The Design of Nanoscale Inorganic Materials with Controlled Size and Morphology by Ionic Liquids

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1. Introduction

Recently, ionic liquids have successfully been employed in the preparation of inorganic materials (Antonietti et al., 2004, Taubert & Li, 2007). Ionic liquids often act as solvents, reactants or morphology templates, which enable the synthesis of inorganic materials with novel morphologies or improved properties. So far only a handful of studies have reported on the fabrications of nano- or micro-scaled materials including particles of metal oxide (Ding et al., 2007, Bühler & Fledmann, 2006) and sulfide (Jiang, et al., 2005, Jiang & Zhu, 2005). Many metal nanoparticles (NPs) such as Ir (Bühler & Fledmann, 2006), Rh (Wang & Zhu, 2005), Ru (Jiang, et al., 2005), Te (Jiang & Zhu, 2005), Al (Mu, et al., 2004), Ag (Zhu et al., 2004), Pt (Foneca et al., 2003), and Au (Dupont et al., 2002) have been prepared in the presence of ionic liquids.

Novel nanostructures can be produced by selecting suitable ionic liquid reaction systems: TiO_2 (Nakashima & Kimizuka, 2003, Yoo et al., 2004, Zhou & Antonietti, 2003), Te nanorods (Zhu et al., 2004), Si (Abedin et al., 2004), CoPt nanorods (Wang & Yang, 2005), and porous silica (Zhou, et al., 2004, Zhou & Antonietti, 2004) have recently been synthesized, as reported. Žilková et al. have used 1-methyl-3-octylimidazolium chloride (C_8mimCl , an ionic liquid) as a template to prepare $\gamma\text{-Al}_2\text{O}_3$ from the hydrolysis and condensation of $\text{Al}_2\text{Cl}(\text{OH})_5$ (Žilková, et al., 2006). It was shown that the molar ratio of $\text{Al}/\text{C}_8\text{mimCl}$ was important to define the porosity, i.e. the framework or textural type. Mumalo-Djokic and coworkers have put forward the concept of “all-in-one” solvent-reactant(-template)s, (Taubert & Li, 2007, Taubert 2004), that is ionic liquids or ionic liquid crystals (Binnemans, 2005) that are at the same time the solvent, the reactant, and the template for the fabrication of an inorganic. These special systems have been termed ionic liquid precursors and ionic liquid crystal precursors respectively (Taubert 2004, Zhu et al., 2006). Ionic liquid crystal precursors allow for the controlled mineralization of inorganics with complex structure and morphology. For example, they have made CaF_2 tubes, CuCl platelets, and Au platelets from ionic liquid crystal precursors or their crystalline analogues (Taubert 2004, Taubert et al., 2007, Taubert et al., 2006, Taubert et al., 2005, Taubert 2005). Furthermore, other research groups have extended this concept of reactive ionic liquid crystals to other compounds (Zhu et al., 2006, Dobbs et al., 2006, Lee et al., 2006, Kem et al., 2006).

Although there are a few inspiring short accounts or perspectives focused on selected topics in materials synthesis using ionic liquids, a relatively comprehensive and updated review of this subject is still a gap, especially considering that the field is growing quite fast. Therefore, in the present contribution, the use of ionic liquids in the preparation of different categories of inorganic materials, including silicas, open framework structures, and ionic liquid-modified materials using ionic liquids by different methods, is systematically reviewed. Due to the abundance of research reported in the literature, the present chapter dealt only with some typical examples and key concepts proposed as highlights.

2. Methods

2.1 Sonochemical synthesis

Ionic liquids have favorable intrinsic properties that make them of interest as solvents for various chemical reactions. The same properties that make the liquids effective solvents also make them interesting liquids for studies involving sonochemistry, acoustic cavitation, and sonoluminescence (Suslick et al., 1991, Suslick, 1988). Recent interest in using ultrasound to accelerate chemical reactions conducted in ionic liquids necessitates an understanding of the effects of acoustic cavitation on these solvents (Flannigan et al., 2005).

The use of ultrasonic irradiation for producing nanomaterials has been a research topic of great interest (Dhasn et al., 1999). This is due to the simplicity of sonochemical method, the cheap price of the equipment and that in many cases the as-prepared material is obtained in the crystalline phase. The ultrasonic-assisted aqueous room temperature ionic liquid method was applied to prepare zinc sulfide and zinc oxide nanomaterials (Zheng et al. 2010; Jia et al. 2010), among many other nanomaterials. Selection of the room temperature ionic liquid was mainly based on the fact that it can be obtained at a relatively low price and the method for its synthesis is simple.

Nanosheet-based microspheres of ZnO with hierarchical structures were prepared by ultrasonic irradiation in acidic ionic liquids by Kowsari (Kowsari 2010). It is found that the ultrasonic irradiation time, ultrasonic frequency, and the acidic ionic liquids influence the growth mechanism and optical properties of ZnO nanostructures. By changing the type of acidic ionic liquids, ultrasonic irradiation time, ultrasonic frequency optical properties of ZnO nanostructure are manageable. The photocatalytic activity test results indicate that the hollow spheres-like ZnO nanophotocatalysts have good photocatalytic activities. Overall, the cited results indicate that the prepared ZnO nanophotocatalysts show good photocatalytic activity and can be considered as a promising photocatalyst for dyes wastewater treatment. Fig. 1. shows the precursor composed of plate-like nanostructures with edge thicknesses of about 40 nm and smooth surfaces. The structures synthesized in this experiment can indicate a new way to construct nanodevices by self-organization in one step.

In other report, flower like ZnO/MgO nanocomposites were prepared by ultrasonic irradiation and chiral ionic liquid, ditetrabutylammonium tartarate, $[TBA]_2[L-Tar]$. It is found that the ultrasonic frequency, the ultrasonic irradiation time and the chiral ionic liquid influence the growth mechanism and optical properties of ZnO/MgO nanocomposites. Enhancement of bandgap in the ZnO/MgO nanocomposites, due to morphology effect, was an interesting observation. The effect of the ultrasonic irradiation time on ZnO/MgO nanocomposites morphology (in the presence of chiral ionic liquid) is shown in Fig 2. As it can be observed in Fig 2, when the ultrasonic irradiation time increases, the thickness of the nanosheets making the flowerlike is reduced. Therefore, the morphology takes a more arranged shape.

Fig. 1. Regular hollow spherical, composed of a number of nanosheets, with an average size of 50–70 μm . and leaf-like ZnO nanostructure, synthesis by acidic ionic liquid, [(mim) hex(mim)][$2\text{H}_2\text{PO}_4$] (kowsari (2010) , accepted for presentation 2nd Asia Pacific Conference on Ionic Liquids and Green Processes September 7-10 , 2010 Dalian • China)

Fig. 2. The effect of ultrasonic irradiation time on the evolution of the morphologies of ZnO/MgO nanocomposite, (a) 2 h and (b) 2.5 h , (Ultrasonic frequencies = 40 kHz, The ultrasonic power was kept at 200 W) (kowsari (2010) , accepted for presentation 2nd Asia Pacific Conference on Ionic Liquids and Green Processes September 7-10 , 2010 Dalian (China)

2.2 Sol-gel synthesis

A good number of works concerning the synthesis of inorganic nanomaterials are based on sol-gel route. The original use of ionic liquids as solvents for inorganic sol-gel reactions is the acid-catalyzed sol-gel synthesis of silica aerogels (Dai et al., 2003). It turned out that such aerogels can be dried without a supercritical drying procedure. Subsequently, 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] was used to synthesize hollow TiO₂ microspheres by interfacial sol-gel reaction (Nakashima & Kimizuka, 2003).

Zhou, et al. used TiCl_4 as the precursor to synthesize very small TiO_2 nanocrystals in $[\text{BMIM}][\text{BF}_4]$ and obtained mesoporous spherical aggregates of TiO_2 nanocrystals (Zhou & Antonietti, 2003). The synthesized titania aggregates exhibits structural mesoporosity with considerable high surface area and narrow pore size distribution, rendering the materials interesting for solar cell conversion, catalysis, and electronic devices. Smarsly, et al. synthesized rutile nanostructures at low temperature by sol-gel chemistry in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (Kaper et al., 2003).

2.2.1 Synthesis Y_2O_3 nano-/microstructured phosphors without metal activators fabricated using functionalized ionic liquids

Flowerlike Y_2O_3 nano-/microstructured phosphors without metal activators were fabricated by an ionic liquid assisted method (acid-catalyzed sol-gel synthesis) involving temperature (600°C) annealing by Kowsari and Faraghi (Kowsari & Faraghi, 2010). Also, the effect of ionic liquid concentration on the morphology of the product was investigated. The results revealed that the ionic liquids play a crucial role in the formation of various morphologies of Y_2O_3 . The effect of the ionic liquids cation and the counter anions on the Y_2O_3 morphology of these nanostructures were studied experimentally. It was observed that Y_2O_3 morphology and PL of these nanostructures was strongly influenced by the type of cation and anion. As the length of the subsidiary chain of cation section of ionic liquid (imidazole cation) reduces, the thickness of the nano-sheets increases. Since Y^{3+} itself is non-luminous, the observed luminescence from the Y_2O_3 samples must be related to chemical-bond breakage with resultant carbon formation and/or non-stoichiometry (from ionic liquid) created by the oxygen deficiency in the system.

In this study, ionic liquid was used as a templating agent and produce different morphologies. The structures of ionic liquids show in Fig.3.

Fig. 3. Structures of ionic liquids (Reproduced from Kowsari & Faraghi, (2010) *Materials Research Bull* 45, 8, 939-945, Copyright (2010), with permission from Elsevier)

Here, the effect of ionic liquid concentration on the morphology of the product was investigated. Fig. 4 shows SEM photographs of products prepared with different ionic liquid concentrations. The results demonstrate that the concentration of ionic liquid is an important factor with regard to the formation of novel Y_2O_3 microstructures. Since no surfactant or capping agent was employed in this synthesis, the ionic liquid used is believed to play an important role in the formation of the novel structure.

Fig. 4. SEM images showing the morphological evolution of Y_2O_3 samples with different concentrations of IL1: (a) 0.036 M, (b) 0.027 M, (c) 0.018 M, and (d) 0.012 M, (Reproduced from Kowsari & Faraghi, (2010) *Materials research Bull* 45, 8, 939-945, Copyright (2010), with permission from Elsevier)

In high concentration of ionic liquid, (0.045 mmol) the Y_2O_3 sample is irregular and crossed microsheets which overlap each other. When 0.012 mmol of ionic liquid is added in hydrothermal solution, the Y_2O_3 sample is shaped as a uniform flowerlike architecture, as shown in Fig. 4c.

The formation mechanism of Y_2O_3 flowers is obviously due to the templating effect in the present ionic liquid- water reaction system. The inset SEM images in Fig. 4e offer a clear view of the morphology from which it can be seen that the flowerlike Y_2O_3 architecture is built up from Y_2O_3 nanoflakes. The results suggested that the morphology of the Y_2O_3 sample prepared by the solution-phase reactions is influenced by adding ionic liquid. The $[C_{17}mim]^+$ cation of $[C_{17}mim]^+[H_2PO_4]^-$ has a hydrophobic chain which, under proper experimental conditions $[C_{17}mim]^+$, could form micells with the positive ends stretch to the outside. After the $Y(NO_3)_3$ is solved in water in the absence of $[H_2PO_4]^-$, which is an ionic liquid anion, there is the possibility of formation of $[Y(H_2O)_2(NO_3)_3 H_2PO_4]^-$. Then, $[C_{17}mim]^+$, which is ionic liquid cation, can interact with precursor $[Y(H_2O)_2(NO_3)_3 H_2PO_4]^-$ ions through electrostatic attraction. Therefore, flowerlike Y_2O_3 architecture can be obtained by hydrothermal route by adding a small amount of $[C_{17}mim]^+[H_2PO_4]^-$.

To further confirm the existence of the carbon impurity, the sample Y_2O_3 -300, temperature (300 °C) annealing, was subjected to XPS analysis, which is a powerful tool for determining the surface composition of a material qualitatively. Fig. 5 shows the XPS analysis results of the sample. Signals of bonding energy from the Y (3d_{5/2}, 158.4 eV), O (1s, 532.1 eV), C (1s, 285.0 eV), and N (1s, 399.0 eV) can be seen clearly in Fig. 10 (Wang & Ong, 2007, Ramírez et al., 2002) This provides additional evidence for the existence of the carbon impurity.

In this study, some Y_2O_3 nanostructures were prepared in the presence of other ionic liquids with different cations, and anions each at a concentration of 0.027 M. The Effect of the ionic liquids cation and the counter anions on the Y_2O_3 morphology of these nanostructures were studied experimentally. It was observed that Y_2O_3 morphology and PL of these nanostructures was strongly influenced by the type of cation and anion. As the length of the

Fig. 5. XPS spectra of Y_2O_3 -300 sample (Reproduced from Kowsari & Faraghi, (2010) *Materials research Bull* 45, 8, 939-945, Copyright (2010), with permeation from Elsevier)

Fig. 6. SEM images showing the morphological evolution of Y_2O_3 samples with different cation and anion of ionic liquids, [concentrations of IL = 0.027 M]: (a) IL1, (b) IL2, (c) IL3 and (d) IL4 [IL1, $([\text{C}_{17}\text{mim}]^+ [\text{H}_2\text{PO}_4]^-)$, 1-heptadecyl-3-methylimidazolium dihydrogen phosphate), IL2, $([\text{C}_{10}\text{mim}]^+ [\text{H}_2\text{PO}_4]^-)$, 1-decyl-3-methylimidazolium dihydrogen phosphate), IL3, $([\text{C}_8\text{mim}]^+ [\text{H}_2\text{PO}_4]^-)$, 1-octyl-3-methylimidazolium dihydrogen phosphate), IL4, $([\text{C}_4\text{mim}]^+ [\text{H}_2\text{PO}_4]^-)$, 1-buthyl-3-methylimidazolium dihydrogen phosphate)]. (Reproduced from Kowsari & Faraghi, (2010) *Materials research Bull* 45, 8, 939-945, Copyright (2010), with permeation from Elsevier)

subsidiary chain of cation section of ionic liquid (imidazole ion) reduces, the thickness of the nano-sheets increase. And as anion section of ionic liquid changes (H_2PO_4^- to HSO_4^-), as shown is Fig. 6, morphology changes from a nano-sheet-like structure to a coral-like one. Since Y^{3+} itself is non-luminous, the observed luminescence from the of Y_2O_3 samples must be related to chemical-bond breakage with resultant carbon formation and/or non-

stoichiometry created by the oxygen deficiency in the system (Fujimaki et al., 1997, Green, 1997, Pifferi et al., 1997, Hayakawa et al., 2003). Here, we assume that the carbon-related impurities play a key role in the luminescence of Y_2O_3 .

2.2.2 Morphogenesis and crystallization of Bi_2S_3 nanostructures by an ionic liquid-assisted templating route

An ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) solution system has been designed for the morphogenesis and crystallization of Bi_2S_3 nanostructures at low temperature and ambient atmosphere by Jiang et al. (Jiang et al., 2005).

Uniform Bi_2S_3 flowers with a size of 3–5 μm , which are composed of nanowires with a diameter of 60–80 nm, can be prepared in large scale by the template effect of the ionic liquid solution, in which vesicles are formed as confirmed by laser light scattering analysis. With prolonged aging time, the flowerlike structures tend to become loose and fall off from the mother flowers, and finally the individual nanowires will form.

The results demonstrated that the shape evolution and phase transformation strongly depend on the reaction conditions, such as pH value, reaction temperature, and reaction time. The pH value of the reaction medium plays a key role in the present procedure for the synthesis of Bi_2S_3 nanoflowers. First, a suitable pH value can effectively prevent BiCl_3 hydrolysis to BiOCl in the initial reaction stage and kinetically control the growth rate of dendrite Bi_2S_3 nanostructures. When the pH value is about 2, even within a short period, for example, about half an hour, large-scale and uniformly shaped Bi_2S_3 nanoflowers with a size of 3.5 μm can be prepared conveniently (Fig. 7).

Fig. 7. SEM images of the product obtained in an ionic liquid system after reaction at 120 °C for 0.5 h. Starting pH = 2 (Reproduced from Jiang et al. *Chem. Mater.* 2005, 17, 6094–6100, Copyright (2009), with permission from American Chemical Society)

2.3 Thermal synthesis

2.3.1 Ionothermal synthesis

Ionic liquids are known for their nonvolatile, nonflammable, and thermally stable properties. These properties make the reactions in open reactor possible. The term “ionothermal” has been used to describe reactions that are conducted in ionic liquids at high temperature with ambient pressures. As a result, ionothermal reactions avoid high pressure of hydrothermal or solvothermal reactions and eliminate safety problems related to high pressure (Taubert & Li 2007). Cooper, et al. have demonstrated that imidazolium-based

ionic liquids can be utilized to synthesize several phosphate-based microporous zeolites by an ionothermal process (Cooper et al., 2004), Dai, et al. reported the use of a newly developed ionic liquid system containing zinc metal ions, which can serve as both solvents and metal-oxide precursors, for manufacturing nanostructured zinc oxide under the ionothermal condition (Zhu et al., 2006). The morphologies of ZnO are strongly dependent on the nature of the ionic liquid precursor (ligands), providing unique methodologies to control the growth conditions.

In ionothermal synthesis, the ionic liquid acts as the solvent, and in many cases also as a template provider playing a structure-directing role in the formation of zeolites and open-framework structures. The use of [EMim][Br] led to the formation of open-framework aluminophosphates SIZ-1, SIZ-3, SIZ-4, SIZ-5, and SIZ-6, (Cooper et al. 2004; Parnham et al. 2006) and the use of choline chloride/urea mixtures led to SIZ-2 and AlPO-CJ2 (Cooper et al. 2004). The ionic liquids acted as both solvent and template provider.

2.3.2 Hydrothermal synthesis

Several research groups have employed ionic liquids for the synthesis of nanostructures by hydrothermal method. Zhang and coworkers (Zhang et al. 2008) reported a hydrothermal method to synthesize sheaf-like CuO self-assembled by nanoplatelets in [BMIM]BF₄. [BMIM]BF₄ was used as a cosolvent and modifiers in the formation of sheaflike CuO. Hollow molybdenum disulfide (MoS₂) microspheres were synthesized in ionic liquids (1-butyl-3-methylimidazolium chloride, [BMIM]Cl)/water binary emulsions using the hydrothermal method at 180 °C by Luo and coworker (Lue et al. 2008). Liu and coworkers (Liu et al. 2009) have also reported a modified hydrothermal method for the synthesis of CdSe nanoparticles-assembled microspheres with macropores using 1-n-butyl-3-methylimidazolium bromide ([Bmim]Br) to assist the reaction. By changing the processing parameters, they fabricate wurtzite CdSe microspheres with an average diameter of about 3 μm. The possible growth mechanism of the CdSe microspheres is investigated.

Nanostructured ZnO was synthesized by a hydrothermal route using different ionic liquids as the morphology templates by Yavari et al. (Yavari et al. 2009). The morphology of ZnO changes from rod-like to star-like and flower-like in different ionic liquids. A 3D nano/micro structure ZnO with unique flower-like morphology has been synthesized (Fig. 9) via the assembly of dicationic ionic liquid and [Zn(OH)₄]²⁻.

A typical SEM image of an individual ZnO hexagonal prism with hexagonal pyramid in tip is presented in Fig. 10. It is indicated that it can grow along the [0001] direction.

It has been known that the adsorption of growth units on crystal surfaces strongly affects the growth speed and orientation of crystals (Li et al., 1999). When a ZnO crystal grew, an ionic liquid (with pyridinium cation, for example) film could form at the interface between solution and the crystal. This landing process on the surface of ZnO [0 0 0 1] crystal face is shown graphically in Fig. 11. Since ionic liquid favors to form a film in which molecules tend to be perpendicular to the absorbed surface, the growth units would tend to face-land onto the growing interface as shown in Fig. 11. This kind of landing and dehydration will result in three Zn–O–Zn bonds, which make it predominant in competition with vertex- and edge-landing. Thus, the ZnO crystals should grow preferentially along the c-axis ([0 0 0 1] direction) as this kind of face-landing on [0 0 0 1] crystal face and the following dehydration steps are repeated (Li et al., 1999).

Fig. 9. SEM image of the flower-like ZnO in $[(C_1)_2C_8(im)_2](Br)_2$, mole ratio $OH^-/Zn^{+2} = 30:1$ and $[(C_1)_2C_8(im)_2](Br)_2 = 0.10$ g. (Reproduced from Yavari et al. (2009) *J. Nanopart. Res.*; 11, 861, Copyright (2009), with permeation from Springer)

Fig. 10. A typical SEM image of an individual ZnO hexagonal prism with hexagonal pyramid in tip (Reproduced from Yavari et al. (2009) *J. Nano part. Res.*; 11, 861, Copyright (2009), with permeation from Springer)

According to the process described earlier, it is supposed that ionic liquid leads to the orientation growth of ZnO rods. Similarly, ZnO flower-like assemblies can be formed in the presence of ionic liquid which has two identical imidazolium cations.

The ZnO has been found to exhibit sensitivity to C_2H_5OH , NH_3 and other species. However, the ZnO based sensing devices possess several critical limitations, which are difficult to overcome, such as a limited maximum sensitivity and the operation at high temperature ($400-500^\circ C$). Flower-like ZnO nanostructures improve performance such as sensitivity and working temperature (room temperature).

Fig. 11. (a) Schematic illustration of ion-pair formed between ionic liquid and $[\text{Zn}(\text{OH})_4]^{2-}$; (b) landing process on the surface of ZnO [0001] crystal face by ionic liquid. (Reproduced from Yavari et al. (2009) *J. Nanopart. Res.*; 11, 861, Copyright (2009), with permission from Springer)

Flower-like ZnO morphology, with different shapes, have been synthesized via a novel and environment-friendly hydrothermal method using zinc acetate and a task specific dicationic dibasic ionic liquid, $[\text{mmpim}]_2[\text{OH}]_2$, which plays an important role in fabrication of ZnO structure (Movahedi et al., 2008). SEM images of ZnO nanostructure synthesized by task specific dicationic dibasic ionic liquid, $[\text{mmpim}]_2[\text{OH}]_2$ is shown in fig. 12.

Fig. 12. SEM images of ZnO nanostructure synthesized by task specific dicationic dibasic ionic liquid, $[\text{mmpim}]_2[\text{OH}]_2$. (Reproduced from Movahedi et al. (2008) *Materials Letters* 62 3856–3858, Copyright (2008), with permission from Elsevier)

The $\alpha\text{-Fe}_2\text{O}_3$ with various morphologies has been synthesized via an ionic liquid assisted hydrothermal synthetic method by Lian and coworkers (Lian et al. 2009). The results indicate that the as-prepared samples are $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, mesoporous hollow microspheres,

microcubes, and porous nanorods. The UV-vis measurements suggest that the as-synthesized pure α -Fe₂O₃ with various morphologies possess different optical properties depending on the shape and size of the samples. The magnetic hysteresis measurements indicate the interesting magnetic property evolution in the as-prepared α -Fe₂O₃ samples, which is attributed to the superstructure or the shape anisotropy of the samples.

2.4 Microwave heating synthesis

The application of microwave heating in synthetic chemistry is a fast-growing research area due to its advantages such as rapid volumetric heating, higher reaction rate, and selectivity, reducing reaction time often by orders of magnitude and increasing yields of products compared with conventional heating methods. As a result, this has opened up the possibility of realizing fast synthesis of materials in a short time. From the perspective of microwave chemistry, one of the key important advantages of room temperature ionic liquids is the presence of large organic positive ions with a high polarizability. Therefore, room temperature ionic liquids are good media for absorbing microwaves, leading to a high heating rate. Lately, by combining the advantages of both room temperature ionic liquids and microwave heating, a new microwave-assisted ionic liquid method has developed for fast controlled synthesis of nanorods and nanowires of Te and ZnO (Jiang & Zhu, 2005). Zhu and coworkers (Zhu et al. 2004) synthesized single-crystal tellurium nanowires using microwave heating in *n*-butylpyridinium tetrafluoroborate ionic liquid in the presence of polymer surfactant of poly(vinylpyrrolidone) (PVP). Li and coworkers (Li et al. 2005) synthesized large-size single-crystal gold nanosheets by microwave heating of HAuCl₄ in [BMIM][BF₄], without any additional template agent. Subsequently, PbCrO₄ rods or bundle-like Pb₂CrO₅, Bi₂Se₃ nanosheets, sulfide M₂S₃ nanorods, single-crystalline cryptomelane-type manganese oxide octahedral molecular sieve (OMS-2) nanoneedles, and nanorods, metal fluorides such as FeF₂, CoF₂, ZnF₂, LaF₃, YF₃, SrF₂, metal-oxide like Fe₂O₃, carbon-coated core shell structured copper or nickel nanoparticles and CNTs/Pt or CNTs/Rh composites have successfully been fabricated by microwave-assisted synthesis method in ionic liquids (Wang & Zhu, 2005, Jiang et al., 2006, Singh et al., 2008, Liu et al., 2006).

Single-crystalline Bi₂S₃ and Sb₂S₃ nanorods have been synthesized using the microwave-assisted ionic liquid method by Jiang and Zhu (Jiang & Zhu, 2005). The starting reagents were Bi₂O₃ or Sb₂O₃, HCl, Na₂S₂O₃, and ethylene glycol (EG) or ethanolamine, and the ionic liquid used was 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]). These experiments showed that the ionic liquid played an important role in the morphology of M₂S₃ (M = Bi, Sb). Single-crystalline Bi₂S₃ nanorods could be prepared in the presence of [BMIM][BF₄]. However, urchinlike Bi₂S₃ structures consisting of nanorods were formed without using [BMIM][BF₄]. Single-crystalline Sb₂S₃ nanorods were obtained in the presence of [BMIM][BF₄]. However, single-crystalline Sb₂S₃ nanosheets could be prepared in the absence of [BMIM][BF₄].

The morphologies of the samples were investigated by transmission electron microscopy (TEM). Figure 13a,b shows TEM micrographs of sample 1 (Bi₂S₃) synthesized under microwave heating at 190 °C for 10 min without using the ionic liquid [BMIM][BF₄], from which one can see the urchinlike morphology of Bi₂S₃.

2.5 Emulsions or microemulsions synthesis

Reverse microemulsions are mostly transparent, isotropic and thermodynamically stable liquid media with nanosized water droplets dispersing in a continuous oil phase and

stabilized by an adsorbed surfactant film at the liquid–liquid interface (Chokshi et al., 1989). One of the important applications of microemulsions involves the preparation of nanoparticles, nanowires, and nanorods (Qi et al., 1997). More recently, some investigations demonstrated that ionic liquids could substitute water or oil to form novel microemulsions in the presence of surfactant

Fig. 13. TEM micrographs of three typical Bi_2S_3 samples: (a and b) sample 1; (d and e) sample 2 synthesized via microwave-assisted ionic liquid method at 190°C for 10 min; (g and h) sample 3 synthesized via microwave-assisted ionic liquid method at 190°C for 30 s. (c, f, and i) Electron diffraction patterns of individual nanorods from samples 1, 2, and 3, respectively. (Reproduced from Jiang & Zhu (2005) *J. Phys. Chem. B*, 109, 4361-4364, Copyright (2005), with permission from American Chemical Society)

Ionic liquid microemulsions have both the advantages of ionic liquids and microemulsion, which can overcome the inability of ionic liquids to dissolve a number of chemicals including some hydrophilic substances and then broaden the utilization of ionic liquids. Some papers reported that ionic liquid could substitute water to form nonaqueous ionic liquid microemulsion and exist as nanosized polar domains dispersed in cyclohexane with the aid of surfactant (Li et al., 2007). Gao, et al. prepared and characterized TX-100/ H_2O /1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF_6) microemulsion using different techniques. Their research results showed that water domains existed in the water-in- bmimPF_6 microemulsion, which could dissolve salts (Gao et al., 2005).

2.6 Electrodeposition synthesis

Electrochemical deposition is an economical and convenient choice for preparing uniform and size controllable nano-materials. It is meaningful to combine the advantages of aqueous ionic liquid microemulsions and the electrodeposition method for preparing materials.

Aqueous ionic liquid microemulsions as electrolytes for electrochemical deposition are special and different from traditional aqueous solution and ionic liquids. Electrochemical approaches have been among the first to be used for the fabrication of inorganic nanoparticles and nanostructured films in ionic liquids. The properties of ionic liquids opened the door to the electrodeposition of metals and semiconductors at room temperature, which was previously only possible from high-temperature molten salts. For example, Al, Mg, Ti, Si, Ge and rare-earth-elements related materials can be obtained from ionic liquids.

Fig. 14. SEM images of the Si NWs prepared with membranes with nominal pore diameter of 400 nm and a thickness of 12 μm (a), 110 nm and 20 μm (b), and 15 and 800 nm (c) after partial or total dissolution of the PC membranes. The inset of the image in panel a exhibits an isolated 400 nm NW after a supplementary washing procedure to show its smooth surface after total dissolution of the membrane. The inset of the image in panel b shows some isolated 110 nm NWs with a good uniformity for the diameters and regular and smooth edges. (d) A TEM picture of isolated 15 nm NWs with the corresponding electron diffraction pattern (Reproduced from Mallet et al (2008) *Nano Letter* 2008 8, 10, 3468-3474 Copyright (2008), with permission from American Chemical Society)

Silicon nanowires were fabricated for the first time by electrochemical template synthesis at room temperature by J. Mallet and coworkers (Mallet et al. 2008). This innovative, cheap, and simple process consists of electroreduction of Si ions using a nonaqueous solvent and insulating nanoporous membranes with average pore diameters from 400 to 15 nm which fix the nanowires diameters

Characterization techniques such as scanning and transmission electron microscopies, infrared absorption measurements, X-ray diffraction experiments, energy dispersive X-ray, and Raman spectrometries show that the as-deposited silicon nanowires are amorphous, composed of pure Si and homogeneous in sizes with average diameters and lengths well matching with the nanopores' diameters and the thicknesses of the membranes. Thanks to

annealing treatments, it is possible to crystallize the Si nanowires, demonstrating the potentiality for this innovative electrochemical process to obtain a wide range of Si nanowires with well controlled diameters and lengths. Figure 14 panels a-c are SEM images of nanowires prepared in PC membrane with pore diameters of 400, 110, and 15 nm, respectively, and thicknesses of 12 μm , 20 μm , and 800 nm, respectively, after partial or total dissolution of the membranes and collection on a HOPG substrate. Figure 14d is a TEM image of 15 nm NWs deposited on a Ni grid.

Ultrafine monodisperse gold nanoparticles (AuNPs) were synthesized by an elegant sputtering of gold onto 1-*n*butyl-3-methylimidazolium hexafluorophosphate (BMI-PF₆) ionic liquid by Khatri and coworkers (Khatri et al. 2008). It was found that the BMI-PF₆ supramolecular aggregates were loosely coordinated to the gold nanoparticles and were replaceable with thiol molecules. The selfassembly of BMI-PF₆-stabilized AuNPs onto a (3-mercaptopropyl)trimethoxysilane (MPS)-functionalized silicon surface in 2D arrays, followed by dodecanethiol (DDT) treatment, have been demonstrated using X-ray photoelectron spectroscopy, field emission scanning electron microscopy, and contact angle measurements. DDT treatment of tethered

AuNPs revealed two types of interactions between AuNPs and the MPS-functionalized surface: (a) AuNPs anchor through Au-S chemisorption linkage resulting in strong immobilization and (b) some of the AuNPs are supported by physisorption, driven by BMI-PF₆. The attachment of these particles remains unchanged with sonication. The replacement of BMI-PF₆ aggregates from physisorbed AuNPs with dodecanethiol molecules advances the dilution of their interaction with the MPS-functionalized surface, and they subsequently detach from the silicon surface. The present finding is promising for the immobilization of ionic liquid-stabilized nanoparticles, which is very desirable for electronic and catalytic device fabrication. Additionally, these environmentally friendly AuNPs are expected to replace conventional citrate-stabilized AuNPs.

2.7 Nanocasting technique and ionic liquid

A nanocasting technique (Attard et al., 1995, Polarz & Antonietti, 2002) was employed for the synthesis of several mesoporous SiO₂ materials. Zhou and Antonietti used [C₁₆Mim][Cl] as the template to prepare monolithic super-microporous SiO₂ (pore diameter 1.3 nm, wall thickness 1.4 nm, surface area 1340 m² g⁻¹) with lamellar order via a nanocasting technique. (Zhou & Antonietti, 2003) They further reported a systematic investigation employing [C₁₀Mim][Cl] ([C₁₀Mim]⁺ = decyl-3-methylimidazolium), [C₁₄Mim][Cl], [C₁₆Mim][Cl], and [C₁₈Mim][Cl] ([C₁₈Mim]⁺ = 1-octadecyl-3-methylimidazolium) as templates, and again obtained lamellar SiO₂ with pore diameters in the range of 1.2–1.5 nm. (Zhou & Antonietti, 2004) In addition, mesoporous SiO₂ with wormlike pores (pore diameter 2.5 nm, wall thickness 2.5–3.1 nm, surface area 801 m² g⁻¹) was synthesized using [BMim][BF₄] as the template. (Zhou & Schattka, 2004) The authors proposed a hydrogen bond-co- π - π stacking mechanism, in which the hydrogen bonds formed between [BF₄]⁻ and the SiO₂ matrix together with the π - π stacking interaction of the neighboring imidazolium rings led to the mutual packing and formation of mesoporous SiO₂ (Fig. 16).

The synthesis of mesoporous SiO₂ using ionic liquids as new templates has furnished new examples in the synthesis of mesoporous materials. However, the efforts made in this regard are still minor, compared to the huge efforts made in the synthesis of mesoporous materials using other templates. The advantages of using ionic liquids instead of conventional solvents are not obvious, the synthesis mechanisms in different cases are not quite clear, and

Fig. 15. Simple Model to Illustrate the Interaction of BMI-PF₆-Stabilized AuNPs on the MPS-Functionalized Surface (Reproduced from Khatri et al. (2008) *Langmuir* 24, 7785-7792, Copyright (2008), with permission from American Chemical Society)

^a Illustration of (a) an MPS monolayer on a silicon surface and (b) the immobilization of BMI-PF₆-stabilized AuNPs on the mercapto-functionalized silicon surface followed by (c) dodecanethiol treatment, which replaces the protective coating of BMI-PF₆ supramolecular aggregates and detaches the physisorbed AuNPs from the silicon surface. (d) Immobilization of new AuNPs. These particles are probably tethered to vacant sites created by the detachment of physisorbed AuNPs. (e). BMI-PF₆-stabilized ultrafine gold nanoparticles in the dispersed phase. (f). Interaction of BMI-PF₆-stabilized AuNPs with a mercapto-functionalized surface. The strong affinity between gold and the mercapto group replaces the BMI-PF₆ aggregates from the localized area and results in Au-S chemisorption bonding. (g). Replacement of the BMI-PF₆ protective layer by dodecanethiol molecules.

Fig. 16. A π - π stacking model proposed to explain the formation of mesoporous SiO_2 using [BMim][BF_4] as the template. In this model, [BF_4] anions interact with the silanol groups and arrange along the pore walls, and [BMim] cations are aligned accordingly, forming π - π stacking interactions between the aromatic motifs. (Reproduced from Zhou et al. (2004) *Nano Lett.* 4, 477, Copyright 2004, with permission of the American Chemical Society)

the knowledge regarding the morphological control of mesoporous SiO_2 is still limited. It is not clear how the use of different ionic liquids may lead to different morphologies and how synthesis conditions may influence the morphology. Regardless of these limitations, this idea has opened up new avenues for the synthesis of hierarchical porous materials and periodic mesoporous organosilicas.

3. Conclusion

The updated application of the ionic liquid in the synthesis of inorganic nanomaterials was briefly outlined. The main emphasis of the outline was a focus on the preorganized structure of the ionic liquid as template effect for inorganic nanomaterials. The particular strength of ionic liquids is their virtually unlimited flexibility of anions and cations combinations. As the cation or anion in the ionic liquid can be tailored by functional substitutes, the size and size distribution of the ionic liquid-stabilized metal nanoparticles can be easily controlled too. In case ionic liquid phase behavior, chemical composition, and reactivity are also considered, ionic liquids provide a flexible toolbox for the fabrication of inorganics with various (and variable) properties simply by designing the appropriate precursor. These precursors are entities which are defined molecularly, which can be well characterized and studied as the transformation to the inorganic proceeds.

Although the application of the ionic liquid in inorganic nanomaterials is still in its early days, many claim that the field of ionic liquid is becoming a promising area of research in the nanomaterials in the years to come.

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

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