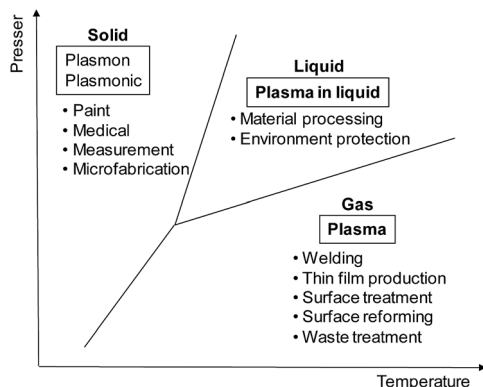


Fig. 2 Relationship between plasma and the three states of matter.

electrical power of this magnitude from the viewpoint of stability and energy saving. Accordingly, many discharges are generated using a pulsed voltage of 1 μs duration or less. An underwater streamer discharge occurs in liquid at a rate of 30 to 100 $\text{mm } \mu\text{s}^{-1}$ while the liquid is being vaporized at the liquid/air interface.^{14,15} The occurrence of an underwater streamer discharge in the liquid phase generates ultraviolet rays, shock waves, and localized heat, together with chemically active species formed by the resulting plasma.¹⁶ The second key method is to generate bubbles by heating, by shock waves, and by gas introduction (or the like) in the liquid to create in-liquid plasma. Since applying electrical power is not always accompanied by a dielectric breakdown of the liquid, in many cases plasma can still be generated with a power of 10 kW or less as a glow discharge, a corona discharge (streamer discharge), and as an arc discharge.

Except for underwater streamer discharge, this review article will restrict its considerations to all in-liquid plasmas as plasma generated in bubbles contained within the liquid.

2.1.3 Chemical composition of plasma generated in a liquid. When plasma is generated in a liquid by ionizing ion-exchanged water, a pale white light is observed (Fig. 3a);¹⁷ the emission spectrum displayed in Fig. 3b is attributed to H_α (at $\lambda = 656 \text{ nm}$) and to H_β (at 486 nm), and to $\cdot\text{OH}$ radicals (at 316 nm). Therefore, the source of plasma is not due to dissolved air in water, but rather to vaporized water that has turned into plasma. Peaks derived from dissolved nitrogen and oxygen gases at $\lambda = 289 \text{ nm}$ (N_β) and $\lambda = 778 \text{ nm}$ (O^*) have also been detected as sharp luminescence.¹⁸

2.2 Methods to generate in-liquid plasma

Fig. 4a shows near surface interactions with plasmas generated outside the liquid.¹⁹ From the cocktail of plasma, such species as radicals, ions, electrons and photons are thought to interact, to differing degrees, with the liquid interface, thereby initiating reactions that cascade well into the liquid phase, possibly *via* biochemical pathways (Fig. 4a). Radicals, ions and photons are often considered, but in attempts to isolate important sources of reactions within liquids, it is also necessary to consider electron interactions directly with the liquid phase (Fig. 4b and

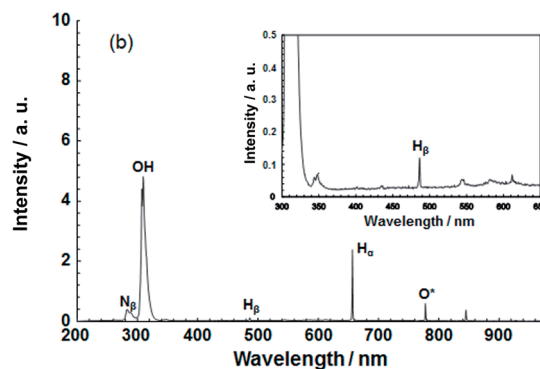
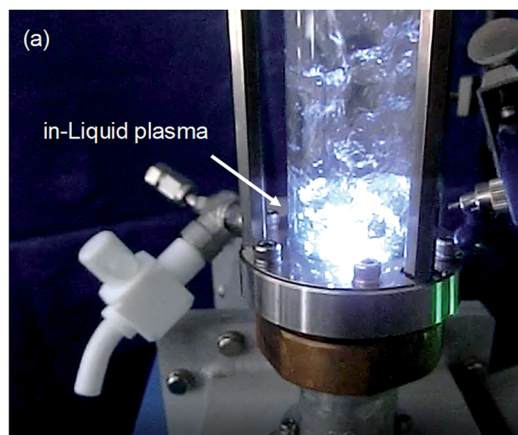


Fig. 3 (a) Photograph illustrating the generation of plasma in liquid using a microwave power supply; (b) spectrum of ultraviolet and visible light emitted by in-liquid plasma generated in ion-exchanged water. Taken from ref. 17. Copyright 2017 by S. Horikoshi.

c); to date, these have received little attention. Accordingly, the focus of this paper will be restricted to phenomena occurring under plasma conditions as illustrated in Fig. 4b and c.

Currently, methods to generate in-liquid plasma can be broadly divided into four categories, and since each possesses

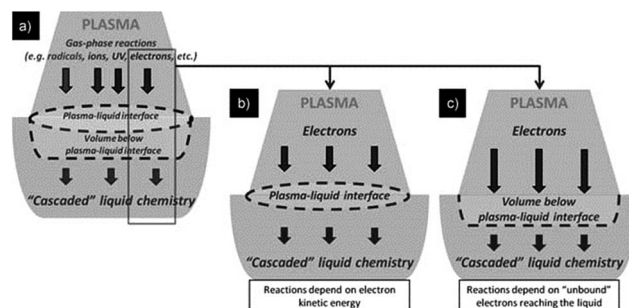


Fig. 4 Schematic diagram of three different types of plasma in-liquid conditions (PiLC): (a) gas-phase species and plasma-radiation-induced liquid reactions at the plasma-liquid interface; (b) and (c) electrons from the plasma can initiate non-equilibrium reactions in the liquid phase where both electron energy distribution (b) and electron density play an important and distinct role (c). Reproduced from Mariotti *et al.*¹⁹ Copyright 2012 by WILEY-VCH.



its own characteristics, it is necessary to select the appropriate plasma according to purpose and end-use. Considering electrode configurations and energy sources, generated in-liquid plasma can be subdivided as:

- (1) Plasma A: direct discharge between two electrodes using an AC (plus) power supply.
- (2) Plasma B: contact discharge between an electrode and the surface of the surrounding electrolyte using a DC power supply.
- (3) Plasma C: plasma generated with either radio frequency (RF) or microwave (MW) irradiation.
- (4) Plasma D: plasma generated using the laser ablation technique.

The schematic of generating Plasma A involves a direct discharge between two electrodes that comes in such forms as solution plasma, discharge plasma in liquid, electric spark discharge, arc discharge, capillary discharge, and streamer discharge (Fig. 5a). Two electrodes of similar size and shape are immersed in the liquid at a short distance. Because of the direct discharge, most liquids containing conductive electrolytes in such media as deionized water, ethanol, and liquid nitrogen can be used. Thus, in-liquid plasma is generated between the two electrodes immersed in the electrolyte solution after passing an electric current through the solution. It is important that the liquid used in this method be conductive.

The schematic of Plasma B is displayed in Fig. 5b. In 1963, Hickling and Ingram reported contact glow discharge electrolysis (CGDE),²⁰ whereby a high-temperature plasma sheath formed between an electrode and the surface of the surrounding electrolyte as a result of a high electric field; this was subsequently accompanied by a glow discharge photo-emission. Consider now two electrodes immersed in a conductive electrolyte in which the distance between them is varied from 5 mm to over 100 mm, and the electrode surface area between the anode and cathode is different; one of the electrodes has a smaller surface area than the other. The electrode

with the smaller surface area is covered with a thin film of water vapor within which a discharge occurs. In a submerged plasma two-electrode generator that uses a direct current power supply, passing the electric current through the electrolyte liquid produces foam owing to Joule heating; the in-liquid plasma is generated at the cathode side. In such a system, as the conductivity of the liquid changes, the conditions under which the in-liquid plasma is generated also change, so that it is necessary to keep the conductivity at an appropriate level. In most cases, the cathode consists of a metal plate with a large surface area (e.g., a Pt mesh), while the anode is a metal wire. A stable DC power supply is often used, although pulsed DC has also been used.

Techniques for generating in-liquid plasma by irradiating an antenna electrode with radio frequency or microwaves for Plasma C have been utilized in a variety of fields (Fig. 5c). These techniques are effective in generating in-liquid plasma at a lower electrical power. In the plasma generating apparatus, the dielectric constant and the dielectric loss of the liquid are important factors in the generation process. Unlike other techniques, however, it is not necessary to use an electrolyte solution. Radio frequency or microwave generated in-liquid plasma can be maintained in water over a wide range of water conductivity (from 0.2 to 7000 mS m⁻¹). When plasma is generated in a solution using radio frequency or microwaves, a lower pressure is often applied because energy is absorbed by water as it possesses a dielectric constant and dielectric loss. An advantage here is that plasma can be generated even in pure water, and so various application developments can be expected.

Another method for generating plasma in a liquid uses the laser ablation technique (Plasma D; Fig. 5d). The laser irradiates a solid substrate immersed in the liquid causing a plasma ball to be generated on the surface of the solid. This technology is applied in such research as nanoparticle production²¹ and deep-sea mass spectrometry.²²

The various techniques for generating Plasma A–C proposed according to usage conditions, reaction conditions, and operating equipment (among others) have been classified in some detail by Saito and Akiyama²³ who explained the classification based on the corresponding engineering diagram for the Plasma A–C summarized in Fig. 6,^{23–84} 7,^{85–128} and 8.^{129–154}

2.3 Problems and countermeasures in plasma generation

To generate plasma continuously in a liquid necessitates application of a large electrical power as compared to the case of generating plasma in vacuum or under atmospheric pressure, so that the thermal load on the electrode is large. Consequently, studies on electrodes used in plasma generation have been carried out for many years. In-liquid plasmas have been generated using electrodes made with such materials as tungsten, aluminum, copper, molybdenum, stainless steel (SUS 304), and carbon. Plasma generation with electrodes made of carbon, molybdenum, and SUS 304 lasted no more than 5 min.¹⁵⁵ Moreover, continuous (for 10 min) in-liquid plasma generation with aluminum and copper electrodes caused

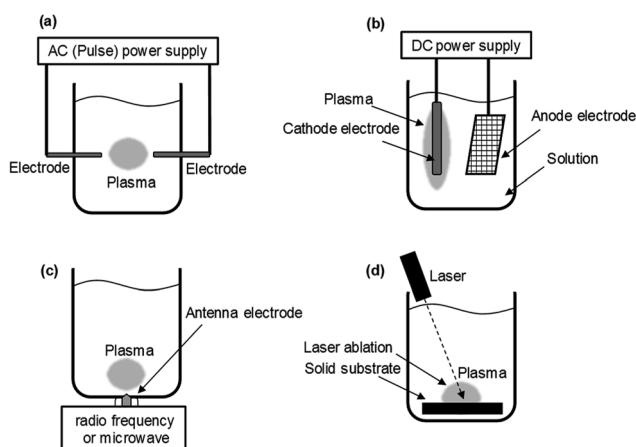


Fig. 5 Images of plasma generation method in a liquid: (a) direct discharge between two electrodes using an AC (plus) power supply; (b) contact discharge between an electrode and the surface of the surrounding electrolyte using a DC power supply; (c) plasma generation with radio frequency (RF) or microwave (MW) irradiation; (d) plasma generation using the laser ablation method.



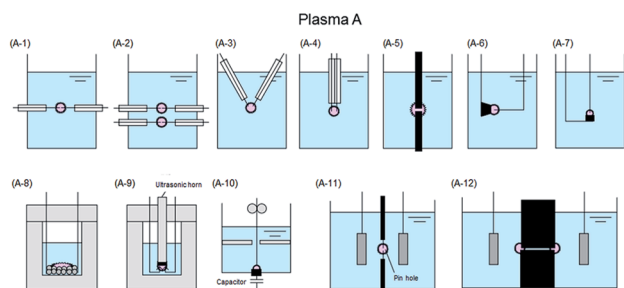


Fig. 6 Typical electrode configuration for Plasma A: (A-1) influence of glow discharge plasma and dielectric barrier discharge;^{24–30} (A-2) dielectric barrier discharge in quartz tube;³¹ (A-3) gliding arc discharge;³² (A-4) gas–liquid interfacial plasma, plasma electrochemistry in ionic liquids, and so forth;^{33–45} (A-5) glow discharge formation over water surface;⁴⁶ (A-6) discharge electrolysis;^{47–64} (A-7) microplasma;^{19,65–75} (A-8) dual plasma electrolysis;⁷⁶ (A-9) plasma in contact with liquids;^{77,78} (A-10) microplasma discharge;⁷⁹ (A-11) glow discharge generated in contact with a flowing liquid cathode;^{80–84} (A-12) AC capillary discharge. Modified with permission from ref. 23. Copyright 2015 by Hindawi.

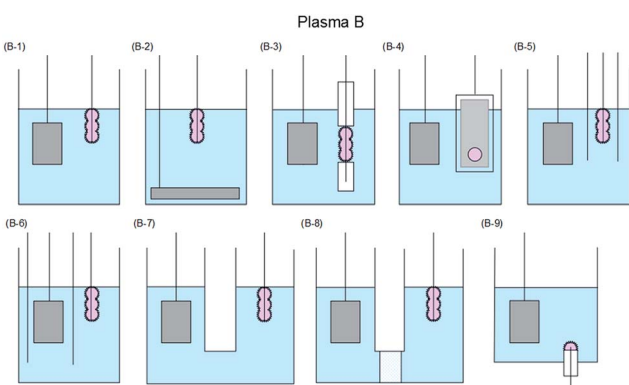


Fig. 7 Typical electrode configuration for Plasma B: (B-1) contact glow discharge;^{85–108} (B-2) electrical discharges,^{109–111} streamer discharge plasma in water;¹¹² (B-3) solution plasma,^{91,93,99,113} electric discharge plasma;¹¹⁴ (B-4) contact glow discharge;^{113,115,116} (B-5) contact glow discharge;¹¹⁷ (B-6) contact glow discharge electrolysis;^{118–120} (B-7) high-voltage cathodic polarization;¹²¹ (B-8) contact glow discharge electrolysis;^{118,122–125} and (B-9) electrical discharge.^{126–128} Modified with permission from ref. 23. Copyright 2015 by Hindawi.

deterioration of the electrode surface. On the other hand, for electrode material with high melting points (*e.g.*, tungsten, mp = 3422 °C), the electrode could, in principle, withstand long-term use (Fig. 9). Nonetheless, deterioration of the electrode surface can still occur depending on the generation conditions of the in-liquid plasma. Therefore, studies on the mechanism of in-liquid plasma heating of the electrodes and improvement measures are ongoing.

Many of the currently reported in-liquid plasmas produce bubbles within which plasma is generated in the liquid. However, if the bubble generating device were to be connected separately, the physical structure of the plasma generating portion would get rather complicated. To resolve this problem, an ultrasonic wave irradiation device is installed in the vicinity

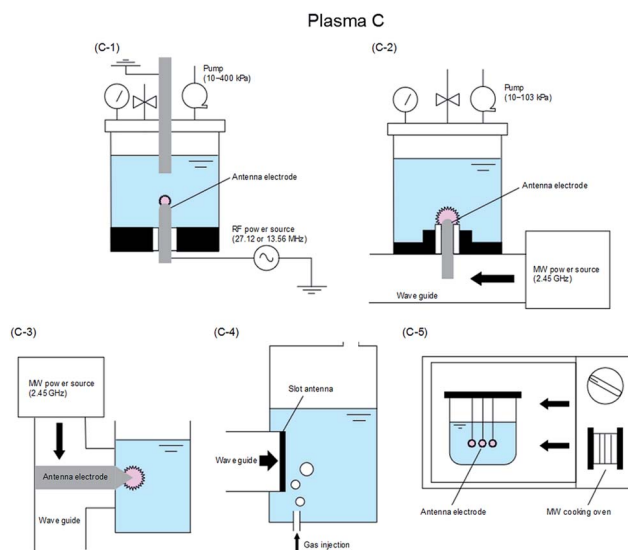


Fig. 8 Typical electrode configuration for Plasma C: (C-1) RF applied in-liquid plasma system under vacuum condition;^{129–140} (C-2) MW applied in-liquid plasma system under vacuum condition;^{134,141–149} (C-3) MW-induced in-liquid plasma system under atmosphere condition;^{150,151} (C-4) slot-excited MW discharge in-liquid plasma system under atmosphere condition;¹⁵² and (C-5) in-liquid plasma generation system with a MW oven.^{153,154} Modified with permission from ref. 23. Copyright 2015 by Hindawi.

of the plasma generating electrode. Even with this method, however, it is not possible to improve the apparatus complexity in the vicinity where plasma is generated. Accordingly, an apparatus has been developed in which the electrode and the ultrasonic homogenizer horn are integrated.

For instance, by sharing the microwave antenna electrode with the ultrasonic homogenizer as an in-liquid plasma apparatus driven by a single microwave power supply, both microwaves and ultrasonic waves can be used to irradiate simultaneously, thereby simplifying the apparatus (Fig. 10).¹⁵⁶ Since the ultrasonic homogenizer can generate fine bubbles in the liquid, they can be produced in the very vicinity where

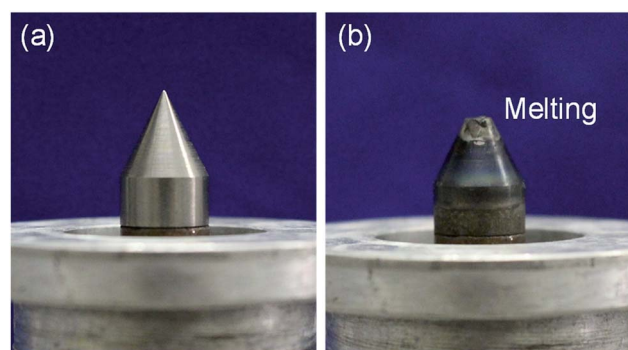


Fig. 9 (a) Photograph of a tungsten pencil-type electrode of an in-liquid plasma generator of the microwave type in an unused state; (b) photograph of a tungsten pencil-type electrode after several minutes of generating in-liquid plasma with continuous microwaves. Taken from ref. 17. Copyright 2017 by S. Horikoshi.



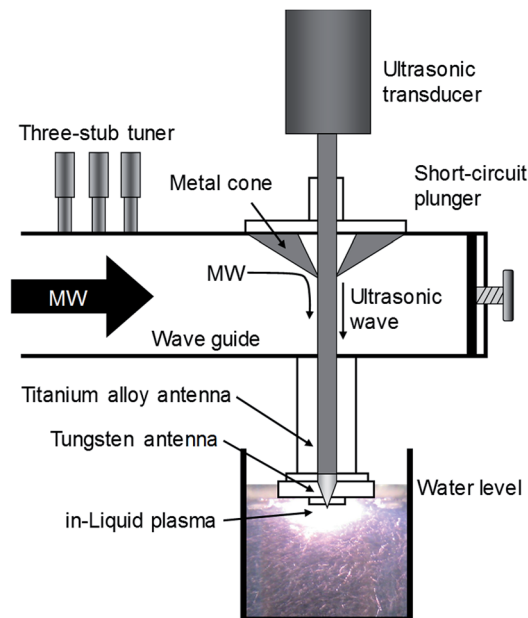


Fig. 10 Schematic diagram of an ultrasonic/microwave simultaneous irradiation type in-liquid plasma generator system. Reproduced from Horikoshi *et al.*¹⁵⁶ Copyright 2017 by Elsevier.

plasma is generated, causing plasma to be generated efficiently in the bubbles. Using the latter method, even if the incident power of the microwaves were reduced by 45% or more, compared to the existing apparatus without ultrasonic waves, in-liquid plasma could still be generated continuously and deterioration of the electrode could be minimized if not suppressed for long periods of use.

3. In-liquid plasma applications

3.1 Nanomaterials synthesis

3.1.1 Noble metals, alloys and metal-oxide nanoparticles.

Two methods have been reported for nanoparticle synthesis using in-liquid plasma. The first method utilizes dissolution of the electrode described in Section 2.3. In the case of in-liquid plasma, dissolution of the electrode surface proceeds by local heating; utilizing this phenomenon provides a method in which nanoparticles are produced by aggregating the electrode metal while evaporating the electrode surface (evaporation method). The second method (reduction method) involves reduction of a metal salt in aqueous media with the in-liquid plasma to synthesize metal nanoparticles. Nanoparticle synthesis by a gas-phase plasma reduction method has already been achieved; however, substituting this by a liquid-phase plasma increases the number of molecules of raw materials contained in the system by orders of magnitude. Hence, at laboratory level, for example, a yield of more than 10 g h^{-1} can be obtained. In addition, unlike the nanoparticle synthesis process occurring by gas-phase plasma, aggregation of generated particles can be prevented immediately by adding a particle agglutination inhibitor (or the like) into the solution.

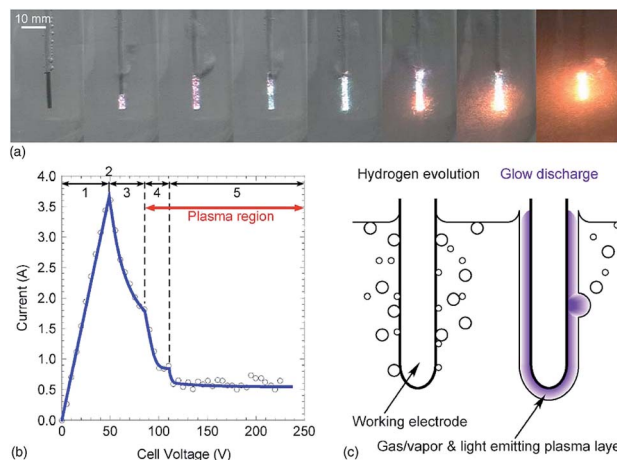


Fig. 11 (a) Photograph of plasma emission during the formation of nanoparticles; (b) relationship between current and voltage; (c) cartoon illustrating the process of nanoparticle generation. Reproduced from Toriyabe *et al.*⁸⁸ Copyright 2007 by the American Institute of Physics.

Dissolution of the electrode method. Studies have been conducted on the evaporation method to form various metallic nanoparticles by placing cathode electrodes of various metals in a potassium carbonate solution, followed by applying a direct current to this solution to evaporate and dissolve the electrodes. Metallic nanoparticles have been formed in solution during the evaporation of Ni, Ti, Ag, and Au nanowire electrodes with in-liquid plasma (Fig. 11).⁸⁸ The advantage of this method is that various kinds of nanoparticles can easily be formed in a liquid by simply changing the kind of metal used for the wire electrode. Along similar lines, Saito and coworkers⁹⁴ reported the syntheses of a single crystal tin oxide plate (SnO) and a $\text{Sn}_6\text{O}_4(\text{OH})_4$ skeleton using tin wire immersed in an electrolyte solution.

The size and shape of these nanoparticles can be controlled by changing the synthesis conditions (reaction temperature, cooling temperature, dispersant) of generating in-liquid plasma (Fig. 12).⁹⁴ And even if plasma conditions were changed, the morphology and the nature of nanoparticles could still be controlled (Fig. 13).⁹⁹ Metal electrodes can be volatilized using wide-area plasma, partial plasma, and partial plasma under high-temperature conditions. Accordingly, it is possible to produce Ti, Fe, Ni, Cu, Zn, Zr, Nb, Mo, Ag, W, Pt, Au, and SUS 316 nanoparticles using in-liquid plasma as the energy source. In addition, alloy nanoparticles of gold and platinum can be made by the simultaneous evaporation of the two electrode materials with in-liquid plasma (Fig. 14).¹⁵⁷ Another study reported the evaporation of a platinum electrode with in-liquid plasma to produce platinum nanoparticles (particle size, 2 nm) supported on a highly conductive carbon black support dispersed in water.¹⁵⁸ This Pt/C catalyst was produced with very high efficiency and used as a catalyst in fuel cells.

Reduced reaction with plasma method. Zinc oxide nanoparticles (ZnO NPs) have been produced using in-liquid plasma.⁹⁰ In this case, a Zn wire (the cathode) and a mesh



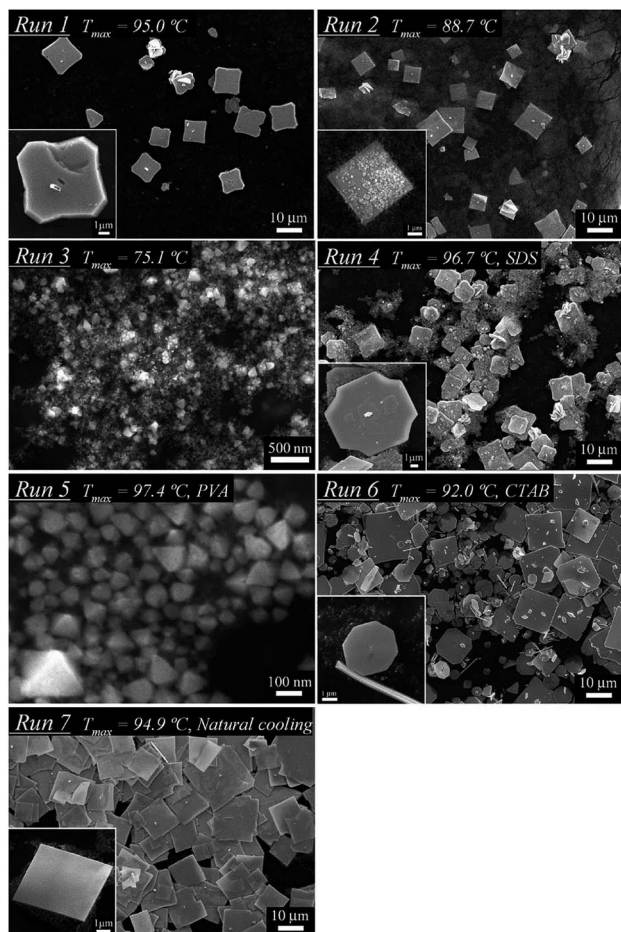


Fig. 12 SEM images of single crystals of a tin oxide SnO plate synthesized by in-liquid plasma under different reaction temperatures, dispersant and cooling conditions. Reproduced from Saito *et al.*⁹⁴ Copyright 2012 by the American Chemical Society.

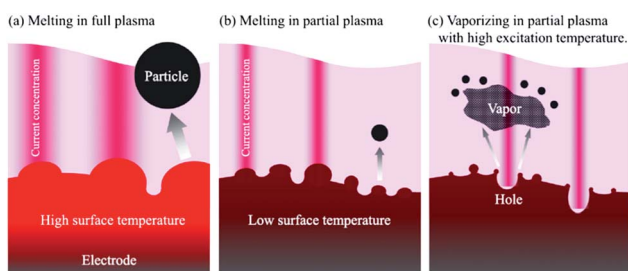


Fig. 13 Images of (a) a wide-area plasma; (b) a partial plasma; and (c) the volatilization of a metal electrode by partial plasma under high temperature conditions. Reproduced from Saito *et al.*⁹⁹ Copyright 2014 by the American Institute of Physics.

made of Pt wire (the anode) were submerged in an aqueous solution of K_2CO_3 . Application of a certain voltage to the solution system generated plasma in the immersed part of the Zn wire. Using medium-power input levels resulted in the formation of flower-like ZnO NPs (Fig. 15a and b),⁹⁰ while applying high-power input levels yielded aggregated ZnO NPs (Fig. 15c);

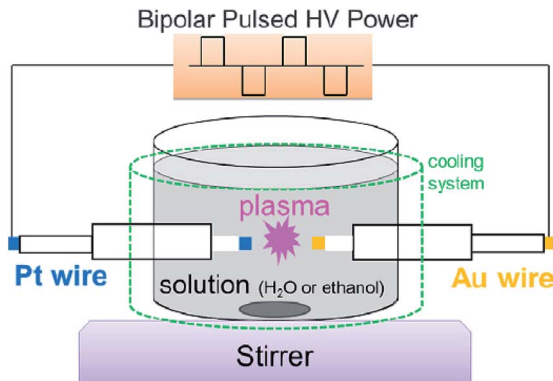


Fig. 14 Image of a synthesis apparatus of a gold/platinum alloy by in-liquid plasma using gold and platinum electrodes. Reproduced from Hua and coworkers.¹⁵⁷ Copyright 2013 by Elsevier.

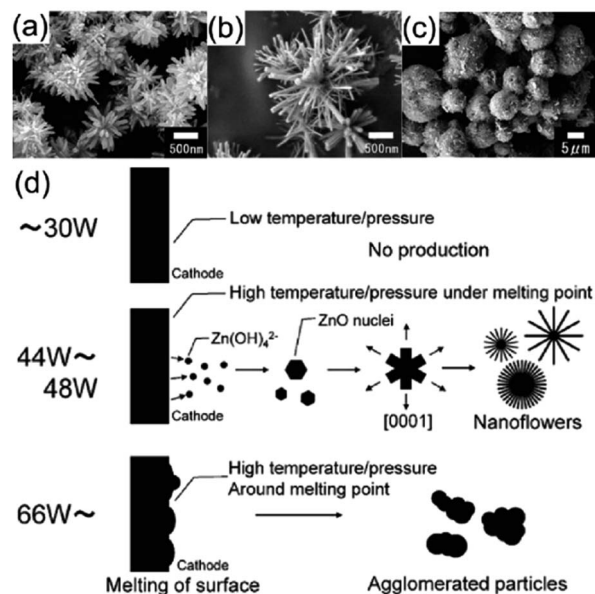
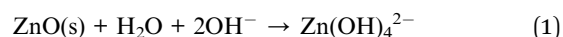
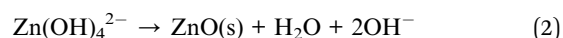


Fig. 15 SEM images of products obtained from in-liquid plasma usage; experimental conditions of K_2CO_3 concentration, and discharge voltage/power are: (a) 1.0 M, 66 V/44 W, (b) 0.5 M, 80 V/48 W, (c) 0.01 M, 200 V/168 W. (d) Schematic processes in the synthesis of ZnO nanoflowers and ZnO aggregates using in-liquid plasma. Modified with permission from ref. 90. Copyright 2011 by Elsevier.

the mechanism of the synthesis is summarized in Fig. 15d. The Zn wire is first oxidized to ZnO on its surface after plasma generation. At low power, the surface temperature of the electrode is below the melting point of zinc and some $Zn(OH)_4^{2-}$ species form around the Zn wire (reaction (1)).



Subsequently, $Zn(OH)_4^{2-}$ migrates to the low-temperature zone and decomposes into ZnO (reaction (2)).



The ZnO nanoparticles grow preferentially along the [0001] direction^{159,160} to form the flower-like ZnO nanoparticles. However, at high power (*i.e.*, at $>300 \text{ W cm}^{-2}$ (ref. 90)), the temperature of the Zn wire reaches its melting point causing rapid evaporation of the Zn wire and the ZnO film resulting in ZnO particle aggregates (Fig. 15c).

Research studies are also being conducted actively on a reduction method to synthesize various nanoparticles. For instance, gold-based bimetallic particles, (*e.g.*, Au-Fe, Au-Ga, Au-In or the like) can be produced using a metal-ion reduction method and a metal nitrate as the precursor from bivalent sp metals, trivalent sp metals, or 3d and 4d metals. A one-step

Table 1 Synthesis of noble metals, alloys and metal-oxide nanoparticles using various in-liquid plasma-related methods (see Fig. 6 for the in-liquid plasma methods)

Nanoparticles produced	Starting materials	In-liquid plasma methods	Ref.
Au	Gold rod or wire	Plasma A	165–169
		Plasma B	88, 99 and 114
		Plasma C	140
Ag	HAuCl ₄ NaAuCl ₄ Silver rod or wire	Plasma A	170–179
		Plasma B	86
		Plasma A	180–183
Pt	AgNO ₃ Ag-zeolite Platinum wire	Plasma B	88 and 99
		Plasma C	140, 147 and 151
		Plasma A	184 and 185
Ni	H ₂ PtCl ₆ Nickel wire	Plasma A	186
		Plasma B	187
		Plasma C	96
Cu	Copper wire CuCl ₂ CuSO ₄	Plasma B	151
		Plasma A	86
		Plasma A	96
Ni	Nickel wire	Plasma B	88, 89, 96 and 106
		Plasma A	188
		Plasma A	189 and 190
Cu	Copper wire CuCl ₂ CuSO ₄	Plasma B	86
		Plasma A	96
		Plasma A	88, 89, 96 and 106
Zn	Zinc plate	Plasma A	188
		Plasma B	189 and 190
		Plasma C	86
Pt–Au	Pt and Au wires	Plasma A	144
		Plasma B	98 and 101
		Plasma A	157
Pt–Au	H ₂ PtCl ₆ , NaAuCl ₄	Plasma B	86
		Plasma A	191
		Plasma B	102
Ag–Pt	Alloy wire	Plasma A	102
		Plasma B	192
		Plasma A	192
Ni–Cu	Ni(NO ₃) ₂ ·6H ₂ O, Cu(NO ₃) ₂ ·4H ₂ O	Plasma B	114
		Plasma A	114
		Plasma B	102
Sn–Ag	Alloy wire	Plasma B	102
		Plasma A	102
		Plasma B	102 and 114
Sn–Pb	Alloy wire	Plasma A	193
		Plasma B	193
		Plasma A	194
Stainless steel	Alloy wire	Plasma A	194
		Plasma B	195
		Plasma A	195
Co–B	Cobalt acetate, KBH ₄	Plasma B	196
		Plasma A	196
		Plasma A	88, 95 and 197
MoS ₂	MoS ₂ powder	Plasma A	109
		Plasma B	109
		Plasma B	198
γ-Al ₂ O ₃	Aluminum rod Aluminum plate	Plasma B	198
		Plasma A	199
		Plasma A	200
TiO ₂	Titanium rod	Plasma A	200
		Plasma B	201
		Plasma B	201
Defective black TiO ₂	Ti wire	Plasma B	202
		Plasma A	202
		Plasma B	203
Pt nanoparticles supported on TiO ₂ nanotube	TiO ₂ nanotube and Pt wires	Plasma B	203
		Plasma A	204
		Plasma A	204
Cellulose–ZnO composite	Zn(O ₂ CCH ₃) ₂ ·2H ₂ O (or anhydrous Zn acetate) and D-glucose	Plasma A	205–209
		Plasma A	210
		Plasma A	210
CuO	Copper foil	Plasma A	211
		Plasma B	211
		Plasma B	211
Cu ₂ O	Copper plate	Plasma B	211
		Plasma A	211
		Plasma B	211
In(OH) ₃ nanocubes	Indium and tin plate	Plasma B	211
		Plasma A	211
		Plasma B	211
Fullerene (C ₆₀)	Graphite in toluene	Plasma B	211
		Plasma A	211
		Plasma B	211
Carbon nanotubes (CNT)	Carbon rods	Plasma B	211
		Plasma A	211
		Plasma B	211
CNT-supported Pt nanoparticles	Pt, H ₂ PtCl ₆ , CNT	Plasma B	211
		Plasma A	211
		Plasma B	211
Carbon–metal nanocomposites	Platinum, aluminium, nickel, copper, tungsten, carbon electrodes	Plasma B	211
		Plasma A	211
		Plasma B	211
Ag on mesoporous silica	Ag NPs, tetraethylorthosilicate (TEOS)	Plasma A	212 and 213



synthesis of nanoparticles in water has also been described.¹⁶¹ Stable gold bimetallic nanoparticles of 5 to 20 nm can be synthesized using this method. On the other hand, in the case of microwave-generated in-liquid plasma (2.45 GHz), Toyota and coworkers¹⁶² succeeded in depositing diamond particles (7 to 8 μm) onto silicon wafers to produce a diamond electrode in methanolic media. Syntheses of Cu, Au, and Pt nanoparticles by the in-liquid plasma reduction method have also been described.¹⁵¹

In fact, syntheses of nanomaterials have been reported extensively as there are many advantages in using the energy from in-liquid plasma to drive a chemical reaction. Thus, various nanoparticles of noble metals, alloys and metal-oxide nano-materials have been synthesized using various types of plasma-related techniques. Some of the nanoparticles, starting materials and type of in-liquid plasma used are summarized in Table 1.

Panomsuwan and co-workers¹⁶³ reported that metal-free N-doped carbon nanoparticles (NCNPs) could be synthesized *via* a solution plasma process with the potential to achieve uniformly distributed nitrogen atoms. Accordingly, they used a set of cyanoaromatic molecules that included benzonitrile, 2-cyanopyridine and cyanopyrazine as a single-source precursor in the synthesis without the addition of a metal catalyst. The resulting NCNPs revealed uniformly nanosized particles (20–40 nm) and an interconnected hierarchical pore structure with a high specific surface area (210–250 $\text{m}^2 \text{g}^{-1}$). The difference in carbon/nitrogen mol ratios of organic precursors gave rise to the variation of nitrogen-doping level in NCNPs from 0.63 to 1.94 atom%. A detailed electrochemical evaluation toward the oxygen reduction reaction (ORR) demonstrated that NCNPs exhibit a significant improvement in terms of both onset potential and current density under alkaline and acidic conditions. The predominant distribution of graphitic-N and pyridinic-N sites on NCNPs played an essential role in enhancing the ORR activity and the selectivity toward a four-electron reduction pathway. More importantly, NCNPs possessed excellent robust long-term durability and strong methanol tolerance compared with those of a commercial Pt/carbon catalyst. The possible formation mechanism of NCNPs is illustrated schematically in Fig. 16. After discharging for 30 min, black solid particles were separated from the liquid precursor by pouring through a filter paper and washed several times with ethanol until the wash solvent was colorless. The solution plasma approach used¹⁶³ should broaden and accelerate further research efforts on nitrogen-doped carbon catalysts, one-step closer to practical fuel cells and other related electrochemical devices.

Morishita and co-workers¹⁶⁴ investigated the routes of solution-plasma-induced nanocarbon formation from hexane, hexadecane, cyclohexane, and benzene; the synthesis from benzene was the most effective. However, the nanocarbons obtained from linear molecules were more crystalline than those from ring molecules. Linear molecules decomposed into shorter olefins, whereas ring molecules were reconstructed in the plasma. C–H dissociation proceeded in the saturated ring molecules, followed by conversion into unsaturated ring

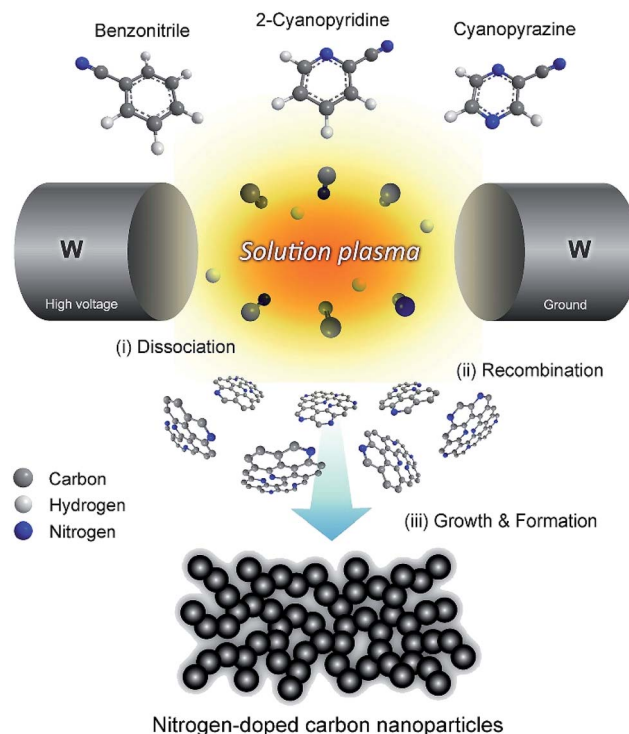


Fig. 16 Schematic illustration of the formation mechanism of nitrogen-doped carbon nanoparticles (NCNPs) *via* a solution plasma process. Modified with permission from ref. 163. Copyright 2016 by Elsevier.

molecules. However, unsaturated ring molecules were directly polymerized through cation radicals (*e.g.*, benzene radical cation) and were converted into two- and three-ring molecules at the plasma–solution interface. The nanocarbons from linear molecules were synthesized in plasma from small C₂ molecules under heat; the products so-obtained were the same as those obtained *via* a pyrolysis synthesis. Conversely, the nanocarbons obtained from ring molecules were directly synthesized through an intermediate (such as benzene radical cations) at the

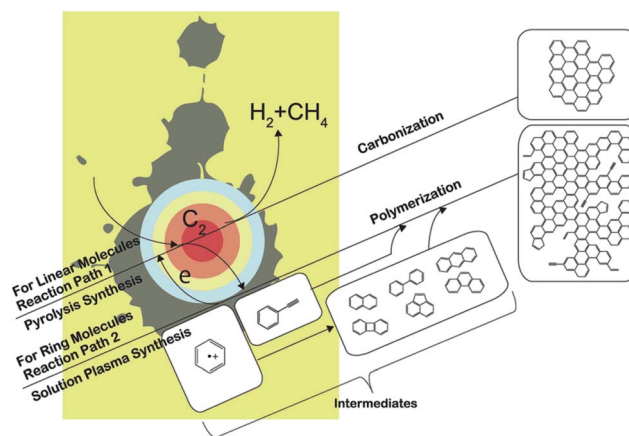


Fig. 17 Reaction routes from hexane, hexadecane, cyclohexane, and benzene. Modified with permission from ref. 164. Copyright 2016 by the Nature Publishing Group.



interface between the plasma and the solution, resulting in the same products as those obtained *via* polymerization. These two different reaction fields provide a reasonable explanation for the fastest synthesis rate observed in the case of benzene. Two reaction paths from monomer to polycyclic aromatic hydrocarbons (PAHs), including graphene, are displayed in Fig. 17. One reaction path (reaction path 1) is from the plasma center. The solution is vaporized by a strong electric field between the electrodes. The vaporized solution forms a gas phase between the electrodes, which is converted into plasma after breakdown. In the plasma, organic compounds were almost completely decomposed, and were similar to the products obtained *via* a pyrolysis synthesis.

3.1.2 Quantum dots. Quantum dots are tiny particles or nanocrystals of a semiconducting material with diameters in the range of 2–10 nanometers (consisting of *ca.* 10–50 atoms), first discovered in 1980 by Ekimov and Onushchenko.²¹⁴ Quantum dots display unique electronic properties that are intermediate between those of bulk semiconductors and discrete molecules, and are partly the result of unusually high surface-to-volume ratios.²¹⁵

The most apparent result of this is the distinctive colors produced owing to different sizes of the nanocrystalline particles. Because of their small size, electrons in quantum dots are confined in small space (a quantum box). When the radii of the semiconductor nanocrystals are smaller than the exciton Bohr radius (exciton Bohr radius is the average distance between the electron in the conduction band and the hole it leaves behind in the valence band), the energy levels are quantized as per Pauli's exclusion principle. Because of the high level of control possible over the size of the nanocrystals produced, quantum dots can be tuned during the manufacturing process to emit light of various colors.²¹⁶ These unique properties render quantum dots versatile in such applications as transistors, solar cells, LEDs, diode lasers, as well as in medical imaging and in quantum computing.²¹⁷

Ultra-small sized (within 5 nm) and monodispersed silicon quantum dots (Si QDs) are ideal candidates for Si/C nanocomposites to be used as anode materials in lithium ion batteries. However, fabrication of these Si QDs/C nanocomposites remains a gigantic challenge in materials chemistry because of the small size, high chemical activity, and low density of Si QDs with Si-H terminated surfaces. Nonetheless, Wei and coworkers²¹⁸ reported a convenient synthetic method for the preparation of Si QDs/C nanocomposites by a novel liquid-phase plasma-assisted synthetic process, with the Si quantum dots embedded in a carbon matrix (Si-QDs/C) *via* a direct discharge between two electrodes powered by an AC power supply. Fig. 18a shows the setup for the liquid-phase plasma synthetic route.²¹⁸ Briefly, the copper and the tungsten (with a quartz shell) electrodes were placed into an ethanol solution containing Si QDs (photograph (i)). After a 20 min continuous sparking discharge, grey Si QDs/C composites were obtained successfully (photograph (ii)). Photograph (iii) shows the spark during the tungsten electrode discharging process. Fig. 18b displays the TEM image of the Si QDs, revealing a diameter within 5 nm and a single crystalline nature with

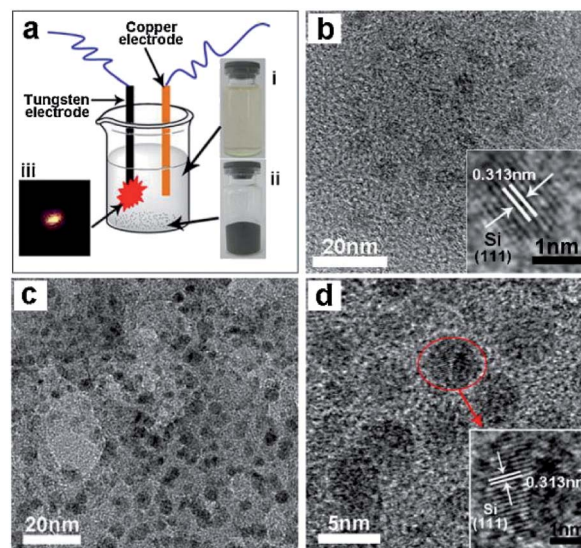


Fig. 18 (a) Setup scheme for the synthetic route. (b) TEM and HRTEM images of Si-quantum dots. (c) TEM image of the Si-quantum dots/C nano-composites. (d) HRTEM image of the Si quantum dots/C nano-composites. Reproduced from Wei *et al.*²¹⁸ Copyright 2013 by Elsevier.

a (111) spacing of about 0.313 nm in the Si crystal (see inset). Fig. 18c depicts the TEM image of the resulting Si QDs/C nanocomposites, and shows that the Si QDs are indeed embedded in large-sized amorphous carbon particles. The HRTEM image of the Si QDs/C nanocomposites is shown in Fig. 18d; the inset image highlights the Si QDs in the nanocomposites maintaining the good crystalline nature and confirms the lattice fringe space of *ca.* 0.313 nm of the (111) plane of the Si crystal. The Si-QDs/C nanocomposites demonstrated high specific capacity, good cycling life and high Coulombic efficiency as anode materials in lithium ion batteries.

3.2 Wastewater treatments

In-liquid plasma techniques in wastewater treatments are associated with the formation of a light emitting plasma around an electrode in a high conductivity electrolyte solution at moderate voltages up to 1 kV. In recent years, these techniques have attracted considerable interest as a tool for generating a large quantity of heat and a high yield of solvent-split radicals.²¹⁹ There are several variations of using in-liquid plasma in the treatment of wastewaters: (A) immersing the electrodes in the waters (Fig. 19a), (B) using a water flow (Fig. 19b), and (C) using bubbles (Fig. 19c) that can be roughly divided into three groups.²²⁰ In method (A) – *i.e.*, in an underwater streamer discharge – to the extent that plasma is generated directly in the liquid, it is suitable for treating wastewaters by means of the resulting shock waves and the generated oxidative active species (*e.g.*, $\cdot\text{OH}$ radicals and ozone). Application studies have treated large quantities of water such as: ballast water, river waters, and dams from high concentrations to smaller scales.²²¹ On the other hand, in methods (B) and (C), since the gas is converted to plasma and is introduced into the liquid, the advantage here is that plasma can be generated easily while concurrently getting



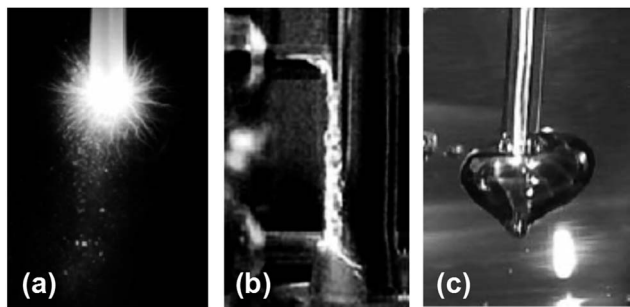
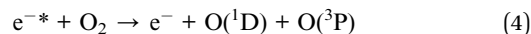


Fig. 19 Method of generating in-liquid plasma for use in water treatment: (a) method of the immersed electrodes in water; (b) method using water flow; (c) method using bubbles. Reproduced from Akiyama *et al.*²²⁰ Copyright 2014 by The Japan Society of Plasma Science and Nuclear Fusion Research.

significant energy saving. These systems generate plasma in bubbles and generate oxidized active species by diffusing them in water as compared with a system in which plasma is directly generated in an aqueous solution. However, compared with method (A), the number of generated $\cdot\text{OH}$ radicals is reduced by about an order of magnitude,¹²⁷ so that the efficiency of the water treatment is lower. For instance, in the concurrent ultrasonic/microwave in-liquid plasma generator described in Fig. 10, the electrode is immersed in the aqueous solution, bubbles are then generated by the ultrasonic waves while plasma is generated in the solution so that the quantity of $\cdot\text{OH}$ radicals generated is decreased. However, because of the cavitation effect of ultrasonic waves, the number of $\cdot\text{OH}$ generated increases such that the total concentration of $\cdot\text{OH}$ radicals produced is also increased.

Various oxidative active species are used in water treatments. Among these, the most powerful oxidative species are the $\cdot\text{OH}$ radicals. Accordingly, studies have been carried out to increase the concentration of $\cdot\text{OH}$ radicals and enhance diffusion efficiency in water in those water treatment processes that involve in-liquid plasma.²²² In addition, generation of $\cdot\text{OH}$ radicals by in-liquid plasma in water and the decomposition of contaminants have also been undertaken.²²³ The mechanism of $\cdot\text{OH}$ radical generation by in-liquid plasma is summarized by eqn (3)–(6). Electrons (e^{-*}) generated by the in-liquid plasma dissociate water and lead to the formation of $\cdot\text{OH}$ radicals (eqn (3)). On the other hand, interaction of these electrons (e^{-*} ; eqn (4)) with dissolved oxygen generates oxygen atoms in their excited $\text{O}({}^1\text{D})$ and ground $\text{O}({}^3\text{P})$ states, which ultimately generate $\cdot\text{OH}$ radicals from water (eqn (5) and (6)).²²³ Therefore, increasing the concentration of dissolved oxygen leads to an increase in the concentration of $\cdot\text{OH}$ species. However, as the concentration of $\cdot\text{OH}$ radicals increases, their subsequent recombination may be facilitated, so that it is disadvantageous to produce too many such species; note that the recombination process depends on the diffusion conditions of the $\cdot\text{OH}$ radical species.



3.2.1 Degradation of persistent organic pollutants (POPs).

Among the many fluorinated organic compounds, perfluorooctanoic acid (PFOA: $\text{C}_7\text{F}_{15}\text{COOH}$) and perfluorooctanesulfonic acid (PFOS: $\text{C}_8\text{F}_{17}\text{SO}_3\text{H}$) possess such excellent chemical and physical characteristics as water repellence, surface-active properties, heat resistance, and chemical resistance. Consequently, they have been used widely as industrial surfactants. However, from the viewpoint of environmental persistence, bioaccumulation and toxicity they are designated as regulated substances by the Stockholm convention (persistent organic pollutants (POPs) convention). Nonetheless, even though PFOS is an alternative albeit difficult surfactant in some industries, its use is exceptionally being permitted; treatment methods to dispose of PFOS have been investigated by Schroder and Maesters²²⁴ who noted that PFOA and PFOS are difficult to decompose with $\cdot\text{OH}$ radicals and ozone. Successful methods to decompose these fluorinated substrates have involved: (i) photochemical decomposition using a photocatalyst,²²⁵ (ii) photolysis by 185 nm vacuum UV light,²²⁶ (iii) sulfuric acid radicals ($\text{SO}_4^{\cdot-}$),²²⁷ (iv) a mechanochemical method,²²⁸ and (v) ultrasonic cavitation.²²⁹

Horikoshi *et al.*¹⁵⁶ achieved successful decomposition of perfluorooctanoic acid (PFOA) in ion-exchange water using in-liquid plasma. The methodology involved concurrent ultrasonic/microwave irradiation in an in-liquid plasma type generator; results are reported in Fig. 20.

Plasma irradiation of PFOA (0.01 mM) in aqueous media for 90 s led to 59% defluorination accompanying the decomposition of PFOA, a substrate noted above as being difficult to decompose even with $\cdot\text{OH}$ radicals. Nonetheless, PFOA was decomposed synergistically by the cavitation effect generated by

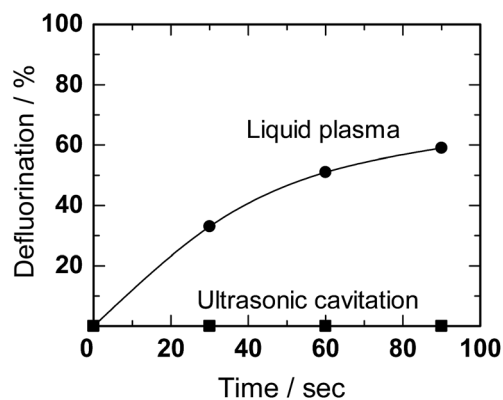


Fig. 20 Defluorination yields (%) from the degradation of aqueous PFOA solutions (0.01 mM) by ultrasonic cavitation alone and by the microwave discharge in-liquid plasma method under simultaneous ultrasonic cavitation (MW power, 220 W; power for cavitation, 90 W). Reproduced from Horikoshi *et al.*¹⁵⁶ Copyright 2017 by Elsevier.





Fig. 22 Photograph of a self-propelled in-liquid plasma apparatus floating over a dam to destroy the harmful *Microcystis aeruginosa*. Reproduced from ref. 251. Copyright Kumamoto University, Japan.

recycled waters. This equipment is expected to become an integral part of a manufacturing process.

4. Summary remarks

This review article has outlined and described in-liquid plasma and has provided application examples of nanomaterials synthesis and wastewater treatment. Related to the present discussion, an earlier article by Kareem and Kaliani²⁵³ reviewed the glow discharge plasma electrolytic technique for nanoparticles synthesis, while Chen *et al.*²⁵⁴ provided a theoretical analysis of the nanomaterial synthetic process from a physics point of view, and most recently Rumbach and Go²⁵⁵ provided a perspectives article on plasmas. It is clear from the literature that compared to gas and solid plasmas the in-liquid plasma technique has yet to fully mature from a physical and engineering viewpoints. In addition, because it has yet to be fully developed exploitation of in-liquid plasma toward new chemical processes is highly desirable without being bound to some fixed concept of the past. Accordingly, in-liquid plasma is a field filled with many possibilities and consequently should trigger the discovery of innovative processes and products.

Conflicts of interest

Authors declare no conflicts of interest.

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