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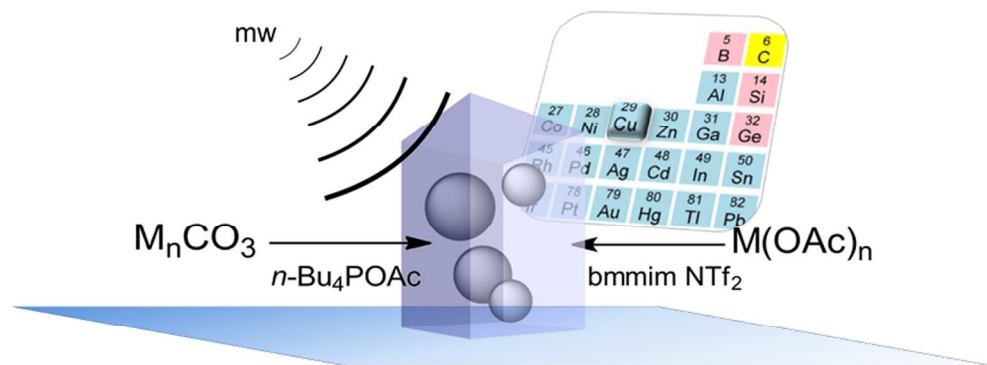


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ARTICLE

Fast track to nanomaterials: Microwave assisted synthesis in ionic liquid media

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Herein we present a general approach to metal and metal oxide nanoparticles using simple metal salts as starting materials. The reducing agent can be delivered in form of the anion incorporated into the metal precursor respectively ionic liquid. Exemplary we demonstrate the synthesis of Cu and Ag as well as ZnO and NiO nanoparticles generated either from acetate or carbonate salts. All particles are synthesised by microwave heating without the necessity of inert conditions. Two different types of ionic liquids have been used as reaction media – tetra-*n*-butylphosphonium acetate (*n*-Bu₄POAc) and 1-butyl-2,3-dimethylimidazolium N,N-bis(trifluoromethylsulfonyl)imid (bmmim NTf₂). In this case, the choice of the ionic liquid seems to have significant influence on size, shape and dispersity of the synthesised particles. It is clearly shown that the acetate anion present in all reaction mixtures can act as an inexpensive and nontoxic reducing agent. The final products in solid, liquid and gaseous phase have been characterised by XRD, TEM, NMR, FT-IR and online gas-phase MS.

Introduction

Ionic liquids (ILs) emerge more and more to highly desirable multipurpose solvents. They show extraordinary chemical and physical properties with low melting points, negligible vapour pressure,^[1] high chemical inertness and tuneable polarity, acidity and basicity.^[2] Due to these properties ionic liquids represent solvents which can be designed for each and every reaction by variation of anion and cation as well as by incorporation of functional and/or coordinating groups.^[3] It is the spirit and purpose of ionic liquids to cover as many objectives as possible. In these terms they can make numbers of classical additives dispensable. Accordingly, ionic liquids are very popular concerning the synthesis of zero- and one-dimensional nanostructures.^[4-7] Ionic liquids can act as solvents, co-solvents,^[8-11] promoters,^[12,13] reducing agents,^[12-15] capping or protective agents and surfactants.^[3,16] Despite their low melting points, ionic liquid phases show structural properties of lower order: they consist of polar and nonpolar nanoscale regimes which make them ideal templates for nanoscale synthesis.^[16-18]

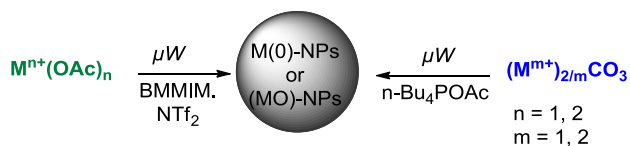
In recent years, metal and metal oxide nanoparticles (NPs) have attracted much attention in academic and industrial research. Their unique properties revealed a completely new field for applications; even for compounds which have been sufficiently investigated in bulk state.^[19-21] Their high surface to volume ratio makes them attractive for catalytic and medical

applications; the quantum size effect of small particles^[22] shows remarkable results in photochemistry and nonlinear optics.^[23,24] However, nanoparticles – as all nanoscale structures – are thermodynamically disfavoured and show high tendency for agglomeration and aggregation. Surfactants, such as polymers/dendrimers,^[25-28] ligands and especially ionic liquids sufficiently shield the nanoparticles' surface and effectively prevent agglomeration.^[12-15,19,29,30]

Nanoparticles can be synthesised in various ways. There are several top-down and bottom-up methods with their inherent advantages and disadvantages.^[15,31-33] Solvothermal syntheses are very well investigated and represent a versatile tool for the preparation of nanomaterials.^[34-36] They bear the advantage to control size and shape by adjusting the reaction parameters. For convincing results solvents or even solvent mixtures must be varied. Additives, surfactants and precursor-loadings have to be adapted.^[37-39] One versatile synthesis of late transition metal(oxide) particles in pure ionic liquid would be favourable because of their high demand in scientific research, which is especially applicable for Cu, Ag, NiO and ZnO.^[5,7,40-43] Reactions should be carried out without any additives, without precautions against moisture or oxygen and at best with an environmentally benign reducing agent.

Herein, we present a general nanoparticle synthesis using tetra-*n*-butylphosphonium acetate (*n*-Bu₄POAc) or 1-butyl-2,3-dimethylimidazolium N,N-bis(trifluoromethylsulfonyl)imid (bmmim NTf₂) as reducing agent respectively stabiliser.

Exemplary we synthesised nanoparticles of NiO-NP, ZnO-NP, Ag-NP and Cu-NP (Scheme 1). The particles - generated from metal carbonates (in *n*-Bu₄POAc) or metal acetates (in bmmim NTf₂) - are synthesised by microwave heating. Further investigation of the solid phase (particles), the liquid phase (IL) and the gaseous phase (by-products) is implemented.



Scheme 1: General synthesis of metal and metal oxide nanoparticles by microwave synthesis. M = Cu, Ni, Ag, Zn

Results and discussion

Microwave Synthesis of Cu(0)- and Ag(0)-nanoparticles

Silver and copper nanoparticles were obtained both in *n*-Bu₄POAc from silver carbonate (Ag₂CO₃) and copper carbonate (CuCO₃), respectively, and in bmmim NTf₂ from silver acetate (AgOAc) and copper acetate monohydrate (Cu(OAc)₂·H₂O). The syntheses were conducted under microwave heating. TEM pictures were taken from the as-synthesised nanoparticles. In figure 1 the copper nanoparticles obtained in *n*-Bu₄POAc are presented as well as a size distribution of the particles. The copper particles obtained in the phosphonium-based IL were synthesised at temperatures of 160 °C within 10 min and show an average diameter of 4.8 nm (±1.7 nm). The monodisperse particles are homogeneously distributed in the ionic liquid film. Previously, we have shown that the thermal decomposition of copper carbonate in *n*-Bu₄POAc at temperatures as high as 120 °C leads to the growth of Cu₂O nanoparticles.^[14] Interestingly, adjusting the reaction parameters (temperature, time and heating method) is suitable as a sensitive tool for the predetermination of the particles final oxidation state, yielding in the present case Cu(0) nanoparticles. The copper nanoparticles obtained in bmmim NTf₂ (see Fig. 2) have been synthesised at temperatures as high as 235 °C within 3 min. The majority of the particles have an average diameter of about 4.9 nm (±1.1 nm) and the incorporation into the ionic liquid effectively prevents further crystal growth or agglomeration but not the aggregation of the small nanoparticles. For both samples the XRD-pattern confirms pure Cu(0) (SI Fig. 1). Due to the smaller particle size obtained in *n*-Bu₄POAc, the XRD reflexes are less intensive compared to those synthesised in bmmim NTf₂.

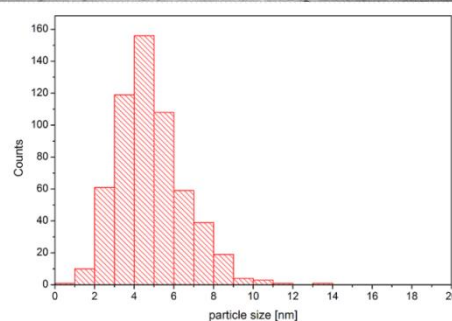


Figure 1: Cu-NPs synthesised in *n*-Bu₄POAc (scale bar 100 nm). The mean particle diameter is 4.8 nm.

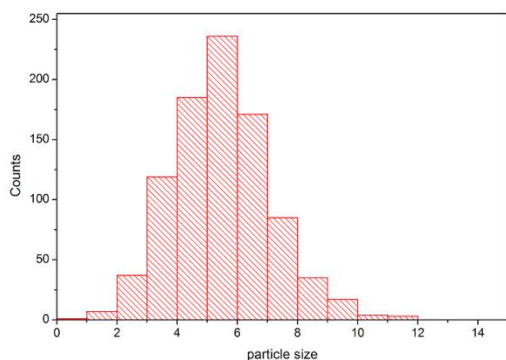
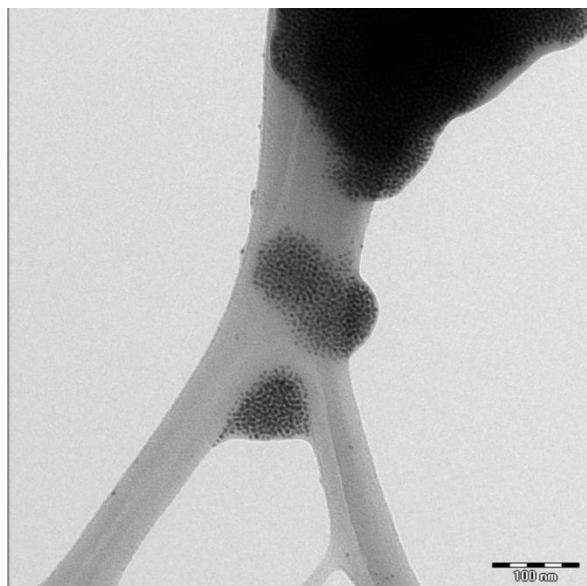


Figure 2: Cu-NPs synthesised in bmmim NTf₂ (scale bar 100 nm). The mean diameter is 4.9 nm.

In an analogous way silver nanoparticles were synthesised in both ionic liquids via microwave irradiation. Figure 3 shows the TEM image depicting the as-synthesised Ag nanoparticles in *n*-Bu₄POAc and in figure 4 the Ag nanoparticles obtained in bmmim NTf₂. The size distribution of the particles is shown in the histogram.

The synthesis of silver nanoparticles in *n*-Bu₄POAc yields small and uniformly shaped particles in the range of 10.1 nm (\pm 5.2 nm). These nanoparticles are very homogeneously distributed and show no agglomerated sites. The silver nanoparticles obtained in *n*-Bu₄POAc have been synthesised at 100 °C in 90 sec.

Contrary silver particles synthesised in bmmim NTf₂ show a higher degree of polydispersity. The particles show a bimodal diameter distribution with the major maximum at 6.7 nm (\pm 0.13 nm) and the minor maximum at 15.6 nm (\pm 0.79 nm). Nevertheless, few particles in the range of 20-60 nm are obtained as well. No residual AgOAc was detected in the

reaction mixture after 5 min at a synthesis temperature of about 200 °C. An XRD-pattern of the particles can be found in SI figure 2 confirming phase purity.

Obviously, the use of different ionic liquids strongly influences the growth of the nanoparticles. *n*-Bu₄POAc is a very polar ionic liquid with low melting point (mp = 55 °C); contrary bmmim NTf₂ is a room temperature ionic liquid (mp = -4 °C) with a relatively low polarity. Apparently, the shielding of the more polar phosphonium ionic liquid seems to be more effective and inhibits the agglomeration of the metal nanoparticles.^[43,44] In contrast, the synthesis of pure metal nanoparticles in the imidazolium-based ionic liquid leads to a higher polydispersity. Additionally, the phosphonium based ionic liquid shows an excellent covering and incorporation of the metal nanoparticles (even on the TEM grid).^[45,46] This can be attributed to the partial charge of the metal particles surface which is beneficial for coulomb interactions between the particle and the polar IL (electrosteric shielding).^[47,48]

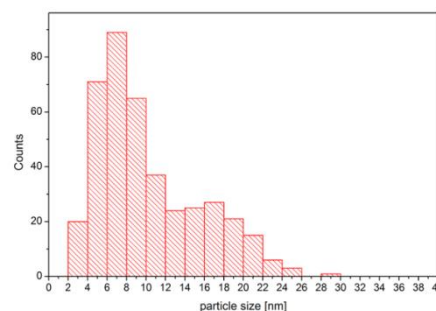
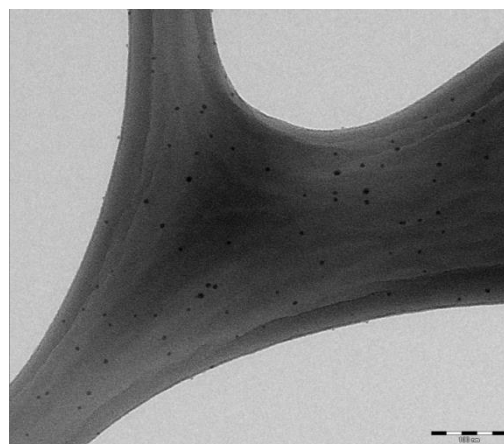


Figure 3: Ag-NPs synthesised in *n*-Bu₄POAc (scale bar 100 nm). The major maximum is at 6.7 nm and the minor maximum at 15.6 nm.

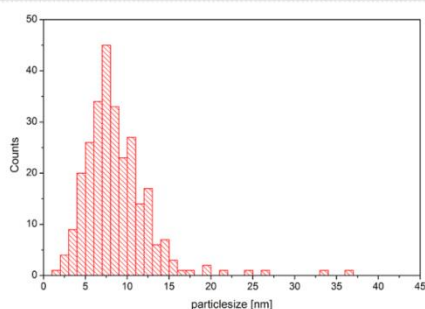
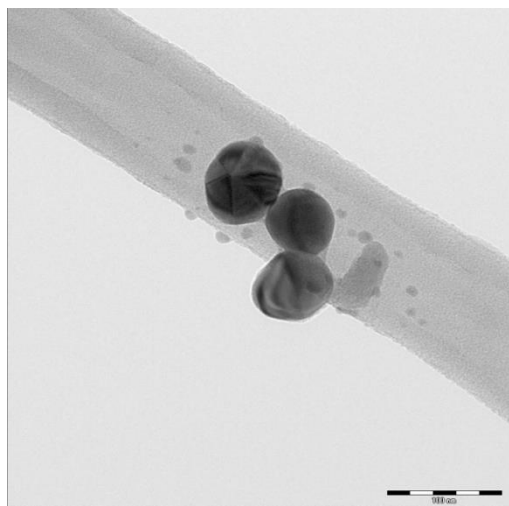


Figure 4: Ag-NPs synthesised in bmmim NTf₂ (scale bar 100 nm). The mean diameter is 12.2 nm.

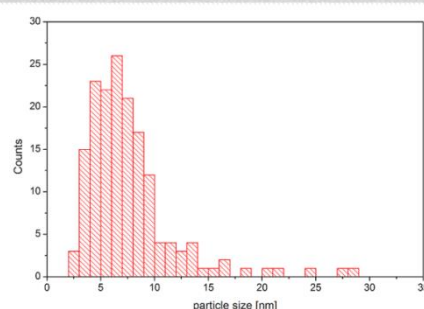
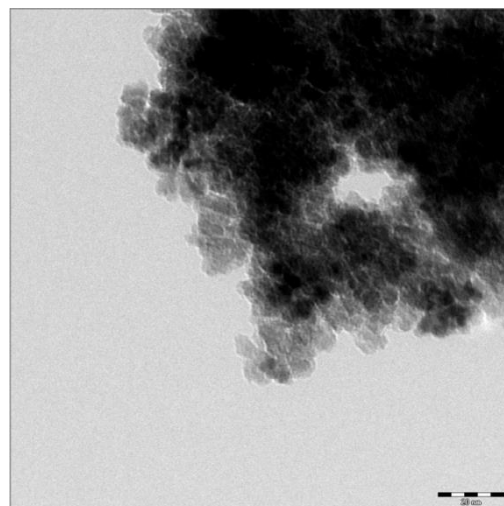


Figure 5: TEM-picture of nickel(II)oxide nanoparticles (5.8 nm) synthesised in *n*-Bu₄POAc (scale bar 20 nm) with size distribution.

Microwave synthesis of NiO and ZnO nanoparticles

NiO- and ZnO-nanoparticles could be obtained both in *n*-Bu₄POAc from nickel carbonate hexahydrate (NiCO₃·6H₂O) and zinc carbonate (ZnCO₃), and in bmmim NTf₂ from zinc acetate dihydrate (Zn(OAc)₂·2H₂O). Due to a better dispersability of nickel acetate in 1-butyl-3-methylimidazolium N,N-bis(trifluoromethylsulfonyl)imid (bmmim NTf₂), the NiO particles are synthesised in the latter.

In figure 5 and figure 6 NiO nanoparticles synthesised in either *n*-Bu₄POAc or bmmim NTf₂ are shown. Particles synthesised in *n*-Bu₄POAc have an average diameter of only 5.8 nm (\pm 1.7 nm), but show a high degree of aggregation. The particles were synthesised at temperatures as high as 200 °C within 10 min. Furthermore, the size distribution is rather broad and even nanoparticles sized between 15 nm and 30 nm are present. The NiO nanoparticles obtained from 1-butyl-3-methylimidazolium N,N-bis(trifluoromethylsulfonyl)imid (bmmim NTf₂) at temperatures of about 250 °C are even smaller – their average diameter is only 2.0 nm (\pm 0.6 nm).

They are all uniformly shaped and show a high tendency for aggregation (due to the small size). Within 30 min only the reflexes of NiO can be detected as shown in the XRD in SI figure 3 indicating no substantial precursor residue or further impurities, moreover no precursor residual could be detected by FT-IR (see SI_Fig. 7). In both cases the XRD reflexes show only a low intensity, due to the small particle size.

ZnO nanoparticles were also synthesised in both ionic liquids via microwave irradiation. The particle precursor ZnCO₃ for the nanoparticles in *n*-Bu₄POAc was converted into zinc oxide within 10 min at 220 °C. The precursor for the zinc oxide nanoparticles in bmmim NTf₂ was zinc(II)acetate dihydrate (Zn(OAc)₂·2H₂O). Nanoparticles could be obtained within 15 min at temperatures of about 225 °C. The TEM pictures of the as-synthesised nanoparticles in *n*-Bu₄POAc are shown in figure 7. Those synthesised in bmmim NTf₂ are shown in figure 8. The nanoparticles obtained in *n*-Bu₄POAc show an average size of 22.2 nm (\pm 10.2 nm), whereas the nanorods synthesised in bmmim NTf₂ have an average length of 189.3 nm (\pm 61.5 nm) and an average diameter of 50.9 nm (\pm 18.2 nm). All nano-sized materials show only a low degree of aggregation and nearly no agglomeration. Both materials were investigated by XRD

techniques as can be seen in SI figure 4. Both XRD patterns are in agreement with the reference pattern (given in red). They show no residual zinc precursor (zinc carbonate or zinc acetate).

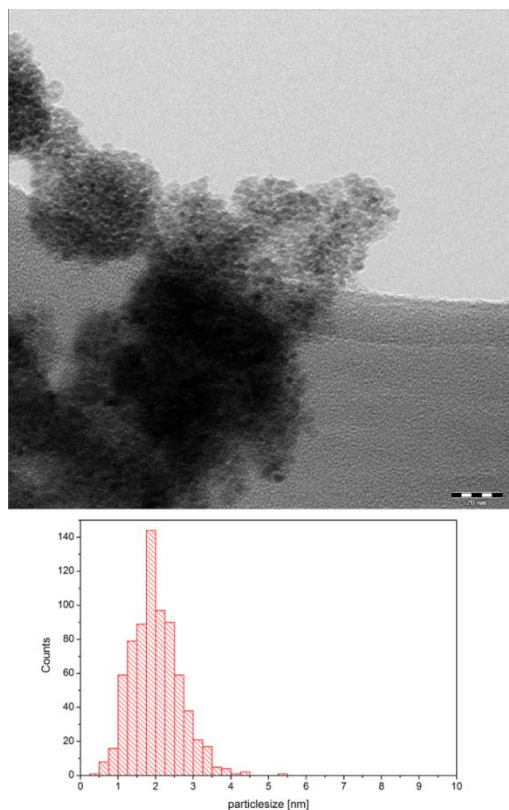


Figure 6: TEM-picture of nickel(II)oxide nanoparticles (2.0 nm) synthesised in bmmim NTf₂ (scale bar 20 nm) with size distribution.

In case of the nickel oxide nanoparticles, those synthesised in bmmim NTf₂ are smaller than those synthesised in *n*-Bu₄POAc. Although the zinc oxide structures synthesised in bmmim NTf₂ are larger than the particles obtained in *n*-Bu₄POAc, they show a high tendency for one-dimensional elongation. From this point of view and in contrast to metal nanoparticles, a rather apolar ionic liquid seems to stabilise metal oxide nanostructures much better and can also lead to a directed growth of 1D nanostructures. This can be attributed to a low ordered *pre-structure* of imidazolium based ionic liquids originating from an intrinsic self-organisation caused by a hydrogen-bond network.^[16,18] Hence, the reaction medium (the ionic liquid) is divided into nanometer-sized polar and nonpolar regions, which are supposed to be beneficial for the growth of metal oxide nanostructures.^[49-51] This can also lead to directed growth of nanostructures which has been already shown by Antonietti *et al.* and summarised by Taubert *et al.*^[42,53]

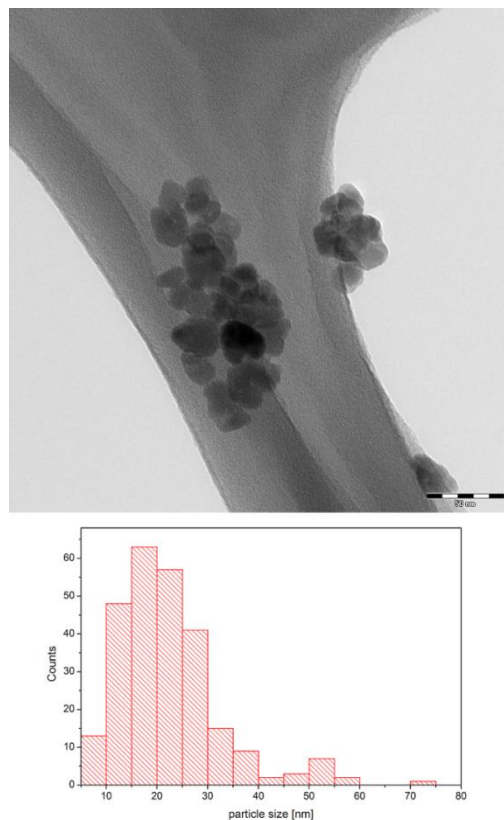


Figure 7: TEM-picture of zinc oxide nanoparticles (22.2 nm) synthesised in *n*-Bu₄POAc (scale bar 50 nm) with size distribution.

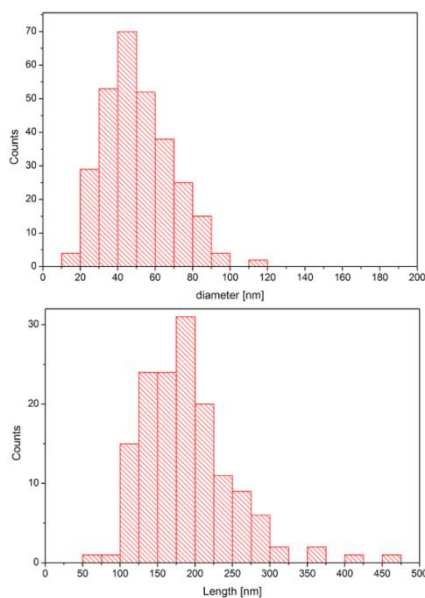
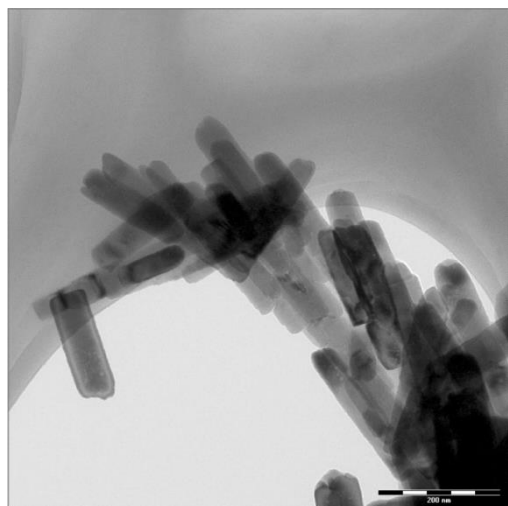


Figure 8: TEM-picture of zinc oxide nanorods (diameter: 50.9 nm, length: 189.3 nm) synthesised in bmmim NTf₂ (scale bar 200 nm) with size distribution.

Investigation of the liquid phase (ionic liquid)

In order to determine the reductive species which are responsible for the reduction of the Cu²⁺ and Ag⁺ ions in the reaction mixture, the ionic liquid was investigated by NMR and ATR-IR methods. The Ni²⁺ and Zn²⁺ species are not reduced by the ionic liquid. The reaction media has been investigated by ¹H-, ¹⁹F- and ³¹P-NMR techniques. As can be seen in SI figure 5 the phosphonium based ionic liquid *n*-Bu₄POAc can act as reducing agent in two ways: On the one hand the acetate ion can act as the reducing medium (forming *n*-Bu₄PCO₃ and carbon dioxide) as previously reported.^[14] Consequently the CH₃ signal for the acetate methyl group at 2.05 ppm vanishes or

shows a loss of intensity. This is the case for all four reactions. In the synthesis of Ag particles the acetate signal only slightly decreases.

On the other hand the phosphonium ion can be converted into tributylphosphine (via Hofmann elimination) and oxidised to tributylphosphin oxide. Accordingly, tributylphosphine can act as reducing agent, too. In SI figure 6 the ³¹P-NMR spectra of all reaction mixtures after the nanoparticle synthesis are shown (including a reference spectrum for pure *n*-Bu₄POAc).

In all ³¹P-NMR spectra one can clearly see the large signal at 33.3 ppm corresponding to the phosphonium species. Another signal at 44.2 ppm appears in the spectra - corresponding to a tributylphosphin oxide - of the high-temperature syntheses of Cu-, Ni(II)O- and Zn(II)O nanoparticles. Due to the high temperature during the synthesis (160 °C – 220 °C) the phosphonium-cations partially undergo Hofmann elimination. The pure ionic liquid and the reaction mixture for the synthesis of Ag nanoparticles (reaction temperature 100 °C) obviously do not show these signals.

In comparison to the IR-spectrum of the pure *n*-Bu₄POAc ionic liquid (see SI Fig. 7) the IR-spectrum of the reaction mixture of Ag(0) nanoparticles in *n*-Bu₄POAc still shows a strong signal at 1580 cm⁻¹ which is in good agreement with the literature known data for acetate-carbonyl and which is already confirmed by ¹H-NMR analysis. In contrast, there is no significant but still a smaller peak (slightly shifted to 1460 cm⁻¹) in the IR-spectrum of the reaction mixture of NiO nanoparticles in *n*-Bu₄POAc indicating the presence of another but different carbonyl species. This confirms the hypothesis that a considerable amount of the acetate is oxidised to carbonate at higher temperatures. This is in good agreement with the already published data which can be found in Ref. [14].

1-butyl-2,3-dimethylimidazolium N,N-bis(trifluoromethylsulfonyl)imide (bmmim NTf₂) is a more temperature stable ionic liquid. Temperatures of up to 250 °C do not lead to decomposition. In the following the ¹H-NMR spectra of pure bmmim NTf₂ and two examples of the reaction mixtures (Cu and Ag nanoparticle syntheses) are shown (SI Fig. 8). Similar to the ¹H- the ¹⁹F-NMR spectra show only one species – corresponding to the trifluoromethyl-groups – confirming that the NTf₂ anions do not decompose or react either (see SI Fig. 9). The IR spectra of bmmim NTf₂ and two corresponding reaction mixtures after the nanoparticle synthesis confirm the above made conclusions that the ionic liquid does not undergo any substantial decomposition (see SI Fig. 10).

Investigation of the gaseous phase

During the particle synthesis the gas-phase was investigated by online gas-phase mass spectrometry (gas-phase MS). We investigated the gas-phase of the reductive decomposition of copper carbonate in *n*-Bu₄POAc and compared it to the reductive decomposition of copper acetate in bmmim NTf₂. One can clearly see in SI figure 11 three main signals. The signal at 44 m/z corresponds to significant amounts of CO₂, generated during the decomposition of the acetate anions of the ionic liquid.^[14] This means that the acetate is not only oxidised

to carbonate, but mainly decarboxylated to carbon dioxide, which correlates with the investigation of synthesis of copper(I)oxide nanoparticles (Cu₂O-NP) in *n*-Bu₄POAc.^[14,54] Signals at 28 m/z and 16 m/z are correlated to dinitrogen and O₂²⁺, respectively.

Due to the lower concentration of acetate ions in the reaction mixture using bmmim NTf₂ as solvent, the amount of extruded carbon dioxide is significantly lower. A constant stream of Argon was used to transport the gas probe into the MS (see Figure 9). Hence, the amount of CO₂ (m/z = 44) in the mass spectrum is rather small, but 1.6-times higher than the oxygen amount, though indicating that the acetate ion acts as reducing agent, regardless whether it originates from the ionic liquid or the nanoparticle precursor.

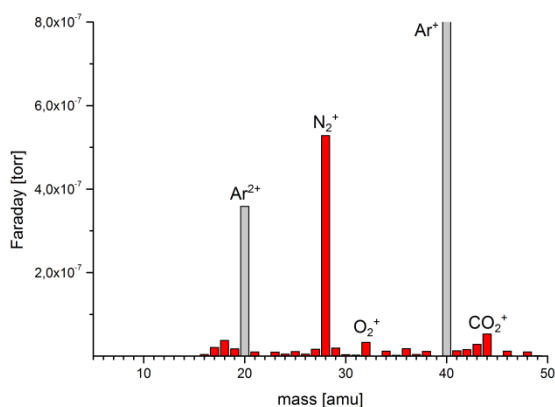


Figure 9: Gas-phase mass spectrogram of volatile compounds of the reductive decomposition of Copper(II)acetate in bmmim NTf₂. Argon (m/z = 40, m/z = 20) is used as carrier gas.

Experimental part

General

All reactions were carried out in a *Monowave 300* microwave (*Anton Paar*[®]) with a maximum power of 850 W at 2.45 MHz. The microwave was equipped with a ruby-thermometer and an IR-reference thermometer as well as a stirring unit. Reactions can be carried out up to a maximum pressure of 30 bar and a maximum temperature of 300 °C. Reaction-mixtures were handled without precautions against water/moisture or air/oxygen in 4 ml microwave-borosilicate vials equipped with a Teflon/silicon septum and a quartz inlet for the thermometer. Aqueous solution of *n*-Bu₄POH (40 wt%), CuCO₃·Cu(OH)₂, Ag₂CO₃, NiCO₃·6H₂O and ZnCO₃ were purchased from *ABCR Chemicals*[®]. Acetic acid (99%), Cu(OAc)₂·H₂O and Ni(OAc)₂·4H₂O were used from the chemicals stock of the institute. AgOAc and Zn(OAc)₂·2H₂O were obtained from *Alfa Aesar*[®]. 1,2-dimethylimidazol, 1-butanol and methane sulfonyl chloride were purchased from *Sigma Aldrich*[®]. All chemicals

were used without further purification prior to use. Tetra-*n*-butylphosphonium acetate (*n*-Bu₄POAc) and 1-butyl-2,3-dimethylimidazolium N,N-bis(trifluoromethyl)sulfonylimid (bmmim NTf₂) were synthesised according to literature known methods.^[3,13,54-57] ¹H-, ¹⁹F- and ³¹P-NMR spectra were recorded on a *Bruker*[®] AVANCE II 300 spectrometer at 298 K (300.1 MHz, 272 MHz, 121 MHz, external standard tetramethylsilane (TMS)). IR spectra were taken on *Bruker*[®] alpha Platinum ATR with a diamond-ATR-module. The obtained nanoparticles were analysed by powder X-ray diffractometry (*STOE*[®]-STADI MP, Cu-Kα irradiation, λ = 1.540598 Å) and by a TEM *Phillips*[®] EM 420, 120 kV. Mass spectra were recorded with *HIDEN*[®] HPR-20QIC equipped with *Bronkhorst*[®] EL-FLOW Select mass flow meter/controller.

Nanoparticle synthesis

An oven-dried 4 ml microwave-borosilicate vial equipped with a Teflon stirring bar, a Teflon/silicon septum and a quartz inlet for a ruby-thermometer was filled with 500 mg of the ionic liquid. 50 mg of precursor (basic CuCO₃ 0.23 mmol, Ag₂CO₃ 0.18 mmol, NiCO₃·6H₂O 0.22 mmol, ZnCO₃ 0.40 mmol, Cu(OAc)₂·H₂O 0.25 mmol, AgOAc 0.30 mmol, Ni(OAc)₂·4H₂O 0.20 mmol, Zn(OAc)₂·2H₂O 0.23 mmol) was filled into the vial and stirred for 2.5 min on a conventional stirring plate to yield a homogeneous mixture. The vial was further equipped with a ruby-thermometer. The maximum irradiation power of the microwave was limited to 75 W when the reaction was about to start. The reaction parameters for the particle syntheses are summarised in the following table.

Table 1: Reaction parameters for the nanoparticle syntheses in ionic liquids by microwave irradiation.

No	Type	Prec.	IL	T [°C]	t [min]	d [nm]
1	Cu(0)	CuCO ₃	<i>n</i> -Bu ₄ POAc	160	10	4.8nm (±1.7nm)
2	Cu(0)	Cu(OAc) ₂	bmmim NTf ₂	235	3	4.9nm (±1.1nm)
3	Ag(0)	Ag ₂ (CO ₃)	<i>n</i> -Bu ₄ POAc	100	1.5	7.0nm, 17nm
4	Ag(0)	AgOAc	bmmim NTf ₂	200	5	12.2nm (±5.4nm)
5	Ni(II)O	NiCO ₃	<i>n</i> -Bu ₄ POAc	200	10	5.8nm (±1.7nm)
6	Ni(II)O	Ni(OAc) ₂	bmim NTf ₂	250	30	2.0nm (±0.6nm)
7	Zn(II)O	ZnCO ₃	<i>n</i> -Bu ₄ POAc	220	10	22.2nm (±10.2nm)
8	Zn(II)O	Zn(OAc) ₂	bmmim NTf ₂	225	15	50.9nm (±18.2nm) ^a
						189.3nm (±61.5nm) ^b

reaction parameters: 500 mg IL, 50 mg precursor, 1000 rpm stirring, 75 W max. power,

^a ZnO nanorods diameter, ^b ZnO nanorods length

Conclusion

The synthesis of copper, silver, nickel oxide and zinc oxide nanoparticles originating from eight inexpensive salt-precursors in two different ionic liquids – tetra-*n*-butylphosphonium acetate (*n*-Bu₄POAc) and 1-butyl-2,3-dimethylimidazolium N,N-bis(trifluoromethylsulfonyl)imid (bmmim NTf₂) – has been investigated. All reactions were carried out in a microwave for chemical reactions within 90 sec - 30 min at temperatures between 100 °C and 250 °C resulting in small sized nanoparticles and nanorods. This clearly demonstrates the general approach of this synthetic protocol for nanostructures using simple ILs; both metal and metal oxide species particles can be obtained. Additionally, the acetate ion can act as nontoxic and environmentally friendly reducing agent, regardless whether it originates from the ionic liquid or the metal salt precursor. Furthermore, it should be emphasised that polarity and geometry differences of the ionic liquids and this clearly influences crystal growth of the nanostructures.

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Notes and references

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Electronic Supplementary Information (ESI) available: XRD, NMR, IR and MS images. See DOI: 10.1039/b000000x/

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