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## Microwave synthesis and inherent stabilization of metal nanoparticles in 1-methyl-3-(3-carboxyethyl)-imidazolium tetrafluoroborate

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The synthesis of Co-NPs and Mn-NPs by microwave-induced decomposition of the metal carbonyls  $\text{Co}_2(\text{CO})_8$  and  $\text{Mn}_2(\text{CO})_{10}$ , respectively, yields smaller and better separated particles in the functionalized IL 1-methyl-3-(3-carboxyethyl)-imidazolium tetrafluoroborate  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$  ( $1.6 \pm 0.3$  nm and  $4.3 \pm 1.0$  nm, respectively) than in the non-functionalized IL 1-n-butyl-3-methylimidazolium tetrafluoroborate  $[\text{Bmim}][\text{BF}_4]$ . The particles are stable in the absence of capping ligands (surfactants) for more than six months although some variation in particle size could be observed by TEM.

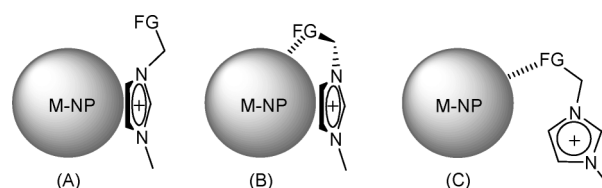
Metal carbonyls  $\text{M}_x(\text{CO})_y$ <sup>1</sup> or other  $\text{M}(0)$  complexes<sup>2</sup> are interesting precursors for the synthesis of metal nanoparticles (M-NPs) because the metal atoms are already in their final zero-valent oxidation state. Thus, no reducing agent is necessary and the carbonyl (CO) side product is largely given off to the gas phase and thereby removed from the M-NP dispersion. Contamination from by- or decomposition products which are otherwise generated during the M-NP synthesis are therefore significantly reduced and very clean particles can thus be obtained.<sup>3</sup>

The small size of nanoparticles results in a large fraction of surface atoms.<sup>4</sup> Unprotected small particles interact *via* van der Waals and (if the particles are magnetic) magnetic interactions which will lead to agglomeration or aggregation from the cohesive surface energy.<sup>5</sup> As a result of their colloidal instability, many nanoparticles need to be stabilized *via* additional (capping) agents such as surfactants or polymers, which provide a steric, electrostatic or electrosteric particle stabilization.<sup>4,6</sup>

Ionic liquids (ILs) can stabilize metal nanoparticles through their high ionic charge, their polarity and high dielectric constants.<sup>7,8</sup> ILs can therefore function both as stabilizer and solvent for the preparation of small (< 5 nm) and (generally) kinetically stabilized M-NPs.<sup>9,10</sup> For these reasons, the chemistry of inorganic compounds and inorganic materials synthesis in

ILs<sup>11,12</sup> and ionic liquid crystals (ILCs)<sup>13,14</sup> has attracted tremendous interest in the recent past.

A scientifically interesting and technologically promising approach is the preparation and stabilization of M-NPs from metal carbonyls in ILs.<sup>3,15</sup> The stabilization of M-NPs in non-functionalized ILs such as 1-butyl-3-methylimidazolium tetrafluoroborate  $[\text{Bmim}][\text{BF}_4]$  is primarily based on the IL-anions, which form the immediate layer around the nanoparticle because the molecular volume of the IL anion influences sizes and shapes of the resulting metal nanoparticles.<sup>3,10,16,17</sup> Functional amino-,<sup>18</sup> carboxylic acid-,<sup>19</sup> hydroxyl-,<sup>20</sup> nitrile-<sup>21</sup> or thiol-,<sup>22</sup> groups on the imidazolium cations exert an additional stabilization on M-NPs because of specific interactions of the functional group with the particle surface. The donor atom(s) of the functional group can attach to the metal nanoparticle much like an extra stabilizing capping ligand.<sup>19</sup> Then, the stabilization of metal-nanoparticles in functionalized-imidazolium-based ILs occurs through the cation with its functional group (Fig. 1).<sup>11,23</sup> For both non-functionalized and functionalized ILs equally charged layers around the M-NPs lead to their separation through electrostatic repulsion and, thus, prevent their aggregation or Ostwald ripening.<sup>24</sup>



**Fig. 1** Three possible stabilization modes of metal-nanoparticles by IL-imidazolium cations with functional groups (FG).

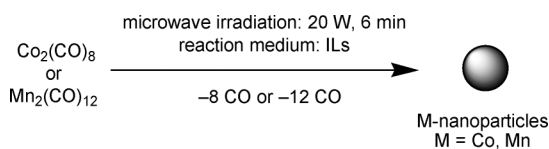
Here we present a simple synthesis method for cobalt and manganese nanoparticles (Co-NPs and Mn-NPs) from their metal-carbonyl precursors  $\text{Co}_2(\text{CO})_8$  and  $\text{Mn}_2(\text{CO})_{10}$ , respectively, in the carboxylic acid functionalized imidazolium ionic liquid (IL) 1-methyl-3-(3-carboxyethyl)-imidazolium tetrafluoroborate  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$ , under microwave irradiation (MWI) (Fig. 2).<sup>†</sup> The results show that the additional carboxylic acid on the IL (Fig. 3) does in both cases (Mn and Co) lead to a more uniform product and a better stabilization of the nanoparticles. Co- and Mn-NPs can be used as catalysts for Fischer-Tropsch reactions (Co-NPs also prepared from  $\text{Co}_2(\text{CO})_8$ )<sup>25</sup> and in the reduction of polycyclic aromatic hydrocarbons and heterocyclic hydrocarbons (Mn and Co).<sup>26</sup>

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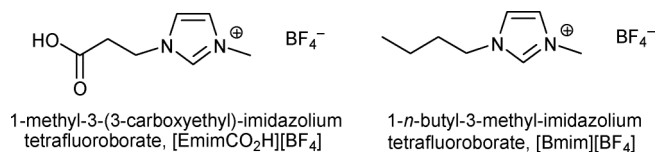
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**Fig. 2** Formation of Co and Mn nanoparticles by microwave irradiation-induced decomposition of metal carbonyls  $M_x(\text{CO})_y$  under argon in ILs.



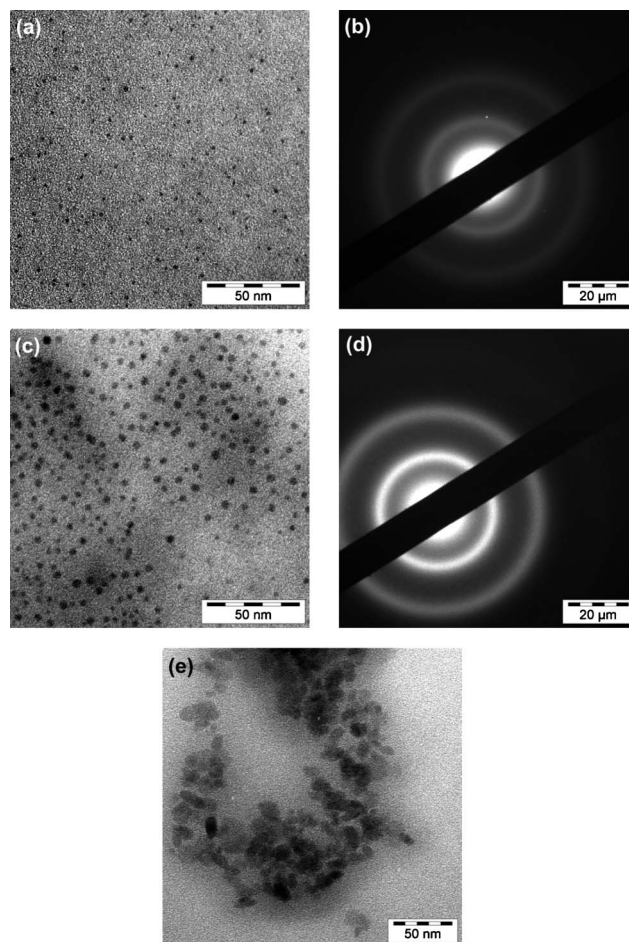
**Fig. 3** Chemical structure of the ILs relevant in this study.

ILs are attractive media for microwave reactions because of their high interaction cross-section resulting from their high ionic charge, high polarity, and high dielectric constant.<sup>1,27</sup> Fig. 4 shows representative transmission electron microscopy (TEM) images of the nanoparticles obtained from the decomposition of  $\text{Co}_2(\text{CO})_8$  in  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$  and  $[\text{Bmim}][\text{BF}_4]$ . Small Co-NPs with narrow size distribution are reproducibly obtained from  $\text{Co}_2(\text{CO})_8$  by microwave irradiation in the functionalized IL  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$  (Fig. 4). All samples grown in  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$  contain small and monodisperse particles with a diameter of  $1.6 \pm 0.3$  nm. Six months after synthesis the particle size has increased to  $3.0 \pm 0.6$  nm; the size distribution is still narrow. In contrast, Co-NPs synthesized from  $\text{Co}_2(\text{CO})_8$  under the same conditions, but in the non-functionalized IL  $[\text{Bmim}][\text{BF}_4]$  exhibit larger, relatively highly aggregated nanoparticles of  $5.1 \pm 0.9$  nm in diameter with somewhat irregular shapes.<sup>15</sup>

The sample identity and crystallinity can be evaluated from selected area electron diffraction (SAED). SAED patterns do not show reflections indicative of a crystalline material. We therefore conclude that the particles obtained from the synthesis are amorphous Co-NPs stabilized by the IL.

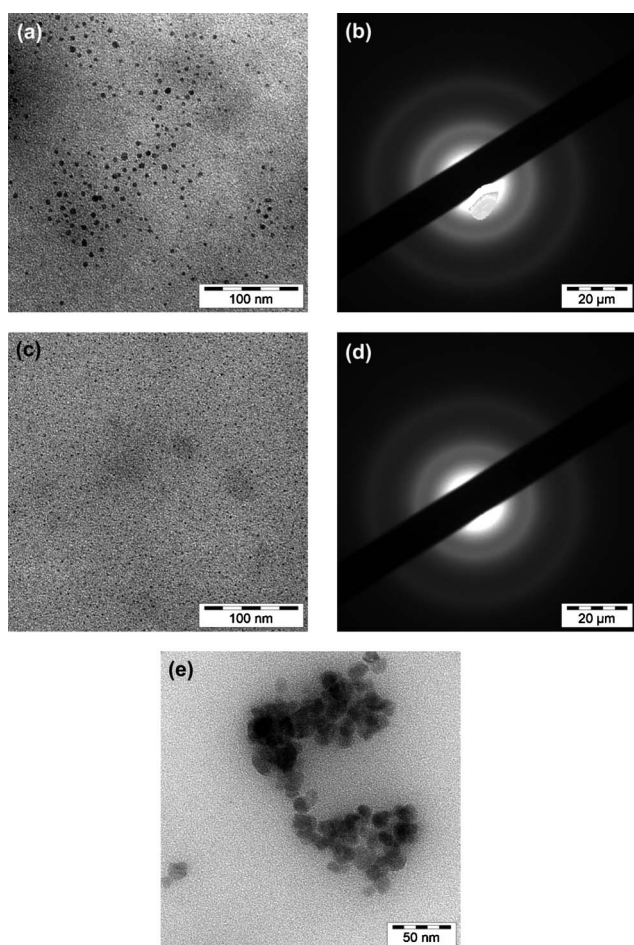
Fig. 5 shows representative TEM data of the nanoparticles obtained from the decomposition of  $\text{Mn}_2(\text{CO})_{10}$  in  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$  and  $[\text{Bmim}][\text{BF}_4]$ . The Mn-NPs are larger than the Co-NPs and have a diameter of  $4.3 \pm 1.0$  nm. The nucleation rate (possibly controlled by the decomposition rate of the carbonyl) may be different for the two precursors. Thus, if the two carbonyls decompose at different rates, the supersaturation will not be the same and consequently, the particle number will not be identical. If we have a fast decomposition, more and smaller particles may form, if the decomposition is slower, we may generate larger particles. Still, the small particle sizes and the narrow size distribution for Mn-NPs are remarkable because under the same conditions in  $[\text{Bmim}][\text{BF}_4]$  the particle diameter is  $28.6 \pm 11.5$  nm. Again, SAED shows that the Mn-particles obtained in the microwave process are amorphous and remain so over time.

Interestingly, TEM images of Mn-NPs in  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$  stored under nitrogen atmosphere show a decrease of the NP sizes to  $2.4 \pm 0.5$  nm with prolonged storage of the NP dispersion. Such a decrease in size is counter-intuitive to the expected slow aggregation or growth of kinetically stabilized small ( $< 5$  nm) metal nanoparticles. With the good coordinating ability of the



**Fig. 4** (a) TEM-images of Co-NPs in  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$  six weeks after synthesis; (b) SAED-image of Co-NPs (the black bar in the SAED is the beam stopper) indicating amorphous material (no well-defined sharp reflections). (c) TEM of Co-NPs in  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$  6 months after synthesis; (d) SAED of Co-NPs in  $[\text{EmimCO}_2\text{H}][\text{BF}_4]$  after 6 months, still indicating an amorphous material; (e) Co-NPs from  $\text{Co}_2(\text{CO})_8$  in  $[\text{Bmim}][\text{BF}_4]$ .

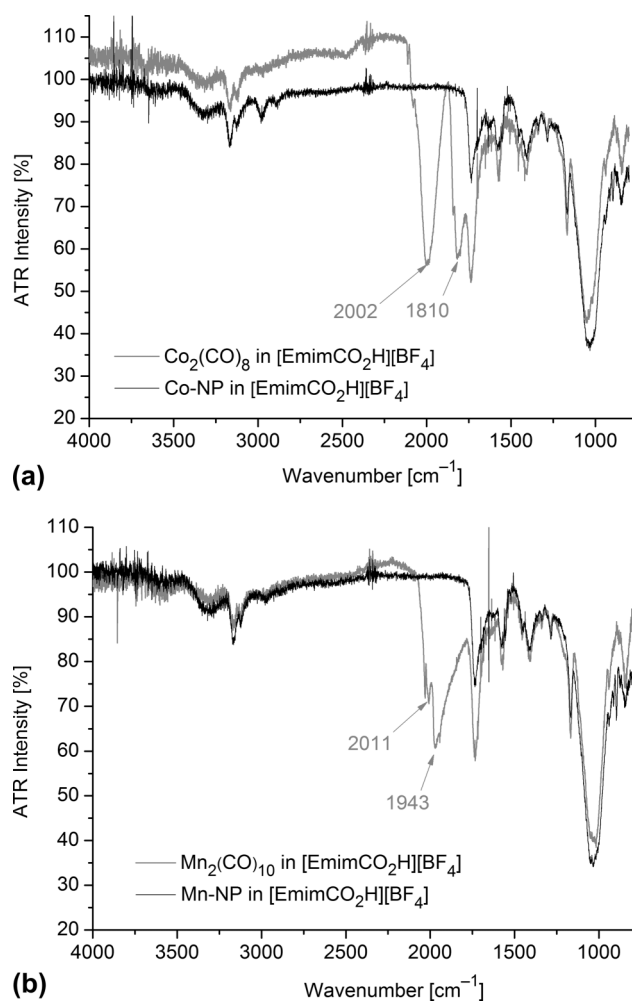
carboxylate group some chemical etching of the M-NPs by the IL may be possible. Binnemans *et al.* use the metal-complex-forming abilities of ILs with carboxyl-functionalized cations for the dissolution of metal oxides and metal hydroxides in carboxylated ILs. The carboxylic acid moiety provides this class of ILs with a good solubilizing ability for basic metal oxides and metal hydroxides leading to molecular metal-carboxylate species in such functionalized ILs.<sup>28,29</sup> The main difference between the current work and the Binnemans study is that in the earlier case, the oxidation state of the metals is positive and the reaction leading to the complexes is an acid-base reaction. In the current case we suspect that a slow redox reaction between reactive surface metal atoms and carboxylic acid yields some molecular metal-carboxylate complexes and  $\text{H}_2$ , effectively leading to a reduced particle size after a few months. A reason for the selectivity of this process (towards Mn- and not Co-NPs) could be the less-noble character of the former (standard reduction potentials  $\text{Mn}^{2+}/\text{Mn} = -1.18$  V,  $\text{Co}^{2+}/\text{Co} = -0.28$  V, both in acidic aqueous solution).<sup>30</sup>



**Fig. 5** (a) TEM-image of Mn-NPs in [EmimCO<sub>2</sub>H][BF<sub>4</sub>] six weeks after synthesis; (b) SAED-image of Mn-NP (the black bar in the SAED is the beam stopper) indicating amorphous material (no well-defined sharp reflections). (c) TEM of Mn-NPs in [EmimCO<sub>2</sub>H][BF<sub>4</sub>] six months after synthesis; (d) SAED of Mn-NPs in [EmimCO<sub>2</sub>H][BF<sub>4</sub>] after 6 months, still indicating an amorphous material; (e) Mn-NPs from Mn<sub>2</sub>(CO)<sub>10</sub> in [Bmim][BF<sub>4</sub>].

As the energy input in the nanoparticle synthesis is rather low (and hence some metal carbonyl may survive the reaction), complete decomposition of the metal carbonyl was ascertained by attenuated total reflection infrared (ATR-IR) spectroscopy.<sup>‡</sup> Fig. 6 compares ATR-IR spectra of the freshly prepared carbonyl/IL dispersion and of the reaction mixture after microwave treatment. The spectra of the initial metal carbonyl/IL dispersion show the typical band structure of metal carbonyls (2002 cm<sup>-1</sup> and 1810 cm<sup>-1</sup> for terminal and bridging CO ligands, respectively, in Co<sub>2</sub>(CO)<sub>8</sub> and 2011 cm<sup>-1</sup> and 1943 cm<sup>-1</sup> for the terminal CO ligands in Mn<sub>2</sub>(CO)<sub>10</sub>). These bands disappeared after microwave treatment. ATR-IR spectroscopy thus indicates that the metal carbonyl precursors are completely decomposed after irradiation for 6 min with 20 W.

The use of a carboxylic acid-functionalized IL has already been described for the synthesis of Pt(0) and Au(0) nanoparticles from H<sub>2</sub>PtCl<sub>6</sub> and HAuCl<sub>4</sub> by reduction with NaBH<sub>4</sub> in aqueous solution. Particle sizes of 2.5 ± 0.5 nm (Pt) and 3.5 ± 1.0 nm (Au) were obtained.<sup>19</sup> The IL used in this previous study, 1-carboxymethyl-3-methylimidazolium chloride, is quite similar to



**Fig. 6** ATR-IR spectra of (a) Co<sub>2</sub>(CO)<sub>8</sub>/IL (gray curve) and the resulting Co-NP (0.5 wt.%) /IL-dispersion after microwave treatment and of (b) Mn<sub>2</sub>(CO)<sub>10</sub>/IL (gray curve) and Mn-NP (0.5 wt.%) /IL after microwave treatment (20 W, 6 min).

the one used in the current work, but it was significantly more hydrophilic and contained a coordinating anion. The effect of the carboxylic acid functionalization could not clearly be discerned because the chloride anions also have a pronounced stabilization effect towards nanoparticles, in particular towards Au-NPs<sup>10</sup> and no comparison to a non-functionalized IL was made.

The main finding of the current work is that carboxylated ILs can also be efficient reaction media and stabilizers if used as pure phases and not in aqueous solution. In particular the acidic group appears to lead to a well-controlled nucleation and growth process, which is illustrated by the narrow size distribution of the resulting particles. Moreover, the carboxylic acid moiety stabilizes the particles over extended periods of time, which (1) is an indication of a rather strong interaction of the IL with the nanoparticles and (2) is useful for practical applications, such as functional fluids. An intriguing feature is the size decrease of the Mn-NPs with time, but, as pointed out above, this could be due to a surface redox process between the NP and the acid group. A more detailed investigation of this process is, however, necessary to conclude on the details of the process.

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## Notes and references

† Experimental: *Materials.*  $\text{Co}_2(\text{CO})_8$  and  $\text{Mn}_2(\text{CO})_{10}$  were obtained from Acros Organics, [Bmim][BF<sub>4</sub>] from IoLiTec. 1-methylimidazole, 3-chloropropionic acid, and NaBF<sub>4</sub> were used as received from Acros. [EmimCO<sub>2</sub>H][BF<sub>4</sub>] *Synthesis.* Under an inert nitrogen atmosphere, equimolar quantities of 1-methylimidazole and 3-chloropropionic acid were dissolved in methanol at room temperature. The mixtures were heated to 75 °C with stirring and allowed to react for 20 h. The resulting reaction mixture was treated with NaBF<sub>4</sub> (1.2 equiv) and allowed to stir for 18 h at room temperature. After separating the NaCl precipitant, the filtrate was concentrated by rotary evaporation. The yellow and viscous product was washed with diethyl ether and dried under vacuum to afford the neat IL. <sup>1</sup>H NMR (D<sub>2</sub>O, ppm relative to TMS): 8.61 (s, 1H), 7.42 (d, 1H), 7.50 (d, 1H), 4.22 (t, 2H), 3.83 (s, 3H), 2.10 (t, 2H).<sup>31</sup> IR (ATR): 3568, 3160, 3115, 2959, 1728, 1572, 1376, 1282, 1169, 1015, 846, 752 cm<sup>-1</sup>. Elemental analysis: calc. for C<sub>7</sub>H<sub>11</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>: C 34.74%, H 4.58%, N 11.58%. Found: C 34.39%, H 4.60%, N 11.64%. Total yield: 68%.

*Nanoparticle synthesis.* Microwave vials with a teflon septum were used. They were charged with ILs and metal-carbonyls by placing the vial in a Schlenk tube or by handling in a glovebox. The general procedure for preparing an 0.5 wt% M–NP dispersion in [EmimCO<sub>2</sub>H][BF<sub>4</sub>] was to add the required mass of metal carbonyl [M<sub>x</sub>(CO)<sub>y</sub>, M = Mn 26.80 mg; Co 21.80 mg] under nitrogen to the dried and degassed IL (0.5 ml, 0.75 g, density 1.51 g mL<sup>-1</sup>). A 0.5 wt% dispersion of M–NP in [Bmim][BF<sub>4</sub>] was prepared by adding the required mass of metal carbonyl [M<sub>x</sub>(CO)<sub>y</sub>, M = Mn 21.30 mg; Co 17.40 mg] under nitrogen to the dried and degassed IL (0.5 ml, 0.6 g, density 1.20 g mL<sup>-1</sup>). The metal carbonyls were finely dispersed in the ILs by stirring for 3 d at room temperature under nitrogen. The magnetic stir bars were removed from the dispersion and the reaction mixture was subsequently heated to 250 °C (20 W, 6 min) by microwave irradiation (MWI, CEM Discover). Dark brown to black metal nanoparticle dispersions were obtained. They were degassed under reduced pressure for 30 min to remove CO.

‡ *Characterization.* ATR-IR-spectroscopy was carried out on a Shimadzu IRAffinity equipped with a ZnSe crystal. TEM images were taken at room temperature on a Zeiss LEO 912 TEM operating at an accelerating voltage of 120 kV. Samples were deposited on 200 μm carbon-coated copper grids.

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