RECENT DEVELOPMENTS IN IONIC LIQUIDS AND NANOMATERIALS

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ABSTRACT

In this paper, the development of Ionic Liquids to synthesize various types of nanoparticles having commercial and viable uses in 21st century is discussed. Nanotechnology is a promising methodology that generates various types of nanoparticles. Research-based on Ionic Liquids is in the progressive stage and by amalgamating it in nanotechnology, amazing results can be accomplished. Thus, efforts must be made to develop advanced techniques to synthesize nanoparticles with desired structures and morphologies in eco-friendly and sustainable Ionic Liquids to reduce environmental pollution in the future. With this perspective, various developments and efforts made by the scientists in the domain of Nanomaterials and Ionic Liquids have been reviewed.

Keywords: Ionic Liquids, Nanoparticles, Synthesis of Nanoparticles, Eco-friendly, Sustainable.

INTRODUCTION

Nanotechnology or “nanoscale technology” is simply the manipulation of matter with at least one dimension sized from 1 to 100 nanometres. This encompasses a myriad of scientific fields such as chemistry, physics, materials science and biology for both its comprehensive understanding and the development of novel applications. The unique fact that the properties of matter (like optical, magnetic and electrical properties) significantly differ at nanometer range from that of its bulk size is exploited successfully to produce nanomaterials. The properties of nanomaterials are controlled by their intricate structures and morphologies. A novel field, nanotechnology, deals with the production of such materials that have extensive application in the fields of medicine, drug delivery, biotechnology, energy harvesting, electronics, and also including many other industrial and household applications.1 With the emergence of these applications, many new fields such as nanoelectronics, nanomedicines, nanophotonics, nanobiotechnology and so on have come into a prominent existence.2-4 Henceforth, there has been an exponential growth in the nanotechnology research activities that have the extensive efforts of scientists and engineers of different branches.5-22, 59,60

Ionic Liquids as a Remarkable Choice in Nanomaterial Synthesis

Ionic Liquid (IL) is a reasonable choice to produce inorganic nanomaterials having specified morphologies, novel structures and refined properties. ILs have some unique properties that blend well with the synthetic procedures of inorganic materials. Because of their low interface tensions, ILs increase the rate of nucleation. They affect the shapes of synthesized materials as they interact with them.

The general methodology to produce nanomaterials involves the use of organic solvents or water though the choice of organic solvents is limited.5 Also, the environmental concern of some organic solvents is a major issue nowadays. Thus, a benign and safer solvent for the reactions is being considered. The ionic liquid is one such example that has a structural organization in the range of nanometers which further can actually instigate the spontaneous self-aggregation of structures of materials in nanoscopic range. Thus, nanomaterials with unique and novel morphologies and functional properties can be created in ionic liquids. The well- synchronization of ionic liquids and nanomaterials has caught the immense attention of researchers.
The organizational behaviour of ionic liquids has been suggested by the neutron scattering experiment.\(^6\) The weak electrostatic interactions such as van der Waals interactions and hydrogen bonding give an intrinsic “nanostructure” to ionic liquids.\(^7,9\) These extensive electrostatic and hydrogen-bonded networks give a three-dimensional structure to them. This network is disrupted with the introduction of some other molecule into it. This triggers the genesis of nano-structures having well-defined polar and non-polar areas.\(^7,10\) This property of ILs is exploited to synthesize the required and well-defined metal nanoparticles.\(^7,10,11\) This network structure of IL prevents the agglomeration of metal nanoparticles and further leads to their stabilization in the media. This has been widely studied and researched upon by many scientists over the years.\(^7,14\) Generally, metal nanoparticles are generated as dispersions by employing any of the methods mentioned below:

- **Reduction:** The appropriate salts of the metals are reduced by the selective reducing agent
- **Decomposition:** The appropriate metal-organic precursors are decomposed using various organic solvents.

This has been described in detail in various research articles.\(^15-22\) Thermodynamically, the large-sized particles are favoured over small-sized ones. The growth of large-sized particles takes place as the smaller ones attach themselves onto the surface of a larger particle by diffusion through the solution. Thus, with the use of additives, a protective layer is formed between these nanoparticles, which prevents their agglomeration and leads to the stabilization of smaller ones.\(^23,24\) The surfactant ions as additives form bilayers which lead to an electrostatic stabilization. A layer of steric coverage is created when surface-capping ligands or polymers are used as additives in nanomaterial synthesis. Thus, the reduced need for additional stabilizers for the preparation and stabilization of the smaller nanomaterials in ILs makes them a remarkable solvent.

Besides acting as a solvent, ILs serve as a template in the formation and stabilization of the small-sized nanostructures owing to its tendency to form hydrogen bonds, \(\pi-\pi\) stacking interactions and self-aggregation.\(^25,26\)

In imidazolium-based ILs, the \(\text{H}\) between two nitrogens has enhanced the ability to form hydrogen bonds with nanomaterials. The positive charge on imidazolium ring is delocalized over the whole ring that actually accentuating the above process. Further, the stability of such ILs is attributed to the \(\pi-\pi\) interaction between the neighbouring stacked imidazolium rings. \(\text{TiCl}_4\) can be hydrolyzed in a composite system composed of water/\([\text{Emim}]\) to give the rutile (\(\text{TiO}_2\)) nanoparticles and rutile-anatase composite nanomaterials.\(^27\) Because of its robust interactions, including hydrogen-bonding and \(\pi-\pi\) stacking interaction with rutile nanoparticles, the IL, \([\text{Emim}]\text{Br}\) served as a template and controlled the phase and morphology of \(\text{TiO}_2\) nanoparticles. It is also proposed that the cationic part of IL, \([\text{Emim}]^+\) has strong interaction with \(\text{TiO}_6\) octahedra molecule, which could be another fundamental reason for the rutile phase formation. The IL template also orients the growth and hence the shape of nanocrystals. In \([\text{Emim}]\text{Br}\), the rutile nanocrystals have rod-like shapes. Based on these observations, a series of shape-controlled ZnO nanostructures have also been generated in imidazole-based ILs at reasonably low temperature.\(^28\) The hydrogen bonds can also be generated between the anions of ILs and nanomaterial. This has been illustrated by the synthesis of mesoporous silica in \([\text{Bmim}][\text{BF}_4]\).\(^29\) Here, the anion \(\text{BF}_4^-\) formed hydrogen bonds with the silanol groups, which might be responsible for the orientation of \(\text{BF}_4^-\) along the walls of pores. The cation, \([\text{Bmim}]^+\) got also arrayed along with the silica. Overall, the silica particles got oriented in a proposed fashion. It is proposed that the \(\pi-\pi\) stack interaction between the imidazolium rings contained in \([\text{Bmim}][\text{BF}_4]\) supplements the stabilization of the mesoporous structure of silica.

Long-chain ILs have a strong tendency for self-aggregation and this fact is exploited to prepare nanostructures.\(^30\) The anisotropic gold nanoparticles with specific shapes and morphologies have been fabricated in the IL, \([\text{C10mim}]\text{Cl}\).\(^31\) The self-assembled structure of \([\text{C10mim}]\text{Cl}\) traps and stabilizes \(\text{AuCl}_4^-\) and induces the formation of gold nanoparticles. If the IL is changed to \([\text{C16mim}]\text{Br}\), then gold nanoplates can be synthesized with a specified shape.\(^32\)

**Different Routes for Synthesis of Nanomaterials in ILs**

To fabricate inorganic nanoparticles, various methods have been designed wherein appropriate ILs is employed as a reaction media. These include: chemical reduction, thermal reduction, photochemical
decomposition, sonochemical reduction, electroreduction, gas-phase deposition and microwave irradiation methods.

**Chemical Reduction**

The salts of metal can be reduced using the reductants like gases, organic and inorganic chemical reagents in the ILs as a solvent to generate metal nanoparticles. This constitutes the most common methodology of forming metal nanoparticles. Using this method, many metal nanoparticles like that of Rh, Pt, Pd have been prepared. The following table lists the reaction conditions required to manufacture various metal nanoparticles.

| Metal Nanoparticle | Metal Salt Precursor | Reductant | Ionic Liquid   | Ref. |
|--------------------|----------------------|-----------|----------------|------|
| Ag                 | AgBF<sub>4</sub>     | H<sub>2</sub> | [BMIm][BF<sub>4</sub>] | 33   |
| Au                 | HAuCl<sub>4</sub>    | NaBH<sub>4</sub> | [BMIm][PF<sub>6</sub>] | 34   |
| Cu                 | Cu(OAc)<sub>2</sub>:H<sub>2</sub>O | H<sub>2</sub>NH<sub>2</sub>:H<sub>2</sub>O | [BMIm][BF<sub>4</sub>] | 35   |
| Pd                 | H<sub>2</sub>PdCl<sub>4</sub> | NaBH<sub>4</sub> | [HSCO<sub>2</sub>Im][Cl] | 36   |
| Pt                 | PtO<sub>2</sub>      | H<sub>2</sub> | [BMIm][BF<sub>4</sub>]; [BMIm][PF<sub>6</sub>] | 37   |
|                    | H<sub>2</sub>Pt(OH)<sub>6</sub> | HCOOH | H<sub>2</sub>O/[BMIm][PF<sub>6</sub>] | 38   |
| Rh                 | RhCl<sub>3</sub>:3H<sub>2</sub>O | H<sub>2</sub> | [BMIm][PF<sub>6</sub>] | 39   |

The fabrication of the nanosized particles of any metal using the above method can be easily accomplished both in the glass flasks and the microfluidic reactors.\(^{46}\)

**Thermal Reduction**

The metal precursors can be simply heated without any reducing agent in appropriate ILs to generate metal nanoparticles. For instance, if the gold salt such as Au(CO)Cl or KAuCl<sub>4</sub> is heated without adding any reducing agent in imidazolium-based ILs, then it activates the production of gold nanoparticles.\(^{41}\) Pd nanoparticles sized ~1nm are formed by heating the palladium acetate (Pd(OAc)<sub>2</sub>) in the concomitance of PPh<sub>3</sub> in imidazolium-based IL, [BMIm][Tf<sub>2</sub>N] at 80°C.\(^{21}\) Another way to produce them is to heat Pd(OAc)<sub>2</sub> in hydroxyfunctionalized ILs.\(^{42}\) On thermal decomposition, an organometallic Pt(IV) precursor in the IL, [BMIm][BF<sub>4</sub>] generates Pt-nanocrystals.\(^{43}\) This process excludes the use of any reducing agent.

The generation of metal nanoparticles and their deposition on the support to produce metal nanoparticles supported hybrid materials is well carried out in ILs. The hybrid of carbon nanotubes and Au nanoparticles are created by heating HAuCl<sub>4</sub>:3H<sub>2</sub>O on poly(ethylene terephthalate (PET) films in IL [BMIm][BF<sub>4</sub>].\(^{44}\) Similarly, Pt nanoparticles are synthesized by thermal decomposition of a Pt precursor and deposited on thiol-functionalized graphene derivatives in the IL.\(^{45}\)

**Photochemical Decomposition**

Metal nanoparticles can be produced by irradiation of metal precursors with UV light and the method is called photochemical reduction. This method excludes the manoeuvring of reducing agents and hence the nanoparticles obtained in this case are not contaminated with the other reagents. This can be illustrated by the formation of Au nanoparticles that can be performed either by the UV-induced decomposition of HAuCl<sub>4</sub> taken in the IL 1decyl-3-methyl-imidazolium chloride for 30 to 70 minute\(^{31}\) or by UV irradiation of HAuCl<sub>4</sub>:4H<sub>2</sub>O taken in a mixture of solvents consisting of an IL, [BMIm][BF<sub>4</sub>] and a small amount of the organic solvent, acetone (ratio by volume 10 : 1) for 8 hours.\(^{46}\) The former procedure results in nanorods of size 100-1000nm, while the latter gives 4µm long and 60 nm thick nanosheets. The other example includes the formation of Pt nanoparticles by the UV-induced decomposition of a Pt precursor in IL, [BMIm][BF<sub>4</sub>].\(^{43}\)

**Sonochemical Reduction**

Here, the modus operandi is the irradiation of metal precursors with ultrasound waves. This prompts the generation of metal nanoparticles. Pd nanoparticles sized 20 nm are fabricated by the IL-assisted sonication of Pd(OAc)<sub>2</sub> or PdCl<sub>2</sub> for 1 hour.\(^{20}\)
Electrochemical Reduction
The properties of ILs that make them inert in electrolytic processes is an advantage and offers an eco-friendly route to generate nanoparticles in ionic liquids using electrochemical reduction where only electrons are used as reducing agents. However, the metal nanoparticles generated using this method are often above 100 nm in size.
The pulsed electrodeposition method is the most common method to synthesize nanocrystalline metals such as nanoNi, nanoPd, nanoCu, nanoFe and nanoCr.\textsuperscript{47-49} Nanostructured iron particles can be accumulated from the electrochemical reduction of FeCl\textsubscript{3} in the presence of anhydrous AlCl\textsubscript{3} and an additive such as benzoic acid in the IL, [BMIm]Cl. The nanoparticles of metals (Mg and Al) which are less-noble in nature can be synthesized successfully by the electrodeposition method if it is carried out in the ILs (Negative results are obtained in aqueous electrolytes). For instance, nanocrystalline Al is obtained by pulsed electrodeposition when carried out using anhydrous AlCl\textsubscript{3} in the electrolyte [EMIm]Cl.\textsuperscript{50} By this method, metal nanoparticles can also be deposited on supporting material, e.g., Ag nanoparticles obtained from electroreduction of AgBF\textsubscript{4} in [BMIm][BF\textsubscript{4}] can be deposited on the surface of TiO\textsubscript{2}.\textsuperscript{51}

Gas-phase Synthesis
High purity nanoparticles are generated using gas-phase synthesis. In this method, the precursors (gaseous or liquid) taken in ILs are decomposed by the method of combustion and nanoparticles are made by using any of the following methods:
(i) magnetron sputtering
(ii) plasma reduction
(iii) physical vapor deposition, and
(iv) electron beam and \(\gamma\)-irradiation
Magnetron sputtering includes the deposition of elements that are ejected by plasma ion bombardment and finally yielding the nanoparticles. This process is done in ILs. This technique is used to generate metal nanoparticles that are of the size of 10 nm and even less and are stable without any requirement of the stabilizing agent. The magnetron sputtering of gold foil when executed in several imidazolium-based ILs effe\textsubscript{c}uated the gold nanoparticles in size range of 3-5 nm.\textsuperscript{52} Plasma deposition or glow discharge electrolysis (GDE) is a methodology wherein the application of high voltage initiates the discharge in the gas that is in between the metal electrode and the solution. In ionic liquid glow discharge electrolysis (IL-GDE), also known as plasma electrochemical deposition (PECD), the discharge starts in the gas between the ionic liquid solution and metal electrode.\textsuperscript{53} Precursor solvated in IL is reduced by the electrons that are generated from the plasma triggers the formation of the nanoparticles.\textsuperscript{54} DNA and HauCl\textsubscript{4} immobilized in the IL is utilized like the liquid electrode to generate gold nanoparticle-DNA encapsulated carbon nanotubes.\textsuperscript{55} Another technique that is subgrouped under this category is physical vapor deposition. This works on the method- solvated metal atom dispersion. For example, the copper powder is dispersed on the surface of IL, [BMIm][PF\textsubscript{6}] and heated till evaporation under a high vacuum. The proliferation of Cu nanoparticles sized 3 nm is achieved by this process.\textsuperscript{56} The electron beam and \(\gamma\)-rays are focused on the metal salts taken in the ILs that give solvated electrons and/or radicals which further generates metal nanoparticles. This is a physical vapor deposition method. Au nanoparticles are generated by the electron beam irradiation of NaAuCl\textsubscript{4}\cdot2H\textsubscript{2}O precursor in the appropriate IL.\textsuperscript{57}

Microwave Irradiation
The peculiar properties of ILs like high polarity and high dielectric constant make it efficient to absorb microwave energy. An easy, prompt and eco-friendly method to synthesize metal nanoparticles is manoeuvring the microwave for the decomposition of metal carbonyls Mx(CO)y dissolved in ILs. Metal carbonyls already have the metal in a zero-valent oxidation state and so eliminate the use of reducing agents in the process. The metal in the precursor should necessarily have the oxidation state of zero for metal nanoparticles synthesis by this process. The side product CO is the main contaminant in the
nanoparticle production process and is dislodged from the dispersion, thereby reducing the contaminations from metal nanoparticles and IL dispersion. Microwave irradiation leads to superheating of the precursor that gives metal particles which also absorb microwaves and gives nanoparticles. The decomposition of the metal carbonyl Cr(CO)_6, which is immobilized in the IL, [BMIm][BF_4] is subjected to microwave. This kind of treatment results in Cr nanoparticles generation. Similarly on microwave irradiation of Fe_2(CO)_9 in [BMIm][BF_4] gives Fe nanoparticles are generated.

CONCLUSION
This review implicates the assorted technologies that can be used for the synthesis of nanosized metal particles deploying ionic liquids as solvents. Nanotechnology is the field of the future that will have revolutionary connotations all over the world in terms of the spectrum of applications ranging from daily uses to specialized ones. To meet the growing demands of nanoparticles, ionic liquids as a solvent for synthesis are found to be green and eco-friendly alternatives. Many technologies sync in well with ionic liquids that are employed in the genesis of metal nanoparticles of desired structures, sizes and morphologies.

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