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Nanoparticle Synthesis

Stabilizer-Free Metal Nanoparticles and Metal–Metal Oxide Nanocomposites with Long-Term Stability Prepared by Physical Vapor Deposition into Ionic Liquids**

*Kai Richter, Alexander Birkner, and Anja-Verena Mudring**

Ionic liquids (ILs) have received substantial attention in recent years. Their inherent properties such as in most cases negligible vapor pressures, wide liquidus ranges, good thermal stabilities, considerable electric conductivities, and wide electrochemical windows have been shown to be advantageous for a large number of applications.[1] As salts, ionic liquids are composed of distinct cations and anions, which makes them widely tunable. They may be designed for specific applications through the choice of the respective cation and anion and the ion combination. In the last decade ILs have been explored for organic synthesis and catalysis[2] and only to a lesser extent for inorganic materials synthesis.[3]

The first account on metal nanoparticles in ILs reports on the formation of palladium nanoparticles from Pd^{II} precursors during a Heck reaction.[4] Since then, especially Dupont and co-workers have dedicated themselves to the preparation of transition-metal nanoparticles from ionic liquids without the use of additional stabilizers either by thermal decomposition of an organometallic precursor or by reduction of the precursor with hydrogen.[5] Nanoparticles (NPs) are thermodynamically and kinetically unstable compared to the bulk. As a consequence, some kind of stabilization needs to be supplied to prevent nanoparticle agglomeration and coalescence of particles. It was proposed that ionic liquids may provide both steric and electrostatic stabilization to NPs, and the term electrosteric stabilization has been coined to describe this circumstance.[6] Unfortunately, in most cases when neat ionic liquids are used, aggregation over time is observed. In response, methods for the long-term stabilization of nanoparticles in ILs were developed that employ additional stabilizers such as poly(*N*-vinyl-2-pyrrolidone) (PVP),[7] IL-like copolymers[8] and IL polymers,[9] or thiol-functionalized ILs.[10]

Since metal nanoparticles alone as well as metal–metal oxide composites are of importance for many applications, we have aimed at synthesizing such materials in ionic liquids without the addition of any stabilizer other than the ionic liquid itself. For example, gold nanoparticles are used in biology and medicine for plasmon-based labeling and imaging, optical and electrochemical sensing, diagnostics, drug vectorization and DNA and gene delivery, and for treatment of various diseases such as cancer, Alzheimer, AIDS, hepatitis, tuberculosis, arthritis, and diabetes.[11] Gold[12] and copper[13] nanoparticles alone have been shown to be efficient catalysts for alcohol oxidation[14] or in the water–gas shift reaction but have also become important in other applications such as conductive films,[15] lubricants,[16] and nanofluids.[17] Coinage-metal nanoparticles have been synthesized by various techniques including reverse micelle methods,[18] reduction of copper salts in water with hydrazine,[19] or in water-in-oil microemulsion with $NaBH_4$,[20] thermodecomposition of organometallic precursors,[21] sonochemical synthesis,[22] gamma radiolysis,[23] with carbon nanotube templates,[24] the electroexploding wire process,[25] pulsed wire discharge,[26] water-in-supercritial-CO_2 microemulsion,[27] photochemistry,[28] microwave irradiation,[29] laser ablation,[30] and many others. Metal vapor synthesis has also been used.[31] Because of their propensity towards oxidation,[32] pure metallic copper particles are difficult to obtain, and only a few reports on oxidation-resistant Cu NPs from aqueous solution exist.[33]

Supported copper nanoparticles are used as highly active heterogeneous catalysts for the synthesis of methanol at moderate pressures and temperatures, and the Cu/ZnO nanocomposite has become the prototype gaining widespread attention.[34] Several methods have been developed for the synthesis of Cu/ZnO nanocomposites involving organometallic[35] or mechanochemical routes.[36] Recently, the synthesis of Cu@ZnO core–shell nanocomposites by solvated metal atom dispersion (SMAD) has been reported.[37] The technique, originally developed by Klabunde and co-workers,[38] consists of cocondensation of substrate vapors together with a cosolvent or stabilizing agent, in this case 2-butanone, under high vacuum onto a target that is maintained at liquid nitrogen temperature. Upon thawing, the desired compound forms. We use a similar approach based on a physical vapor deposition setup initially developed by Timms, Skell, Klabunde, and Green for the synthesis of low-valent main-group halides and transition-metal arene complexes and used for work by Ozin, Burdett, and Turner in matrix cryochemistry.[39]

[*] K. Richter, Prof. Dr. A.-V. Mudring
FRSC, Anorganische Chemie I—Festkörperchemie und Materialien
Fakultät für Chemie und Biochemie
Ruhr-Universität Bochum, 44780 Bochum (Germany)
Fax: (+49) 234-32-14951
E-mail: anja.mudring@rub.de
Homepage: http://www.anjamudring.de
Dr. A. Birkner
Physikalische Chemie I, Fakultät für Chemie und Biochemie
Ruhr-Universität Bochum, 44780 Bochum (Germany)

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Simply using ionic liquids with negligible vapor pressure rather than conventional volatile organic solvents (VOCs) or stabilizing agents with significant vapor pressure makes it possible to work at ambient temperature under high vacuum rather than freezing the volatile compounds. Physical vapor deposition by sputtering of metal targets into ILs has been reported recently.[40] However, the substantially higher pressures likely lead to formation of thin metal films at the IL surface. In consequence, this technique has been explored for manufacturing of lunar telescopes.[41] One major disadvantage is that the high-energy particle impact on the IL leads to decomposition.

We investigated the milder physical vapor deposition of the coinage metals copper and gold under high vacuum and ambient temperature. For example, in a typical experiment to prepare Cu nanoparticles in an IL, pure copper (80 mg) was evaporated onto the surface of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophospate ($[C_4mim][PF_6]$, 40 mL) at a vapor pressure of 10^{-6} Torr. During the deposition the color of the ionic liquid changed from transparent colorless to red-brown, thus indicating the formation of the copper colloid. Figure 1 a, b shows the TEM images of the particles measured directly in the ionic liquid. The image reveals spherical particles with a mean diameter of 3 nm. The particles themselves self-assemble to domains with hexagonal arrangements on the TEM grid (similar to a 2D close-packed layer of circles). Interestingly in such arrays, the particles are about 20 Å apart from each other. We ascribe this phenomenon to the formation of an electrostatic protection layer of ionic liquid around the Cu particles. The colloids are very stable, and we observed no color change or precipitation over months.

The powder X-ray diffraction (PXRD) pattern of the red-brown powder obtained after precipitation by dilution with dry acetonitrile and centrifugation at 2000 rpm confirms the crystallinity and absence of any other crystalline impurities of the samples, which show the expected reflections for face-centered cubic (fcc) copper at $2\theta = 43.32°$ (111), 50.49° (200), and 74.04° (220) (see the Supporting Information).

To investigate the optical properties, UV/Vis spectroscopy was carried out (Figure 1 e). The absorption maximum at 576 nm can be attributed to the surface plasmon resonance of small copper particles. The position of the maximum depends on the environment of the particles and the polarity of the solvent. It was possible to predict the surface plasmon resonance (SPR) peak based on Mie theory according to the BHMIE algorithm[42,43] by assuming spherical particles of 3 nm and a size distribution of 20 %.

To examine the oxidation behavior of the particle surface, in situ oxidation was carried out by opening the cuvette and aging the colloids in air. During the oxidation process the SPR shifts to higher wavelengths and the sample color changes gradually from red-brown to green. After 20 minutes the maximum was found at 600 nm owing to surface oxidation. After leaving the cuvette open to air overnight, no significant absorption maximum could be detected (Figure 1 e, inset, right). Similar observations were made for evaporation of copper into the ionic liquid $[C_4mim][Tf_2N]$ (Tf_2N = bis(trifluorosulfonyl)amide; see also below for Cu@ZnO composites).

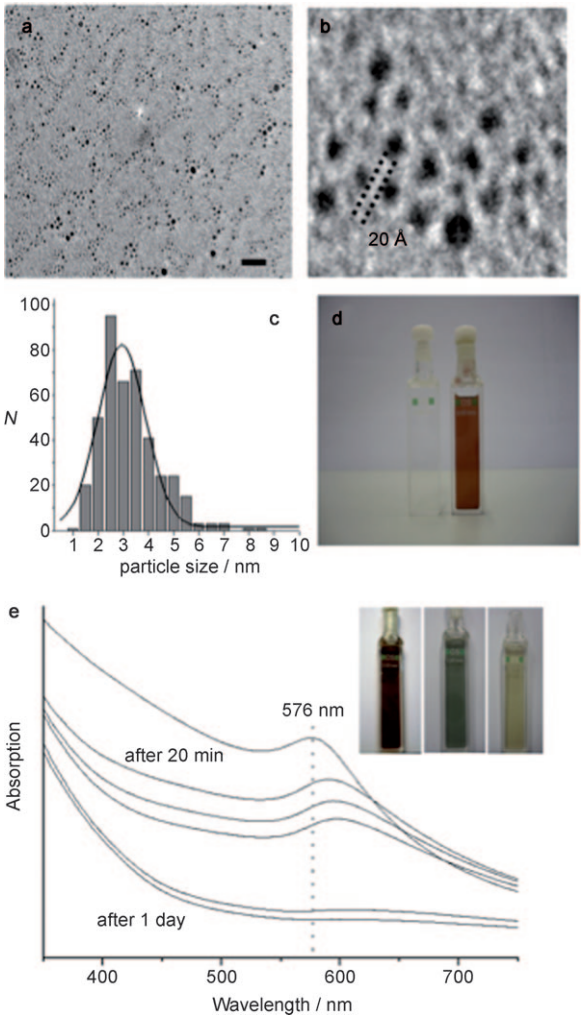

Figure 1. a,b) TEM images of copper nanoparticles in the ionic liquid $[C_4mim][PF_6]$. Scale bars: 40 nm. c) Particle size distribution of the as-prepared copper particles. d) Photographs of pure $[C_4mim][PF_6]$ (left) and of $[C_4mim][PF_6]$ after copper deposition (right). e) UV/Vis spectra of the copper colloids in $[C_4mim][PF_6]$. Inset: Color change during air oxidation of the copper particles.

To investigate the influence of the ionic liquid on the metal particle formation in more detail, we switched from copper to gold. As gold is the more noble metal, it is less apt to oxidize and thus is easier to handle. Evaporation of gold into the ionic liquids $[C_4mim][BF_4]$, $[C_4mim][Tf_2N]$, $[C_4mpyr][Tf_2N]$ (C_4mpyr = *N*-butyl-*N*-methylpyrrolidinium), $[C_4mim][DCA]$ (DCA = dicyanamide), and [P66614][DCA] (P66614 = trishexyltetradecylposphonium) was studied. As for copper (see also below), the gold colloids obtained by evaporation of the metal into $[C_4mim][BF_4]$ and $[C_4mim][Tf_2N]$ showed good long-term stability against precipitation. For $[C_4mim][Tf_2N]$, TEM imaging shows 4 nm large round particles with a small size distribution as the reaction product (Supporting Information). PXRD and UV/Vis spectroscopy confirm the formation of gold particles of this small size. The rsults of UV/Vis spectroscopy indicate that initially smaller

particles had formed, which underwent ripening (see the Supporting Information).

When the imidazolium cation is exchanged for pyrrolidinium as in $[C_4mpyr][Tf_2N]$, substantially larger particles form, which start to precipitate after a few days. Evaluation of the absorption spectrum and TEM as well as PXRD data, also undertaken for the following experiments, indicate a particle size of about 20–40 nm. This result suggests that the imidazolium cation is responsible for particle stabilization. The aromatic π system or the acidic C2 proton may play an important role in the direct interaction with the metal particle. A second layer formed by the counteranion may lead to an electrostatic stabilization shell. Recently, XPS studies confirmed such a bilayer structure for ultrathin $[C_2mim][Tf_2N]$ films.[44]

To test this hypothesis, other ILs with $[C_4mim]$ as the cation and BF_4 as well as DCA (dicyanamide) as anions were employed in the synthesis. In the case of $[C_4mim][BF_4]$, a colloid with long-term stability formed. However, the metal particles were slightly larger after ripening (ca. 7 nm) than in the case of $[C_4mim][Tf_2N]$. For $[C_4mim][DCA]$, initially small particles form (ca. 10 nm). However, larger particles (40–79 nm) grew with time, and gold precipitation was almost complete after three days. However, the particle size cannot be correlated with the molecular volume of the IL anion, as suggested for the formation of silver NPs by hydrogen reduction in ILs.[45] That NP formation and stabilization is more complex becomes obvious when the extremely hydrophopic ionic liquid [P66614][DCA] is used. In this case, the immediate formation of a metallic layer on top of the IL surface during the evaporation process is observed. This film then breaks up, and fairly large particles (ca. 50 nm) form, which soon precipitate.

We assume that the formation and the particle size distribution of the copper particles depend on the physical and chemical properties of the ionic liquid. The transition metal evaporates as mono- or diatomic species into the gas phase and forms a thin layer on the ionic liquid surface (Figure 2). The initial formation of a thin layer is supported by the observation that high evaporation rates lead to a reflective metal surface on the ionic liquid film. This thin layer breaks, and metal fragments diffuse into the bulk IL and form nanoparticles, which are shielded by alternating cation–anion layers around the particle. The obtained particle size is the energetic optimum for the given metal aggregates in the corresponding IL matrix.

The versatility of the methods is demonstrated by the fact that not only metal colloids but also nanoscale Cu/ZnO composite materials can be stablized over long periods of time in ILs such as $[C_4mim][Tf_2N]$. To obtain such mixed materials, copper was deposited on zinc oxide (NanoTec, Nanophase, and Puratronic, AlfaAesa) dispersed in the ionic liquid by ultrasound. After the zinc oxide dispersion was placed in the vacuum chamber, copper was evaporated onto the surface of the ionic liquid. During the evaporation process, the color of the dispersion changed from white to brown. The product was siphoned into a Schlenk tube under inert conditions for further investigations.

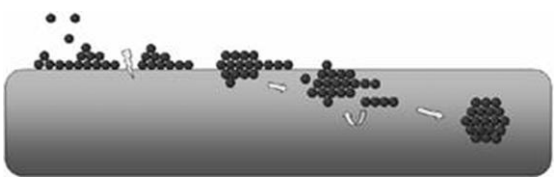

Figure 2. Postulated formation mechanism of nanoparticles.

The TEM analysis of the reaction product (in the IL) reveals that the zinc oxide nanoparticles are covered with copper. Most of the formed copper particles are on or close to the zinc oxide substrate surface. Only a few free particles were observed. This result is backed by energy-dispersive X-ray (EDX) spectroscopy. The EDX emission spectra measured directly in the neighborhood of zinc oxide particles also show intense copper signals. If an area further away from zinc oxide is chosen for the measurement, only signals which can be attributed to the ionic liquid are detected (see the Supporting Information).

After separating the Cu/ZnO composite material from the IL by centrifugation and washing with polar and apolar solvents (acetonitrile, dichloromethane), flaking and agglomeration of copper from the zinc oxide surface was observed (see the Supporting Information). To enhance the contact of copper to the zinc oxide surface, microwave irradiation and ultrasound treatment were used. After the deposition experiment, one sample of the as-prepared colloid was treated with microwave irradiation and the other sample with ultrasound several times. Using both strategies it was possible to fix the copper nanoparticles to the zinc oxide substrate. Figure 3 shows the TEM images of the separated and washed composite particles. In the case of annealing with microwave radiation (Figure 3a) the size of the copper particles on the ZnO surface is on average 3.5 nm, which corresponds quite

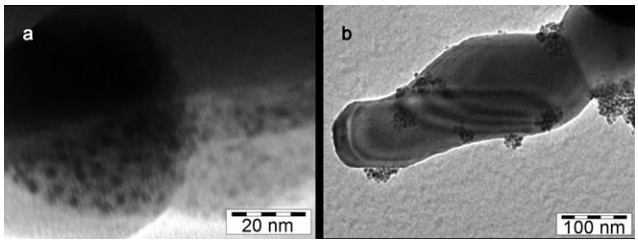

Figure 3. TEM image of Cu/ZnO nanostructures after treating with a) microwave irradiation and b) ultrasound.

well with the particle size distribution of the neat copper colloids (Figure 1c). When the sample is treated with ultrasound, the copper particles tend to form larger aggregates (Figure 3b) and cover the substrate surface less uniformly than in the case of microwave heating. We assume that the fast heating with microwave irradiation leads to a partial melting of the copper surface and that the particles form an alloy with the substrate. This process is faster than the formation of agglomerates or Ostwald ripening observed in the case of the ultrasound treatment. The EDX spectra for all cleaned Cu/ZnO samples reveal only the characteristic

emission lines of zinc oxide and copper (see the Supporting Information).

Physical vapor deposition of substrates into suitable ionic liquids under high vacuum represents a simple and facile way to prepare nanoparticle suspensions that show good long-term stability. We were able to show that no stabilizers other than the solvent itself are needed to keep the particles in solution. The advantage of the ionic liquid is two-fold. For the first time, freezing or cooling of the solvent during the synthesis can be omitted, as the solvent has negligible vapor pressure. This advance may open completely new paths for inorganic synthesis. Secondly, only the IL (solvent) is needed to keep the nanoparticles in solution, as its constitution allows it to provide enough stabilization. We are currently trying not only to elucidate the nature of stabilization but are also broadening this synthesis method for the preparation of fluoridic and oxidic NP materials[46] as well as mixed-metal alloys.

Experimental Section

Materials: Copper (99.9995%) and gold (99.99%) were purchased from smart-elements.com (Vienna, Austria). Zinc oxide was purchased from Nanophase (NanoTec) and AlfaAesar (Puratronic) and dried at 400°C under vacuum for 6 h. The ionic liquids [C_4mim]]-[BF_4], [C_4mim]][PF_6], [C_4mim]][Tf_2N], and [C_4mpyr][Tf_2N] were purchased from IoliTec (Denzlingen, Germany) and were dried at 80°C under vacuum for two days prior to use. The other ionic liquids were prepared as described below.

[P66614][DCA]: Trihexyl(tetradecyl)phosphonium chloride (50 g, 0.0963 mol) and sodium dicyanamide (10.3 g, 0.116 mol) were added to a mixture of acetone (150 mL) and water (150 mL). The mixture was stirred overnight at room temperature. After removal of the acetone under vacuum, the residual layer was extracted with dichlormethane (4 × 50 mL). The combined organic layers were washed intensively with deionized water (10 × 15 mL) to remove any excess dicyanamide. The solvent was evaporated to give a colorless low-viscosity liquid. Yield: 95.2%, 50.41 g. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.89$ (m, 12H), 1.25 (m, 32H), 1.47 (m, 16H), 2.10 ppm (m, 8H).

[C_4mim][DCA]: 1-Butyl-3-methyl-imidazolium chloride (50 g, 0.286 mol) was melted at 80°C in an argon-flushed three-neck flask, and sodium dicyanamide (28.00 g, 0.315 mol) was added to the melt. The mixture was then stirred at 80°C under argon overnight. After cooling to room temperature, the remaining solid was extracted with 100 mL dichlormethane, and the organic layer was washed with a small amount of deionized water. The solvent was evaporated to give a low-viscosity colorless liquid. Yield: 92.8%, 54.48 g. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.88$ (t, 3H), 1.32 (m, 2H), 1.84 (m, 2H), 4.02 (s, 3H), 4.24 (t, 2H), 7.46 (s, 1H), 7.51 (s, 1H), 9.36 (s, 1H).

Preparation of Cu and Au nanoparticles: Typical SMAD equipment (TVP 800, Torrovap, Canada) as described in detail in reference [37], was used to prepare the coinage-metal colloids. In a typical experiment, the ionic liquid (40 mL) was placed in the glass bulb of the reactor and of the desired metal (80 mg) was placed in a tungsten crucible for evaporation. The setup was evacuated with an oil diffusion pump to 10^{-6} Torr; the ionic liquid was allowed to degas for 4 h. Then rotation of the glass bulb was started. When a homogeneous thick film of the ionic liquid had formed on the glass surface, the metal was evaporated onto the ionic liquid under dynamic vacuum. After evaporation, the as-prepared colloid was siphoned into a Schlenk tube under argon and subjected to further analysis.

Preparation of Cu/ZnO composites: Before evaporation, zinc oxide (100 mg) was dispersed in the ionic liquid (40 mL) by aging with the help of ultrasound. This dispersion was placed in the SMAD equipment and vaporized with copper as described above. One sample of as-prepared colloid was then treated under argon with ultrasound for 30 min, and the other sample was treated with microwave irradiation (CEM Discover) for 10 min at 300 Watt power. The particles were then centrifuged and washed with dry acetonitile several times.

Instrumentation: TEM was carried out with a Hitachi H-8100 microscope equipped with a LaB_6 cathode and operated at an acceleration voltage of 200 kV. Energy-dispersive X-ray spectra (EDS) were obtained from an attached EDX system (Oxford Link) with a Si(Li) crystal and an ultrathin ATW2 window. Samples measured directly in the ionic liquid were prepared by dropping a small amount on the gold grid; excess liquid was wiped away with a tissue. Powder samples were dispersed in dichloromethane, and the solvent was allowed to evaporate before the measurement. PXRD was carried out using a Huber G670 Guinier camera. The powders were sealed in 0.5 mm Lindemann capillaries under argon. UV/Vis spectra were recorded using a Varian Cary 5000 UV/Vis spectrometer under argon, except for the measurements during the in situ oxidation process.

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