

# APPLICATIONS OF IONIC LIQUIDS (ILS) IN THE CONVENIENT SYNTHESIS OF NANOMATERIALS

Xiaodi Liu<sup>1,2</sup>, Jianmin Ma<sup>2</sup> and Wenjun Zheng<sup>2</sup>

<sup>1</sup>College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, Henan 473061, P. R. China

<sup>2</sup>Department of Materials Chemistry, College of Chemistry, Nankai University, Tianjin 300071, P. R. China

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**Abstract.** In the past few decades, ionic liquids (ILs), “green” solvents, have attracted tremendous attention in the inorganic nanomaterials synthesis owing to their unique physico-chemical properties, such as nonvolatile, negligible vapor pressure, low toxicity, and high thermal stability. Most recently, many technological advances have occurred in the use of ILs, served as solvents, reactants, or templates, in the synthesis of nanomaterials with controllable structures, morphologies and properties. In this paper, we provide an in-depth discussion of recent developments, in which ILs have been employed for the preparation of inorganic nanomaterials based on their reasonable properties.

## 1. INTRODUCTION

Over the past few decades, nanoscience has experienced exponential growth in its research activities [1]. It is known that the properties of nanomaterials strongly depend on their structures and morphologies; therefore, the controlled synthesis of nanostructures with novel morphologies and functional properties has recently attracted tremendous attention [2-4]. Generally, nanomaterials are fabricated in molecular solvents (organic solvents or water); nevertheless, a limited number of molecular solvents can be used and some organic solvents cause environmental pollution [5]. Thus, it is desirable to explore novel and “green” solvents that allow special reactions to occur.

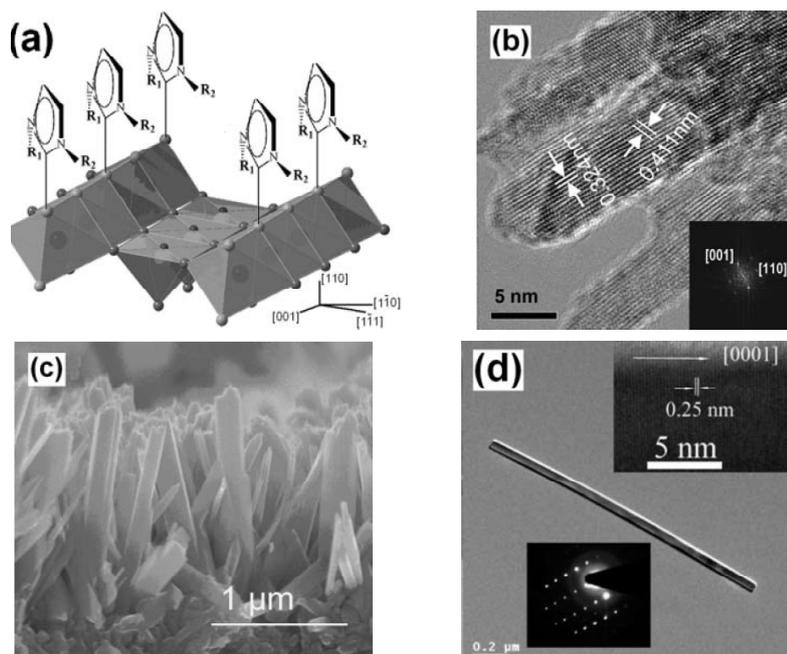
Recently, ionic liquids (ILs) have attracted increasing attention due to their appealing physical and chemical properties, such as low melting point, negligible vapor pressure, nonvolatile, high thermal stability, and high ionic conductivity [6]. ILs are usually composed of organic cations (e.g., imidazole

ring) and inorganic anions and their properties are strongly dependent on the species of cations and anions; thereby, ILs are referred to as “designed liquids” with tunable properties by adjusting their cations and anions [7]. Actually, the possible combination number of the cations and anions is uncountable (high to  $\sim 10^{18}$ ) [8]. Mainly on account of these unique properties, ILs show an increasing potential to innovate in the synthesis techniques.

At the beginning, ILs have been used as functional solvents in the field of organic chemistry [9]. Gradually, the advantages of ILs in the inorganic synthetic procedures have been realized, for instance: (1) ILs have low interface tensions in spite of their polar features, which results in high nucleation rate; (2) ILs can react with products via some interaction (e.g., hydrogen bond) and accordingly affect the shape of the products; (3) ILs are immiscible with a number of organic solvents and can provide a nonaqueous and polar alternative for the two-phase systems [10,11]. Several groups have selected reasonable ILs to synthesize inorganic

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Corresponding author: Xiaodi Liu, e-mail: liuxd1983@yahoo.com.cn



**Fig. 1.** (a) Schematic illustration of a projected view of [Emim]<sup>+</sup> ions adsorbing on the rutile (110) plane to form tight coverage layer. (b) HRTEM image of the as-prepared pure rutile nanorods. (c) SEM image of the rutile films consisting of rectangular nanorods. (d) TEM image of the ZnO nanorods [15,17,18].

nanomaterials with special morphologies, novel structures, and improved properties. On the basis of the above discussions, it is rational to expect that the application of ILs may offer a wide variety of possibilities for the fabrication of nanomaterials and develop into a mainstream in the field of synthetic chemistry.

As a burgeoning field, the development of ILs-assisted routes for the synthesis of nanomaterials offers both opportunities and challenges for the future development in the nanomaterials synthesis [12]. To the best of our knowledge, a number of successes on the fabrication of nanostructures in ILs have been continually reported; thereby, it seems timely to review the developments in the ILs-assisted synthesis of nanomaterials. In this paper, we provide an update on currently available methods for the synthesis of inorganic nanomaterials in ILs. To facilitate a discussion, the range of the properties and functions of ILs for the synthesis of nanomaterials has been divided into three major groups: (1) templates; (2) reaction media; (3) “all-in-one” solvents.

## 2. TEMPLATES

Considering the structures of ILs, in fact, they are quaternary ammonium salts; therefore, it can be deduced that ILs can be used as templates. The

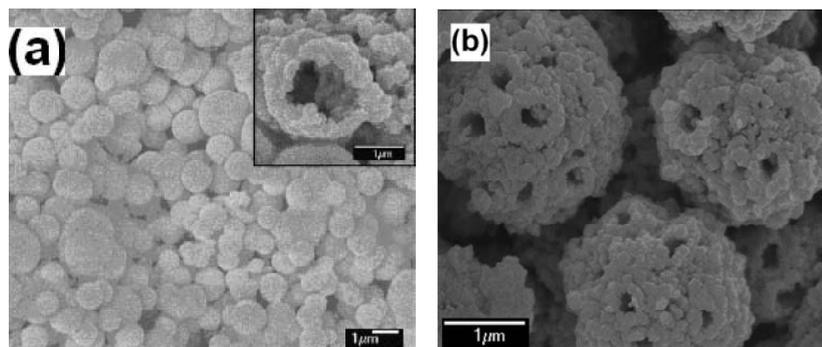
structures of ILs are different from those of the traditional quaternary ammonium salt; moreover, their structures can be easily regulated and ILs have relatively strong self-assembled abilities. ILs thus have been widely used as templates for the synthesis of nanomaterials. ILs have significant influence on the shapes and structures of the samples based on different mechanisms, including hydrogen bonds and  $\pi$ - $\pi$  stack interactions, self-assembled mechanism, electrostatic attraction, and so on.

### 2.1. Hydrogen bonds and $\pi$ - $\pi$ stack interactions

One of the most important properties of ILs is a very rare and unconventional property that has not received sufficient attention: ILs can form extended hydrogen bonds and are highly structured in the liquid state. It can be speculated that this important property can be used as the “entropic driver” for the spontaneous and highly ordered nanoscale structures [13]. Additionally,  $\pi$ - $\pi$  stacking interactions between the neighboring imidazolium rings are always responsible for the self-assembly of ILs in some systems [14].

In our research group, we have reported a novel synthesis route, hydrolysis of  $\text{TiCl}_4$  in a water/[Emim]Br composite system, to prepare rutile





**Fig. 3.** (a) SEM image of the ZnSe hollow microspheres. (b) SEM image of the CdSe nanoparticles-assembled microspheres [42,43].

nism. Zhou et al. have proposed that this reasonable mechanism was accountable for the self-assembly of [Bmim]BF<sub>4</sub> in the synthesis of mesoporous silica [19]. It was believed that BF<sub>4</sub><sup>-</sup> interacted with the silanol groups and formed hydrogen bonds, which might induce the oriented arrangement of BF<sub>4</sub><sup>-</sup> along the pore walls. Along with BF<sub>4</sub><sup>-</sup>, as presented in Fig. 2, driven by the coulomb coupling force with the anion, [Bmim]<sup>+</sup> were also arrayed along the silica. Moreover, the fluid state of [Bmim]BF<sub>4</sub> facilitated the proposed relocation of molecules, which could be then stabilized by the additional  $\pi$ - $\pi$  stack interaction between the imidazolium rings of [Bmim]BF<sub>4</sub>.

The hydrogen bond-co- $\pi$ - $\pi$  stack mechanism with ILs as templates have opened a novel and effective pathway to preparing nanostructures. Chen et al. have described the synthesis of 2D patterned Pt nanostructures at the air-water interface, in which [Emim]BF<sub>4</sub> played an important part in the shape of the 2D Pt nanostructures [20]. Also, in one of our studies, we have presented an IL-assisted microwave irradiation method to synthesize Zn(OH)F nanofibres in the presence of [Tmim]BF<sub>4</sub> [21]. It was found that [Tmim]BF<sub>4</sub> served as both F source and template. The phases and shapes of the products, from ZnO nanorods to Zn(OH)F nanofibres, could be controlled by changing the content of [Tmim]BF<sub>4</sub>. In the synthesis, the F-F distance in the BF<sub>4</sub><sup>-</sup> anion (2.28 Å) was close to the distance between coplanar anions placed at each Zn(OH)<sub>3</sub>F<sub>3</sub> octahedron. Thus, [Tmim]BF<sub>4</sub> self-assembled into ordered structures on the Zn(OH)F (110) plane and accordingly had major influence on the growth habit of Zn(OH)F. Besides the above successes, some suitable imidazole-based ILs have been used to prepare other highly organized nanostructures [22,23]. According to the above results, it can be concluded that the

self-organized ILs can be described as polymeric “supramoleculars” and extended to synthesize many other nanomaterials.

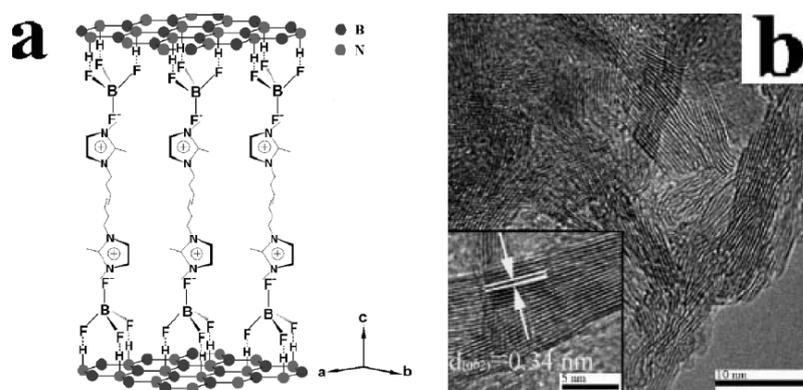
## 2.2. Self-assembly of long-chain ILs

ILs derived from 1-alkyl-3-methylimidazolium ([C<sub>n</sub>mim]<sup>+</sup>) are of particular interest to chemists. Long-chain ILs display the behavior of both lyotropic and thermotropic liquid-crystal in different solvents [24]. Long-chain ILs have tolerance toward perturbations in the supramolecular templates and show a relatively strong tendency to self-aggregation [25]. Therefore, Long-chain ILs have been used as templates to prepare nanostructures.

Long-chain ILs have been extensively used to prepare mesoporous silica materials. Adams and co-workers have demonstrated that [C<sub>16</sub>mim]Cl can be employed to synthesize MCM-41-type mesoporous silica through a hydrothermal route [26]. Moreover, long-chain ILs have been used to synthesize many other nanomaterials. For example, Firestone et al. [27] have fabricated anisotropic Au nanoparticles with different sizes and shapes in the highly constrained aqueous domains of a ionogel template, formed via self-assembly of [C<sub>10</sub>mim]Cl in water. [C<sub>10</sub>mim]<sup>+</sup> served initially to trap or localize AuCl<sub>4</sub><sup>-</sup> through electrostatic interactions and accordingly stabilized them. Triangular, hexagonal, and truncated triangular gold nanoplates have been synthesized using Langmuir monolayer of [C<sub>16</sub>mim]Br via the interfacial reduction of AuCl<sub>4</sub><sup>-</sup> by the formaldehyde, in which IL [C<sub>16</sub>mim]Br served as both template and stabilizer for the products [28].

## 2.3. Other possible mechanisms

Because of their special properties, some ILs have been employed as templates to synthesize



**Fig. 4.** (a) Schematic illustration of the proposed hydrogen bond-co- $\pi$ - $\pi$  stack interaction mechanism. (b) HRTEM image of the as-obtained t-BN nanoflakes [40].

nanomaterials based on other possible mechanisms. Nakashima et al. have developed a simple synthesis route to hollow  $\text{TiO}_2$  microspheres by using  $[\text{Bmim}]\text{PF}_6$  as templates. Microsized droplets were formed due to the limited miscibility of toluene with  $[\text{Bmim}]\text{PF}_6$ , then  $\text{Ti}(\text{OBu})_4$  in the microdroplets were hydrolyzed selectively at the interface. In addition,  $[\text{Bmim}]^+$  were adsorbed to the surfaces of the hollow spheres by electrostatic interactions [29]. Also, hierarchical Au dendrites and  $\text{TiO}_2$  nanoparticles have been prepared by using IL as effective templates [30,31].

### 3. REACTION MEDIA

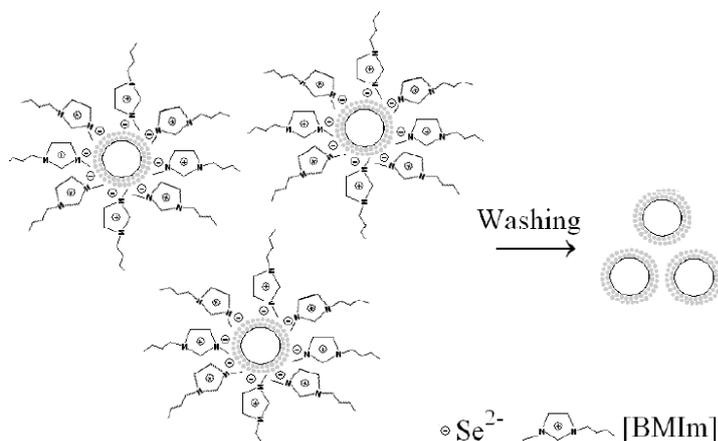
Nanomaterials are mostly synthesized in various molecular solvents, and the most frequently used solvents are organics that may have potential pollution implications. To minimize pollution has become a major concern and some conventional organic solvents should be replaced by a new class of green solvents for the long-lasting development of human society [32]. A wide range of ILs offer a potentially wide range of solvent properties and are considered to be excellent solvents for their versatility and green credentials [33]. It can be concluded that in the near future, ILs will be explored as “green” solvents to replace conventional volatile solvents in a variety of processes. 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.

#### 3.1. Ionothermal synthesis

Ionothermal synthesis is the use of ILs as the reaction solvent and, in many cases, structure directing

agent (SDA) in the synthesis of materials [34,35]. 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 [36]. In addition, there are at least a million binary ILs compared to only about 600 molecular solvents. Therefore, ionothermal synthesis can offer a lot of opportunities to fabricate nanomaterials by using appropriate ILs.

It was claimed that ionothermal synthesis could be used in any situation where hydrothermal/solvothermal methods were implemented. Indeed, many chemists have synthesized several different types of nanomaterials through this excellent synthetic technique. Recham et al. have reported the use of ILs as solvent and template to enable the growth of  $\text{LiFePO}_4$  powders with controlled size and morphology. Two inherent advantages of this route are that the reactions carried out at atmospheric pressure and ILs were SDA for the orient crystal growth of  $\text{LiFePO}_4$  powders [36]. Park and co-workers have also developed an ILs-based environmentally benign ionothermal technology to manipulate the sizes and shapes of a series of iron-based nanomaterials ( $\alpha\text{-Fe}_2\text{O}_3$  and  $\alpha\text{-Fe}$ ) [37]. In the experiment, the cylindrical micelles of  $[\text{Bmim}]\text{Cl}$  were capped on the specific crystalline planes of the building blocks ( $\beta\text{-FeOOH}$  nanoparticles) via H-bonding-co- $\pi$ - $\pi$  stack interactions, and then  $\beta\text{-FeOOH}$  had a tendency to grow in a special direction. As a result, the self-assembled  $\beta\text{-FeOOH}$  nanorods were obtained. Additionally, the ionothermal method has been used to synthesize g- $\text{C}_3\text{N}_4$  hexagonal nanoprisms [38], ZnO nanostructures [39], turbostratic BN nanoflakes [40].



**Fig. 5.** Adsorption of  $[\text{BMIm}]^+$  on the surfaces of the ZnSe hollow nanospheres [65].

### 3.2. ILs-assisted hydrothermal/solvothermal methods

Broadly speaking, the synthesis of crystalline solid state materials in the liquid phase is much easier than in the solid phase. The archetypes of this synthesis technique are hydrothermal/solvothermal method. Nevertheless, hydrothermal method usually requires relatively high reaction temperature; as to solvothermal method, the ability to control the phases and shapes of the nanomaterials is still not entirely satisfied and some synthetic systems use hazardous volatile organic solvents. Therefore, according to some unique properties of ILs, such as low surface tension, viscosity, and high ionic conductivity, the traditional hydrothermal/solvothermal methods could be modified by adding suitable ILs.

Our research team has been concentrating on the employment of ILs-assisted hydrothermal/solvothermal methods in preparing nanomaterials, including  $\text{TiO}_2$ ,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{MSe}$  ( $\text{M} = \text{Cd}, \text{Zn}$ ),  $\text{Se}$ , and  $\text{Te}$  [17,41-45]. For example, we have used a novel and facile ILs-assisted hydrothermal method to prepare dispersible ZnSe hollow microspheres, which were composed of ZnSe nanoparticles of about 18.8 nm (Fig. 3a) [42]. The application of  $[\text{Bmim}]\text{Br}$  allowed the reactions to be completely carried out under mild conditions. We considered that the reasons mainly involved of three aspects: (1)  $[\text{Bmim}]\text{Br}$  had high ionic conductivity, and simultaneously the solubility of  $\text{Se}$  increased as the ionic strength of media increases. As a result, the reactions were promoted in the presence of  $[\text{Bmim}]\text{Br}$ ; (2) ILs had lower surface tensions compared with water, which resulted in high nucleation rate, a large number of ZnSe crystal nuclei could be formed in the nucle-

ation process and then very small nanoparticles could easily be generated; (3)  $[\text{Bmim}]\text{Br}$  had effect on the sizes of the hollow spheres for the low surface tension and high viscosity of IL-water media. Also, based on the similar special properties of  $[\text{Bmim}]\text{Br}$ , as shown in Fig. 3b, we have synthesized wurtzite CdSe nanoparticles-assembled microspheres with macropores through a modified hydrothermal method using  $[\text{Bmim}]\text{Br}$ -water as solvent [43]. Many other nanomaterials, such as  $\text{CuO}$  nanostructures [46],  $\alpha\text{-Fe}_2\text{O}_3$  hollow spheres [47], and  $\text{ZrO}_2$  nanowires [48], have been prepared through the modified hydrothermal/solvothermal methods with different ILs.

### 3.3. ILs-assisted microwave method

From the perspective of microwave chemistry, one of the key important advantages of ILs is the presence of large organic cations (e.g.,  $[\text{C}_n\text{mim}]^+$ ); therefore, ILs are excellent microwave-absorbing agents for their high ionic conductivity and polarizability. Moreover, the polarization of ions under the electric field of microwave results in the anisotropic growth of crystals [49]. On the basis of the advantages of ILs and microwave-heating, some researchers have developed a novel ILs-assisted microwave method for the fast controllable synthesis of nanomaterials. Zhu et al. have demonstrated that the ILs-assisted microwave route is a fast, template-free, high-yield, and green route for the synthesis of  $\text{Te}$  nanorods and nanowires [49]. Subsequently, this novel synthetic method has been extended to other nanostructures, such as  $\text{Bi}_2\text{S}_3$ , and  $\text{Sb}_2\text{S}_3$ ,  $\text{LaPO}_4\text{:Ce,Tb}$  [50,51].

#### 4. "ALL-IN-ONE" ILs

As the research works went further, in the synthesis of nanomaterials, it has been found that ILs not only just acted as templates or solvents but also could serve as multifunctional solvents. In analogy to the "solvent-template" ILs mentioned above, ILs with special cations and anions can be appropriately tailored, according to the initial crystal structures, compositions, and crystal habits of the products, to obtain several special functions and accordingly act as "solvent-stabilizer", "solvent-template-reactant" and so on.

##### 4.1. Solvent-stabilizer

Nanoparticles have attracted tremendous attention due to their unique properties and potential applications. Their excellent properties are mainly due to the quantum size effect; thereafter, the precise control of the size of nanoparticles has been recognized as an important task. As to ILs, their low surface tensions are beneficial to improve the stability of the as-formed nanoparticles and helpful to accelerate the nucleation rate; ILs can be easily manufactured to be hydrophobic or hydrophilic by designing their structures [52]. In these regards, ILs could be used as "solvent-stabilizer" solvents to prepare monodispersible nanoparticles. Stable transition-metal nanoparticles (2-3 nm in size) have been synthesized by reduction of transition-metal compounds dissolved in [Bmim]PF<sub>6</sub> without using any capping reagent [53]. Moreover, compared with the original imidazolium ILs (I-ILs), I-ILs with functional groups (e.g., thiol-, ether-, amino-) could stabilize aqueous dispersed nanoparticles much more easily owing to the special functional groups [54]. The "solvent-stabilizers" ILs have also provided powerful strategies for the fabrication of other nanomaterials [55,56].

##### 4.2. Solvent-template-reactant

It is known that ILs containing anions like sulfate, phosphate, carbonate, chloride, and metal cations can be viewed as IL precursors for the synthesis of nanomaterials [57]. Hence, ILs are sometimes not only solvents but also reactants and templates for the fabrication of inorganic materials. This concept has been carried out further by a series of research groups, who have introduced alternative approaches to prepare nanomaterials with well-defined properties from "solvent-template-reactant" "all-in-one" ILs.

Taubert's group has synthesized nanomaterials from various "all-in-one" ILs [58,59]. For example,

they have 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 a thermotropic liquid crystal with lamellar self-assembled structures and the plate morphology was therefore caused.

Designable characteristic is one of the most important properties of ILs; thereby, ILs can be tailored to purposefully synthesize nanomaterials. For example, on the basis of the composition of products, ZnO, Zhu et al. have developed a Zn-containing IL, Zn(L)<sub>4</sub>(NTf<sub>2</sub>)<sub>2</sub> (L = alkylamine), for the synthesis of ZnO nanomaterials with controllable shapes. Zn(L)<sub>4</sub>(NTf<sub>2</sub>)<sub>2</sub> were used as both solvents, templates, and precursors [60]. Also, three F-containing ILs, [Omim]PF<sub>6</sub>, [Omim]BF<sub>4</sub>, and [Bmim]PF<sub>6</sub>, have been used as "solvent-template-reactants" to fabricate rare earth fluoride nanomaterials in a large scale [61].

Closely related to the above examples, we have recently synthesized t-BN nanoflakes, BiOCl nanostructures, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous nanoflakes from "all-in-one" ILs [40,62,63]. For instance, in the synthesis of t-BN, we have used a B-containing IL [Bdmim]BF<sub>4</sub> in terms of boron precursor, solvent, and template. The formation of t-BN nanoflakes could be explained by hydrogen bond-co- $\pi$ - $\pi$  stack interaction mechanism. As shown in Fig. 4a, the spatial structure of t-BN is consisted of a nearly flat network of B<sub>3</sub>N<sub>3</sub>. The H radicals are electron-deficient, so it is favorable for them to bind perpendicularly to the N atoms of B<sub>3</sub>N<sub>3</sub>. Thus, the *ab* plane of t-BN is suitable for forming a coverage layer by BF<sub>4</sub><sup>-</sup> adsorbing model. Along with BF<sub>4</sub><sup>-</sup>, [Bdmim]<sup>+</sup> will be arrayed along the t-BN layer. It can be deduced that [Bdmim]BF<sub>4</sub> form an extended hydrogen bond system and can be adsorbed on the (002) plane of t-BN to effectively inhibit the crystalline growth in the [001] direction. Finally, t-BN crystal grows perpendicularly to the *c*-axis and form flake-like t-BN (Fig. 4b).

Besides the above discussions, ILs can also be used as other multifunctional solvents [64,65]. Most recently, we have used a novel Se-containing IL [Bmim][SeO<sub>2</sub>(OCH<sub>3</sub>)] to purposely prepare ZnSe hollow nanospheres through a facile one-pot hydrothermal method. It was found that [Bmim][SeO<sub>2</sub>(OCH<sub>3</sub>)] not only served as Se precursor but also acted as stabilizer for the hollow nanospheres. As displayed in Fig. 6, we speculated that [Bmim]<sup>+</sup> could adsorb on the ZnSe spheres surfaces possible driven by the electrostatic attractions; therefore, [Bmim]<sup>+</sup> hindered the agglomeration of the obtained ZnSe nanospheres in the solution. It could be expected that this task-special IL

would be used to prepare other metal selenides nanomaterials with novel morphologies.

## 5. CONCLUSIONS

In conclusion, we have briefly reviewed the recent developments of the fabrication of nanomaterials in ILs. The ILs-assisted synthesis of nanomaterials is still a burgeoning field; nevertheless, it also enters an exciting stage of its development. It can be considered that, in the near future, we will face many scientific challenges in many hot spot problems which need to be studied further: (1) the effect of ILs on the synthesis of nanomaterials should be deeply understood, which is beneficial to the purposely expanding ILs for the controlled synthesis of analogous nanomaterials and will, in turn, motivate the developments of ILs; (2) there are some limitations for employing ILs in some synthetic systems (e.g., strongly basic environment); therefore, we should recognize the reasons for these limitations and try our best to explore methods to expand the application range of ILs; (3) how to advisably choose and "mix" the various unique features of ILs in one synthetic system? According to the characterizations of the resulting products, we should design ILs to enhance their performance; (4) some less expensive ILs should be developed and gradually be applied in the chemical industry. In short, we hope that this review will not only display the recent developments of ILs, but also give the readers some inspirations to explore novel and effective routes for the synthesis of various nanomaterials.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] C. Burda, X. Chen, R. Narayanan and M.A. El-Sayed // *Chem. Rev.* **105** (2005) 1025.
- [2] C.N.R. Rao, S.R.C. Vivekchand, K. Biswasa and A.Govindaraja // *Dalton Trans.* (2007) 3728.
- [3] B.L. Cushing, V.L. Kolesnichenko and C.J. O'Connor // *Chem. Rev.* **104** (2004) 3893.
- [4] A. Hagfeldt and M Grätzel // *Chem. Rev.* **95** (1995) 49.
- [5] P.J. Dyson and T.J. Geldbach // *Electrochem. Soc. Interface* **16** (2007) 50.
- [6] J. Dupont, R.F. Souza and P.A.Z. Suarez // *Chem. Rev.* **102** (2002) 3667.
- [7] K. Fukumoto, M. Yoshizawa and H. Ohno // *J. Am. Chem. Soc.* **127** (2005) 2398.
- [8] J. Fuller, R.T. Carlin and R.A. Osteryoung // *J. Electrochem. Soc.* **144** (1997) 3881.
- [9] R. Sheldon // *Chem. Commun.* (2001) 2339.
- [10] T. Welton // *Chem. Rev.* **99** (1999) 2071.
- [11] M. Antonietti, D. Kuang, B. Smarsly and Y. Zhou // *Angew. Chem. Int. Ed.* **43** (2004) 4988.
- [12] R.E. Morris // *Angew. Chem. Int. Ed.* **47** (2008) 442.
- [13] S.N. Baker, G.A. Baker and F.V. Bright // *Green Chem.* **4** (2002) 165.
- [14] A.G. Avent, P.A. Chaloner, M.P. Day, K.R. Seddon and T. Welton // *J. Chem. Soc., Dalton Trans.* (1994) 3405.
- [15] W. Zheng, X. Liu, Z. Yan and L. Zhu // *ACS Nano* **3** (2009) 115.
- [16] K. Dong, S.J. Zhang, D.X. Wang and X.Q. Yao // *J. Phys. Chem. A* **110** (2006) 9775.
- [17] P. Peng, X. Liu, C. Sun, J. Ma and W. Zheng // *J. Solid State Chem.* **182** (2009) 1003.
- [18] L. Wang, L. Chang, B. Zhao, Z. Yuan, G. Shao and W. Zheng // *Inorg. Chem.* **47** (2008) 1443.
- [19] Y. Zhou, J.H. Schattka and M. Antonietti // *Nano Lett.* **4** (2004) 477.
- [20] H. Chen and S. Dong // *Langmuir* **23** (2007) 12503.
- [21] L. Wu, J. Lian, G. Sun, X. Kong and W. Zheng // *Eur. J. Inorg. Chem.* (2009) 2897.
- [22] D.G. Tong, W. Chu, X.L. Zeng, W. Tian and D. Wang // *Mater. Lett.* **63** (2009) 1555.
- [23] H. Park, S.H. Yang, Y.S. Jun, W.H. Hong and J.K. Kang // *Chem. Mater.* **19** (2007) 535.
- [24] T.A. Bleasdale, G.J.T. Tiddy and E. Wyn-Jones // *J. Phys. Chem.* **95** (1991) 5385.
- [25] Y. Zhou and M. Antonietti // *Adv. Mater.* **15** (2003) 1452.
- [26] C.J. Adams, A.E. Bradley and K.R. Seddon // *Aust. J. Chem.* **54** (2001) 679.
- [27] M. Firestone, M.L. Dietz, S. Seifert, S. Trasobares, D.J. Miller and N.J. Zaluzec // *Small* **1** (2005) 754.
- [28] X. Bai, L. Zheng, N. Li, B. Dong and H. Liu // *Cryst. Growth Des.* **8** (2008) 3840.

- [29] T. Nakashima and N. Kimizuka // *J. Am. Chem. Soc.* **125** (2003) 6386.
- [30] Y. Qin, Y. Song, N. Sun, N. Zhao, M. Li and L. Qi // *Chem. Mater.* **20** (2008) 3965.
- [31] H. Imai // *Top. Curr. Chem.* **270** (2007) 43.
- [32] D. Adam // *Nature* **407** (2000) 938.
- [33] R.D. Rogers and K.R. Seddon // *Science* **302** (2003) 792.
- [34] L. Wang, Y.P. Xu, B.C. Wang, S.J. Wang, J.Y. Yu, Z.J. Tian and L.W. Lin // *Chem. Eur. J.* **14** (2008) 10551.
- [35] E.R. Parnham and R.E. Morris // *J. Am. Chem. Soc.* **128** (2006) 2204.
- [36] N. Recham, L. Dupont, M. Courty, K. Djellab, D. Larcher, M. Armand and J.M. Tarascon // *Chem. Mater.* **21** (2009) 1096.
- [37] H.S. Park, Y.C. Lee, B.G. Choi, Y.S. Choi, J.W. Yang and W.H. Hong // *Chem. Commun.* (2009) 4058.
- [38] M.J. Bojdys, J.O. Muller, M. Antonietti and A. Thomas // *Chem. Eur. J.* **14** (2008) 8177.
- [39] H. Zhu, J.F. Huang, Z. Pan and S. Dai // *Chem. Mater.* **18** (2006) 4473.
- [40] J. Lian, T. Kim, X. Liu, J. Ma and W. Zheng // *J. Phys. Chem. C* **113** (2009) 9135.
- [41] T. Kim, J.B. Lian, J.M. Ma, X.C. Duan and W.J. Zheng // *Cryst. Growth Des.* DOI: 10.1021/cg901422v.
- [42] X.D. Liu, J.M. Ma, P. Peng and W.J. Zheng // *Mater. Sci. Eng. B* **150** (2008) 89.
- [43] X.D. Liu, P. Peng, J.M. Ma and W.J. Zheng // *Mater. Lett.* **63** (2009) 673.
- [44] J.M. Ma, X.D. Liu, L.Y. Wu and W.J. Zheng // *Crys. Res. Technol.* **43** (2008) 1297.
- [45] J.M. Ma, X.D. Liu, Y. Wu, P. Peng and W.J. Zheng // *Crys. Res. Technol.* **43** (2008) 1052.
- [46] M. Zhang, X. Xu and M. Zhang // *Mater. Lett.* **62** (2008) 385.
- [47] S.W. Cao and Y.J. Zhu // *Acta Mater.* **57** (2009) 2154.
- [48] W.S. Dong, F.Q. Lin, C.L. Liu and M.Y. Li // *J. Colloid Interface Sci.* **333** (2009) 734.
- [49] Y.J. Zhu, W.W. Wang, R.J. Qi and X.L. Hu // *Angew. Chem. Int. Ed.* **43** (2004) 1410.
- [50] Y. Jiang and Y. Zhu // *J. Phys. Chem. B* **109** (2005) 4361.
- [51] G. Bühler and C. Feldmann // *Angew. Chem. Int. Ed.* **45** (2006) 4864.
- [52] L.A. Blanchard, D. Hancu, E.J. Beckman and J.F. Brennecke // *Nature* **399** (1999) 28.
- [53] J. Dupont, G.S. Fonseca, A.P. Umplerre, P.F.P. Fichtner and S.R. Teixeira // *J. Am. Chem. Soc.* **124** (2002) 4228.
- [54] K.S. Kim, D. Demberelnyamba and H. Lee // *Langmuir* **20** (2004) 556.
- [55] M. Green, P. Rahmana and D. Smyth-Boyle // *Chem. Commun.* (2007) 574.
- [56] H. Zhang, H. Cui // *Langmuir* **25** (2009) 2604.
- [57] A. Taubert and Z. Li // *Dalton Trans.* (2007) 723.
- [58] A. Taubert // *Angew. Chem. Int. Ed.* **43** (2004) 5380.
- [59] Z. Li, A. Shkilnyy and A. Taubert // *Cryst. Growth Des.* **8** (2008) 4526.
- [60] H. Zhu, J.F. Huang, Z. Pan and S. Dai // *Chem. Mater.* **18** (2006) 4473.
- [61] C. Zhang, J. Chen, Y. Zhou and D. Li // *J. Phys. Chem. C* **112** (2008) 10083.
- [62] J.M. Ma, X.D. Liu, J.B. Lian, X.C. Duan, T. Kim, H.B. Li and W.J. Zheng // *Cryst. Growth Des.* **10** (2010) 2522.
- [63] J.B. Lian, J.M. Ma, X.C. Duan, H. Tong and M.L. Ruan // *Chem. Commun.* **46** (2010) 2650.
- [64] Y. Gao, A. Voigt, M. Zhou and K. Sundmacher // *Eur. J. Inorg. Chem.* (2008) 3769.
- [65] X.D. Liu, J.M. Ma, P. Peng and W.J. Zheng // *Langmuir* **26** (2010) 9968.