Ionic Liquids - Novel Tenside like Materials for size controlled Preparation of Nanoparticles and safe-to-handle Nanoparticle Dispersions

Dr. Thomas J. S. Schubert*, Dr. Tom F. Beyersdorff**, Dr. Frank Stiemke*

*IoLiTec Ionic Liquids Technologies GmbH, Heilbronn, Germany
**IoLiTec Ionic Liquids Technologies Inc., Tuscaloosa, AL, USA

ABSTRACT

Ultra small Ag and Ru nanoparticles with a narrow size distribution have been synthesized in ionic liquids using reductive, thermal or photochemical conditions. The influence of the ionic liquid on the size of the nanoparticles has been investigated. In addition stable dispersions of different kinds of MWCNT in water have been prepared by the addition of ionic liquids as novel tenside like materials to a mixture of the MWCNT in water. These dispersions have been characterized by Photon Cross Correlation Spectroscopy (PCCS).

Keywords: ionic liquids, nanoparticles, dispersions

1 INTRODUCTION

Ionic Liquids (ILs) are a 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. 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].

2 SYNTHESIS OF NANO PARTICLES

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.

A problem that occurs during the reduction of metal salts MX_n with hydrogen gas is the formation of the corresponding acids HX, which leads to a destabilization of the MNPs and clustering. In order to prevent the MNPs from clustering a base has to be added to scavenge the HX byproducts.

Janiak *et al.* demonstrated the 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]. Different Ag precursors were dissolved in dried ILs and reacted with hydrogen (4atm, 85°C) in the presence of n-Butylimidazole in a stainless steel reactor.

Selected results for these experiments are summarized in Table1.

Table 1: Ag nanoparticle size and distribution from different precursors and ILs

Ionic Liquid	Scavenger	Silver Precursor	AgNP median (min-max diameter/nm)	Standard deviation
BMIM BF4	BuIm	AgBF4	2.8 (1.2-4.7)	0.8
BMIM PF6	BuIm	AgPF6	4.4 (2.0-9.8)	1.3
BMIM OTf	BuIm	AgOTf	8.7 (3.5-18.4)	3.4

From the results in Table 1 it is obvious, that the size of the anion in the ionic liquid has a dramatic influence on the particle size and the size distribution of the synthesized Ag nanoparticles. All synthesized Ag-IL-dispersions were stable under Argon over a period of at least 3 days.

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 BMIM BF4 under argon up to 250°C for several hours or by irradiation at 200-450nm for 15 minutes.

Selected results of these experiments are summarized in Table 2.

Table 2: Nanoparticle Size and Distribution in BMIM BF_4

NSTI-Nanotech 2010, www.nsti.org, ISBN 978-1-4398-3401-5 Vol. 1, 2010

Ionic Liquid	Metal carbonyl (wt % in IL)	Product	TEM median diam/nm (standard deviation *σ*)*c*
BMIM BF4	$Fe_2(CO)_9$ (0.2)	Fe	5.2 (±1.6)
BMIM BF4	$Ru_3(CO)_{12}$ (0.2)	Ru	1.6 (±0.4)
BMIM BF4	$Ru_3(CO)_{12}$ (0.08)	Ru	2.0 (±0.5)
BMIM BF4	$Os_3(CO)_{12}$ (0.2)	Os	2.5 (±0.4)

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.

3 STABILIZATION OF NANOMATERIALS IN IL

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 *nanomaterials* 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 and sediments will be obtained.

Samples of prepared dispersion were analyzed by Photon Cross Correlation Spectroscopy (PCCS)[5] 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. 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.

Decays of several repeated individual measurements for long and short MWCNTs with same diameter have been measured.

The sample of dispersed long MWCNTs (0.5%wt in water) is a very stable dispersion even over a period of 24 hours..

The stability analysis of the second sample (short MWCNTs, 0.5%wt in water) results in statistical distributed correlation functions. 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.

4 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

[1] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2007.
[2] T. J. S. Schubert, *Nachr. Chem.* **2005**, *53*, 1222.
[3] a) E. Redel, R. Thomann, C. Janiak, *Inorg.Chem.* **2008**, ***47***, 14-16. b) C. Janiak, E. Redel, M. Klingele, T. F. Beyersdorff, T. J. S. Schubert, DE102007038879.
[4] a) J. Kraemer, E. Redel, R. Thomann, C. Janiak, *Organometallics* **2008**, *27*, 1976-1978. b) C. Janiak, E. Redel, M. Klingele, T. F. Beyersdorff, T. J. S. Schubert, DE102007045878.
[5] Sympatec GmbH, www.sympatec.com