REVIEWS

Glow discharge plasma electrolysis for nanoparticles synthesis

T. Abdul Kareem · A. Anu Kaliani

Abstract There are many methods available to synthesize nanomaterials and the glow discharge plasma electrolysis is a novel and a green method in this category. It is seen that most of the papers are published after 2005 and the interest in it is growing due to its applicability in the industry for preparing nanomaterials at large scale. But, only few results are available yet and most of them are on metal nanoparticle preparation, so that more studies are needed to understand the nature of growth of the nanoparticles under glow discharge in liquid and its applicability in preparing semi-conductor nanomaterials. Many have tried many methods to prepare nanoparticles by the glow discharge and a review like this is the need of the time to understand its present status that helps to modify the present situation to a better one. This review classifies all the available methods of nanomaterials synthesis in liquid by glow discharge in to three and it is discussed in detail.

Keywords Nanomaterials synthesis · Glow discharge plasma electrolysis

Introduction

As there is plenty of room at the bottom [1], we have plenty of methods to reach at the bottom. At the bottom, the nanoparticles behave differently even if they are made up of the same chemistry of their bulk counterpart. Peculiar properties are observed due to their size below a characteristic length scale of a specific property since most of their atoms are at their surface. There are many methods available today to synthesize nanomaterials, and of course, glow discharge plasma electrolysis is a new generation green technology in this category. It is seen that most of the papers discussing the synthesis of colloidal nanoparticles by glow discharge plasma are published after 2005 and the interest in it is growing due to its applicability in industrial production of nanomaterials at large scale. But, only few results are available now and most of them are on metal nanoparticle preparation, so that more studies are needed to understand the particle growth nature under glow discharge in liquid and its applicability in preparing semi-conductor nanoparticles. Many have tried many methods to synthesize nanoparticles in liquid under glow discharge and a review like this is the need of the time to understand its present status that helps to modify the present situation to a better one. This paper discusses the possibility of glow discharge electrolysis for the preparation of nanoparticles, since the glow discharge electrolysis occupy a special place among the new technologies developed to prepare nanomaterials due to the fact that the discharge allows one to create active species that can react with the selected target molecules very fast and very easily. There are three excellent reviews discussing the discharges and the chemical reactions when the discharge in and in contact with liquid [2–4] and a review on plasma liquid application in nanoscience [5], but those reviews have not given full attention to the colloidal nanomaterial preparations by plasma electrochemical method. Of course, this review will give you an insight into the nanoparticles preparation by glow discharge plasma.

Nanoparticles can be synthesized via solid [6–8], liquid, gas, and plasma phase routes [9–27]. For high purity

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products, gas-phase synthesis is most effective. Gas-phase synthesis methods are gas-phase condensation [8, 26–28] and flame pyrolysis [29, 30]. In the gas-phase condensation, the material is being vaporized using heated crucibles, electron or laser beam evaporation or sputtering, but when we replace the evaporative source with precursor for decomposition, then the gas-phase condensation is known as chemical vapor condensation or chemical vapor synthesis. In the case of flame pyrolysis, the gaseous or liquid precursors are decomposed by the combustion reaction.

Evaporation and condensation are also the basic principles of the thermal plasma-based nanoparticles synthesis. There are several ways to produce the fourth state of matter, plasma such as direct current plasma, microwave plasma, and radio frequency plasma.

A gas is called a plasma when it is partially ionized and having collective behavior [31, 32] by introducing energy that makes electrical breakdown so that the gas become electrically conductive. There are two kinds of plasma, thermal equilibrium plasma and non-thermal equilibrium
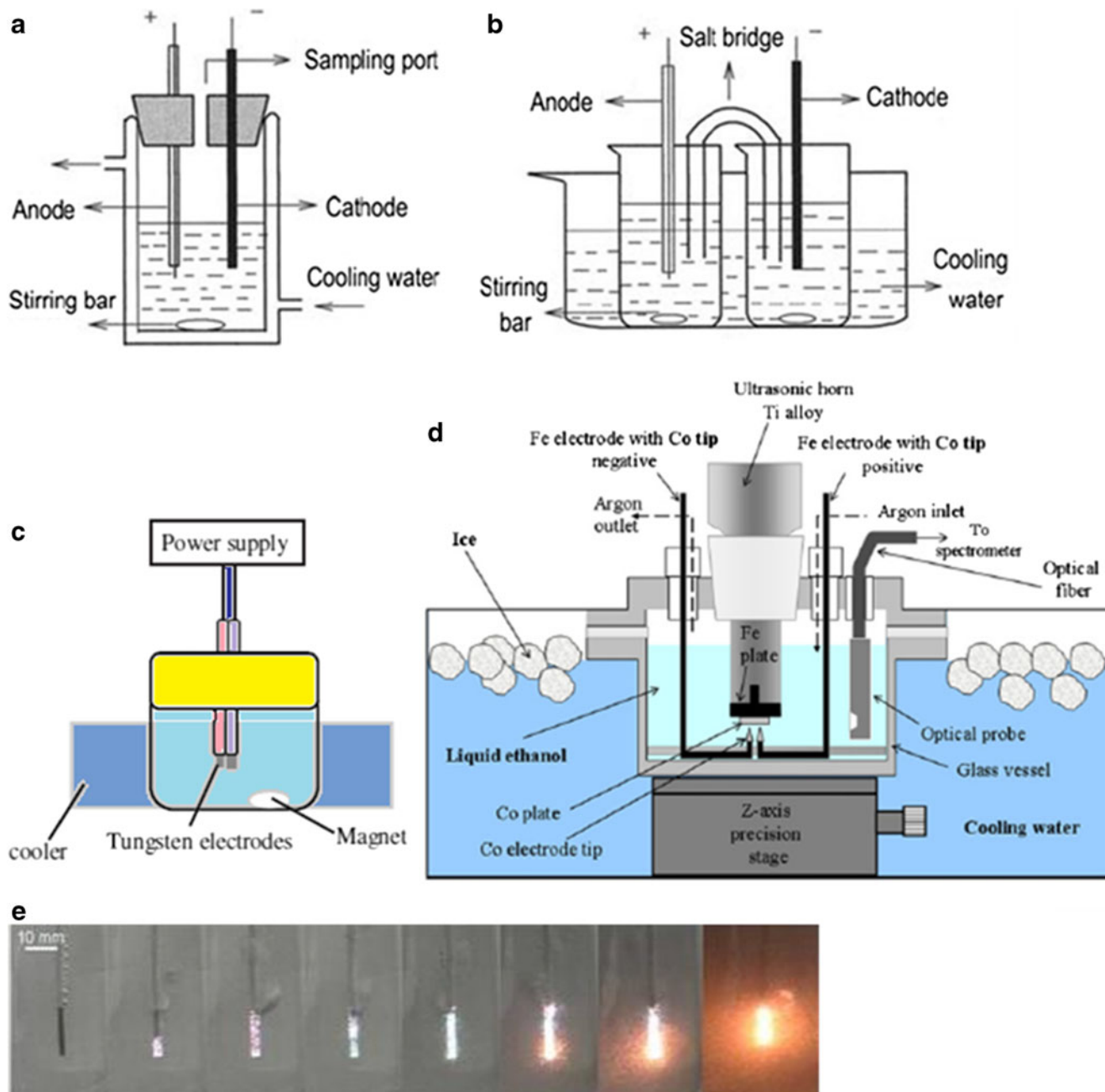

Fig. 1 a–d Experimental setup of glow discharge electrolysis, e photographs of the CGDE at different voltages (images from [59], [77], [82], Reproduced with permission of ELSEVIER S.A. and AMERICAN INSTITUTE OF PHYSICS in the format Journal via Copyright Clearance Center)

plasma. In the case of thermal equilibrium plasma, the temperature of all the electron, ion, and neutral species are the same, whereas in the case of non-thermal equilibrium plasma the temperature of all the species are not same, where electron has much higher temperature than other species. The importance of the non-thermal equilibrium plasma is that, non-thermal equilibrium plasma can drive high-temperature chemistry at low ambient temperatures using lower input energy.

Plasma can be produced by applying a potential difference between two electrodes inserted in a gas-filled cell. Electrons are accelerated away from cathode and collide with the gas atoms. The excited species due to the excitation collisions decays to lower levels by glow or emission of light. Ion–electron pair is produced due to ionization collision and the ions release secondary electrons when they are accelerated towards cathode. The release of secondary electrons gives more ionization collision and the plasma sustains. Plasma can be characterized by different quantities such as electron temperature, gas-phase composition, plasma gas enthalpy using characterization techniques like Langmuir probe, enthalpy probe, and spectroscopy.

In the case of DC glow discharge, a continuous potential difference is applied across the cathode and anode and this gives rise to a constant current. Glow discharge plasma [33] is a complicated gas mixture because of the interactions of a number of different plasma species, where the electron possesses energies in the range of 1–10 eV with density of about 10^9–10^{11} cm^{-3} [34].

In 1887, Gubkin [35] demonstrated the possibility of the electrolysis of aqueous solution of metallic salts using glow discharge and a new field of research was started called plasma electrochemistry. Plasma electrochemistry is the study of the interaction of plasma with the electrolyte solution, and it uses plasma to drive the chemical reactions. This paper reviews the nanomaterials synthesis using plasma electrochemical method. Nanomaterials synthesis using the classical electrochemical methods [36] comes under the liquid-phase synthesis and plasma electrochemical method is a fusion of liquid and plasma phases. Electrochemical reactions are taking place in between an electronic conductor (electrodes) and an ionic conductor (electrolyte) with charge transfer across the interface between these two. Electrochemical reactions are carried out using aqueous electrolytes [36], solid electrolytes [37, 38], and molten salts or ionic liquids or room-temperature ionic liquids [39–43]. In the case of plasma electrolysis, plasma can be considered as a conductive fluid because of the presence of ions and electrons.

Plasma electrolysis is a generic term used to describe high-voltage electrochemical processes where the plasma discharge occurs at the electrode–electrolyte interface.

Discharge phenomena have been observed in both positive and negative biasing of the electrodes, and depending on the electrode–electrolyte combination. Discharge vary in appearance with the gas used and the electrolyte solution. Many have studied about the discharges in electrode–electrolyte interface [35, 44–62] in the past for the degradation of toxic substances [63–68], but the plasma–liquid interaction is still not well-understood due to complex and dynamical nature of the plasma–liquid interface. Based on the discharge mechanism, electrodes positions with electrolyte, and the nature of electrolytes, the plasma electrolysis can be broadly classified in to three as (1) contact glow discharge electrolysis (CGDE), (2) glow discharge electrolysis (GDE), and (3) ionic liquid glow discharge electrolysis (IL-GDE). Bruggeman and Leys [2] have classified the discharges in liquid and in contact with liquids as (a) direct liquid-phase discharges, (b) discharges in the gas phase with liquid electrodes, and (c) discharges in bubbles in liquids. But the discharges in bubbles in liquids are actually contact glow discharge electrolysis, because both the electrodes are in contact with the electrolyte when we consider the position of electrodes with the electrolyte. Here, we are not going to explain discharge mechanisms in liquid or water electrolytes because it is already well-explained by Bruggeman and Leys [2].

Contact glow discharge electrolysis

Contact glow discharge electrolysis (CGDE) [44–46, 59, 63, 66, 69, 70] is an electrochemical process, where the plasma is sustained in between an electrode and the surface of surrounding electrolyte. On the other hand, when a high voltage is applied in the conventional electrolysis, it becomes CGDE, where the electrodes are immersed in the electrolyte and it is also called plasma under liquid, that includes discharge produced at the ultrasonic cavity in the liquid also [59, 60, 71]. The experimental setup used for the CGDE and photographs of the discharge are given in
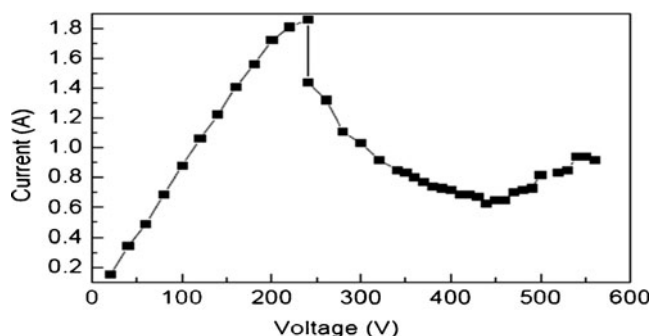

Fig. 2 A typical I–V curve characteristics of contact glow discharge plasma

Table 1 Nanoparticles produced by plasma electrochemical methods

No.	Method	Electrodes		Precursor and electrolytes	Products	Particle size	Discharge and particle growth details	Ref.
		Anode	Cathode					
1	CGDE	Fe	Fe	Ethanol	Carbon encapsulated iron carbide nano particles	5–600 nm	Ultrasonic cavitation method, electrodes are 1mm apart, 55 V, 1.58A, 1 h treatment	[59, 71]
2	CGDE	Co	Co	Ethanol	Graphite encapsulated cobalt	4–40 nm	Electrode dissolution method, electrodes are 1mm apart, Ar plasma, 55 V,3A,15 min treatment	[60]
3	CGDE	Pt	Ni, Ti, Ag, Au	K_2CO_3	Ni, Ti, Ag, Au	10–30 nm	Electrode dissolution method, 160V at atmospheric pressure.	[77]
4	CGDE	Ni	Ni	H_2SO_4	Ni	ca. 50 nm	32 V with stirrer	[78]
5	CGDE	N.M	N.M	N.M	Cu	5–30 nm	32 V with stirrer	[78]
6	CGDE	Pt	Pt	$CuSO_4+H_2SO_4$	Cu	50–400 nm	10 μs treatment, Ar gas, with stirrer	[79]
7	CGDE	Pt	Pt	$H_2PtCl_6+HClO_4$	Pt	30–200 nm	10 μs treatment, Ar gas, with stirrer	[79]
8	CGDE	Pt	Pt	$NaAuCl_4+HClO_4$	Au	ca. 125 nm	10 μs treatment, Ar gas, with stirrer	[79]
9	CGDE	Pt	Pt	$H_2PtCl_6+NaAuCl_4+HClO_4$	Pt+Au	80–140 nm	10 μs treatment, Ar gas, with stirrer	[79]
10	CGDE	N.M	Cu	$Ti(OC_3H_7)_4+HCl+Ethanol$	TiO_2	ca. 200 nm	300–900 s treatment, 500 V.	[80]
11	CGDE	W	W	$HAuCl_4+KCl+gelatin$	Au	10 nm	Electrode distance 0.3 mm, 2.5 kV	[81]
12	CGDE	W	W	$HAuCl_4,4H_2O+Sodium dodecyl sulfonate$	Au	10–20 nm	Electrode distance 0.3 mm, 25 °C, pulse DC 1,600–3,200 V(15 KHz)	[82]
13	CGDE	Ti	Ti	DI	TiO_2	10–30 nm	100 V, 2.5A, 50 T, 10 min	[83]
14	GDE	Ag	Plasma	Acid+DI	Ag	ca.10 nm	Electrode dissolution method, Ar gas, electrode is 1–2 mm above the liquid, 5 mA, 5–15 min treatment,	[26]
15	GDE	Pt	Plasma	$HAuCl_4$	Au	ca.10 nm	5 mA, 10 min	[26]
16	GDE	Pt	S.S	$AgNO_3+DI+CV$	Ag	ca.7.5 nm	Electrode is 1 mm above liquid, Ar gas, 290 V, 2 mA, 1–30 min	[87]
17	GDE	Ag	S.S	HNO_3+Ag with fructose	Ag	ca.10 nm	Electrode dissolution method, 2 kV, 5 mA,	[89]
18	GDE	Au	S.S	HCl+Au with fructose	Au	ca.10 nm	Electrode dissolution method, 2 kV, 5 mA	[89]
19	IL-GDE	Pt	N.M	$AgNO_3/AgCF_3SO_3$+[BMIM]OTf	Ag	ca. 5 nm	10 mA, 470 V,1 mbar	[57]
20	IL-GDE	Al or Au	Al or Au	$GeCl_2$dioxane+(EMIm)TFSA	Ge	Below 50 nm	10 mA,400 V and 500 V, 30 min, 0.75 T	[90]
21	IL-GDE	Pt	Pt	(EMIM)TfO	Ag	ca.20 nm	Electrodes are 10 cm apart, 10 mA, 500 V, 1 mb.	[42]
22	IL-GDE	Pt	Pt	$(BMP)Tfo+Cu(TfO)_2$	Cu	ca.50 nm	Electrodes are 10 cm apart, 10 mA, 500 V, 1 mb.	[42]
23	IL-GDE	Pt	Pt	$Cu+(EMIm)Tf_2N$	Cu	ca.11 nm	10 mA,1,000 V, Ar gas, 30 min treatment, 0.75 T	[93]
24	IL-GDE	Pt	Pt	$Cu+(Py1,4)Tf_2N$	Cu	ca.26 nm	1 mA, 1,000 V, Ar gas, 30 min treatment, 0.75 T	[93]

N.M not mentioned, *S.S* stainless steel

Fig. 1. The other approach in the CGDE is keeping either one of the electrodes, cathode, or anode fully immersed in the solution and the other electrode kept as just contacting the surface of the solution [47, 66]. There are two ways to grow particles by this method. One is the dissolution of either one electrode, and the other is from the particle species dissolved in the liquid electrolyte. Growth of the particle is faster when the growth by the particle species of the electrolyte is chosen, since the charged species are available from the beginning of the process, but this process is constrained by the limited reservoir of the species in the liquid electrolyte. When the particle growth by the electrode dissolution is chosen, there is an infinite supply of the growth species, but the growth of the particle is slow. CGDE method is also used for the preparation of oxide or metal films and that process is known as "plasma electrolytic oxidation" or PEO where the film will be deposited in any one of the electrode [69, 71–75].

There is a clear deviation seen from the Faradays' electrochemical law [48] in the contact glow discharge electrolysis, so that high yield is obtained during the material preparation [49]. It is a well-known fact that novel material productions are not possible by the conventional electrolysis, but even water decomposition [50, 51] is also possible by the CGDE. The reason is nothing but the high energetic charged species and the presence of the two reaction zones such as the liquid near the plasma–electrolyte interface and the plasma around the electrode. No doubt that these two reaction zones are the reason for the high yield [45, 50]. The plasma around the electrode is produced by the dissociation of solvent and solute molecules by appropriate energy transfer and there are a number of radicals, ions, and other active species produced via electron impact dissociation, excitation, and ionization.

The reaction zone is located in a fixed position and constantly renewed during the diffusion of the active species in to the solution. In the reaction zone within the plasma around the electrode, the generation of primary products occurs via ionization in the liquid phase at the expense of the kinetic energy of accelerated particles entering the solution during the discharge.

When the potential between the electrodes is high enough, the solution vaporizes and a gaseous sheath is formed around one electrode [62, 76, 77]. Glow discharge plasma occurs in this gaseous sheath when the gaseous sheath breakdown at high potential. The color of the discharge depends on the constituents of the electrolyte [44, 61] and orange light is seen for the Na_2CO_3 electrolyte [44]. A typical I–V characteristic of the CGDE is shown in Fig. 2. It is observed from the characteristic curve that the CGDE is undergoing in three processes [3, 4, 65, 66, 69,
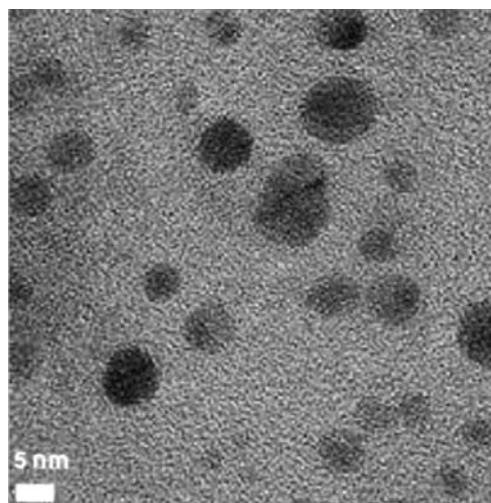

Fig. 3 Nickel nanoparticles prepared by CGDE method ([78], Reproduced with permission from Elsevier)

70, 78–80]. It is deduced that CGDE obeys ohm's law until a particular applied voltage only that is the current increased almost proportionally with the rising of the applied voltage. It is known as conventional/classical electrochemical region in the I–V characteristic curve. With a further increase in applied voltage, a thin gas film starts to form [66, 78, 80] and insulate the working electrode from the bulk solution. The equivalent resistance of the gas-solution interface increases sharply due to the lower electrical conductivity of the gas film than the electrolytic solution, which results in a sudden decrease of the electric current. This region in the I–V characteristics is known as unstable region. The voltage at which the current starts to decrease is known as the critical voltage. With a further
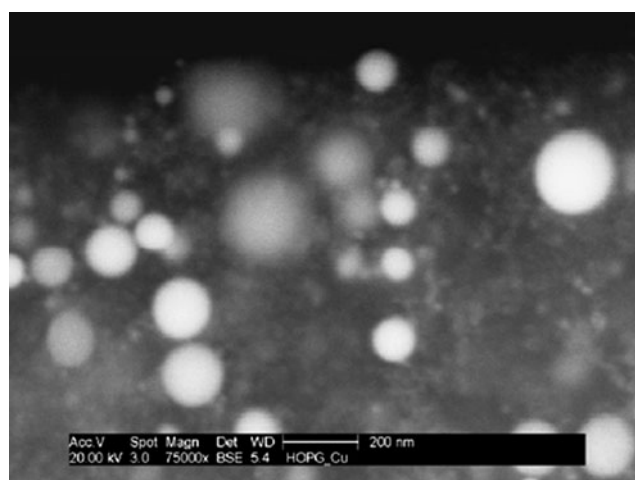

Fig. 4 Copper nanoparticles prepared by CGDE method ([79], Reproduced with permission of ELSEVIER INC. in the format Journal via Copyright Clearance Center)
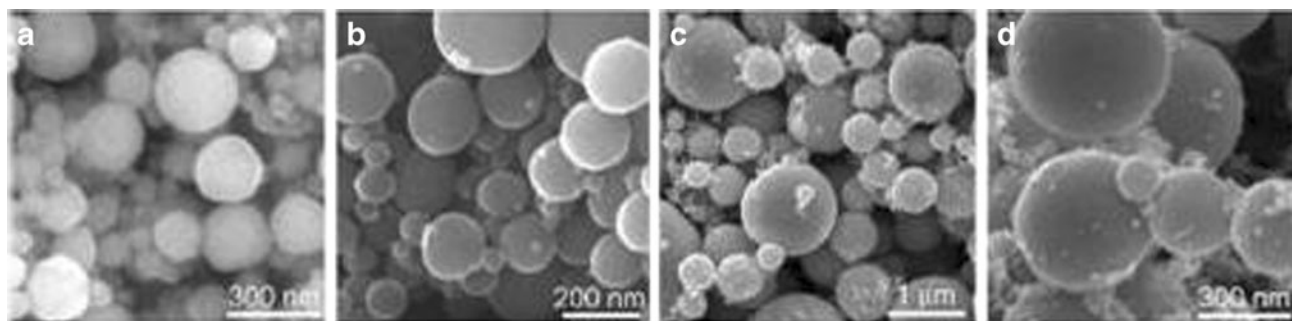
Fig. 5 Micrographs of Ni, Ti, Ag, and Au nano balls ([77], Reproduced with permission of AMERICAN INSTITUTE OF PHYSICS in the format Journal via Copyright Clearance Center)

increase in applied voltage the current starts to increase again and starts to obtain the electrochemical discharges. Colloidal nanoparticles can be synthesized by applying a voltage above the critical voltage. Carbon-encapsulated iron carbide [59, 71], carbon-encapsulated cobalt [60], Ag [77], Ti [77], nickel [77, 78], copper [78, 79, 81], Pt [79], Au [77, 79, 82, 83], TiO$_2$ [76, 80] nanoparticles have been synthesized by this method so far and the details are tabulated in Table 1. TEM image of the nickel particles prepared by this method is shown in Fig. 3 [78].

Lal et al. [79] prepared Cu nanoparticles of sizes 50–400 nm using CuSO$_4$+H$_2$SO$_4$ electrolyte solution and it is shown in Fig. 4. The same group has prepared Pt particles of 30–200 nm sizes [79] using H$_2$PtCl$_6$+HClO$_4$ as electrolytic solution. They have also used NaAuCl$_4$+HClO$_4$ electrolyte for preparing Au nanoparticles [79], and H$_2$PtCl$_6$+NaAuCl$_4$+HClO$_4$ electrolyte for Pt+Au nanoparticles. In all the above cases, the discharge lasted only for about 10 μs with 1A current.

Paulmier et al. [80] reports the preparation of TiO$_2$ nanorods with a diameter of about 200 nm using this CGDE method, where the plasma discharge occurs at a voltage of about 500 V at atmospheric pressure. They observed that the density and the orientation of the nanorods perpendicular to the substrate surface are increasing with increase in voltage from 500 to 700 V. They have also reported that amorphous TiO$_2$ was formed at lower voltages and this amorphous is converted to anatase phase as the intensity of plasma is increased. They have used HCl with the precursor solution to control the current. The experiments by increasing the treatment time give longer bended nanofibers with higher disorientation [80].

Different shapes of gold nanoparticles with size ranges in between 25–50 nm were synthesized from the solution of HAuCl$_4$.4H$_2$O with sodium dodecyl sulfonate as stabilizer by applying voltage from 1,600 to 3,200 V in between two tungsten electrodes in a setup similar to the picture shown in Fig. 1c [82], and Osamu Takai [81] also reported the preparation of 10 nm gold nanoparticles from HAuCl$_4$ with gelatin and KCl in a similar setup by applying a voltage of 2,500 V. It is deduced from their results that the size and shapes of the particles are depended on the time of treatment, applied voltage, and concentration of the dissolved species.

Electrode dissolution method can also be utilized to prepare nanomaterials as described in the previous paragraphs. Nano-balls of Ni, Ti, Ag, and Au [77] as depicted in Fig. 5 have been prepared by the dissolution of the electrodes using the same setup described above, but Ruslan Segiienko [59, 60, 71] and his colleagues have performed the electrode dissolution in a different way, where the discharge was produced with the help of ultrasonic cavitation method. They [59, 60, 71] have used a setup shown in Fig. 1d where the ion electrodes were melted and reacted with the ionized ethanol electrolyte that made carbon-encapsulated iron carbide nanoparticles of sizes ranging in between 5 and 600 nm as given in Fig. 6. Ultrasonic cavitation creates highly localized high temperature and pressure regions that enhance the electrical conductivity, so that plasma discharge can be generated at relatively low electric power, so that they [59, 60, 71] have prepared the metal nanomaterials by electrode dissolution by creating a constant potential difference of 55 V in between the electrodes.
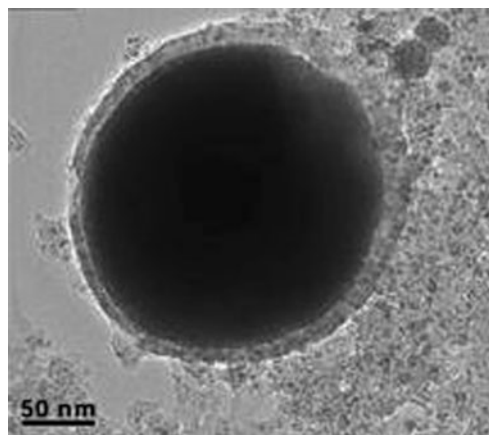

Fig. 6 Carbon nanocapsule with an amorphous core ([59], Reproduced with permission of ELSEVIER S.A. in the format Journal via Copyright Clearance Center)
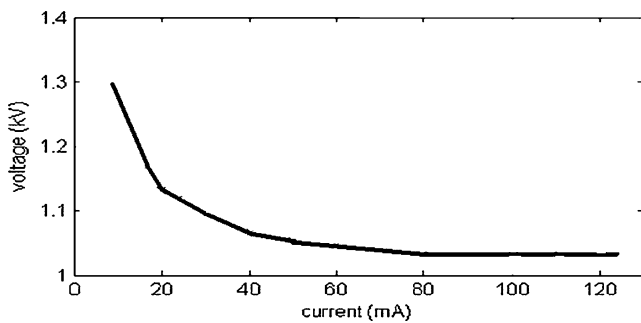
Fig. 7 Current–voltage characteristic of filamentary glow discharge plasma

Glow discharge electrolysis

Glow discharge electrolysis (GDE) [52, 53, 65, 84–86] is an electrochemical technique in which the discharge is initiated in the gas in between the metal electrode and the aqueous solution by applying high voltage.

One gets corona discharge when distilled water is used as an electrolyte solution and stainless steel as pin electrode [53, 84] and can observe a liquid elevation before the corona onset due to the Coulomb force. It is found that water surface deformations have a significant influence in the electrical breakdown formation and the current–voltage characteristic is relatively independent of the voltage in a particular current range [53] for filamentary glow when the water acts as cathode, but I–V characteristic exhibits a glow like behavior for higher currents. A cathode spot is seen on

the surface of the water and its diameter increases with current. A typical I–V characteristic is shown in Fig. 7.

Vyalykh group [54] conducted a photographic investigation to study the interface of the liquid electrolyte and the plasma of a low-pressure dc glow discharge. The photographs of the plasma–electrolyte interface are shown in Figs. 8 and 9. This group [54] conducted experiments for copper sulfate ($CuSO_4$) water solution and for the water solution of potassium permanganate ($KMnO_4$). A complicated kinetic process is involved at the plasma–electrolyte interface as well as the surface is also affected by intense acoustic oscillations due to the current flow through the electrolyte and the exchange of energy from electronic current to the ionic current. During the discharge over the smooth electrolyte surface, the surface warped and the electrolyte and the plasma underwent a turbulent mixing after intense surface waves. Later, the discharge was extinguished when the mixture was ejected to the upper electrode after the turbulent mixing. This may be due to the coulombic attraction as shown by Bruggeman et al. [53]. But, a slight change is seen in the discharge of the copper sulfate solution that the discharge was quieter and passed through different quasi-steady modes, such as smooth surface, a solitary wave perturbation, regular ripples (Faraday waves) and churning foamed turbulent mixing zone. It is evident from the churning foamed turbulent mixing zone that coulombic attraction also prevails here. But we do not have much theoretical and experimental study available to date to confirm what happens at the
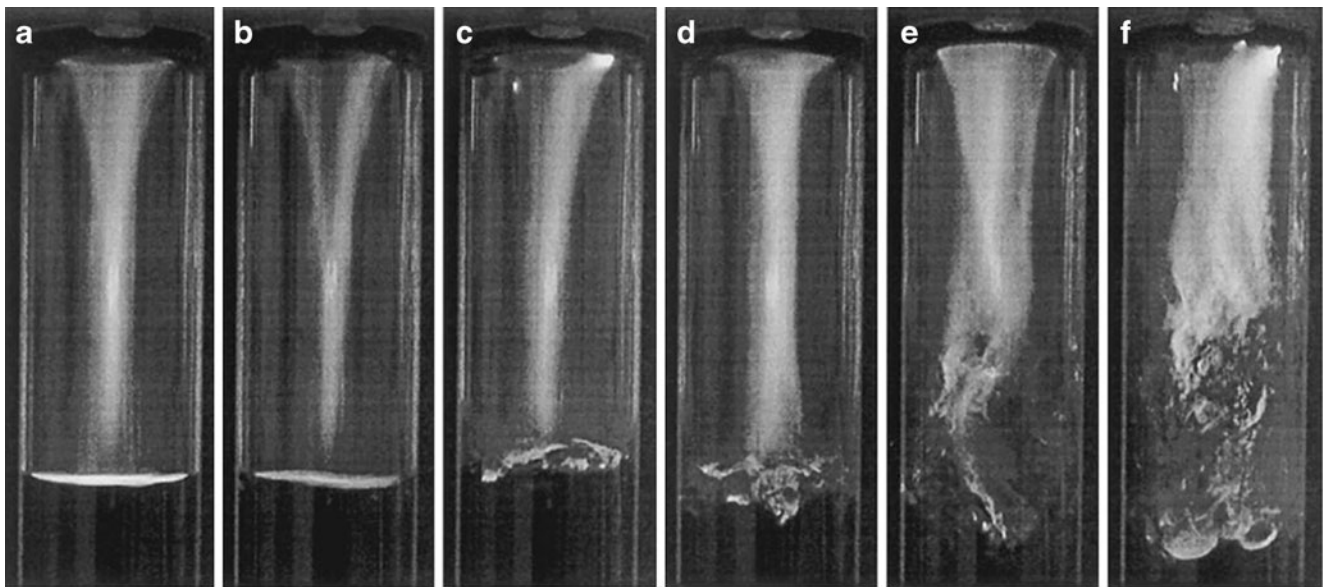

Fig. 8 Dynamics of a glow discharge over a potassium permanganate solution: **a** smooth surface, **b** warped surface, **c** wave perturbation of the surface, **d** growing perturbation, **e** turbulent ejection of the plasma–electrolyte mixture into the discharge zone, and **f** another turbulent ejection of the plasma electrolyte mixture into the discharge zone (with kind permission from Springer Science+Business Media: experimental study of the stability of the interface between a liquid electrolyte and the glow discharge plasma [54] Fig. 1)
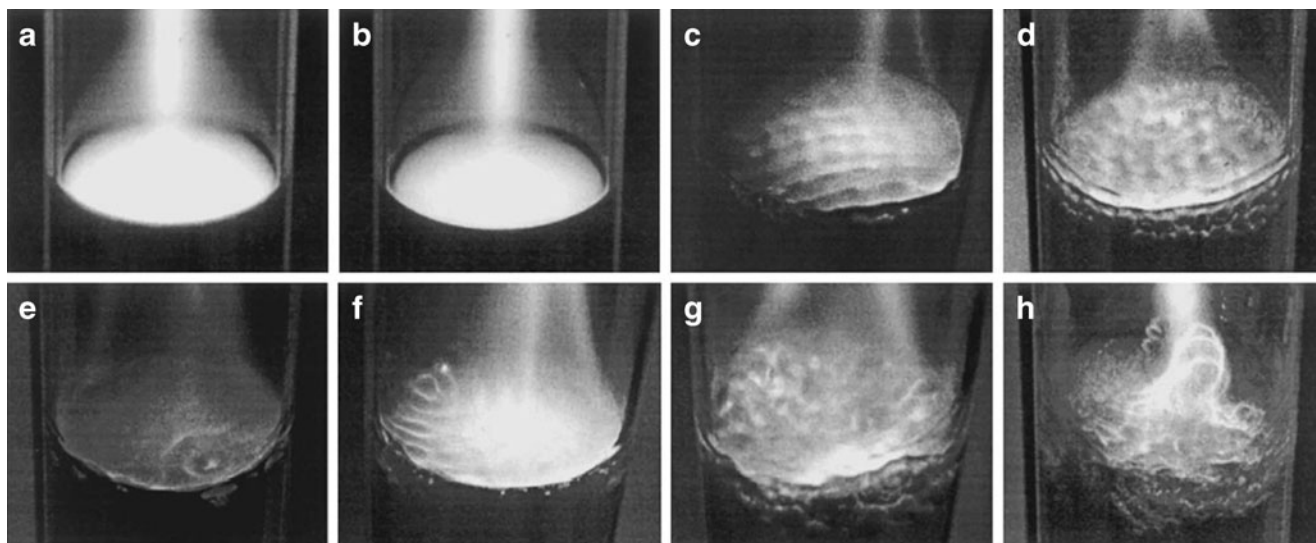
Fig. 9 Modes of a glow discharge over a copper sulfate solution: **a**, **b** smooth surface, **c**, **d** solitary wave perturbation, **e**, **f** regular ripples, and **g**, **h** churning foamed turbulent mixing zone (with kind permission from Springer Science+Business Media: experimental study of the stability of the interface between a liquid electrolyte and the glow discharge plasma [54] Fig. 2)
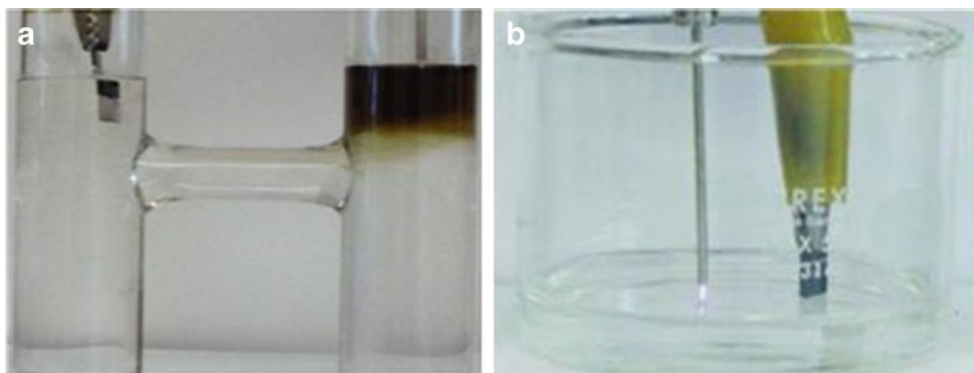
plasma–liquid interface. The basic principle in this reaction is that plasma occurs above the surface of the solution and then moves into the solution by transferring energetic plasma particles into aqueous solution and collide with ions in the aqueous solution. That the charged species in the plasma accelerated towards the solution and enters into the solution with high magnitude of kinetic energy so as to make chemical reactions in the solution [65]. An overview of important reactions in the plasma–liquid interactions is well-explained in the review published by Bruggeman and Leys [2]. The most probable reaction may be due to the collision of high energetic electrons with the molecules in the electrolytic solution [65]. The electron density increases with increase in plasma power which increases the plasma volume so that the electrons have greater chance to interact with the molecules in the solution [65] and a similar effect is reported in the CGDE also [79] where the amorphous TiO_2 is converted to anatase when the plasma intensity increased to a certain level.

The team of R. Mohan Sankaran [26, 87–89] has designed a microplasma method to prepare nanomaterials by electrode dissolution and nucleation from the electrolyte solution, this method comes under the GDE based on the classification used here, since one of the electrodes is in contact with the electrolyte and other is plasma. They have prepared silver nanoparticles by the electrode dissolution (Ag anode) [26] with a stabilizer in an H-shaped setup as shown in Fig. 10a, further Au and Ag nanoparticles were also prepared by the growth of the particle species dissolved in the electrolyte $HAuCl_4$ and $AgNO_3$ using the setup shown in Fig. 10b.

Ionic liquid glow discharge electrolysis

Ionic liquid glow discharge electrolysis (IL-GDE) is developed by the group of Frank Endres [43, 53, 56], who developed the electrodeposition of nanoscale materi-

Fig. 10 **a** Nanoparticles by electrode dissolution method **b** nanoparticles from the dissolved species in the electrolyte [26, 87, Reproduced with permission of IOP and AMERICAN IN-STITUTE OF PHYSICS in the format Journal via Copyright Clearance Center]

als in ionic liquid. Here, the discharge is initiated in the gas in between the metal electrode and the ionic liquid solution. This group [43, 53, 56] named it as plasma electrochemical deposition (PECD) at the interface of plasma/ionic liquid by considering plasma as an electrode. Ionic liquids are defined as molten salts with melting point below 100 °C with large number of cations and anions. Frank Endres et al. defined the ionic liquid as "an ionic material that is liquid below 100 °C" [56]. Ionic Liquids (IL) have high ionic conductivity, low viscosity, high thermal stability, wide electrochemical window up to 7 V, and have negligible vapor pressure as well as they are environmentally friendly [56]. The IL-GDE concept is based on the reduction of precursor material dissolved in IL with free electrons from the plasma. Here, the plasma considered as an electrode because of the deposition of the materials at the interface of ionic liquid and plasma like electroplating at one electrode. The negligible vapor pressure of the IL helps to make an extended and stable plasma [42, 90] cloud rather than a localized corona discharge and the larger electrochemical window helps to electro-deposit materials that cannot be deposited from aqueous solutions. A photograph of ionic liquid glow discharge and the schematic representation of ionic liquid glow discharge electrolysis are shown in Fig. 11.

Understanding the stability of ionic liquids when they bring in contact with plasma is very important, so that Yong-Bing Xie et al. [91] have studied the stability of [BMIM]Cl, [BMIM][PF$_6$] and [BMIM][BF$_4$] ionic liquids under glow discharge plasma exposure for 10 min when neither of the electrodes are in contact with the ionic liquid. They [91] have produced argon plasma by applying a DC voltage of 1.0 kV at a pressure of 100 Pa in between two stainless steel electrodes of diameter 40 mm kept 100 mm away while maintaining the flow rate as 10 ml/min in a quartz tube of 40 mm diameter. They [91] have used

Fourier transform infrared and NMR spectroscopy to determine the structural changes in the ionic liquid after the application of the glow discharge. After comparing chemical shift values of the samples before plasma treatment and after treatment, Yong-Bing Xie et al. [91] and the team of Frank Endres [92] have concluded that the structure of imidazolium ionic liquids is stable under the influence of these plasmas due to the low temperature of the glow discharges.

But, de-composition of ionic liquid is [55, 58] reported when any one of the metal electrode is in contact with the ionic liquid.

Sebastian A. Meiss and M. Poelleth's [55, 57] group synthesized silver nanoparticles using IL-GDE for about 10 min. From their observations, the reactions started at the IL–argon plasma interface and it spread all over the solution, which was observable from the dark color of the solution. During the reaction time, a change in the pink/blue emission of argon plasma is observed and then the reaction started at the IL–plasma interface.

The physicochemical properties of ionic liquids also influences the particles growth and size [58] and it was confirmed by preparing copper nanoparticles in different air and water stable IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide ([EMIm]Tf$_2$N) and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) amide ([Py$_{1,4}$] Tf$_2$N). Where, the decomposition of the IL takes place at the anode and the materials starts to deposit at the IL–plasma interface, at the gaseous electrode [55, 58].

Metal nanoparticles of platinum, palladium [58], silver [39, 40, 58] can also be synthesized using the same technique by dissolving metal salts in different ionic liquids; the dissolved metal salts can be reduced with the help of free electrons from plasma [56]. Germanium particles of sizes about 50 nm were prepared using the

Fig. 11 a Photograph of ionic liquid glow discharge plasma, **b** schematic drawing of ionic liquid glow discharge plasma electrochemical setup. (Reproduced by permission of The Royal Society of Chemistry, DOI: 10.1039/b614520e)
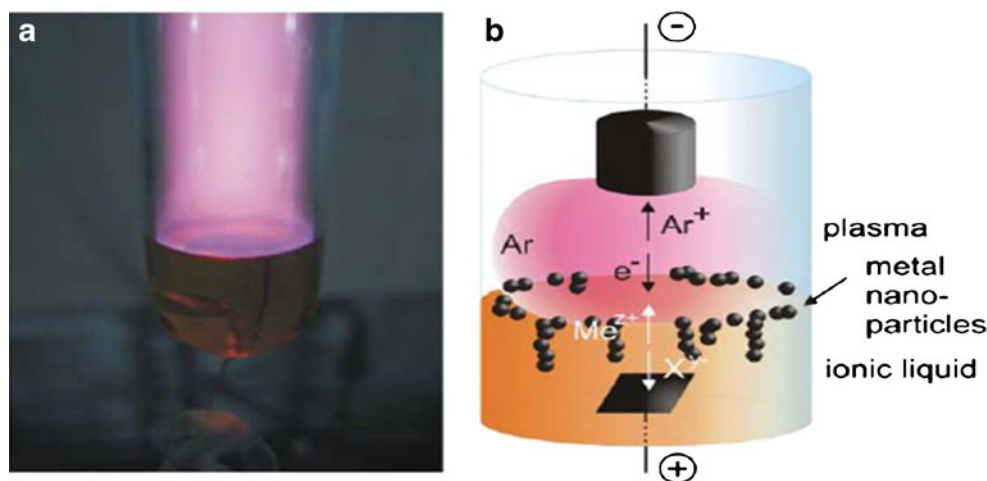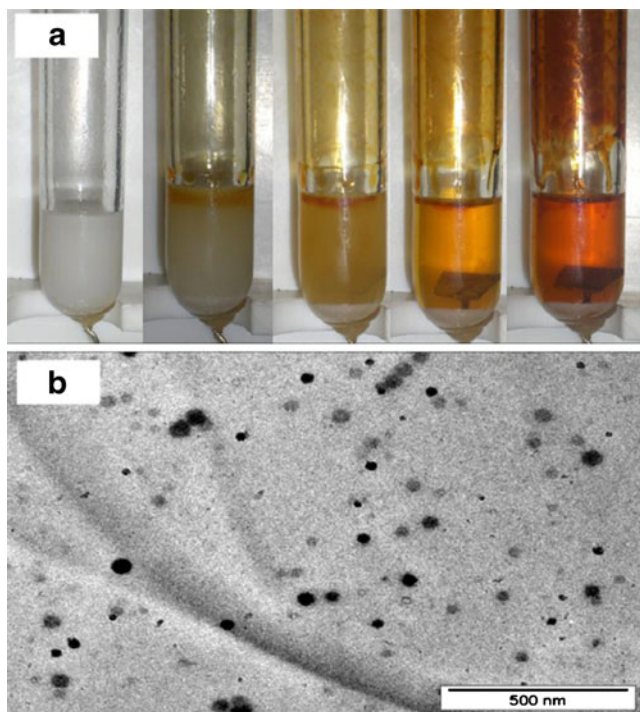
Fig. 12 The color change during the preparation of Ge nanoparticles and the prepared Ge nanoparticles ([90], Reproduced with permission from Elsevier)

electrolyte $GeCl_2C_4H_8O_2$+[EMIm]TFSA as anode with an applied voltage in between 450 V and 500 V for about 30 min [90] where the plasma is ignited at 1,000 V with a current of 10 mA at 100 Pa. So that the electrons are accelerated towards the surface of ionic liquid electrolyte. The resulting Ge particles are shown in Fig. 12.

Copper nanoparticles of 11 nm [93] were prepared by dissolving copper in 1-ethyl-3-methylimidazolium bis(tri-fluoromethylsulfonyl)amide ([EMIm]Tf$_2$N and copper nanoparticles of 26 nm [93] by dissolving copper in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) amide([Py$_{1,4}$]Tf$_2$N) by igniting plasma at 1,000 V at 100 Pa with a current of 10 mA for 30 min. After the

ignition, the voltage dropped from 1,000 to 450–500 V and the resulting particles are shown in Fig. 13. This work [93] indicates that the nature of ionic liquid also affects the particles size when they are prepared by the plasma electrolytic method.

Theoretical aspects of plasma–liquid interface

A priori, electrolytes are purely ionic conductor and metallic electrodes are electron conductor, but plasma is a fluid of ionic and electronic conductors. It is assumed that the glow discharge plasma as an electronic conductor since the electrons have high kinetic energy while neglecting the inhomogeneity of the glow discharge plasma, so that the glow discharge plasma can be considered as an electrode. But, when the plasma sheath becomes poor in electrons under a negative polarization and thus ionic conduction predominates and thus the plasma sheath act as an electrolyte.

Charged species from plasma diffuses to the plasma boundaries and leads to a negative charging of the plasma walls and leaves a positive space charge in front of the wall, called sheath. This sheath can be treated as the diffusion potential in conventional electrolytes.

When we are considering plasma as an electrolyte, this means that there are pairs of electrolytes that are in mutual contact, that forms liquid electrolyte–plasma electrolyte interfaces and this interface is not stable because these are immiscible and this interface is in between two immiscible electrolytes. But from the reports of Vyaluk et al. [54], it is seen that the ions in both phases diffuse across the plasma electrolyte–liquid electrolyte interface and disappearing the interface (evident from the movement of liquid electrolyte to the upper electrode after a turbulent mixing), which means it brings a potential equilibrium between these two phases. Even though, from the IL-GDE [53, 56], these inhomogeneous immiscible electrolyte systems preserve its interface. Because of the difference in charge driving forces in these dissimilar media, there are some nontransferring components

Fig. 13 a Copper nanoparticles prepared in [EMIm]Tf$_2$N and b copper nanoparticles prepared in [Py$_{1,4}$]Tf$_2$ ([93], Reproduced by permission of the PCCP Owner Societies, DOI: 10.1039/ b906567a)
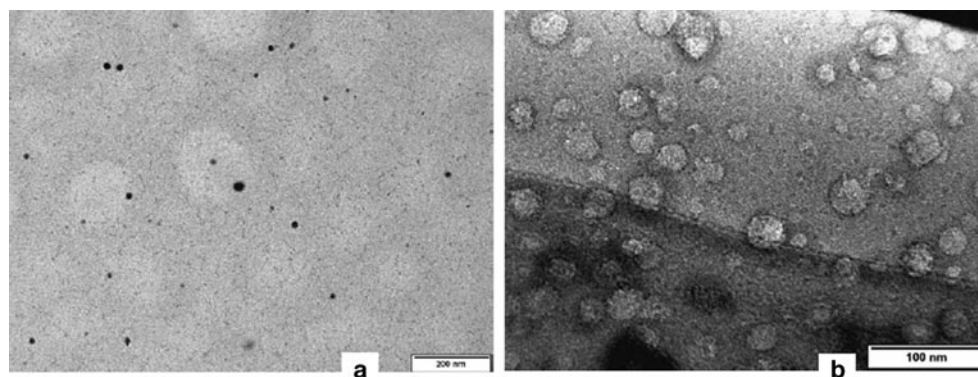
in each of the phases and there is a Galvani potential (in the case of Galvanic cell) at the interfaces between these two electrolytes and that cannot be measured [94]. More detailed studies are needed to unravel the secret of the plasma-liquid interface and their interactions to form nanomaterials.

In conclusion, it is observed that only few studies are available about the nanoparticle preparation in liquid under plasma and this is not enough to tell the nucleation and the growth process of nanoparticles in liquid under plasma.

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