

## Ionic liquids for synthesis of nanoparticles (A review)

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Received: 2 July 2018; Accepted: 5 September 2018

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**ABSTRACT:** An ionic liquid (IL) is a salt in the liquid state. In some contexts, the term has been restricted to salts whose melting point is below some arbitrary temperature, such as 100 °C. While ordinary liquids such as water and gasoline are predominantly made of electrically neutral molecules, ionic liquids are largely made of ions and short-lived ion pairs. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses. They are known as "solvents of the future" as well as designer solvents. Very polar reactions can be carried out in these liquid in the absence of or with a controlled amount of water, and crystalline nanoparticles can be synthesized conveniently at ambient temperatures. The pronounced self-organization of the solvent is used in the synthesis of self-assembled, highly organized hybrid nanostructures with unparalleled quality. The extraordinary potential of ionic liquids in materials synthesis is described in this mini-review and a physicochemical explanation is given.

**Keywords:** *Ionic liquid; Nanoparticle; Polarity; Synthesis; Sol-Gel.*

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## INTRODUCTION

Room temperature ionic liquids (ILs) constitute a new class of substances, which are considered as potential substitutes to many traditional organic solvents in reaction and separation systems (Freyland, *et al.*, 2003). An expanding interest in ionic liquids has been observed during the last decade. ILs are composed of bulky ions, have very small vapor pressure, low melting point, high solvating capacity, high ionic conductivity and high thermal stability, which make them attractive for practical applications (Zhou, *et al.*, 2003). ILs is ideal

solvents for green chemistry, clean synthesis and can be used in many cyclic processes. IL's are claimed to be useful as heat transfer fluids in solar heating and absorption refrigerating systems (Nakashima and Kimizuka, 2003). Ionic liquids (ILs) are organic salts with low melting points, sometimes as low as -96 °C. ILs has received much attention in many areas of chemistry and industry due to their potential as a "green" recyclable alternative to traditional organic solvents (Itoh, *et al.*, 2004). The ILs is liquid over a wide range of temperatures, in some cases in excess of 400 °C. Because

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of their properties, such as high polarity, negligible vapor pressure, high ionic conductivity, and thermal stability, ILs can be used in catalysis, as inert solvents in electrochemistry, for polymer synthesis, and in the adaptation of enzymatic reactions to organic media. ILs can also be used to replace water in chemical or technical processes (Zhou, *et al.*, 2004).

The synthesis and processing of nanoparticles consisting of metallic nanocrystal cores and organic monolayer shells promise interesting technological applications (Zhou, *et al.*, 2003). In recent years, optical nanoprobe have been developed by modifying the surface of gold nanoparticles with various functional molecules. Gold nanoparticles have tremendously high molar absorptivity in the visible region (Endres, *et al.*, 2002). Particle aggregation results in further color changes of gold nanoparticle solutions due to mutually induced dipoles that depend on antiparticle distance and aggregate size. Gold nanoparticle aggregation-induced analytes have been demonstrated for DNA, several metal ions (Welton, 2004). Although ionic liquids have found application only recently in chemistry, they are an old class of substances: the first description of an IL with a melting point of 128 °C was published in 1914 (Sheldon, *et al.*, 2001). The most extensively studied ILs is the 1-alkyl-3-methylimidazolium salts. Newer systems include species with additional functionality, for example, long-chain amphiphilic ILs with both lyotropic and thermo tropic liquid crystallinity. Organic reactions can be conducted with increased selectivity in these ILs. Other liquid crystalline species with wide phase regions and a very high dipole moment and polarizability are described by (Itoh, *et al.*, 2004).

In this study, we will not focus on the use of ILs in catalysis and organic/inorganic synthesis, as there are already excellent reviews and books available. Instead we will describe recent developments in which the advantages of ILs for materials chemistry and especially for the synthesis of novel nanostructures have been gradually realized.

### **IONIC LIQUIDS FOR THE SYNTHESIS OF NANOSTRUCTURES**

First, ILs was used in electrosynthesis: various metallic nanoparticles, such as palladium, iridium, and

semiconductor nanoparticles such as stable Ge nano-clusters have been synthesized. The preparation of Ti nanowires onto graphite by electroreduction as described by (Frey, *et al.*, 2003) is exciting but still requires final proof. In all of these examples the large operation window for electrochemical reactions and the high polarity of ILs are exploited. Very fine and stable noble-metal nanoparticles can also be synthesized in ILs by chemical reduction (Kubisa, 2000). The colloidal system metal-nanoparticle/IL-stabilizer is extraordinarily stable and no ligands are required; extraordinarily high turnover numbers are achieved with this system in catalytic hydrogenation. Besides the large electrochemical window, other advantages of ILs can be considered (Welton, 2004):

I) Although polar, ILs can have low interface tensions which in addition seems to adapt to the other phase (e.g. for 1-butyl-3-methylimidazolium tetrafluoroborate the  $\gamma = 38 \text{ mNm}^{-1}$  against air). Since low interface tensions result in high nucleation rates, very small particles can be generated which undergo Ostwald ripening only weakly.

II) Low interface energies for larger objects can be translated into good stabilization or solvation of molecular species. Obviously, the IL structures “adapt” too many species, as it provides hydrophobic regions and a high directional polarizability which is oriented parallel or perpendicular to the dissolved species. Put simply: reactions in ILs are like reactions in a pure “universal” ligand.

III) Owing to the high thermal stability of ILs, reactions can be conducted at temperatures well beyond 100°C in nonpressurized vessels.

IV) ILs facilitates inorganic synthesis from very polar starting materials under ambient conditions and under anhydrous or water-poor conditions. In this way, hydroxide or oxihydrate formation and the coupled generation of amorphous species can be suppressed, as low amounts of water drive the mass balance to completely condensed systems, which are usually directly crystalline.

V) The most important advantage of ILs, however, is an unconventional and very rare property that cannot be emphasized sufficiently: ILs form extended hydrogen bond systems in the liquid state and are therefore highly structured. ILs is therefore “supramolecular”

solvents. Solvent structuration is the molecular basis of most molecular recognition and self-organization processes, with water being the most prominent and pronounced example. This special quality can be used as the “entropic driver” for spontaneous, well-defined, and extended ordering of nanoscale structures.

### **SOL-GEL REACTIONS IN WATER-POOR IONIC LIQUIDS**

First work on inorganic sol–gel reactions focused on the formation of silica aerogels. It turned out that such aerogels can be dried without a supercritical drying procedure (Kubisa, 2000). This again speaks for a very low interface tension of the binary system and coupled low capillary forces. It is, however, even more interesting to make crystallizable species by sol-gel reactions in water-poor reaction media. Zhou *et al.* (2003) hydrolyzed titanium tetrachloride in 1-butyl-3-methylimidazolium tetrafluoroborate with some reaction water (water-poor conditions) in a low-temperature synthesis (at 80 °C). Anatase powders consisting of 2-3 nm-sized particles and with surface areas of 554 m<sup>2</sup>/gr were obtained, which assembled to larger, spherical sponge like superstructures. These experiments look simple but they illustrate the multiple advantages of ILs. First, sol-gel reactions in water usually provide amorphous titania, which has to be calcined above 350 °C to result in the desired crystalline anatase. This usually prevents direct employment of anatase in organic/inorganic hybrid systems (Sheldon, *et al.*, 2001). Also, the nucleation rate of titania in the bulk is rather low (usually particles with diameters of ca. 20 nm are obtained). The IL solvent therefore not only facilitates direct synthesis of crystalline species under ambient conditions, it also increases the nucleation rate by more than a factor of 1000, owing to its low interface energy and adaptability. Only with this combination is the delicacy of the resulting structures possible (Zhou, *et al.*, 2003). The anatase obtained has a sponge like structure with high surface area and narrow pore-size distribution, and due to its increased volume it is easy to handle. This material is expected to have potential in solar energy conversion, catalysis, and optoelectronic devices, for example, for the potential one-step synthesis of dye-sensitized titania solar cells. IL-based quasi-solid-state electrolytes were just recently

employed for such regenerative photoelectrochemical cells and yielded %7 energy efficiency, but nanostructure synthesis still took place by classical means (Zhou, *et al.*, 2004). In another synthetic application Nakashima and Kimizuka (2003) reported the preparation of TiO<sub>2</sub> hollow microspheres in ionic liquids by means of a so-called interfacial sol-gel reaction.

The strong surface binding of ILs onto various nanoparticles was employed by Itoh *et al.* (2004), who showed that hydrophilic and hydrophobic properties of gold nanoparticles can be tuned by exchange of anions in the IL moiety. Backed by the same set of advantages of ILs as a reaction medium, microwave-assisted syntheses of single-crystalline tellurium nanorods and nanowires have been recently reported. Solvent self-structuration and supramolecular effects become important when reactions are conducted with higher concentrations of inorganic reactant. Even standard ILs such as the 1-butyl-3-methylimidazolium tetrafluoroborate gives nicely nanostructured gels (Zhou, *et al.*, 2003). The reaction of silica gave a sponge like, bicontinuous phase with a characteristic length of 5 nm. NMR and Raman spectrometry indicated the IL molecules spontaneously form a double layer by binding to silica. This sounds unusual for such a small molecule but just reflects the very strong tendency of the ILs to form extended hydrogen-bonding networks, in this case an undulating two-dimensional structure (Welton, 2004). The liquid structure of ILs and their mixtures with other solvents are probably organized in a similar fashion. The self-organization of ILs can be supported by using amphiphilic species with a longer hydrophobic tail (Zhou, *et al.*, 2004). Again, due to a combination of hydrogen-bonding networks and polarity contrast (amphiphilicity), very well-organized lyotropic phases are obtained for both the pure RTILs as well as their mixtures with water, oils, and reactants. This tolerance of self-organization against loading is again very unusual, and even in water it is found only for some special surfactants that form microemulsions (Sheldon, 2001).

### **THE EFFECT OF WATER**

The role of extra water in ILs is complex and depends on the supramolecular structure of the ionic liquid. It seems to be safe to state that its structure and chemical

reactivity is far from that of bulk water, as it is tightly bound and activated in the H-bonding system of the IL. As a result reactions with water take place quite rapidly in these systems. On the other hand, water cannot function here as a solvating ligand since it is too involved in IL binding; this was deduced, for instance, from the absence of so-called solvent pores (Zhou, *et al.*, 2004). This is a quite singular situation for colloid chemistry and material synthesis. Water modifies the patterns of IL self-organization, and this is why the structural outcome of such reactions depends strongly on the water content. The peculiar self-aggregation behavior of the IL/water system is evident by comparing two sol-gel-derived IL-silica hybrid materials, prepared with varying amounts of water, but the same ratio of IL to silica (Welton, 2004). These results demonstrate that ILs can also be applied in water-rich media. Here, they only play the role of a classical surfactant, however, with a very strong tendency towards self-organization with high order. The combination of polymer latexes and amphiphilic ILs in water-rich media as templates for porous silica indeed led to bimodal structures where both typical textures coexisted. The resulting supermicroporous opals were discussed as optical sensor elements where reflection contrast depends critically on the absorption of trace amounts of organic molecules (Nakashima and Kimizuka, 2003).

## CONCLUSIONS

Ionic liquids (ILs) have presented as green revolution in chemical industries and academic studies. ILs can reduce the chemical waste and improve the safety of processes. They can also solve a large number of polar, non-polar, organic and inorganic components. In this study, We suppose that ILs will find, in addition to organometallic synthesis, catalysis, and electrochemistry, a fourth area of application the synthesis of nanostructured solids, either to make nanoobjects (e.g. particles and fibers) or for the design of nanopores and nanochannels in solids. The unique combination of adaptability towards other molecules and phases plus

the strong H-bond-driven solvent structure makes ionic liquids potential key tools in the preparation of a new generation of chemical nanostructures.

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