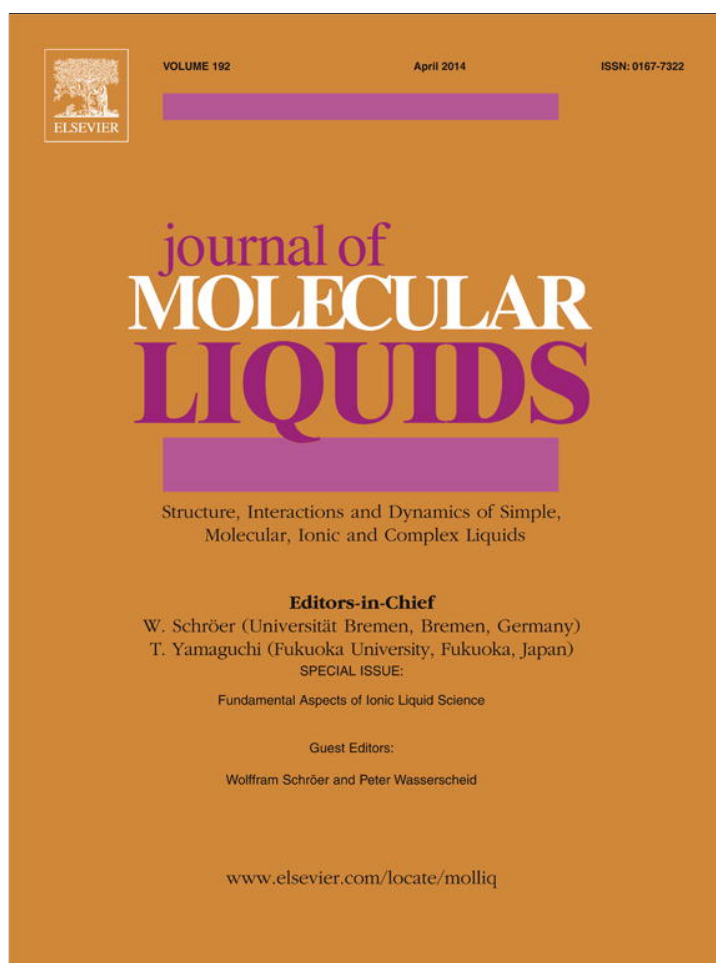


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# Plasma electrochemistry in ionic liquids: from silver to silicon nanoparticles



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## ABSTRACT

In this paper an overview will be given about the generation of metal and semiconductor nanoparticles with plasma electrochemistry using the example of the plasma electrochemistry project in the DFG framework of SPP1191. After an introduction in nanoparticle synthesis and plasma electrochemistry in ionic liquids, we focus on our own results on the synthesis of silver, copper, germanium and silicon nanoparticles. We will present the results in chronological order to exemplify the assumptions, the difficulties and consequences. At the end we will give first indications for the particle forming process during plasma electrochemistry.

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## 1. Introduction

Ionic liquids (ILs), which are salts usually consisting mostly of large ions with melting points of below 100 °C, are of high interest in chemistry and physics due to a number of distinct physical properties. ILs are characterised by large electrochemical (up to 6 V) and wide thermal windows (~–50 °C to ~+250 °C), good ionic conductivities, the ability to solubilise many chemical species and especially they have a negligible vapour pressure. Due to this very low vapour pressure ILs can be analysed in ultra high vacuum quite easily [1]. These unique properties can be tuned by just changing the cation or the anion, respectively. In particular for electrochemical applications (e.g. electrodeposition [2], capacitors [3], dye sensitised solar cells [4], corrosion inhibition [5], lithium batteries [6], etc.) ILs are very promising solvents, especially as they are not flammable. Also the generation of free nanoparticles in ionic liquids and their possible applications in this field are hot topics in the field of ionic liquid research. For example, transition metal nanoparticles in ionic liquids can be applied for catalytic reactions [7]. In their review article Dupont et al. pointed out that an important advantage of ILs is the ability to stabilise metal nanoparticles and metal oxide particles without the addition of any stabilising agent [8]. In two reviews the different approaches of the synthesis of nanoparticles and their applications in ILs were addressed and highlighted [8,9]. The important routes to make metal nanoparticles in ionic liquids are: the chemical reduction method, sputter deposition of metals onto surfaces of the liquids in vacuum, reduction with free electrons in a scanning electron microscope and the plasma electrochemical approach. In a recent feature article Richter et al. report about the synthesis of metal nanoparticles in ionic liquids

by the chemical reduction method, sputter deposition and physical vapour deposition [10]. For the chemical reduction process it was for example reported that iridium and rhodium nanoparticles with 2.0 nm–2.5 nm diameter can be synthesised in the dry ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF<sub>6</sub>) from [Ir(cod)Cl]<sub>2</sub> (cod = 1,5-cyclooctadiene) and RhCl<sub>3</sub>·3H<sub>2</sub>O, respectively [11]. After isolation, the nanoparticles can be re-dispersed in ionic liquids [11]. Furthermore, platinum nanoparticles within a narrow size regime can be obtained by decomposition of Pt-organometallic precursors in [BMIm]PF<sub>6</sub> [12]. The synthesis and functionalisation of gold nanoparticles modified by ionic liquids with imidazolium cations has been reported by Itoh et al. [13]. Already bimetallic Au–Pd nanoparticles were successfully prepared by a co-decomposition from Pd(OAc)<sub>2</sub> and Au(OAc)<sub>3</sub> in hydroxyl-functionalised ionic liquid 1-(2'-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)amide [C<sub>2</sub>OHmim]Tf<sub>2</sub>N [14].

Due to the above mentioned very low vapour pressures which range at or near room temperature typically between 10<sup>–9</sup> and 10<sup>–8</sup> Pa and at 100 °C between 10<sup>–4</sup> and 10<sup>–2</sup> Pa – depending on the particular liquid – it is possible to synthesise materials in a controlled environment [15]. In vacuum, metal nanoparticles can be obtained by sputter deposition of metals onto ionic liquid surfaces. Torimoto et al. reported e.g. that gold nanoparticles and even gold silver alloys can be made with this method [15–18]. Vanecht et al. have investigated the influence of the viscosity of ionic liquids on the particle growth for gold particles made by sputter deposition [19]. They found two growth processes, a fast one which stops directly after the sputtering and subsequently followed by a second slow growth. In their experiments the particle growth has stopped at particle sizes of 6 nm, this behaviour was attributed to a formation of a stabilising IL layer around the particles [19]. The rate of the second process depends on the viscosity of the IL. Physical vapour deposition into ionic liquids is a similar way to create nanoparticles in a vacuum environment [10,20].

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Richter and co-workers have evaporated copper on [BMIm]PF<sub>6</sub> at a pressure of 10<sup>-4</sup> Pa and have received particles with a size around 3 nm [20]. Also nanoparticles can be synthesised in a scanning electron microscope or a scanning Auger electron microprobe, respectively. Here the electron beam reduces the metal precursors. This approach was introduced by Roy et al. [21] and Imanishi et al. [22]. Another way to produce nanoparticles in ILs under reduced pressure is the plasma electrochemical approach, where the plasma acts as a mechanically contact-free electrode [23,24]. 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 Gubkin used a plasma above an aqueous solution of silver nitrate [25], to generate silver 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 [26,27].

Within the last 8 years plasma electrochemistry, has developed to an alternative route to generate free metal nanoparticles in ionic liquids. Until now, this research field has been carried out mainly by 4 groups: R. Hatakeyama and T. Kaneko at Tohoku University in Sendai [24], C.-J. Liu at the Tianjin University in China [28], J. Janek at Gießen University and our group. A joint project between J. Janek and us was part of the DFG priority program "Ionic Liquids" (SPP 1191) and the important results will be summarised in this article. In literature there are different methods reported to ignite stable plasmas above ionic liquids. DC plasma reactors were very often used, whereby mostly one electrode is placed in the liquid and the other one is placed in the gas phase above the liquid [29]. Hatakeyama has introduced 2 operating modes (A-mode and B-mode) for the DC setup [30]. In the A-mode the electrode in the liquid acts as a cathode, in the B-mode the cathode is the electrode in the gas phase. With both electrode configurations the generation of nanoparticles is possible. In the A-mode secondary electrons, created due to the interaction of the plasma gas ions with the IL interface, act as reducing agents, whereas in the B-mode the primary electrons in the plasma reduce the dissolved species. In the DC plasma experiments mostly argon is used as process gas at a pressure around 1 mbar. Liu et al. use also a DC plasma, but in their plasma reactor, both electrodes are in the gas phase above the liquid, which was placed in a quartz crucible located at the "positive column" of the glow discharge [28]. In addition, they showed, that a sub-atmospheric dielectric barrier discharge (SADBD) plasma can act as a reducing agent, too [31]. As third major plasma type radio frequency discharge plasma can be applied for plasma electrochemistry [23,32].

Mainly metal particles were synthesised with plasma electrochemistry. Gold, platinum and palladium particles were generated from HAuCl<sub>4</sub>·3H<sub>2</sub>O, PtCl<sub>2</sub> and PdCl<sub>2</sub>, respectively in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF<sub>4</sub>) by Hatakeyama et al. [30,33]. Liu et al. also have produced gold and palladium from HAuCl<sub>4</sub>·3H<sub>2</sub>O and (PdCl<sub>2</sub>)/[BMIm]BF<sub>4</sub> [28]. We will summarise here our results for the generation of silver nanoparticles from AgCF<sub>3</sub>SO<sub>3</sub> in 1-butyl-3-methylimidazolium trifluoromethylsulfonate ([BMIm]TfO) and 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ([Py<sub>1,4</sub>]TfO) and of copper nanoparticles in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]Tf<sub>2</sub>N), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py<sub>1,4</sub>]Tf<sub>2</sub>N) and 1-butyl-3-methylimidazolium dicyanamide ([BMIm]dca) [23,34–36]. Despite a lot of information, it is not yet possible to comment on a general trend of the particle size dependency on the individual ionic liquid and on the kind of the plasma reactor. Our own results in comparison with data obtained by the Kuwabata group in Japan imply that the anion plays an important role for the particle size [37], this will be discussed later. The influence of different alkyl chain lengths of the imidazolium cation in [RMIm]TfO (R = Alkyl) liquids and the resulting change in the surface tension has been investigated within the PhD thesis of M. Pölleth in the group of Janek [38]. No exact correlation between physical properties like surface tension and the particle size could be found. An interesting fact is that knowledge about the stability of the ionic liquids

during the plasma is scarce. Hatakeyama et al. have shown with their setup, that there is a strong colour change of an ionic liquid, containing an imidazolium cation during plasma interaction [33]. With optical emission spectroscopy they observed methylidyne radicals (CH) in the plasma [33,39], due to a loss of an alkyl chain of the imidazolium cation. We found a colour change of 1-butyl-3-methylimidazolium dicyanamide and of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide after the plasma process, too [36]. Unfortunately, neither IR nor XPS spectroscopy delivered any reliable information on the reaction products, and NMR investigations for plasma treated [Py<sub>1,4</sub>]Tf<sub>2</sub>N performed by us in cooperation with the NMR group at Clausthal University (Prof. A. Schmidt) also showed no changes in the NMR spectra compared to the pure liquid.

In the framework of the SPP1191 project we started as the first ones the investigation of the generation of semiconductor nanoparticles (silicon and germanium), by plasma electrochemistry. Semiconductor nanoparticles have interesting properties like for example a size dependent band gap, and we have shown by electrodeposition experiments that nanoscale silicon and germanium films can be easily made from different SiCl<sub>4</sub> and GeCl<sub>4</sub> ionic liquid solutions [40–42]. Nowadays semiconductor nanoparticles can – in principle – be produced by chemical reduction, etching or plasma reduction in the gas phase [43], or by metathesis reactions between KGe and excess GeCl<sub>4</sub> in glyme solvents [44]. The liquid-solution-phase synthesis of crystalline silicon was first developed by Heath. In this route silicon was made by reduction of SiCl<sub>4</sub> and RSiCl<sub>3</sub> (R = octyl) with sodium in a nonpolar organic solvent, like hexane, at high temperatures in a high pressure bomb over 3 to 7 days [45]. The size of the silicon crystal strongly depends on the chosen "alkyl chain" length. Crystals made with C<sub>8</sub>H<sub>17</sub>-SiCl<sub>3</sub> were in the range between 3 and 7 nm, the particles with HSiCl<sub>3</sub> showed in contrast a much wider size distribution (5–3000 nm). Afterwards, further solution based methods working at less extreme conditions were developed. An overview on the evolution of synthesis routes in solution has been given by Masala and Seshadri [46]. Recently Kamyshny et al. have shown that Si nanoparticles, synthesised by chemical reduction of SiBr<sub>4</sub> with metallic Na in diglyme, can be stabilised by the ionic liquid dimethylimidazolium iodide as capping agent [47]. The authors found that the capping is due to interaction of the imidazolium ring with the silicon resulting in a formation of a carbene-Si surface complex [47]. Kortshagen and co-workers have introduced a low-pressure nonthermal plasma method to synthesise silicon nanoparticles [48]. In this approach the electrons in the plasma dissociate the silane in an argon-silane gas mixture. They received particles with sizes around 5 nm. An electrochemical synthesis of silicon nanocrystals has been reported by Choi et al. [49]. They generated the silicon particle by ultrasound assisted electrochemical C<sub>8</sub>H<sub>17</sub>-SiCl<sub>3</sub> reduction in a tetrahydrofuran lithium perchlorate solution. Particles with diameters between 3 and 25 nm were found, and with infrared spectroscopy an alkyl terminated surface was detected. Recently, Liu et al. showed that silicon nanostructures can be obtained by electron reduction of the liquid precursor SiCl<sub>4</sub> in a transmission electron microscope (TEM) and a scanning electron microscope [50]. This approach is very similar to the above mentioned introduced by Roy et al. and Imanishi et al. The disadvantage in this particular case is that the high vapour pressure precursor SiCl<sub>4</sub> has to be encapsulated between silicon nitride membranes to be applicable in a TEM. Recently Kareem and Kaliani were able to produce ZnS nanoparticles in [BMIm]BF<sub>4</sub> with plasma electrochemistry [51]. Here we will present our results for obtaining germanium and silicon nanoparticles with the plasma method.

## 2. Results: from silver to silicon

In our initial studies together with Jürgen Janek we asked ourselves if, based on the pioneering paper by Gubkin using aqueous solutions, it is possible to generate silver (nano)particles with the help of a glow

discharge plasma in ionic liquids. Our approach was simple: ionic liquids have at or near ambient temperatures usually a negligible vapour pressure, and consequently an argon plasma should “burn” stably over an ionic liquid. For this fundamental approach we decided for quite a simple chemical system and investigated the reduction of silver trifluoromethylsulfonate ( $\text{AgCF}_3\text{SO}_3$ ) in the ultrapure ionic liquid  $[\text{BMIm}]\text{CF}_3\text{SO}_3$  [23]. Fig. 1 shows the experimental setup. Argon is fed into a reactor which contains the electrolyte with an electrode. The cylinder like electrode is located above the electrode. After equilibration a pressure of around 1 mbar is adjusted and a voltage between 500 and 1000 V is applied between the electrodes. In this setup argon is ionised and electrons move towards the electrolyte, the argon ions move towards the counter electrode. At the interface plasma/ionic liquids the electrons can react with the silver ions forming silver particles. In the beginning the liquid is yellowish and when the plasma is switched on, a dark cloud is formed at the interface moving slowly to the bottom of the reactor. After about 10 minutes the whole of the reactor was filled with a black suspension and the experiment was stopped. The particles from the suspension were collected and analysed both by scanning electron microscopy and transmission electron microscopy. The analysis showed that silver nanoparticles with a size between about 8 and 30 nm were obtained.

With these fundamental studies we could show for the first time that

- ionic liquids allow a stable glow discharge plasma over the liquid and
- that silver nanoparticles with sizes between 8 and 30 nm can be made by reduction of  $\text{Ag}^+$  ions with the electrons of the plasma.

Based on these promising results we investigated the reduction of copper salts by plasma electrochemistry.

The motivation for these experiments was the following: in ionic liquids copper ions can both exist as  $\text{Cu}^+$  and as  $\text{Cu}^{2+}$  ions. This is due to the different complex chemistry, compared to water. Whereas in aqueous solutions hydrated  $\text{Cu}^+$  ions would undergo a disproportionation to  $\text{Cu}^{2+}$  and  $\text{Cu}$ , this does not occur in ionic liquids. Thus, it was of interest to test if there is a difference whether copper particles are made from  $\text{Cu}^+$  or from  $\text{Cu}^{2+}$ . Furthermore at that time we had the first hints that cations and/or anions influence the particle size of electrochemically or chemically made metal particles, thus we varied both cations and anions. The abstract in ref. [35] is the following:

“We report on the synthesis of copper nanoparticles in two different water- and air-stable ionic liquids using plasma electrochemical

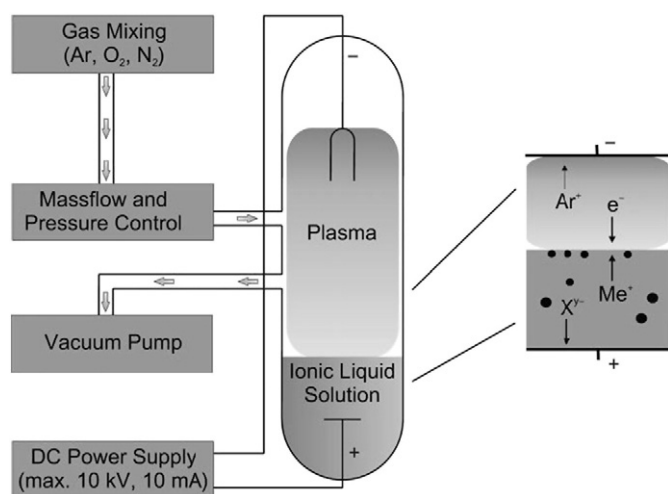


Fig. 1. Sketch of the plasma reactor [23]. Figure reproduced with permission from Wiley (Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

deposition. The copper nanoparticles were deposited in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ( $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ ) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ( $[\text{EMIm}]\text{Tf}_2\text{N}$ ). To get information on the dimensions of the particles made, we have applied *in situ* transmission electron microscopy (particles in ionic liquid). The chemical composition was investigated by *ex situ* X-ray photoelectron spectroscopy (XPS). We found that the copper particles produced in  $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$  were larger in size compared to the particles obtained in  $[\text{EMIm}]\text{Tf}_2\text{N}$  (roughly 20 vs. 10 nm). The chemical composition of the particle surface differs, too. In both cases the particles are partly oxidised leading to a  $\text{CuO}$  shell, but the particles obtained in  $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$  carry a lot of residues from the ionic liquid.”

Whereas in the case of silver the surface chemistry is comparably simple, copper nanoparticles are subject to a surface oxidation, likely due to *ex situ* handling. With the setup available at that time it was not avoidable to handle the samples outside of the glove box, e.g. to analyse them by TEM and XPS. With the new setup which we will get in the course of the year this problem will be solved. Fig. 2 shows a TEM image of the Cu particles obtained in  $[\text{EMIm}]\text{Tf}_2\text{N}$ . We applied a droplet of the liquid with the particles on a TEM grid and analysed them. Due to ionic liquid adsorbed on the surfaces of the particles we could not resolve the atomic layers of the Cu particles. Nevertheless the TEM image shows that tiny particles are obtained. Fig. 3 shows an XPS analysis of the particles, done in cooperation with Stefan Krischok, Ilmenau.

The XPS spectrum shows a complicated surface chemistry and besides metallic copper we see shake up lines and signals for  $\text{CuO}$ . Furthermore, the structure at 932.3 eV can either be assigned to clean copper or to copper in  $\text{Cu}_2\text{O}$ . The conclusion of this study, published in ref. [35] is as follows:

“We have shown that the particles produced in  $[\text{EMIm}]\text{Tf}_2\text{N}$  are smaller in diameter (~11 nm) compared to those ones produced in  $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$  (~26 nm). This is in contrast to the classical electrochemical deposition of copper in these liquids and might be due to the viscosity of the liquids. Moreover from the experiments there are strong hints that  $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$  is more strongly adsorbed on these particles than  $[\text{EMIm}]\text{Tf}_2\text{N}$ . In both liquids the particles are to a certain extent oxidised to  $\text{CuO}$ , most likely due to a surface attack during *ex situ* treatment. In contrast to earlier published results on the plasma electrochemical deposition of Ag nanoparticles, the production of copper nanoparticles is surprisingly much more complicated. In order to elucidate the surface chemistry future studies will involve further ionic liquids as reaction media as well as higher resolution TEM measurements.”

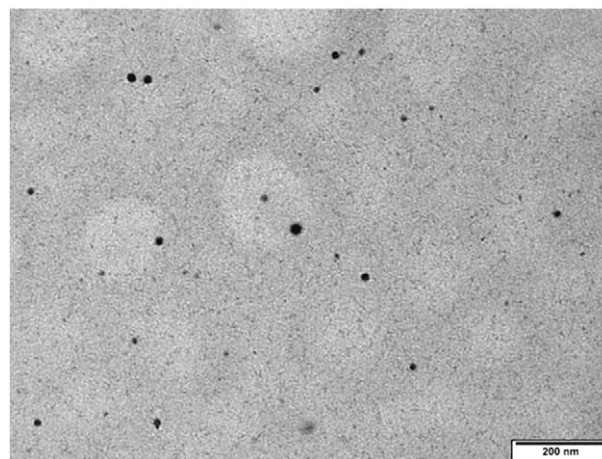


Fig. 2. TEM of Cu nanoparticles made in  $[\text{EMIm}]\text{Tf}_2\text{N}$  [35]. Reproduced by permission of the PCCP Owner Societies.

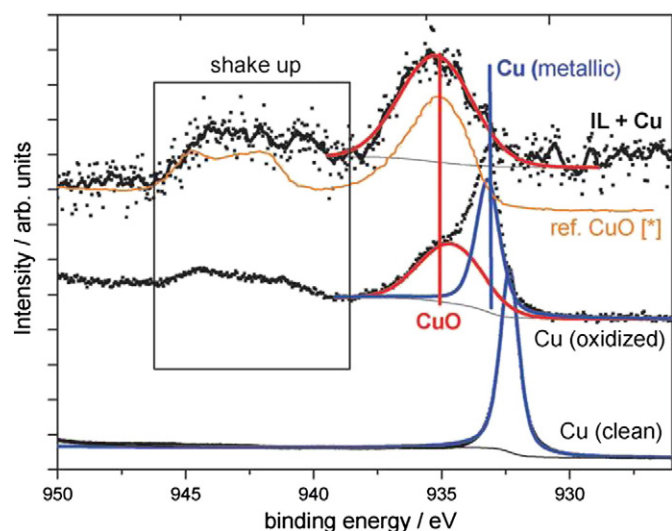


Fig. 3. XPS Cu  $2p_{3/2}$  region of the nanoparticles in [EMIm]Tf<sub>2</sub>N [35]. Reproduced by permission of the PCCP Owner Societies.

In the following experiments we decided to use another ionic liquid in which we could dissolve copper halides. There was one more complication: When we introduced copper ions electrochemically into the liquids with the Tf<sub>2</sub>N anion, at elevated temperature we got quantitatively CuF<sub>2</sub>, due to an unexpected decomposition of the anion. Therefore we selected an as pure as possible liquid with the dicyanamide ion. Such liquids can dissolve many metal halides. The abstract of [36] summarises the key results:

“We report on the reaction of CuCl and CuCl<sub>2</sub>, 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 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 CuCl<sub>2</sub>/[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.”

Fig. 4 shows photos of the experiments in the beginning, in the middle and after 30 minutes.

Due to the different complexation CuCl gives a yellowish solution, CuCl<sub>2</sub> a green solution. After 30 minutes of reaction we get both a suspension of particles and a tiny copper mirror at the reactors surface. The latter one is the result of a convection, likely induced by the evolution of chlorine at the electrode inside the liquid. Fig. 5 summarises the particle size distributions obtained in both cases. Within the limit of uncertainty the results are identical with particle sizes between 1 and 10 nm.

We can conclude from these studies the following: “We showed that there is no clear influence of the dissolved copper species (CuCl and CuCl<sub>2</sub>) 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 oxidised. In addition, we could show that the pure IL reacts with the plasma themselves. ILs 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<sup>-1</sup> regime.”

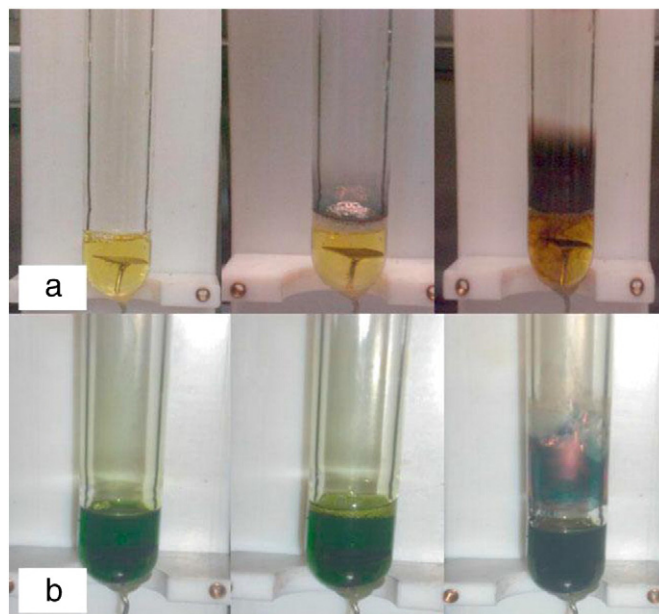


Fig. 4. (a) Plasma experiment (0–30 min) CuCl/[BMIm]dca, (b) Plasma experiment (0–30 min) CuCl<sub>2</sub>/[C<sub>4</sub>mim]dca [36]. Figure reproduced with permission from Wiley (Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

In our electrodeposition experiments we are able to deposit Ge and Si from GeCl<sub>4</sub> and from SiCl<sub>4</sub>, respectively, and this is relatively straightforward. Not too surprisingly our attempts to reduce these compounds by plasma electrochemistry failed totally as the precursors were simply pumped off due to too high vapour pressures. For this purpose we selected a GeCl<sub>2</sub>·dioxane complex (GeCl<sub>2</sub>C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>). With this complex it was possible to deposit germanium films in [Py<sub>1,4</sub>]Tf<sub>2</sub>N and in [EMIm]Tf<sub>2</sub>N.

Both the SEM images and the corresponding EDX analysis showed that elemental Ge is obtained by electrodeposition. As this compound has quite a low vapour pressure we used it for the electrochemical experiment. The upper left image of Fig. 6a shows the pure 0.1 M solution/suspension of the complex in [EMIm]Tf<sub>2</sub>N. It is clearly visible that during plasma interaction the liquid changes from “milky” to an orange coloured liquid, and the colourisation starts at the plasma ionic liquid interface. The TEM analysis (Fig. 6b) done after separation of the particles from the solution reveals particle sizes smaller than 50 nm. In cooperation with the group of Stefan Krischok we could analyse the chemical composition of the solution before and

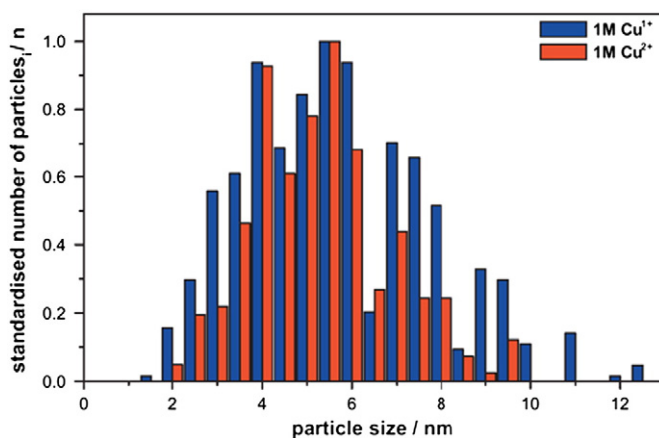
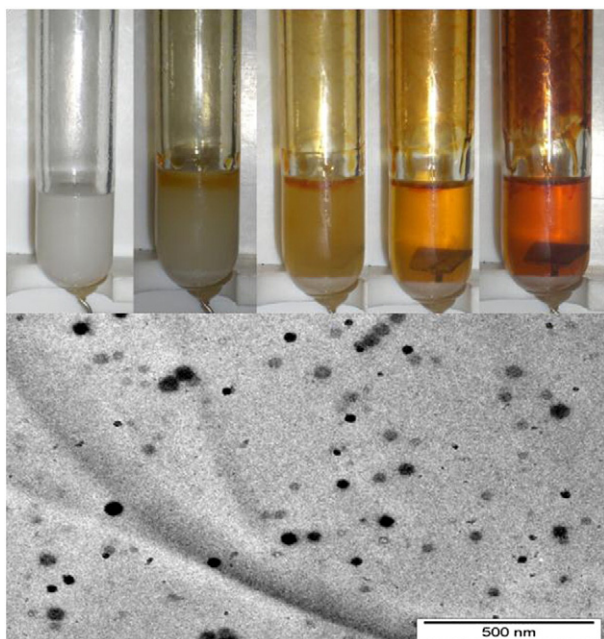


Fig. 5. Histograms of the copper nanoparticles [36]. Figure reproduced with permission from Wiley (Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).



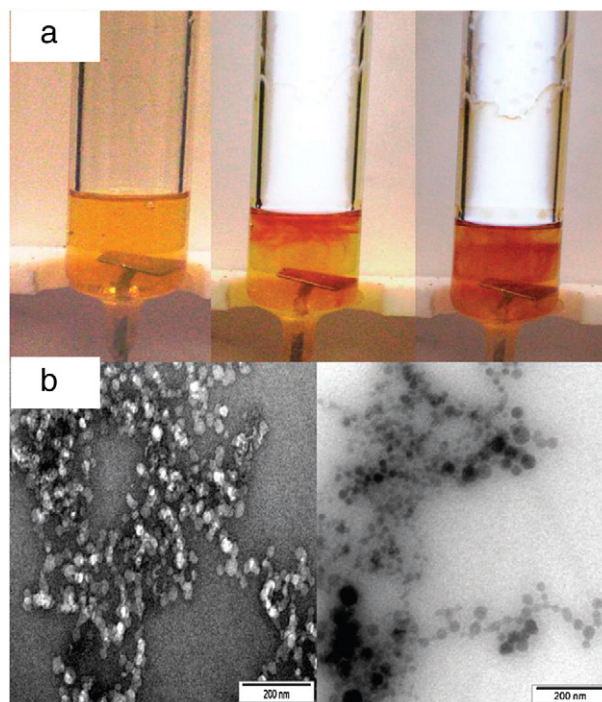
**Fig. 6.** (a) Plasma experiment with  $\text{GeCl}_2 \cdot \text{dioxane}/[\text{EMIm}]\text{Tf}_2\text{N}$ . (b) TEM image of the obtained particles [52]. Figure reproduced with permission from Elsevier (Copyright © 2011).

after the plasma treatment. At the interface germanium can be detected and the detail spectrum of the germanium 2p region shows the development of an additional component in the spectrum, which can be attributed at least to the oxidation state of  $\text{Ge}^+$ . This demonstrates that the plasma solution interaction leads to a reduction of the germanium from  $\text{Ge}^{2+}$  to  $\text{Ge}^+$  and even to  $\text{Ge}^0$ . We were told by a colleague (Ingo Krossing) that  $\text{Ge}^{1+}$  species can be orange, too. However, an analysis of our suspension in the group of Professor Schnepf (Tübingen) gave no hint for that so that the particles obtained are due to elemental Ge.

### 3. First results on the formation of silicon nanoparticles

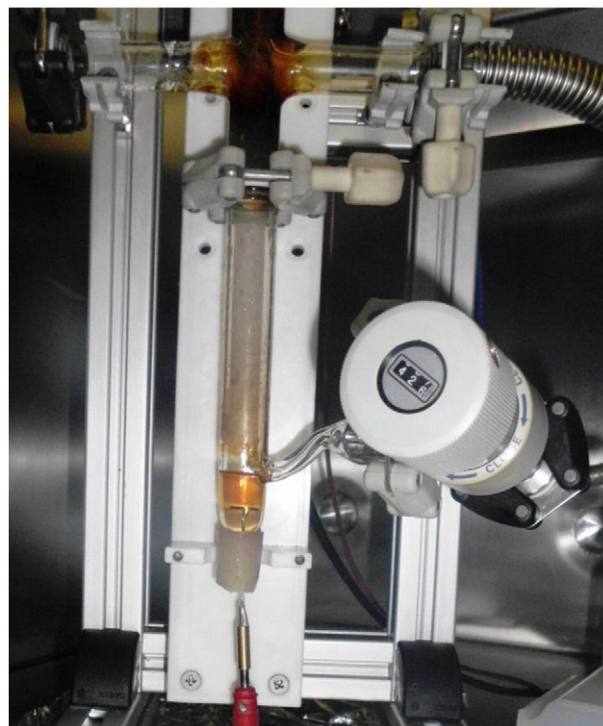
As the precursors  $\text{SiCl}_4$  and  $\text{SiBr}_4$ , from which elemental silicon can be electrodeposited classically, have a too high vapour pressure for the plasma reactor which we have used so far, we chose for our first attempts  $\text{SiI}_4$ , which is a solid material avoiding to be pumped off from the reactor. A classical electrodeposition experiment performed together with Andreas Bund (Ilmenau) revealed that from  $\text{SiI}_4/[\text{Py}_{1,4}]\text{Tf}_2\text{N}$  solutions elemental Si could not be obtained, rather subvalent  $\text{Si}_x\text{I}_y$  compounds were obtained. Nevertheless, these first results showed that  $\text{SiI}_4$  can be reduced electrochemically. We performed a plasma electrochemical experiment with this solution, which can be seen in the upper part of Fig. 7a. The left image shows the solution before the experiment, and with time a colour change of the solution occurs and a precipitate appears in the liquid. The corresponding TEM image is shown in Fig. 7b, where particles with diameters of below 20 nm are visible. A reliable *ex situ* XPS investigation was not possible, and taking all results into account we think that the plasma reduction also leads to  $\text{Si}_x\text{I}_y$  compounds.

Although not the desired result, this experiment showed at a minimum, that the approach to make, by this method, Si nanoparticles is – in principle – possible. As there are only a few Si-precursors available we modified our reactor such, that it can cope with the high vapour pressure of  $\text{SiCl}_4$ . We have added an inlet for  $\text{SiCl}_4$  so that the pumped off precursor is replaced. With this setup there is a continuous diffusion of  $\text{SiCl}_4$  through the solution to the surface. Fig. 8 shows a photo of this new reactor.



**Fig. 7.** (a) Plasma experiment (30 min)  $\text{SiI}_4/[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ . (b) SEM and TEM images of  $\text{Si}_x\text{I}_y$  particles from  $\text{SiI}_4/[\text{Py}_{1,4}]\text{Tf}_2\text{N}$  [29]. Reproduced by permission of the PCCP Owner Societies.

With this new plasma cell we have investigated the interaction of the plasma with  $\text{SiCl}_4$  passed through  $[\text{EMIm}]\text{Tf}_2\text{N}$ . In Fig. 9 the corresponding plasma experiment is shown. It is again visible that during the experiment a colour change of the liquid occurs.



**Fig. 8.** New plasma reactor for plasma electrochemical reduction of high vapour pressure precursors.



Fig. 9. Plasma experiment (30 min)  $\text{SiCl}_4/[\text{EMIm}]\text{Tf}_2\text{N}$ .

After the experiments the solution was analysed with TEM and dynamic light scattering (photon cross correlation spectroscopy; PCCS). In TEM particles were observable. Therefore, we can conclude that the  $\text{SiCl}_4$  was reduced by the plasma electrons. In contrast to the above mentioned results for silver and copper no distinct information about the size distribution of the particles has been achieved with TEM. Particles around 20 nm were seen but also much smaller and much larger ones were detectable. For this reason we have applied, in cooperation with the Sympatec company, PCCS measurements to get a reliable particle size distribution (Fig. 10). Due to the fact that this method is based on the Stokes–Einstein equation we had to dilute the sample with a less viscous solvent.

The high viscosity of the used ionic liquids leads to multiple scattering events of the particles, which causes falsified results. The results of the particle IL solution in methanol confirm our TEM observation. But in contrast to the TEM results most of the particles were smaller than 5 nm. This result shows that with PCCS it is possible to get rapidly particle size distributions. The PCCS results also indicate a decomposition of the particles with time, because the size distribution has shifted to smaller values. We attribute this behaviour to an interaction of the silicon nanoparticles with the methanol (residues of water), maybe in combination with chlorine in the solution. Due to this reaction  $\text{SiO}_x$  species might be formed on the particle surface, which lead to a slow decomposition of the particles. In the future dry aprotic solvents without halide-groups like toluene for example have to be used to avoid such decomposition. The chemical composition could not be determined

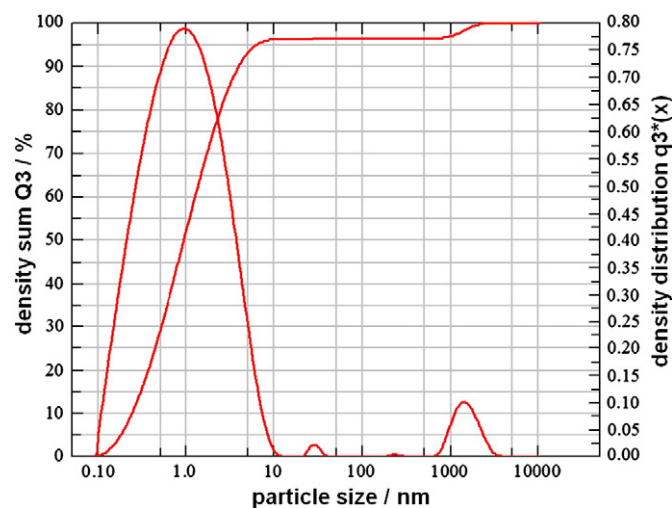


Fig. 10. Particle size distribution of silicon nanoparticles.

with XPS, but additional photoluminescence and UV/Vis measurements imply the formation of pure silicon nanoparticles.

As mentioned above it is not yet possible to see a general trend of the particle size dependency on the individual ionic liquid and on the kind of the plasma reactor. The particles synthesised so far were larger in size compared to the particles generated with the chemical reduction method and the sputtering technique. For example the copper nanoparticles produced with physical vapour deposition in  $[\text{BMIm}]\text{Tf}_2\text{N}$  and  $[\text{BMIm}]\text{PF}_6$  exhibit particles sizes around 3 nm [20]. These sizes are comparable with observed sizes for copper particles generated with the chemical method [53]. Just our copper nanoparticles in  $[\text{BMIm}]\text{dca}$  were in this size regime, the Cu particles in  $[\text{EMIm}]\text{Tf}_2\text{N}$  and  $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$  were larger. When we compare the particle dimensions from plasma electrochemistry in ionic liquids, consisting of imidazolium cations and different anions, with the particle dimensions achieved by reduction with low-energy electrons, done by the Kuwabata group [37] then we end in the same size regime. Interestingly Kuwabata et al. found that the anion plays an important role for the particle size, whereas the change of the alkyl chain length at the cation has a minor influence on the size [37]. Here the particles in imidazolium liquids containing the  $[\text{Tf}_2\text{N}]$  anion were around a factor of 2 larger compared to liquids containing the  $[\text{PF}_6]$  anion.

In Fig. 11 a comparison of TEM images of germanium and silicon nanoparticles in  $[\text{EMIm}]\text{Tf}_2\text{N}$ ,  $[\text{EMIm}]\text{FAP}$  and  $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$  is shown. On the one hand it is visible that there is no big difference between the germanium and silicon particles in the same liquid, whereas on the other hand the germanium particles in the FAP liquid are smaller and exhibit a narrower size distribution. In addition, the pyrrolidinium cation has nearly no influence on the silicon particle size. Here the same trend has been observed for copper, the particles in  $[\text{BMIm}]\text{dca}$  were smaller compared to the particles in  $[\text{EMIm}]\text{Tf}_2\text{N}$  and  $[\text{Py}_{1,4}]\text{Tf}_2\text{N}$ . A final statement is not possible, because the silicon results, with PCCS, indicate that there are much smaller particles in the liquids, which were barely detectable with the TEM. There are more measurements of the particles size with different methods necessary to decide to which extent the anion is a determining factor for the particle size in plasma electrochemistry. For the sputtering technique and the physical vapour deposition method, two comparable growth models were proposed. As mentioned above, Vanecht et al. found two growth processes for gold particles made by sputtering. The first one is fast and it stops directly after the sputtering and subsequently followed by a second slow growth. The rate of the second process depends on the viscosity of the IL. They attributed the particle size of around 6 nm to a formation of a stabilising IL layer around the particles [19]. Richter et al. introduced a similar process for the evaporation of metals on ionic liquids [10,20]. There, the beginning of the particle growth is an interplay between the mass transport to the IL surface, the diffusion through the surface and the ripening in the bulk of the IL. They claim

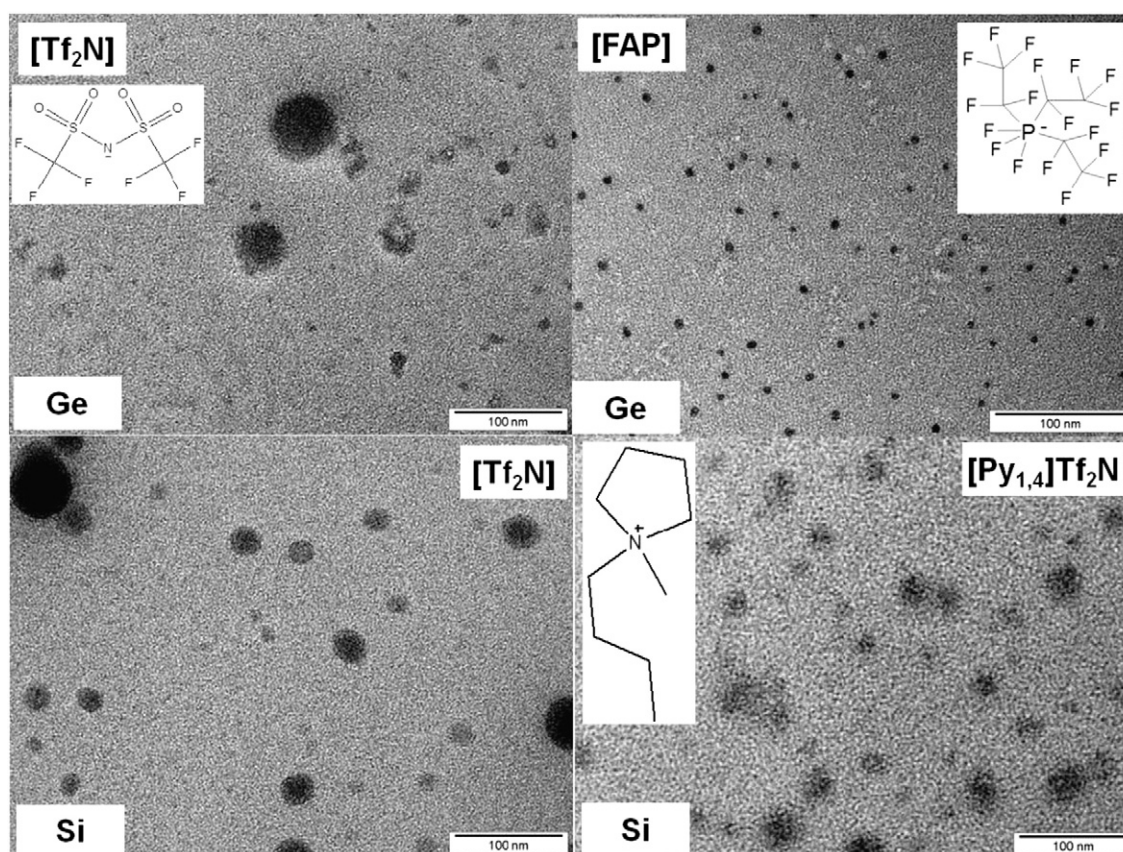


Fig. 11. TEM of semiconductor particles in [EMIm]Tf<sub>2</sub>N, [EMIm]FAP and [Py<sub>1,4</sub>]Tf<sub>2</sub>N.

that for smaller particles is it necessary to have a higher diffusion rate than the mass transport to the surface. Moreover, they state for the final particle size the following: "This final size seems to be independent of the concentration of metal and bulk properties of the IL and depends on the chemical identity of the respective IL matrix" [10]. In addition, they found, that for long term stabilisation of transition metal nanoparticles imidazolium ILs with weakly coordinating perfluorinated anions, like the Tf<sub>2</sub>N anion, are suited. With the highly coordinating dicyanamide anion, for example, they were not able to get nanoparticles. This is in contrast to our results for copper nanoparticles in [BMIm]dca. So the proposed growth model cannot be transferred one-to-one, and there are open questions. But terms like mass transport and diffusion in the IL have to be taken into account to explain the growth process during plasma electrochemistry. The mass transport, for example due to convection, in the plasma experiment, is the transport of the dissolved species from the bulk to the interface. Interestingly the start concentration of the compounds seems to have no influence on the particle size. The copper particles from a 60 mmol/L Cu<sup>+</sup> [EMIm]Tf<sub>2</sub>N solution were larger compared to the particles from a 1 mol/l Cu<sup>+</sup> [BMIm]dca solution. Then the electron density above the liquid and the penetration depth of the electrons into the liquid should play a role in the first step of the growth process. Also secondary species, like IL decomposition products, could have influence on the reduction process, especially for the A-mode where these products are proposed to be necessary for the reduction. Obviously the plasma induced growth process is in some contrast to vapour induced ones, with more parameters. In our opinion more work is necessary to get insight in the particle growth during plasma interaction.

#### 4. Conclusion

In the present paper we have summarised the key results of the plasma electrochemistry project in the framework of the SPP1191 of the

DFG. We have reported, that with this method it is possible to synthesise different kinds of metal and semiconductor nanoparticles. Using the example of the generation of copper nanoparticles in [EMIm]Tf<sub>2</sub>N, [Py<sub>1,4</sub>]Tf<sub>2</sub>N and [BMIm]dca we have demonstrated the ability of this technique to produce nanoparticles from reactive metals. Also we have presented the possibility of plasmaelectrochemistry to synthesise free germanium and especially silicon nanoparticles in ionic liquids. In comparison with particles achieved by reduction with low-energy electrons, we found hints that the anion has an influence on the particle size. At the end we have discussed the growing process of the particles in the context of the proposed growth model for nanoparticles produced by physical vapour deposition in ionic liquids.

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