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Use of Ionic Liquids for the Synthesis of Iron, Ruthenium, and Osmium Nanoparticles from Their Metal Carbonyl Precursors

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Summary: Stable iron, ruthenium, and osmium nanoparticles are obtained reproducibly by thermal or photolytic decomposition under an argon atmosphere from $Fe_2(CO)_9$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$, dissolved in the ionic liquid $BMim^+BF_4^-$, with a very small and uniform size for Ru and Os nanoparticles of about 1.5−2.5 nm without any additional stabilizers or capping molecules (characterization by transmission electron microscopy (TEM), dynamic light scattering, and transmission electron diffraction (TED) analysis).

Transition-metal nanoparticles are very important for technological applications in several areas of science and industry, including catalysis or chemical sensors.[1,2] In particular, Ru nanoparticles can be used for olefin hydrogenation reactions.[3] The controlled and reproducible synthesis of defined and stable metal nanoparticles (MNPs) is of high importance.[4,5]

Ionic liquids (ILs) as a "*nanosynthetic template*" stabilize metal nanoparticles on the basis of their high ionic charge, high polarity, high dielectric constant, and supramolecular network.[6] According to DLVO (Derjaugin−Landau−Verwey−Overbeek) theory,[7] ILs provide an electrostatic protection in the form of a "*protective shell*" for MNPs, so that no extra stabilizing molecules or organic solvents are needed.[8]

Most metal nanoparticle syntheses in ILs are carried out through the reduction of metal salts by hydrogen gas,[9] by photochemical reduction,[10] or by electroreduction.[11] Here we report the preparation of Fe, Ru, and Os metal nanoparticles by decomposition of the di- and trinuclear metal carbonyls $Fe_2(CO)_9$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$, respectively, in *n*-butylmethylimidazolium tetrafluoroborate, $BMim^+BF_4^-$. In a typical experiment the metal carbonyl was dissolved/suspended under an argon atmosphere in dried and deoxygenated $BMim^+BF_4^-$. For the MNP synthesis the mixture was heated under argon up to 250 °C for several hours to thermally decompose the metal carbonyl. Alternatively, the mixture was irradiated at 200–450 nm for 15 min for photolytic decomposition (Scheme 1).[12,13]

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(12) Materials and instrumentation: $Fe_2(CO)_9$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ were obtained from Strem, and $BMim^+BF_4^-$ was purchased from IoLiTec (H_2O content ≪100 ppm; Cl^- content ≪50 ppm). All manipulations were done using Schlenk techniques under argon, since the metal carbonyl salts are hygroscopic and air sensitive. The ionic liquids were dried under high vacuum (10^{-3} mbar) for several days. Transmission electron microscopy (TEM) photographs were taken at room temperature from a carbon-coated copper grid on a Zeiss LEO 912 transmission electron microscope operating at an accelerating voltage of 120 kV.

(13) Thermal decompositions were carried out under argon (air) in a vessel which was connected to an oil bubbler. In a typical experiment the metal carbonyl $M_n(CO)_m$ (M = Fe, Ru, Os; 0.020, 0.014, and 0.008 g, respectively) was dissolved/suspended (~1 h) under argon at room temperature in 3.0 g of the ionic liquid to give a 0.2−1 wt % M solution. The solution was slowly heated to 180–200 °C for Fe and Ru and to 250 °C for Os over a period of 12 h under stirring. After the mixture was cooled to room temperature under argon, an aliquot of the ionic liquid was collected under an argon atmosphere for in situ TEM and dynamic light scattering characterization. Photolytic decompositions of a solution/suspension of $Ru_3(CO)_{12}$ (0.005 g) in 3.0 g of $BMim^+BF_4^-$ were carried out in a Kürner UV 1000 reactor from Kürner-Analysentechnik in quartz tubes for 15 min under argon with an Hg-UV lamp (1000 W) in the range 200–450 nm.

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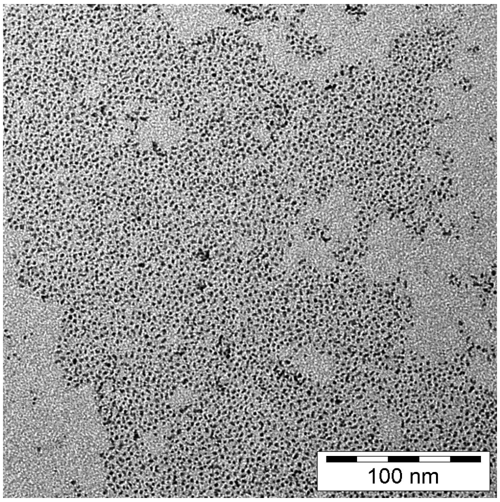


Figure 1. Ru nanoparticles from $Ru_3(CO)_{12}$ in $BMim^+BF_4^-$ by thermal decomposition (entry 5 in Table 1).

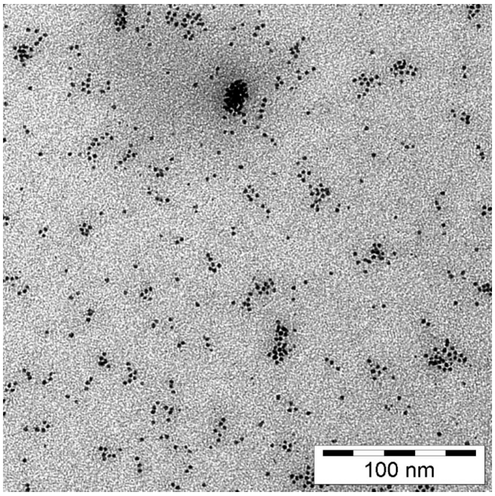
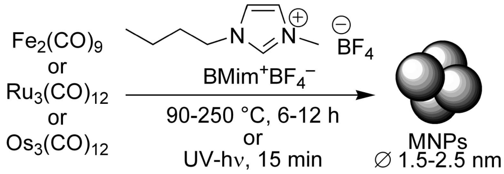


Figure 2. Ru nanoparticles from $Ru_3(CO)_{12}$ in $BMim^+BF_4^-$ by photolytic decomposition (entry 8 in Table 1).

Scheme 1. Formation of Fe, Ru, and Os Nanoparticles by Thermal and Photolytic Decomposition of Metal Carbonyls under Argon in $BMim^+BF_4^-$



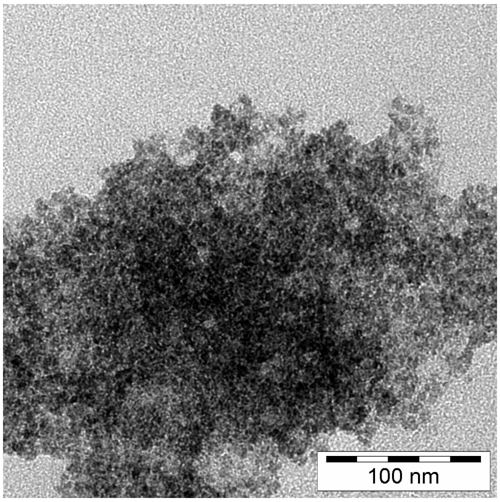


Figure 3. Fe nanoparticles from $Fe_2(CO)_9$ in $BMim^+BF_4^-$ by thermal decomposition (entry 3 in Table 1).

Table 1. Nanoparticle Size and Distribution in $BMim^+BF_4^-$ Analyzed by TEM and Dynamic Light Scattering.

entry	metal carbonyl (wt % in IL)[a]	product[b]	TEM median diam/nm (standard deviation σ)[c]	dynamic light scattering median diam/nm (σ)[d]
1	$Fe_2(CO)_9$ (0.2)	Fe_2O_3		6.2 (±1.2)
2	$Fe_2(CO)_9$ (1)	Fe_2O_3	4.2 (±1.1)	6.4 (±1.1)
3	$Fe_2(CO)_9$ (0.2)	Fe	5.2 (±1.6)	10.1 (±2.1)
4	$Fe_2(CO)_9$ (1)	Fe		10.7 (±2.4)
5	$Ru_3(CO)_{12}$ (0.2)	Ru	1.6 (±0.4)	2.9 (±0.5)
6	$Ru_3(CO)_{12}$ (0.6)	Ru		2.9 (±0.6)
7	$Ru_3(CO)_{12}$ (1)	Ru		2.8 (±0.6)
8[e]	$Ru_3(CO)_{12}$ (0.08)	Ru	2.0 (±0.5)	3.9 (±1.0)
9	$Os_3(CO)_{12}$ (0.2)	Os	2.5 (±0.4)	
10	$Os_3(CO)_{12}$ (1)	Os		5.6 (±1.5)

[a] The solubility of metal carbonyl precursors in $BMim^+BF_4^-$ is limited to a maximum value of about 1 wt %. [b] Fe_2O_3 assignment/analysis through electron diffraction. [c] Statistical evaluation of the total sample pictures (see also the Supporting Information). Transmission electron microscopy (TEM) photographs were taken at room temperature from a carbon-coated copper grid on a Zeiss LEO 912 transmission electron microscope operating at an accelerating voltage of 120 kV. [d] Hydrodynamic radius, median diameter from the first three measurements at 633 nm. [e] Photolytic decomposition.

Black Fe, dark brown Ru, or orange-red Os nanoparticle dispersions (Figure S15, Supporting Information) were reproducibly obtained and are stable for several months under argon. The median metal nanoparticle size for Ru and Os of 1.5−2.5 nm is extremely small with a narrow or uniform, albeit not monodisperse, size distribution (Figures 1 and 2). It is, at present, not trivial to routinely and easily prepare uniform nanoparticles of such small 1–2 nm size. No extra stabilizers or capping molecules are needed to achieve this small particle size. Fe nanoparticles are magnetic and agglomerate as a result of their superparamagnetic properties (Figure 3).[4] Ru nanoparticles produced by thermal and photolytic decomposition show only slight differences in median size and size distribution (Figures 1 and 2 and Table 1). Nanoparticles produced by photolysis give somewhat larger particles because of a faster decomposition and growth process in the ionic liquid.

Furthermore, we synthesized Fe_2O_3 nanoparticles (Figure 4) in air as a comparison and reference to the Fe NP synthesis, so as to ensure the absence of significant oxidation in the latter. For Fe_2O_3 the $Fe_2(CO)_9$/IL mixture was subjected to the same decomposition conditions, albeit under air.[13] The rusty colored Fe_2O_3 NP are not magnetic at room temperature, different to the black Fe NPs (see Figure S16, Supporting Information). The Fe_2O_3 NPs are obtained as crystalline nanomaterials, on the basis of electron diffraction analysis, again different from the case for Fe nanoparticles, which are amorphous under the same synthesis conditions (Figure 5).

MNPs (*core*) are considered stabilized in ILs by the formation of "*protective*" anionic and cationic layers (shells) around them in a "*core-shell system*".[8,14] ILs are regarded as supramolecular polymeric structures with a high degree of self-organization and weak interactions among supramolecular imidazolium−anion

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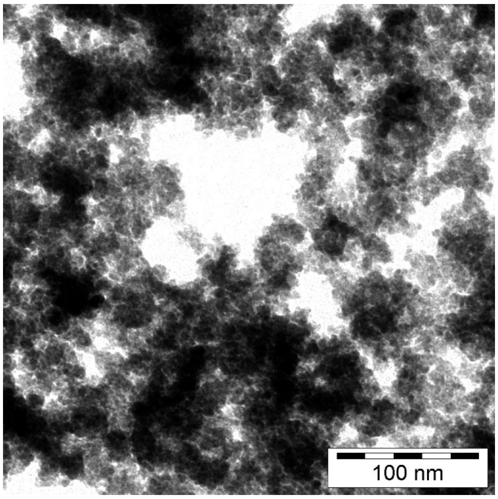

Figure 4. Fe_2O_3 nanoparticles from $Fe_2(CO)_9$ in $BMim^+BF_4^-$ by thermal decomposition in air (entry 2 in Table 1).

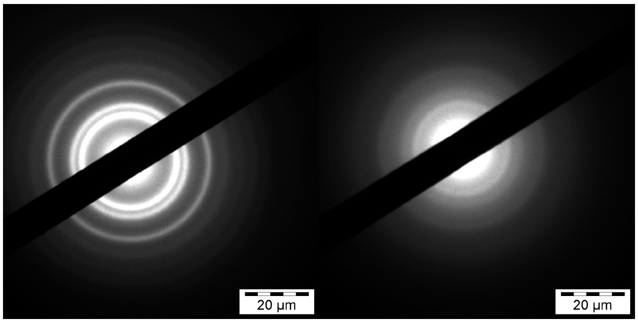

Figure 5. Transmission electron diffraction (TED) pattern of crystalline Fe_2O_3 nanoparticles (left) and amorphous Fe nanoparticles (right) from $Fe_2(CO)_9$ in $BMim^+BF_4^-$ by thermal decomposition under air and argon, respectively (entries 2 and 3 in Table 1; the black bar is the beam stopper). The diffraction rings (Å) at 2.7 (very strong), 2.2 (strong), 1.6 (strong), and 1.3, 1.1, and 1.0 (all weak) match with *D* spacing of the Fe_2O_3 (iron oxide) diffraction pattern.[17]

clusters.[6] We suggest that the thickness of the stabilizing shells around an MNP depends on the IL molecular ion volumes. According to DLVO theory the first inner shell must be anionic:[7] then the IL anion will have the highest influence on the size and electrostatic stabilization of the resulting nanoparticles. Recently it was shown that the anion molecular volume can determine the range of the metal nanoparticle size.[5] When mixed with other molecules or MNPs, ILs become nanostructured materials with polar and nonpolar regions.[6,15,16]

Furthermore, we suggest that ionic liquids act as a "*novel nanosynthetic template*". The particle size does not significantly change with a 5-fold difference in concentration of the precursor (0.2 vs 1 wt %, Table 1). In nanoparticle syntheses through sol–gel, microemulsion, and other processes with stabilizers or capping molecules the concentration of the precursor plays a crucial role in determining the particle size and size distribution.[4,8]

In conclusion, we describe here a simple and reproducible method for the synthesis of Fe, Ru, and Os metal as well as Fe_2O_3 nanoparticles in the ionic liquid $BMim^+BF_4^-$ with an extraordinarily small and uniform MNP size of about 1.5−2.5 nm for Ru and Os nanoparticles. No extra stabilizers or capping molecules are needed to achieve this small particle size. The synthesis uses easily commercially available metal carbonyl precursors and can readily be expanded to the broad range of other metal carbonyl complexes. Metal carbonyls are attractive starting materials for nanosyntheses, as they are available in high purity or are easily purifiable: e.g., by sublimation. Also, the IL $BMim^+BF_4^-$ is produced in large quantities. The nanoparticles can be separated by centrifugation (10 min at 2000 rpm under argon) from the ionic liquid, and the ionic liquid can be reused.[17,18] The resulting NP residue can be redispersed in various polar solvents such as *n*-butylimidazole, acetone, methanol, ethanol, and CH_2Cl_2. Investigations on the characteristics and properties of the above MNPs in ILs, mixed with and redispersed in various solvents, are currently underway in our laboratory.

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Supporting Information Available: Figures giving statistical graphs for dynamic light scattering, additional TEM pictures, pictures showing the color of nanoparticle dispersions. This material is available free of charge via the Internet at http://pubs.acs.org.

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