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Ionic Liquids as Advantageous Solvents for Preparation of Nanostructures

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1. Introduction

Nanoparticles are defined as solid particles with a size in the range of 10-1000 nm, depending on the applied synthesis method different structural motifs can be obtained: nanoparticles, nanorods, nanowire, nanoclusters or nanospheres. The nanoparticles have drawn great attention across various areas of science and nanotechnology due to their exclusive physicochemical properties, which are attributable to the quantum size effect and single-electron transitions.

The sciences as chemistry, physics, biology, medicine and electrical engineering are becoming more and more connected with nanotechnology and strongly interrelated. (Kumar, 2010; Suh et al., 2009).

When one talks about nanoparticle synthesis, characterization and their properties, it is today obligatory to consider issues related to a tight control over size, shape, crystal structure and morphological purity. Obviously, chemical composition is also critical, but important aspects in the (nano)materials science have been widely demonstrated to correlate with the morphological/structural parameters (Mudring et al., 2009).

First, the ionic liquids were used in electrosynthesis of various metallic nanoparticles, such as palladium (Pd), iridium (Ir) and semiconductor nanoparticles such as stable germanium or Ge nanoclusters (Deshmukh et al., 2001; Dupont et al., 2001; Endres & Abedin, 2002; Endres et al., 2003). Then the preparations of Ti nanowires onto graphite by electroreduction (Mukhopadhyay & Freyland, 2003) were extremely stimulating. In all of these examples the potential for electrochemical reactions and the high polarity of ionic liquids are exploited.

In addition to electrochemical reactions different other techniques are used to fabricate nanostructures, wherein often various solvents are applied. As a recent and very effective technique also ionic liquids are employed in the creation of nanostructured materials, because of their unique properties such as extremely low volatility, wide temperature range in liquid state, good dissolving ability, high thermal stability, excellent microwave absorbing ability, high ionic conductivity, wide electrochemical window, non-flammability, etc (Antonietti et al., 2004; Suh et al., 2004). Many ionic liquids are not only non-flammable but also stable in a broad temperature range from room temperature to 400 °C. These unique properties can be exploited in an effective preparation of nanostructures with control of size

and size distribution. This aspect is crucial for a number of applications of nanostructures such as in medicine, where nanoparticles should have a size in the range of 2 to 10 nm. The heat stability of ionic liquids can be exploited for example in the preparation of iron oxide at high temperature, in this case the nanoparticle size can be controlled by the temperature of their preparation. Furthermore alloy nanoparticles are obtained at a high temperature, ionic liquids can act as a promising solvent for their preparation.

The present review presents a study of selected exemplary works that outline the progress in research on the application of ionic liquids in the nanoparticle field covering the last ten years period. Diverse types of nanoparticles are presented which were synthesized in ionic liquids, using different techniques. Our aim is to provide a comprehensive overview on the synthesis of different nanoparticles in ionic liquids, and also the possibility to influence the morphology, structure and properties of nanoparticles using ionic liquids. Very recently a review appeared (Patzke et al., 2011) describing the application of ionic liquids in the preparations of metal nanoparticles excluding metal oxides which however are also very important from several points of view.

Ionic liquids are able to offer exceptional properties as media for the synthesis of nanoparticles. The low surface tension of many ionic liquids leads to high nucleation rates and, in consequence, to small particles. The ionic liquid itself can perform as an electronic as well as a steric stabilizer and thus can lower particle growth. As highly structured liquids, ionic liquids have a strong effect on the morphology of the particles formed (Mudring et al., 2009).

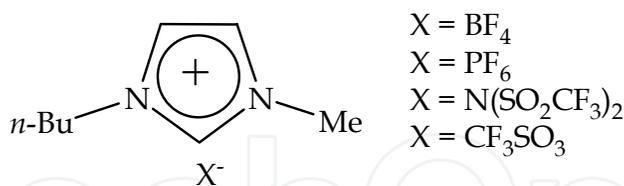
Ionic liquids that have an imidazolium ring as cation can interact with many different species, as they provide hydrophobic or hydrophilic regions and a high directional polarizability. This is one of the special qualities of imidazolium ionic liquids that differentiate them from the classical ion aggregates of which ion pairs and ion triplets are widely recognized examples. This structural organization of ionic liquids can be used as "entropic drivers" for spontaneous, well-defined, and extended ordering of nanoscale structures. Indeed, the unique combination of adaptability towards other molecules and phases plus the strong hydrogen-bond-driven structure makes ionic liquids potential key tools in the preparation of a new generation of chemical nanostructures.

The morphology and the properties of the nanoparticles are very well correlated, therefore depending on the size and shape of nanoparticles their properties can change very much. However, the size and shape can be tailored by the synthesis method and certainly at the same time the properties of nanoparticles. That means that by synthesis method one can achieve nanoparticles with required properties for different applications.

Owing to their outstanding properties, ionic liquids have been exploited successfully in the synthesis of different inorganic nanoparticles. Therefore a variety of inorganic nanostructures including metal nanoparticles, metal oxide nanoparticles, metal complexes nanoparticles, alloys etc. have been produced in various room temperature ionic liquids. However, in contrast to their application in organic chemistry, the use of ionic liquids in inorganic synthesis in particular in the synthesis of inorganic nanoparticles is still in its primary stage, and more exploration is necessary to utilize their advantages fully.

The first part of this chapter describes the synthesis of metal nanoparticles in ionic liquids, in the second part we will illustrate the synthesis of some metal oxide nanoparticles in ionic liquids and the last part points out the type of alloys that can be obtained in ionic liquids.

Ionic liquids mostly applied in the preparation of metal, metal-oxide and alloy nanoparticles are shown in Scheme 1.



Scheme 1. Examples of imidazolium ionic liquids used in the preparation of metal nanoparticles.

2. Synthesis of metal nanoparticles in ionic liquids

The optical and electrical properties of metal and semiconductor nanoparticles have been extensively utilized in the creation of advanced materials for use in electronics, sensors, and photonics. Metal nanoparticles have also served as precursors to form nanowires or nanorods. The extraordinary properties of metal nanoparticles largely depend on their morphology and particle size. Accordingly, both the precise control of the particle size and a clear understanding of their chemical phenomena remain a research task. Various synthetic methods for metal nanoparticles have been reported, but most of them were based on the reduction of a metal ion by toxic reducing agents such as NaBEt_3H , LiBEt_3H , and NaBH_4 .

To obtain stable nanoparticles consisting exclusively of chemically pure transition metals, without using any stabilizing agent, is still an unsolved topic that remains the subject of contrasting opinions (Ott & Finke, 2007). In the case of physical preparation techniques, traces of hydrocarbons deriving from the vacuum systems, gases present in the deposition environment, or other contaminants that come into contact with the nanoparticles during real applications, always give rise to an outer shell, even of a small thickness, which stabilizes the pure metal core nanoparticles. Even in solution when the stabilizers are not added on purpose, either the solvent itself or dissolved oxygen can be responsible for interactions with the nanoparticles surface, leading to a stabilizing zone that surrounds the particle and has its own composition, this shell being different from that of the pure metal nanoparticle core.

Metal nanoparticles are easily prepared using the following methods:

- controlled decomposition of organometallic compounds in the formal zero oxidation state such as $[\text{Pt}_2(\text{dba})_3]$ (Scheeren et al., 2003), $[\text{Ru}(\text{cod})(\text{cot})]$ (Silveira et al., 2004), or $[\text{Ni}(\text{cod})_2]$ (Migowski et al., 2007) (dba=dibenzylideneacetone, cod=1,5-cyclooctadiene, and cot=1,3,5-cyclooctatriene) dispersed in ionic liquids;
- chemical reduction (usually with hydrogen or a hydride source) of transition-metal compounds such as $[\text{Pd}(\text{acac})_2]$ (Umpierre et al., 2005), (acac=acetylacetonate), $[\text{Ir}(\text{cod})\text{Cl}]_2$, RhCl_3 (Fonseca et al., 2003), and RuO_2 (Rossi et al., 2004) dispersed in ionic liquids;
- simple transfer of the nanoparticles freshly prepared in water or “classical” organic solvents to the ionic liquids (Zhao et al., 2006).

Alternatively, *in situ* laser radiation may be used to induce the fragmentation of relatively large nanoparticles dispersed in ionic liquids into smaller particles with a narrow size distribution (Gelesky et al., 2005).

The formation of the nanoparticles from the first two methods apparently follows the autocatalytic mechanism (Besson et al., 2005; Besson et al., 2005) that basically involves two steps: nucleation and surface growth. In various cases these ionic liquids colloidal mixtures can be used directly as catalysts or they may be isolated and used as powders in solventless conditions (the substrates/products are per definition the solvent) or re-dispersed in the ionic liquids.

Nevertheless one has to know that metals which are obtainable in nanophases are basically unstable materials difficult to handle. Therefore, storage and using uncovered metal nanoparticles in nanotechnological applications is almost impossible. In aiming to avoid or to slow down the instability of the metal nanoparticles, a large number of investigations have been conducted to determine how the correct stabilization of metal nanoparticles can be achieved. However, it should also be noted that the alternative of a specific stabilizer is currently driving the bibliographic classifications. Many papers are specifically titled in terms of the most important stabilizer selected for the nanoparticles preparation. The number of agents that have been successfully applied to the synthesis of good nanoparticles has undergone a vast increase, thus evidencing the need for a comprehensive examination of this field.

Those species capable of stabilizing a nanosized metal phase can be classified in three classes, according to their mechanisms of action: (i) electrostatic, based on the classical theory of electrostatic colloidal stabilization, (ii) steric; and (iii) electrosteric, which is a combination of the electrostatic and steric modes (Ott & Finke, 2007).

The stabilization of nanoparticles in solution can be achieved by electrostatic and/or steric protection using among others, quaternary ammonium salts that are the most popular and investigated classes of stabilizing agents for soluble metal nanoparticles.

Due to the fact that the metal nanoparticles cannot be handled without a former stabilization, several synthetic routes for producing different metal nanoparticles covered with different stabilizers came out in the literature. This variety of synthetic routes allowed manufacturing a large diversity of metal nanoparticles having different morphology and in particular different properties. Anyway, the assignment of stabilizing the nanoparticles remains a very important issue to solve. For this reason a main part of the published papers describe not only the synthesis of nanoparticles in ionic liquids but also the stabilization of nanoparticles and the influence of the stabilizer molecule on the nanoparticles size, shape and properties.

2.1 Ionic liquid assisted of eighth metal group nanoparticles Ru(0)

Very fine and stable metal nanoparticles as Ru(0) were synthesized in ionic liquids by chemical reduction (Fonseca et al., 2003). The colloidal system metal-nanoparticle/ionic liquids-stabilizer is extraordinarily stable and ligands are not required. Extraordinarily high turnover numbers are achieved with this system in catalytic hydrogenation.

Few years ago ionic liquids were investigated as suspension media for catalytically active nanoclusters (Ott & Finke, 2007; Calò et al., 2005). The main advantages of synthesizing nanoparticles in ionic liquids resides in the direct possibility of using them as highly recyclable catalysts in several processes, thus providing a low environmental impact (Jacob et al., 2006). The so - called 'green' character of such a synthetic approach is that it does not require conventional solvents; rather, separation of the reaction products can be easily achieved by physical treatments, such as distillation inducing solidification of the ionic

liquid solvent, etc. Furthermore, the ionic liquids may itself afford the nanoparticles stabilization, thus greatly facilitating catalyst recycling and improving the total turnover number.

Although the nanoscale Ru(0) particles can be prepared by decomposition of Ru(0) organometallic precursors or reduction of RuCl₃ in the presence of stabilizing agents such as polymers or ligands, the development of a more simple and efficient method for the preparation of Ru(0) nanoparticles is still a challenge in nanocatalysis (Rossi et al., 2004).

Quaternary ammonium salts are one of the most popular and investigated classes of stabilizing agents for soluble metal nanoparticles. It is assumed that the stabilization in these cases is essentially due to the positive charge on the metal surface which is ultimately induced by the adsorption of the anions on to the coordinatively unsaturated, electron-deficient, and initially neutral metal surface.

The Ru(0) nanoparticles can be prepared via a very simple method based on H₂ reduction of the commercially available precursor RuO₂·3H₂O, which avoids the use of an organometallic precursor. An efficient catalyst for hydrogenation of benzene and other benzene derivatives was obtained in this way. In biphasic experiments, the RuO₂ was dispersed in the ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆], 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] or 1-*n*-butyl-3-methylimidazolium trifluoromethane sulphonate [BMIM][CF₃SO₃] prior to the addition of the substrate. The reactor was submitted to vacuum, placed in an oil bath at 75 °C under stirring (700 rpm) and connected to the hydrogen gas reservoir. The reaction was initiated by the admission of H₂ gas of 4 atm. The reaction was monitored by the fall in hydrogen pressure (Rossi & Machado, 2009).

The reduction of [Ru(COD)(2-methylallyl)₂] (COD = 1,5-cyclooctadiene) dispersed in various ionic liquids, namely, 1-*n*-butyl-3-methylimidazolium and 1-*n*-decyl-3-methylimidazolium, associated with the N-bis(trifluoromethanesulfonyl)imides (NTf₂) and the corresponding tetrafluoroborates (BF₄) with hydrogen gas at 50 °C leads to well-dispersed immobilized nanoparticles. Nanoparticles with a smaller mean diameter were obtained in the ionic liquids containing N-bis(trifluoromethanesulfonyl)imides than that in the tetrafluoroborate analogues, which is less coordinated (Precht et al., 2008).

2.2 Ionic liquid assisted of metal nanoparticles: Ir(0), and Rh(0)

Very fine and stable noble-metal nanoparticles of Ir(0) were synthesized in ionic liquids by chemical reduction (Fonseca et al., 2003). By monodispersed Ir(0) nanoparticles with a mean diameter of 2.1 nm were prepared by reduction of [Ir(cod)Cl]₂ (cod=1,5-cyclooctadiene) dissolved in 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid at 75 °C (Dupont et al., 2002) with molecular hydrogen. It is important to note that the synthesis of Ir(0) nanoparticles should be performed in the absence of water (Sweeny & Peters, 2001).

Accordingly, the addition of a ligand constitutes an alternative approach to increase the stability of rhodium nanospecies.

A particularity in the case of Rh(0) colloids, is that the precipitation of nanoparticles has been reported during catalytic applications such as the hydrogenation of substituted arene compounds (Migowski & Dupont, 2007; Léger et al., 2008). The same paper explains that a very robust stabilization of small nanoparticles with a very narrow size distribution provides almost inactive catalysts for the hydrogenation reactions. In contrast, the

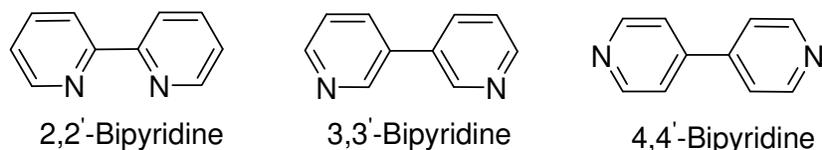
nanoparticles stabilized by compounds binding less strongly to the metal surface generate higher catalytic activity.

Recent study described an efficient approach for the preparation of Rh(0) nanoparticles by reduction of RhCl₃ with NaBH₄ (scheme 2) followed by the stabilized by different isomers of bipyridine (scheme 3), the most used was 2,2'-bipyridine as ligand (Léger et al., 2008). These colloidal suspensions have shown interesting activities and selectivity for the hydrogenation of aromatic compounds in several non-aqueous ionic liquids according to the nature of the anion and cation fragments (scheme 2).



Scheme 2. Synthesis of 2,2' bipyridine-stabilized rhodium nanoparticles in ionic liquids.

It is important to note that the synthesis of Rh(0) nanoparticles should be performed in the absence of water (Sweeny & Peters 2001).



Scheme 3. Bipyridine isomers used in the preparation of Rh-nanoparticles.

A phenomenon, which was studied in the literature, is the role of extra water in ionic liquids. This phenomenon is complex and depends on the supramolecular structure of the ionic liquid. It is assumed that its structure and chemical reactivity is far from that of bulk water, as it is tightly bound and activated in the H-bonding system of the IL. As a result, reactions with water take place quite rapidly in these systems. On the other hand, water cannot function as a solvating ligand here since it is too involved in IL binding. This was deduced, for instance, from the absence of so-called solvent pores and represents a quite singular situation for colloid chemistry and material synthesis.

Gelesky et al. showed that *in situ* laser radiation of relatively large Rh(0) nanoparticles dispersed in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid induces their fragmentation into smaller particles with narrow size distribution. The Rh nanoparticles were prepared by simple hydrogen reduction of [Rh(cod)- μ -Cl]₂ (cod=1,5-cyclooctadiene) dispersed in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate at 75 °C. After 60 minutes darkening of the solution was observed indicating the formation of Rh(0) nanoparticles (Gelesky et al., 2005).

Stable ruthenium, rhodium, and iridium metal nanoparticles have been reproducibly obtained by facile, rapid, and energy-saving microwave irradiation under an argon atmosphere from their metal-carbonyl precursors [M_(x)(CO)_(y)] in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (Redel et al., 2009; Vollmer et al., 2010). The metal nanoparticles synthesized have a very small (<5 nm) and uniform size and are prepared without any additional stabilizers or capping molecules as long-term stable metal nanoparticles-ionic liquid dispersions. The ruthenium, rhodium, or iridium nanoparticles dispersed in ionic liquids are highly active and easily recyclable catalysts for the biphasic liquid-liquid hydrogenation of cyclohexene to cyclohexane.

The treatment of an orange solution of $[\text{IrCl}(\text{cod})]_2$ (cod=1,5-cyclooctadiene) in 1-butyl-3-methylimidazolium hexafluorophosphate with hydrogen at 75 °C for 10 min affords a black solution. This ionic solution promotes the biphasic hydrogenation of various olefins under mild reaction conditions, and the products were isolated almost quantitatively by simple decantation. The catalytic activity of this system is significantly superior to those obtained in biphasic conditions by classical transition-metal catalyst precursors in ionic liquids under similar reaction conditions. A mercury test clearly indicated the presence of Ir(0) particles in the system formed by the reduction of the Ir(I) precursor in 1-butyl-3-methylimidazolium hexafluorophosphate. These nanoparticles could be isolated by centrifugation from the catalytic mixture (Dupont et al., 2002).

2.3 Ionic liquid assisted metal nanoparticles: Ni(0), Pd(0) and Cu(0)

Colloidal suspensions of Ni(0) nanoparticles were obtained by thermal decomposition at 75 °C and 5 bar of molecular hydrogen from bis(-1,5-cyclooctadiene) Ni(0) as organometallic precursor in 1-butyl-3-methylimidazolium ionic liquids with three different anions, BF_4^- , CF_3SO_3^- and $\text{N}(\text{Tf})_2^-$ (Cassol et al., 2006).

Different N-donor compounds have already proved their efficiency as protective agents in the case of colloidal suspensions in non-aqueous ionic liquids. As an example, the synthesis of phenanthroline stabilized palladium nanocatalysts and their use for olefin hydrogenation in 1-butyl-3-methylimidazolium hexafluorophosphate media was reported (Huang et al., 2003).

The reduction of $\text{Pd}(\text{acac})_2$ (acac=acetylacetonate), dissolved in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate $[\text{BMIM}][\text{PF}_6]$ or 1-*n*-butyl-3-methylimidazolium tetrafluoroborate $[\text{BMIM}][\text{BF}_4]$ as ionic liquids, by molecular hydrogen (4 atm) at 75 °C affords stable, nanoscale Pd(0) particles with sizes of 4.9 ± 0.8 nm. In as much as 1,3-butadiene is at least four times more soluble in the 1-*n*-butyl-3-methylimidazolium tetrafluoroborate than butenes, the selective partial hydrogenation could be performed by Pd(0) nanoparticles embedded in the ionic liquid (Umpierre et al., 2005).

Gelesky et al., showed that *in situ* laser radiation of relatively large Pd(0) nanoparticles dispersed in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid induces the fragmentation into smaller particles with narrow size distribution. The Pd nanoparticles were prepared by simple hydrogen reduction of PdCl_2 dispersed in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate at 75 °C. After 15 minutes a dark solution was obtained which indicate the formation of Pd(0) nanoparticles (Gelesky et al., 2005).

Reduction of copper precursors was carried out by borohydride (Singh et al., 2008; Singh et al., 2008), by microwave irradiation (Jacob et al., 2006), or even by spontaneous dissolution of macroscopic copper powders (copper bronze) reacting with the counterions of the ionic liquids through an oxidation/reduction multistep process that occurs while using nanoparticles in heterogeneous catalysis (as a part of the overall catalytic cycle). Tetraalkylammonium halides, imidazolium derivatives and other ionic liquids with ammonium moieties (Singh et al., 2008; Singh et al., 2008) have been employed as dispersing media where copper nanoparticles have been generated and successfully used as catalysts.

2.4 Ionic liquid assisted of Ge(0) and Te(0) nanoparticles

Tellurium Te(0) nanorods and nanowires were prepared in ionic liquids applying microwave irradiation. By combining the advantages of both ionic liquids and microwave

heating a fast and controlled synthesis of tellurium nanorods and nanowires was obtained. By controlling experimental parameters, it was possible to manufacture either Te nanorods or nanowires (Zhu et al., 2004).

Germanium nanoclusters and quantum dots with dimensions of only a few nanometers have been intensively investigated in the past. Such small Ge(0) clusters show, for example, a photoluminescence which is shifted to higher energies with decreasing particle size, thus quantum size effects are present. Most of such studies were performed under ultrahigh vacuum conditions which would complicate a possible future nanotechnological process. Therefore scientists were seeking for a new method to prepare germanium nanoclusters. Endres et al., developed a synthesis method for germanium nanoclusters with a narrow height distribution by electrodeposition from a diluted solution of GeCl₄ in 1-butyl-3-methylimidazolium hexafluorophosphate. Under the reported conditions, the lateral sizes of most of the clusters ranged between 20 and 30 nm while their heights vary from 1 to 10 nm with most of them between 1 and 5 nm (Endres & Abedin, 2002).

2.5 Ionic liquid assisted Au, Ag, Pt nanoparticles

The controlled decomposition of the organometallic Pt(0) precursor Pt₂(dba)₃ (dba = dibenzylideneacetone) was reported in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] as ionic liquid (Scheeren et al., 2006). Stable and catalytically active Pt(0) nanoparticles with a mean diameter of 2.3 nm (Scheeren et al., 2003) were obtained. Moreover, from transmission electron microscopy (TEM) contrast density fluctuations around the metal nanoparticles in the ionic liquid, and different thicknesses of mass density between the ionic liquid and crystalline structures were observed.

Spherically shaped Ag and Au nanoparticles of 20 nm diameters were synthesized through the reduction of silver nitrate and tetrachloroauric acid, respectively in ionic liquids (Singh et al., 2009). A facile one-pot synthesis of gold nanoparticles took place in an aqueous solution using *N*-(2-hydroxyethyl)-*N*-methylmorpholinium tetrafluoroborate (Kim et al., 2006). Single-crystal gold nanosheets and nanoparticles have been successfully prepared by microwave irradiation process in 1-butyl-3-methylimidazolium tetrafluoroborate (Li et al., 2005). Aggregation-induced colour changes of the gold nanoparticles in an aqueous solution were used as an optical sensor for anions via anion exchange of ionic liquid moiety (Itoh et al., 2004).

Because there is no additional template agent in such syntheses, the synthetic procedures and the related treating processes are very simple. The synthetic route is fast and the size of the resultant nanosheets is very large, and it is favourable to produce gold nanosheets in large scale. Ag and Pt (0) nanoparticles with a very narrow size distribution were prepared in 1-butyl-3-methylimidazolium bis(triflymethyl-sulfonyl) imide process (Wang & Yang 2006), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (Scheeren et al., 2008) using oleic acid as the major capping agent. In this case the combination of oleic acid with 1-butyl-3-methylimidazolium bis(triflymethyl-sulfonyl)imide led to an automatic separation of colloidal metal nanoparticles from the ionic liquid mixtures through a settling process (Wang & Yang 2006). Gold nanoparticles were also directly synthesized in pure 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ionic liquid via addition of HAuCl₄, followed by reduction with a ten times excess of NaBH₄. Alternatively, Au nanoparticles were prepared in 1-*n*-butyl-3-

methylimidazolium tetrafluoroborate ionic liquid to which 1-methylimidazole had been added. The presence of 1-methylimidazole at a level of 1.0 mM was found to have a significant effect on the stability of the final Au nanoparticles (Dash & Scott, 2009).

The influence of the temperature on the size distribution of the gold nanoparticles was also studied using small-angle X-ray scattering (SAXS) technique (Hatakeyama et al., 2010). The results showed that the particle size and its distribution were greatly affected by the temperature of the capture ionic liquid. The temperature change caused a drastic change in the viscosity of the ionic liquid and the diffusive velocities of the sputtered Au nanoparticles. In addition to the diffusion factor, the stabilities of the formed Au nanoparticles and the coordination and stabilization by the constituent ions of the ionic liquid, especially the anion, influenced the generating process of Au nanoparticles. Once prepared and stabilized by ions, Au nanoparticles were stably dispersed in the ionic liquid at lower temperatures. This study indicates that one can control the size and dispersion of Au nanoparticles only by regulating the temperature of the capture ionic liquid. In this way very small nanoparticles of less than 1nm diameter can be produced.

A new one phase method for the synthesis of uniform monodisperse crystalline Ag nanoparticles in aqueous systems was developed by using newly synthesized mono and dihydroxylated ionic liquids and cationic surfactants based on 1,3-disubstituted imidazolium cations and halogens anions. The hydroxyl functionalized ionic liquids and hydroxyl functionalized cationic surfactants simultaneously act both as the reducing and protective agent. By changing the carbon chain length, alcohol structure and anion of the hydroxy-functionalized 1,3-imidazolium based ionic liquids and the hydroxyl functionalized cationic surfactants the particle size, uniformity and dispersibility of nanoparticles in aqueous solvents could be controlled (Dorjnamjin et al., 2008).

One-phase synthesis of gold and platinum nanoparticles using new thiol-functionalized ionic liquids is also described in the literature (Kim et al., 2004). Thiol-functionalized ionic liquids as stabilizing agents for gold and platinum nanoparticles were designed to have thiol groups on either the cation or anion and symmetrical or unsymmetrical positions at the cation. The metal nanoparticles formed using thiol-functionalized ionic liquids are crystalline structures with face-centred cubic packing arrangements and have small sizes (the average diameters 3.5, 3.1, and 2.0 nm for Au and 3.2, 2.2, and 2.0 nm for Pt, respectively) and uniform distributions. It is believed that the nanoparticle size and distribution depend on the number and position of thiol groups in the ionic liquid.

3. Synthesis of metal oxide nanoparticles in ionic liquids

Traditionally, synthetic approaches for the production of functional metal oxide materials have involved high-temperature reaction environments with energy-intensive techniques such as laser ablation, ion implantation, chemical vapour deposition, photolithography or thermal decomposition. Therefore, ionic liquids which by definition are salts existing in liquid form typically below 100 °C can be used as thermally stable and non-volatile solvents, which can be beneficial to the reduction of solvent emission in comparison to conventional volatile organic compounds. Several imidazolium-based ionic liquids, including 1-butyl-3-methylimidazolium bis(triflylmethylsulfonyl)imide [BMIM][Tf₂N], are not only non-flammable but also stable in a broad temperature range-from room temperature to over 400 °C.

3.1 Ionic liquid assisted iron oxide nanoparticles

Magnetic iron oxide nanoparticles (Fe_2O_3 and Fe_3O_4) have been extensively studied because of their potential applications in biomedical fields. The fluid dispersions of magnetic iron oxide nanoparticles are known as ferrofluids. These ferrofluids are much used in medicine. A main problem of these magnetic nanoparticles is their aggregation, due to the magnetic attractive forces combined with inherently large surface energies. Therefore, many attempts have been made to prepare magnetic nanoparticle dispersions in the presence of surfactants or polymeric compounds with functional groups as stabilizers.

All these technological and medical applications require that the nanoparticles are superparamagnetic with size smaller than 20 nm and the overall particle size distribution is narrow so that the particles have uniform physical and chemical properties. In the last years, various methods for the preparation of such particles have been developed and optimized. High-quality monodisperse iron oxide nanoparticles with high crystalline and narrow size distribution have been prepared by a high-temperature organic phase decomposition method.

A simple and economical method to achieve stable water-soluble iron oxide nanoparticles is based on dispersions in an ionic liquid containing acrylic acid anion. Distinct particles were synthesized by an organic phase decomposition method. The synthesis of magnetite nanoparticles in our laboratories was carried out only by simple precipitation of ferrous salts in alkaline aqueous solutions at low temperature. It was found that the ionic liquid can be used as solvent and stabilizer to efficiently tune the particle growth and prevent nanoparticle aggregation (Zhai et al., 2009).

The synthesis of iron oxide nanostructures with well-defined shapes, including rods, cubes, and spheres, in 1-butyl-3-methylimidazolium bis(triflylmethyl-sulfonyl) imide ([BMIM][Tf₂N]), was also reported. Surfactants including oleic acid and oleylamine, which are commonly used as surface capping agents for size and shape control in molecular solvents, can be employed for making morphologically well defined nanostructures in this ionic liquid. Iron pentacarbonyl thermally decomposes at elevated temperatures in 1-butyl-3-methylimidazolium bis(triflylmethyl-sulfonyl) imide ionic liquid and subsequently form nanoparticles. Nanorods, nanocubes, and spherical particles were synthesized depending mainly on the reaction temperatures and surfactants (Wang & Yang, 2009). It was also reported that this ionic liquid can be recycled and reused without detrimental effects on size and size distribution of the particles made (Wang et al., 2007). $\alpha\text{-Fe}_2\text{O}_3$ with various morphologies has been successfully synthesized *via* an ionic liquid-assisted hydrothermal synthetic method (Cao & Zhu, 2009; Lian et al., 2009). Good photocatalytic activities of $\alpha\text{-Fe}_2\text{O}_3$ nanospheres were obtained by microwave-hydrothermy in 1-butyl-3-methylimidazolium tetrafluoroborate ionic. This ionic liquid influences not only the crystal phase but also the morphology of the final product (Cao & Zhu, 2009).

We also prepared iron oxide magnetic nanoparticles using as ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄]. Iron (II) chloride and iron (III) chloride which dissolves in [BMIM][BF₄] are coprecipitated in the presence of potassium hydroxide yielding magnetite. The stabilization of magnetite was realized without further purification with glycolic acid. The coprecipitation reaction of iron(II) and iron(III) in ionic liquid and basic condition is published in a Romanian patent (A. Nan et al., 2010)

3.2 Ionic liquid assisted titanium oxide nanoparticles

Titanium oxide nanostructures have versatile applications, for example, in photocatalysis, solar-energy conversion, sensors, and ductile ceramics. The synthesis of derivatives with all kinds of size and shape (spherical particles, nanotubes, and nanorods) has been described in numerous studies. Out of the three main titanium polymorphs (anatase, brookite, rutile), research so far has been centred on the synthesis of anatase nanoparticles. However, recently the generation of nanometer-sized rutile has received growing attention due to its promising potential as a photocatalyst and as an electrode material.

Although the photocatalytic activity of rutile is still unclear, several groups found that rutile phase shows higher photocatalytic activity than anatase, and a lot of experimental evidence supported that the existence of a synergistic effect between the anatase and rutile phases is beneficial for reducing the recombination of photogenerated electrons and holes, which usually results in an enhancement of photocatalytic activity. However, it is known that anatase modification of TiO_2 can be obtained first in all solution synthesis pathways and it is even believed that anatase with particle size of 10-20 nm is a thermodynamically stable modification of TiO_2 , when considering the contribution of surface energy.

The synthesis of 2-3 nm sized titanium dioxide nanocrystals and their self-assembly toward mesoporous TiO_2 spheres was achieved in an ionic liquid under mild conditions. The resulting structures combine the convenient handling of larger spheres with a considerable high surface area and narrow pore size distribution and are expected to have potential in solar energy conversion, catalysis, and optoelectronic devices. In a typical synthesis of TiO_2 nanoparticles, 1-butyl-3-methylimidazoliumtetrafluoroborate was used as solvent (Zhou & Antonietti, 2003).

Pure rutile and rutile-anatase nanocomposites have been successfully synthesized by hydrolysis of titanium tetrachloride in hydrochloric acid with the assistance of (1-ethyl-3-methyl-imidazolium bromide). The content of rutile in the composites can be controlled by simply adjusting the amount of (1-ethyl-3-methyl-imidazolium bromide) added to the reaction mixture. According to this approach, the composites with arbitrary content of rutile have been rationally and reproducibly prepared in high yields. This method has the following obvious advantages: a simple process; high yield, reaction can be performed under atmospheric pressure in a glass vessel and because high-pressure and high temperature is unnecessary. Products are highly crystalline and their components are controllable. The method can be developed into a general way to synthesize other metal oxide nanoparticles on a large scale (Zheng et al., 2009).

Highly crystalline, well-defined rutile nanorods were synthesized directly by a modified sol-gel reaction in ionic liquid containing imide moieties. In particular, the crystallization was performed under ambient temperature conditions. Compared to previously reported syntheses of rutile and anatase, the present approach features several peculiarities. In essence, the crystallization starts from an amorphous TiO_2 network, which is stabilized by the ionic liquid and converted to rutile upon removal of the ionic liquids simply by extraction. This mechanism is markedly different from the water-based nucleation of rutile in solution, which requires delicate control of various parameters, especially the pH. It is believed that the nucleation of rutile from amorphous TiO_2 , stabilized by the ionic liquid through binding of the imide or amide, has a lower barrier compared to the situation in aqueous solution, in which the crystallization of anatase in the form of nanocrystals is usually regarded as favoured due to its lower interfacial energy. These findings point to a different option for controlling the crystallization of nanostructured oxides in general by the

stabilization of an intermediate amorphous oxide, which is then converted into its crystalline counterpart by removal of the stabilizer (Kaper et al., 2007).

Nanocrystalline particles of TiO_2 were synthesized via an alkoxide sol-gel method employing water-immiscible ionic liquids as a solvent medium and later modification with non-ionic surfactant as a pore-templating material. Detailed information on the preparative method, crystallographic and structural properties, and photocatalytic activity of the TiO_2 particles are described (Choi et al., 2006). The possible synthetic route and mechanism of the formation of TiO_2 particles and the advantages of using water-immiscible ILs [BMIM][PF₆] in this sol-gel method are discussed in comparison with the challenges of conventional solvent systems (Choi et al., 2006). In the same study, nanostructured TiO_2 particles with high surface area, controlled porosity, and narrow pore size distribution have been synthesized via a sol-gel method modified with ionic liquids and surfactant molecules. Due to the special characteristics of the [BMIM][PF₆] as well as the role of surfactant as a pore templating material in sol-gel network, highly porous TiO_2 particles with anatase crystalline structure were formed even at low temperatures. The TiO_2 particles were thermally stable and thus resistant to pore collapse and anatase-to-rutile phase transformation during calcinations. The thermal stability induced high photocatalytic activity after heat treatment of TiO_2 particles up to 800 °C. This synthesis method has important implications since obtaining crystal structure at low temperatures and keeping good photocatalytic activity at high temperatures can make it possible to utilize the TiO_2 particles and their preparative method in various applications. This new methodology using ionic liquid and surfactant in combination can also be useful for preparing similar crystal nanostructures of other oxide materials at low temperatures.

3.3 Ionic liquid assisted ruthenium oxide nanoparticles

The reaction of NaBH_4 with RuCl_3 dissolved in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] and 1-*n*-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] as ionic liquid is a simple and reproducible method for the synthesis of stable ruthenium oxide nanoparticles with a narrow size distribution within 2 - 3 nm. These nanoparticles showed high catalytic activity either in the solventless or liquid-liquid biphasic hydrogenation of olefins and arenes under mild reaction conditions. Nanometric ruthenium oxide confined in a zeolitic framework was recently reported as an efficient catalyst for alcohol oxidation under mild aerobic conditions. The nanoparticles could be re-used in solventless conditions up to 10 times in the hydrogenation of 1-hexene yielding a total turnover number for exposed Ru(0) atoms of 175,000 (Rossi et al., 2004; Rossi et al., 2004).

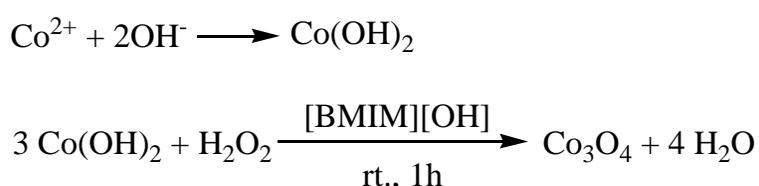
3.4 Ionic liquid assisted vanadium pentoxide, zinc oxide and cobalt oxide nanoparticles

A methodology for the generation of vanadium pentoxide nanostructures was developed based on ionic liquids serving as both reaction medium and structure providing template at the same time (Kaper et al., 2008).

ZnO nanostructures with different shapes have been synthesized via a hydrothermal route, using zinc acetate and sodium hydroxide as the reactants in the presence of different ionic liquids. The ionic liquids can act as morphology templates for ZnO. The ionic liquids can be considered as potential candidates for constructing novel nano-sized ZnO. The morphology

of ZnO changes from rod-like to star-like and flower-like in the presence of different ionic liquids.

Zou and co-workers have used a relatively new technique incorporating ionic liquids to direct the synthesis of the Co_3O_4 nanocrystals (Zou et al., 2008). Ionic liquids have recently attracted attention as stable, highly reactive solvents, with good electrical conductivity, high ionic mobility and good chemical and thermal stabilities. In this synthesis 1-*n*-butyl-3-methylimidazolium hydroxide [BMIM][OH] was dissolved in $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at room temperature (Scheme 3) and both NaOH and H_2O_2 were added separately to the solution, over a period of 30 min. After a 6 h period of stirring, a black - brown precipitate was collected, purified and dried in the oven at 80°C for 10 h. The ionic liquid was collected and reused.



Scheme 3. Ionic reaction of cobalt precursors in the presence of NaOH and H_2O_2

4. Synthesis of alloy nanoparticles in ionic liquids

Alloy nanoparticles, exhibit different catalytic, magnetic, optical and other chemical and physics properties to those of single metal nanoparticles. They are potentially useful for applications such as chemical and biochemical sensing, catalysis, optoelectronics devices, medical diagnostic and therapeutic.

In the case of preparation of alloy nanoparticles in ionic liquid the literature only a few publications have appeared so far. The properties of alloy nanoparticles do not only depend on the size and shape of nanoparticles but also on their composition.

Although various synthetic methods have been developed for the morphological controls of nanoparticles, rods, and wires of semiconductors, metals, and metal oxides, only limited success has been made in making alloy or intermetallic nanoparticles, such as FePt, CoPt, and AuCu (Lee et al., 2002; Shevchenko et al., 2002; Hyeon, 2003; Manna et al., 2003; Zhang et al., 2003; Milliron et al., 2004; Teng & Yang, 2004).

The formation of one-dimensional nanorods and nanowires has rarely been reported. For technologically important Co-Pt and Fe-Pt systems, shape, crystal phase, and composition are essential for the outstanding catalytic, magnetic, and other properties. For example, the structured CoPt_3 and FePt_3 have been predicted to have higher electrocatalytic activities than pure Pt in hydrogen oxidation reactions. The face centred tetragonal FePt nanoparticles are the most designable material among the Fe-Pt system for magnetic data storage media applications. Cobalt platinum nanorods were made in freshly dried 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [BMIM]-[Tf₂N] at 350°C . Platinum acetylacetonate ($\text{Pt}(\text{acac})_2$) and cobalt acetylacetonate ($\text{Co}(\text{acac})_3$) were used as Pt and Co precursors, respectively. The reaction temperature is usually high in order to obtain crystal phase- and composition-specific alloy nanomaterials (Reiss et al., 2004). These temperatures are typically above the boiling points of most of the conventional solvents. Post synthesis high-temperature treatments often affect the particle size, size distribution, and structural

property of the nanoparticles. For this type of reaction, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide was chosen as the solvent because of its thermal stability. The combined high-temperature environment and the unique property of ionic liquid bis(trifluoromethylsulfonyl)imide could attribute to the observed formation of CoPt alloy nanoparticles and nanorods with different compositions and crystal phases. The decrease in melting point of nanoparticles could be relevant for the formation of stable CoPt alloys (Wang & Yang, 2005).

A new methodology which allowed identifying peptide sequences that both specifically bind to the ferromagnetic phase of FePt and control the crystallization of FePt nanoparticles using a modified arrested precipitation technique was also described in the literature (Reiss et al., 2004). They applied a peptide-based synthetic strategy for the synthesis of the technologically important magnetic material FePt, in which biological interactions control the nucleation of nanoparticles that have no isomorphous complement in nature. In addition, this biological strategy has several advantages over more recent chemical methods, including the potential synthesis of the desired high anisotropy ferromagnetic crystalline phase in aqueous conditions under ambient temperature, pressure, and atmosphere. Bacterial amplification of the "organic" virus templates makes the production of both the nucleating peptides and FePt nanoparticles easy and cost-effective.

Au–Ag bimetallic nanoparticles have been fabricated by one-step simple electrochemical deposition method using ionic liquid as green electrolyte (1-butyl-3-methylimidazolium tetrafluoroborate). The indium tin oxide (ITO) surface has been utilized for the fabrication of Au–Ag bimetallic nanoparticles.

The use of a stabilizing agent to prepare alloy nanoparticles in ionic liquids can be avoided by using a technique known as sputter deposition. The technique ejects atoms from a solid surface by the energetic impact of gaseous ions, typically used are Ar⁺ ions. This technique was used for the first time to synthesize gold-silver alloy nanoparticles in an ionic liquid (Okazaki et al., 2008). The chemical composition and optical properties of the Au–Ag alloy nanoparticles were easily controlled just by varying the area ratio of the individual pure metal foils in the sputtering targets.

PdAu alloy nanoparticles were also directly synthesized in pure 1-*n*-butyl-3-methylimidazolium hexafluorophosphate as ionic liquid (particle size 6.0 - 2.9 nm) and in the presence of a 1-methylimidazole additive in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (particle size 3.0 - 0.5 nm). Investigations of the stability of the PdAu alloy nanoparticles revealed aggregation in pure ionic liquid, while stability was observed in the presence of 1.0 mM 1-methylimidazole or other stabilizers. The activity of the nanoparticles synthesized directly in the pure ionic liquid began to drop dramatically within 10 min upon addition of the substrate, while PdAu nanoparticles synthesized in the presence of 1.0 mM 1-methylimidazole showed dramatically improved retention of catalytic activity over time. Finally, PdAu nanoparticles were also synthesized in 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate in order to demonstrate the generality of this mode-of-stabilization. PdAu nanoparticles in pure 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate solutions precipitated within 1 h in the absence of 1-methylimidazole additives during the hydrogenation reaction, whereas stability for prolonged periods of times was achieved in the presence of 1-methylimidazole, however higher concentrations of 1-methylimidazole (ca. 10–100 mM) were needed to stabilize the nanoparticles (Dash & Scott, 2009).

Nanocrystalline alloys were also possible to obtain by deposition. In this way several aluminium alloys from ionic liquids based on AlCl_3 were prepared. Of particular interest are electrochemically made Al-Mn alloys, which are widely used in the automobile industry for lightweight construction. An attempt was made to obtain nanocrystalline Al_xMn_y alloys electrochemically by adding MnCl_2 and nicotinic acid to a Lewis acidic ionic liquid. The deposition was performed by using a current density of $I=0.5 \text{ mAcm}^{-2}$ on glassy carbon.

5. Conclusion

In summary, preparation of metal or metal oxide nanoparticles in ionic liquids is an upcoming method providing several advantages over conventional methods. The metal nanoparticles are often of great interest as catalysts. As an additional effect imidazolium-based ionic liquids also form protective layers at the metal nanoparticles thus providing improved stability. By the formation of such ionic liquid protective layers discrete supramolecular species appear through the loosely bound anionic moieties and/or NHC carbenes together with an oxide layer when present on the metal surface. These loosely surface-bound protective species are easily displaced by other substances present in the media. This on the one hand is responsible to some extent for their catalytic activity, but on the other hand explains their relatively low stability that leads to aggregation/agglomeration and eventually to the bulk metal. Therefore the stability and the catalytic activity of metal nanoparticles in imidazolium ionic liquids are also highly influenced by coordinative strength of the aggregates with the metal surface and the type and nature of the substrates/products.

Moreover, metal nanoparticles dispersed in these fluids are stable and can serve as active catalysts for reactions in multiphase conditions. The catalytic properties (activity and selectivity) of these soluble metal nanoparticles indicate that they possess a pronounced surface like (multi-site) rather than single site like catalytic properties. In other cases the metal nanoparticles are not stable and tend to aggregate or alternatively they serve as simple reservoirs of mononuclear catalytically active species. However, the ionic liquid provides a favourable environment for the formation of metal nanoparticles with, in most cases, a small diameter and size distribution under very mild conditions.

In the hydrogenation of simple alkenes the recovered ionic dispersion can be re-used several times without any significant loss in catalytic activity, as observed with ionic liquid-dispersed $\text{Ir}(0)$, $\text{Rh}(0)$, $\text{Pt}(0)$, and $\text{Ru}(0)$ nanoparticles. However, in the case of aromatic compounds and ketones some metal nanoparticles tend to aggregate with loss of their catalytic activity such as $\text{Rh}(0)$ in the hydrogenation of benzene and $\text{Ir}(0)$ in the reduction of ketones. However, these nanoparticles are more stable in the hydrogenation reactions when dispersed in the ionic liquids than in solventless conditions. It has to be mentioned that aromatics, ketones, and alcohols are much more soluble in the ionic liquids than the alkenes and alkanes.

In some cases, which were described for the synthesis of iron oxide, the different solubility of precursors, reactive intermediates and nanoparticles in ionic liquid helps to regulate the delivery of agents in different phases. This shows that high level morphological control of nanomaterials is feasible using ionic liquids by selecting proper capping agents and reaction conditions, which is an important step forward in using ionic liquids as solvents for controlling the size and shape of nanomaterials.

Another important conclusion which comes out is that the simultaneous sputter deposition of different kinds of pure materials can be applied to prepare alloy nanoparticles containing three or more elements, the physicochemical properties being tunable for desired purposes, such as catalysts for fuel cells.

We expect that ionic liquids will find, in addition to organometallic synthesis, catalysis, and electrochemistry, a fourth area of application—the synthesis of nanostructured solids, either to make nanoobjects (e.g. particles and fiber) or for the design of nanopores and nanochannels in solids. The unique combination of adaptability towards other molecules and phases plus the strong H-bond-driven solvent structure makes ionic liquids potential key tools in the preparation of a new generation of chemical nanostructures.

6. References

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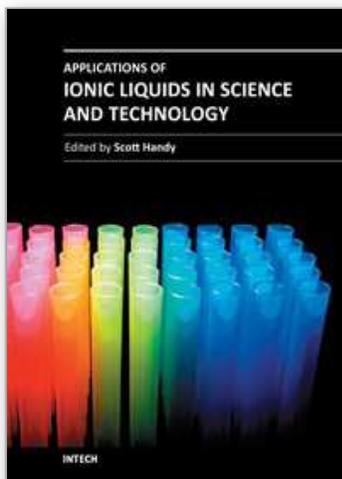
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This volume, of a two volume set on ionic liquids, focuses on the applications of ionic liquids in a growing range of areas. Throughout the 1990s, it seemed that most of the attention in the area of ionic liquids applications was directed toward their use as solvents for organic and transition-metal-catalyzed reactions. Certainly, this interest continues on to the present date, but the most innovative uses of ionic liquids span a much more diverse field than just synthesis. Some of the main topics of coverage include the application of RTILs in various electronic applications (batteries, capacitors, and light-emitting materials), polymers (synthesis and functionalization), nanomaterials (synthesis and stabilization), and separations. More unusual applications can be noted in the fields of biomass utilization, spectroscopy, optics, lubricants, fuels, and refrigerants. It is hoped that the diversity of this volume will serve as an inspiration for even further advances in the use of RTILs.

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