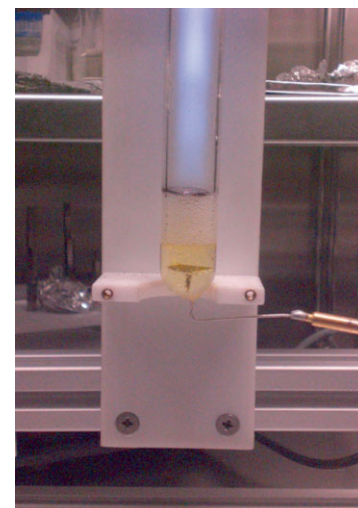


Plasma Electrochemistry in 1-Butyl-3-methylimidazolium dicyanamide: Copper Nanoparticles from CuCl and CuCl₂

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We report on the reaction of CuCl and CuCl₂, each dissolved in 1-butyl-3-methylimidazolium dicyanamide ([BMIm]dca), with a glow discharge argon plasma. The interaction of the plasma with the solutions exhibits a strong reaction with gas evolution and the growth of copper nanoparticles. The particle size was determined with transmission electron microscopy (from the particle/ionic liquid, IL solution). The chemical composition was investigated by ex situ X-ray photoelectron spectroscopy (XPS). We found that the mean diameter of the copper particles produced in CuCl/[BMIm]dca and CuCl₂/[BMIm]dca was in the same order of magnitude (between 2 and 10 nm). Despite the strong reaction we found no hints for IL degradation products in the liquids with infrared spectroscopy. XPS showed that ex situ treatment of the particles leads to the formation of CuO.



Introduction

Ionic liquids (IL) are well suited for the synthesis and stabilization of metal nanoparticles and metal oxide particles without the addition of stabilizing agents,^[1] a

result of their usually low surface tension in the 20–40 mN·m⁻¹ regime. They show a wide range of interesting chemical and physical properties like, for example very low vapour pressures which range at or near room temperature typically between 10⁻⁹ and 10⁻⁸ Pa and at 100 °C between of 10⁻⁴ and 10⁻² Pa – depending on the particular liquid. One possibility is to synthesize metal nanoparticles by chemical reduction. It was reported that by chemical reduction very fine and stable nanoparticles of Ir(0) and Rh(0) with 2.0–2.5 nm diameter can be synthesized in the dry IL 1-butyl-3-methylimidazolium hexafluorophosphate from [Ir(cod)Cl]₂ (cod = 1,5-cyclooctadiene) and RhCl₃·3H₂O, respectively.^[2] After isolation, the nanoparticles can be re-dispersed in IL.^[2] Furthermore, the decomposition of Pt-organometallic precursors in 1-butyl-3-methylimidazolium hexafluorophosphate, leads to stable Pt(0) nanoparticles with diameters between 2 and 3 nm having a narrow size distribution.^[3] Pt nanoparticles are recyclable catalysts for the solventless or biphasic hydro-

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generation of alkenes and arenes under mild reaction conditions. Itoh et al.^[4] reported the synthesis and functionalization of gold nanoparticles modified by IL with imidazolium cations. Due to their very low vapour pressures IL can be employed in vacuum experiments as fluid substrates or solvents. Torimoto et al. reported, e.g. that very fine gold nanoparticles and even AuAg alloys can be obtained by sputter deposition of metals onto ILs.^[5–7] In 2007 we reported for the first time that free, isolated silver nanoparticles can be obtained from silver salts dissolved in the IL 1-ethyl-3-methylimidazolium trifluoromethylsulphonate [EMIm]TfO by applying a plasma as a mechanically contact-free electrode.^[8,9] Due to their negligible vapour pressure, ILs are well suitable electrolytes for plasma electrochemical processes, and stable and homogeneous plasmas are obtained.^[10,11] In aqueous media plasma electrochemistry is possible too. Because of the high vapour pressure of water atmospheric-pressure microplasmas or plasma jets have to be used to generate colloidal metal nanoparticles.^[12,13] The plasma-electrochemical approach is hitherto the only electrochemical route to the synthesis of free nanoparticles. In aqueous media this method is, in contrast to ionic liquids, restricted to the generation of noble metal particles. In our case an argon glow discharge plasma was employed as a gaseous electrode and the other (solid) electrode was immersed in the IL containing the desired metal salt. This method was also successfully applied for the reduction of HAuCl₄ and PdCl₂ in 1-butyl-3-methylimidazolium tetrafluoroborate [BMIm]BF₄ by Xie and Liu.^[11] Hatakeyama and co-workers^[14] showed recently that not only the electrons from the plasma can reduce the dissolved metal species but also generated hydrogen atoms from the IL are able to conduct the reduction process. The second process is only possible if the anode is placed above the liquid surface.

In a recent publication, we presented the surprisingly complicated generation of copper nanoparticles in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulphonyl)amide ([Py_{1,4}]Tf₂N) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulphonyl)amide ([EMIm]Tf₂N).^[15] In the present paper we report on the synthesis of free, dispersed copper nanoparticles in the air and water stable IL, 1-butyl-3-methylimidazolium dicyanamide ([BMIm]dca), by employing plasmas as mechanically contact-free electrodes and using CuCl and CuCl₂ as precursors. Cu nanoparticles are interesting due to their catalytic and electrocatalytic properties. Nanocrystalline compact copper layers with an average crystallite size of about 50 nm can, e.g. be electrodeposited without additives in the IL [Py_{1,4}]TfO and in [Py_{1,4}]Tf₂N.^[9,16] Meanwhile, there is a lot of evidence in the literature that even slight variation in the ion structure (e.g. different alkyl chain lengths) can have an influence on the outcome of (physico-) chemical reactions.^[17] Furthermore, liquids with the dicyanamide

dissolve a range of metal halides quite well.^[18] For this reason we selected a liquid with the dca anion to dissolve CuCl and CuCl₂, respectively, and to investigate the plasma electrochemical deposition of Cu from both salts. As CuCl₂ can react with Cu to CuCl the Cu precursors might have an influence on the particle size.

Experimental Part

Preparation of the Samples

CuCl and CuCl₂ (Sigma–Aldrich, >99.999%) were dissolved in two concentrations (0.5 and 1 mol·L⁻¹) in [BMIm]dca (Iolitec: >98%). The IL was dried under vacuum for about 10 h at a temperature of 100 °C, to a water content of about 36 ppm (by Karl–Fischer titration) and stored in an argon filled glove box, with water and oxygen levels below 1 ppm (OMNI-LAB from Vacuum-Atmospheres). The liquids contain ~100 ppm of Cl⁻. Apart from that, they were not purified over Al₂O₃ or SiO₂ so that further inorganic impurities are excluded. The low amount of Cl⁻ will be complexed by CuCl_x. All solutions were characterized with cyclic voltammetry (CV) and X-ray photoelectron spectroscopy (XPS) before the plasma experiments. The CV of the liquid with either CuCl or CuCl₂ shows that it is easy to electrodeposit copper from these solutions. This is in a good agreement with our previous results and literature data obtained in [EMIm]dca.^[16,18,19] XPS shows, besides the expected elements, a small amount of oxygen. This might be due to some water content as liquids with dca absorb water rapidly. Consequently it is difficult to dry them below the 10 ppm level. Despite the water in the liquid, XPS provides no evidence for the well known disproportionation of CuCl to Cu and CuCl₂ usually occurring in water, as concluded from the absence of shake up structures indicative for Cu²⁺ in the Cu2p core level spectra (see Discussion Section). The setup for the particle production consists of a DC plasma reactor with a controlled argon atmosphere inside an inert gas glove box (OMNI-LAB from Vacuum Atmospheres). The argon for the plasma is taken directly from the glove box, thus it is of the highest quality. This glove box is also reserved for the plasma experiments, thus there are no contaminants in the atmosphere. The plasma reactor consists of a glass cell with usual KF vacuum connectors and is made of two parts which facilitates filling of the cell. One of the two platinum electrodes is fused in the cell, the other one is welded on a feed through flange. In our setup the electrode in the liquid serves in every experiment as the anode. The cell is evacuated with a common rotary pump. A photo of the cell can be found in ref.^[15] The plasma was ignited with a common DC power supply at a current of 10 mA and at a voltage 1 000 V, leading finally to stable voltages between 400 and 500 V. All experiments were done at room temperature (~20–22 °C).

Spectroscopic and Microscopic Measurements

The size of the copper particles was directly determined in the solution by transmission electron microscopy (TEM). The TEM used is a JEOL JEM-2100 and the acceleration voltage was 120 kV. For the TEM measurements a small drop of the IL with the produced nanoparticles was placed onto a TEM grid. The chemical composi-

tion of the used IL, with and without Cu, as well as that of the particles was analyzed *ex situ* with XPS. For the *ex situ* measurements the particles were separated by centrifugation and washed several times with acetone to remove most of the IL. After washing, the particles were put onto a carbon tape. The present experimental investigation was performed in a UHV chamber (base pressure $< 2 \times 10^{-10}$ mbar) using monochromated Al K α radiation ($h\nu = 1486.7$ eV) produced by a PHI 10-610 X-ray source (14 kV, 300 W) in combination with an Omicron XM1000 monochromator. The spectra were recorded with a hemispherical electron analyzer (Type EA125, Omicron) equipped with seven channeltrons. The emitted electrons were analyzed at an emission angle of $\Theta = 53^\circ$ with respect to the surface normal. The chosen pass energy was 50 eV in case of the survey spectra and 15 eV for the high resolution core level spectra. The operation conditions lead to a total energy resolution below 0.6 eV (FWHM of Ag3d $_{5/2}$ at a pass energy of 15 eV) and below 1.2 eV (pass energy of 50 eV) for the survey scan as deduced from measurements of a polycrystalline Ag sample, which was in addition used as a reference for determining the Fermi energy in the spectra. The survey spectra provide information on the chemical elements present in the near surface region (outermost 5–10 nm of the sample), whereas the better resolved scans of single peaks have been used for determining the stoichiometry and to determine the chemical/bonding states (here in particular of the Cu). The IR measurements on the liquids were carried out with a Bruker IFS 66v Fourier Transform Infrared spectrometer. The bulk sample was prepared by pressing a liquid droplet between two KBr pellets.

Results

Two to 3 ml of [BMIm]dca containing $0.5 \text{ mol}\cdot\text{L}^{-1}$ CuCl and $0.5 \text{ mol}\cdot\text{L}^{-1}$ CuCl $_2$, respectively, were put in the glass cell and carefully out-gassed at 0.1 Pa. Then the plasma was ignited at a pressure of 100 Pa at a current of 10 mA. In our experiments the electrode above the liquid acted as a cathode and the other one as an anode. Thus, electrons are accelerated to the surface of the IL. After ignition the voltage drops rapidly from 1 000 V to 450–500 V. Immediately after ignition a strong gas evolution sets in at the anode (mainly Cl $_2$). Therefore, the current was decreased to the minimum value of 1 mA, leading to just a low gas evolution. The pure liquid shows no gas evolution during interaction with the plasma, although a reaction with the plasma has to be expected, as the pure [BMIm]dca has changed its colour from clear to yellow after the plasma treatment. We observed this for [Py $_{1,4}$]Tf $_2$ N too, but not for [EMIm]Tf $_2$ N. It is still an open question how the plasma exactly interacts with ILs. The plasma experiments (30 min) for both solutions are shown in Figure 1a/b. In both cases the left image shows the solution before the experiment. With plasma the mentioned gas evolution sets in and on the bubbles/plasma interface a dark ring appears (middle picture). Due to intermixing (right picture) the whole liquid changes its colour in both cases. The CuCl solution changes its colour from yellow to brown and the CuCl $_2$ solution from

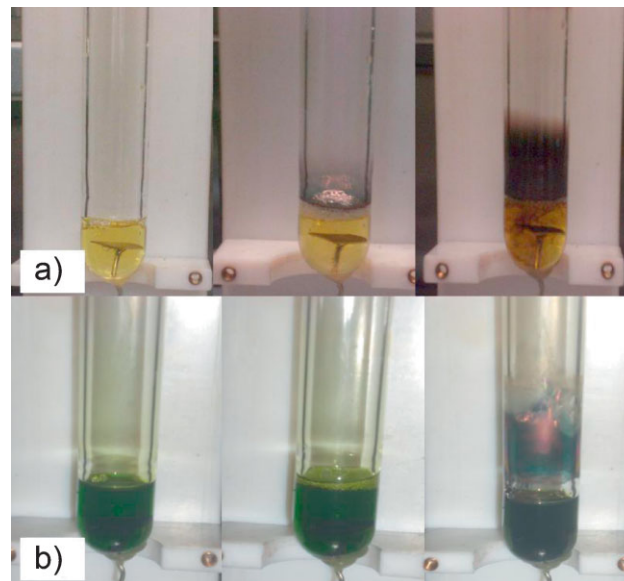


Figure 1. (a) Plasma experiment (30 min) CuCl/[BMIm]dca. (b) Plasma experiment (30 min) CuCl $_2$ /[BMIm]dca.

dark green to black. We attribute the appearance of the dark ring and the colour change mainly to the formation of copper nanoparticles at the liquid/plasma interface. Additionally, due to the outgassing process a thin film of the IL solution remains at the walls of the plasma cell, leading to a thin metallic film.

Figure 2a/b shows TEM images of the obtained copper nanoparticles inside both liquids ($0.5 \text{ mol}\cdot\text{L}^{-1}$ CuCl or CuCl $_2$). Small particles with an average size of about 6 nm are clearly seen. Unfortunately, a better resolution can currently not be achieved for the particles in the liquid and thus electron diffraction patterns cannot be obtained. This is due to the circumstance that the particles are covered by a thin film of the IL. Addition of solvents and the subsequent centrifugation lead to particle agglomeration which we wanted to avoid for this very fundamental study. The particles made from CuCl $_2$ seem to form groups. The size distribution functions of the particles from both $1 \text{ mol}\cdot\text{L}^{-1}$ solutions are shown in Figure 3. There are only small differences in the size distribution between the CuCl and the CuCl $_2$ containing liquids. The particles have diameters between 1 and 10 nm, and in some TEM images even sheets are visible. This might be due to a detachment of the above described metallic like film from the cell walls. The amount of the dissolved CuCl or CuCl $_2$ (0.5 or $1 \text{ mol}\cdot\text{L}^{-1}$) also does not seem to influence the particle size. This effect was also found by Chang et al. for the production of Ag nanoparticles in aqueous media with atmospheric plasmaelectrochemistry.^[20] Only the amount of particles slightly increases with increasing the concentration of CuCl and CuCl $_2$ in [BMIm]dca, respectively.

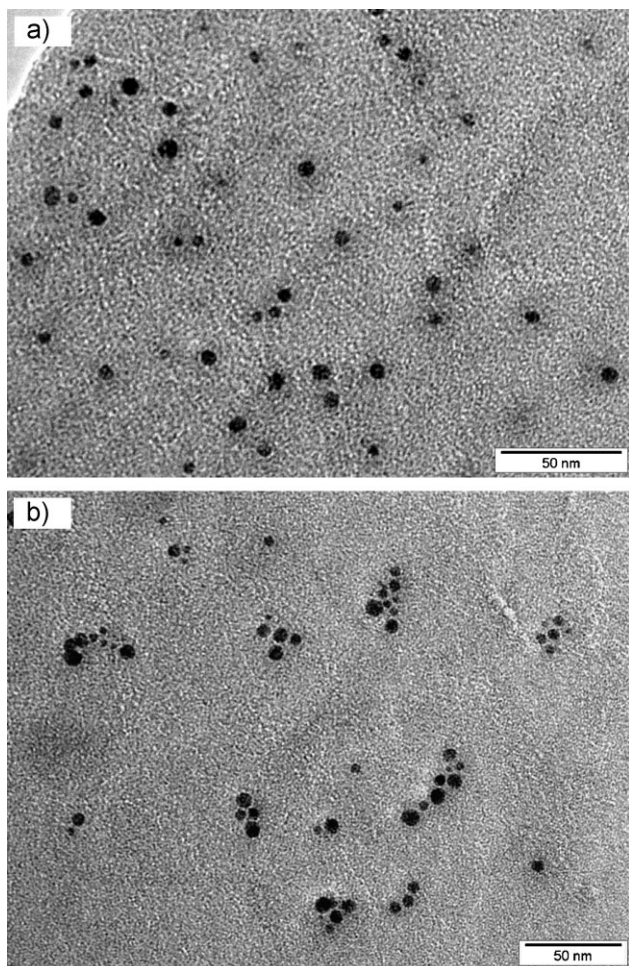


Figure 2. (a) TEM image of Cu particles from CuCl/[BMIm]dca. (b) TEM image of Cu particles from CuCl₂/[BMIm]dca.

An XPS analysis of a layer of particles obtained from the CuCl containing liquid reveals that the major spectral contributions consist of copper, carbon, oxygen, nitrogen and chlorine (see Figure 4). Nitrogen and chlorine are residues of the electrolyte. The carbon signal is to some extent also a residue of the IL, but mostly this is due to the used carbon tape as support. A detailed spectrum of the Cu 2p peak region of the particles is shown in Figure 5 (black curve). Due to charging the binding energy of the Cu 2p from the particles is shifted by 5.85 eV to lower binding energy. The Cu 2p peak region is comprised of four contributions with binding energies at 935 eV, around 943, 955 and 963 eV. The features at 935 and 955 eV are due the excitation from the Cu 2p_{3/2} and the Cu 2p_{1/2} orbitals. The additional peaks at around 943 and 964 eV are due to a shake up process (the ejected core electron simultaneously transfers some of its energy to another electron). This structure is an indication for Cu²⁺ as, e.g. present in CuO,^[21,22] because this shake up is due to the open 3d⁹ shell

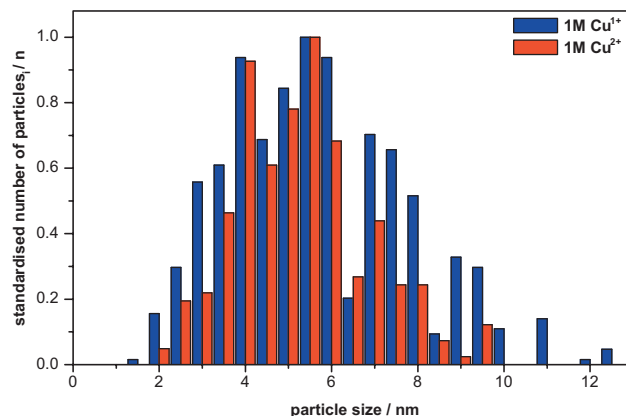


Figure 3. Standardised size distribution curves of Cu particles from CuCl and CuCl₂ in [BMIm]dca.

of Cu²⁺. Such a shake up structure is completely absent for CuCl dissolved in the IL (red curve), underlining that indeed only Cu¹⁺ ions are present in this solution as already stated. In case of CuCl₂ (blue curve) the structure is more complicated and seems to consist of at least two different Cu species (Cu²⁺ and Cu¹⁺).

Figure 6a/b presents a comparison of the IR spectra of the pure [BMIm]dca, the CuCl/[BMIm]dca and the plasma treated solution (Figure 6a) and the same for the CuCl₂ (Figure 6b). The results show just the C≡N stretching vibrations of the [dca] anion between 2 000 and 2 300 cm⁻¹ and the alkyl C–H plus the ring C–H stretching vibrations of the [BMIm] cation between 2 800 and 3 200 cm⁻¹, because in this wave number region the major contributions of the stretching vibrations of both ions are visible. The IR spectra do not show striking alterations due to the plasma treatment. The whole measured spectral range between 600 and 3 200 cm⁻¹ shows no differences compared to the pure solutions. The origin of the additional

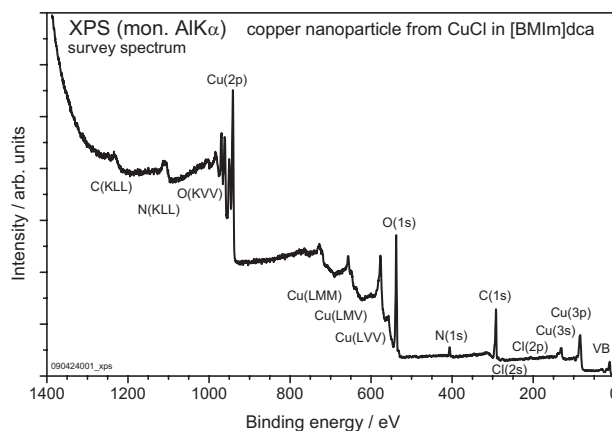


Figure 4. XPS survey spectrum of a Cu nanoparticle film (CuCl/[BMIm]dca).

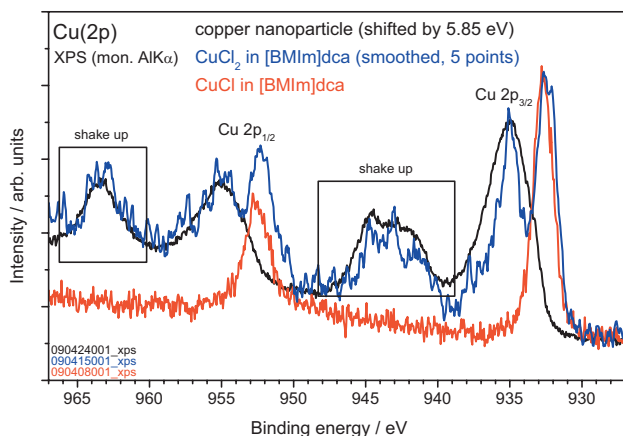


Figure 5. XPS Cu 2p region of the copper nanoparticle film CuCl/[BMIm]dca; (black curve), the CuCl₂ in [BMIm]dca (blue curve) and the CuCl in [BMIm]dca (red curve).

feature around 2280 cm^{-1} (* in Figure 6b) in the CuCl₂ is a hint for the formation of a copper dicyanamide complex [Cu(N(CN)₂)₂], because for this complex the combination band of the symmetric and antisymmetric N–C stretching modes shift to 2290 cm^{-1} compared to 2230 cm^{-1} for the stretching mode in the pure liquid.^[23,24]

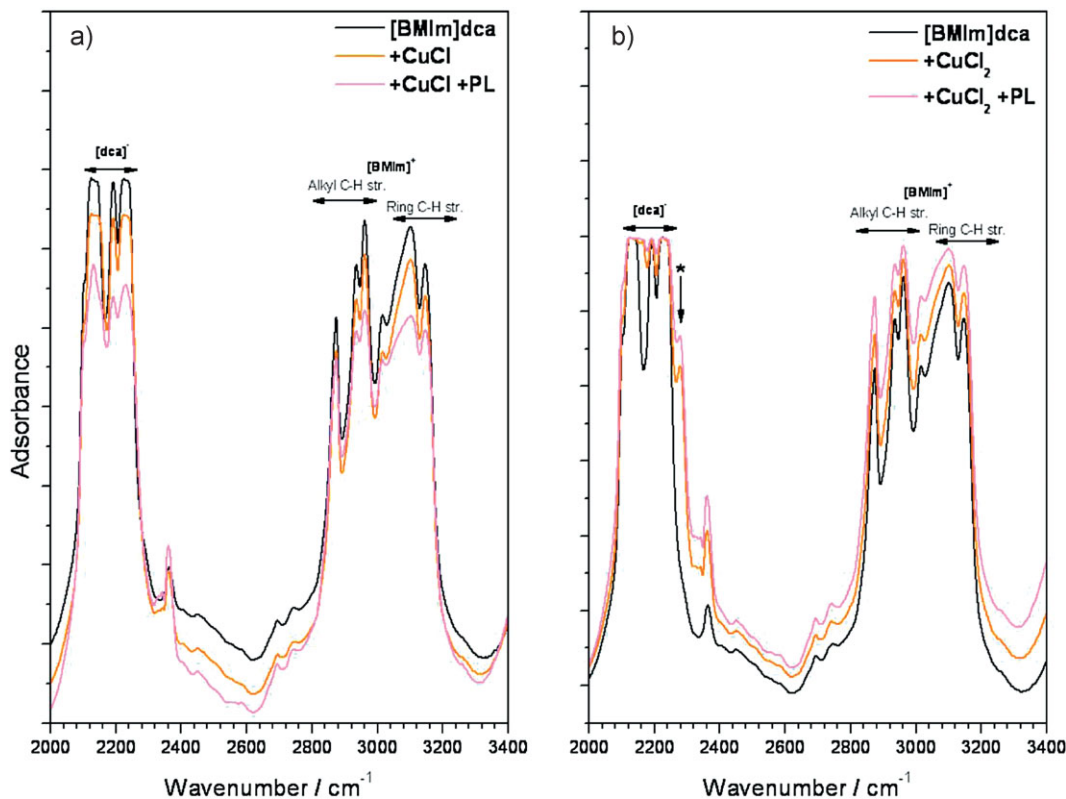


Figure 6. (a) IR spectra of CuCl/[BMIm]dca (before and after plasma treatment). (b) IR spectra of CuCl₂/[BMIm]dca (before and after plasma treatment).

Discussion

We find from this study that the plasma interacts with both types of copper salts in IL similarly, as indicated by the synthesis of copper nanoparticles with similar sizes. Therefore we can conclude at a minimum that in addition to the one step reduction process in the case of CuCl, a two step reduction process in the CuCl₂ solution is possible, too. The particle size distributions of copper from CuCl and CuCl₂ show no striking differences, which we attribute mainly to the strong reaction during the plasma process. Furthermore, due to the gas evolution the intermixing of the liquid causes a fast removal of the particles from the reaction zone, which prevents a further growing of the particles. As mentioned above, we suggest that the gas evolution is caused by chlorine evolution at the counter electrode. Hydrogen formation 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. However, the colour change of the pure liquid after the plasma process shows that a reaction has occurred. Unfortunately, neither IR nor XPS deliver any reliable information on the reaction products. In earlier studies we observed a similar colour change for [Py_{1,4}]Tf₂N but not for [EMIm]Tf₂N.^[15] Xie and Liu^[11] did also not report

any decomposition of [BMIm]BF₄/HAuCl₄ and [BMIm]BF₄/PdCl₂ solutions during plasma treatment as analyzed with IR spectroscopy and NMR. However, they have used a different setup, where both electrodes are separated from the liquid. Recent NMR investigations by us for plasma treated [Py_{1,4}]Tf₂N show no changes in the NMR spectra compared to the pure liquid. Baba et al.^[25] in contrast found a colour change of pure [BMIm]BF₄ through irradiation with 220 eV argon plasma ions. The colour did not change when the liquid was irradiated with 20 eV plasma ions. Their setup is comparable to ours, but the colour change was only observed if the cathode is placed inside the liquid and the anode is above the liquid. In a recent paper Hatakeyama and co-workers^[14] observed with optical emission spectroscopy in the gas plasma region the formation of methylidyne radicals, but only if they change the polarity (cathode is inside the liquid). In our setup the cathode was always placed above the IL, therefore in future these phenomena's must investigated in more detail.

As in the case of Cu particles made from Cu⁺ in [Py_{1,4}]Tf₂N and [EMIm]Tf₂N the particles are oxidized to CuO in both cases, in our opinion due to a surface attack during the intensive ex situ treatment as Cu nanoparticles are quite reactive. An in situ oxidation inside the reactor cannot be excluded totally, especially because of the higher water content in [BMIm]dca compared to other IL. But earlier results on the electrodeposition of Cu-, Al- and Si-films from IL support more the ex situ treatment assumption.^[16,26]

Conclusion

In this paper we have reported on the synthesis of free, dispersed copper nanoparticles in the air and water stable IL, [BMIm]dca, by employing plasmas as mechanically contact-free electrodes. We showed that there is no clear influence of the dissolved copper species (CuCl and CuCl₂) on the particle size. The particle sizes are between 1 and 10 nm in both cases. We attribute this mainly to the strong intermixing due to gas evolution during the plasma process. The ex situ investigation with XPS has shown that the particles are oxidized. In addition, we could show that the pure IL reacts with the plasma themselves. IL with the dicyanamide anion facilitate the plasma electrochemical process as commercially available copper halides can be used, leading to quite high concentrations in the mol·L⁻¹ regime.

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- [1] J. Dupont, J. D. Scholten, *Chem. Soc. Rev.* **2010**, *39*, 1780.
- [2] G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira, J. Dupont, *Chem. Eur. J.* **2003**, *9*, 3263.
- [3] C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner, S. R. Teixeira, *Inorg. Chem.* **2003**, *42*, 4738.
- [4] H. Itoh, K. Naka, Y. Chujo, *J. Am. Chem. Soc.* **2004**, *126*, 3026.
- [5] T. Torimoto, K. Okaszaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata, *Appl. Phys. Lett.* **2008**, *89*, 243117.
- [6] T. Suzuki, K. Okaszaki, T. Kiyama, S. Kuwabata, T. Torimoto, *Electrochemistry* **2009**, *77*, 636.
- [7] K. Okaszaki, T. Kiyama, K. Hirahara, N. Tanaka, S. Kuwabata, T. Torimoto, *Chem. Commun.* **2008**, *6*, 691.
- [8] S. A. Meiss, M. Rohnke, L. Kienle, S. Zein El Abedin, F. Endres, J. Janek, *Chem. Phys. Chem.* **2007**, *8*, 50.
- [9] S. Zein El Abedin, M. Pölleth, S. A. Meiss, J. Janek, F. Endres, *Green Chem.* **2007**, *9*, 549.
- [10] J. Janek, M. Rohnke, M. Pölleth, S. A. Meiss, Plasma Electrochemistry With Ionic Liquids, in: *Electrodeposition From Ionic Liquids*, F. Endres, D. MacFarlane, A. Eds., Wiley-VCH, Weinheim 2008, p. 259.
- [11] Y. B. Xie, C. J. Liu, *Plasma Process. Polym.* **2008**, *5*, 239.
- [12] C. Richmonds, R. Mohan Sankaran, *Appl. Phys. Lett.* **2008**, *93*, 131501.
- [13] H. Furusho, K. Kitano, S. Hamaguchi, Y. Nagasaki, *Chem. Mater.* **2009**, *21*, 3526.
- [14] T. Kaneko, K. Baba, T. Harada, R. Hatakeyama, *Plasma Process. Polym.* **2009**, *6*, 713.
- [15] M. Brettholle, O. Höfft, L. Klarhöfer, S. Mathes, W. Maus-Friedrichs, S. Zein El Abedin, S. Krischok, J. Janek, F. Endres, *Phys. Chem. Chem. Phys.* **2010**, *12*, 1750.
- [16] S. Zein El Abedin, A. Y. Saad, H. K. Farag, N. Borissenko, Q. X. Liu, F. Endres, *Electrochim. Acta* **2007**, *52*, 2746.
- [17] Themed Issue: Physical chemistry of ionic liquids, *PCCP* **2010**, *12*, 1631.
- [18] M. Y. Deng, P. Y. Chen, T. L. Leong, I. W. Sun, J. K. Chang, W. T. Tsai, *Electrochem. Commun.* **2008**, *10*, 213.
- [19] T. I. Leong, I. W. Sun, M. J. Deng, C. M. Wu, P. Y. Chen, *J. Electrochem. Soc.* **2008**, *155*, F55.
- [20] F. C. Chang, C. Richmonds, R. Mohan Sankaran, *J. Vac. Sci. Technol. A* **2010**, *28*, L5.
- [21] P. E. Larson, *J. Electron. Spectrosc.* **1974**, *4*, 213.
- [22] G. Schön, *Surf. Sci.* **1973**, *35*, 96.
- [23] H. Köhler, A. Kolbe, G. Lux, *Z. Anorg. Allg. Chem.* **1977**, *428*, 103.
- [24] C. Aliaga, S. Baldelli, *J. Phys. Chem. B* **2007**, *111*, 9733.
- [25] K. Baba, T. Kaneko, R. Hatakeyama, *Appl. Phys. Lett.* **2007**, *90*, 201501.
- [26] F. Bebensee, N. Borissenko, M. Frerichs, O. Höfft, W. Maus-Friedrichs, S. Zein El Abedin, F. Endres, *Z. Phys. Chem.* **2008**, *222*, 671.