

Ionic Liquids as Novel Dispersing Agents for Nanoparticles:

Synthesis and Stabilization of Nanomaterials - Safe-to-Handle Dispersions

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ABSTRACT

Nanomaterials, in particular ultra small metal ones, become more and more interesting in numerous different technologies, e.g. printed electronics or energy applications. Ionic liquids (ILs) with their interesting profiles of physical and chemical properties allow the safe use as media for synthesis and dispersion of nanomaterials. 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 carbon allotropes (CNTs, graphenes) in various solvents have been prepared by the addition of ionic liquids as novel tenside like materials. These dispersions have been characterized by Photon Cross Correlation Spectroscopy (PCCS).

Keywords: dispersions, ionic liquids, nanomaterials, carbon nanotubes, graphenes

1 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 (Fig. 1). The lower symmetry of the cations or anions and the delocalization 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 and electrochemical stability, negligible vapor pressure, non-inflammability, 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 making ILs the media of choice for dispersing nanoparticles.^[2]

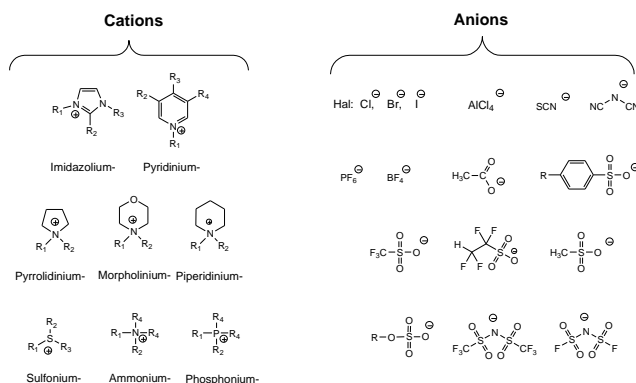


Fig.1. Examples of typical cations and anions.

2 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. In particular 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^[1].

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. Selected results for these experiments are summarized in Table 1.

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 BF ₄	BuIm	AgBF ₄	2.8 (1.2-4.7)	0.8
BMIM PF ₆	BuIm	AgPF ₆	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.^[2]

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 200-450 nm for 15 min.

Selected results of these experiments are summarized in Table 2.

Table 2. Nanoparticle Size and Distribution in BMIM BF₄.

Ionic Liquid	Metal carbonyl (wt % in IL)	Product	TEM median diam/nm (standard deviation σ) ^c
BMIM BF ₄	Fe ₂ (CO) ₉ (0.2)	Fe	5.2 (\pm 1.6)
BMIM BF ₄	Ru ₃ (CO) ₁₂ (0.2)	Ru	1.6 (\pm 0.4)
BMIM BF ₄	Ru ₃ (CO) ₁₂ (0.08)	Ru	2.0 (\pm 0.5)
BMIM BF ₄	Os ₃ (CO) ₁₂ (0.2)	Os	2.5 (\pm 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.

The work was carried on by Janiak *et al.*^[3] They have furthermore synthesized so called “naked” metal nanoparticles in Ionic Liquids without the addition of stabilizers. They used the microwave-activity of Ionic liquids including good energy uptake for heating the metal carbonyl precursor/IL mixture. As a consequence, easy and rapid microwave induced decomposition of metal carbonyls M_x(CO)_y in ILs occurs and MPs were formed.

3 DISPERSING NANOPARTICLES WITH IONIC LIQUIDS

Dispersions in general become more and more interesting for all kind of applications. Among the various nanoparticles the carbon allotropes like carbon nanotubes (CNTs), graphene or fullerenes play an increasing role in: e.g. energy applications for hydrogen storage^[4] or electrode materials for batteries^[5], OPV^[6] or printed electronics. But for all these applications long term stable and easy as well as safe to handle dispersions are of great importance in manufacturing processes, also with the background of uncertainties concerning the specific toxicity of certain nanoparticles (NPs). Currently it is e.g. under investigation if some types of nanotubes may cause cancer like asbestos.^[7] Due to this fact, it is an important issue to avoid any type of nanoparticle contamination. For this reason solutions or stable dispersions are needed. Since carbon allotropes are hardly soluble in most common solvents, it is usually necessary to synthesize cost-intensive chemical modifications of these particles to make them e.g. more hydrophilic. In addition, some of the original properties may be lost by using this method. By using these Ionic Liquids, which can be designed to have similar properties as the NP and to be environmentally friendly, the (Carbon-)NPs can be dispersed in different solvents without any chemical modification. Thus, stable IL-based dispersions of these nanomaterials will overcome the mentioned drawbacks: they are not dusty, non-volatile, non-inflammable and can be designed to be biodegradable

3.1 Choice of suitable dispersant

Ionic liquids are well known to have similar properties compared to surface active agents. Thus ionic liquids can be used as surfactants to stabilize aqueous and non aqueous dispersions of various nanopowders. For the preparation of a stable dispersion parameters like size and shape of nanoparticles, concentration of particle and solvent have to be taken into consideration. To identify suitable ionic liquids, we proceed as follows:

- pre-selection of ionic liquids by evaluation of Iolitec's database and consequential matrix-setup
- identification of lead-structures by screening processes
- modification of structures by rational design

Dispersions which are optically stable after ultrasound treatment are exposed to 20.000 rcf in a centrifuge for 1 min. Samples, which remain stable after this treatment, are analyzed by Photon Cross Correlation Spectroscopy (PCCS; SympaTec NANOPHOX®), which uses the principle of dynamic light scattering

3.2 Dispersion of carbon nanotubes

While using the above described method, 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 (Fig. 2, on the right) and sediments will be obtained.



Fig. 2. Seven MWCNT-dispersions in water (left); centrifuge (middle); dispersions without or with suitable IL after 20000 rcf, 1 min (right).

Samples of the prepared dispersions 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 detecting the decay of light intensity and elimination of multiple scattered light (Fig. 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.



Fig. 3: NANOPHOX®[®], setup-scheme.

In Fig. 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.

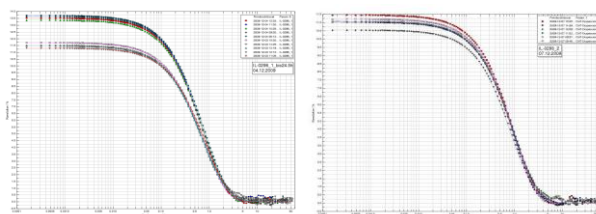


Fig. 4. Stability measurements of dispersions of long (left) and short (right) MWCNT in water.

The two sets of decays in Fig. 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 (Fig. 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.

3.3 Dispersion of Graphenes

Graphene with its extraordinary electronic, thermal and mechanical properties play an increasing role in energy applications: Graphene-composite materials are investigated for application in super-capacitors^[9], for photoelectrochemical solar cells and photocatalysis.^[10] Furthermore, graphenes are also interesting for applications like lubricants additives^[11] or in biosensing.^[12]

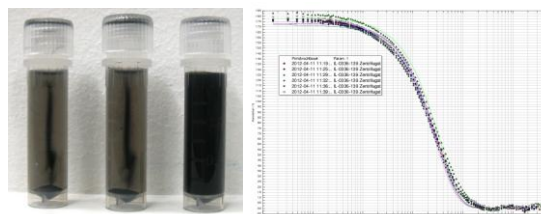


Fig. 5. Graphene dispersions in water after 20.000 rcf for 1 min (left); Stability measurements of graphene dispersion (right).

In our labs we have investigated the dispersion of nine different types of graphenes (diameter from less than 2 μm to 15 μm , thickness from 2 nm to 12 nm with surface areas from 60 to 750 m^2/g) in solvents like water and alcohols by using selected ILs and standard dispersing agents.

It was found that graphene no.9 having the highest surface area could be dispersed best in water by the IL-additive, and surprisingly well with standard agents, too. But by using the IL you can add more value to the

dispersions, in particular for non-low costs applications: additional conductivity of the dispersion due to the ionic structure of the IL is created. Furthermore, the non-volatile ILs remains on the particle surface even after evaporating the carrier fluid. Simple re-addition of the fluid and simple mixture often generates again homogenous and stable dispersions.

In Fig. 5, left, a selection of three different graphene dispersions in water after application for centrifugal forces of 20.000 rcf for 1 min is shown. Two of them immediately collapsed, while graphene no.9 remains completely dispersed due to the suitable dispersing agent. This sample was further investigated by PCCS. In Fig. 5 on the right can be seen the statistical distributed correlation functions of this sample with not decrease in altitude. This sample is identified as a very stable dispersion. Not until application of the highest centrifugal force for more the 20 min the dispersion starts to form sediments.

The same type of graphene was dispersed in a higher alcohol at 0.5 wt% concentration. By simple optical observation without applying centrifugal forces no changes of the dispersion quality could be observed. Even after 15 min at 20.000 rcf no sedimentation could be detected (Fig. 6). Dilution of this very stable dispersion with ethanol in different ratios does not have any influence on the stability of this solution.

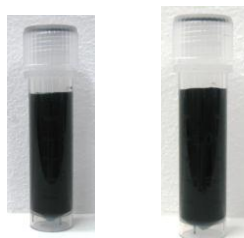


Fig. 6. Graphene dispersions in alcohol before (left) and after 20.000 rcf for 15 min (right).

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 solutions. This procedure is not limited to CNTs, graphenes or fullerenes, it can be applied also to other nanomaterials, e.g. to metal oxides. Furthermore, water, alcohols, common organic solvents or even Ionic Liquids themselves are suitable solvents for dispersing nanomaterials. The stability of the dispersions - for highly viscous carrier fluids dilution might be necessary - can be followed by PCCS measurements.

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