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Ionic Liquids as Designer Solvents for the Synthesis of Metal Nanoparticles

Vipul Bansal and Suresh K. Bhargava
RMIT University
Australia

1. Introduction

Size and shape-controlled synthesis of metal nanostructures has received significant interest in materials research, as metal nanoparticles are likely to have a considerable impact upon the fields of catalysis, sensing, photonics, optoelectronics and biology, due to their unique size- and shape-tunable physico-chemical properties (Hao et al., 2004; Burda et al., 2005; Shukla et al., 2005; Lu et al., 2009; Sardar et al., 2009). With significant developments in this field, the current focus is predominantly on synthesis of ultra-fine (sub-10 nm) metal nanoparticles with narrow size distribution that remain stable in reaction media, tuning the shape of metal nanostructures, to understand the metal nanoparticles shape-guiding mechanisms, and to understand their structure-property correlation (Lu et al., 2009). To prepare metal nanoparticles (colloids), the most commonly employed approach is the bottom-up wet-chemistry approach. In this approach, typically in the presence of a capping/stabilizing agent, metal ions are controllably reduced, wherein individual metal atoms combine to form metal nanoparticles stabilized by capping agents. Although in few instances reducing agents themselves act as stabilizers, capping agents are generally considered essential to minimize the surface free energy of metal nanoparticles, which would otherwise aggregate in the absence of these capping agents. In most of the well established wet-chemistry routes of metal nanoparticles synthesis, aqueous or organic solvents are generally employed, while the use of ionic liquids (ILs) for synthesis of metal nanoparticles is a relatively recent phenomenon.

As an aqueous solvent, water is although a naturally-available, environmentally-benign, non-toxic and non-inflammable media for nanomaterials synthesis, it remains liquid only in a narrow temperature range (0-100 °C), and have low solubility for organic molecules. Conversely, organic solvents might although offer diverse physico-chemical properties (e.g. density, polarity and solubility), most of them are highly toxic, flammable, have low boiling points and low solubility of inorganic reactants. These drawbacks associated respectively with water and organic solvents may therefore limit their applicability as versatile solvents for nanomaterials synthesis conducted at relatively higher or lower temperatures. Similarly, although few traditional molten salts have been tested as alternative reaction media, their high melting points (usually above 100 °C) limit the practical applicability of such solvents for nanomaterials synthesis.

Ionic liquids (ILs), conventionally refereed as 'room temperature ionic liquids' (RTILs) or 'room-temperature molten salt' have recently become attractive reaction media for the

"green" synthesis of inorganic nanomaterials due to their interesting physico-chemical properties. For instance, ILs are typically liquid over a range of temperatures (RTILs are liquid at room temperatures, with some showing melting point down to -80 °C), possess negligible vapour pressures, high thermal and chemical stability, high ionic conductivity, broad electrochemical potential window, and high ionic density (Dobbs et al, 2006; Dupont and Scholten, 2009; Ma et al., 2010; Neouze, 2010). These interesting properties of ILs offer distinct advantages over conventional aqueous and organic solvents to explore a range of organic and inorganic materials synthesis.

The history of ILs goes as early as 1914, when Walden reported the first ionic liquid [$C_2H_5NH_3$][NO_3] with melting point 13-14 °C. This was termed as a protic ionic liquid (PIL), since it involved a proton-transfer reaction during synthesis (Walden, 1914). In 1951, Hurtley and Weir synthesized aprotic ionic liquids (APILs) by mixing alkylpridinium chlorides with $AlCl_3$ (Hurtley & Weir, 1951). However these ILs were found to be sensitive to moisture and air and are not in active use nowadays. Thereafter in 1992, Wilkes and Zaworotko developed a new series of water-stable ILs containing tetrafluoroborate {[BF_4]}, hexafluorophosphate {[PF_6]}, nitrate {[NO_3]}, sulphate {[SO_4]} and acetate {[CH_3COO]} anions (Wilkes and Zaworotko, 1992). Since then, a range of ILs containing organic cations and organic or inorganic anions has been developed (Gordon and Muldone, 2008).

In the recent development of ILs, imidazolium (Im)-based ILs have attracted particular attention because Im-based compounds are very versatile with generally high solubilisation ability and high thermal and electrochemical stability. Moreover, varying the counter-anion in Im-based ILs can drastically influence the physicochemical properties of these systems. For instance, considering a butylmethylimidazolium {[BMIm]} cation, a strongly coordinating anion like chloride will render the [BMIm][Cl] IL as hydrophilic, while a low coordinating anion like hexafluorophosphate will create a hydrophobic [BMIm][PF_6] IL (Mehdi et al., 2010; Soni et al., 2010). The current chapter aims to predominantly focus on use of Im-based ILs for synthesis of metal nanoparticles, mainly because imidazolium moieties have been the most investigated until now with a significant potential for further development. It is also noteworthy that in context of nanomaterials synthesis, Im-based ILs not only play a role of versatile solvent, but they also stabilize nanoparticles, which is particularly important for use of nanoparticles towards various applications including catalysis. Therefore, when combining Im salts and nanoparticles, the need to understand the interactions occurring between Im species and nanoparticles begins to be pressing that will also be touched upon in this chapter. In addition, the chapter will also discuss some of the interesting applications that IL-mediated synthesis of metal nanoparticles may offer.

2. ILs as solvents for stabilization of metal nanoparticles

ILs, in general, differ from the classical ammonium salts, at least in one very important aspect: ILs possess pre-organized structures, mainly through hydrogen bonds (Hardacre et al., 2003; Tsuzuki et al., 2005; Dupont & Suarez, 2006), which induce 3-D structure dimensionality in these systems (*IL effect*). Conversely, aggregates of classical salts display charge-ordered structures. Since ILs can form extended hydrogen-bond networks at the liquid state, therefore they demonstrate this very unique property of high self-organization on the nanomolecular scale, and can be classified as 'supramolecular' fluids. This nanoscale structural organization of ILs can be used to drive the spontaneous extended ordering of nanomaterials (Pearson et al., 2010; Soni et al., 2010). Some of the classical examples that

have illustrated this concept include IL-mediated synthesis of ordered mesoporous materials and microporous aluminophosphates, wherein ILs served both as the solvent and structure-directing agents (Endres, 2002; Antonietti et al., 2004; Zhou, 2005). One another example in this category includes synthesis of protein and silica nanocapsules in [BMIm][BF$_4$] IL via self-organization process, as was demonstrated recently by our group (Soni et al., 2010). It has also been established that the properties of Im-based ILs are dependent on their organized nano-aggregates, rather than merely on their isolated cations and anions (Suarez et al., 1998; Neto et al., 2006). The 3-D arrangement of the Im-based ILs is generally formed through chains of the cationic imidazolium rings, which generates supramolecular channels in which anions are typically accommodated as chains (Lopes & Padua, 2006) (Figure 1). The formation of this 3-D ionic network entails high directional polarizability, which provides an opportunity to adapt a range of external species in either hydrophilic or hydrophobic regions of ILs (Dupont & Suarez, 2006). Therefore, size and shape of the metal nanoparticles synthesized in ILs is typically modulated by the volume of these 3-dimensionally arranged regions within IL environment. It would probably not be an overstatement to classify ILs as nanostructured solvents, with a potential to direct the tailored synthesis of nanoscale materials.
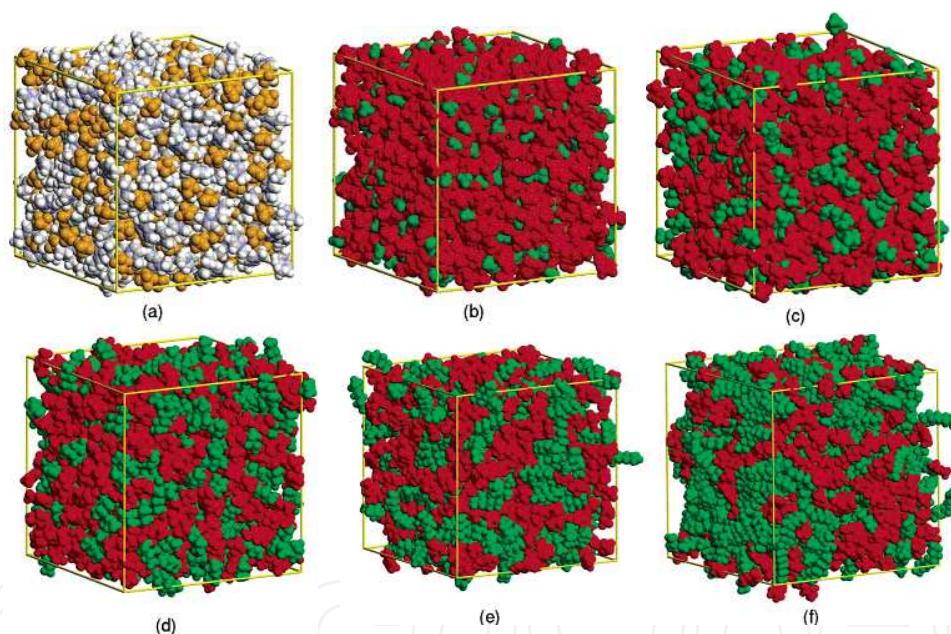

Fig. 1. Snapshots of simulation study of [C$_n$MIm][PF$_6$] ILs (boxes contain 700 ions) showing the polar (red) and non-polar (green) domains of ILs. In panels (a)-(f), *n* corresponds to 2, 2, 4, 6, 8 and 12 respectively (adapted from Lopes & Padua, 2006 with permission from the American Chemical Society).

A series of studies in the literature suggests that ILs interact relatively strongly with the surface of metal nanoparticles, which have been summarized in a recent report (Neouze, 2010). In fact, transition metal nanoclusters and nanoparticles stabilization by Im-based ILs is now considered as a classical stabilization method (Ott & Finke, 2007). Although capping agents are generally considered essential during metal nanoparticles synthesis in conventional solvents to stabilize them (Neouze & Schubert, 2008), they are typically not required for nanomaterials synthesis in Im-based ILs. However, it is notable that ligand-free

synthesis of metal nanoparticles in ILs, as reported in few reports, is probably a misleading assumption because in these synthesis protocols, although no external ligand is added to stabilize nanoparticles, the Im moiety itself plays the role of both as a solvent, and a stabilizer (Campbell et al., 2010; de Caro et al., 2010; Neouze, 2010; von Prondzinski et al., 2010). Considering the importance of nanoparticles stabilization feature of ILs, we will elaborate on this concept later in this chapter.

3. ILs as solvents for synthesis of metal nanoparticles

3.1 Serendipitous discovery of metal nanoparticles formation in ILs

The discovery that ILs can act as novel media for the preparation and stabilization of metal nanoparticles is rather serendipitous. It began with the isolation of metal nanoparticles during catalytic hydrogenation and C-C coupling reactions using organometallic or metal salt catalysts in ILs. For instance, when Deshmukh and co-workers carried out the Heck reaction using $Pd(OAc)_2$ and $PdCl_2$ catalysts in 1,3-dibutylimidazolium bromide {[BBIm][Br]} IL under ultrasonic irradiation conditions, they observed formation of 20 nm Pd nanoparticles composed of 1 nm nanoclusters formed via reduction of Pd^{2+} ions during catalytic reaction (Deshmukh et al., 2001). Similarly Hamill and co-workers observed formation of 0.8-1.6 nm Pd clusters during the Heck reaction in several ILs (Hamill et al., 2002). Following these, among the first publications in this field, Dupont and co-workers made a deliberate attempt towards synthesis of uniform-sized Ir nanoparticles in [BMIm][PF_6] IL and used them as catalysts for the hydrogenation of olefins (Dupont et al., 2002). This pioneering work stimulated many subsequent studies, leading to synthesis of Ir (Fonseca et al., 2003; 2006; Singh et al., 2008a), Rh (Fonseca et al., 2003; Bruss et al., 2006), Pt (Scheeren et al., 2003; 2006), Ru (Silveira et al., 2004; Gutel et al., 2007), Pd (Umpierre et al., 2005; Durand et al., 2008), Ni (Migowski et al., 2007), Cu (Singh et al., 2008b; 2008c; 2009) and Ag (An et al., 2009) nanoparticles by reducing the corresponding transition metal salts or by decomposing organometallic compounds in different ILs (Dupont & de Oliveira Silva, 2008). Similarly, uniform Ru nanoparticles were obtained by reducing RuO_2 hydrate by H_2 in a range of Im-based ILs with [BMIm] as a cation and [BF_4], [PF_6] or [SO_3CF_3] as anions (Rossi et al., 2004; 2009). These Ru nanoparticles synthesized in ILs demonstrated excellent performance towards the hydrogenation of olefins. In another study, importance of external parameters such as temperature and stirring during synthesis of Ru nanoparticles was highlighted to control nanoparticle size by utilizing the self-organization feature of [BMIm][$N(SO_2CF_3)_2$] IL (Gutel et al., 2007). Additionally, in a series of reports, [BMIm][BF_4] IL was utilized towards the synthesis of Cr, Mo, W, Fe, Ru, Os, Co, Rh and Ir nanoparticles (Redel et al., 2008a; 2009; Kramer et al., 2008). It is notable that in most of these studies, ILs themselves acted as stabilizing agents without requiring any external capping agent during synthesis of uniform, ultrasmall metal nanoparticles. This is significantly different from metal nanoparticles synthesis in conventional aqueous and organic solvent, wherein an external stabilizing/ capping agent is typically required during synthesis.

3.2 Metal nanoparticles synthesis in ILs using "task-specific" ILs

In addition to the aforementioned reports on use of non-functionalized ILs towards synthesis of metal nanoparticles, a recent noteworthy trend is towards synthesis of functionalized ILs, e.g. metal ion-containing ILs, which can be directly reduced, leading to metal nanoparticles synthesis in ILs without requiring any additional metal salts. One of the

examples of these include synthesis of Ag nanoparticles via reducing Ag-containing ILs such as bis(N-2-ethylhexylethylenediamine)silver nitrate {[Ag(eth-hex-en)$_2$][NO$_3$]} and bis(N-hexylethylenediamine)silver hexafluorophosphate {[Ag(hex-en)$_2$][PF$_6$]} by NaBH$_4$ (Iida et al., 2008).

Another category of functionalized ILs includes those which contain certain functional groups that may bond onto metal surfaces, and thus stabilize the formed metal nanoparticles more effectively. This has led to development of a range of new functionalized ILs, which are also often termed as "task-specific ILs" (Davis, 2004; Fei et al., 2006; Lee, 2006; Li et al., 2006; Davis & Wasscheid, 2008). To this end, thiol-containing ILs are particularly notable towards stabilization of metal nanoparticles, as thiols are well-known to interact strongly with metal surfaces. For instance, IL 3,3'-[disulfanylbis(hexane-1,6-diyl)]-bis(1-methyl-1H-imidazol-3-ium)dichloride was utilized for the synthesis of 5 nm, water-soluble Au nanoparticles via reducing HAuCl$_4$ with NaBH$_4$ (Itoh et al., 2004). Lee and co-workers developed a range of thiol-functionalized ILs to prepare Au, Pt, and Pd nanoparticles, wherein the sizes of nanoparticles was found to be reduced with an increase in the number of thiol groups in ILs (Kim et al., 2004; Kim et al., 2005). Additionally, Au nanoparticles were stabilized by using a zwitterionic imidazolium sulfonate-terminated thiol (Tatumi & Fujihara, 2005), and Au nanoparticles and Pd nanowires could be prepared by using a thiol functionalized IL, 1-methyl-3-(2'-mercaptoacetoxyethyl) imidazolium chloride (Gao et al., 2005). Similarly, nitrile-functionalized (Zhao et al., 2004; Chiappe et al., 2006; Fei et al., 2007) and amine-functionalized (Wang et al., 2008) ILs were also used towards metal nanoparticles stabilization, and superior ability of nitrile-functionalized ILs over non-functionalized ILs was demonstrated in this particular context (Zhao et al., 2004; Chiappe et al., 2006; Fei et al., 2007). Since synthesis of thiol- and nitrile-functionalized ILs usually involves hazardous and odorous raw materials and multiple synthesis steps, other functionalized ILs such as N-(2-hydroxyethyl)-N-methylmorpholinium) tetrafluoroborate {[HEMMor][BF$_4$]} were prepared using more environmentally-benign synthesis and utilized for the synthesis of 4.3 nm Au nanoparticles (Kim et al., 2006). By using longer chain ILs such as [C$_{12}$HEMIm][Cl] and [C$_{14}$HEMIm][Cl], the same authors could also prepare 3.1 and 2.8 nm Au nanoparticles respectively. In another interesting study, Choi and co-workers could prepare 4.1 and 2.1 nm Ag nanoparticles by reducing AgNO$_3$ in 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate {[HEMIm][BF$_4$]} IL (Choi et al., 2007). More recently, Dinda and co-workers utilized several ascorbic acid-based ILs to prepare Au nanostructures, wherein ascorbate present in the anionic part of IL acts a reducing agent during nanoparticles synthesis (Dinda et al., 2008). Some of the metal nanostructures formed in ILs have been illustrated in Figure 2.

The examples discussed above demonstrate the potential of using task-specific ILs in the stabilization and preparation of metal nanoparticles. As is evident from the above discussed examples, one of the major advantages of using ILs for synthesis of metal nanoparticles is that the metal nanoparticles prepared in ILs are generally monodispersed and very small in size, predominantly due to the IL stabilization effect and low interface tensions of ionic liquids (Antonietti et al., 2004; Migowski & Dupont, 2007; Dupont & de Oliveira Silva, 2008). However it should also be noted that in certain cases ILs by themselves cannot effectively stabilize metal nanoparticles and additional stabilizing/capping agents may still be needed to assist with their stabilization in ILs. This indicates that more research is warranted to correlate the influence of type of ILs with metal nanoparticles stabilization and their size profile. Particularly interesting is the observation that ILs can themselves be functionalized

to either incorporate metal ions (Iida et al., 2008) or reducing agent (Dinda et al., 2008) within the IL structure. This provides a great deal of flexibility towards facile synthesis and stabilization of metal nanoparticles towards narrow and small size range with a potential ability to control their shape anisotropy (Davis, 2004; Fei el al., 2006; Lee, 2006; Li et al., 2006; Davis & Wasserscheid, 2008). However, in our opinion, it is not truly remarkable if one seeks to use functionalized ILs just for the sake of making nanoparticles. The true potential of functionalized ILs towards metal nanoparticles synthesis will require extensive exploration of additional advantages associated with IL-based synthesis of nanomaterials. This may include phase transfer ability of such nanomaterials or their improved catalytic and sensing properties, some of which will be discussed later in this chapter.
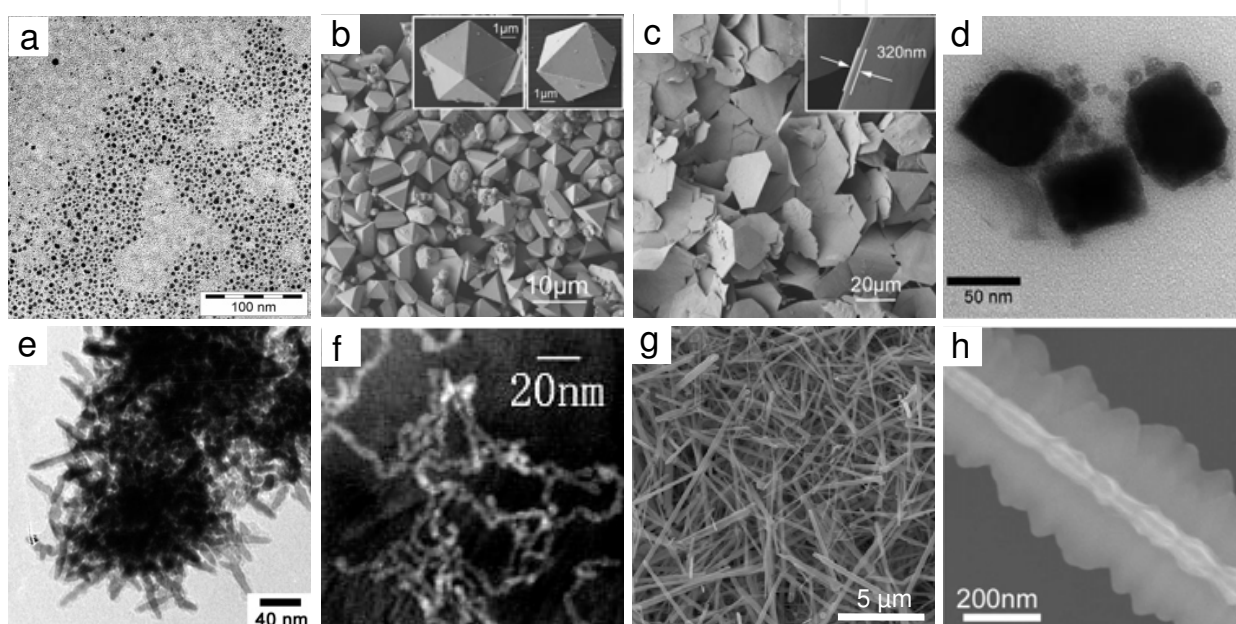

Fig. 2. Transmission and scanning electron micrographs exemplifying different morphologies of metal nanoparticles formed in ILs. (a) Ag nanospheres formed in [BMIm][BF$_4$] with *n*-butylimidazole as a scavenger; (b & c) Au nanostructures synthesized via microwave heating of 150 (b) and 100 mg (c) of HAuCl$_4$.4H$_2$O in [BMIm][BF$_4$] at 200 °C for 5 min; (d) Co nanocubes prepared in {DMI][NTf$_2$]; (e) Co-Pt nanorods obtained in [BMIm][NTf$_2$]; (f) Pd nanowires synthesized in a thiol-functionalized IL; (g) Ag nanowires formed in [BMIm][MeSO$_4$]; (h) Au nanodendrites formed in [BMIm][PF$_6$]. (adapted from (a) Redel et al., 2008b; (b & c) Ren et al., 2008; (d) Scariot et al., 2008; (e) Wang & Yang, 2005; (f) Gao et al., 2005; (g) Kim et al., 2009; (h) Qin et al., 2008 with permissions).

3.3 Metal nanoparticles synthesis in ILs using additional stabilizers or scavengers

In sections 3.2 and 3.3, we discussed some of the cases wherein ILs used during metal nanoparticles synthesis acted as a stabilizer, which predominantly resulted in small sized nanoparticles. However, sometimes additional stabilizing agents are required for metal nanoparticles stabilization in IL, which provide additional flexibility for the phase transfer of metal nanoparticles to different solvent media. Stabilizing agents such as citrate (Wei et al., 2004), oleic acid (Wang & Yang, 2006), dendrimers (Ou et al., 2008), phenanthroline (Huang et al., 2003), bipyridine (Leger et al., 2008), poly(vinylpyrrolidone) (Yang et al., 2008), and IL-like polymers (Zhao et al., 2007) have been used during metal nanoparticles

synthesis in ILs. Despite these studies, it is still not encouragingly clear how ILs and additional stabilizing agents interact with metal nanoparticles surface.

An interesting alternative to using additional stabilizing agents in IL during metal nanoparticles synthesis is the use of scavenging agents to remove the acidic products typically formed as by-products during nanoparticles synthesis. For instance, reduction of a metal salt by H_2 may lead to formation of acidic molecules, which might promote unwanted aggregation of metal nanoparticles during their synthesis. To address this issue, Redel and co-workers reduced $AgBF_4$ in the presence of both [BMIm][BF_4] and *n*-butylimidazole (Redel et al., 2008b). In this particular case, HBF_4 formed as a reaction by-product spontaneously reacted with *n*-butylimidazole and got neutralized that resulted in 2.8 nm Ag nanoparticles. Conversely, 66 nm Ag particles were formed in the absence of *n*-butylimidazole. Although interesting and with significant potential for further development, such scavengers have not been explored in great details for metal nanoparticles synthesis in ILs. We believe that the future studies in this area will focus upon use of such scavenging molecules, stabilizers, shape-directing agents, etc to achieve highly functional metal nanostructures in IL solvents for various applications.

3.4 Shape-controlled synthesis of metal nanoparticles in ILs

Shape-controlled synthesis of metal nanostructures is as important as size-control, because different morphologies of metal nanoparticles may lead to distinctly different physico-chemical properties (Lu et al., 2009). Considering the importance of metal nanoparticles shape control, significant efforts have been directed towards shape-controlled synthesis of metal nanostructures in ILs. For instance, Co-Pt nanorods were synthesized in [BMIm][NTf_2] IL while using cetyltrimethylammonium bromide (CTAB) as a shape-directing agent (Wang & Yang, 2005). The ionic nature and thermal stability of imidazolium-based ILs also make them good absorbers of microwaves. The microwave absorbing ability of ILs was utilized for the formation of Au nanosheets of 50 nm thickness and size larger than 30 μm by microwave heating of $HAuCl_4$ in [BMIm][BF_4] IL, wherein role of both the IL and the microwave heating in shape control was claimed (Li et al., 2005). In another microwave-mediated synthesis of Au nanoparticles in ILs, miscellaneous Au nanostructures were obtained in [BMIm][BF_4], [BMIm][NTf_2], [BMIm][PF_6], [BMIm][Br], [BMIm][Cl] and [BMIm][Tos] ILs (Ren et al., 2008). Zhu and co-workers synthesized 60 nm thick hexagonal- and triangular-shaped Au nanosheets by a photochemical reduction method in [BMIm][BF_4] (Zhu et al., 2007). Other metal nanostructures reported in ILs include anisotropic Au nanoparticles (Firestone et al., 2005), Au nanorods (Kumar et al., 2007), Pd nanowires (Kumar et al., 2007), Co nanocubes (Scariot et al., 2008) and Ag nanorods (Kim et al., 2009).

Similarly electrochemical syntheses of metal nanostructures in the presence of ILs have also been reported, and readers are encouraged to look at associated references for a detailed understanding of these systems (Endres, 2002; Huang & Sun, 2004; Huang & Sun, 2005; Abbott & McKenzie, 2006; Dobbs et al., 2006; El Abedin & Endres, 2006; Yeh et al., 2006; Endres & El Abedin, 2008). It is however noteworthy that the use of ILs, particularly Im-based ILs as solvents for electrochemical reactions is predominantly dominated due to their electrochemical stability, excellent oxidative and reductive stability, and a large electrochemical potential window, which is typically notably larger than the electrochemical window of conventional molecular solvents (MacFarlane & Pringle, 2006; Endres et al., 2008).

3.5 Galvanic replacement-mediated shape-controlled synthesis of metal nanoparticles in ILs

Another interesting aspect of metal nanostructure synthesis that is becoming interesting popular, and thus deserves particular focus is galvanic replacement reactions, which are also termed as transmetallation reactions. Galvanic replacement reactions are single-step reactions that utilize the differences in the standard electrode potentials of various elements, leading to deposition of the more noble element and dissolution of the less noble component without any applied external potentials. A classical example of this includes dipping an iron nail in aqueous $CuSO_4$ solution, which will result in spontaneous deposition of Cu onto Fe nail, while Fe will be leached out in the surrounding aqueous environment in the form of Fe^{2+} ions. Notably, since these reactions involve atom-by-atom replacement of metal template with a more noble metal ion, these reactions have the potential to develop high surface area nanostructures materials. Although these types of reactions are well known, it has been only recently that such facile electroless chemistry has been used for nanomaterials development. For instance, galvanic replacement reactions involving sacrificial metal nanoparticles and suitable metal ions have been employed by various groups (Sun et al., 2002; Sun & Xia, 2004; Liang et al., 2004; 2005; Shukla et al., 2005; Selvakannan & Sastry, 2005) for the synthesis of hollow/porous metal (Sun et al., 2002; Sun & Xia, 2004) and metal alloy (Liang et al., 2004; 2005) nanostructures in aqueous (Sun & Xia, 2004; Liang et al., 2004; 2005; Shukla et al., 2005) and organic environments (Selvakannan & Sastry, 2005). The electroless nature of galvanic replacement reactions also provides them the unique and significant advantage of simplicity. It is noteworthy that galvanic replacement reactions have hitherto mostly been confined to aqueous and organic solvents, wherein predominantly formation of hollow nanoarchitectures, without significant solvent effect has been observed (Figure 3).
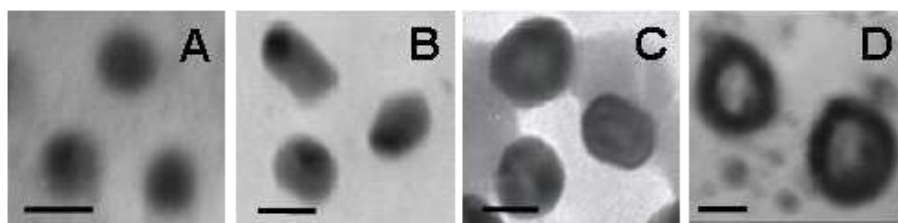

Fig. 3. Transmission electron micrographs of Ag nanoparticles in water before (A), and after galvanic replacement with (B) 0.1 %, (C) 1 %, and (D) 10 M % of $[AuBr_4]^-$ ions for 48 h. Scale bars correspond to 20 nm (adapted from Pearson et al., 2010 with permission from the Royal Society of Chemistry).

To this end, our group has also previously demonstrated that highly active bimetallic nanocatalysts can be developed in aqueous media by using galvanic replacement approach (Bansal et al., 2008; Bansal et al., 2009). In an interesting work, Qin and co-workers could synthesize threefold symmetrical dendritic Au nanostructures by galvanic replacement reaction between a Zn plate and a solution of $HAuCl_4$ in $[BMIm][PF_6]$ IL (Qin et al., 2008). In this study, the choice of the Zn plate and the IL $[BMIm][PF_6]$ were both claimed to be important for the formation of Au dendrites. Similarly Cu substrates have been used as templates for the growth of anisotropic Ag nanostructures in IL (Abbott et al., 2008). More recently, we performed a systematic study to explore galvanic replacement reaction in the IL $[BMIm][BF_4]$, wherein when spherical Ag nanoparticles were reacted with $KAuBr_4$, this led to the shape transformation of Ag nanospheres into hierarchical Au-Ag dendritic

nanostructures (Figure 4; Pearson et al., 2010), which showed high electrocatalytic activity and good surface enhanced Raman scattering (SERS) sensing ability (unpublished findings).
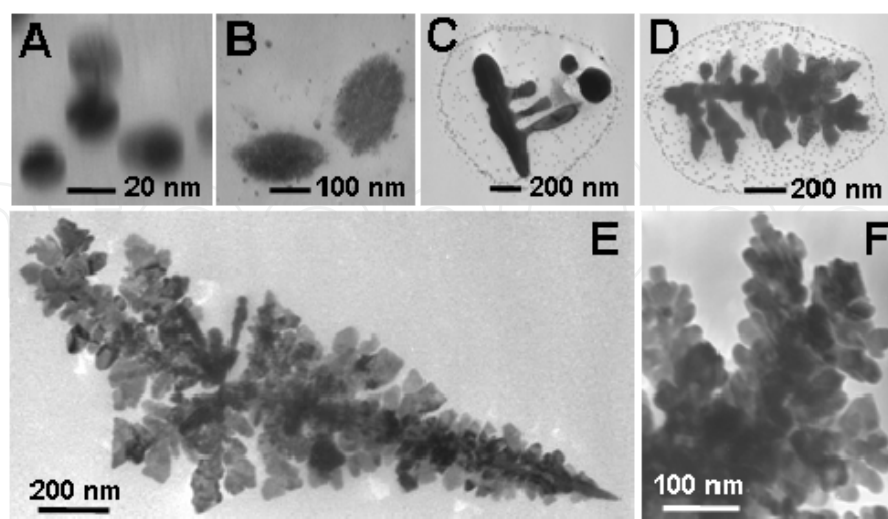

Fig. 4. Transmission electron micrographs of Ag nanoparticles in ionic liquid [BMIm][BF$_4$] before (A), and after galvanic replacement with (B) 0.1 M%, (C and D) 1 M%, and (E and F) 10 M % of [AuBr$_4$]$^-$ ions for 48 h (adapted from Pearson et al., 2010 with permission from the Royal Society of Chemistry).

The detailed investigation of the reaction mechanism of nanodendrites formation in [BMIm][BF$_4$] revealed the stabilization of Au^{+1} species in the highly viscous IL followed by a diffusion-limited-aggregation (DLA) mediated self-organization process, that led to such dendritic forms (Figure 5). Stabilization of Au^{+1} species in IL [BMIm][BF$_4$] is rather
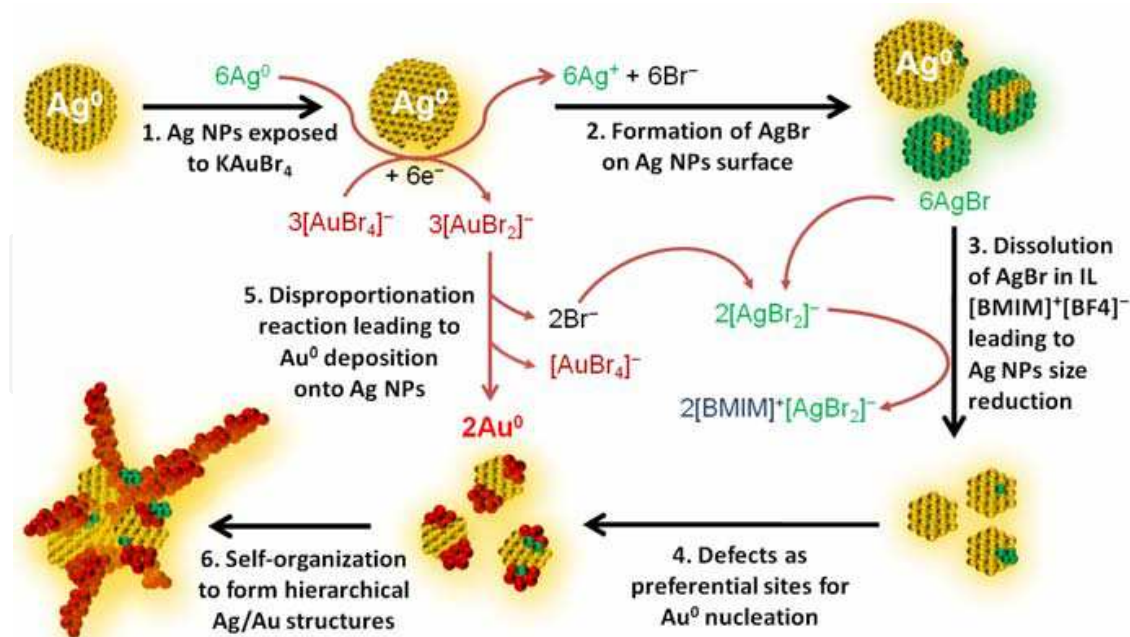

Fig. 5. Reaction scheme explaining the mechanism for synthesis of Au-Ag hierarchical dendritic structures in the IL [BMIm][BF$_4$] (adapted from Pearson et al., 2010 with permission from the Royal Society of Chemistry).

interesting, because it is extremely difficult to stabilize such metastable metal species in aqueous environments. This report also suggests that if regularly employed aqueous and organic solvents are replaced with non-conventional (e.g. viscous) solvents such as ILs during replacement reactions, the reaction kinetics may change significantly either due to restricted movement of ions and/or stabilization of intermediate reaction species in such solvents. Hence, this may lead to markedly different reaction nanoproducts in ILs and the ability to control shape anisotropy, thus posing ILs as true designer solvents for the shape-controlled synthesis of anisotropic nanomaterials. This is only one of the very few examples wherein a detailed reaction mechanism of anisotropic metal nanoparticles formation has been undertaken in an IL. However, systematic knowledge regarding the metal nanoparticles formation mechanisms and control of shape anisotropy is yet to be generalized, which will also most possibly also require understanding of these systems through computational modelling studies.

4. Applications of metal nanoparticles synthesized in ILs

It has been well established that physico-chemical properties of metal nanoparticles for various applications strongly depend on their surface properties, in addition to the more commonly known size and shape effects. These surface properties of metal nanoparticles may vary significantly from one synthesis protocol to another, predominantly because concentration and type of stabilizing agents used in these synthesis methods can be quite different. Since ILs generally act as *in situ* stabilizing agents during synthesis of metal nanoparticles, the nanomaterials synthesized in ILs may offer significantly new properties for a myriad of applications. For this reason, among others, when combining ILs and metal nanoparticles, the need to understand the interactions between ILs and metal nanoparticles surface is becoming increasing important. To this end, in order to understand the interactions between an Im-based IL and Au nanoparticles, Schrekker and co-workers used an ether-modified imidazolium species, which could absorb the near-infrared radiation, and thus made SERS study of the surface of Au nanoparticle feasible (Schrekker et al., 2007). The SERS study clearly showed an interaction of imidazolium cation with Au nanoparticles surface by means of a parallel coordination, however almost no interaction between the methanesulfonate anion and Au nanoparticle surface was observed (Figure 6). A series of other reports also strongly suggested interaction between metal nanoparticles and Im-based ILs. However it was found that this interaction with metal surface can take place either via cationic imidazolium ring or the anion or both, which may vary from one IL system to another (Neouze, 2010).

In a pioneering work, Dupont and co-workers demonstrated that metal nanoparticles synthesized in Im-based ILs possess outstanding catalytic properties for biphasic hydrogenation reactions, with almost 100% yield (Dupont et al., 2002). From this work, the high catalytic performance of the metal nanoparticles could be linked to the presence of imidazolium medium, which allowed the synthesis of monodispersed, 2 nm sized small nanoparticles. In another study, 3 nm sized, monodispersed Rh nanoparticles synthesized in [BMIm][BF$_4$] IL in the presence of a copolymer, were used for benzene hydrogenation reaction (Mu et al., 2005). These Rh nanoparticles showed unprecedented activity and recyclability, thus performing the catalytic reaction in five complete recycles of 4000 total turnover each. In another interesting report, Rh and Ir nanoparticles dispersed in an Im-based IL were employed as reusable active catalysts in the biphasic hydrogenation of cyclohexane (Redel et

al., 2009). In a more recent study, to understand the high catalytic performance of metal nanoparticles synthesized in Im-based ILs, Au nanorods were synthesized using an ionic capping agent dodecyltrimethylammonium bromide (CTAB), and its imidazolium equivalent, 1-dodecyl-3-methylimidazolium bromide (Bai et al., 2009). Following this, the interaction energies of these molecules with Au (111) plane were calculated using COMPASS force fields which yield smaller interaction energies for imidazolium (174.1 kcal mol^{-1}) than that for CTAB (216.5 kcal mol^{-1}). The authors claimed that due to the smaller interaction between Au and imidazolium group, more active sites of Au were accessible during catalytic reactions, which led to higher catalytic activity in IL-based systems.
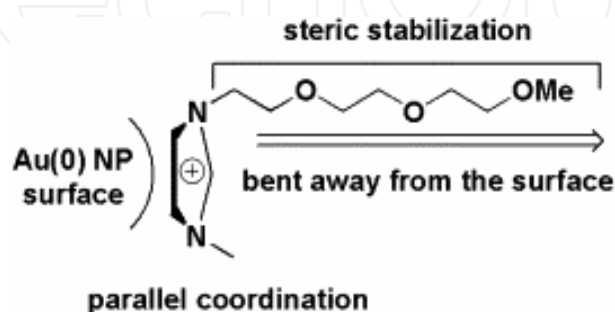

Fig. 6. Imidazolium cation coordination and stabilization mode demonstrating the parallel coordination of the imidazolium cation onto the Au nanoparticle surface (adapted from Schrekker et al., 2007 with permission from the Elsevier Inc.).

Metal nanoparticles formed in other solvents when incorporated in Im-based ILs, also demonstrated interesting catalytic properties (Cassol et al., 2005). Notably, in a large number of Im-based systems, different groups detected the presence of an *N*-heterocyclic carbine (NHC) species associated with metal nanoparticles (Ott et al., 2005; Zhao et al., 2009). The NHC radical species can on one hand significantly enhance the catalytic performance of these materials in ILs, while on another, it might promote nanoparticles aggregation. The promising catalytic activity of NHC species associated with various metal nanoparticles such as Ir, Au and Rh in Im-based ILs was outlined by various groups (Cavell, 2008; CAi & Liu, 2009; Aldeco-Perez et al., 2009). Conversely, Ott and co-workers suggested that presence of these NHC species associated with Ir nanoparticles can act as potent inhibitor of Heck reactions (Ott et al., 2005).

In addition to the above highlighted few cases, several other studies have investigated the catalytic performance of metal nanoparticles in ILs. All these studies point to the fact that careful choice of the IL is the key to obtain desired catalytic performance. If chosen appropriately, ILs can not only enhance the catalytic activity, but can also provide much desired substrate and product stability. As is clear from these illustrations, the presence of NHC species in Im-based systems cannot be omitted, and therefore metal nanoparticles associated with ILs can even be considered as one material, a single catalytic system. In fact, in one of the studies, it was demonstrated that during Suzuki C-C coupling reactions, Pd nanoparticles were catalytically active only when they were formed *in situ* in an Im-based IL (Fernandez et al., 2007).

5. Conclusion

Through this chapter, our aim was to discuss some of the most important developments in the field of ionic liquid-assisted synthesis of metal nanoparticles and their promising

applications in the area of catalysis. It was not an intention of this chapter to provide an exhaustive review of the developments in this field; however the aim was to familiarize the readers with this developing field by discussing few of the leading case studies. Although most of the illustrations discussed in this chapter are from imidazolium-based IL systems, the scope of this chapter can also be equally extended to other ILs. From the illustrations provided in this chapter, some major outcomes can be drawn: (i) ILs can act as new designer solvents for the size- and shape-controlled synthesis of metal nanoparticles, wherein synthesis of ultra-small size, monodispersed metal nanoparticles of different compositions is achievable in ILs. (ii) The interactions between metal nanoparticle surface and IL can be a bit complex: while ILs can assist in *in situ* stabilization of metal nanoparticles, nanoparticles can themselves influence the nanostructural organization of ILs in which they form. (iii) ILs play multiple roles towards metal nanoparticles synthesis which include their solvent, template, and stabilizing capabilities. (iv) In case of imidazolium-based ILs, formation of NHC radical species is particularly notable for catalysis reactions, because this can either positively or negatively influence the catalytic performance of metal nanoparticles. Therefore choice of an appropriate IL and metal nanoparticles for a particular catalysis reaction can be considerably important. (v) Moreover, in future, potentially numerous ILs can be synthesized by a combination of appropriate cations and anions. This creates a huge potential for use of ILs as preferred solvent system for nanomaterials synthesis in general, and metal nanoparticles in particular. The large scale commercial implications of IL-mediated synthesis of metal nanoparticles cannot be overemphasized.

6. References

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Ionic Liquids: Theory, Properties, New Approaches

Edited by Prof. Alexander Kokorin

Ionic Liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering. This book, consisting of 29 chapters gathered in 4 sections, reviews in detail and compiles information about some important physical-chemical properties of ILs and new practical approaches. This is the first book of a series of forthcoming publications on this field by this publisher. The first volume covers some aspects of synthesis, isolation, production, modification, the analysis methods and modeling to reveal the structures and properties of some room temperature ILs, as well as their new possible applications. The book will be of help to chemists, physicists, biologists, technologists and other experts in a variety of disciplines, both academic and industrial, as well as to students and PhD students. It may help to promote the progress in ILs development also.

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