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Chapter 4

Progress in Green Solvents for the Stabilisation of Nanomaterials: Imidazolium Based Ionic Liquids

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Additional information is available at the end of the chapter

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Abstract

For over a decade, ionic liquids (ILs) have attracted enormous attention from scientists across the globe. The history of these compounds traces back to 1914 where the inception of the first IL with a melting point of 12°C was made. Years later, a progression of the remarkable related compounds have been discovered. Out of many analogous compounds realized from time to time, the imidazolium class of ionic liquid is the most studied because of their air and moisture stability. The physicochemical properties of ILs differ significantly depending on the anionic/cationic species and alkyl chain length. ILs have found application in many scientific fields the most recent being good solvents and stabilizing agents in the nanomaterial synthesis. Studies have showed that ILs not only stabilize as synthesized nanomaterials but also provide environmentally green routes towards nanomaterials engineering.

Keywords: ionic liquids, green solvent, nanomaterials, imidazolium-based ionic liquid, stabilization, capping agents

1. Introduction

Nanomaterials have penetrated numerous multidisciplinary research fields in both science and engineering domains, leading to the development of next generation products which have already made a debut in the commercial marketplace [1]. To date, synthetic methods and protocols remain of fundamental importance in accessing and harnessing unique properties of materials as their particle sizes approach the nanometer size regime. Suspended nanomaterials are usually desired due to their suitability with various applications and they are

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easily prepared from chemical approaches. These approaches provide opportunities in tailoring and tuning the properties of the nanomaterials to suit desired applications by tweaking reaction parameters. Two main reaction parameters have received attention, namely, (1) the type and nature of the precursor/s [2–4], as well as (2) the nature of the solvent used during and after completion of the fabrication process [5–7]. Nanomaterials have, however, received their share of potential negative implications on the environment and its inhabitants [8]. Thus, efforts in devising eco-friendly reaction protocols have been seen as a proper response. In this chapter, imidazolium-based ILs are reviewed as green solvents over conventional organic solvents for use in the synthesis of nanomaterials.

The general use of conventional organic solvents in various laboratory and industrial processes has presented issues over the years. For example, in pharmaceutical production, the high energy consumption (*ca.* 60% of the overall energy) and 50% of the post-treatment greenhouse gas emissions are attributed to the incorporation of organic solvents in the production process [9, 10]. Thus, the search for alternative green solvents that do not compromise the process and quality of the end-product has become popular. As a result, different tools, methods and guidelines have been established to ascertain the proper selection of alternative solvents for synthesis; Ghandi [11] has categorized these solvents into three classes, namely: (i) preferred, (ii) usable and (iii) desirable. Ionic liquids are among solvents have become a central focus as alternatives to toxic solvents and subsequently exploited in various reactions.

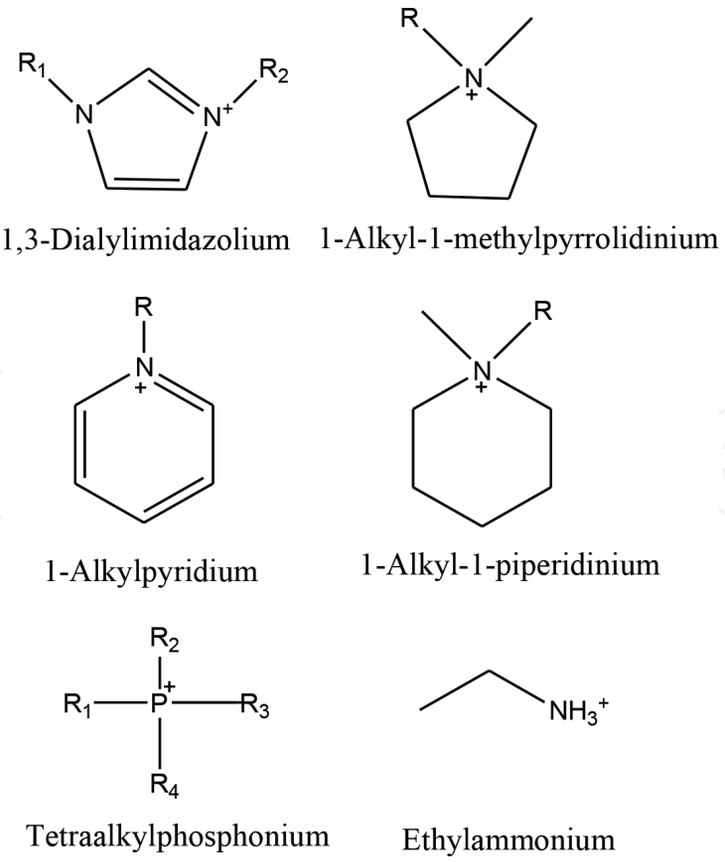


Figure 1. Commonly used cations for ILs synthesis.

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Ionic liquids (ILs) are generally molten salts composed of organic cations and organic or inorganic anions, with characteristic melting points below 100°C. They possess unique physicochemical properties such as low viscosity [12], negligible vapor pressure [13], non-flammability [14], good thermal and chemical stability [15], high ionic conductivity [16], and tunable solubility for both organic and inorganic molecules. They are thus regarded as environmentally-friendly and may lead to the formation of novel materials that have never been achieved by conventional solvents or even water. ILs are normally characterized by their cationic components of which imidazolium [17], pyridinium [18], ammonium [19], pyrrolidinium [20], piperidinium [21] and phosphonium [22] cations with different alkyl chain lengths being the most common (**Figure 1**). Examples of some commonly used anions are shown in **Figure 2**. ILs can be classified further into groups, *viz.* polyionic liquids (PILs) [23, 24], room temperature ionic liquids [25–27], task-specific ionic liquids [28, 29] and supported ionic liquid membranes [30, 31]. IL composites are also known, such as the metal organic frameworks-supported ILs [32, 33].

The complexity and suitability of ILs in various applications have been debated over the years. Many questions have been asked about the complexity (and sometimes even the simplicity) associated with the usefulness of ionic liquids in various fields of science specifically their use as solvents. However, the hybrid ionic nature of ILs and the resultant intermolecular interactions

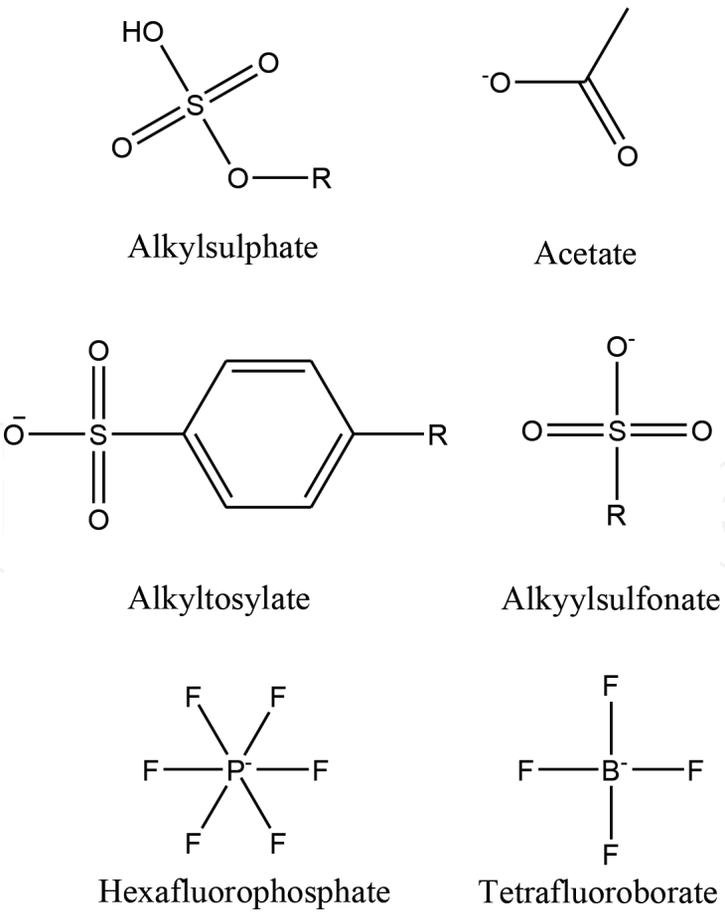


Figure 2. Most familiar anionic specie used in ILs synthesis.

give rise to a complex set of phenomena, creating an area of study that is both interesting and challenging. Furthermore, they have been extensively studied and researched as potential solvents for inorganic nanomaterial synthesis, organic chemical reactions, polymer synthesis and electrochemical applications [34–38]. Thus, the aim of this chapter is to rather highlight the recent developments and breakthroughs in exploiting the interesting physicochemical properties of ILs in the world of nanomaterials. The scope will be restricted to the use of room temperature ILs as green solvents for the synthesis and stabilization of inorganic nanomaterials. Prior to this, the physicochemical properties of ILs will be briefly outlined.

2. Physicochemical properties of ILs

The physicochemical properties of ILs (e.g. viscosity, melting point, hydrophobicity, solvation, and catalytic activity) can be tuned by changing the alkyl chain length in the cationic and/or the anion groups [39, 40]. Task specific or targeting ILs can be synthesized by careful choice and combination of the cationic and anionic groups, to suit a specific application. A catalysis-themed review article by Sheldon [35], for example, outlines the potential use of ILs as both reaction media and catalysts. The former was, however, found to have a profound effect on the catalytic activities and selectivity.

2.1. Viscosity

Greater van der Waals forces and hydrogen bonding are typical attributes of materials exhibiting high viscosities [41, 42]. Generally, ILs are highly viscous than most common molecular solvents, with viscosity ranging between 10 and 500 mPa s at room temperature [43]. The cation structure influences the IL viscosity with minimal values reported for ethylmethylimidazolium, $EtMeIm^+$ ILs. Furthermore, $EtMeIm^+$ ILs have adequate side chain mobility and low molecular weight. Generally, the viscosity of ILs increases with alkyl chain length and degree of fluorination [44]. Anions also have an influence over the viscosity of ILs, e.g. $[BMIm]PF_6$ = 312 mPa [45], $[BMIm]BF_4$ = 154 mPa [46] and $[BMIm]TF_2N$ = 52 mPa [44].

2.2. Conductivity

ILs have relatively good ionic conductivities compared to organic solvents and electrolytic systems (up to about 10 mS cm^{-1}) [43]. Susan et al. [47] first demonstrated that fused ammonium salts can be used as proton conductors in polymer membrane fuel cells [47]. According to Greaves et al. [48], "ionic conductivity is a transport property and is governed by the degree of dissociation of the ions, viscosity, ion mobility, and ionic charge". These aforementioned factors depend on the effective ion sizes and shapes. Furthermore, ionic conductivity of ILs is inversely proportional to viscosity and molar volume [48].

2.3. Melting point

The general description of ILs is that of ionic salts that are in a liquid phase below an arbitrary temperature of 100°C; the majority of ILs are solids at standard room temperature. From a

practical point of view, ILs are desirable in their molten state e.g. transportation of ILs across multiple unit operations in industrial applications is most effective in their liquid phase. ILs exhibiting of significantly lower melting points or "room temperature ILs" (T_m < 25°C) are critically important to researchers searching for new industrial applications [49]. One main reason for their demand is their usage as solvents or absorbents for separation tasks involving selective dissolution of solutes in gas (e.g. CO_2), liquid (e.g. toluene), or solid (e.g. cellulose) states. They are also widely considered as liquid solvents to promote chemical reactions [50].

2.4. Density

ILs are generally denser than water, with values ranging from 1 to 1.6 g cm^{-3} and their densities decrease with increase in alkyl chain length in the cation [51]. For example, ILs composed of substituted imidazolium-type cations and $CF_3SO_3^-$ anion display densities of 1.39, 1.33, 1.29 and 1.27 g cm^{-3} for $[EMIm]^+$, $[EEIm]^+$, $[BMIm]^+$ and $[BEIm]^+$, respectively [52]. The densities of ILs are also affected by the nature of anions, e.g. the densities of 1-butyl-3-methylimidazolium-type ILs with different anions, such as BF_4, PF_6, TFA and Tf_2N in literature are recorded to be 1.12, 1.21, 1.36 and 1.43 g cm^{-3}, respectively [44, 53]. The order of increasing density with respect to anions is: $[CH_3SO_3]^- \approx [BF_4]^- < [CF_3CO_2]^- < [CF_3SO_3]^- < [C_3F_7CO_2]^- < [(CF_3SO_2)_2N]^-$, in Ref. [52].

2.5. Electrochemical window

The electrochemical window allows ILs to be used in the electrodeposition of semiconductors and metals. The electrochemical window, by definition, is the electrochemical potential range over which the electrolyte is neither reduced nor oxidized at an electrode. Thus, the magnitude of the electrochemical value determines the solvent's electrochemical stability. The electrodeposition of elements and compounds in water is limited by its low electrochemical window of only about 1.2 V. On the contrary, ILs have significantly larger electrochemical windows, for example, 4.15 V for $[BMIm]PF_6$ at a platinum electrode, 4.10 V for $[BMIm]BF_4$ and 5.5 V for $[BMP]Tf_2N$ at a glassy carbon electrode [54, 55]. Generally, the wide electrochemical windows of ILs have opened the new horizon for the electrodeposition-assisted synthesis of metals and semiconductors at room temperature, which were previously achieved only from molten salts at high reaction temperatures.

2.6. Thermal stability

Most solvents are thermally stable at high temperatures only for short durations; long time exposure habitually leads undesirable decomposition [43]. On the other hand, ILs are known to be thermally stable up to 450°C. Their thermal stability is limited by the strength of their hydrocarbon bonds [43]. It is common knowledge that ILs with larger proton transfer energies prematurely decompose before reaching their boiling points with varying decomposition temperatures ranging between 100 and 360°C [56]. Protic ILs with a bis(trifluoromethane) sulfonamide anion and alkylammonium, imidazolium and a range of other heterocyclic cations are identified as the most stable ILs due to their bond strength resulting from resonance stabilization [57]. Specifically, ILs such as 1-ethyl-3-methyl-imidazolium tetrafluoroborate, 1-butyl-3-methyl-imdazolium tetrafluoroborate and 1,2-dimethyl-3-propyl imidazolium

bis(trifluorosulfonyl)imide are thermally stable up to 445, 423 and 457°C, respectively [43]. The anionic components is known to predominantly contribute to the thermal stability of the ILs over the cationic counterparts. Furthermore, the hydrophilicity of the anions decreases thermal stability of the ILs [58].

3. Imidazolium-based ionic liquids

ILs with the 1,3-dialkylimidazolium cation are by far the most studied class of ILs due to their interesting properties. The class can interact with various chemical species, as they offer hydrophobic or hydrophilic regions and a high directional polarizability. The structural organization of these solvents can be used as 'entropic drivers' for spontaneous, well-defined, and prolonged ordering of nanoscale structures. Certainly, the unique combination of flexibility towards other molecules (and phases) with strong hydrogen-bond-driven structures make ILs potential key tools in the preparation of a new generation of chemical nanostructures [13].

4. Imidazolium-based ionic liquids in nanomaterial synthesis

Generally, ILs have chemical attributes such as non-volatility, negligible vapor pressure and most importantly, high thermal stability [59]. The majority of the fabrication protocols require heat to be applied, thus controlling both nucleation and growth rates to ensure monodispersity in suspended nanomaterials [60]. Functional groups of organic solvents determine stability and coordination mode towards nanomaterials [5]. Similarly, the composition of the ILs (combination of organic cation with organic or inorganic anion) play a major role in determining the final chemical attributes. The early reports have demonstrated ILs as dual-action reagents, i.e. as both solvent media and template or structure/shape-directing agent [61, 62]. Furthermore, the recovery of ILs after completion of nanomaterials synthesis strengthens their classification as eco-friendly solvents. The negligible vapor pressure feature enables reactions in ILs to proceed in ambient pressure when subjected to synthetic protocols common for hydro- and solvothermal methods, hence the reactions are rather termed ionothermal synthesis [59].

In recent years the advantages of incorporating ILs in the synthesis of inorganic nanomaterials have been thoroughly demonstrated, due to their unique physicochemical properties [63, 64]. Several ILS-incorporated methods and protocols have been reported for the fabrication of inorganic nanomaterials. Synthetic reactions, in the presence of ILs, offers nanomaterials to display exceptional and/or unique properties [34].

4.1. Electrostatic stabilization of nanomaterials by ILs

Ionic compounds such as carboxylates, polyoxoanions and fluorides usually generate double layers between the nanoparticles, thereby introducing repulsive forces between individual nanoparticles. Thus, electrostatic repulsions prevent aggregations and agglomeration of nanoparticles suspended in the solution phase. This type of electrostatic stabilization is sensitive to reaction parameters such as pH, concentration and temperature. This has been demonstrated in metal nanoparticles stabilized by ILs composed of sulfonium, tertiary butyl

ammonium, phosphonium and imidazolium moieties [65]. A graphical illustration of this kind of stabilization is shown in **Figure 3**.

4.2. Steric stabilization of nanomaterials by ILs

Steric stabilization of nanoparticles is another significant parameter. This usually happens through the use of surfactants, alcohols and a variety of polymers/oligomers. These compounds are adsorbed on the nanoparticle's surface, thereby forming a protective layer [66]. When the nanoparticles are sterically stabilized, their free motion in solution is limited. Furthermore, the thickness of the protective layer has an important role in the stabilization process and greatly depends on the alkyl chain length and nature of the stabilizing agent, where applicable [65].

4.3. A combination of electrostatic and steric stabilization of nanomaterials by ILs

Both electrostatic and steric stabilization processes can co-exist in the stabilization of nanoparticles in solution phase. Ionic surfactants with long alkyl chains ordinarily provide this type of stabilization. This is mostly achieved through ILs which have polar heads groups which generate electric double layer around the nanoparticle and a lipophilic tail group providing the steric repulsions between nanoparticles [65]. Examples of IL-stabilized nanoparticles are listed in **Table 1**.

4.4. Practical examples of imidazolium-based ILs used in the synthesis of nanomaterials

The diversity of ILs presents a challenge is identifying the relationship/trend between their physiochemical properties and morphological (also crystal phase) control of the nanomaterials. It is for these reasons ILs have been used in conjunction with conventional organic solvents to synthesize nanomaterials [68, 74, 75]. Since the influence of ILs on the

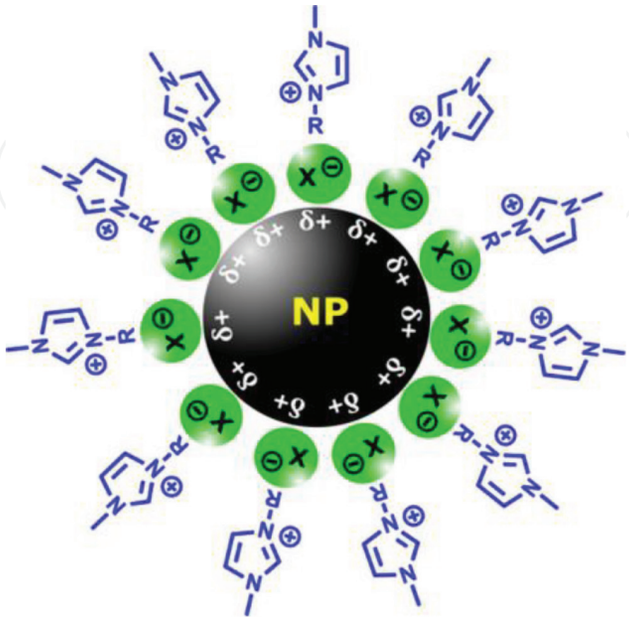


Figure 3. Electrostatic stabilization of nanoparticles by the imidazolium based ILs. Reproduced from Ref. [65] with permission granted by Springer.

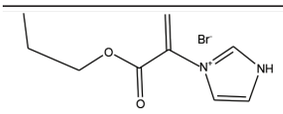
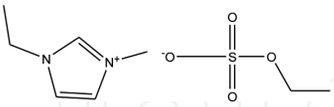
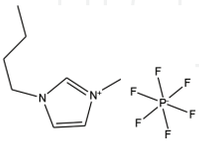
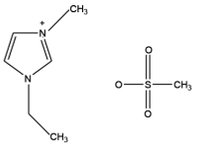
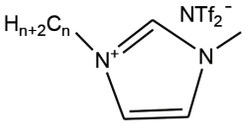
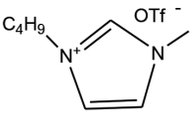
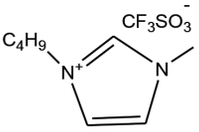
IL used	NP synthesized	Size (nm)	IL name and reference
	Al_2O_3, TiO_2, Fe_3O_4	80–100	1-methacryloyloxypropyl-3-methylimidazolium bromide [67]
	ZnSe	70–100	1-butyl-3-methylimidazolium methyl sulfate [68]
	PbS	100	1-n-butyl-3-methylimidazolium hexafluorophosphate [69]
	CdS, PbS	2–15, 102–160	1-ethyl-3-methylimidazolium methanesulfonate [70]
 n=3,7,9,11,13,15	Ni	4.9–5.9	1-alkyl-3-methylimidazolium N-bis(trifluoromethane sulfonyl) [71]
	Au	140	n-butyltrimethylammonium N-bis(trifluoromethylsulfonyl)imide [72]
	Ir	2.4–2.6	1-n-butyl-3-methyl trifluoromethane sulfonate [73]

Table 1. Examples of nanoparticles stabilized by imidazolium based ILs.

properties of nanomaterials is not predictable at this stage, there are efforts in conducting investigations for the sake of rather establishing databases. A good example is the work by Duan et al. [76] where ILs are demonstrated as both solvent and shape-directing agent in the synthesis of γ-AlOOH and well-dispersed $NH_4Al(OH)_2CO_3$ nanostructures. The same group extended the study on ferric giniite crystals (**Figure 4**) which revealed interesting photocatalytic behavior which could only be linked to exposed facets of the crystals, as opposed to the surface area [77]. There are reports that have documented evidence of imidazolium-based ILs having acted as capping agents [78, 79]. Zheng and co-workers [79, 80] have given plausible reasons that support capping through interaction modes of imidazolium-based ILs with TiO_2 nanoparticles, for example, hydrogen bonding between the positively charged (due to delocalization) position-2 H atom in the imidazole ring with O on the TiO_2 surface.

IL-nanomaterial composites have also been reported for use in biological applications, e.g. the study by Alavi-Tabari et al. [81] demonstrates the use of 1-butyl-3-methylimidazolium

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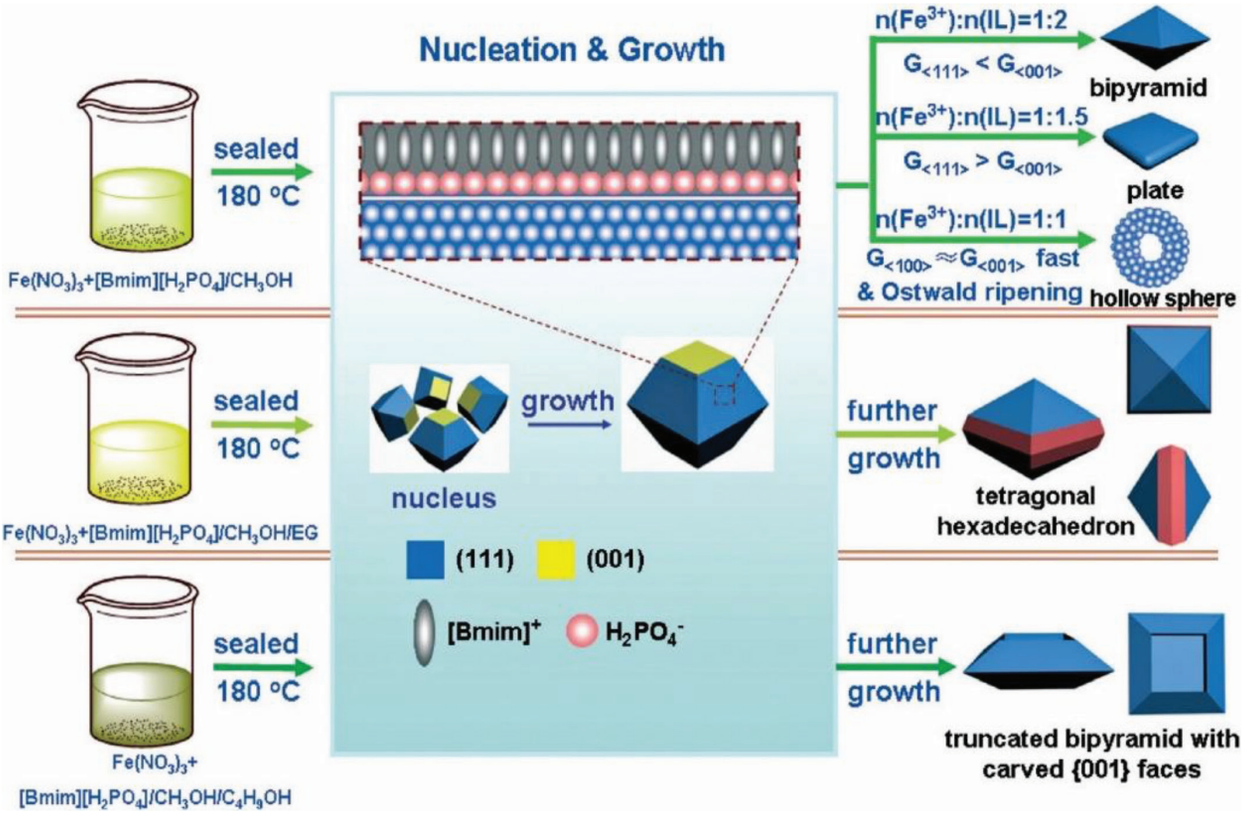


Figure 4. Synthesis of ferric giniite crystals exhibiting different shapes as a result of varying reaction parameters. Reproduced from Ref. [70] with permission from the Royal Society of Chemistry.

tetrafluoroborate IL to form IL-ZnO composites for potential activity enhancement of doxorubicin and dasatinib for breast anticancer remedies. In their study the outcome showed that ZnO-NPs/BMTFB/CPE reveals two different oxidation signals for the simultaneous examination of doxorubicin and dasatinib, which eventually showed a good linear relationship between the oxidation peak current of doxorubicin and its concentration. They concluded that ZnO-NPs/BMTFB/CPE showed good capacity for analysis of doxorubicin and dasatinib in injection and serum samples. Husanu et al. [82] reported an easy synthetic method focusing on preparing citrate-based ILs which showed a dual-action feature, an ability to act as both capping agents and reducing agents towards the preparation of inorganic nanomaterials.

Although the topic "ILs in the synthesis of nanomaterials" is not of novel origin, the 'novelty' is observed where a new class of ILs is prepared through the incorporation of new anionic groups. This subsequently results in the synthesis of nanomaterials bearing desired properties. For example; 3-(hydroxypropyl)-3-methylimidazolium bis(salicylato)borate (OHMimBScB) IL has been used for the covalent grafting of carbon quantum dots via a bottom up approach [83]. Since ILs have strong adsorption capabilities, the surface on the carbon quantum dots was protected against friction, which then improved their stability efficiency in tribological evaluations. Saien and Hashemi [84] used 1-hexadecyl-3-methyl imidazolium chloride IL as a surfactant to study its interaction with Fe_3O_4 nanoparticles in a biphasic oil/water system. In a study by Okoli et al. [85] it was found that the sole use of ILs without additional co-surfactants is capable of producing good quality (monodispersity with narrow size distribution) metal alloy nanoparticles which display enhanced catalytic activities.

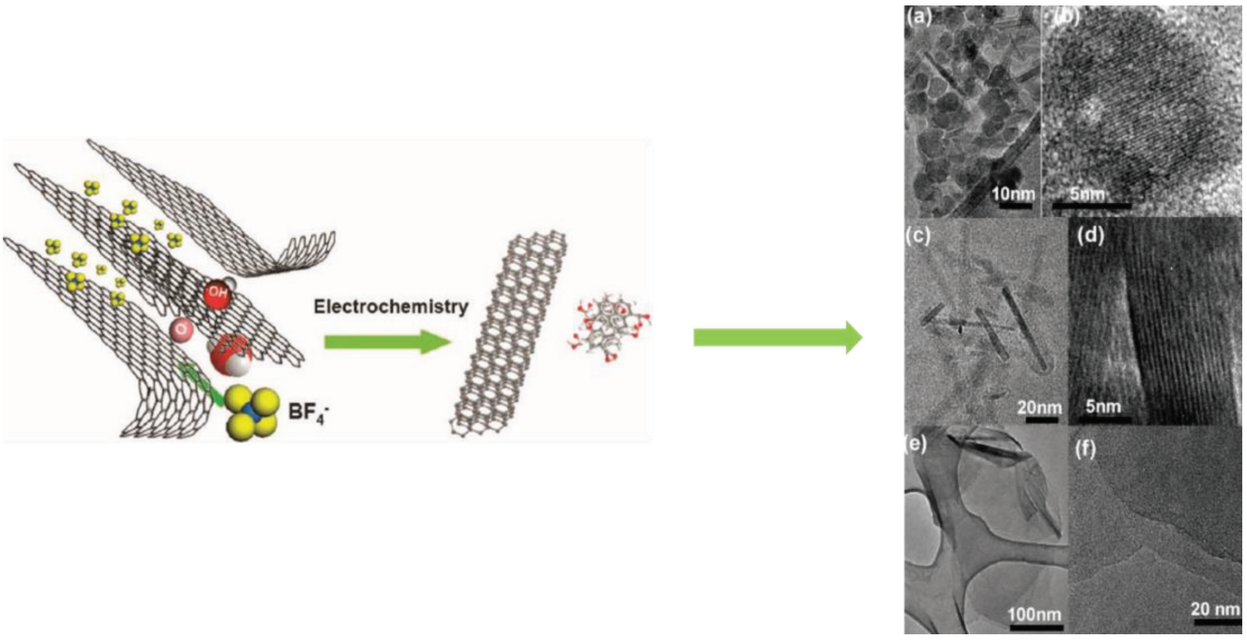


Figure 5. The electrochemical exfoliation of graphite into (a and b) carbon nanoparticles, (c and d) carbon nanoribbons and (e and f) graphene sheets. Reprinted with permission from Ref. [87]. Copyright 2009 American Chemical Society.

A pre-concentration technique based on the use of graphene oxide (GO) functionalized with an IL was established for the determination of Hg traces in water [86]. In this study, the hybrid IL-GO nanomaterial was fabricated by a simple procedure, where the IL used was 1-butyl-3-dodecylimidazolium bromide ([C_4C_{12}im]Br). The incorporation of [C_4C_{12}im]Br led to high sorption performances on Hg. Furthermore, functionalization of the imidazolium ring with long alkyl chains increased the retention competence of GO for the analyte, consequently providing additional physicochemical properties that were beneficial for the extraction of Hg and its control at trace levels.

Other interesting reports include the use of ILs as a solvent medium in the electrochemical exfoliation of graphite to obtain nanomaterials of significant technological importance i.e. fluorescent carbon nanoribbons, nanoparticles and graphene (**Figure 5**) [87]. ILs are most suited for this task due to their broad electrochemical window, as well as high dielectric constant necessary to counteract stacking in nanomaterials resulting from van der Waals interactions. Furthermore, imidazolium-based IL-capped carbon quantum dots have been prepared by pyrolysis [88]. Recently, imidazolium-based IL has been used to exfoliate 2D transition metal chalcogenide, WS_2 nanosheets [89]. Prechtl et al. [90] demonstrated the use of ILs as both stabilizing and reducing agents in the preparation of metal nanoparticles from organometallic complexes. Similarly, citrate-modified ILs were recently used to prepare IL-capped Ag nanoparticles [90].

5. Tuning the properties of nanomaterials (NMs) through the use of IBILs

Stabilization of nanoparticles using different media has been necessary to suit various applications. The medium plays a key role in modifying and tuning the chemical and physical

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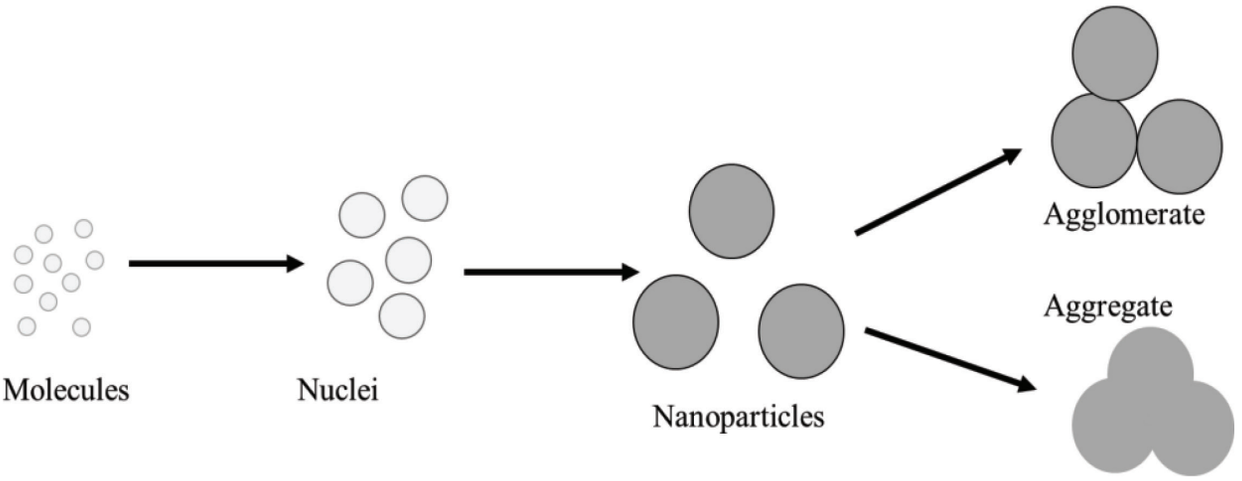


Figure 6. Mechanism of nanoparticle production using colloidal methods. The methods differ in the way the starting molecules are generated by chemical reaction/precipitation. The nuclei may be amorphous or crystalline and lead to amorphous or crystalline nanoparticles. Because of their intrinsic instability, the nanoparticles may form agglomerates that can be easily redispersed or form non-dispersible aggregate clusters.

properties of the nanomaterials [91, 92]. Various synthetic routes such as colloidal methods use solvent-mediated chemical procedures to form colloids via self-assembly or other processes related to the tuning of physicochemical properties [93]. The former process usually proceeds via the homogeneous nucleation of particles and subsequent particle growth by condensation, coagulation and arrest of particles (**Figure 6**).

Imidazolium-based ILs have been reported to improve the electric conductivity of multi-walled carbon nanotubes for electrochemical or electro catalytic applications [65]. Covalent interaction linkage ensures improved oxidation and hydrogenation reactions. Imidazolium-based

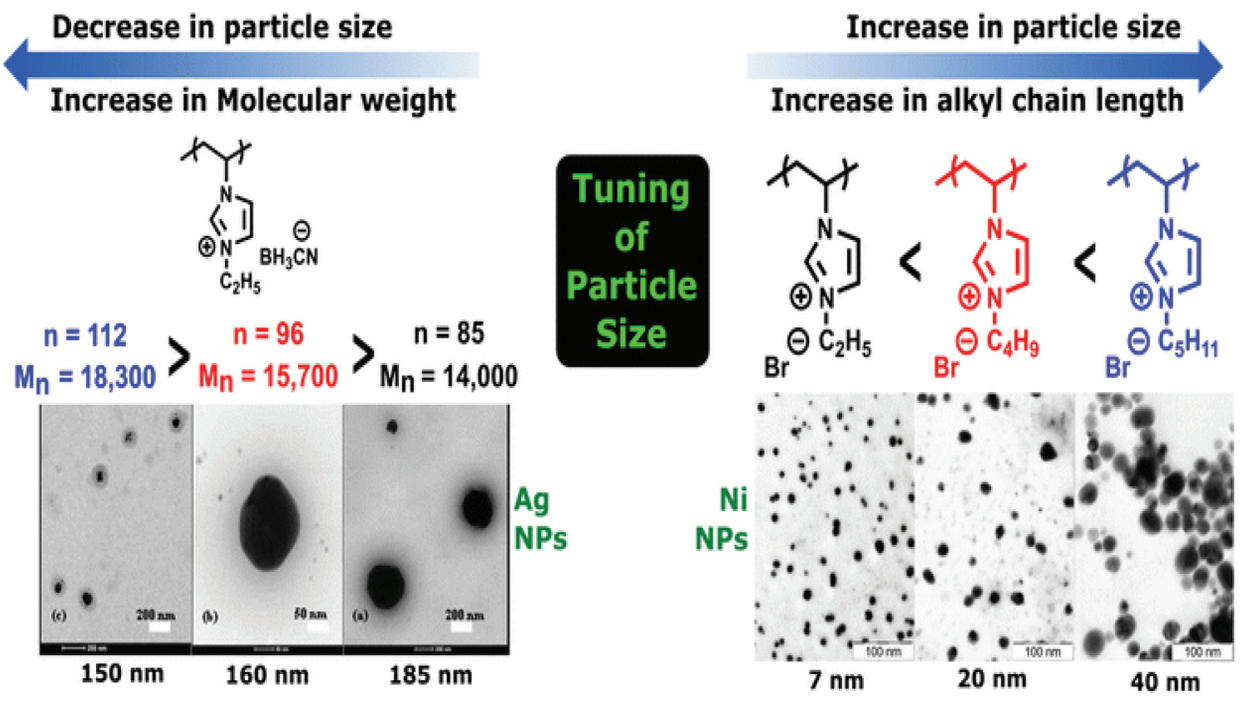


Figure 7. Tuning of nanoparticles size by imidazolium based ionic liquid (reprinted with permission from Refs. [65, 95, 97]).

ILs provide surface stabilization of nanoparticles over a long period of time with insignificant or no change in particle size and size distribution, providing re-usable or recyclability capabilities in applications such as catalysis [65]. Photocatalyst stabilized by imidazolium-based ILs are known to bind strongly and could be easily separated from the reaction mixture without contamination or significant loss in catalytic performance [65].

Interestingly, small-sized Cu nanoparticles (6.6 nm) have reportedly been synthesized *in situ* using [BMIM][PF_6] and [BMIM][BF_4] ILs as stabilizing agent and later used in cycloaddition catalytic reactions between azides and alkynes [94]. The particle size of imidazolium-based IL-capped nanoparticles can be easily tuned by varying the molecular weight, alkyl chain lengths and substituents on the imidazolium ring [71, 95]. Gracia et al. [96] demonstrated

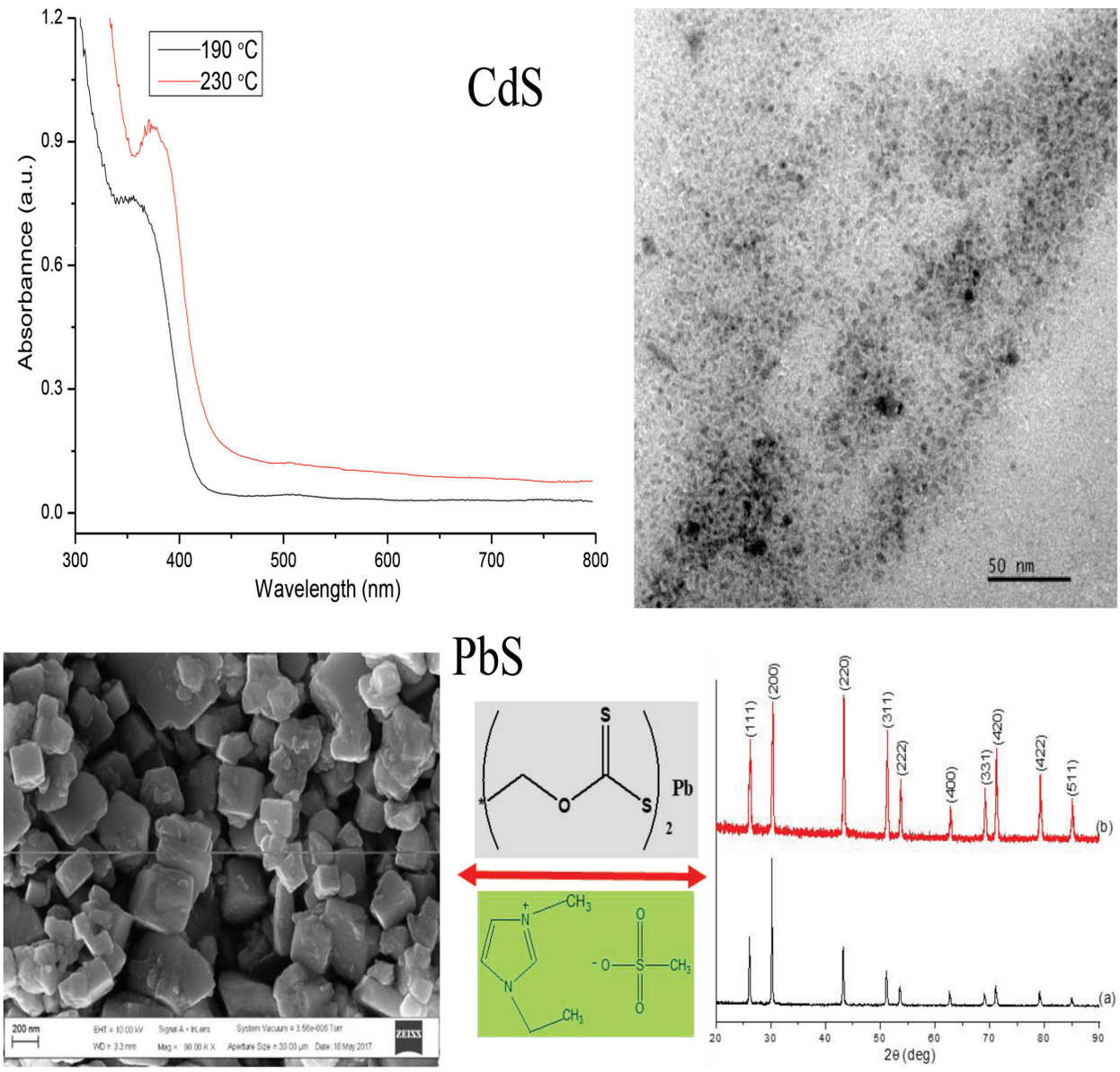


Figure 8. Top = optical properties and transmission electron microscopy image of 1-ethyl-3-methylimidazolium methanesulfonate stabilized CdS nanoparticles. Bottom = scanning electron microscope image, structure of the IL and X-ray diffraction patterns of 1-ethyl-3-methylimidazolium methanesulfonate stabilized PbS nanoparticles (reprinted with permission from Refs. [70, 98]).

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the decrease of Ag nanoparticle sizes with an increase of the molecular weight of P[ViEtIm][BH_3CN] IL. In another report, Vijayakrishna et al. [97] studied the effect of alkyl chain lengths in the imidazolium-based poly-ILs of the general formula (P[ViRIm][OH]) where R = ethyl, butyl and pentyl, on particle sizes of magnetic Ni nanoparticles; average particle sizes increased with alkyl chain length (**Figure 7**).

The type of functional group present in the IBIL determines the mode of interaction with the nanoparticle. Furthermore, tweaking of the reaction parameters has become a common practice to manipulate these interaction modes, thus, enabling particle size and shape-directing capabilities. The chemical structure of 1-ethyl-3-methylimidazolium IL, in the recent study, afforded covalent, coordinate, electrostatic/steric or weak chemisorption interactions via their cations and counter anions (**Figure 8**) to produce CdS and PbS nanoparticles [70, 98]. The 1-ethyl-3-methylimidazolium IL efficiently produced very small and well dispersed CdS quantum dots in the size range of 2.3–4.3 ± 0.265 nm, attributed to the presence of both cationic and anionic components [70]. Cubic-shaped and highly crystalline PbS nanoparticles in the particle size range of 64 ± 18 nm were synthesized using the same 1-ethyl-3-methylimidazolium IL (**Figure 8**) [98].

6. Conclusion

Ionic liquids (ILs), imidazolium-based ILs (IBILs) in particular, have been exploited in various applications including its use as both reactants and stabilizing agents in the synthesis of functional nanomaterials. The remarkable merit of IBILs and ILs in general is their diversified design which involves a vast selection of cations and anions species. The physicochemical properties of ILs play a major role in improving, modifying and tuning important properties of nanomaterials such as particle size and morphology to suit various applications. Interestingly, the physicochemical properties of ILs further provide unique stability for nanomaterials, which guarantees longer shelf life. In addition, ILs are known to be less toxic, thus enabling them to be used as alternative eco-friendly candidates in various studies as means of applying green chemistry principles. The properties of ILs change with cation/anion composition and there is currently no model to predict its interactions and subsequent influence on the properties of nanomaterials. Hence, an increasing interest observed in evaluating ILs as both reactants and stabilizing agent in the synthesis of different classes of nanomaterials.

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Conflict of interest

We declare no conflict of interest.

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