Stable chromium, molybdenum and tungsten nanoparticles are obtained reproducibly by thermal or photolytic decomposition under argon from mononuclear metal carbonyl precursors $\text{M(CO)}_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) suspended in the ionic liquids $\text{BMim}^+\text{BF}_4^-$, $\text{BMim}^+\text{OTf}^-$ and $\text{BtMA}^+\text{Tf}_2\text{N}^-$ ($\text{BMim}^+ = \text{n-butyl-methyl-imidazolium}, \text{BtMA}^+ = \text{n-butyl-trimethyl-ammonium}, \text{Tf}_2\text{N} = \text{N(O_2SCF_3)_2}, \text{OTf} = \text{O_3SCF_3}$) with a very small and uniform size of 1 to 1.5 nm in $\text{BMim}^+\text{BF}_4^-$ which increases with the molecular volume of the ionic liquid anion to ~100 nm in $\text{BtMA}^+\text{Tf}_2\text{N}^-$ [characterization by transmission electron microscopy (TEM), dynamic light scattering and transmission electron diffraction (TED) analysis].

Syntheses and applications of transition-metal nanoparticles are of contemporary interest in several areas of science. In particular, W and Mo nanoparticles can be used for olefin metathesis reactions. The synthesis of defined and stable metal nanoparticles (M-NPs) is of high importance.

Metal nanoparticles can be stabilized by the ionic charge, high polarity, high dielectric constant and supramolecular network of ionic liquids (ILs). According to the DLVO (Derjaguin–Landau–Verwey–Overbeek) theory, ILs provide an electrostatic protection in the form of a “protective shell” for M-NPs, so that no extra stabilizing molecules are needed. Most known metal nanoparticle syntheses in ILs are carried out through the reduction of metal salts by hydrogen gas, photochemical or electroreduction/electrodeposition. Recently, $\text{Fe}_2\text{O}_3$ nanoparticles were synthesized by thermal decomposition of $\text{Fe(CO)}_6$ + stabilizers in $\text{BMim}^+\text{Tf}_2\text{N}^-$. Here we report the preparation of Cr, Mo and W M-NPs by thermal or photochemical decomposition under argon of the mononuclear metal carbonyls $\text{M(CO)}_6$ in ILs (Scheme 1). The range of about 1 to 1.5 nm with a narrow, albeit not monodisperse, size distribution could be reproducibly synthesized in $\text{BMim}^+\text{BF}_4^-$ (Fig. 1 and Fig. 2, Table 1). Nanoparticles of this small size are novel. Nanoparticles obtained in $\text{BtMA}^+\text{Tf}_2\text{N}^-$ are larger, ranging from about 70 to 150 nm (Table 1). Such large nanoparticles can easily be separated, e.g. by simple centrifugation (10 min at 2000 rpm under argon) from the IL. TED (transmission electron diffraction) studies show that the larger Cr, Mo and W NPs produced under argon are crystalline (Fig. 3, ESI† Fig. S14, S18, S23), with the diffraction patterns corresponding to the metal lattices, thereby proving their metallic character and the absence of significant oxidation.

Furthermore, we synthesized the M-oxide nanoparticles (Fig. 4) for comparison to the Cr, Mo and W NPs. For the M-oxides the $\text{M(CO)}_6$/IL mixture was subjected to the same decomposition conditions, albeit under air. The M-oxide NPs have different colors from the MNP suspensions (ESI† Fig. S25–S27) are obtained through decomposition from their metal carbonyl in ionic liquids. Also, extremely small M-NPs of Cr, Mo and W in the range of about 1 to 1.5 nm with a narrow, albeit not monodisperse, size distribution could be reproducibly synthesized in $\text{BMim}^+\text{BF}_4^-$ (Fig. 1 and Fig. 2, Table 1). Nanoparticles of this small size are novel. Nanoparticles obtained in $\text{BtMA}^+\text{Tf}_2\text{N}^-$ are larger, ranging from about 70 to 150 nm (Table 1). Such large nanoparticles can easily be separated, e.g. by simple centrifugation (10 min at 2000 rpm under argon) from the IL. TED (transmission electron diffraction) studies show that the larger Cr, Mo and W NPs produced under argon are crystalline (Fig. 3, ESI† Fig. S14, S18, S23), with the diffraction patterns corresponding to the metal lattices, thereby proving their metallic character and the absence of significant oxidation.

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S23–25), have a broader size distribution (Table 1) and show no crystallinity (ESI† Fig. S15 and S24).

A comparison of Mo NPs produced under thermal and photolytic decomposition shows only slight differences in median size and size distribution (Table 1). Nanoparticles produced by photolysis give somewhat larger particles because of a faster decomposition process in the ionic liquid.

A correlation exists between the molecular volume of the anion in the ionic liquid and the synthesized metal nanoparticles, shown here for, but not limited to, tungsten. The size of the Cr, Mo and W nanoparticles increases with the molecular volume of the IL anion (Table 1, Fig. 5). MNPs (core) are

![Fig. 2 TEM of Mo NPs from Mo(CO)₆ in BMim⁺BF₄⁻ by photolytic decomposition (entry 7 in Table 1). See footnote e in Table 1.](image1)

![Fig. 3 TED patterns of a single W NP (left) and an ensemble of W NPs (right) from W(CO)₆ in BtMA⁺Tf₂N⁻ by thermal decomposition under Ar (entry 4 in Table 1). The black bar is the beam stopper. The d-values match with the d-spacing of W metal.](image2)

![Fig. 4 TEM of Cr-oxide NPs from Cr(CO)₆ in BtMA⁺Tf₂N⁻ by thermal decomposition (entry 12 in Table 1).](image3)

![Fig. 5 Correlation between the molecular volume of the ionic liquid anion (VᵢL) and the observed W nanoparticle size with standard deviations as error bars (from TEM and dynamic light scattering, ESI† Fig. S1–S11).](image4)

A correlation exists between the molecular volume of the anion in the ionic liquid and the synthesized metal nanoparticles, shown here for, but not limited to, tungsten. The size of the Cr, Mo and W nanoparticles increases with the molecular volume of the IL anion (Table 1, Fig. 5). MNPs (core) are

**Table 1** MNP and M-oxide NP (M = Cr, Mo and W) size and size distribution in different ionic liquids

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>VᵢL-anion/nm³ (standard deviation σ)</th>
<th>Metal carbonyl</th>
<th>TEM NP median diameter/nm, (standard deviation σ)</th>
<th>Dynamic light scattering NP median diameter/nm, (standard deviation σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMe₃BF₄</td>
<td>0.073 (±0.009)</td>
<td>Mo(CO)₆</td>
<td>5.7 (±2.1)</td>
<td>11.7 (±2.3)</td>
</tr>
<tr>
<td>BMe₃OTf</td>
<td>0.131 (±0.015)</td>
<td>Mo(CO)₆</td>
<td>33 (±11)</td>
<td>45 (±11)</td>
</tr>
<tr>
<td>BMe₃Tf₂N⁻</td>
<td>0.232 (±0.015)</td>
<td>Mo(CO)₆</td>
<td>67 (±32)</td>
<td>97 (±33)</td>
</tr>
<tr>
<td>BtMA⁺Tf₂N⁻</td>
<td>0.232 (±0.015)</td>
<td>Mo(CO)₆/air</td>
<td>91 (±83)</td>
<td>163 (±47)</td>
</tr>
<tr>
<td>BMe₃BF₄</td>
<td>0.073 (±0.009)</td>
<td>Mo(CO)₆</td>
<td>1.5 (±0.3)</td>
<td>2.5 (±0.6)</td>
</tr>
<tr>
<td>BMe₃BF₄</td>
<td>0.073 (±0.009)</td>
<td>Mo(CO)₆/air</td>
<td>~1.0–2.0 (±0.6)</td>
<td>3.8 (±1.1)</td>
</tr>
<tr>
<td>BtMA⁺Tf₂N⁻</td>
<td>0.232 (±0.015)</td>
<td>Mo(CO)₆/air</td>
<td>150 (±30)</td>
<td>258 (±89)</td>
</tr>
<tr>
<td>BtMA⁺Tf₂N⁻</td>
<td>0.232 (±0.015)</td>
<td>Mo(CO)₆/air</td>
<td>— (layers, ESI S19)</td>
<td>— (layers)</td>
</tr>
<tr>
<td>BtMA⁺Tf₂N⁻</td>
<td>0.073 (±0.009)</td>
<td>Cr(CO)₆</td>
<td>1.5 (±0.3)</td>
<td>3.0 (±0.6)</td>
</tr>
<tr>
<td>BtMA⁺Tf₂N⁻</td>
<td>0.232 (±0.015)</td>
<td>Cr(CO)₆</td>
<td>33 (±10)</td>
<td>51 (±12)</td>
</tr>
<tr>
<td>BtMA⁺Tf₂N⁻</td>
<td>0.232 (±0.015)</td>
<td>Cr(CO)₆/air</td>
<td>—</td>
<td>62 (±16)</td>
</tr>
</tbody>
</table>

See Scheme 1. † From TEM measurements, statistical evaluation of the total sample pictures. ‡ Hydrodynamic radius, median diameter form the first 3 measurements at 633 nm in n-butyl-imidazole (see ESI Fig. S1–S11). § Photolytic decomposition for 15 min at 200 to 450 nm. The TEM pictures with particles of average median diameters of less than 1.5 nm show electron dense cloudy structures. Due to scattering caused by the surrounding ionic liquid resolution of the TEM is limited and particles below 1.5 nm are hardly resolved.
considered stabilized in the ILs by the formation of “protective” anionic and cationic layers (shells) around them in a “core–shell system”.6,15 We suggest that the thickness of the stabilizing shells around an MNP depends on the IL molecular parameters like density, viscosity, conductivity and surface tension also correlate with the volume of the anion in the ionic liquid and could influence nanoparticle nucleation and growth,16 although the supramolecular imidazolium–anion clusters of the IL should be taken into account.4

The IL cation can be used as a fine-tuning tool in nanosynthesis,9 “Pure” imidazolium based ILs should be considered as three-dimensional networks of anions and cations, linked by weak interactions (such as hydrogen bonds, van der Waals and Coulomb forces). ILs should be regarded as supramolecular polymeric structures with a high degree of self-organisation and weak interactions. When mixed with other molecules or MNPs, ILs become nanostructured materials with polar and nonpolar regions.4,17,18

We describe here a simple and reproducibly method for the synthesis and size tailoring of Cr, Mo and W metal nanoparticles with median diameters between ~1–100 nm and narrow size distribution in ionic liquids. The synthesis uses easily nonpolar regions.4,17,18

Notes and references


14 STOE WinXPOw version 1.10, data base, STOE & Cie GmbH, Darmstadt, Germany, 2002.


19 Metalcarbonyls are poisonous due to the possible liberation of CO and, thus, should be handled with care, yet Fe(CO)5 and Ni(CO)4 are industrially produced on a multi-ton scale; see D. G. E. Kerfoot, X. Nickel, E. Wildermuth, H. Stark, G. Friedich, F. L. Ehnhöök, B. Kühborth, J. Silver and R. Ritzper, Iron Compounds, in Ullmann’s Encyclopaedia of Industrial Chemistry, Wiley, 5th edn (online), 2008.