

Inorganic Materials Synthesis – a Bright Future for Ionic Liquids?

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Materials Science goes back to prehistoric times, where people started to utilize rocks, bones, leather, and other things they found in Nature to fabricate tools and clothing. Later, this knowledge evolved and metals, alloys, ceramics, and fabrics replaced the older materials with inferior properties. In historic times, the knowledge of materials and processing improved further and more sophisticated materials for more sophisticated (or fashionable) applications became available.

An example of a historic high-tech material is Damascus Steel, which is responsible for the extraordinary sharpness of historic sword blades from the Middle East. No European blacksmith at the time was able to produce anything that came even close to the blades of the Damascus swords. In the mid 19th century, the knowledge of how to make those blades apparently got lost. Only very recently, Verhoeven and colleagues have been able to fabricate blades that appear to be comparable to the historic materials. It turns out that many of the superior properties of the metal blade come from its highly sophisticated processing, microstructure, and chemistry, including a variety of impurities like C, V, Mo, Cr, Mn, and Nb.¹

Much more recently, “nano” has become the new hot topic in materials science. The common theme here is always “size matters” and over the last decades, researchers have developed exciting new materials with unique and tunable properties. For example, Brust et al.^{2,3} have in the early 1990s triggered an immense interest in gold nanoparticles, which is reflected in

the dramatic increase in publications and patents with this topic, Figure 1. The interest in nanostructured inorganic and organic/inorganic composite materials has further grown to now include other metallic, alloy, and inorganic nanoparticles, assemblies, 2D and 3D structures, and many more.

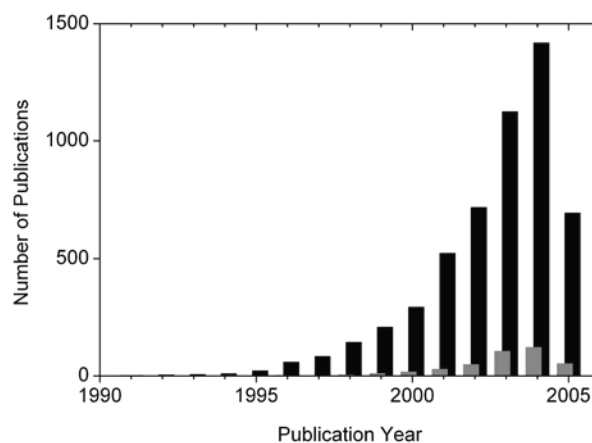


Figure 1. Results of a Chemical Abstracts (SciFinder) search on numbers of publications containing the term “gold nanoparticles” from 1990 to 2005. Black columns represent the total number of publications and gray columns the corresponding patents. Data for 2005 are obviously not complete yet, but on a good way to top 2004. Date of the search was June 2, 2005.

Unlike metals, alloys, and other inorganic materials that have historically been very important, ionic liquids (ILs) are a topic of the present times. ILs are

Biographical Sketch



Andreas Taubert obtained a Diploma in Chemistry from the University of Basel in 1997 working with W. Meier. From 1997 to 2000 he was a graduate student at the Max-Planck-Institute for Polymer Research in Mainz with G. Wegner. During his thesis he spent some time in the lab of D.C. Martin at the University of Michigan and from 2000 to 2003 he worked with K.I. Winey at the University of Pennsylvania. After returning to Basel he established a small research group focusing on organic/inorganic hybrid materials, especially on biologically inspired materials. A second line of research is devoted to using ionic liquids for the fabrication of inorganic materials with defined structures and properties.

essentially salts that are liquid at room temperature. Classical examples are the AlCl_3 -based systems or the imidazolium ILs. Originally, ILs have attracted interest as reaction media for organic reactions, for extraction, and for electrochemistry.⁴ Recently, ILs have also been explored with respect to their potential as reaction media for the fabrication of inorganic matter.^{5–15} These developments have also recently been reviewed.¹⁶

Thinking about the outcome of the experiments published so far, we may now ask ourselves: realistically, what is the potential of ILs for materials synthesis compared to other (established) procedures? Can ILs make a difference to the average materials chemist?

It is very unlikely that ILs will entirely replace organic solvents or aqueous systems or gas phase processes for the fabrication of inorganic matter. However, ILs can in many cases add value to (inorganic) materials synthesis by providing a means to fabricate materials that are not otherwise available. Moreover, reactions in ILs are often much shorter or occur under milder conditions than in regular solvents. Some recent examples that illustrate the special role of ILs in inorganic materials chemistry shall be introduced and briefly discussed now.

The first examples show that ILs can be very efficient templates for inorganic materials synthesis. Nakashima et al.⁵ have shown that when titanium tetrabutoxide is dissolved in anhydrous toluene and injected into 1-butyl-3-methylimidazolium hexafluorophosphate under vigorous stirring, hollow titania microspheres form via an interfacial sol-gel reaction. In a similar approach, Jiang and Zhu have reacted Bi_2O_3 with $\text{Na}_2\text{S}_2\text{O}_3$ in IL/ethylene glycol mixtures that were heated up to 190 °C via microwave irradiation.¹⁴ The morphology of the obtained Bi_2S_3 nanorods could be tuned by simply adjusting the reaction times or temperatures.

Despite their differences, both approaches have the beauty that particles, which are not otherwise accessible or at least not as easily, can be made quickly and in a controlled and tunable manner. For comparison, a conventional synthesis of hollow TiO_2 spheres requires the fabrication of a suitable template, the precipitation onto this template, the removal of the template, etc. In the above examples however, the ILs act as very efficient, yet chemically simple, all-in-one systems for advanced materials synthesis. As a result, the advantages are in these cases overwhelmingly speaking for the use of an IL-assisted process and not for a conventional synthesis.

Several authors have pointed out that ILs act not only as a template, but that they also stabilize the formed structures. Antonietti and colleagues have shown that ILs are efficient solvent-templates for tuning the nanostructure of silica.^{6,7,17} They point out that the IL-templated materials do not contain the

typical “solvent pores” of regular sol-gel silica. As a result, the material exhibits a significantly increased mechanical stability compared to materials that were fabricated conventionally. ILs thus again provide a useful advantage over more traditional approaches. Figure 2 shows an example of a silica material that was fabricated with the help of an ionic liquid.¹⁶

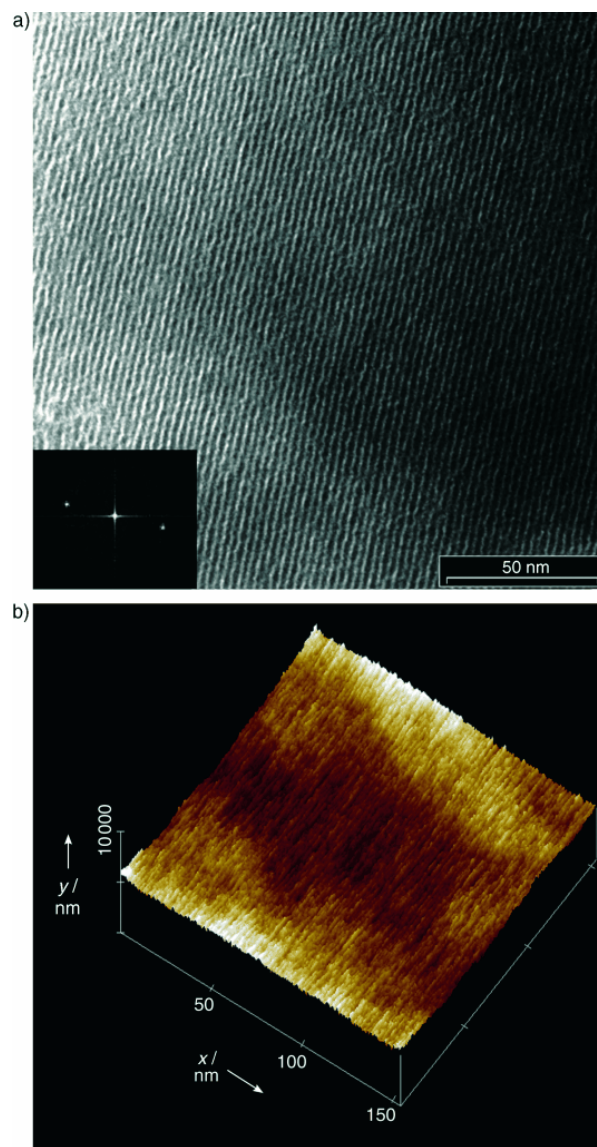


Figure 2. a) TEM image of porous silica prepared in a sol-gel reaction of 1-hexadecyl-3-methylimidazolium chloride at 40 °C. Inset: Fourier transform of the TEM image. b) AFM image of a surface of the same material. Images from ref.¹⁶ copyright Wiley-VCH 2004.

In some cases, ILs are even solvent-template-reactants. That is, their chemical structure is such that they do not only interact with an inorganic material that forms in the IL, but they are also part

of the reaction that leads to the inorganic material: we have recently found that a Cu-containing liquid crystal can act as a Cu source, as a solvent, and as a morphology-modifying template for the fabrication of CuCl nanoplatelets at the same time, Figure 3.¹²

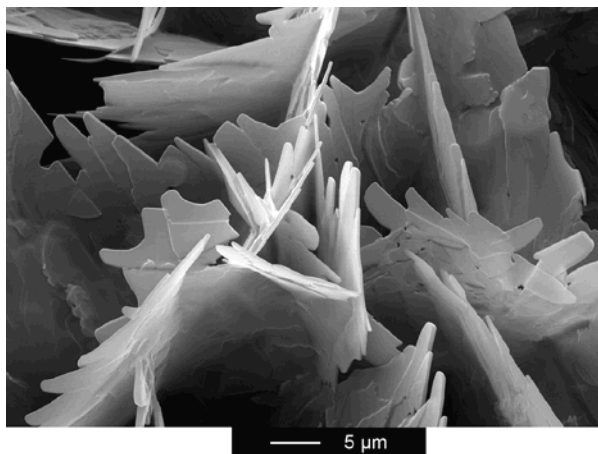


Figure 3. SEM image of CuCl nanoplatelets formed at 85 °C in an ionic liquid crystal that acts as reactant, solvent, and template at the same time.¹²

ILs have yet another effect on crystallization that is currently under investigation: they seem to lower nucleation energies¹⁵ and to have an influence on the selection of polymorphs of inorganic matter. Figure 4 gives an example from our laboratory showing polymorph selectivity. Calcium carbonate precipitation from aqueous CaCl₂ solutions without an IL but with rapid stirring affords micrometer-sized spherical vaterite particles. They are composed of nanometer-sized subunits and some of them are porous.

However, the precipitation of CaCO₃ in a water/IL emulsion containing 10% (v/v) of the hydrophobic IL 1-hexyl-3-methyl imidazolium tetrafluoroborate [HMIM][BF₄] yields the well known calcite rhombohedra. Moreover, an increase of the IL content to ca. 50% yields particles with a finely structured surface with features roughly on the order of 100 nm.

The details of this polymorph selection are currently under investigation as is the mechanism of surface structure formation. Nevertheless, these preliminary results already demonstrate that ILs can not only affect shapes of inorganic matter, but they can also act on different length scales *at the same time*: in the absence of an IL spherical (micrometer length scale) vaterite (Ångstrom length scale) particles that are composed of nm-sized subunits form. The addition of an IL yields rhombohedral (micrometer length scale) calcite (Ångstrom length scale) crystals with a surface structure on the 100 nm scale.

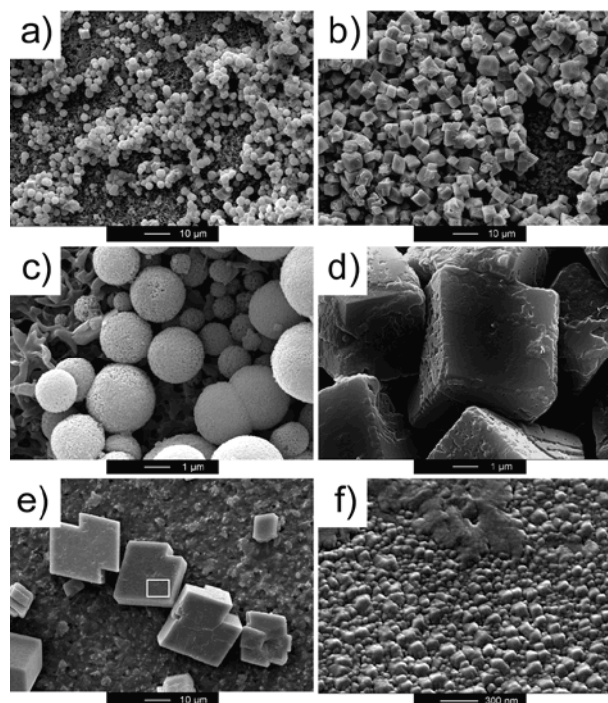


Figure 4. SEM images of CaCO₃ precipitated from IL/water emulsions. a, c) control sample precipitated without IL at 1500 rpm. b, d) CaCO₃ precipitated in the presence of 10% (v/v) HMIM][BF₄] at 1500 rpm. e) CaCO₃ precipitated at ca. 50% (v/v) [HMIM][BF₄] and 1500 rpm. f) High magnification image of the surface of a crystal (frame in Fig. 3e).

The common feature of the studies highlighted in this perspective article is precisely this: all examples clearly show that ILs add value to inorganic materials chemistry. They do so without overlooking the advantages and achievements of classical materials synthesis like additive-driven aqueous precipitation reactions. However, the unique adaptability and flexibility of ILs generates a niche that is potentially inaccessible for other synthetic protocols. ILs thus provide us with a new, flexible, and powerful tool for the fabrication of novel, interesting, and highly sophisticated nanostructures via chemical approaches.

Consequently, we can now go back to the title question: *inorganic materials synthesis – a bright future for ionic liquids?* What will the answer be? The answer will currently most likely be “yes, but ...”. As stated above, ILs will not replace other processes, but they can in many cases provide an attractive alternative or complementary synthetic protocol or an extension for very specific requirements. Time will tell exactly how successful this new and interesting approach of using ILs for materials synthesis will be.

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