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Chapter 4

Applications of Ionic Liquids (ILs) in Synthesis of Inorganic Nanomaterials

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Additional information is available at the end of the chapter

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1. Introduction

These years, inorganic nanomaterials, which stands out as an important class of advanced materials, received great attention due to the technological applications in fields as diverse as optoelectronics, energy conversion/production, catalysis, and biomedicine [1-3]. Formation and size or morphology control of nanoparticles are crucial issues in inorganic nanomaterials research. Among the investigated strategies for the synthesis of inorganic nanomaterials, the solution-based chemical process underwent rapid progress over the last two decades and has developed into a promising field in materials chemistry. The most common media for conducting chemical reactions and materials synthesis are aqueous and organic solvents. Nevertheless, a limited number of molecular solvents can be used and some of them may cause environmental problems. Although traditional molten salts have been used as alternative reaction media, their high boiling points (above 100 °C) significantly restricts the scope of applications and make the process impractical [4,5]. In this regard, it remains a great challenge to explore novel and green media that allow particular reactions to occur.

As an organic salts with low melting points (as low as -96°C), ionic liquids (ILs) have received much attention in many areas of chemistry and industry due to their potential as a "green" recyclable alternative to traditional organic solvents. Ionic liquids are not new; the first ionic liquid, $[C_2H_5NH][NO_3]$ (melting point 13-14 °C), was synthesized by Walden via the neutralization of ethylamine with concentrated HNO_3, as reported in 1914 [6]. However, it is only in the past few years that ILs have began to be used in the inorganic synthesis. The first attempt at using ILs as the reaction medium instead of conventional molecular solvents for the synthesis of inorganic materials was pioneered by Dai and co-workers in 2000 [7]. They introduced ILs for the fabrication of porous silica gels termed as "ionogels", which are being extensively investigated. After this study, ILs have been actively employed for the synthesis

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of a broad range of inorganic materials, and many interesting inorganic materials with various properties have been fabricated [8,9].

ILs offers many distinct advantages (such as negligible vapor pressures, good thermal stability, high ionic conductivity, broad electrochemical potential windows, and high synthetic flexibility) for a wide variety of inorganic and organic materials. This Chapter will focus on the use of ILs in inorganic materials synthesis. We will describe some recent development of synthesizing inorganic nanomaterials (including metal nanoparticles, metal oxides, metal chalcogenides, and zeolites) in ILs. Especially, we focus on the versatile role of ILs that plays in the synthesis of the inorganic nanomaterials.

2. Advantages of ILs in synthesis of inorganic nanomaterials

At the beginning, ILs have been used as functional solvents in the field of organic chemistry. The special physical properties of the ionic liquids that render them interesting as potential solvents for inorganic synthesis, as follows [10]: (1) They are good solvents for a wide range of inorganic materials and unusual combinations of reagents which can be brought into the same phase. (2) They are often composed of poorly coordinating ions, so they have the potential to be highly polar yet noncoordinating solvents. (3) ILs are immiscible with a number of organic solvents and can provide a nonaqueous and polar alternative for the two-phase systems. Hydrophobic ionic liquids can also be used as immiscible polar phases with water. (4) Ionic liquids are nonvolatile, hence they may be used in high-vacuum systems and eliminate many containment problems. Recently, ILs have been employed as reaction media to fabricate inorganic nanomaterials via various routes, such as ionothermal synthesis, ILs-assisted modified hydrothermal/solvothermal methods, and ILs-assisted microwave method [11]. Especially, ionothermal synthesis, which mainly uses ILs as the reaction solvent and, in many cases, structure directing agent (SDA) shows many advantages in the inorganic synthesis [12]. For example, the negligible vapor pressure produced from ILs when heated makes the ionothermal synthesis take place at ambient pressure. This property not only eliminates the safety concerns associated with the high pressure, but also allows for the ionothermal synthesis of materials in glass vessels.

Ionic liquids cannot be regarded as merely a “green” alternative to conventional organic solvents. The most important advantage of using ionic liquids for the preparation of inorganic materials is that ionic liquids form extended hydrogen bond systems in the liquid state and are therefore highly structured, which can be defined as supermolecular fluids [13]. This property of structural organization makes ionic liquids suitable for use as entropic drivers for the generation of well-defined nanostructures with extended order. ILs thus have been wildly used as templates for the synthesis of nanomaterials, especially the hollow and porous materials [14,15]. ILs have significant influence on the shapes and structures of the samples based on different mechanisms, including hydrogen bonds and π-π stack interactions, self-assembled mechanism, electrostatic attraction, and so on.

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Since ionic liquids can serve as "tailored solvents", they thus give us an opportunity for designing the ionic liquid according to the crystal structures, compositions, and crystal habits of the target products. ILs containing ions like sulfate, phosphate, carbonate, chloride, and metal cations can be regarded as reactive liquid precursors for the fabrication of inorganic materials. The IL is not only a solvent or template, but it acts as a tailored molecular precursor with a well-defined composition, structure, and reactivity. These parameters can be exploited for the fabrication of uniformly structured inorganic materials with various properties and these ILs can be viewed as "all-in-one" ILs. The hypothesis of ionic liquids as "all-in-one" solvents was first tested on cuprous chloride by Taubert and co-workers [16]. In that study, they introduced a protocol for the synthesis of CuCl nanoplatelets from a Cu-containing IL **1** and 6-O-palmitoyl ascorbic acid **2**. It was found that the mixtures of **1** and **2** could form thermotropic liquid crystals with lamellar self-assembled structures and the plate morphology was therefore caused (Figure 1). After this study, a large range of inorganic nanomaterials with interesting phases and morphologies were fabricated from various all-in-one ILs [13].

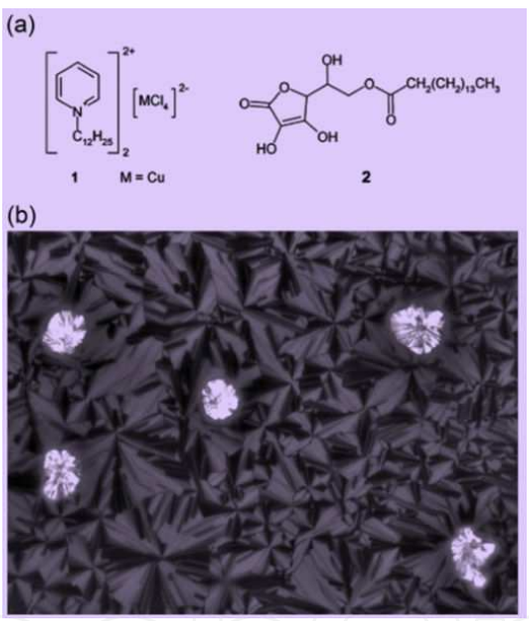


Figure 1. (a) Components of the ionic liquid precursors used for CuCl platelet synthesis: Cu-containing IL **1** and 6-O-palmitoyl ascorbic acid **2**. (b) Optical micrograph (crossed polarizers) of a demixed ionic liquid precursor.

3. Development of ILs in synthesis of inorganic nanomaterials

3.1. Metal nanoparticles

Metal nanoparticles (NPs) have become one of the hottest fields in nanoscience due to their diverse applications in the fields of catalysis, biology, optics, electronics, and nanotechnology [17,18]. Metal NPs can be fabricated by a variety of methods, such as chemical reduction of metal salts, thermal, photochemical or sonochemical decomposition of metal complexes,

hydrogenation of olefinic ligands of metal complexes, vapour phase deposition and electrochemical reduction of metals in high oxidation states. Majority of the metal NPs synthesized in the ILs medium needs the additional reducing reagents such as molecular hydrogen gas, complex hydrides, hydrazine, alcohols, and thiols, leading to a complex synthesis, where the shapes and sizes of the products are strongly affected by the concentration, addition sequence, and rate of addition of the capping and reducing agents. In contrast, ILs have unique and tunable properties useful in the synthesis of metal nanocrystals via chemical or physical routes. The main advantages of using ILs are their dual role of reaction solvent and nanoparticles stabilizer [19] (Figure 2). Thiol-, ether-, carboxylic acid-, amino-, hydroxyl-, or nitrile-functionalized imidazolium cations can stabilize metal NPs even more efficiently through the added functional group[20].

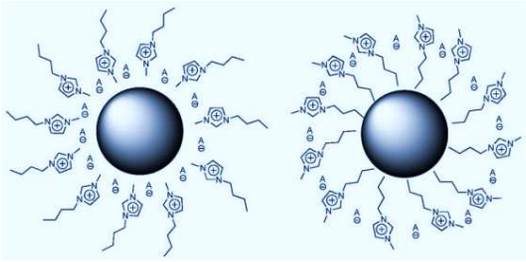


Figure 2. Potential NPs tabilisation in ILs for surface charged/polar NPs (left) and for surface neutral, non-polar NPs (right) [19].

In some cases, ILs acts as reducing agent for the formation of various metal NPs by simple reduction of metal salt compounds. Recently, there are very few reviews on the synthesis of metal NPs [19-22]. For instance, Dupuont and co-workers discussed the structural/surface properties of soluble metal NPs dispersed in ILs, with particular attention paid to the stabilization models proposed to explain the stability and properties of these metal NPs [21]. Luska and Moores reviewed the use of functionalized ILs in the synthesis of metal NPs, with an emphasis on the application of NP:IL catalysts [22]. In this part, we will present the current progress mainly on the chemical reduction synthesis of metal NPs in the presence of ILs.

3.1.1. Monometallic NPs

3.1.1.1. Ir, Ru and Pt

In 2002, Dupont and co-workers for the first time reported the synthesis of Ir NPs with an average size of 2 nm in the IL [BMIM][PF_6] medium with the absence of any surfactant [23]. By using the similar strategies, they later synthesized the stable and isolable nanometric Pt NPs of 2.0-2.5 nm in diameter from the reaction of $Pt_2(dba)_3$ (dba=bis-dibenzylidene acetone) dispersed in ionic liquid [BMIM][PF_6] with molecular hydrogen (4 atm) at 75 °C [24] (Figure 3). They found that a plethora of imidazolium ILs with different physical-chemical properties can be easily prepared by varying the anion and the alkyl chain on the aromatic ring, and this thereby opens the possibility for the preparation of distinct NPs, for biphasic catalysis. Very

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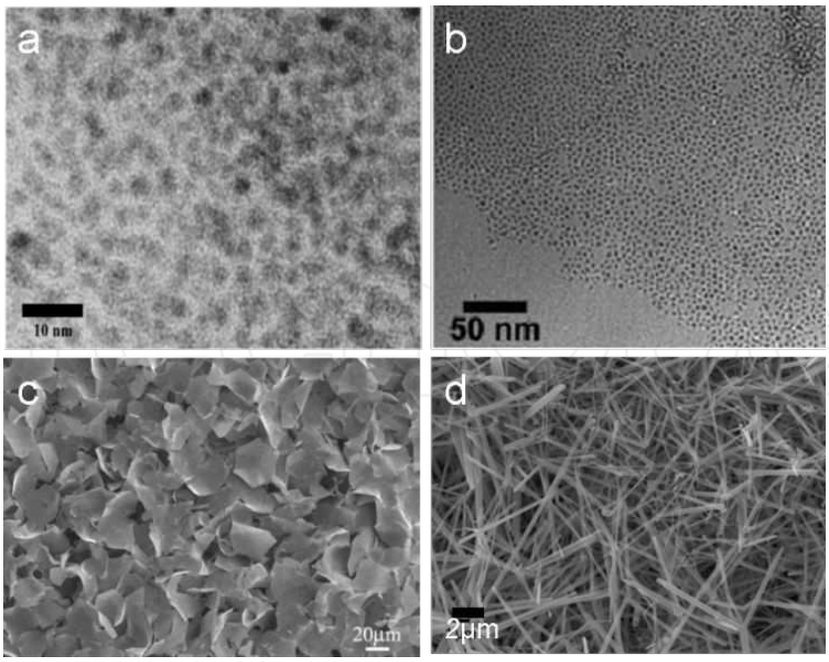


Figure 3. TEM and SEM images exemplifying metal NPs exhibiting different shapes prepared in the presence of ILs: (a) Pt stablized by ILs [24], (b) Ru stablized by ILs [26], (c) Au nanosheets [28], (d) Ag nanowires [32].

recently, Zhang et al. [25] reported the electroless deposition of Pt NPs by dissolving $K_2[PtCl_4]$ or $K_2[PtCl_6]$ in 1-ethyl-3-methylimidazolium ILs containing bis-(trifluoromethylsulfonyl)imide (NTf_2^-) or tetrafluoroborate (BF_4^-) anion and small cations such H^+, K^+, and Li^+ at various temperatures. The ultrasmall and uniform Pt NPs of ca. 1-4 nm in diameter were produced and the Pt-NPs/[EMIM][Tf_2N] dispersion was kept stably for several months without adding any additional stabilizers or capping molecules.

Dupont and co-workers [26] have presented a simple organometallic approach for the synthesis and catalytic application of Ru NPs in imidazolium ionic liquids using a clean straightforward hydrogenation route with the readily available versatile ruthenium precursor [Ru(COD)(2-methylallyl)$_2$] (Figure 3). The particles with 2.1-3.5 nm in diameter dispersed in the ionic liquid, no significant agglomeration of the Ru NPs can be observed. Recently, Prechtl and co-workers synthesized the Ru nanoparticles from the reduction and decomposition of ([Ru(COD)(2-methylallyl)$_2$] precursor, which were dissolved in imidazolium ILs undergo reduction and decomposition, respectively [27].

3.1.1.2. Au, Ag and Cu

On the other hand, some ILs itself, such as hydroxylated imidazolium salts, can perform as the reducing agent in the synthesis of metal NPs. For example, Li et al. [28] prepared Au nanosheets with very large size by directly microwave heating of [BMIM][BF_4] or [BMIM][PF_6] solutions (Figure 3). It can be found that the formation of the large-scale Au nanosheets is likely directly related to two-dimensional polymeric structure by hydrogen bonds between the cations and anions in the ILs, which has a template effect for the formation of Au sheets.

In another report, Gao et al. [29] used [BMIM][PF_6] and [BMIM][Tf_2N] as multifunctional molecules and synthesized regular-shaped single-crystal Au nano-and microprisms with controlled sizes (a very broad size range of 3-20 μm in diameter and 10-400 nm in thickness) without the need for additional capping agents and reducing agent. Ren et al. also fabricated Au nano-and microstructures such as polyhedral crystals, large single-crystalline nanoplates, hollow trapeziform crystals, holey polyhedra, and dendrites via microwave heating of $HAuCl_4 \cdot 4H_2O$ in a variety of ionic liquids (ILs) in the absence of capping agents or additional reducing agents [30]. The authors supposed that IL ions act as the capping agent directing Au crystal growth and consequently determining the final shape, owing to the fact that ILs having different absorption abilities and thus leading to the various morphologies observed. Qin et al. [31] reported the synthesis of hierarchical, three-fold symmetrical, single-crystalline Au dendrites were synthesized by the reaction between a zinc plate and a solution of $HAuCl_4$ in the ionic liquid [BMIM][PF_6]. The significantly lowered ion diffusivity and reaction rate in the ionic liquid medium could largely contribute to the formation of the pure single-crystalline Au dendrites.

Suh and co-workers [32] synthesized the Ag nanowires by the simple reduction of a silver precursor in the presence of [BMIM][$MeSO_4$] (Figure 3). By chosing the different IL, they also synthesized well-defined Ag NPs with cubic and octahedral shape in the presence of [BMIM]Cl and [BMIM]Br, respectively. Importantly, they found that ILs distributed over the nanoparticle surface play an important role in the determination of interparticle interactions, leading different assembly processes with respect to the types of ILs employed. It was speculated that [BMIM][$MeSO_4$] provides a higher degree of directional polarizability than either [BMIM]Cl or [BMIM]Br, as a result of the bulky and delocalized charge state of the anions. Kim and co-workers [33] reported the water-phase synthesis of Ag nanoparticles with average size of 4.1 and 2.2 nm using 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([HEMIM][BF_4]) and 1-(2'-hydroxyethyl)-2-methyl-3-dodecylimidazoliumchloride ([C_{12}HEMIM]Cl), respectively, in the absence of any other reducing agent. They also found that the size of IL-Ag could be tuned by varying the side chain length of the cation.

IL-mediated nanobelt self-assembly from nanoparticles has been much less well investigated and an intermediate state that transiently appears during the self-assembly process has seldom been observed. Very recently, Zhou and co-workers presented the controlled self-assembly of copper nanoparticles into nanobelts bridged by an IL [34]. They first synthesized Cu nanoparticles via the addtion of hydrazine hydrate into the mixture solution of $Cu(AcO)_2$, ethanol and IL. The formed Cu nanoparticles can assembley into Cu nanobelts in around one week. It was found that the template-like effect of the ionic liquids was the key for the formation of Cu nanobelts.

3.1.2. Bimetallic NPs

The possibility of controlling the electronic and geometric structures of bimetallic NPs by the addition of a second metal is one of the most important approaches to obtain more efficient catalysts [35]. Compared to the monometallic NPs, the synthesis of bimetallic NPs in the ionic liquids was less studied. In 2004, Yang and co-workers [36] for the first time demonstrated the

syntheis of CoPt nanorods, hyperbranched nanorods, and nanoparticles with different CoPt compositions in ionic liquid [BMIM][Tf_2N], from the ($Pt(acac)_2$) and ($Co(acac)_3$) precursors in the presence of CTAB. Very recently, Dupont and co-workers [37] prepared unsupported bimetallic Co/Pt NPs with size of 4.4 ± 1.9 nm by a simple reaction of [bis(cylopentadienyl)cobalt(II)] and [tris(dibenzylideneacetone) bisplatinum(0)] complexes in IL [BMIM][PF_6] at 150 °C under hydrogen for 24 h. The formed bimetallic Co/Pt NPs display core-shell like structures in which mainly Pt composes the external shell ($CoPt_3$@Pt-like structure). Different from these two works, Vallés and co-workers [38] demonstrated an electrochemical synthesis of alloyed CoPt NPs of different sizes (10-120 nm), using CoPt aqueous solution/[BMIM][PF_6]/Triton X-100 water-in-ionic liquid microemulsions by electrodeposition. The relative amount of aqueous solution to ionic liquid determines the size of the nanoreactors, which serve as nanotemplates for the growth of the nanoparticles and hence determine their size and distribution.

In addtion to CoPt, other bimetillic NPs or composties were prepared in the presence of IL. For example, Helgadottir et al.[39] reported the preparation of core-shell Ru@CuNPs with small diameters and narrow size distributions via the simultaneous decomposition of Ru and Cu organometallic precursors in IL. Ding et al. [40] reported the synthesis of Pd_xNi_y bimetallic NPs (the nominal atomic ratios of Pd to Ni are 2:1, 3:2 and 1:1) supported on multi-walled carbon nanotubes (MWCNTs) by a thermal decomposition process using N-butylpyridinium tetrafluoroborate ([BPy][BF_4]) as the solvent. Fischer and co-workers [41] sythesized Ni/Ga alloy materials by microwave induced copyrolysis of [$Ni(COD)_2$] (COD=1,5-cyclooctadiene) and GaCp* (Cp*=pentamethylcyclopentadienyl) the ionic liquid [BMIM][BF_4]. They found that, without additional hydrogen, the current method selectively yields the intermetallic phases NiGa and Ni_3Ga from the respective 1:1 and 3:1 molar ratios of the precursors.

3.2. Metal oxides

Metal oxides have been regards as promising solid-state materials for a wide variety of applications in the fields of nanotechnology and materials science due to their unique chemical, physical and mechanical properties. Till now, many metal oxides have been prepared in ionic liquids or mixed solutions containing ionic liquids by the wet chemical method.

3.2.1. TiO_2

It is widely known that TiO_2 is an important wide band gap semiconducting material and is widely used in the photocatalytic field. Up to now, TiO_2 of different phases (anatese or rutile) and morphologies were synthesized by using ILs as the medium. Zhou et al. [42] used IL [BMIM][BF_4] as medium and synthesized mesoporous spherical anatase aggregates self-assembled from very fine anatase nanocrystals with an average diameter of 2-3 nm under mild conditions. The high crystallinity of the obtained particles underlines the unique advantages of the IL method compared to other synthetic pathways towards TiO_2 nanocrystals. Very interestingly, Nakashima and co-worker [14] synthesized hollow TiO_2 microspheres by subjecting a mixture of [BMiM][PF_6], toluene, and $Ti(OBu)_4$ to vigorous stirring. The $Ti(OBu)_4$ molecules dissolved in toluene droplets reacted with trace amount of water at the

interface between the toluene droplets and ionic liquid, leading to the formation of hollow TiO_2 microspheres (Figure 4). It is worth mentioning that no other hard template was needed in the synthesis, indicating the advantages of the ILs as the efficient, simple all-in-one systems for the inorganic synthesis.

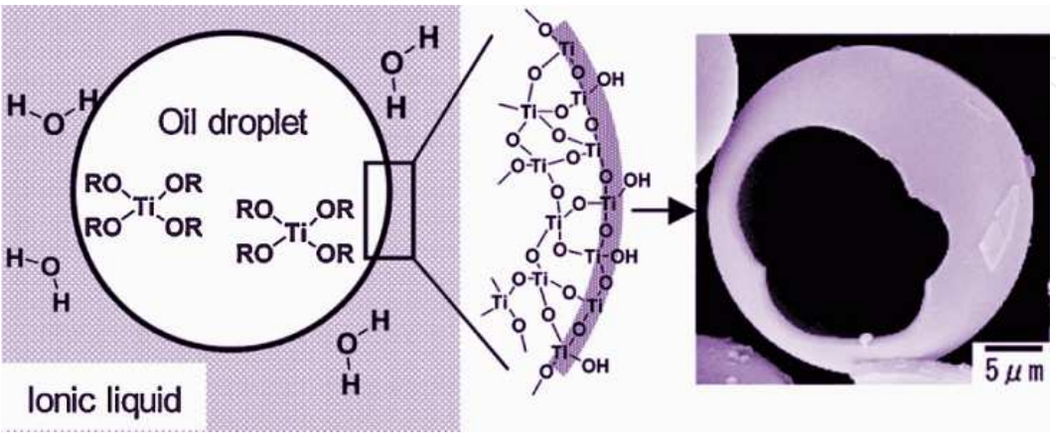


Figure 4. Left: Schematic illustration of the mechanism proposed for the formation of hollow TiO_2 microspheres at the interface between the oil droplet and ionic liquid. Right: SEM image of a hollow TiO_2 microsphere with a broken shell. [14]

In another report, Ding et al. [43] reported a facile method to synthesize cubelike anatase nanocrystals with uniform size and shape via a microwave-assisted route in [BMIM][BF_4]. Dai and co-workers [44] fabricated hierarchically patterned macroporous TiO_2 architectures via the spontaneous self-assembly of TiO_2 prepared from a mixture of 1-octadecene (ODE) and an ODE-immiscible 1-alkyl-3-methylimidazolium-based ionic liquid as the reaction medium. Wessel et al. [45] reported a fast way to synthesize pure TiO_2(B) in a mixture of [C_{16}MIM]Cl/[C_4MIM][BF_4]. In addtion to pure TiO_2, element-doped TiO_2 nanomaterials were also fabricated. Yu et al. [46] employed, ionic liquid [BMIM][BF_4] as both a structure-directing agent and a dopant and prepared fluorinated B/C-codoped anatase TiO_2 nanocrystals through hydrothermal hydrolysis of tetrabutyl titanate. Our group recently reported a facile ionic liquid-assisted synthesis of pure rutile and rutile-anatase composite nanoparticles by hydrolysis of titanium tetrachloride in hydrochloric acid [47]. The ionic liquid, [EMIM]Br, can serve as a capping agent based on its strong interaction with the (110) facet of rutile. More specifically, we demonstrate that [EMIM]Br favors the formation of rutile structure with a rod-like shape due to the mutual π-π stacking of imidazole rings. The ratios of rutile to anatase in the products can be controlled and TiO_2 nanoparticles with arbitrary phase compositions can be obtained in high yields by means of this simple method.

3.2.2. ZnO

Zinc oxide (ZnO), a wide band gap semiconductor, plays an important role in many applications because of its extraordinary electrical and optical properties. Recently, ILs have attracted much attention in the synthesis of ZnO since it can not only acts as functional solvents for

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reaction precursors but also morphologic templates for nanostructures. Zhou et al. [48] synthesized ZnO hexagonal micro-pyramids with all their exposed surfaces consisting of polar ±(0001) and {101} planes by using a mixture of oleic acid and ethylenediamine as the solvent, which can be regarded as one kind of ionic liquid ($R\text{-}COOH+R\text{-}NH_2 \rightarrow RCOO^-+R\text{-}NH_3^+$). Zhu et al. [49] prepared hierarchical ZnO structures with diverse morphologies from the metal-containing ILs acting as both solvents and metal-oxide precursors. Our group [50] recently found that low-dimensional ZnO nanostructures from nanoparticles to nanorods to nanowires can be successfully synthesized in ionic liquid at low temperature (Figure 5). We found that the longer alkyl chain at position-1 of the imidazole ring of the ionic liquid will hinder the ZnO nanostructures from growing longer, and the hydrogen bonds may play a crucial role for the directional growth of the 1D nanocrystals. The as-obtained ZnO nanostructures in different ionic liquids show strong size/shape dependence of photocatalysis activity.

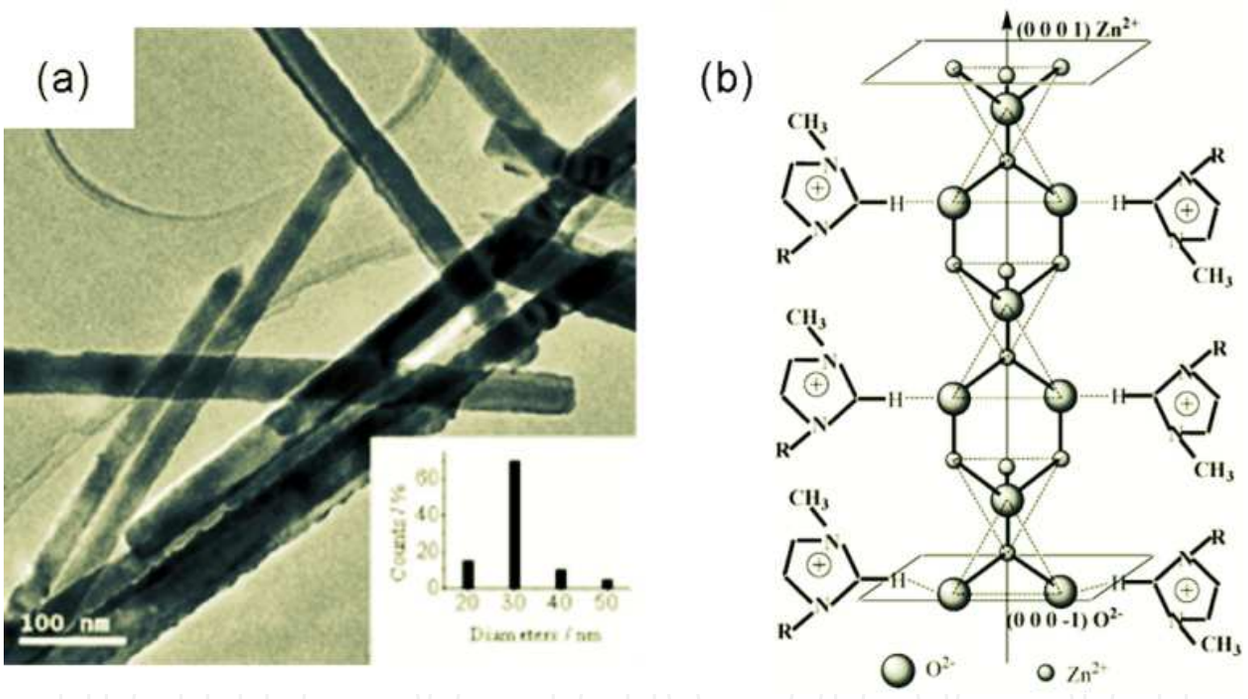


Figure 5. (a) TEM image and size distribution histogram (inset) of the ZnO nanorods prepared in [EMIM][BF_4] at low temperature. (b) Proposed growth schematic diagram of 1D ZnO nanostructures in ionic liquid. [50]

3.2.3. Copper oxide

Copper oxide is a transition-metal oxide with a narrow band gap, and is widely used as a photocatalyst. Li et al. [51] reported the morphology control synthesis of Cu_2O crystals by the electrodeposition method in the presence of ionic liquids. They found that the hydrophilic ionic liquids, 1-methyl-3-ethylimidazolium salts containing ethyl-sulfate anions, have dramatic effects on the morphology changes of electrochemically grown Cu_2O crystals. The shape of Cu_2O crystals evolves from cubic to octahedral and spherical shape only by adding a varied

small amount of ionic liquids in the deposited solutions. Shen and co-workers [52] presented the synthesis of flowerlike Cu_2O architectures in the presence of ionic liquid [BMIM][BF_4] with the assistance of microwave irradiation. It was shown that flowerlike Cu_2O architectures with a band gap of about 2.25 eV and a high surface area of 65.77 cm^2g^{-1} consist of many thin nanosheets that could be obtained by adjusting the amount of used [BMIM][BF_4] and exhibited high and stable photochemical activity for the reduction of Cr(VI) to Cr(III) under visible-light irradiation. Recently, stable nanouids comprising of CuO nanoparticles suspended in 1-butyl-3-methylimidazolium acetate and trioctyl(dodecyl) phosphonium acetate have been synthesized and it was found that these ionic liquids provide stabilization to CuO nanoparticles [53]. Gusain et al. [54] prepared CuO nanorods by ultrasound assisted shape regulation in the presence of 1-hexyl-3-methylimidazolium acetate and tetrabutylammonium acetate ionic liquids. The results showed that CuO nanorods, stabilized by ionic liquids, exhibit excellent friction-reduction (15-43%) and improved anti-wear properties (26-43%) compared to the PEG 200 and 10W-40 engine oil.

3.2.4. Iron oxide

Hematite (α-Fe_2O_3) and magnetite (Fe_3O_4) has attracted a great deal of attention owing to potential applications in fields of catalysis, gas sensors, adsorbent, rechargeable Li-ion batteries, magnetic storage, etc. Recently, our group have successfully prepared α-Fe_2O_3 with various morphologies, such as nanoparticles, mesoporous hollow microspheres, microcubes, and porous nanorods, via an [BMIM]Cl ionic liquid assisted hydrothermal synthetic method [55]. Importantly, we found that the hydrogen bond-co-π-π stack mechanism is used to be responsible for the present self-assembly of the [BMIM]Cl ionic liquid in the reaction systems for the formation of the α-Fe_2O_3 with various morphologies. We also successfully synthesized aggregated α-Fe_2O_3 nanoplates under ionothermal conditions through the self-assembly of nanoplatelets in a side-to-side manner [56]. [PMIM]I ionic liquid was used in the synthesis and is essential for the assembly and coalescence of small nanoplatelets into final nanoplates. Using the similar method, self-assembled Fe_3O_4 nanoflakes with an average diameter of about 15 nm have been synthesized with the assistance of ionic liquid [C_{16}MIM]Cl, which plays a critical role for the self-assembly of nanoparticles into nanoflakes by adsorbing onto the surfaces of the primary Fe_3O_4 nanoparticles [57]. Most recently, Xu et al. [58] prepared α-Fe_2O_3 hollow microspheres in the presence of metal ion-containing reactable ionic liquid ([OMIM][$FeCl_4$]) under the solvothermal condition. It was found that [OMIM][$FeCl_4$] acted not only as Fe source but also as solvent and template for the fabrication of α-Fe_2O_3 hollow microspheres. In addition, the electrochemical and photocatalytic properties of α-Fe_2O_3 were investigated. The α-Fe_2O_3 hollow microspheres exhibited high conductivity, high photocurrent, and high photocatalytic activity. The designed hollow microsphere showed potential applications in photocatalysis.

3.2.5. Other oxides

BiOX (X=Cl, Br and I) has drawn considerable attention because of its optical properties and promising inductrustrial applications, such as catalysts and photocatalysts, ferroelectreic

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materials, pigments, photoluminescence, and so on. Recently, ionic liquids as "designer liquids" have attracted great interest for the synthesis of BiOX micro/nanostructures. Our group has successfully synthesized ultrathin BiOCl nanoflakes, nanoplate arrays, and curved nanoplates via an ionothermal synthetic route by using an ionic liquid [C_{16}MIM]Cl as "all-in-one" solvent, simply adjusting reaction temperature (Figure 6) [59]. The formation of plate-like BiOCl may be due to fact that the [C_{16}MIM]Cl prefers to selectively adsorbed on the (001) plane of BiOCl, which can effectively inhibit crystalline growth in the (001) direction. Li and co-workers[60] have been successfully synthesized BiOI uniform flowerlike hollow microspheres with a hole in its surface structures through an EG-assisted solvothermal process in the presence of ionic liquid [BMIM]I. In this work, ionic liquid [BMIM]I not only acted as solvents and templates but also as an I source for the fabrication of BiOI hollow microspheres and was vital for the structure of hollow microspheres. Yu and co-workers [61] fabricated bismuth BiOBr micropsheres with hierarchical morphologies via an ionothermal synthesis route. Ionic liquid [BMIM]Br acts as a unique soft material capable of promoting nucleation and in situ growth of 3D hierarchical BiOBr mesocrystals without the help of surfactants.

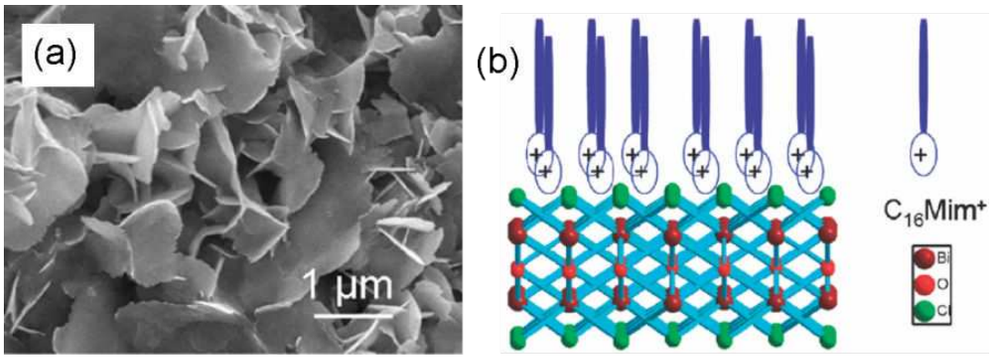


Figure 6. (a) SEM images of BiOCl nanoplates obtained in [C_{16}Mim]Cl at 180 C for 24 h. (b) Schematic illustration of the interaction of BiOCl crystal planes and the head parts of [C_{16}MIM]Cl. [59]

Recently, Lian et al. [62] prepared γ-Al_2O_3 mesoporous nanoflakes via a one-step ionothermal synthetic method under mild conditions using an ionic liquid [BDMIM]Cl as multifunctional material in terms of solvent and template. Duan et al. [63] prepared well-dispersed ammonium aluminum carbonate hydroxide (NH_4-Dw) and γ-AlOOH nanostructures with controlled morphologies have been synthesized by employing an ionic liquid ([BDMIM]Cl) assisted hydrothermal process. These as-prepared NH_4-Dw and γ-AlOOH nanostructures were converted into porous γ-Al_2O_3 nanostructures by thermal decomposition, whilst preserving the same morphology. Very rencently, Li et al. [64] reported a simple and facile hydrothermal method for the synthesis of hierarchical α-GaOOH architectures assembled by nanorods as a precursor, in which ionic liquid ([BMIM][OH]), as green and efficient recyclable solvents, play a key role in the formation of the hierarchical structures. After calcining the precursor in air, mesoporous α-Ga_2O_3 hierarchical structures were successfully obtained. Furthermore, the as-prepared mesoporous α-Ga_2O_3 hierarchical structures display good photocatalytic activity in the degradation of RhB molecules.

3.3. Metal Chalcogenides

3.3.1. M_2X_3 (M=Bi or Sb; X=S or Se)

Metal chalcogenides have been previously studied and employed in many applications, such as catalysis, light harvesting, energy conversion and storage devices [65,66]. Like metal oxides, a few kinds of metal chalcogenides have been synthesized using methods based on ionic liquids. Jiang et al. [67] synthesized single-crystalline Bi_2S_3 nanorods and Sb_2S_3 nanorods via the microwave-assisted ionic liquid method by using [BMIM][BF_4] as the reaction medium. Later, they synthesized Bi_2Se_3 nanosheets with thicknesses of 50-100 nm by the microwave-assisted ionic liquid method, where selenium powder, $Bi(NO_3)_3\,5H_2O$, HNO_3 aqueous solution, ethylenediamine or ethylene glycol, and an ionic liquid [BMIM][BF_4] were used [68]. Yu and co-workers [69] prepared uniform Bi_2S_3 flowers composed of uniform nanowires (diameter 60-80 nm) using $BiCl_3$ and CH_3CSNH_2 as the precursors and a mixture of [BMIM][BF_4] and water as the reaction medium (Figure 7).

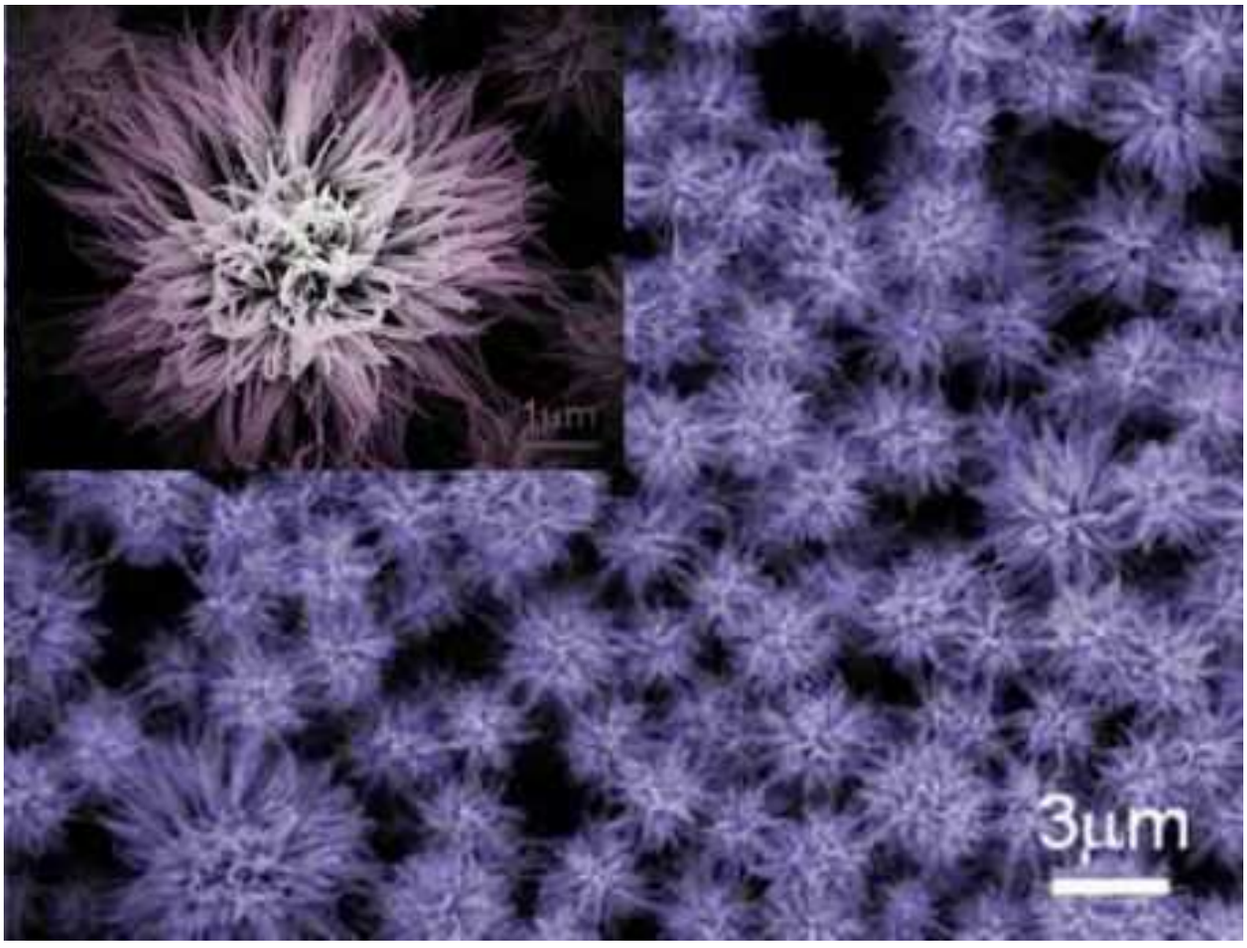


Figure 7. SEM images of Bi_2S_3 nanoflowers synthesized using $BiCl_3$ and CH_3CSNH_2 as the precursors and [BMIM][BF_4] as the solvent and template [69].

Our group recently achieved a morphology control synthesis over the Bi_2S_3 nanostructure by via an ionic liquids-assisted hydrothermal route. One dimensional nanorods, two dimensional nanofabrics, and three dimensional urchin-like microspheres and crossed nanofabrics have been obtained [70]. In another study, we also achieved the morphology-control synthesis of Sb_2S_3 nanostructures [71]. By introducing different organic complex reagents or the amount of ionic liquid [BMIM]Cl in the reaction system, one-dimensional nanorods, two-dimensional nanowire bundles, three dimensional sheaf-like superstructures, dumbbell-shaped superstructures, and urchin-like microspheres can be obtained. It should be noted that, the self-assembly effect of ionic liquid, which could attribute to a combination of the van der Waals forces between the ionic liquid molecules and the hydrogen-bond interactions and electrostatic forces between the citrate cations and ionic liquid, play an important role in the formation of different morphologies.

3.3.2. MX (M=Cd or Zn; X=S or Se)

The Cd-containing metal chalcogenides have motivated much more interest due to their size-dependent optical and electronic properties, and potential applications in the fields of nonlinear optics, light-emitting devices, electronics, and so on. However, there are very few reports on the synthesis of Cd-containing metal chalcogenides using ILs. More recently, Rao and co-workers [72] synthesized CdS nanostructures in the presence of [BMIM][$MeSO_4$] (where [$MeSO_4$] is methylsulfate), [BMIM][BF_4], and [BMIM][PF_6]. They also prepared CdSe nanoparticles in [BMIM][BF_4] and ZnSe in [BMIM][$MeSO_4$]. Arce and co-workers [73] recently successfully synthesized CdS nanoparticles with very small size (3-7 nm) by simply using an ionic liquid and the bulk powder of the material of the target nanoparticle. The method is very simple: First, a mixture of the bulk solid material and the ionic liquid trihexyl(tetradecyl)phosphonium cation ($[P_{66614}]^+$) is heated, with stirring, then, the mixture is allowed to cool down, and it is centrifuged to remove any excess of the bulk material from the generated nanodispersion. The ionic liquid plays a dual role as nanoparticle former and as a stabilizing agent.

The ability of ionic liquids to act as a reactant, solvent, and surfactant, as a function of other synthesis parameters, also denoted as ionic liquid precursors (or task-special ionic liquids), which offer many advantages over traditional solution-phase methods [13]. Our group recently used a Se-containing ionic liquid 1-n-butyl-3-methylimidazolium methylselenite ([BMIM][$SeO_2(OCH_3)$]) as a new Se precursor to prepare ZnSe hollow nanospheres with bubble templating through a facile one-pot hydrothermal method [74]. It was found that [BMIM][$SeO_2(OCH_3)$] not only serves as Se source but also acts as stabilizer for the ZnSe hollow nanospheres. We further reported the synthesis of CdSe dendrites from nanoparticles using ionic liquid precursor [BMIM][$SeO_2(OCH_3)$] [75]. Our experimental results demonstrate that the CdSe dendrites are obtained by self-assembly through oriented attachment, in which secondary mono-crystalline particles can be obtained through attachments of primary particles in an irreversible and highly oriented fashion.

Differently, we developed a Brønsted acid-base ionic liquid-assisted method for the synthesis of flower-like CdSe dendrites [76]. The CdSe dendrites were synthesized under solvothermal conditions at 150 °C for 24 h, using a mixed solution of water, ethanol, an ionic liquid based

on formic acid and N,N-dimethylformamide, cadmium chloride and selenium dioxide as solvents, cadmium and selenium sources, respectively. Mechanism study reveals that formation of flower-like dendrites depends on the interaction between the polar structure of CdSe crystals and the ionic liquid [DMFH][HCOO].

3.3.3. Other metal chalcogenides

Recently, we prepared ferrimagnetic Fe_3S_4 nanowalls and triple hierarchical microspheres via an ionic liquid-modulated solution-phase process [77]. The nanowalls of Fe_3S_4 were obtained via an ionic liquid modulated hydrothermal process with ascorbic acid and [BMIM]Cl as the reducing reagent and modulating additive, respectively. The Fe_3S_4 hierarchical microspheres assembled from nanoplates were formed under solvothermal process with ethylene glycol as a co-solvent and reducing reagent, and [BMIM]Cl as a modulating additive, respectively. It was found that the organized structure of the [BMIM]Cl possibly has a template effect on the formation of the nanobuilding blocks of Fe_3S_4 superstructures.

Ge and co-workers [78] prepared CuS nestlike hollow spheres assembled by microflakes were successfully synthesized through an oil-water interface route employing copper chloride, carbon disulfide, and sulfur as the starting materials in the presence of the ionic liquid [BMIM][BF_4]. It was found that [BMIM][BF_4] IL played a key role as a surfactant and structure-directing agent in the formation of CuS hollow spheres. By using an ionic liquid precursor 1-n-butyl-3-ethylimidazolium methylselenite ([BMIM][$SeO_2(OCH_3)$]), we synthesized $Cu_{2-x}Se$ nanocrystals and CuSe nanoflakes a through a convenient hydrothermal method [79]. It is found that the [BMIM][$SeO_2(OCH_3)$] not only serves as Se source but also has influence on the shapes of CuSe nanoflakes. The length of the alkyl unit linking the imidazolium ring can be altered and may have an influence on the morphologies of products.

3.4. Zeolites materials

Microporous and open-framework materials such as zeolites and coordination polymers, have been extensively studied for their potential applications in catalysis, ion-exchange, gas storage, separation, and sensor technology [80,81]. Zeolites are an important class of crystalline porous materials that have been employed for numerous catalytic applications because of their uniform channel size, strong acidity, high thermal/hydrothermal stability, and unique molecular shape selectivity. Generally, most zeolites are synthesized under hydrothermal conditions in an autoclave using an organic template or structure directing agent, commonly a tetraalkylammoniumcation, such as tetrapropylammonium cation (TPA^+) [82]. Howerver, the hydrothermal synthesis of zeolites was not regarded as a green process [83]. Therefore, the development of green or sustainable route for the synthesis of zeolites is important task. As a green medium, ILs-assisted ionothermal synthesis was recently found to be an alternative to the reported hydrothermal method. Because of the vanishingly low vapor pressure of ionic liquids, ionothermal reactions address safety concerns associated with the high pressures of hydrothermal reaction, thus allowing for the synthesis of zeolites at ambient pressure. In addtion, separate template was not required in the ionothermal synthesis of molecular sieves.

3.4.1. Aluminophosphate zeolites

In 2004, Cooper et al. [84] for the first time reported the ionothermal synthesis of zeolite and zeotype materials, using the ionic liquid 1-ethyl-3-methylimidazolium bromide ([EMIM]Br) and urea/choline chloride deep eutectic solvents to synthesize aluminophosphate zeolites (designed as SIZ-n, Figure 8). The use of [EMIM]Br resulted in the formation of aluminophosphates SIZ-1, SIZ-3, SIZ-4, SIZ-5, and SIZ-6 [84,85], and the use of choline chloride/urea mixtures resulted in SIZ-2 and AlPO-CJ2 (Figure 3,7). After this study, the ionothermal synthesis has shown to be a highly promising synthetic route for a wide variety of zeolites and zeolites analogues. The ionothermal synthesis method is also employed for the preparation of other metal phosphates. For instance, cobalt aluminophosphate molecular sieves SIZ-7, SIZ-8, and SIZ-9 with zeotype SIV, AEI, and SOD, respectively, were synthesized by the ionothermal synthesis in the presence of [EMIM]Br [86]. SIZ-7 exhibits a novel zeolite framework structure featuring double-crankshaft chains, which run parallel to the crystallographic a-axis, characteristic of a family of zeolites such as the PHI, GIS, and MER structure types. Furthermore, magnesium, gallium, and silicon can be incorporated into the ionothermally prepared aluminophosphate zeolites [87,88]. Very recently, Tian and co-workers [89] successfully achieved the ionothermal synthesis of permeable aluminophosphate molecular sieve membranes on porous alumina disks by substrate-surface conversion. Different types of molecular sieve membranes were synthesized, including CHA, AEL, AFI, and LTA, and the reported method is a simple, and environmentally benign process suitable for large-scale production.

To get more new structures, organic templates such as amines have been introduced into the ionothermal synthesis system. Tian and co-workers [90] have studied the structure-directing role of amines in ionothermal synthesis in the presence of IL [BMIM]Br. It was found that the addition of amines to the IL strongly influenced the dynamics of the crystallization process and improved the phase selectivity of the crystallization, leading to the formation of pure AFI and ATV structures. Therefore, it is possibly an effective way to control the structure of molecular sieves by combining the ionic liquid and organic amine in the synthesis. Later, Xing et al. [91] prepared a novel aluminophosphate (denoted as JIS-1) consisting of an anionic open framework $[Al_6P_7O_{28}H]^{2-}$ with 1-methylimidazole (MIA) and [EMIM]Br as cotemplates. Protonated $[MIAH]^+$cations along with $[EMIM]^+$ cations act as co-templates and were found to coexist in the intersection of the three-directional channels in the structure. Recently, Tian and co-workers [92] demonstrated the successful ionothermal synthesis of thermally stable aluminophosphate zeolites (denoted as DNL-1) with 20-membered ring pore openings (CLO) by use of 1,6-hexanediamine (HDA) and [EMIM]Br as co-templates for the first time. Both $[EMIM]^+$ and protonated HDA remained intact upon occlusion inside the CLO structure, suggesting that the protonated HDA is essential and acts as a co-template together with the ionic liquid cations in the crystallization process of DNL-1.

With the combined advantages of the ionic liquids and microwave heating method, microwave-enhanced ionothermal synthesis is a novel method to prepare molecular sieves. Its advantages are its fast crystallization rate, low synthesis pressure, and high structural selectivity. Xu et al. [93] synthesized a series of aluminophosphate molecular sieves (AlPO4-11 and SAPO-11) in the [EMIM]Br under ionothermal conditions. The microwave heating led to

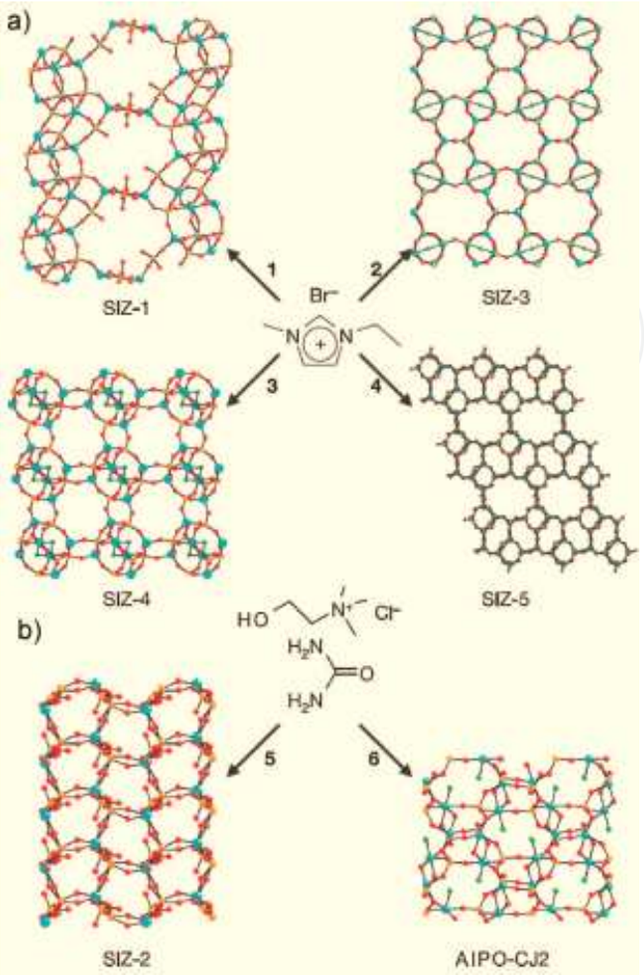


Figure 8. (a) Ball-and-stick diagrams of aluminophosphate materials SIZ-1, SIZ-3, SIZ-4, and SIZ-5 synthesized ionothermally using [EMim]Br. b) SIZ-2 and AlPO-CJ2 synthesized using a choline chloride/urea eutectic mixture [84,85]. The structure-directing agents are omitted for clarity. Orange, cyan, and red spheres correspond to phosphorus, aluminum, and oxygen atoms, respectively.

a more rapid growth of crystalline molecular sieve compared with that by conventional heating during ionothermal synthesis.

3.4.2. Silica-based zeolites

To date, there are only a few literatures on the synthesis of silica-based materials using ionic liquids as templates in the synthesis of silica-based zeolites. The problems associated with the synthesis of siliceous zeolites from ILs can be attributed to the poor solubility of the silica starting materials. In many of the successful attempts at synthesis of silica-based zeolites, the organic additives have been utilized in their hydroxide form in hydrothermal synthesis. Therefore, exchanging the anions of the ILs to those of the hydroxide type is strongly desirable for the ionothermal synthesis of silica-based zeolites [83]. Recently, Wheatley et al.[94] successfully synthesized siliceous zeolites silicalite-1 (MFI) and theta-1 (TON) via an ionothermal method using ionic liquid 1-butyl-3-methylimidazolium hydroxide ([BMIM]

http://dx.doi.org/10.5772/59048

[OH]) as both solvent and structure directing agent. The [BMIM][OH] was obtained from [BMIM]Br via ion-exchange with an anion exchange resin in water, which finally yields a ternary liquid of approximate formula [BMIM]-$OH_{0.65}Br_{0.35}$. The approximate initial molar composition was 20IL: tetraethyl orthosilicate (TEOS): $4H_2O$: 0.38HF, confirming that the IL is indeed the major solvent. The chemical formula of the formed zeolites crystals was determined to be $[Si_{48}O_{96}]$-$F_4(C_8N_2H_{15})_2(C_2H_7O)_2$. This result indicates that it is possible to alter the chemistry of ionic liquids so that they are suitable for the preparation of crystalline silica-based zeolites materials [94].

4. Concluding remarks

In summary, we have briefly highlighted the applications of ionic liquids in the preparation of inorganic nanomaterials, including metal NPs, metal oxides, metal chalcogenides, metal salts, and zeolites. Compared with traditional solvents, ionic liquids have many advantages, such as negligible vapor pressures, good thermal stability, wide electrochemical potential windows, and tunable solubility for inorganic substances. Notably, ionic liquids cannot be only regarded as a "green" alternative, but also provide a powerful medium for the synthesis of inorganic nanomaterials with unique morphologies and controlled phases. As one of the most rapidly growing fields, one can envision that there will certainly be intensified interest in this promising direction. One of the most distinctive features of ionic liquids is that they can be treated as "tailored solvents" due to their unlimited flexibility of combinations of anions and cations. Therefore, one can design the appropriate ionic liquid precursor according to the initial crystal structures, compositions, and crystal habits of target products. These precursors are molecularly defined entities, which can serve as both the reactant and solvent for the reaction, and as the template over the final inorganic material morphology at the same time. This"all-in-one" synthesis route which can make the reaction system simpler, and thus giving more control over the phases and morphologies of the final products.

Although the use of ILs for the synthesis of inorganic nanomaterials has been widely studied, a comprehensive and fundamental understanding on the effect type of ionic liquids and on the rational design of ionic liquids at the molecular level is still lacked. For example, it is also not clear how ionic liquids interact with inorganic or organic species, reactants, and products; how ionic liquids influence the nucleation and growth of materials; how self-assembly processes in ionic liquids differ from those in conventional solvents; and how ionic liquids influence the morphology. We believe that the synthesis of new inorganic materials should go hand-in-hand with the development of understanding of the effect type of ionic liquids. Since the research on well established rules and correlations between molecular structures of the adopted ionic liquids and the morphologies of the resulting inorganic materials is limited, it is highly expected that this understanding will improve with the accumulation of knowledge and the systematic design of experiments.

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