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PERSPECTIVE

Plasma electrochemistry in ionic liquids: an alternative route to generate nanoparticles

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In this perspective, the application of stable glow discharge plasmas as free electrodes for the generation of nanoparticles in ionic liquids is reported. The basic concepts of plasma electrochemistry as well as a few other concepts in this field will be presented. One focus is the interaction of the plasma with the ionic liquids itself and possible influences on the production process of the particles. Several examples of the plasma generation and characterisation of nanoparticles in ionic liquids will be presented. The starting point is thereby the generation of noble metals and at the end the efforts to synthesize semiconductor nanoparticles will be discussed. In all examples the benefits, the difficulties and the challenges of this method and the outcome for the future will be addressed.

Introduction

Ionic liquids open several opportunities to synthesize and stabilize metal nanoparticles and metal oxide particles without the addition of further stabilizing agents.^{1,2} One route to synthesize metal nanoparticles is the chemical reduction method. It was reported that by chemical reduction very fine and stable nanoparticles of Ir(0) and Rh(0) with 2.0 nm–2.5 nm diameter can be synthesized in the dry ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate from [Ir(cod)Cl]₂ (cod = 1,5-cyclooctadiene) and RhCl₃·3H₂O, respectively.³ After isolation, the nanoparticles can be re-dispersed in ionic liquids.³ Furthermore, the decomposition of Pt-organometallic precursors in 1-butyl-3-methylimidazolium hexafluorophosphate leads to stable Pt(0) nanoparticles with a narrow size distribution.⁴ However, purity issues have to be considered when liquids with PF₆⁻ or BF₄⁻ are used. Itoh *et al.* reported the synthesis and functionalization of gold nanoparticles modified by ionic liquids with imidazolium cations.⁵ One of the key physical properties is the very low vapour pressure which ranges at or near room temperature typically between 10⁻⁹ and 10⁻⁸ Pa and at 100 °C between 10⁻⁴ and 10⁻² Pa—depending on the particular liquid. This property opens the way to material synthesis routes in a controlled environment in ionic liquids. The application of ILs in vacuum for particle synthesis was highlighted in a recent paper by Kuwabata *et al.*⁶ For the particle generation in vacuum Torimoto *et al.* reported *e.g.* that very fine gold nanoparticles and even AuAg alloys can be obtained by sputter deposition of metals onto ionic liquid surfaces.^{7–9} The other possibility to

produce nanoparticles in ILs under reduced pressure is the plasma electrochemical way, where the plasma acts as a mechanically contact-free electrode. With this electrode it is possible to reduce dissolved metal species directly at the IL plasma interface. This method is quite old, as more than hundred years ago J. Gubkin ignited a plasma above an aqueous solution of silver nitrate,¹⁰ leading to silver formation at the water surface. Because of the high vapour pressure of water nowadays atmospheric-pressure microplasmas or plasma jets are used to generate colloidal metal nanoparticles in aqueous media.^{11,12} However, this method is more or less restricted to the generation of noble metal particles. In 1997 Janek and co-workers applied this technique to grow AgBr layers on the solid ion conductor AgCl.¹³ In 2007 we reported in cooperation with the Janek group for the first time that with the plasma electrochemical approach free, isolated silver nanoparticles can be obtained from silver salts dissolved in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate [BMIm]TfO.^{14,15} Due to their very low vapour pressure, ionic liquids are well suitable electrolytes for the plasma electrochemical processes, because compared to water it is much easier to obtain stable and homogeneous plasmas.^{16–18} This method was also successfully applied by the groups of Hatakeyama and Liu.^{14–24} As reduction *via* a plasma is facilitated by free electrons in the plasma phase, an electron beam may also be used for spatially focused reduction processes at the surface of ILs. This approach was indeed used for the synthesis of nanoparticles by Roy *et al.* and Imanishi *et al.*^{25,26} Both groups have used a scanning electron microscope or a scanning Auger electron microscope, respectively, for the formation of metal particles from ILs. In the following these in part different approaches of the plasma electrochemical method onto ionic liquids for the nanoparticle generation are presented and discussed.

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Experimental setups and the plasma IL interface

For an understanding and a comparison of the results it is important to introduce the different plasma cell concepts presented so far in the literature. Furthermore it is important to discuss a possible interaction of the plasma with the ionic liquid, because the resulting reaction products might be a source for impurities in the IL.

Most of the used setups are DC plasma reactors, where one electrode is placed in the liquid and the other one is placed above the liquid.^{14,19} In Fig. 1 (left image) a scheme of our setup is shown. Hatakeyama *et al.* described 2 operating modes for the DC setup.¹⁹ In the A-mode the electrode in the liquid acts as a cathode, in the B-mode this electrode acts as an anode. In the DC plasma experiments mostly argon is used as process gas. Xie and Liu used a DC plasma too, but in their case, both electrodes were in the gas phase and the liquid was placed in a quartz crucible located at the “positive column” of the glow discharge.¹⁸ Furthermore, they used a sub-atmospheric dielectric barrier discharge (SABDD) plasma as a reduction agent.²⁷ The third plasma type above an IL surface is the radio frequency discharge plasma.¹⁷

In Fig. 2 the plasma profiles of potentials in the plasma region and in the liquid (1-butyl-3-methyl-imidazolium tetrafluoroborate; [BMIm]BF₄) in (a) the A-mode and in (b) the B-mode are shown. This was measured by Hatakeyama *et al.* with a Langmuir probe and published in ref. 20. In the A-mode (an argon pressure of 40 Pa and a current of 1 mA) the discharge voltage (the potential at the cathode) is -290 V, therefore the potential in the IL is nearly the same. In the plasma region the potential is about -5 V, thus the potential difference between plasma and IL is 285 V. This electric field above the IL leads to acceleration of positive ions from the plasma towards the ionic liquid surface. In the B-mode the potential in the IL is 0 V and the resulting potential difference is 5 V, too. The voltage drop occurs at the cathode where electrons are emitted and consequently accelerated, finally

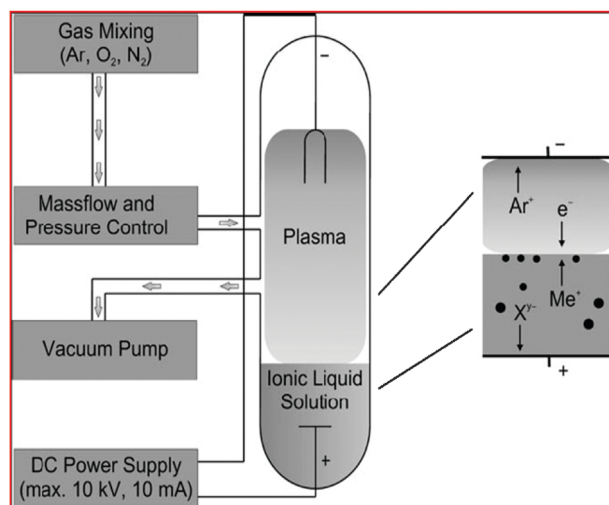


Fig. 1 Schematic experimental setup and the plasma-electrochemical reduction of a metal-containing salt in a liquid solvent (B-mode).¹⁴ Figure from ref. 14. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

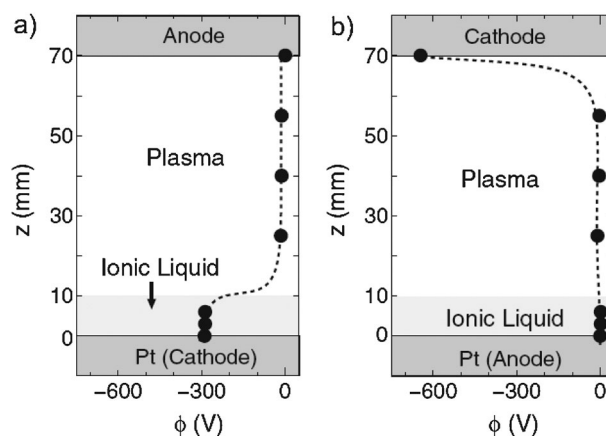


Fig. 2 Axial profiles of the space potential (Φ) in the plasma region and the floating potential in the ionic liquid in (a) the A-mode and (b) the B-mode.²⁰ Figure from ref. 20. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

hitting the ionic liquid surface. In the same paper it was shown that the ionic liquid itself acts as the cathode electrode in the A-mode. This was proved in an additional experiment, where they compared the plasma properties from a plasma cell with and without liquid.²⁸ They found that in the A-mode secondary electrons are emitted more efficiently compared to a stainless steel and a nickel electrode. In both modes there is no remarkable increase of the ionic liquid temperature, as in the experiments by Liu *et al.* The question arises, if there is an influence of the plasma mode on the ionic liquid itself. For the A-mode it was shown that there is a strong colour change in the liquid.^{17,19–21} With optical emission spectroscopy in the gas plasma the methylidyne radicals (CH) were observed.^{20,27} This can be explained by the dissociation of the alkyl chain of the [BMIm] cation, furthermore the dissociation of the IL is enhanced with increasing ion energy. Hatakeyama found no colour change in the B-mode. In contrast we found that there is a colour change of 1-butyl-3-methylimidazolium dicyanamide ([BMIm]dca) and of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py_{1,4}]Tf₂N) after the plasma process.^{22,23} Thus, a reaction has occurred during the electron IL interaction. Unfortunately, neither IR nor XPS deliver any reliable information on the reaction products, and NMR investigations for plasma treated [Py_{1,4}]Tf₂N performed at TU Clausthal also show no changes in the NMR spectra compared to the pure liquid. Independent of the different liquids employed we had slightly higher discharge currents (5–10 mA compared to the 1 mA from Hatakeyama *et al.*) and a slightly higher pressure (100 Pa compared to pressure > 80 Pa). Xie and Liu did also not report (using their setup) any decomposition of [BMIm]Cl, [BMIm]BF₄ and [BMIm]PF₆ solutions during plasma treatment as analyzed with IR spectroscopy and NMR.¹⁸ The corresponding FTIR spectra before and after the plasma treatment are shown in Fig. 3 for these three liquids (assigned structures of the imidazolium cation are marked in the figure; further details to the peak assignment can be found in ref. 18 and the references there in). It is visible that all peaks representing cations and anions have not changed after the interaction of the plasma with the liquids. In our opinion more detailed investigations are

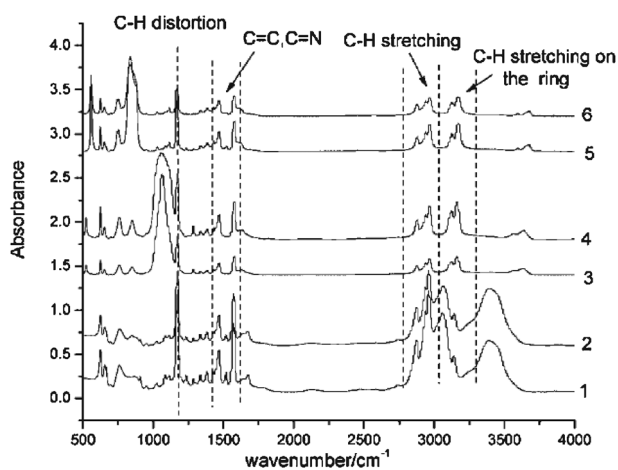


Fig. 3 FTIR spectra of the ionic liquids [BMIm]Cl (1, 2), [BMIm]BF₄ (3, 4) and [BMIm]PF₆ (5, 6) before (odd numbers) and after the plasma treatment (even numbers).¹⁸ The peaks assigned to the imidazolium cation are marked with dashed lines. The peak representing the BF₄⁻ anion can be found at 1062 cm⁻¹ and the peak for the PF₆⁻ anion at 835 cm⁻¹.¹⁸ Figure from ref. 18. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

needed for the understanding of the reaction processes of either the electron or the plasma ions with the ionic liquids. These results have then to be compared with the existing concept for radiation chemistry in ionic liquids.²⁹

It is of particular interest to study the interaction of the electrons with the ILs, because from pulse radiolysis measurements it was suggested that aromatic cations, especially imidazolium based cations, serve as electron trapping centres during radiolysis resulting in the formation of neutral radicals and radical ions.^{30,31} Additionally we showed in cooperation with Krischok *et al.* that there is an influence of non-monochromated AlK α X-rays on the surface composition of the ionic liquid [EMIm]Tf₂N.³² These results suggest that the [Tf₂N] anion is more subject to a beam damage than the imidazolium cation. In γ -ray irradiation experiments of [BMIm]Tf₂N Le Rouzo *et al.* found an opposite behaviour.³³ There the cation loss rate (2.8×10^{-7} mol J⁻¹) after a dosage of 2 Megagray (MGy) is slightly higher than the loss rate of the anion (2.2×10^{-7} mol J⁻¹). In addition they showed that the cation loss rate depends on the chosen anion. However, as stated above for the plasma experiments in the B-mode, only reaction products from the imidazolium cation could be found, and until now, there is no information on the influence of the plasma on the anion. Hints for an interaction could be found in a TOF-SIMS study of [EMIm]Tf₂N, using He⁺ ions with an energy of 2 keV.³⁴ Here smaller fragments of the Tf₂N anion were observed, too. The possible influence on these effects for the material synthesis will be addressed in the following section.

Synthesis of nanoparticles

In general, with all plasma setups discussed here it is possible to synthesise metal nanoparticles. Hatakeyama *et al.* generated gold nanoparticles from HAuCl₄·3H₂O/[BMIm]BF₄, platinum and palladium nanoparticles from PtCl₂/[BMIm]BF₄ and

PdCl₂/[BMIm]BF₄ solutions, respectively.^{19,20} Xie and Liu produced gold and palladium from HAuCl₄·3H₂O (PdCl₂)/[BMIm]BF₄.¹⁸ We ourselves showed that silver nanoparticles can be made from AgNO₃ and AgCF₃SO₃ in [BMIm]TfO and [Py_{1,4}]TfO.^{14,15} The synthesis of copper nanoparticles was successful in [EMIm]Tf₂N, [Py_{1,4}]Tf₂N and [BMIm]dca.^{22,23} Due to the low solubility of copper species in [EMIm]Tf₂N and [Py_{1,4}]Tf₂N, Cu⁺ was dissolved electrochemically in the liquids. A major disadvantage is the low amount of copper introduced (62 mmol L⁻¹) by this method, whereas no other ions are involved in the reaction process. In [BMIm]dca CuCl and CuCl₂ can be easily dissolved in high amounts, but chlorine evolution occurs as a side reaction. In Fig. 4 the temporal evolution of the plasma electrochemical generation of copper particles in [EMIm]Tf₂N/Cu Tf₂N is shown (B-mode). It is clearly visible that the reaction starts directly at the plasma IL interface and with time the reaction products are growing downwards the cell, whereas the rest of the liquid remains clear. At the anode some small bubbles are formed, which is likely to be due to a decomposition of the liquid at the anode of the cell.

The main technique to determine the particle sizes is transmission electron microscopy (TEM) and in the case of ionic liquids the particle sizes can be measured directly in the IL due to its very low vapour pressure. Thus, secondary reactions during separation of the particles from the IL can be avoided. This is especially important for the particles made from reactive metals. As a disadvantage a detailed analysis of the particles structure is hindered by an IL film around the particles. We summarize now shortly the determined particle sizes reported in the literature. In general, all particles exhibited sizes of well below 100 nm. The Au particles from Hatakeyama *et al.* have sizes around 60 nm and those from Liu 32 nm in the "same" liquid.^{18,20,21} The shapes of the particles range from spherical to hexagonal.¹⁹ Gold particles made with the (SADB) plasma

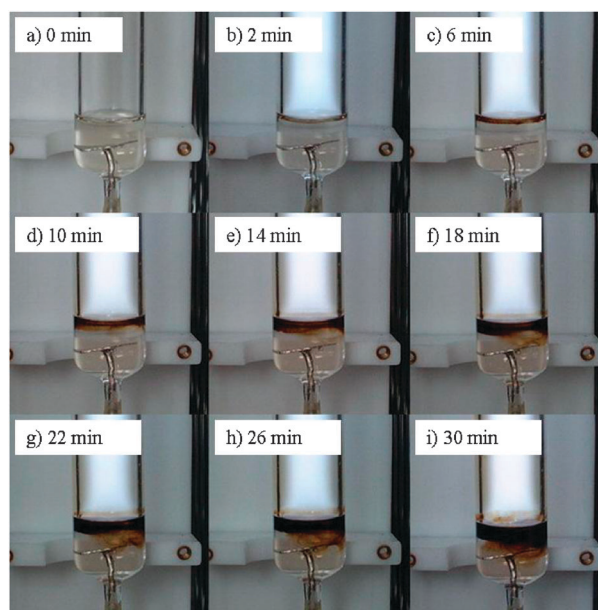


Fig. 4 Temporal evolution of the plasma electrochemical reduction (30 min) of Cu⁺ in [EMIm]Tf₂N. Figure from ref. 22 reproduced with permission of the PCCP Owner Societies.

in [BMIm]BF₄ had an average size of 1.7 nm.²⁷ Pt particles exhibited a diameter of 1–2 nm and Pd particles had a mean diameter of around 5 nm.^{18,20,21} In the case of silver the particles had an average size of 30 nm.¹⁴ The copper particles made in [EMIm]Tf₂N (B-mode) are smaller compared to the ones made in [Py_{1,4}]Tf₂N (roughly 10 vs. 20 nm),²² whereas the diameter of copper particles in [BMIm]dca is between 2 and 10 nm (B-mode too).²³ Thus an influence of the plasma on the particle size is likely.

Indeed, Hatakeyama *et al.* found that the particle sizes and the obtained amount depend on the plasma mode. With the A-mode, where ions interact with the liquid, the particles are smaller and the amount was higher compared to B-mode.^{19–21} Apparently the resulting hydrogen radicals from the imidazolium cation reduce the dissolved gold species more efficiently than the electrons. This effect can be enhanced by replacement of the argon with H₂.¹⁹ The higher amount was attributed to the higher penetration depth of the ions compared to the electrons and the resulting higher reaction rate of hydrogen radicals. Tsuda *et al.* found a similar influence of the ionic liquids on the particle generation process in γ -ray experiments.³⁵ Here irradiation of the ionic liquids 1-butyl-3-methylimidazolium Tf₂N and 1-methyl-1-propylpiperidinium Tf₂N with high energy electron beams (4.8 MeV accelerated energy with a beam current of 10 mA) and γ -rays (irradiation dose: 6 or 20 kGy in both cases) leads to the formation of gold particles whereas in tributylmethylammonium ([Bu₃MeN])Tf₂N no particle formation was found. They suggested that radiochemically unstable ILs tend to produce nanoparticles.³⁵ In contrast γ -ray experiments at higher dosages (2 MGy) from Bossé *et al.* and Le Rouzo *et al.* showed that the cation loss rate in [Bu₃MeN]Tf₂N is higher than that in [BMIm]Tf₂N.^{33,36} Therefore not only the stability of the ions in general has to be taken into account but also the formed degradation products have to be investigated. As mentioned above, from pulse radiolysis measurements it was suggested that aromatic cations, especially imidazolium based cations, serve as electron trapping centres during radiolysis resulting in the formation of neutral radicals and radical ions.^{30,31} These radicals, formed from plasma electrons or from γ -radiolysis, can either reduce the solvated metal ions, too, or hinder the reduction process. This argument is also true for hydrogen atom radicals interacting with ILs. An example for the influence of radiation products on the particle formation in ILs is the work of Chen *et al.*³⁷ Here gold nanoparticles were prepared under γ -radiation in a 0.1 mM HAuCl₄ quaternary ammonium-based ionic liquid [Me₃NC₂H₄OH]Zn₂Cl₅ solution. They suggested that the solvated electrons, generated from γ -radiolysis, reduce first the zinc from Zn²⁺ to Zn⁺ and this Zn⁺ reduces then the gold ions to gold. In addition J. F. Wishart pointed out in his perspective paper that solvated electrons react very fast in ILs with imidazolium cations compared to liquids with ammonium ions where the electrons react very slow.²⁹ These observations could be an explanation for the missing gold particles in [Bu₃MeN]Tf₂N of Tsuda *et al.* These results support again the need for a detailed knowledge on the stability of the ionic liquids and the resulting products during ion irradiation. An overview on the interaction of ionic liquids with ionizing radiation can be found in the perspective paper by J. F. Wishart.²⁹

Interestingly, the generation of palladium was not possible in the B-mode, what Hatakeyama *et al.* attributed to the low amount of dissolved PdCl₂ in [BMIm]BF₄.²⁰ In the case of copper in [BMIm]dca we ourselves attributed the smaller particle size compared to copper in [EMIm]Tf₂N and [Py_{1,4}]Tf₂N mainly to the strong reaction of the plasma with the CuCl, respectively, CuCl₂ in [BMIm]dca,²³ leading to chlorine evolution. Most likely the gas evolution (leading to an intermixing of the liquid) causes a fast removal of the particles from the reaction zone, which prevents a further growing of the particles. Hydrogen formation as mentioned above either due to water dissociation or decomposition of [BMIm]dca can be excluded, as the interaction of the plasma with the pure liquid exhibits no gas evolution at all. In addition these copper experiments have shown no difference in the particle sizes due to the number of reduction steps. The published data from other groups and ours do currently not allow to comment on a general trend of the particles size dependency on the individual ionic liquid and the kind of the plasma mode. In addition the reactions at the electrode in the liquid have to be unveiled as well as a possible influence on the particle formation. Our own results with Cu nanoparticles furthermore suggest that the viscosity plays an important role for the particle size, because the particles were slightly larger in the more viscous liquid [Py_{1,4}]Tf₂N.²² On the other hand we know from classical electrodeposition experiments in ionic liquids that just the change of the cation can change the crystallite size in the deposit. For example, the deposition of aluminium from AlCl₃ in [Py_{1,4}]Tf₂N leads to nanocrystalline deposits, whereas in [EMIm]Tf₂N a microcrystalline deposit is obtained,^{38,39} although the Al species are virtually identical.³⁸ One future option might be to change the viscosity of the IL by increasing the temperature. Additionally a higher temperature might make it possible to enhance the amount of the produced particles.

Besides the particle size it is important to get insight in the chemical composition and the crystallinity, especially in the case of the “reactive” particles. The method of choice is X-ray diffraction (XRD). Unfortunately a high amount of particles is often needed. To some extent it is possible to determine the crystallinity by TEM, provided the IL film around the particles is thin or the particles were separated from the liquid. Xie and Liu found for their Au and Pd particles that they are crystalline.¹⁸ The silver particles made by us were also crystalline after the plasma process,¹⁴ showing that with plasma it is possible to receive crystalline nanoparticles.

Information on the chemical composition can be obtained by X-ray photoelectron spectroscopy (XPS), especially as in the last few years XPS was used to investigate the ionic liquid interface directly.⁴⁰ We found for the particles separated from [EMIm]Tf₂N, [Py_{1,4}]Tf₂N and [BMIm]dca that in all cases the particles are oxidized to CuO.^{22,23} This oxidation is in our opinion due to a surface attack during the intensive *ex situ* treatment as Cu nanoparticles are quite reactive. The Pd particles from Liu *et al.* are to some extent oxidized, too. In the case of copper in [EMIm]Tf₂N it was possible to inspect the particles directly in the liquid with XPS. Again the particles were oxidized in the surface region to CuO. We cannot exclude an oxidation process during the plasma

process, but we have to take into account the transport time to the XPS facility. In addition we found a strong enrichment of the electrochemically dissolved copper species in the near surface region of the [EMIm]Tf₂N.⁴¹ Such enrichment behaviour can play a role in the particle growth process.

With XPS it is also possible to get information about the interaction of the liquids with the particle. Scheeren *et al.* found with XPS for isolated Pt particles made by chemical reduction in [BMIm]BF₄ and [BMIm]PF₆ different fractions of fluorine around the particles.⁴² As both liquids are pretty unstable in air/water liberating HF a chemical reason cannot be excluded. Moreover they found the different chemical oxidation states (Pt(0), Pt²⁺ and Pt⁴⁺). Besides the oxidation of platinum they claim that these different fractions and states are due to an interaction of the IL with the metal surface. With small-angle X-ray scattering (SAXS) they supported this assumption, because anionic supramolecular aggregates were found around the Pt particles.⁴² These aggregates were attributed as a protective layer around the particles. In the case of the gold nanoparticles generated by Chen *et al.* (see above) the quaternary ionic liquid with ammonium ions can act as an effective stabilizer.³⁷ For the copper particles made in [Py_{1,4}]Tf₂N compared to those in [EMIm]Tf₂N we found a similar behaviour of different fractions of residues on the particles.²² We suggested that [Py_{1,4}]Tf₂N is more strongly adsorbed on these particles than [EMIm]Tf₂N. A detailed investigation of the surface condition of the particles generated by plasma in the ILs is missing until now. In conclusion these results show how important it is to use a combination of several methods to gain information on the interaction of ILs with the particles and the change of the ILs itself. From our point of view it is important to ensure liquid quality as impurities might segregate at the surface of the particles. Adding other organic molecules with functional groups, like thiols, as possible stabilizers is not straightforward, because these additional molecules can also interact with the electrons from the plasma. Thus the plasma process or other radiation induced processes in ILs might become more complicated.

The next question is if it is possible to make semiconductor nanoparticles directly in ionic liquids with the plasma approach. Semiconductor nanoparticles have interesting properties like for example a size dependent band gap. Our own studies showed that nanoscale silicon and germanium films can be electrodeposited in different ionic liquid solutions from SiCl₄, SiBr₄ and GeCl₄.^{43–45} Unfortunately, due to the high vapour pressures of these common semiconductor precursors most of the dissolved compound is pumped out of the liquid during the outgassing and the following plasma process. To suppress the high vapour pressure of SiBr₄ (~1000 Pa at RT) we started with the more viscous [Py_{1,4}]Tf₂N. With this mixture we found no hints of particle formation in the liquid. In our opinion during the outgassing process before the plasma experiment all SiBr₄ was removed. Therefore we did experiments with SiI₄ dissolved in [Py_{1,4}]Tf₂N, as the vapor pressure of SiI₄ is low enough to avoid outgassing during the experiment. At first we tried to electrodeposit pure silicon from this solution on Au(111). This step was important because there is no information available on the electrochemistry of SiI₄ in [Py_{1,4}]Tf₂N. With SiI₄ in [Py_{1,4}]Tf₂N it was indeed possible

to deposit a film consisting of particles. EDX showed that this film consists mainly of silicon and oxygen. This complete oxidation could be due to the *ex situ* treatment of the film, but this is in contrast to our results for silicon films from SiCl₄ in [Py_{1,4}]Tf₂N,^{43,44} where it was possible to obtain pure silicon films. Fig. 5a presents the plasma experiment for the SiI₄/[Py_{1,4}]Tf₂N solution. The left image shows the solution before the experiment. During the plasma interaction a colour change of the solution is visible and a precipitate appears in the liquid. The corresponding SEM and TEM images are shown in Fig. 5b. Particles in the 20 nm regime are visible. Unfortunately the particles could not be separated from the liquid. Together with the electrodeposition results, that also did not give evidence for elemental Si, we think that we produce non-stoichiometric Si_xI_y compounds during the plasma process. Such compounds could be easily dissolved in solvents like acetone which we use for the separation of the particles from the ionic liquid. To overcome this problem for a proof of principle we used the GeCl₂-dioxane complex (GeCl₂C₄H₈O₂) as a precursor for our plasma experiments. We dissolved 0.1 mol L⁻¹ of the GeCl₂-dioxane complex in [EMIm]Tf₂N. Before the experiments, the solution was characterized with cyclic voltammetry (CV), and the CV of the liquid with the complex shows that it is easy to electrodeposit germanium from such suspensions. In Fig. 6a the plasma experiment (B-mode) with the GeCl₂-dioxane-[EMIm]Tf₂N suspension is shown.²⁴ The upper image shows the pure 0.1 M suspension. It is clearly visible that during plasma interaction (*ca.* 30 min) the liquid changes from milky to an orange colored liquid. The colorization starts at the plasma ionic liquid interface. It seems that the plasma interaction leads to better solubility of the complex in the surface region.

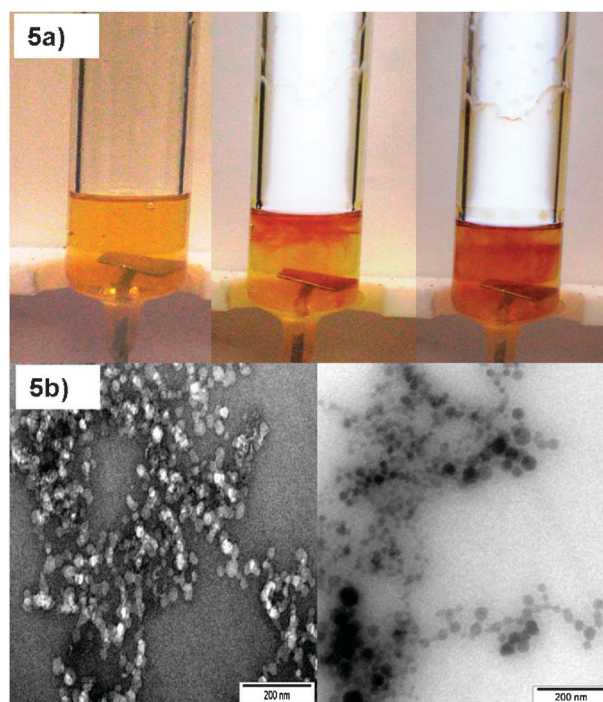


Fig. 5 (a) Plasma experiment (30 min) SiI₄/[Py_{1,4}]Tf₂N, (b) SEM and TEM images of Si_xI_y particles from SiI₄/[Py_{1,4}]Tf₂N.

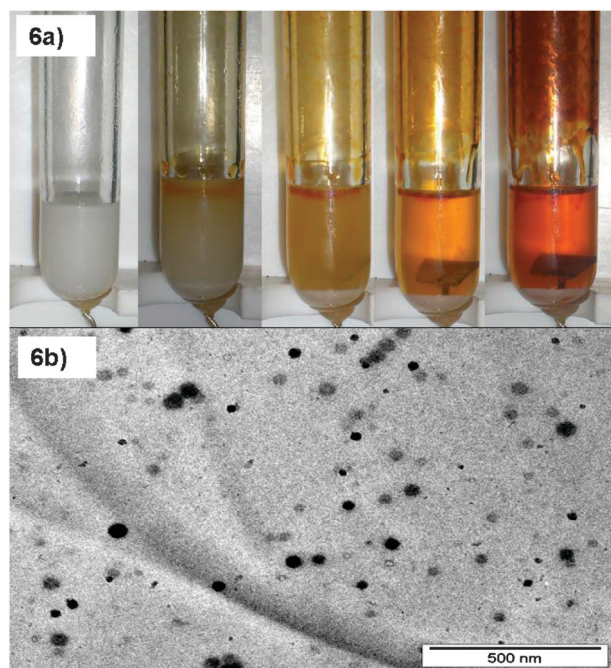


Fig. 6 (a) Plasma experiment (30 min) GeCl_2 -dioxane/[EMIm]Tf₂N, (b) TEM image of Ge particles from GeCl_2 -dioxane/[EMIm]Tf₂N. Reprinted from ref. 24. Copyright 2011, with permission from Elsevier.

Whether this phenomenon is caused by a slight temperature increase or due to the interaction of the complex with the plasma is not clear at the moment. In the lower figure the corresponding TEM measurement is shown. Here particles smaller than 50 nm are observable (see Fig. 6b). A similar colour effect was observed during the electrodeposition of $\text{Si}_x\text{Ge}_{x-1}$ films,⁴⁵ where the films consist of different particles with variable sizes (around 2–20 nm) and due to the film growth the colour changed from red to blue–green. This change in colour was attributed to the absorbing of different wavelengths from the visible spectrum, because the particles exhibit different band gaps. We might explain the different colours observed here by a size-dependent quantum effect, too. We can conclude that the formation of semiconductor particles with a plasma is in principle possible. The high vapour pressure of typical semiconductor precursors is limiting. A backdoor could be the SADBD approach from Liu, because this method works at sub-atmospheric and even at atmospheric pressures. Thus the experiments are independent of the vapour pressures of the dissolved species. With this approach it could be possible to use the electrochemically well characterized SiCl_4 or SiBr_4 for the plasma electrochemical experiment.

Conclusion and outlook

This perspective was intended as an introduction in plasma electrochemistry. We showed that with the plasma electrochemical approach it is possible to generate metal nanoparticles in ionic liquids with different sizes. So far all groups started with noble metals, as a proof of principle. In addition the growth of copper nanoparticles and even the possibility of

the generation of semiconductor particles were demonstrated. Comparing all available data, there are strong indications that the kind of the plasma and the used ionic liquid play a role for the particle size, although currently there is no trend visible which property has the major influence on the growth and on the chemical composition of the more reactive particles. Moreover until now it is not clear if Dupont and Scholten are right with their statement in a recent review “*Electrochemical reductions of metal compounds in ILs are likely the cleanest methods for preparing metal NPs since only electrons are involved*”,¹ because the interaction with ions and with the electrons from the plasma is leading to a certain amount of beam damage of the ILs. Due to this damage residues remain in the liquid and have a possible positive or negative influence on the reduction process. For the A-mode plasma this damage is essential for the reduction process. In addition we found with XPS more residues of the liquid, which showed more beam damage, on the surface of the isolated particles.

In contrast, the physical and chemical properties of ILs, like the very low vapour pressure, make these liquids easily accessible to different kinds of analytical methods, like *e.g.* vacuum-based methods, without major problems. Due to the usual temperature stability of ILs experiments at elevated temperatures are also feasible. Consequently it should be possible to get more insight in the plasma ionic liquid interaction process and in the subsequent nucleation and growth. For the semiconductor experiments it is furthermore important to get species with very low vapour pressure and the plasma range has to be expanded to atmospheric plasmas. A first step was done by Liu *et al.* with the introduction of the SADBD plasma. In future these kinds of plasmas could be very interesting for industrial applications, because no vacuum is needed.

In another way, the properties of ionic liquids could lead to interesting new kinds of experiments with plasmas or just electron beams. For example Rutten *et al.* wrote images in a frozen ionic liquid with SIMS.⁴⁶ This way could be extended to create nanostructures by reducing metal ions with a focused ion or electron beam. It was already shown that with a SEM it is possible to produce metal particles on a surface. The use of templates is a further way for nanostructures. Hatakeyama *et al.* have impregnated carbon nanotubes with dissolved Au (Pd) chloride in an ionic liquid and exposed them to plasma; with that template assisted method nanoparticles in the range of 2 nm were produced.^{21,47} These examples show clearly that in the future interesting new results with different ionic liquid plasma experiments can be expected.

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References

- J. Dupont and J. D. Scholten, *Chem. Soc. Rev.*, 2010, **39**, 1780–1804.
- T. Torimoto, T. Tsuda, K. Okazaki and S. Kuwabata, *Adv. Mater.*, 2010, **22**, 1196.
- G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira and J. Dupont, *Chem.–Eur. J.*, 2003, **9**, 3263.
- C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner and S. R. Teixeira, *Inorg. Chem.*, 2003, **42**, 4738.
- H. Itoh, K. Naka and Y. Chujo, *J. Am. Chem. Soc.*, 2004, **126**, 3026.
- S. Kuwabata, T. Tsuda and T. Torimoto, *J. Phys. Chem. Lett.*, 2010, **1**, 3177.
- T. Torimoto, K. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka and S. Kuwabata, *Appl. Phys. Lett.*, 2008, **89**, 243117.
- T. Suzuki, K. Okazaki, T. Kiyama, S. Kuwabata and T. Torimoto, *Electrochemistry (Tokyo, Jpn.)*, 2009, **77**, 636.
- K. Okazaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata and T. Torimoto, *Chem. Commun.*, 2008, 691.
- J. Gubkin, *Ann. Phys. (Leipzig)*, 1887, **32**, 114.
- C. Richmonds and R. Mohan Sankaran, *Appl. Phys. Lett.*, 2008, **93**, 131501.
- H. Furusho, K. Kitano, S. Hamaguchi and Y. Nagasaki, *Chem. Mater.*, 2009, **21**, 3526.
- J. Janek and C. Rosenkranz, *J. Phys. Chem. B*, 1997, **101**, 5909–5912.
- S. A. Meiss, M. Rohnke, L. Kienle, S. Zein El Abedin, F. Endres and J. Janek, *ChemPhysChem*, 2007, **8**, 50.
- S. Zein El Abedin, M. Pölleth, S. A. Meiss, J. Janek and F. Endres, *Green Chem.*, 2007, **9**, 549.
- J. Janek, M. Rohnke, M. Pölleth and S. A. Meiss, *Plasma electrochemistry with ionic liquids*, in *Electrodeposition from Ionic Liquids*, ed. F. Endres, D. MacFarlane and A. Abbott, Wiley-VCH, Weinheim, 2008, p. 259.
- K. Baba, T. Kaneko and R. Hatakeyama, *Appl. Phys. Lett.*, 2007, **90**, 201501.
- Y. B. Xie and C. L. Liu, *Plasma Processes Polym.*, 2008, **5**, 239.
- K. Baba, T. Kaneko and R. Hatakeyama, *Appl. Phys. Express*, 2009, **2**, 035006.
- T. Kaneko, K. Baba, T. Harada and R. Hatakeyama, *Plasma Processes Polym.*, 2009, **6**, 713.
- T. Kaneko, K. Baba and R. Hatakeyama, *Plasma Phys. Controlled Fusion*, 2009, **51**, 124011.
- M. Brettholle, O. Höfft, L. Klarhöfer, S. Mathes, W. Maus-Friedrichs, S. Zein El Abedin, S. Krischok, J. Janek and F. Endres, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1750.
- N. Kulbe, O. Höfft, A. Keppler, S. Zein El Abedin, S. Krischok, J. Janek, M. Pölleth and F. Endres, *Plasma Processes Polym.*, 2011, **8**, 32–37.
- A. A. Aal, R. Al-Salman, M. Al-Zoubi, N. Borissenko, F. Endres, O. Höfft, A. Prowald and S. Zein El Abedin, *Electrochim. Acta*, 2011, DOI: 10.1016/j.electacta.2011.02.063.
- P. Roy, R. Lynch and P. Schmuki, *Electrochem. Commun.*, 2009, **11**, 1567.
- A. Imanishi, M. Tamura and S. Kuwabata, *Chem. Commun.*, 2009, 1775.
- Z. Wie and C. L. Liu, *Mater. Lett.*, 2011, **65**, 353–355.
- T. Kaneko, K. Baba and R. Hatakeyama, *J. Appl. Phys.*, 2009, **105**, 103306.
- J. F. Wishart, *J. Phys. Chem. Lett.*, 2010, **1**, 3225–3231.
- I. A. Shkrob, S. D. Chemerisov and J. F. Wishart, *J. Phys. Chem. B*, 2007, **111**, 11786.
- I. A. Shkrob and J. F. Wishart, *J. Phys. Chem. B*, 2009, **113**, 5582.
- A. Keppler, M. Himmerlich, T. Ikari, M. Marschewski, E. Pachomow, O. Höfft, W. Maus-Friedrichs, F. Endres and S. Krischok, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1174.
- G. Le Rouzo, C. Lamouroux, V. Dauvois, A. Dannoux, S. Legand, D. Durand, P. Moisy and G. Moutiers, *Dalton Trans.*, 2009, 6175.
- J. Günster, O. Höfft, S. Krischok and R. Souda, *Surf. Sci.*, 2008, **602**, 3403.
- T. Tsuda, S. Seino and S. Kuwabata, *Chem. Commun.*, 2009, 6792–6794.
- E. Bossé, L. Berthon, N. Zorz, J. Monget, C. Berthon, I. Bisel, S. Legand and P. Moisy, *Dalton Trans.*, 2008, 924.
- S. Chen, Y. Liu and G. Wu, *Nanotechnology*, 2005, **16**, 2360.
- P. Eiden, Q. X. Liu, S. Zein El Abedin, F. Endres and I. Krossing, *Chem.–Eur. J.*, 2009, **15**, 3426.
- N. M. Rocher, E. I. Izgorodina, T. Ruther, M. Forsyth, D. MacFarlane, T. Rodopoulos, M. D. Horne and A. M. Bond, *Chem.–Eur. J.*, 2009, **15**, 3435.
- K. R. J. Lovelock, I. J. Villar-Garcia, F. Maier, H.-P. Steinrück and P. Licence, *Chem. Rev.*, 2010, **110**, 5158.
- A. Keppler, O. Höfft, V. Kempter, F. Endres and S. Krischok, *J. Phys. Chem.*, submitted.
- C. W. Scheeren, G. Machado, S. R. Teixeira, J. Morais, J. B. Domingos and J. Dupont, *J. Phys. Chem. B*, 2006, **110**, 13011.
- F. Endres and S. Z. El Abedin, *Phys. Chem. Chem. Phys.*, 2002, **4**, 1649.
- S. Z. El Abedin, N. Borissenko and F. Endres, *Electrochem. Commun.*, 2004, **6**, 510.
- R. Al-Salman, S. Zein El Abedin and F. Endres, *Phys. Chem. Chem. Phys.*, 2008, **10**, 4650.
- F. J. M. Rutten, H. Tadesse and P. Licence, *Angew. Chem., Int. Ed.*, 2007, **46**, 4163.
- K. Baba, T. Kaneko, R. Hatakeyama, K. Motomiya and K. Tohji, *Chem. Commun.*, 2010, **46**, 255.