Size controlled Preparation of Nanoparticles and safe-to-handle Nanoparticle Dispersions by the use of Ionic Liquids

Frank M. Stiemke, Adriana Willm, Thomas J. S. Schubert

IOLITEC Ionic Liquids Technologies GmbH, Salzstraße 184, Heilbronn, Germany, www.iolitec.de

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Introduction

Ionic Liquids (ILs) are a new class of materials, consisting entirely of ions, which are liquid at unusual low temperatures[1]. Typical structural motifs combine organic cations with inorganic or, more rarely, organic anions (Figure 1). The lower symmetry of the cations or anions and the delocalisation of the charge over larger parts of the ions by resonance are mainly responsible for the low melting points of ionic liquids. The manifold combinations of cations and anions provide a large number of liquid materials with (tunable) unique properties such as high conductivity, high thermal stability, negligible vapor pressure, non-flammability, good solubility of many inorganic precursor salts as a consequence of the tunable polarity of ILs and their tenside like character. As a consequence, this unique combination of properties makes ILs – among many other different applications - the media of choice for synthesis and dispersing nanoparticles[2].

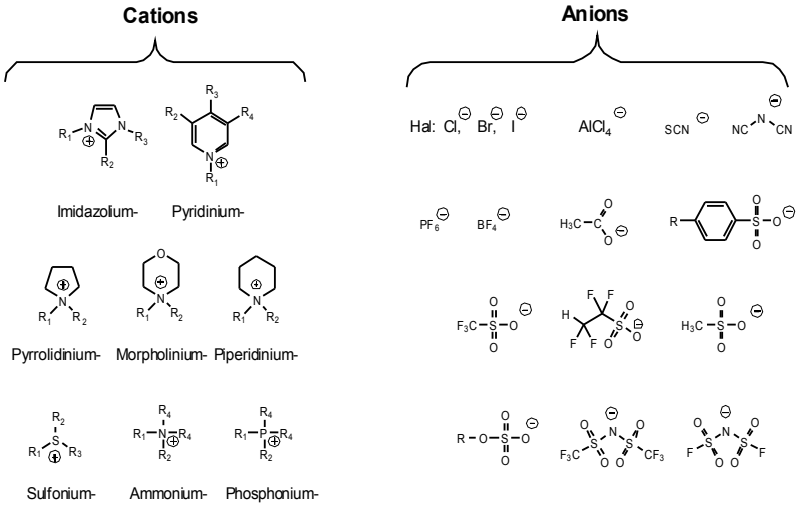

Figure 1: Examples of typical cations and anions.

Synthesis of Nanoparticles

The controlled and reproducible synthesis of metal nanoparticles (MNPs) is of great interest since many properties of MNPs relate directly to the size of these materials. Especially transition metal MNPs are of interest due to their application in many different areas of sciences, including catalysis or chemical sensing. MNPs can be synthesized in different ways including reduction of metal salts with hydrogen gas, electrochemical reduction or photochemical reduction.

Janiak et al. demonstrated the dramatic influence of the size of the ionic liquid ions on the size and size distribution of silver nanoparticles synthesized by the reduction of a silver salt AgX with

hydrogen gas in an ionic liquid and an alkylimidazole base as scavenger[3] for the emerging acids HX, which leads to a destabilization of the MNPs and clustering. Different Ag precursors were dissolved in dried ILs and reacted with hydrogen (4 atm, 85°C) in the presence of n-Butylimidazole in a stainless steel reactor in order to give Ag-IL-dispersions with Ag-particle less than 10 nm in size.

In addition, *Janiak et al.* synthesized other transition metal nanoparticles such as iron, ruthenium or osmium in ionic liquids by photochemical and thermal procedures of the respective metal carbonyl precursors[4].

The synthesis was performed by heating a mixture or suspension of the metal carbonyl precursors in 1-butyl-3-methyl-imidazolium tetrafluoroborate (BMIM BF_4) under argon up to 250°C for several hours or by irradiation at 200-450 nm for 15 min. Extremely small and uniform MNPs were received as stable dispersions in the ionic liquid in all cases. The nanoparticles produced by photolysis were somewhat larger than those produced by thermolysis due to faster decomposition and growth of the particles in the ionic liquid.

Stabilization of Nanoparticles

Dispersions in general are interesting for the easy and the even more important safe handling of nanoparticles, also with the background of uncertainties concerning their specific toxicity. It is e.g. assumed that some particles can cause cancer like asbestos. Due to this reason it is crucial to avoid any type of nanoparticle contamination. Stable IL-based dispersions of these materials will overcome these drawbacks: they are not dusty, non-volatile, non-inflammable and can be designed to be biodegradable.

IOLITEC succeeded in dispersing MWCNTs with same size in diameter but different length (5-15 µm and 1-2 µm) in water by using a suitable IL and treatment with ultrasound. The stabilizing effect of the IL is extremely obvious if the dispersions are stressed by centrifugal forces. If no or an unsuitable additive was added, the dispersion will collapse even at low centrifugal force impact (Figure 2, on the right) and sediments will be obtained.

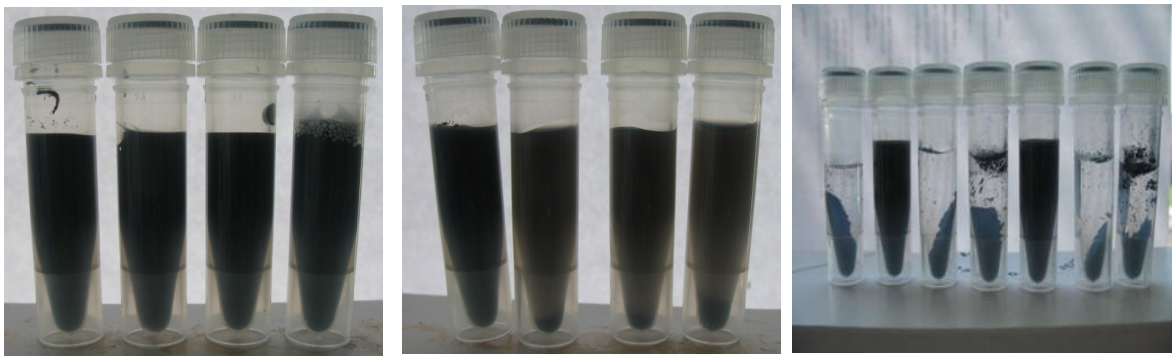

Figure 2: Four MWCNT-dispersions in water (left); dispersions after 20'000 rcf, 5 min (middle); dispersions without or with suitable IL after 5'000 rcf, 1 min (right)

Samples of prepared dispersion were analyzed by Photon Cross Correlation Spectroscopy (PCCS) which allows analysis of particles in the range of 1 nm – 1 µm using the principle of dynamic light scattering. Furthermore, measurements can be conducted often without any dilution or even at opaque samples. This is possible due to the 3D-measurement setup with two independent crossbred lasers and detectors allowing to detect the decay of light intensity and elimination of multiple scattered light (Figure 3). At the same time information about particle size and stability of the dispersion can be obtained from the measured correlation functions of the decays of the light intensity.

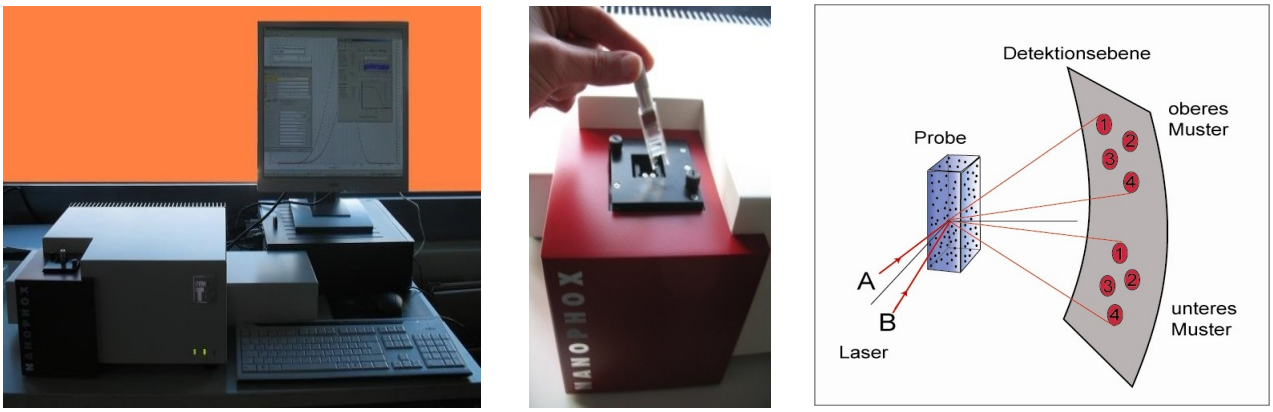

Figure 3: NANOPHOX®, [5], scheme of setup

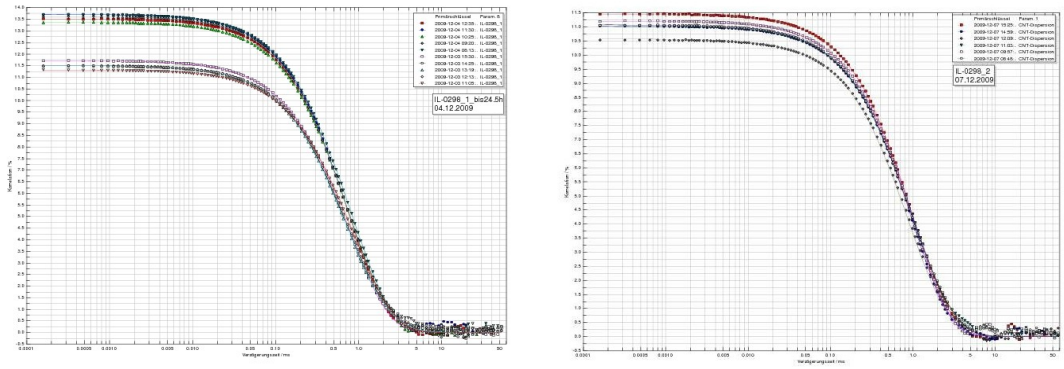

Figure 4: Stability measurements of dispersions of long (left) and short (right) MWCNT in water

In Figure 4 decays of several repeated individual measurements can be seen for long MWCNTs (left) and short MWCNTs (right) with same diameter. It is obvious that the curves are not stacked one by another following the order of measurement (see colors) - this would be the case for unstable dispersions - but the amplitudes of the curves alter around a certain value statistically. The two sets of decays in Figure 4 (left) are not the result of an unstable dispersion, but the consequence of a laser readjustment during the 24 h measurement time. Accordingly, the sample of dispersed long MWCNTs (0.5%wt in water) is a very stable dispersion.

The stability analysis of the second sample (short MWCNTs, 0.5%wt in water) results in statistical distributed correlation functions (Figure 4, right). Although in this case a stabilizing effect of a suitable ionic liquid as dispersing additive (a few mol% based on particle concentration) can be seen and a very stable dispersion is obtained.

Conclusions

Ionic liquids are suitable solvents for the size controlled synthesis of metal nanoparticles. By variations of the anions different particle sizes and size distributions can be obtained. The dispersion of nanomaterials by using ionic liquids as additives leads to very stable, easy and safe-to-handle dispersions. This procedure is not limited to CNTs or water, but is rather applicable to different other particles or solvents, also the stability measurement by PCCS.

References

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