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Ionic Liquids: Sustainable Media for Nanoparticles

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Abstract: In this paper, an incompressible viscous fluid flow over a flat plate is presented. In the past decade, ionic liquids have attracted great interest both in scientific research world and amongst the most diverse technological and industrial sectors. This fact, together with the growing contribution of the industrial sector, is turning ionic liquids into a key component for the most diverse fields of science, such as nanotechnology, electrochemistry, green chemistry, physics, materials science and engineering, among many others. First, before talking about the ionic liquids' applications, one should answer this question; what are the main properties that make ionic liquids so attractive? In general, ionic liquids are salts formed by very asymmetric and large ions, due to which they have attractive cation-anion forces weaker than those that occur in conventional ionic salts, such as table salt, which causes them to be liquids in a wide range of temperatures, including the ambient temperature in most cases. The term "ionic liquid" is considered a synonym of a "molten salt", although in practice it began to be used when molten salts started to be popular at low temperatures. Indicatively, a compound is usually called a molten salt when the melting temperature is above 100 °C, while an ionic liquid melts at lower temperatures. Due to the growing applications of ionic liquids as engineering fluids, their ability to functionalize or surface-modify materials in the form of nanoparticles has recently been described. Therefore, ionic liquids have been used as solvents for nanoparticle synthesis with a wide variety of sizes and morphologies.

Keywords: Ionic Liquids, Nanoparticles, Nanotechnology, Green chemistry, Green Synthesis.

Introduction

Ionic liquids are salts with low melting points, lower than 100ºC. They are composed of an anionic part and a cationic part and due to their great thermal and chemical stability; they can be used in high-temperature processes up to 300ºC, since temperatures higher than this cause decomposition. Most of ionic liquids are remaining liquids at temperatures above room temperature, which is the main advantage of these solvents [1]. The main characteristic that differentiates ionic liquids from molten salts is the wide temperature range in which ionic liquids are liquid compared to traditional salts (Fig. 1).

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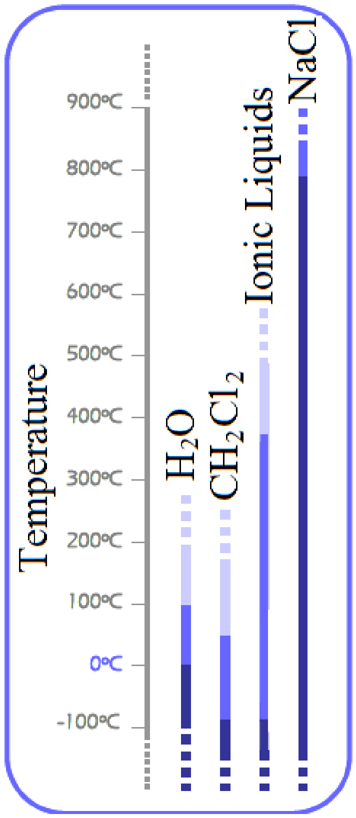

FIG. 1. Comparison of physical states and temperature ranges of different compounds [1].

Many of the Ionic liquids are formed by an organic cation and an anion that can be organic or inorganic. Some properties, such as thermal stability and miscibility, are mainly dependent on the anion, while other properties, such as viscosity, surface tension and density, depend on the length of the alkyl group of the cation and /or its shape and symmetry [2].

Due to all combination possibilities of cations and anions, there are a large number of ionic liquids. Thus, ionic liquids offer a wide range of physicochemical properties suitable for different applications. Ionic liquids are considered green liquids of design, because their properties can be adjusted or modified by varying the cation and/or the anion, without generating polluting emissions to the environment [3].

Initially, these materials were developed for their exclusive use in electrochemistry [3], although they have been receiving importance and a particular interest making them present in many fields of sciences [4]. As a representative figure, Fig. 2 shows the spectacular growth in terms of the number of scientific articles on ionic liquids that have been published in the past 20 years.

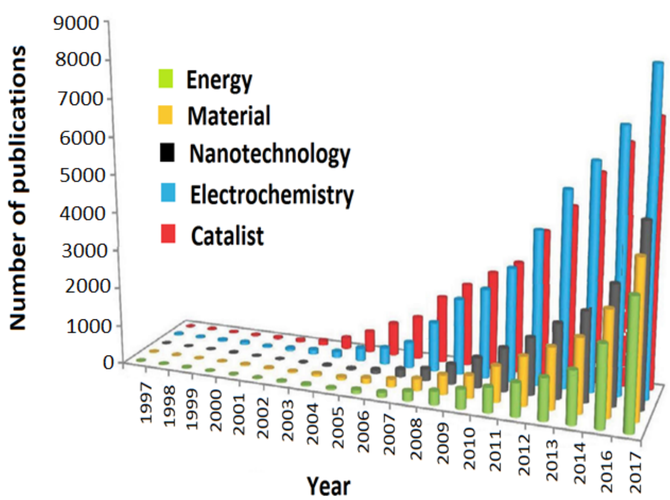

FIG. 2. Number of scientific publications related to ionic liquids in different fields in the period (1997-2017) according to the Institute for Scientific Information (ISI) Web of Science.

However, ionic liquids have a multitude of applications due to possessing many important characteristics. These properties comprise; zero volatility [5], almost zero vapour pressure [6], being simply liquids composed entirely of ions [7], negligible flammability [8], a wide range of potential windows [9], high thermal stability [10], a low melting point [11] and a controlled miscibility with organic compounds and water [12].

Due to the possibility of combining the cation; generally organic, voluminous and asymmetric, with various generally inorganic anions although they can also be organic, the term "design solvents" has emerged, since the choice of ions determines the physico-chemical properties of ionic liquids (melting point, viscosity, solubility, …, etc.). The most common cations are the di- or tri-substituted imidazolium, the substituted pyridiniums, tetraalkyl-ammoniums and tetraalkylphosphoniums and their partners are usually halide anions, sulphates, sulphonates, triflates, amides and imides, borates and phosphates [13]. Fig. 3. illustrates some of the most common ions, anions and cations in the formation of ionic liquids. Since there are many more, the combinations are very numerous due to the fact that their ionic and hybrid organic-inorganic nature as well as ionic liquids possessing unique properties make them interesting for diverse applications [14].

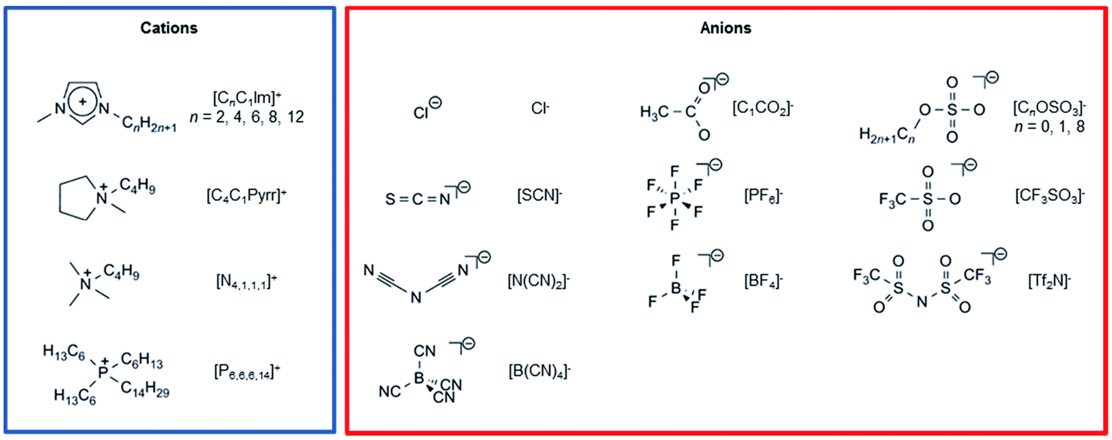

FIG. 3. Most common cations and anions in the formation of ionic liquids [15].

Thus, these liquids are generally good solvents for both organic and inorganic compounds, including metal salts. This is due to the fact that ionic liquids are a highly solvating medium, but a very little coordinating one. In addition, one of their most acknowledged properties is their very low vapour pressure which is a good indicator to consider them non-volatile solvents [16]. This characteristic is the basis of the great interest that these compounds raise in green chemistry to replace volatile organic compounds as solvents in chemical reactions. In addition, as mentioned above, the choice of cation and anion determines the solubility and miscibility of ionic liquids in water and in traditional organic solvents, the existing combinations being countless [17]. This makes them interesting in extraction processes, since we can always find adequate ionic liquids for our concrete extraction system. The ionic liquids also have a high thermal stability up to temperatures above 450 °C in some cases, as well as a high specific heat. In addition, ionic liquids present a wide range of potential in which they are stable and which we will refer to as the electrochemical stability interval [18]. Finally, it is worth mentioning their high ionic conductivity which, together with the large range of electrochemical stability, makes them potentially attractive as electrolytes in different electrochemical devices [15].

Short Historical Review

From the historical perspective, the first material that would fit with the definition of ionic liquid was observed in the middle of the 19th century, in a Friedel-Crafts reaction [19], where a liquid phase was obtained, being designated with the name "red oil". Later, research determined that this "red liquid" was an ionic liquid. The first known bibliographical reference in this respect is when Walden [20] in 1914 synthesized ethylammonium nitrate with a melting point of 12 °C [21]. Later, in 1948, the development of ionic liquids formed by chloroaluminium ions. Hurley and Weir [22] discovered that mixing alkylpyridinium chloride with aluminium chloride produces a reaction that yields colourless ionic liquids. This discovery has remained a curiosity for a long time, until its singular properties have become known and electrochemical studies have been initiated. Fig. 4 presents an overall model of an asymmetrical system of ions in the IL structure.

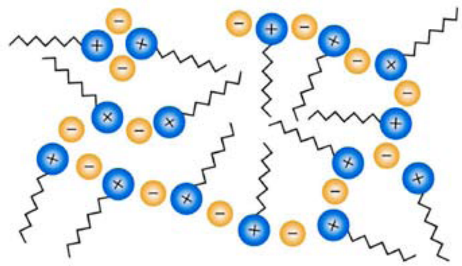

FIG. 4. Reorganized model of an ionic liquid [23].

The real history of ionic liquids began in the US military, with Lowell King, in charge of a research project in piles, to find viable substitutes for the molten salts of LiCl/KCl, at that time used as electrolytes [14]. The chloroaluminates were introduced in the field of electrochemistry, since they achieved much lower melting temperatures than expected. In addition, they did not behave as simple binary mixtures. The system they formed and their Lewis acid-base characteristics provided an anion series of the Cl^- type; $[AlCl_4]^-$, $[Al_2Cl_7]^-$ and $[Al_2Cl_{10}]^-$. For a long period, research and development focused mainly on electrochemical applications [24].

To overwhelm the restrictions of a particular ionic liquid in some areas and feat its greater properties in other areas, combinations of ionic liquids are currently being largely discovered. Ionic liquid mixtures represent a comparatively novel area evolving in the field that has gathered substantial curiosity [25], since they tolerate for extra change of the ionic liquid characteristics for precise requests. The ionic liquids containing the slight part of the mixture can be correspondingly intended to enhance anticipated physical or chemical characteristics. There are numerous requests described for binary ionic liquids as solvents for chemical production and procedures [26], for electrochemical requests such as dye-sensitized solar cells [27, 28], batteries [29, 30] and in chromatography [31].

One can realize that the acid-base chemistry of the components results in a binary ionic liquid material, which is a mixture of two nitrate salts [32]. The specific instance is a glass forming salt with a glass transition temperature of 2100 °C. This ionic liquid is not a one-off curiosity, since there have been many articles and patents for this example alone up to now.

In 1967, a publication by Swain modified the direction of the applications by the use of benzoate tetra-n-hexylammonium as a solvent for kinetic studies. In the 1980s, Hussey and Seddon [33] studied the application of chloroaluminate ionic liquids as polar solvents in the creation of transition metal complexes. At the same time, the first publications appeared where chloraluminates were effective Friedel-Craft catalysts [34]. The main problem with these liquids was their sensitivity to water. In 1990, Michael Zaworotko [35] became able to develop, synthesize and completely characterize salts with new cations, but at the same time being stable anions in water. By this way, the work in the laboratory became easier, with no longer need to work in free moisture atmosphere. These new salts, with anions of the types tetrafluoroborate, hexafluorophosphate, nitrate, sulphate and acetate, proved to be much more stable liquids, at least at low temperatures and although the initial purpose was to use them as electrolytes in piles, they proved to be particularly suitable in other applications [13].

As different studies are carried out in chemical reactions, it is becoming clear that their behaviour is different from that observed in conventional polar and non-polar media. By means of different cations and anions, a large number of compounds can be obtained; their characterization shows the great variety of properties offered by ionic liquids. Nowadays, the catalogue of cations and anions is even bigger, which means that the possibility of creating new ionic liquids is practically unlimited and the applications of ionic liquids are only limited by the imagination of researchers. One way to demonstrate the wide dissemination of these compounds in the scientific field and in the industrial applications is the growing number of publications in this area [14].

The Role of Ionic Liquids in Green Chemistry

The objective of "Green Chemistry" is to create a cleaner and more sustainable chemistry that does not harm the environment. More specifically, "Green Chemistry" is the design of products or processes that reduce or eliminate the use or production of hazardous substances by offering alternatives with greater environmental compatibility. Along with the use of supercritical fluids, the replacement of traditional volatile organic solvents with non-volatile ionic liquids as a reaction medium can offer a convenient solution to some of the environmental problems suffered by the current chemical industry, such as the emission of harmful gases, issues associated with the existing aqueous Cr(VI) electroplating solution [36] and the recycling of catalysts [37].

One of the most researched cases is the use of ionic liquids in catalysis, since these cannot only be used as a solvent, but also can act as a catalyst or co-catalyst increasing the speed of the reaction, the yield or changing its selectivity [38]. There are numerous examples and applications of ionic liquids in catalytic reactions, such as the Heck reaction, Diels-Alder reactions, Friedel-Crafts, esterifications or regioselective alkylations as illustrated in several recent reviews [39]. In addition, the solubility of certain gases such as H_2, CO and O_2 in ILs is generally good, which allows them to participate in reactions such as hydrogenations, carbonylations, hydroformylations and aerobic oxidations.

Another outstanding application within "Green Chemistry" is to replace traditional organic solvents in liquid-liquid extraction processes (Fig. 5). Thus, the data presented by the Robin D. Rogers group reflects that the distribution coefficients for different types of solutes in the ionic liquid system [BMIM [PF_6] - water are more suitable for practical applications than the classical system 1- octanol- water. These two-phase systems are being actively studied by various groups that intend to develop a new and clean separation technology [40].

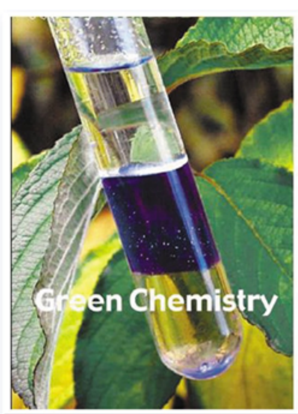

FIG. 5. Green chemistry [40].

Although the applications of ionic liquids have been studied since the 1980s as a means of reaction or catalysis, it was recently when the first industrial process using ionic liquids was developed. Specifically, the process consists in adding methylimidazole instead of triethylamine to eliminate hydrochloric acid in the production process of dichlorophenylphosphine, improving up to ten times the yield of said reaction thanks to the easy separation of the ionic liquid obtained as a secondary product; Dario [41]. For this reason, the BASF Company has received the prestigious 2004 Innovation Award from the European Chemical News and has gone in history to implement the first chemical process that uses liquids of large-scale ionics [42]. BASF currently offers a process license called BASIL [43] (biphasic acid scavenging utilizing ionic liquids), which can be used in other reactions such as acylations, phosphorylations, sulphonations and silylations (Fig. 6).

FIG. 6. Photograph of a BASIL process reactor. The ionic liquid is separated from the reaction medium allowing the improvement of the reaction yield [43].

As a last application within "Green Chemistry", it is worth highlighting the use of ionic liquids as solvents in reactions catalyzed by enzymes. One of the main advantages that have been identified is that, unlike other polar organic solvents, ionic liquids do not deactivate enzymes, allowing reactions with polar substrates that were previously not possible. In other cases, the use of ionic liquids in biocatalysts offers a greater selectivity, a higher reaction speed and even a greater stability of the enzymes [44].

Ionic Liquids in Electrochemistry

Ionic liquids present a series of properties (high ionic conductivity, wide range of electrochemical stability) that make their presence in the different branches of electrochemistry more and more consolidated, presenting applications, such as electrolytes in electrochemical synthesis, solvents in electrodeposition of metals, batteries, super-condensers, fuel cells, solar cells and devices based on conductive polymers, such as electrochemical sensors, artificial muscles and electro-chromic devices [45].

One of the topics of greatest industrial interest in electrochemistry is that of electrodeposition of metals. As a general rule, the variety of metals that can be electrodeposited in a given medium is limited by the electrochemical stability of said medium. In this sense, the main advantage of the ILs compared to the technologies in aqueous media is their wide range of electrochemical stability [15]. While aqueous solutions have a range of electrochemical stability of 2 V, the range of electrochemical stability that some ILs have exceeds 4 V depending on the pH of the medium, reaching up to 6V (Fig. 7) [46]. The studies carried out so far have focused on the electrodeposition of metals, such as aluminum, which are too electropositive to be deposited from conventional aqueous solutions. That is, it is necessary to apply a very high potential to the solution in order to achieve the deposition of the metal, producing undesired electrochemical reactions in the aqueous electrolyte. In addition to aluminum, the electrodeposition of lithium, nickel, copper, cadmium, tin, antimony, zinc, silver or semi-conductors, such as germanium and silicon, has also been studied [47].

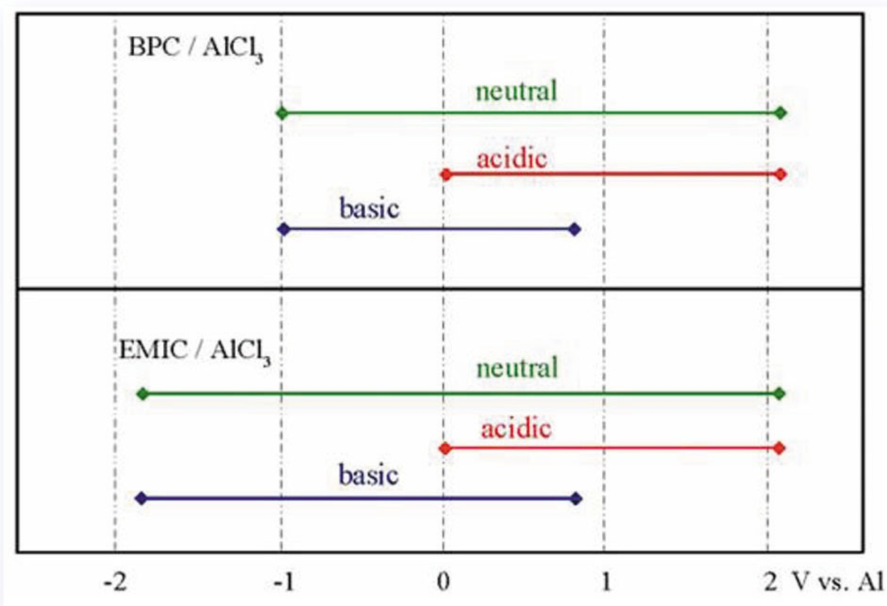

FIG. 7. Electrochemical stability interval for the electrodeposition of aluminum in ionic liquid medium BPC / $AlCl_3$ and EMIC / $AlCl_3$ [48].

Nanotechnology

In 1959, Richard Feynman was the first to propose that, at some point, materials could be manufactured with atomic sizes. Feynman stated that: “The principles of physics, as far as I can see, do not speak against the possibility of manoeuvring things atom by atom " [49].

Nanotechnology is the result of the individual manipulation of molecules or atoms with the aim of creating new materials with better properties. It is a relatively new field of research, where structures with dimensions from 1 to 100 nanometers are studied. One nanometer is one trillionth of a meter (1 nm $=1\times10^{-9}$ m) [50]. Fig. 8 shows a comparative diagram between 1 picometer (1×10^{-12} m) and 1 meter [51].

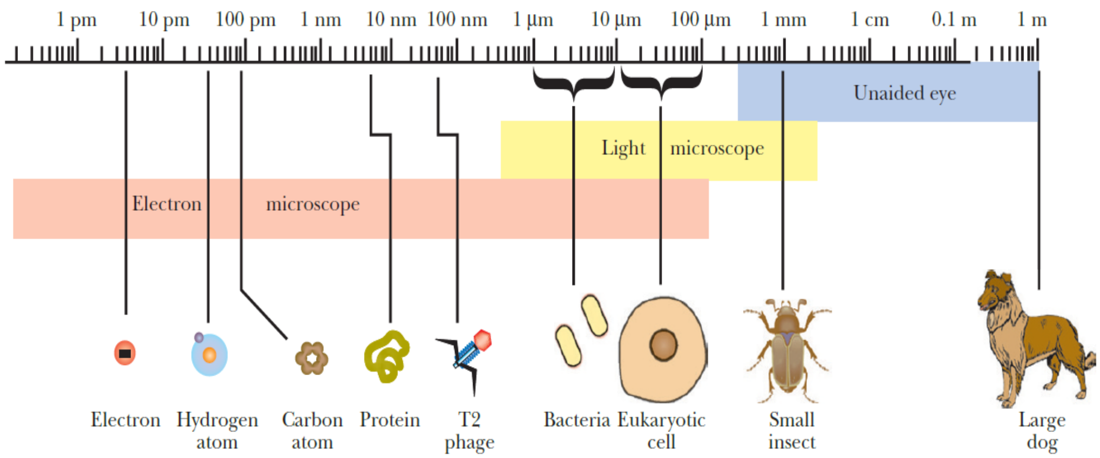

FIG. 8. Size comparison of objects ranging in size from 1 meter to 1 picometer [51].

Nowadays, the study of nanotechnology has been possible in microscopy, biochemistry, physical chemistry, among other sciences, where with the aid of these today it is possible to understand, design, manipulate, characterize and produce nanometric structures. One of the greatest advances in nanotechnology is the production and application of nanoparticles in biological sciences; an instance is its use in antitumor cells [52], pathogens, among others. Some nanomaterials have the characteristic of being antibacterial; for instance, silver, selenium, copper or carbon has shown antimicrobial activity [53].

Nanotechnology is an area of research that, in the past decades, has had great, amazing and irresistible achievements [54]. It has applications in microscopy and science, such as physics, chemistry, biology, medicine, materials science and engineering [55]. There are currently opportunities to design and produce articles, on a nanometric scale capable of satisfying the needs of this increasingly globalized world. In some areas, the use of nanotechnology has great relevance in energy, electronic and medical industry. The study and development of nanotechnology is so important, because it is the key to solving many of the problems facing the world, such as hunger [56], disease [57], lack of drinking water [58], the need to make better use of energy resources [59], among many others [60] (Fig. 9).

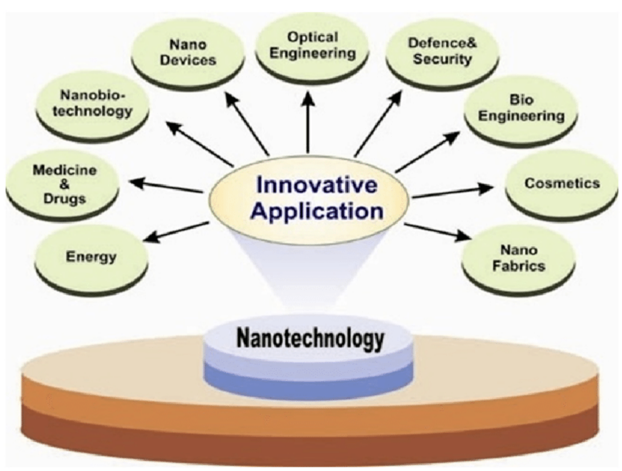

FIG. 9. Numerous uses of nanotechnology [61].

It can be stated that an area that generates a lot of interest and a lot of research is medicine [62], where efforts are aimed at improving quality and life expectancy; some time ago, for example, it was impossible to think that there would be particles that could directly attack a tumor. At present, this is a reality and there are advances in the treatment of cancer [63], autoimmune [64] or cardiovascular diseases [65].

An alternative of the medical area is the use of nanoparticles as therapeutic agents [66], as well as the coatings with antimicrobial characteristics to prevent the transmission of diseases, spread of infections and bad odours caused by microorganisms [67]. Thus, textile fibres, such as sportswear, underwear or medical textile fibres, such as gauze, bandages or surgical clothing, are today an area to exploit nanotechnology focused on anti-microorganisms [68].

In recent times, science has a revolutionary look at the area of nanotechnology. As the name specifies, the motivation has come from following applied requests, particularly in the fields of electronics and materials science, more willingly than a search for theoretical information. Nanotechnology comprises the separate manipulation of single particles or even atoms. Structure components atom-by-atom or molecule-by-molecule so as to produce materials with different or massively better properties represented possibly the unique aim of nanotechnologists. Nevertheless, the field has extended in a somewhat unclear way and inclined to comprise any structures so small that their investigation or manipulation was intolerable or unfeasible until now. At the nanoscale, quantum effects appear and materials frequently act oddly, related to their bulk properties [51].

Metallic Nanostructures and Metallic Nanoparticles

Nanotechnology has had a progressive development in recent years, because it describes the creation and exploitation of materials with controlled structural characteristics, with at least one dimension in the nanometer range. Nanotechnology presents a huge potential of applications in different scientific areas and technologies; for this reason, one of its objectives is to obtain nanoparticles of different metallic elements with different shapes and sizes, since they have unique optical [69], electronic [70], magnetic [71] and catalytic [70] properties. It should be noted that, when handling substances, particles and compounds in the nanometric scale, their physical and chemical properties are significantly altered, which creates a completely new perspective for the design of novel materials.

As presented in Fig. 10, the nanostructures possess different shapes. These nanostructures can be spheres, cubes, bi-pyramids, octahedrons, flowers, bars, rices, rods, carrots and wires. Within the ionic liquids, the size of the nanostructures is manageable. For instance, the size of silver nanocubes might be changed from 30 nm to 70 nm through presenting a drop quantity of sulphide or hydrosulphide into reaction-solution or through fluctuating silver forerunners [72]. The dimension of nano-carrots may possibly alter from 120 nm to 250 nm by changing the concentration of forerunners or reaction period.

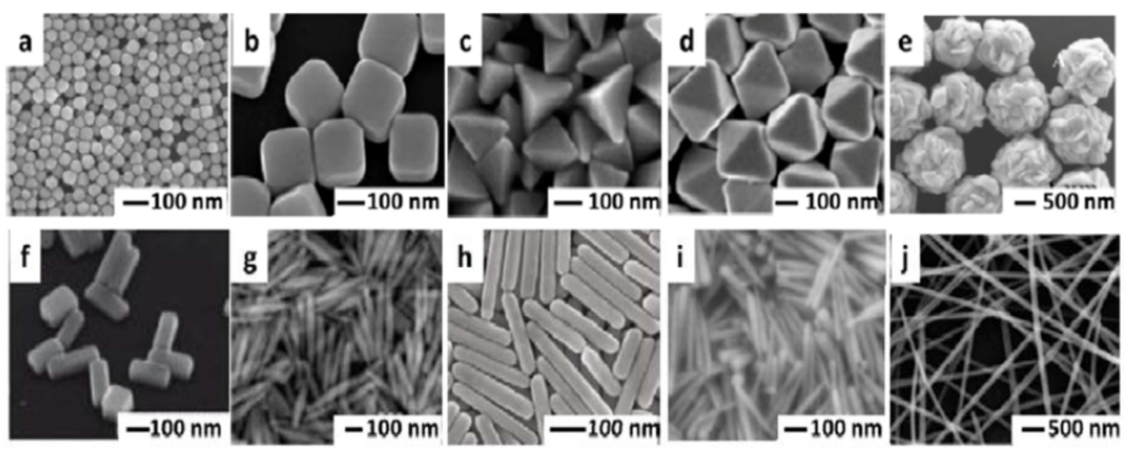

FIG. 10. Altered natures of silver nanostructures. (a) spheres [73], (b) cubes [74], (c) right bi-pyramids [75], (d) octahedrons [76], (e) flowers [77], (f) bars [78], (g) rices [79], (h) rods [80], (i) carrots [81] and (j) wires [82].

However, in the past twenty years, the interest has remarkably increased in nano-chemistry, the science that is responsible for studying and generating new synthetic routes for the production of building blocks of different sizes (within the nanometric scale) and investigating their shape, composition, structural surface, load and functionality, or for the construction of self-assembly processes spontaneously directed by defined surface pattern chemistry or lithography; these can form architectures that act in an intelligent function and predict a particular use [83]. For the formation of nanoparticles, one can use the metal salt reduction method with a synthetic reducing agent or with a bioreductor. Another alternative is to use surfactants for their formation. There are also physical techniques, such as laser ablation or reactive vapour deposition, among others; all these techniques are used in a general known method called "bottom-up" method, in which nanostructures are formed atom by atom until you reach materials with nanometric dimensions [84]. Another general method is the well-known one as "top-down" method, where macroscopic materials are fractionated until reaching the nanoscale; within this group of materials we find mechanical polishing and mechanical grinding.

There are different types of nanomaterials which are classified according to the type of material that makes them being divided into: metals, semiconductors and polymers [85]. Some nanoparticles are in the form of dots, tubes, nano-sheets, nano-tubes, nano-discs, spheres, bars and many others [86].

Nanoparticles are currently of great scientific interest due to their wide applications; they are a new type of materials, either based on ceramics, metals, polymers or composite materials (for example: polymer-metal, polymer-ceramic), where at least one of the dimensions of the nanoparticles is in the range of 1 to 100 nm [87]. The nanoparticles retain a large surface area /volume ratio, which allows their use in applications for catalytic materials, drugs or energy storage [88]. Among the most common metallic nanoparticles are those of gold, platinum, palladium and silver these can be synthesized by means of some methods where, in each of them, the morphology of the obtained nanoparticles is checked. There are physical and chemical techniques and among them is the chemical reduction of metallic salts in the presence of a stabilizing agent, which is a well spread technique [89].

Within metallic nanostructures, the most common and most used to date are nanoparticles, due to the relative ease with which they are obtained and the possibility of controlling their size and shape. A nanoparticle is defined as the smallest unit that can still behave as a complete unit in terms of property and transportation. At least, one of its dimensions lies between 1 and 100 nm. As nanoparticles approach the range of 1 to 10 nm, the effects of size and surface are made more obvious. This has implications that can be manifested in their magnetic properties, in electronic driving, in the melting temperature or chemical reactivity, among others. It is possible to control these properties selectively by modification of size, morphology and composition [90, 91].

These new particles have properties that are improved or completely different from those of their original materials, which open up the possibility of designing systems with specific properties. Many applications of nanoparticles are currently being developed in various fields, such as: image improvement, biological markers, bio-bactericides, solar cells, photonic crystals, among others.

The first object in which metallic nanoparticles were used was the Lycurgus calice of the fifteenth century, in Rome. It contained gold nanoparticles [92]. Mayan pigments dating to the eleventh century in the Chichen Itza ruins contain iron and chromium nanoparticles [93]. At the beginning of the sixteenth century, it was known to obscure silver compounds due to light; however, it was not until the nineteenth century when, with the work of Fox-Talbot and Daguerre [94], silver halide was used in the form of nanoparticles in photochemistry and photography [95]. Gold particles have also been used in the melting of glass, better known as "ruby glass" [96].

There are two chief methods for the production of metal nanoparticles: a bottom-up method and a top-down method (Fig. 11) [97]. Bottom- up method contains the creation of a structure; atom by atom, molecule by molecule or by self-assembly. In the top-down method, the suitable preliminary materials are reduced in size by means of physical and chemical procedures [98].

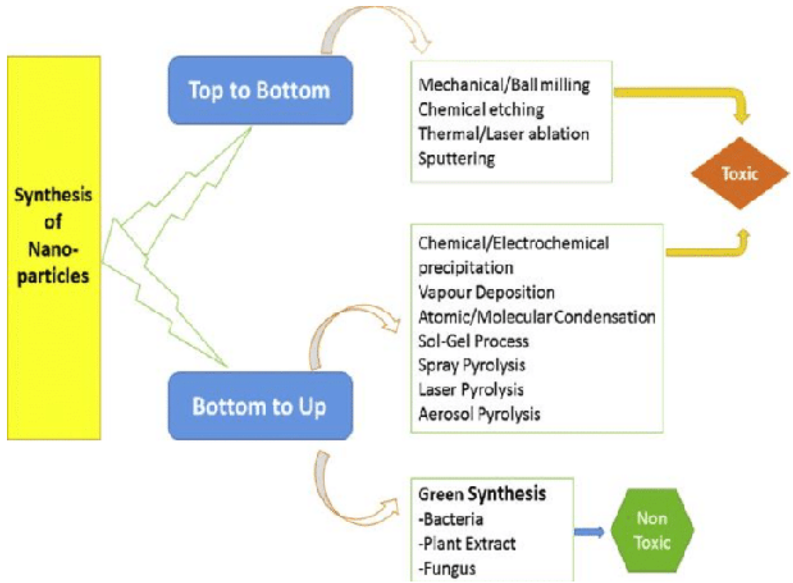

FIG. 11. Dissimilar methods for the production of metallic nanoparticles : (a) Top-bottom and (b) Bottom-up methods [97].

Ionic and Nanomaterial Liquids

The contribution of ionic liquids to the synthesis of materials and more particularly to that of nanostructures has been gradual during the past decade; however, it is very promising in view of the work [99] having been carried out for the time being. Ionic liquids are a perfect stabilizer system of metallic nanoparticles, which makes them excellent catalysts for very diverse reactions. In addition to the characteristics that were extensively detailed in previous sections, these ionic compounds have the rare property of forming extended systems [100] of hydrogen bonding when they are in a liquid state, which classifies them as "supramolecular solvents" and allows them to provide a certain nanostructural order to some spontaneous reactions (it is an almost essential property in the chemistry of colloids and surfactants).

The term nanotechnology refers to the design, manufacture and use of materials (which receive the generic name of nanomaterials) or devices (nano-devices) of dimensions in the nanometer scale [101]. This range of length ranges from individual atoms and molecules to polymer chains and proteins of considerable length, which makes nanotechnologies a multidisciplinary field of preferential interest for scientific disciplines, such as chemistry, electrochemistry, physics, molecular biology, among others. Perhaps, the clearest and most popular example of nanomaterial with promising applications is carbon nanotubes. Since their discovery in 1991 by the Japanese Sumio Iijima, carbon nanotubes have received considerable attention due to their extraordinary structural and electronic properties. One of the limitations of nanotubes is that they are strongly entangled with each other in a complex structure that provides them with unique properties, but with difficult processes at the same time [102].

Recently, a group of Japanese researchers has published the possibility of using carbon nanotubes and ILs to form physical gels that can be used in new electronic devices, antistatic materials and electro-conductive inks [103]. The formation of the gels is attributed to interactions of type π -π through which nanotubes are surrounded by ionic liquid molecules and form an ordered three-dimensional structure that has physical gel behaviour (Fig. 12). Due to the non-volatility of the ILs, the gels obtained are thermally stable and do not dry or wrinkle even when subjected to vacuum. In a subsequent experiment, these authors used a gel formed by a polymerizable ionic liquid to prepare a highly electro-conductive plastic material. Fukushima *et al.* [103] also explain that, incorporating only 4% by weight of carbon nanotubes, the mechanical properties of the polymer are increased by around 400%, with an electrical conductivity of 0.56 S/cm. On the other hand, several groups are investigating the carbon-IL nanotube pair as electrolyte-electrolyte material, studying the electrochemical behaviour of this particular system and its possible applications [104].

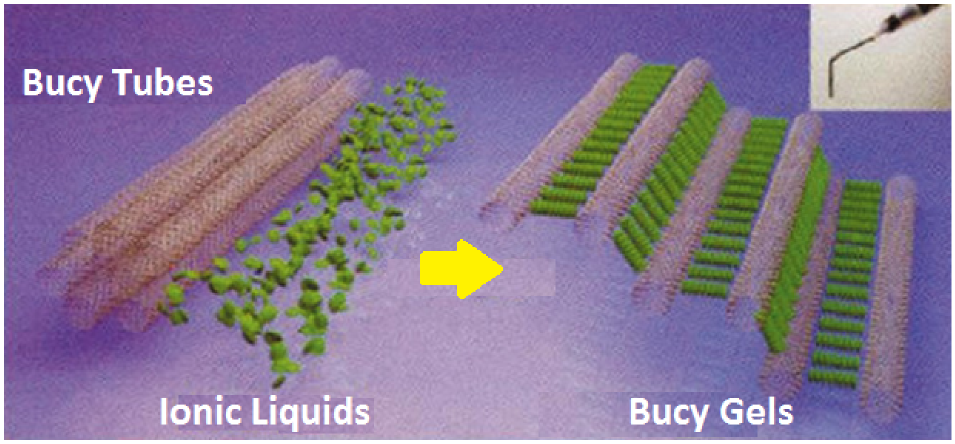

FIG. 12. Representative diagram of the gels obtained using carbon nanotubes and ILs [103].

Another classic example of nanomaterial are metallic nanoparticles that have very particular physico-chemical properties, which makes them interesting in electronic, magnetic, optoelectronic, pharmaceutical, biomedical, cosmetic, energy, sensor or catalytic applications. There are several recent investigations related to ILs and nanoparticles. Thus, Kim *et al.* [105] have developed a new method of synthesizing gold and platinum nanoparticles in one step using new ILs functionalized with thiols. These ILs function as stabilizing agents for the nanoparticles that are obtained with the added attraction that this method gives rise to small particles (2-4 nm) and uniform distributions. Other similar investigations are related to the formation and stabilization of nanoparticles of other metals, such as iridium, rhodium, ruthenium or TiO_2. But, the ILs are not only useful as a means of synthesis of these nanoparticles, since they can also be used to modify the surface of the nanoparticles. Itoh *et al.* [106] have recently published the synthesis and properties of gold nanoparticles modified with ILs based on the imidazolium cation. These authors have proposed the use of gold nanoparticles modified with an IL as an optical sensor for anions, since the presence of certain anions in the medium can induce changes in the colour of the aqueous dispersion of gold nanoparticles (Fig. 13).

FIG. 13. Photograph of dispersion of gold nanoparticles functionalized with an imidazolium LI in the presence of different anions: Cl^-, Br^-, BF_4^-, PF_6^- [106].

It can be agreed that room-temperature ionic liquids, such as $[C_4mim]^+$ BF_4^-, can be utilized as templates to formulate massive mesoporous silica through the nano-casting method [107]. Also, self-assembly does not depend on amphiphilic interfaces and the attendance of water It is estimated that the anticipated hydrogen bond stack mechanism with room temperature ionic liquids as templates might open innovative corridors to manufacture mesoporous materials beneath altered circumstances than currently utilized [108].

However, supramolecular structures are big molecules shaped by combination or bonding of smaller molecules. Correspondingly, they go to the nanoscience field as they are frequently likely to improve molecules of an anticipated form or functionality [109]. The prearranged “supramolecular” behaviour of ionic liquids delivers a soft pattern to direct the creation of bimodal porous carbon systems or the development of electrodeposits. Numerous crucial factors, such as: viscosity, polarity, surface tension, hydrogen bonding and overcoordination with solutes or surfaces, altogether show important roles in moderating class reactivity and mass transportation characteristics leading the origin of nanostructure [110].

Finally, ILs can also be used for transferring metallic nanoparticles from an aqueous phase to an organic phase. The group of Wei *et al.* [111] have developed a method for transferring gold nanoparticles to different organic solvents including ILs by simple agitation. More recently, CIDETEC has proposed a simple method of capture and transfer of liquid-liquid phase of silver nanoparticles (Fig. 14) [112].

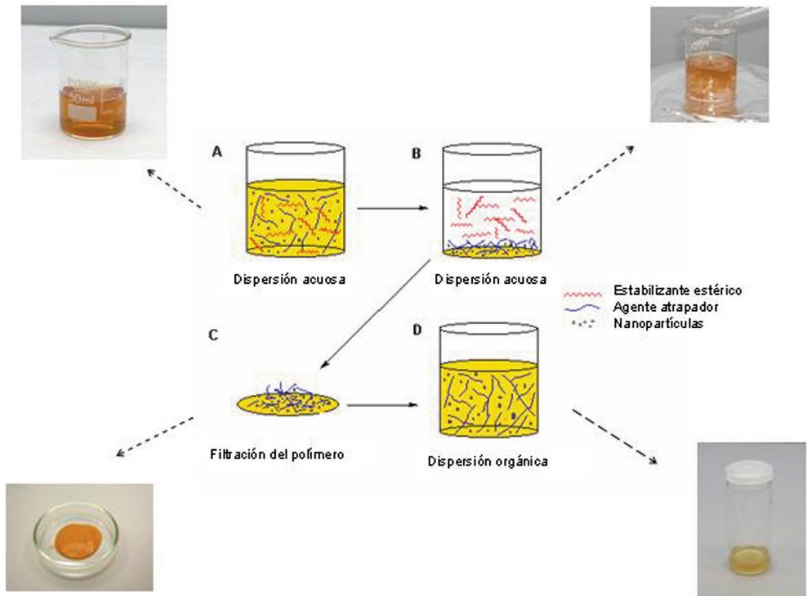

FIG. 14. Phase transfer process of silver nanoparticles using a polymer ionic liquid (PIL) [113].

This new method uses a polymer with a chemical structure similar to an ionic liquid called PIL (polymeric ionic liquid) as a phase transfer vehicle. This PIL precipitates in water by adding certain salts, trapping quantitatively the silver nanoparticles inside it. The polymeric solid can be easily recovered by filtration and subsequently dissolved in different organic solvents. The silver nanoparticles are red dispersed maintaining their initial shape and size [114]. This method not only offers the possibility of keeping the nanoparticles stored in a solid polymer, but also serves to transfer the nanoparticles or other nano-objects from the water to all kinds of organic solvents.

Nanoparticle Synthesis

In this review article, the authors deliver a summary of typical ionic liquids as exclusive solvents to produce precise nanomaterials comprising shape-organized nanoparticles, electrodeposited films, metal-organic outlines, colloidal gatherings, hierarchically absorbent carbons and DNA or RNA constructions. These revolutions demonstrate how ionic liquids can achieve manifold roles in leading chemistry and physics at the nanoscale: performing as supramolecular template, metal and carbon source, sacrificial agent and redox agent, altogether in the nonappearance of official steadying ligand.

Electrochemical Approaches

Nano-crystals possessing extraordinary index planes often display events greater than those of the most communal thermodynamically steady, low index; for instance, (111), (100) and even (110) planes because of the attendance of an extraordinary density of atomic stepladders, brackets and twist portion as energetic spots. Unluckily, crystal development rates orthogonal to a high index plane are characteristically quicker; consequently, high index planes are generally reduced throughout nano-crystal growing. Certainly, this leaves a task to manufacture well distinct nano-crystals surrounded by high index surfaces.

Sun et al. have participated extensively to this field in recent times, inventing a forthright electrochemical way to identical ~200 nm platinum nano-flowers (Fig. 15) even-handed shrill single crystalline petals through straight electrodeposition on top of a glassy-carbon electrode in chloro-platinic acid comprising reline ionic liquid at 80 °C [115]. The electro-catalytic action of the Pt nano-flowers for ethanol oxidation in acid solution demonstrated to be approximately twice that of marketable Pt black substance built upon the oxidation current density. Fascinatingly, running the production at other temperatures produced imprecise petals, demonstrating the gentle association among diffusive transference, nucleation and growth in ionic liquids.

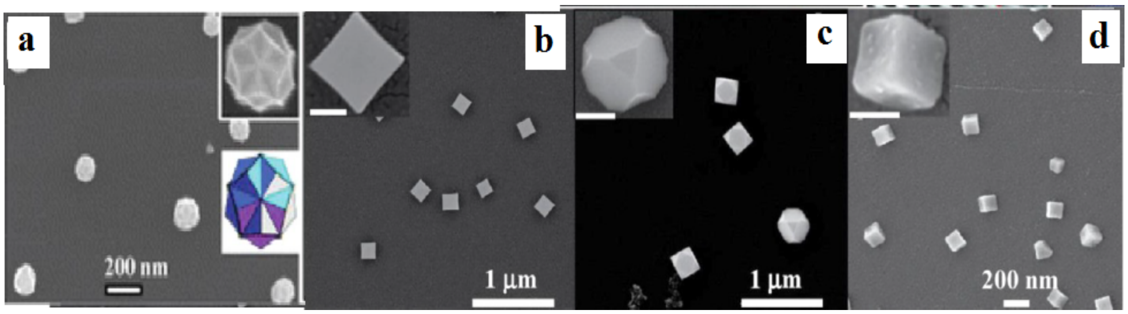

FIG. 15. (a) High amplification SEM image of Pt nano-composites, (b-d) SEM images of Pt nanostructures electrodeposited on glassy carbon at 80 °C for 60 min growth at different combinations of applied square-wave potentials [115].

Anti-Solvent Approaches

Wong et al. [116] invented an ingenious two-stage anti-solvent approach to 10-nm thick single crystalline mesoporous ZnO nano-sheets by means of firstly liquefying ZnO powders in reline ionic liquid at 70 °C shadowed by relaxed inoculation into a water bath as shown in Fig. 16. Calcination of the recuperated precipitous, which enclosed a combination of wurtzite ZnO and $Zn_4CO_3(OH)_6{\cdot}H_2O$ segments the latter shaped by cohort of carbonate and hydroxide ions resulting from urea breakdown activated a topotactic conversion connecting combination of vacuums to create superior arbitrarily dispersed holes. The calcined mesoporous ZnO nano-sheets displayed great precise superficial areas and showed approximately as active as profitable TiO_2 in the photo-catalytic deprivation of methylene blue.

Wet Chemical Production of Nanostructures

With a convenient room-temperature insignificant reduction of $HAuCl_4$ by a selected acid in anhydrous reline ionic liquid, Sun and his group acquired approximately 300-nm polycrystalline gold-star moulded NPs restricted through (331) and adjacent extraordinary index surfaces [117]. The outcome is an outstanding result in that neither kernels nor surfactant additives were necessary. Besides the NPs showing a steady pentagonal regularity, additional star moulded gold NPs of numerous outlets were likewise detected and, through solely regulating the gratified water, additional single morphologies were obtained, comprising snow-flake shape NPs and nano-thorns, as presented in Fig. 17. Moreover, the star-formed NPs verified to be active electro-catalysts, through a 150 mV optimistic change of the start potential for H_2O_2 drop and over a 14 folding improvement in drop current density associated with that on a polycrystalline gold electrode, a product qualified to the attendance of high-index surfaces.

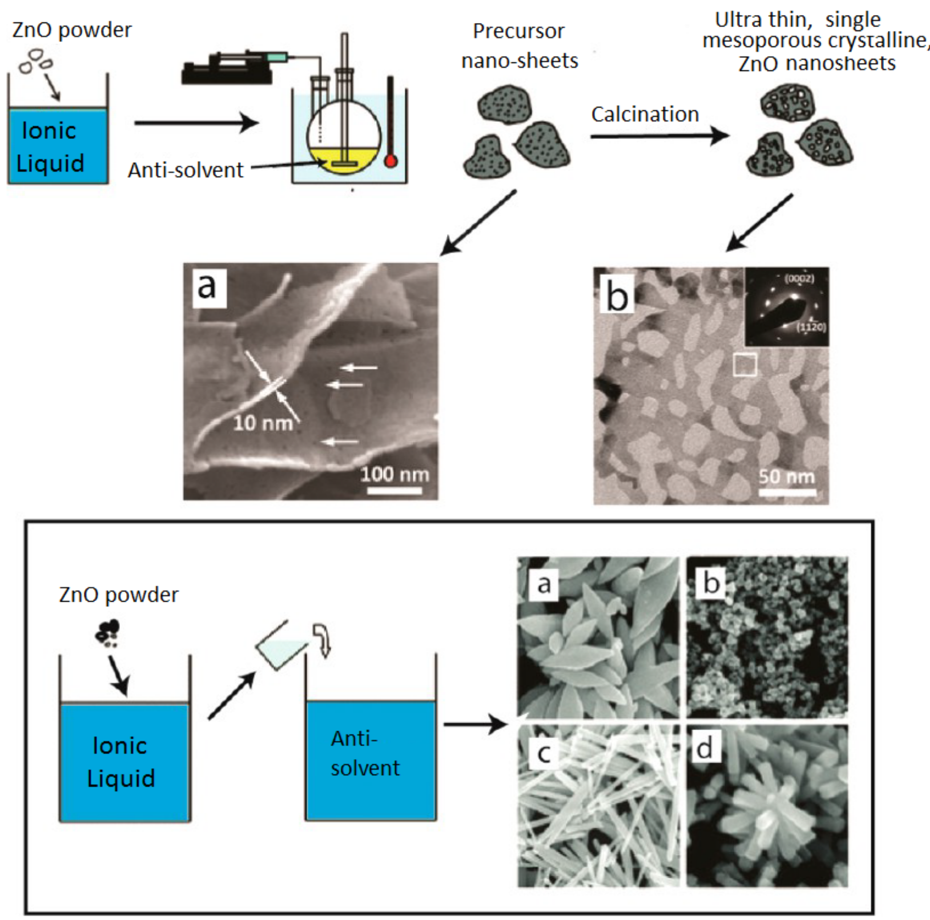

FIG. 16. (Top) An anti-solvent methodology for the production of ZnO nanosheets. (Bottom) Graphical demonstration of the anti-solvent technique for shape-controlled synthesis of varied ZnO nanostructures [118].

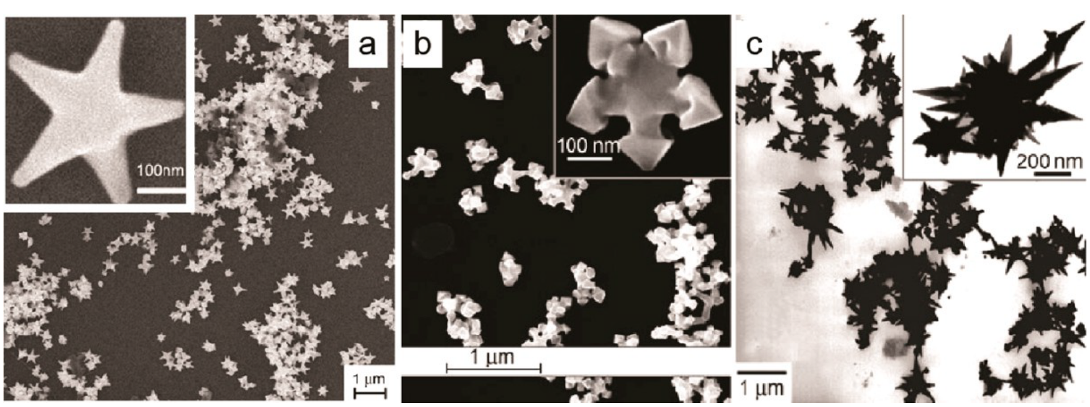

FIG. 17. SEM images of (a) star-shaped and (b) snow-flake-like gold NPs. (c) TEM image of gold nano-thorns [117].

Toxicity of Ionic Liquids

Up to now, what the authors mentioned regarding the ionic liquids and their roles in nanoparticle preparation is promising. Nevertheless, ionic liquids frequently utilized up to the present time are toxic in nature, which has been verified by numerous toxicological statistics intended at an extensive choice of creatures. However, scientists need to discover innovative approaches to take benefit of the non-volatile nature of ionic liquids not exposed by typical liquid media [119]. Moreover, this feature must also be deliberated when the toxicological concern of ionic liquids is studied. The toxicological investigation of ionic liquids has been always verified; for instance, toxicity bioassessment consuming plants [120] and measurable construction property association modeling [121] have together appeared in the articles. The adaptable nature of ionic liquids once more represents the authority of designer-solvents; specifically, ionic liquids can be intended to be harmless. Through the adjacent partnership between toxicologists and scientists, greener and better-organized ionic liquids can be achieved.

Conclusions

Nanostructured metals represent an important class of nanomaterials with multiple applications, such as: optics, sensors, catalysts and magnetic recording media, among others. The properties (optical, electronic, magnetic and catalytic) that metallic nanoparticles exhibit have a strong dependence on their shape and size, as well as on the nature of the metal or metals involved.

Ionic liquids and their technological applications constitute an exciting and emerging field of research. Although in the beginning, most of the research was related to their use in "Green Chemistry", great advances were subsequently made using the ILs in various applications and advanced electrochemical devices. In addition, the use of ILs in the design of nanomaterials is one of the most current and promising fields in nanotechnology due to the very diverse applications of these compounds.

A rapid growth with a great potential can be noticed in metallic nanoparticle synthesis, which potentially leads to generate functional materials. To achieve this objective, it is clear that a multidisciplinary interaction and collaboration between biologists, chemists, physicists and engineers is needed in order to solve this synthesis issue of particles with desired characteristics. This, perhaps, leads to study their properties and their effects on the environment, as well as to explore new applications of the nanostructured metallic materials that are sustainable to be utilized.

Finally, ionic liquids propose incredible chances and open fascinating viewpoints for producing well-arranged nanostructures inside an anhydrous or low containing water medium. The authors accomplish this review article by proposing their views on the progress of the arena, indicating to zones of unblemished and fascinating service which will confidently realize achievement in the upcoming years.

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