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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.

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_6) from $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) and $RhCl_3 \cdot 3H_2O$, 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_6 [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 $Pd(OAc)_2$ and $Au(OAc)_3$ in hydroxyl-functionalised ionic liquid 1-(2′-hydroxylethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)amide [C_2OHmim]Tf_2N [14].

Due to the above mentioned very low vapour pressures which range 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 — 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_6 at a pressure of 10^{-4} 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 $HAuCl_4 \cdot 3H_2O$, $PtCl_2$ and $PdCl_2$, respectively in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) by Hatakeyama et al. [30,33]. Liu et al. also have produced gold and palladium from $HAuCl_4 \cdot 3H_2O$ and ($PdCl_2$)/[BMIm]BF_4 [28]. We will summarise here our results for the generation of silver nanoparticles from $AgCF_3SO_3$ in 1-butyl-3-methylimidazolium trifluoromethylsulfonate ([BMIm]TfO) and 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ([$Py_{1,4}$]TfO) and of copper nanoparticles in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([EMIm]Tf_2N), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([$Py_{1,4}$]Tf_2N) 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 [$Py_{1,4}$]Tf_2N 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 $SiCl_4$ and $GeCl_4$ 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 $GeCl_4$ 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 $SiCl_4$ and $RSiCl_3$ (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_8H_{17}–$SiCl_3$ were in the range between 3 and 7 nm, the particles with $HSiCl_3$ 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 $SiBr_4$ 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_8H_{17}–$SiCl_3$ reduction in a tetrahydrofurane 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 $SiCl_4$ 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 $SiCl_4$ 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_4 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