Review Article
Nanomaterial Synthesis Using Plasma Generation in Liquid

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Received 20 August 2015; Revised 27 September 2015; Accepted 28 September 2015

Academic Editor: Wei Chen

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Over the past few decades, the research field of nanomaterials (NMs) has seen rapid development due to the unique electrical, optical, magnetic, and catalytic properties of these materials [1–7]. Pure metallic and metal alloy nanoparticles (NPs) have been applied as materials for catalysis, microelectronics, optoelectronics, and magnetics, as well as conductive pastes, fuel cells, and battery electrodes [8]. Among the various methods available today for NM synthesis, techniques for plasma generation in liquid are relatively new. Various types of plasma such as arc discharge and glow discharge can be applied to produce metal, alloy, oxide, inorganic, carbonaceous, and composite NMs. Many experimental setups have been reported, in which various parameters such as the liquid, electrode material, electrode configuration, and electric power source are varied. By examining the various electrode configurations and power sources available in the literature, this review classifies all available plasma in liquid setups into four main groups: (i) gas discharge between an electrode and the electrolyte surface, (ii) direct discharge between two electrodes, (iii) contact discharge between an electrode and the surface of surrounding electrolyte, and (iv) radio frequency and microwave plasma in liquid. After discussion of the techniques, NMs of metal, alloy, oxide, silicon, carbon, and composite produced by techniques for plasma generation in liquid are presented, where the source materials, reaction media, and electrode configurations are discussed in detail.

1. Introduction

In the past few decades, the research field of nanomaterials (NMs) has seen rapid development due to the unique electrical, optical, magnetic, and catalytic properties of these materials [1–7]. Pure metallic and metal alloy nanoparticles (NPs) have been applied as materials for catalysis, microelectronics, optoelectronics, and magnetics, as well as conductive pastes, fuel cells, and battery electrodes [8]. Among the various methods available today for NM synthesis, techniques for plasma generation in liquid are relatively new. Most reports studying plasma in liquid NM syntheses have been published after 2005 [9] and the growing interest in this technique is due to its many advantages such as simplicity of experimental design. When discussing techniques for plasma generation in liquid, we should make a mention of the application of this technique in water purification, given its longer history compared to its use in NM synthesis. Locke et al. reviewed the use of electrohydraulic discharge and nonthermal plasma [10] in water treatment, and some of their configurations can be applicable to NM synthesis. A similar review on electrical discharge plasma technology for wastewater remediation has also been reported by Jiang et al. [11]. In addition, Bruggeman and Leys reviewed the research on atmospheric pressure nonthermal discharges in and in contact with liquids [12]. These reviews will be helpful for the design of new methods for NM synthesis. In addition, a significant number of review articles on NM synthesis by using techniques for plasma generation in liquid have been published recently. These reports mainly focus on certain types of plasma including microplasma [13], electrical arc discharge in liquids [14], glow discharge plasma electrolysis [9], and atmospheric pressure plasma-liquid interactions [15], providing in-depth information about each plasma type. Moreover, general reviews covering a variety of plasma types have also been published. Graham and Stalder summarized a variety of plasma-in-liquid systems from the viewpoint of nanoscience [16]. Chen et al. have presented a general review of plasma-liquid interactions for NM synthesis [17]. However, despite their importance, several important points have not been considered, including the electrode configuration for NM synthesis, the method to supply the source materials for NMs, and the kind of liquid used. Hence, there is an urgent need for information on these various aspects, as they can be
expected to play a significant role in further development of NM synthesis by techniques for plasma generation in liquid.

Herein, this review classifies and introduces all available plasma in liquid for application in a variety of fields such as NM synthesis, analytical optical emission spectrometry, hydrogen production, polymerization, and water treatment. The liquid and electrode configurations used for generating plasma are also presented in detail. Moreover, the metal, alloy, oxide, inorganic, carbonaceous, and composite NMs produced by techniques for plasma generation in liquid are discussed, along with the power sources and raw materials of NMs in each method. Thus, the information presented in this review will help to develop for plasma generation in liquid for NM synthesis, in terms of new fabrication methods, equipment design, and strategies for scale-up. In addition, recent trends and further research have also been summarized in this review.

2. Plasma Generation in Liquid

Many experimental setups of plasma in liquid generation have been reported, in which the liquid medium, electrode material, electrode configuration, electric power source, and other parameters were varied. By examining electrode configurations and power sources, plasma in liquid generation can be subdivided into four main groups:

(i) Gas discharge between an electrode and the electrolyte surface.
(ii) Direct discharge between two electrodes.
(iii) Contact discharge between an electrode and the surface of surrounding electrolyte.
(iv) Radio frequency (RF) and microwave (MW) generation.

2.1. Gas Discharge between an Electrode and the Electrolyte Surface (Group i). Figure 1 shows the electrode configurations for gas discharge techniques between an electrode and the electrolyte surface (Group i). In the i-1 to i-3 schematics of Figure 1, both electrodes are solid metals and the liquid comes into contact with the plasma. Liu et al. reported glow-discharge plasma reduction using ionic liquids (ILs) [18–20] or aqueous solutions containing metal ions [21, 22] to produce NPs (i-1). Dielectric barrier discharge was also applied in the setup shown in Figure 1(i-1) [23, 24]. Figure 1(i-2) shows dielectric barrier discharges generated inside the quartz cylindrical chamber that is filled with fuel gas and liquid water [25]. Gliding arc discharge techniques (i-3) were also applied, with humid air as a feeding gas [26]. Note that, in the abovementioned methods, as the liquid is only in contact with the plasma, the conductivity of the liquid does not affect plasma generation.

The methods in which the liquid acts as the conductive electrode are discussed below. Kaneko et al. demonstrated gas-liquid interfacial plasma generation [27–33] as shown in Figure 1(i-4), in which the cathode was immersed into the IL and the discharge was generated between the anode and the IL surface. Argon gas was passed through the system in a continuous flow to generate glow discharge plasma. Similar techniques such as plasma electrochemistry in ILs [34–37] have been reported by Endres et al. Recently, Yang et al. reported the synthesis of carbon nanotubes decorated with Au and Pd NPs (CNT) [38, 39] by using the plasma generation setup seen in design i-4. A low-pressure glow discharge was generated over the water surface using a plate electrode designed for wastewater treatment [40]. In the designs shown in i-4 and i-5, the distance between the electrode and the liquid surface was in the range of 4–60 mm. In the case of design i-6, the electrode was closely contacted to the liquid surface to better concentrate the electric field in a specific area. When the anode is placed above the surface of an electrolyte and a high direct-current (DC) voltage is applied between the anode and cathode immersed in the electrolyte, glow discharge occurs between the anode and surface of the electrolyte. An electrode under such conditions has been labeled a “glow discharge electrode” (GDE) by Hickling and Ingram [41], who reviewed light-emission generated by such GDEs. A typical experimental setup of GDE is shown in Figure 1(i-6). Note that this technique was applied for NM synthesis. Kawamura et al. synthesized NPs of various materials such as Ag [42], Si [43, 44], SiC [44], Al [43], Zr [43], Fe [45], Ni [46, 47], Pt [43], CoPt [43], Sm-Co [48], and FePt [45, 49] using plasma-induced cathodic discharge electrolysis in a molten chloride electrolyte under Ar at 1 atm pressure. They also developed an apparatus with a continuous rotating disk anode for cathodic discharge electrolysis [46]. Others have reported the formation of plasma [50] and synthesis of NMs using conductive electrolyte solution in Ar or air [51–53]. Recently, the formation of graphene [54, 55] and carbon dendrites [56] was also reported by using ethanol.

In the case of Figure 1(i-7), a metallic capillary tube, acting as the cathode, was positioned above the surface of the liquid, and Ar or He gas was injected through this tube to form plasma. This small plasma, or microplasma, is a special class of electrical discharge formed in geometries where at least one dimension is reduced to submillimeter length scales [13]. Conventionally, microplasma has been used to evaporate solid electrodes and form metal or metal-oxide nanostructures of various compositions and morphologies. Microplasma has also been coupled with liquids to directly reduce aqueous metal salts and produce colloidal dispersions of NPs [15, 57–67]. Richmonds et al. reported synthesis of Ag [58, 60], Au [58], Ni [62], Fe [62], and NiFe [62] NPs using such techniques. Mariotti et al. also synthesized Au [15, 64] and Si [61] NPs in a similar fashion. In microplasma with DC, the metal plate inserted in the liquid acts not only as a counter electrode but also as a source material of metal ions [62, 65]. In a similar vein, dual plasma electrolysis (shown in Figure 1(i-8)) has also been reported. In the case of i-9 and i-10, the nozzle was directly inserted to the liquid [68–70]. Since glow discharge generated in contact with a flowing liquid cathode (shown in Figure 1(i-11)) has a small cell size, this setup is used for compact elemental analysis of liquid by optical emission spectrometry [71–75]. Although the i-11 configuration has not been applied for NM synthesis, it has the potential for continuous NM synthesis.
Summary. In Group i, the raw materials for the NMs were supplied from the liquid. Since the plasma temperature was relatively low as compared to the arc or spark discharge, ionic liquid was not decomposed in the reaction field. However, the reduction of metal ions by excited species and nucleation and growth reactions occur in the plasma field. Therefore, it is very important to understand these chemical reactions in order to control the synthesis of NMs. In addition, the synthesis of composite NMs and alloy NPs have become much more important in the current areas of research. In most cases, Group i uses the batch process, in which the concentration of the metal ions decreases during NMs synthesis. Therefore, the development of continuous synthesis techniques, like rotating disk anode or flowing liquid cathode, will become essential in the future.

2.2. Direct Discharge between Two Electrodes. This second group of plasma generation technique involves a direct discharge between two electrodes and comes in forms such as “solution plasma,” “discharge plasma in liquid,” “electric spark discharge,” “arc discharge,” “capillary discharge,” and “streamer discharge.” The schemes of these discharges are summarized in Figure 2. In contrast to gas discharge (Group i), 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 such as deionized water, ethanol, and liquid nitrogen (LN) can be used in such systems. For NP production, both electrode and ions in the liquid serve as raw materials for NP formation.

Takai et al. reported using solution plasma techniques for various NP syntheses [79–98], surface functionalization [99], and chemical reactions [100]. When the solid electrode was used as a source material of NMs, this was referred to as “solution plasma sputtering.” A typical setup for solution plasma generation is shown in Figure 2(ii-1) [79–111]. The applied voltages were between 1.6 and 2.4 kV, with pulses at around 15 kHz and pulse widths at 2 µs. Typical Au NP synthetic conditions use chloroauric acid (usually HAuCl₄) as a starting material; it is believed that hydrogen atoms are essential as reducing agents for the NP formation process. This technology has been applied for alloy and composite NM synthesis; the PtAu and PtAu/C NMs were synthesized using Pt and Au electrodes within the carbon-dispersed solution [84, 88]. Ag NP-embedded mesoporous silica was also produced via solution plasma [90, 92], for use in catalysis. Tarasenko et al. also reported using electric discharge techniques in water for NP synthesis, in which the peak current was 60 A, and AC, DC, and pulsed power sources were used [112–114]. C₆₀ fullerene and carbon nanotubes (CNTs) were also produced by electric discharges in liquid toluene [105, 107]. Figure 2(ii-2) shows the setup for
producing NPs supported on carbon nanoballs, in which the discharge occurred in benzene [115].

The configuration seen in Figure 2(ii-3) has also been used for producing NPs. Abdullaeva et al. synthesized carbon-encapsulated Co, Ni, and Fe magnetic NPs [116], spherical ferromagnetic Fe$_3$O$_4$ NPs [117], Wurtzite-type ZnMgS [118], and Fe and Ni NPs coated by carbon [119] using pulsed plasma techniques. In this system, one of the electrodes was kept vibrating in order to keep the discharge process stable. Without vibration of the electrode, the discharge process continues until the electrodes become eroded enough to make the gap between the electrodes larger than the required distance for the breakdown [118]. The CNT [120] and graphene layers [121] were synthesized from two graphite electrodes by arc discharge. Tong et al. used the configuration in Figure 2(ii-4) for the cutting of CNTs [124], as well as the synthesis of honeycomb-like Co–B amorphous alloy catalysts [125] and zinc oxide nanospheres [126].

Figure 2(ii-5) shows the setup of DC or pulsed arc discharge in water [130–141, 153, 242–245, 250, 251]. In the arc discharge process at higher currents (15 ~ 25 A) and lower voltages, the electrode material is vaporized to form NPs. Lo et al. reported on a submerged arc nanoparticle synthesis system (SANSS) to synthesize Cu [138], Ag [139, 141], and Au [140] nanofluids. Ashkarran et al. produced Au [131], Ag [132, 135], ZnO [133, 134], WO$_3$ [130], ZrO$_2$ [136], and TiO$_2$ [137] NPs by arc discharge with currents ranging between 10 and 40 A. In the case of using a DC power source for arc discharge in liquid [130, 131, 135, 140], the reaction time was less than 5 minutes. In contrast to the arc discharge with low voltage and high current, high-voltage and low-current plasma was also generated in the liquid.

Sano et al. is famous for the synthesis of carbon “onions” by submerged arc discharge in water [142–144]. Their research group has synthesized various carbon-based NMs and composite materials using the configurations seen in ii-6 and ii-7. In these systems, the anode is smaller than the cathode and the gap distance between the two was maintained at less than 1 mm. The small anode is mostly consumed during discharge [143]. Multiwalled CNTs [145], single-walled CNTs [154], single-walled carbon nanohorns [146], multishelled carbon NPs [155], and carbon NPs [156] were all synthesized using this arc discharge method. They also presented the synthesis of Gd-hybridized single-wall carbon nanohorns using a graphite-rod anode doped with 0.8 mol% Gd [157]. The formation of single-walled carbon nanohorns dispersed with NPs of a Pd alloy was recently reported using a gas-injected arc-in-water method, in which the graphite rod and solid Pd alloy acted as raw materials [158]. Other research groups have also reported on arc discharge methods for NM synthesis [147–152], with a recent trend in this category of fabricating carbon NM-supported metal NPs for fuel cells application [150, 151].

Figure 2(ii-8) shows the spark discharge method [166, 167], which involves a spark discharge reaction conducted in an autoclave. Pure metallic plates were used as the electrode, pure metallic pellets with diameters of 2–6 mm as starting materials, and liquid ammonia and n-heptane as dielectric liquid media.

Sergienko et al. reported electric plasma discharge in an ultrasonic cavitation field [246–249, 252, 253] as shown in Figure 2(ii-9), in which an iron tip was fixed on top of a titanium ultrasonic horn and two wire electrodes were inserted 1 mm away from the iron tip [249]. They explained that an
ultrasonic cavitation field enhanced electrical conductivity due to the radicals and free electrons formed within it, which allowed for an electric plasma discharge to be generated at a relatively low electric power.

Wire explosion processes in water [168] can also be included in Group ii, as shown in Figure 2(ii-10), in which the stored electrical energy of a capacitor is released through a triggered spark gap switch to the wire. The electrical energy is dissipated mainly in the wire because its resistivity is very low compared to distilled water. Thus, the part of wire located between the electrodes is heated, vaporized, and turned into plasma, eventually allowing for NP formation.

For configurations ii-1 to ii-10, the direct discharge occurs between two solid electrodes. In the case of DC diaphragm discharge [169] (ii-11) and AC capillary discharge [170] (ii-12), the electrode is the electrolyte itself. When a high voltage is applied on electrodes separated by a dielectric barrier (diaphragm) with a small pinhole in it, the discharge is ignited just in this pinhole [169]. The diaphragm discharge does not reach the electrode surface and thus the electrode erosion is minimized and the electrode lifetime is prolonged in this configuration. During discharge, the material surrounding the pinhole was damaged. While diaphragm discharge has mainly been applied to water purification, this discharge also has potential for use in NM synthesis.

Summary. As compared to Group i, Group ii plasma generation techniques use spark or arc discharge with high excited temperature. Here, both ions in the liquid and electrode can be used as the NM source. Because of the direct discharge, it is not necessary to consider the conductivity of the liquid. The distilled water, organic solvent, and LN can be applied in this system. This group of techniques is used for the synthesis of carbon-based NMs by using graphite rods or organic solvent as the raw materials. When the NMs are precipitated from the liquid, impurities from the electrode should be carefully considered. The use of diaphragm discharge or capillary discharge is an attractive solution to this problem. The solid electrodes allow the synthesis of NMs with high degree of purity by using distilled water. On the other hand, for continuous NM production, a continuous supply method of metallic wire such as wire explosion will be required.

2.3. Contact Discharge between an Electrode and the Surface of Surrounding Electrolyte. In 1963, Hickling and Ingram reported contact glow discharge electrolysis (CGDE) [204], where a high-temperature plasma sheath was formed between an electrode and the surface of the surrounding electrolyte due to a high electric field, accompanied by a glow discharge photoemission. This model of plasma formation using CGDE was also supported by Campbell et al. [171], Sengupta et al. [208], and Azumi et al. [207]. In CGDE, two electrodes are immersed in a conductive electrolyte and the distance between them is changeable from 5 to over 100 mm. The electrode surface area is different between the anode and cathode. One electrode has a smaller surface area than the other. The electrode surface which has small surface area is covered with a thin film of water vapor, and the discharge proceeds inside this thin film. Schematics of CGDE are given in Figure 3. In most cases, the cathode consists of a metal plate with a large surface area such as a Pt mesh, while the anode is a metal wire. A stable DC power supply is often used, but sometimes pulsed DC can be applied.

In order to synthesize NPs from CGDE, two different methods are possible. One is the dissolution of one of the electrodes used in the process, while the other is from the particle species dissolved in the liquid electrolyte. Lal et al. reported the preparation of Cu NPs using a CuSO$_4$ + H$_2$SO$_4$ solution [172] and this technique. They also produced Pt, Au, and Pt/Au alloy NPs in a H$_3$PtCl$_6$ + NaAuCl$_4$ + HClO$_4$ electrolyte by using the configuration seen in Figure 3(iii-1) [172]. The formation of various metal and oxide NPs has been reported by the dissolution of the electrode wire [173–187, 195, 201]. For metal NP synthesis, selection of the electrolyte is important. Cu and Sn NPs were produced using citric acid and KCl solutions, respectively [178, 184]. In addition, the electrode configuration also affected the product composition. In the cases of iii-1 and iii-2, the current tends to be concentrated at the tip of the electrode, which causes oxidation and agglomerations of the particles. To avoid producing an inhomogeneous electric field, the electrode tip was shielded by a glass tube (iii-3) [177, 179, 185, 200]. The metal-plate electrode was also applied to CGDE, in which the side of the metal plate was covered to avoid the current concentration to the edge (iii-4) [201, 202]. Alloy NPs of stainless steel, Cu-Ni, and Sn-Pb were also synthesized from alloy electrodes [188, 200]. These configurations were also applied for degradation of dye in solution [205, 206, 209–212].

Summary. The simple Group iii configuration allows us to customize the setup more easily, where the distance between the two electrodes does not affect the plasma generation dramatically. The size and shape of the electrode can be changed. However, the liquid that can be used is limited to a conductive solution because vapor formation triggers plasma generation. Since the generated glow-like plasma in Group iii does not effectively reduce the metal ions in the solution, a solid electrode is often used as the raw materials for NM synthesis. Since the plasma is generated over the entire electrode surface, NMs can be continuously generated in the reactor. Unlike Group ii, in Group iii configuration, it is difficult to fabricate composite NMs as they are immediately quenched by the surrounding solution. However, this quenching is beneficial in the production of nonoxidized metal NPs. The challenges for the future include product minimization and a decrease in the input energy, which is mainly consumed in the resistive heating of the solution.

2.4. Radio Frequency and Microwave Plasma in Liquid Techniques. Techniques for generating plasma in liquid by irradiation with RF or MW have been utilized in a variety of fields. Such techniques are considered to be effective to generate plasma at lower electric power. RF and MW plasma can be generated and maintained in water over a wide range of water conductivity (0.2 ∼ 7000 mS/m). When plasma is generated in a solution using RF or MW, lower pressure is often applied because energy is absorbed in water with dielectric constant and dielectric loss. Nomura et al. have demonstrated the
synthesis of NPs by using RF and MW plasma under pressures ranging from 10 to 400 kPa. Configurations (iv-1), (iv-2), and (iv-3) in Figure 4 show different configurations of plasma generation using RF irradiation. Plasma was generated in water by irradiation at a high frequency of 13.56 MHz, with the plasma bubbles forming around the electrode [215–217]. Optical emission spectroscopy and a high-speed camera were used to investigate this plasma in detail. WO$_3$, Ag, and Au NPs were also produced by RF plasma, by using a plate to control the behavior of the plasma and the bubbles, which in turn enhanced the production rate of NPs (iv-3) [226]. MW plasma can also be generated in liquid media. In the case of MW, a MW generator and waveguide are required. Similar to the RF plasma, the metal plate was placed 4 mm away from the tip of the electrode [233]. To produce Ag, ZnO, and WO$_3$ NPs, a precursor rod with a diameter of 1-2 mm was inserted vertically through the top of the reactor vessel (iv-5) [233, 234].

The generation of MW plasma in liquid media has been reported by others. Yonezawa et al. have reported the generation of MW plasma at atmospheric pressure to produce ZnO [236], Ag [237], and Pt [237] NPs as shown in Figure 4(iv-7). Slot-excited MW discharge (iv-8) [238] and MW irradiation by MW oven (iv-9) [239, 240] are also reported; as the frequency of the MW oven is regulated to be fixed at 2.45 GHz, the wavelength of MW surrounding the oven is 122.4 mm. The configuration, including distance of electrodes, size, and other parameters, is selected based on the wavelength for MW resonance.

**Summary.** Among the various types of plasma, RF and MW plasma has been newly applied for NM synthesis. This technology shows promise in NM synthesis, including composite NM synthesis and element doping. Different from Group iii, distilled water can be used in RF and MW plasma. This is an advantage for NMs synthesis without impurities. Compared to DC and AC, generation of RF and MW required special equipment. Recently, these power sources are commercially available. Since the bubble formation surrounding electrode is important for plasma generation, the electrode shape and configuration should be sophisticated. Research on reaction area surrounding the electrode and evaluation of energy efficiency is also required in the future.

### 3. Nanomaterials Produced by Plasma in Liquid Techniques

The various types of plasma discussed previously have been applied for producing NMs. Figure 5 shows a breakdown of papers published on NM synthesis by plasma in liquid, based on the composition of the target NM. A large number of papers regarding the synthesis of noble metal NPs (Au, Pt, Pd, and Ag) have been published because noble metal ions are more easily reduced. In particular, the synthesis of Au NPs is
Figure 4: Showing configurations of radio frequency and microwave plasma in liquid techniques; (iv-1) [215–222], (iv-2) [223–225], and (iv-3) [226], (iv-4) [220, 227–232], (iv-5) [233, 234], and (iv-6) [235], (iv-7) MW-induced plasma in liquid [236, 237], (iv-8) slot-excited MW discharge [238], and (iv-9) MW irradiation by MW oven [239, 240].

Figure 5: Breakdown of papers published on NM synthesis by plasma in liquid, based on the composition of the target NM with different categories of (i) gas discharge, (ii) direct discharge, (iii) contact discharge, and (iv) RF and MW plasma.
often used in such studies because colloidal Au NP solutions display a red color, owing to their surface plasmon resonance, which affords an easy way to confirm NP formation. NPs comprised other metals such as Ni, Cu, Fe, and Sn which have also been synthesized. The (ii) direct discharge between two electrodes method has been applied for producing carbon NMs and composite materials of metal and carbon, in which the solid carbon electrode is used as a source material.

Three methods exist for supplying raw materials for NP formation. First, the metal ions can be present in the liquid, such as AgNO₃, HAuCl₄, and H₂PtCl₄, which can then be reduced by the plasma to form metallic NPs. In this process, the product size is controlled by the plasma irradiation time and surfactant. The solution, IL, molten salt, or organic solvent can be used as a liquid. Second, conductive solid electrode of metal wire, plate, pellet, and carbon rod can be consumed during plasma generation to form NPs. The merit of this method is its versatility for use with different raw materials such as metals, alloys, and carbon. Moreover, in the limited case of DC plasma, the metallic anode is sometimes anodically dissolved as metal ions, which are then reduced by the plasma generated near the cathode to produce metallic particles. This section focuses on the produced NMs, their raw materials and used configurations for these studies.

3.1. Noble Metals. Metal NPs containing Au, Ag, Pd, and Pt were synthesized using various types of plasma techniques, as shown in Table 1. Size control of the synthesized NPs is the main subject of this category. In most cases, spherical NPs with diameter less than 10 nm are produced. In other instances, nanorods and polygonal NPs are generated [20, 91, 96] instead. The ultraviolet-visible (UV-vis) spectra of NPs dispersed in solution were measured due to their observable surface plasmon resonances; it is well known that the resonance wavelength varies with size and shape of the particle and hence this method of analysis can be used as another way to confirm a desired synthesis. In the case of (i) gas discharge, the IL is used because it does not evaporate under vacuum conditions. However, when (iii) contact discharge was applied, the liquid was limited to the conductive solution. To supply the source materials, two methods are commonly used: metallic electrodes and ions of chlorides or nitrates. NP synthesis using metallic electrodes is a surfactant-free and high-purity method; however, size control of the synthesized particles is difficult in this technique. Conversely, the plasma reduction of metal ions with a surfactant allows for synthesis with a high degree of size control. Recently, this technology has extended to the field of noble metal alloy and composite NPs such as Pt supported on carbon.

3.2. Other Metals. In spite of their instability at high temperatures, NPs of Ni, Cu, Zn, and Sn have been synthesized by plasma in a solution (Table 2). Generally, these materials can react with water vapor, which causes them to undergo oxidation. However, in the solution plasma the short reaction time and cooling effect of surrounding water might prevent the produced NPs from undergoing oxidation. Additionally, experimental conditions such as electrode temperature, electrolyte additives, and solution pH were carefully optimized to fabricate metal NPs. For producing Cu NPs, surfactant of cetyltrimethylammonium bromide (CTAB) and ascorbic acid as the reducing agent were added to the solution [241]. Gelatin and ascorbic acid were selected as the capping agents to protect the particles against coalescence and oxidation side reactions [85]. In addition, Cu NPs were formed in a citrate buffer where Cu₂O was stable at low concentrations in a K₂CO₃ electrolyte (0.001 M); the clear formation of CuO was observed with increasing K₂CO₃ electrolyte concentration (0.01–0.5 M). These results were consistent with the Cu E–pH diagram [178]. Compared to the aforementioned materials, Al, Ti, Fe, and Zr are more active and undergo oxidation more readily. Therefore, a solution-based synthesis has not been reported for these metals, and molten salts are most frequently used to synthesize them as these salts do not contain oxygen.

3.3. Alloys and Compounds. Techniques for plasma generation in liquid have been used to synthesize alloy NPs with unique properties suitable for many applications. Noble bimetallic alloy NPs have been investigated for plasmonics-related applications, catalysis, and biosensing, utilizing properties that can be tuned by changing the composition [67]. Similar to noble-metal NP synthesis, metal ions in solution or solid electrodes were supplied as raw materials (Table 3). In the case of the solid electrodes, an alloy electrode [188, 200] and a pair of two different pure-metallic electrode [88] were used. Magnetic NPs of Co-Pt, Fe-Pt, and Sm-Co have also been synthesized using plasma in molten salt for use in ultra-high density hard drives, bioseparations, and sensors applications [43, 45, 48, 49, 76]. Compounds of Co-B, MoS₂, and ZnMgS were also synthesized, using a KBH₄ solution and liquid sulfur.

3.4. Oxides. When oxide NMs were synthesized via techniques for plasma generation in liquid, the solid electrode was consumed under high-temperature plasma conditions (such as arc discharge), followed by the subsequent reaction of produced NPs or generated metal vapor with the surrounding electrolyte to synthesize oxide NPs (Table 4). From the Cu electrode, the CuO nanorods with a growth direction of [010] were produced [82, 178]. ZnO nanorods or nanoflowers with a growth direction of [001] were also synthesized [82, 176]. It is believed that the precursor ions Cu(OH)₂⁺ and Zn(OH)₂⁻ were generated and precipitated to form rod-like structures. During the oxide precipitation, the surfactant and liquid temperature also affected the final morphology and composition of the synthesized NMs [180]. Because the products are quickly synthesized and immediately cooled down in the plasma process in liquid, the synthesized oxide crystals tend to have lower crystallinity. Sometimes, metastable phases and defect structures were observed after synthesis. When the ZnO nanospheres were formed in the agitated solution, the produced particles contained a large amount of defects [186]. The formation of TiO₂₄ phase was also reported [183].

3.5. Silicon. Si NPs have the potential to be applied to anode materials for lithium-ion batteries, optoelectronic devices,
### Table 1: Noble metal NP synthesis via techniques for plasma generation in liquid.

<table>
<thead>
<tr>
<th>NPs</th>
<th>Raw materials</th>
<th>Liquid</th>
<th>Configuration and reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Au rod or wire</td>
<td>Solution</td>
<td>ii-1: solution plasma (pulsed) [81, 87, 101] (AC) [103], ii-5: arc discharge [140], iii-1: plasma electrolysis (DC) [174, 185], iii-3: electric discharge (DC) [185, 200], and iv-3: RF plasma (20 kPa, 27.14 MHz) [226]</td>
</tr>
<tr>
<td></td>
<td>LN</td>
<td>Ethanol</td>
<td>ii-1: solution plasma (pulsed) [87, 93]</td>
</tr>
<tr>
<td></td>
<td>Au plate</td>
<td>Solution</td>
<td>iii-4: solution plasma (DC) [201]</td>
</tr>
<tr>
<td>Au</td>
<td>Au metal foil</td>
<td>Solution</td>
<td>i-7: microplasma [58]</td>
</tr>
<tr>
<td></td>
<td>HAuCl₄</td>
<td>Solution</td>
<td>i-1: influence of glow discharge [20, 22], i-4: gas–liquid interfacial discharge plasma [32], i-6: gas–liquid interfacial discharge plasma [32], i-7: plasma–liquid interactions [15], plasma-induced liquid chemistry [64], microplasma [66], i-8: DC glow discharge [78], ii-1: solution plasma (DC 0.9–3.2 kV, 12–20 kHz, bipolar pulsed) [79, 83, 91, 93, 94, 96–98], ii-4: solution plasma (DC 960 V, 15 kHz, pulsed) [128], and ii-5: arc discharge [131]</td>
</tr>
<tr>
<td>NaAuCl₄</td>
<td>IL</td>
<td></td>
<td>i-1: room temperature plasma [19], influence of glow discharge [18], i-4: plasma electrochemistry [36], and i-4: gas–liquid interface plasma [29]</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag rod or wire</td>
<td>Solution</td>
<td>i-5: arc discharge [132], submerged arc [139], electric spark discharge [141], i-10: wire explosion [168], ii-1: plasma electrolysis (DC) [174, 185], iv-3: RF plasma in water (20 kPa) [226], iv-5: MW plasma [233], and iv-7: MW-induced plasma [237]</td>
</tr>
<tr>
<td></td>
<td>Molten salt</td>
<td></td>
<td>i-6: discharge electrolysis (DC 200–400 V) [42]</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag metal foil</td>
<td>Solution</td>
<td>i-7: microplasma [58]</td>
</tr>
<tr>
<td></td>
<td>AgNO₃</td>
<td>Solution</td>
<td>i-7: microplasma [60, 63], i-8: DC glow discharge [78], ii-1: liquid phase plasma reduction (25–30 kHz) [111], and ii-5: Arc discharge [133]</td>
</tr>
<tr>
<td></td>
<td>IL</td>
<td></td>
<td>i-4: plasma electrochemistry in ILs [34, 36]</td>
</tr>
<tr>
<td>Pd</td>
<td>PdCl₂</td>
<td>IL</td>
<td>i-1: influence of glow discharge plasmas [18] and i-4: plasma electrochemistry [36]</td>
</tr>
<tr>
<td>Pt</td>
<td>Pt wire</td>
<td>Solution</td>
<td>ii-1: plasma sputtering (DC 15 kHz) [80], ii-3: cathodic contact glow discharge (DC) [182], and iv-7: MW-induced plasma [237]</td>
</tr>
<tr>
<td></td>
<td>Pt plate</td>
<td>IL</td>
<td>i-4: gas–liquid interfacial plasmas [27]</td>
</tr>
<tr>
<td></td>
<td>H₂PtCl₆</td>
<td>Solution</td>
<td>i-7: plasma–chemical reduction [37] and iii-1: electrochemical discharges (DC) [172]</td>
</tr>
</tbody>
</table>

### Table 2: Other metal NP syntheses via techniques for plasma generation in liquid.

<table>
<thead>
<tr>
<th>NPs</th>
<th>Raw materials</th>
<th>Liquid</th>
<th>Configurations and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Al plate</td>
<td>Molten salt</td>
<td>i-6: plasma-induced cathodic discharge electrolysis (DC) [43]</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti disk</td>
<td>Molten salt</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>Fe plate</td>
<td>Molten salt</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>CoCl₂</td>
<td>Solution</td>
<td>ii-1: liquid-phase plasma (pulsed) [110]</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni wire</td>
<td>Solution</td>
<td>iii-1: cathodic contact glow discharge (DC) [182], plasma electrolysis [174, 175, 182, 192], iii-2: solution plasma (DC) [177, 179, 185]</td>
</tr>
<tr>
<td></td>
<td>Ni disk</td>
<td>Molten salt</td>
<td>i-6: plasma-induced cathodic discharge electrolysis (DC) [43, 46, 47]</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu wire</td>
<td>Ethylene glycol</td>
<td>i-6: arc discharge (AC) [51], ii-3: arc discharge (pulsed) [241], iii-1: solution plasma (DC) [178], and iii-3: electric discharge plasma (DC) [200]</td>
</tr>
<tr>
<td></td>
<td>CuCl₂</td>
<td>IL</td>
<td>i-5: SANS [138]</td>
</tr>
<tr>
<td></td>
<td>CuSO₄</td>
<td>Solution</td>
<td>i-1: pulsed electrical discharge (AC or DC) [113] and ii-1: solution plasma (pulsed) [85]</td>
</tr>
<tr>
<td></td>
<td>CuCl, CuCl₂</td>
<td>IL</td>
<td>i-1: electrochemical discharges (DC) [172] and i-4: plasma electrochemistry [37]</td>
</tr>
<tr>
<td>Zn</td>
<td>zinc plate</td>
<td>Solution</td>
<td>iv-4: MW plasma [230]</td>
</tr>
<tr>
<td>Ge</td>
<td>GeCl₂C₆H₆O₂</td>
<td>IL</td>
<td>i-4: plasma electrochemistry [36]</td>
</tr>
<tr>
<td>Zr</td>
<td>Zr plate</td>
<td>Molten salt</td>
<td>i-6: plasma-induced cathodic discharge electrolysis (DC) [43]</td>
</tr>
<tr>
<td>Sn</td>
<td>Sn rod</td>
<td>Solution</td>
<td>iii-1: solution plasma (DC) [184, 187]</td>
</tr>
<tr>
<td>NPs</td>
<td>Raw materials</td>
<td>Liquid</td>
<td>Configurations and references</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------------------------</td>
<td>--------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Au-Ag</td>
<td>HAuCL₄, AgNO₃</td>
<td>Solution</td>
<td>i-7: microplasma-chemical synthesis [67]</td>
</tr>
<tr>
<td>Au core-Ag shell</td>
<td>HAuCL₄, AgNO₃</td>
<td>Solution</td>
<td>i-8: dual plasma electrolysis [78]</td>
</tr>
<tr>
<td>Pt-Au</td>
<td>H₂PtCl₆, NaAuCl₄</td>
<td>Solution</td>
<td>ii-i: solution plasma sputtering (DC, pulsed) [88]</td>
</tr>
<tr>
<td>Ag-Pt</td>
<td>Ag and Pt wires</td>
<td>Solution</td>
<td>ii-i: arc-discharge solution plasma (DC, pulsed) [89]</td>
</tr>
<tr>
<td>Co-Pt</td>
<td>CoCl₂, PtCl₂</td>
<td>Molten salt</td>
<td>i-6: plasma-induced cathodic discharge electrolysis [76]</td>
</tr>
<tr>
<td>Fe-Pt</td>
<td>FeCl₂, PtCl₂</td>
<td>Molten salt</td>
<td>i-6: plasma-induced cathodic discharge electrolysis [49]</td>
</tr>
<tr>
<td>Sm-Co</td>
<td>SmCl₃, CoCl₂</td>
<td>Molten salt</td>
<td>i-6: plasma-induced cathodic discharge electrolysis [48]</td>
</tr>
<tr>
<td>Ni-Cr</td>
<td>Alloy wire</td>
<td>Solution</td>
<td>iii-i: solution plasma (DC) [188]</td>
</tr>
<tr>
<td>Sn-Ag</td>
<td>Alloy wire</td>
<td>Solution</td>
<td>iii-i: electric discharge plasma [200]</td>
</tr>
<tr>
<td>Sn-Pb</td>
<td>Alloy wire</td>
<td>Solution</td>
<td>iii-i: solution plasma (DC) [188]</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>Alloy wire</td>
<td>Solution</td>
<td>iii-i: solution plasma (DC) [188], electric discharge plasma [200]</td>
</tr>
<tr>
<td>Co-B</td>
<td>Co acetate, KBH₄</td>
<td>Solution</td>
<td>ii-i: solution plasma (pulsed) [125]</td>
</tr>
<tr>
<td>MoS₂</td>
<td>MoS₂ powder</td>
<td>Solution</td>
<td>ii-i: arc in water (DC 17 V, 30 A) [159]</td>
</tr>
<tr>
<td>ZnMgS</td>
<td>ZnMg alloy</td>
<td>Liquid sulfur</td>
<td>ii-i: pulsed plasma in liquid (AC) [118]</td>
</tr>
</tbody>
</table>

**Table 4: Oxide NM synthesis via techniques for plasma generation in liquid.**

<table>
<thead>
<tr>
<th>NMs</th>
<th>Raw materials</th>
<th>Liquid</th>
<th>Configurations and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)₂</td>
<td>Mg rod</td>
<td>Solution</td>
<td>iv-i: MW plasma [233]</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Al rod</td>
<td>Solution</td>
<td>ii-i: arc-discharge (DC) [242]</td>
</tr>
<tr>
<td>γ-Al₂O₃, α-Al₂O₃</td>
<td>Al rod</td>
<td>Solution</td>
<td>ii-i: arc-discharge (DC) [152]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>TiCl₄</td>
<td>Solution</td>
<td>i-i: arc-discharge (AC) [26]</td>
</tr>
<tr>
<td></td>
<td>Ti(OCH₃)₂H₄</td>
<td>Ethanol</td>
<td>iii-i: plasma electrolytic deposition (DC) [191]</td>
</tr>
<tr>
<td></td>
<td>Ti foil</td>
<td>Solution</td>
<td>ii-i: electrochemical spark discharge (DC) [129]</td>
</tr>
<tr>
<td></td>
<td>Ti rod</td>
<td>Solution</td>
<td>ii-i: arc-discharge (DC) [137], iii-i: plasma electrolysis (DC) [174, 181], and iii-i: high-voltage discharge (DC) [195]</td>
</tr>
<tr>
<td>TiO₂₋ₓ</td>
<td>Ti rod</td>
<td>Solution</td>
<td>iii-i: plasma discharge (DC) [183, 185]</td>
</tr>
<tr>
<td></td>
<td>Ti plate</td>
<td>Solution</td>
<td>iii-i: solution plasma (DC) [201]</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>BaTiO₃ powder</td>
<td>Solution</td>
<td>ii-i: arc-discharge (DC) [165]</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Fe rod</td>
<td>Solution</td>
<td>ii-i: pulsed plasma [117] and iii-i: solution plasma (DC) [185]</td>
</tr>
<tr>
<td>CoO</td>
<td>Co(II) acetate tetrahydrate</td>
<td>Solution</td>
<td>ii-i: discharge plasma (DC, pulsed, 20 kHz) [109]</td>
</tr>
<tr>
<td>CuO</td>
<td>Cu rod</td>
<td>Solution</td>
<td>i-i: arc discharge (DC) [51], ii-i: plasma-induced technique (pulsed DC) [82], ii-i: SANSS [138], and ii-i: arc discharge [152]</td>
</tr>
<tr>
<td></td>
<td>Cu sheet</td>
<td>Solution</td>
<td>iii-i: solution plasma (DC) [178]</td>
</tr>
<tr>
<td></td>
<td>CuCl₂</td>
<td>Solution</td>
<td>i-i: arc discharge (DC) [51], ii-i: SANSS [138], and iii-i: solution plasma (DC) [178]</td>
</tr>
<tr>
<td></td>
<td>i-i: microplasma (Ar) [65]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>Zn rod</td>
<td>Solution</td>
<td>ii-i: electric discharge (DC pulsed) [82, 112, 114] (DC) [113], ii-i: arc discharge (DC (DC pulsed) [126], ii-i: submerged arc discharge (DC) [134], iii-i: solution plasma (DC) [176, 186], iv-i: MW plasma [230], and iv-i: MW plasma [233]</td>
</tr>
<tr>
<td></td>
<td>Zn plate</td>
<td>Solution</td>
<td>iii-i: solution plasma (DC) [201]</td>
</tr>
<tr>
<td></td>
<td>ZnO powder</td>
<td>Solution</td>
<td>ii-i: arc discharge (DC) [165]</td>
</tr>
<tr>
<td></td>
<td>zinc acetate</td>
<td>Solution</td>
<td>iv-i: MW-induced plasma [236]</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Zr rod</td>
<td>Solution</td>
<td>ii-i: arc discharge (DC) [136]</td>
</tr>
<tr>
<td>Ru₂O₃</td>
<td>RuCl₃</td>
<td>NaOH</td>
<td>i-i: dielectric barrier discharge (Ar + O₂) [24]</td>
</tr>
<tr>
<td>SnO</td>
<td>Sn rod</td>
<td>Solution</td>
<td>iii-i: solution plasma (DC) [180]</td>
</tr>
<tr>
<td>Ta₂O₃</td>
<td>Ta rod</td>
<td>Solution</td>
<td>ii-i: DC arc discharge [243]</td>
</tr>
<tr>
<td>WO₃</td>
<td>W rod</td>
<td>Solution</td>
<td>ii-i: arc discharge (DC) [130], iv-i: RF plasma [226], and iv-i: MW plasma [234]</td>
</tr>
</tbody>
</table>
Table 5: Silicon NP synthesis via techniques for plasma generation in liquid.

<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Liquid</th>
<th>Configurations and references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si disk</td>
<td>Molten salt</td>
<td>i-6: Plasma-induced cathodic discharge electrolysis [43]</td>
</tr>
<tr>
<td>SiO₂ particle</td>
<td>Molten salt</td>
<td>i-6: Plasma-induced cathodic discharge electrolysis [44]</td>
</tr>
<tr>
<td>Silicon wafer</td>
<td>Ethanol</td>
<td>i-7: microplasma-induced surface engineering [61]</td>
</tr>
<tr>
<td>Si electrode</td>
<td>LN</td>
<td>ii-5: arc discharge (DC) [244]</td>
</tr>
<tr>
<td>Si rod</td>
<td>Solution</td>
<td>ii-6: arc discharge (DC) [149], iii-1: solution plasma (DC) [194], iii-2: high-voltage discharge (DC) [195], and iii-3: electric discharge plasma (DC) [200]</td>
</tr>
</tbody>
</table>

full-color displays, and optoelectronic sensors. As shown in Table 5, techniques for plasma generation in liquid have been applied to Si NP synthesis. Molten salt systems have been used to synthesize Si NPs, in which the electrochemical reduction of SiO₂ particles occurs according to the following [44]:

\[
\text{SiO}_2 + 4e^- \rightarrow \text{Si} + 2\text{O}_2^{-} \quad (1)
\]

When a Si rod was used as an electrode to produce Si NPs in solution, the electric conductivity of Si electrode was an important factor because high-purity Si has high electric resistance. To prevent the electrode from overheating, a Si rod with an electric resistance of 0.003–0.005 Ω·cm was used [194, 244].

3.6. Carbon. A wide variety of carbon NMs have been synthesized using plasma in liquid, in which the graphite electrode was consumed during arc discharge (Table 6). The organic solvent was also used as a carbon source. Under high-temperature plasma conditions, carbon atom sublimation and subsequent reaggregation into solid carbon have been shown to occur [250]. When catalytic particles such as Ni, Fe, and Co are present in the reaction field, CNT generation can be enhanced as well [154]. The decomposition of organic solvents such as toluene, ethanol, and butanol is also used for synthesizing carbon NMs. For toluene in particular, the decomposition is expected to occur uniformly because of its symmetric structure [107]. During plasma generation in alcohol, 2,3-butanediol, phenylethylenyl, indene, naphthalene, and biphenylene can be formed as by-products [54]. Arc discharge methods have also been applied for synthesizing composite materials of carbon and metal NPs.

3.7. Composite Materials. Table 7 shows published trends for composite NM synthesis via techniques for plasma generation in liquid. Noble metal NPs such as Au, Pt, Pd, and Ag supported on carbon NMs have been synthesized via solution plasma because these composite materials have great potential for catalysis, electroanalysis, sensors, fuel cells, and Li-air batteries. In these instances, carbon was sourced from graphite rods, benzene, and carbon powders, while the noble metals were supplied from metallic rods or metal ions in solution. In other reports, magnetic metal NPs encapsulated in carbon or other organic and inorganic coatings could be used in medicine as localized RF absorbers in cancer therapy, bioengineering applications, and drug delivery [116, 150]; the carbon coating provides good biocompatibility while protecting from agglomeration. They also have physical applications such as magnetic data storage, electromagnetic-wave absorption, and ferrofluids. Co, Ni, and Fe NPs encapsulated in carbon have been synthesized by techniques for plasma generation in liquid, where an ethanol solvent was used as a carbon source.

4. Summary of Recent Developments and Future Research

4.1. Applications of Synthesized NMs. During the early stages of development of the field of NM synthesis, the synthesis of noble metal NPs was reported, in which their particle size, crystal structure, and UV-vis properties were evaluated. Over the years, the field has expanded gradually with studies on the various applications of the synthesized NMs such as catalysis, fuel cells, battery electrodes, magnetic materials, and nanofluids. Composite materials and alloy NPs have been synthesized recently in order to further enhance the properties of NMs. However, synthesized materials have already been reported from other methods. Although plasma in liquid has many advantages, it is very essential to fabricate noble NMs only by the plasma in liquid technique.

4.2. Formation Mechanism of NMs. Recent research has clarified the plasma characteristic of excitation species, excitation temperature, and current density by using the optical emission spectroscopy where high speed camera investigated the plasma generation. These studies are very helpful to understand the plasma phenomena. However, the mechanism of NM synthesis is still unclear because of the difficulty associated with in situ observations during NM formation. In the case of the chemical reduction route, the excited species and possible reactions have been discussed. On the other hand, NM synthesis from solid electrodes, used as raw materials, requires an understanding of the interfacial phenomena between the liquid and solid electrode surface. The change in surface morphology will be helpful for the prediction of the surface phenomena. Besides, physical models and a comparison of parameters with the theoretical values are also important, especially for the effective production and control of NMs.

4.3. Energy Efficiency and Productivity. In published research articles, authors often mention the advantages of techniques for plasma generation in liquid, such as simple setup, high energy efficiency, and high productivity. However, the actual measurement of energy efficiency and productivity is rarely reported. For example, Sn NPs were synthesized at 45 Wh/g by using plasma in liquid [184]. Such quantitative information can be effective in explaining the advantages of the plasma in liquid technique. The authors should mention the total...
amount of material (kg/hour) and the input energy (W) along with a comparison with other NM synthesis methods.

### 4.4. Scale-Up and Continuous Processes.

The presented setups of the plasma in liquid technique are operated on a batch scale with a small cell size. To produce large amounts of NMs, scale-up and continuous processes are necessary. It is possible to have a continuous flow design with the use of metal ions in the liquid as the source materials of NMs. In the case of solid electrode, the electrode needs continuous supply. Additionally, we should consider the total process containing the supplement of raw materials, synthesis, separation of products, purification, and dispersion. As a case of success, NP synthesis by using supercritical fluid technology has been reported by Byrappa et al. [254]. They have developed a continuous setup with a productivity of 10 t/year, where the technology of dispersion of synthesized NMs was most important for application.

### 5. Conclusion

In this review, the configuration of techniques for plasma generation in liquid was systematically presented. By examining their electrode configurations and power sources, all available plasma in liquid was classified in four main groups, and the features of each group and the relevant studies were discussed in detail. Further, the formation of NMs composed of metals, alloys, oxides, silicon, carbon, and composites produced by techniques for plasma generation in liquid was presented,
and the source materials, liquid media, and electrode configuration were summarized. Metal ions in liquid or solid electrodes were mainly used to supply source materials for NP formation. The used liquid was not limited to the distilled or electrolyte solution, as organic solvent, IL, LN, and molten salt were also applied in such techniques. The arc discharge method has been mainly adopted to synthesize carbon-based materials. In contrast, the glow-like plasma method was used for metal NP synthesis. Techniques for plasma generation in liquid for NM synthesis still remain an area of research, including process scale-up, design of produced NMs, and applications of produced NMs. The authors hope that this review of NM synthesis using techniques for plasma generation in liquid will help to lead the way for enhanced NM synthesis.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References


[57] C. Richmonds and R. M. Sankaran, “Plasma-liquid electrochemistry: rapid synthesis of colloidal metal nanoparticles by...


