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Communication

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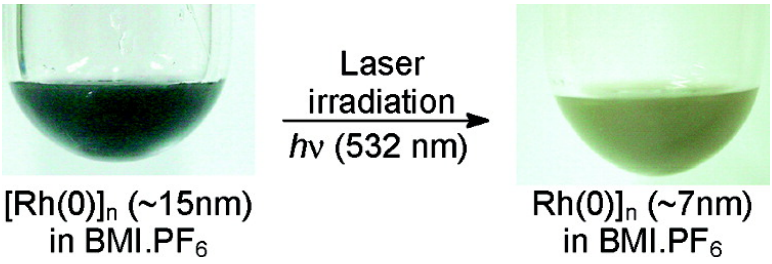

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Laser-Induced Fragmentation of Transition Metal Nanoparticles in Ionic Liquids

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It is expected that transition-metal nanoparticles of 1−10 nm in size will exhibit physical−chemical properties intermediate between those of the smallest element from which they can be composed and those of the bulk material.[1] However, in solution nanoparticles are solely kinetically stable, and they should be stabilized against aggregation into larger particles and bulk material. The stabilization of nanoparticles in solution can be achieved by electrostatic and/or steric protection by, for example the use of water-soluble polymers, quaternary ammonium salts, surfactants, or polyoxoanions.[2] In this respect we and others have recently demonstrated that ionic liquids[3] are a suitable medium for the preparation and stabilization of transition-metal nanoparticles and are also ideal for the generation of recyclable biphasic catalytic systems for hydrogenation and C−C coupling reactions.[4] Indeed, the pronounced self-organization of imidazolium ionic liquids—that can be described as polymeric supramolecules[5]—has been used for the preparation of various highly organized hybrid nanostructures.[6] It has been suggested that the combined intrinsic high charge plus the steric bulk of these salts can create an electrostatic and steric colloid-type stabilization of transition-metal nanoparticles, similar to the proposed model for the stabilization of nanoclusters by polyoxoanions or by tetralkylammonium salts.[7]

However, in some cases the transition-metal nanoparticles, in particular those of Rh(0) and Pd(0), dispersed in the ionic liquid tend to aggregate into larger structures with loss of their catalytic activity.[8] It is worth pointing out that the valence band emission for these metal particles occurs at binding energies (measured by XPS analysis with respect to the Fermi level) that are quite similar to that of the pure metals. This suggests that in these cases the development of electron deficiencies at the nanoparticle surface is not sufficient to approximate the ionic liquid and thus to create an effective electronic/steric protection layer.[7] It is also known that laser irradiations of metal particles promote the photoejection of electrons, which induces subsequent fragmentations, and this constitutes an alternative and selective method for the breakup of large or irregular particles into smaller and regular ones.[9] Therefore, the irradiation of nanoparticles dissolved in ionic liquids may provide a new method for the generation of transition-metal nanoparticles with a small and narrow size distribution dispersed in ionic liquids or restructure those particles that tend to aggregate into larger particles after use as, for example, in catalysis. Moreover, since imidazolium ionic liquids possess negligible vapor pressure, it is possible to investigate their size and shape modification before and after radiation by in situ transmission electron microscopy (TEM) experiments,[10] thus avoiding sample treatments such elimination of the solvents, which may be involved in the stabilization of the nanoparticles.

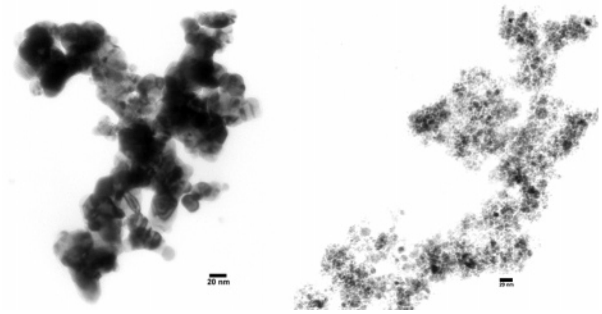

Figure 1. Parts of the TEM micrographs showing the Pd nanoparticles dispersed in $BMI\cdot PF_6$ ionic liquid, observed at 200 kV, before (left side) and after (right side) photolysis with 532 nm laser excitation for 120 min.

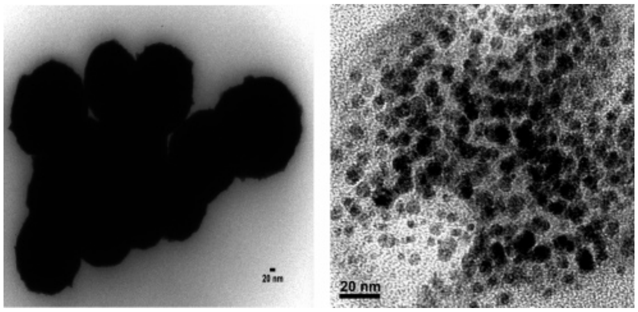

Figure 2. Parts of the TEM micrographs showing the Rh nanoparticles dispersed in $BMI\cdot PF_6$ ionic liquid, observed at 200 kV, before (left side) and after (right side) photolysis with 532 nm laser excitation for 120 min.

We disclose herein that indeed the in situ laser radiation of relatively large Pd(0) and Rh(0) nanoparticles dispersed in 1-*n*-butyl-3-methylimidazolium ($BMI\cdot PF_6$) ionic liquid induces their fragmentation into smaller particles with narrow size distribution.

The Rh and Pd nanoparticles were prepared by simple hydrogen (4 atm) reduction of $PdCl_2$ or $[Rh(cod)\text{-}\mu\text{-}Cl]_2$ (cod = 1,5-cyclooctadiene) dispersed in 1 mL of $BMI\cdot PF_6$ at 75 °C. In both cases the transition-metal suspensions darken after 15 min in the case of Pd and after 60 min in the case of Rh. Small portions of these ionic liquid “solutions” were transferred to a holey carbon grid and analyzed by TEM (Figures 1 and 2).

Another part of the ionic liquid sample was centrifuged affording a black powder that was washed with dichloromethane and dried under reduced pressure; a thin 1.0-mm layer of Pd or Rh power was deposited into a small cavity on a glass substrate and analyzed by X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS). The WAXD pattern confirmed the crystalline Pd(0) and Rh(0), by indexation of Bragg reflections obtained by a pseudo-Voigt profile fitting using the FULLPROF code. The X-ray diffraction patterns (Figures 3 and 4) could be adjusted to the predicted lines of the Pd(0) and Rh(0) fcc structures, and the cell

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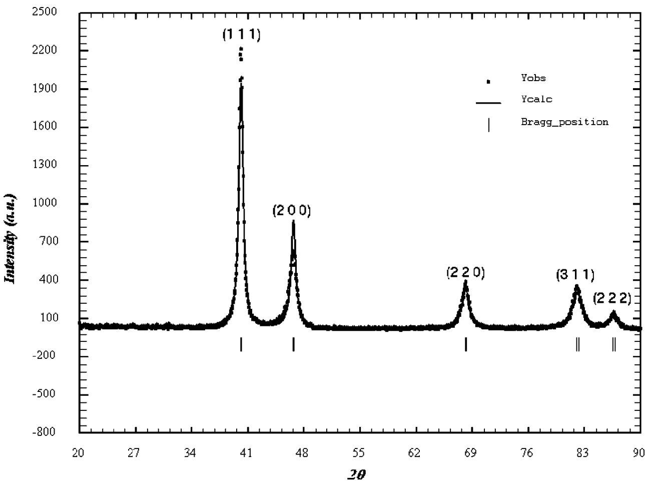

Figure 3. X-ray diffraction pattern of Pd(0) nanoparticles before laser irradiation.

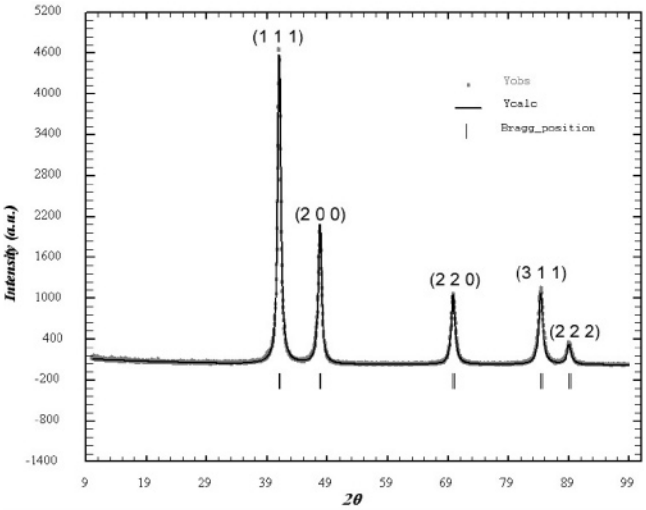

Figure 4. X-ray diffraction pattern of Rh(0) nanoparticles before laser irradiation.

unit parameters obtained were $a = 3.890$ Å and $a = 3.807$ Å for Pd and Rh, respectively. The XPS analysis showed mainly the presence of palladium and rhodium, and the valence band (4d, 5s) emission occurs at a binding energy ca. 0−8 eV, measured with respect to the Fermi level, which is quite similar to that of pure Rh and Pd metals (see Figure S5).

The remaining ionic liquid dispersion was submitted to Nd:YAG laser irradiation at 532 nm with a fluence of 200 mJ/cm^2 (8 ns pulses, 20 Hz) for 120 min and then also placed in a holey carbon grid and analyzed by TEM (Figures 1 and 2).

The TEM micrographs of the particles dispersed in BMI·PF$_6$, before laser irradiation, show large aggregates for both Pd(0) and Rh(0), and their size could not be determined from the TEM micrographs (Figures 1 and 2). The metallic nature of these Pd(0) and Rh(0) nanoparticles was also confirmed by energy dispersion spectrometry and selected area diffraction (see Figures S3 and S4 of the Supporting Information). Nevertheless, a mean diameter of 12 and 15 nm for Pd(0) and Rh(0) nanoparticles, respectively, could be estimated from the XRD diffraction pattern by means of the Debye−Scherrer equation and assuming spherical shape for the metallic particles.

However, both the Pd(0) and Rh(0) nanoparticles dispersed in the ionic liquid after the laser radiation displayed an irregular shape with a monomodal size distribution of 4.2 (±0.8) nm for Pd(0) and 7.2 (±1.3) nm for the Rh(0) as determined from the TEM micrographs (Figures 1 and 2).

It is interesting to note that nanoparticles isolated from the ionic liquid can be easily redispersed by simple laser radiation, and the colloidal solution thus formed is stable for weeks without any change in their size as determined by TEM analysis of Rh(0) nanoparticles after 8 weeks of the laser treatment (see Figure S4). The fragmentation of transition-metal nanoparticles with laser excitation is most probably a result of the electron ejection from the metal nanoparticles. The ionic liquid is probably playing different roles in the fragmentation process. Since the plasmon absorption of metal nanoparticles is sensitive to the surrounding environment,[9b] the ionic liquid may alter the refractive index surrounding the nanoparticles and also complex with the metal surface. The photoejection generates an electronic deficiency on the particle surface that facilitates the approximation of the ionic liquid, consequently forming a protective layer that renders its agglomeration into larger clusters difficult.

In summary we have demonstrated for the first time that imidazolium ionic liquids are the media of choice for in situ investigations of the changes in shape and size of colloidal Pd and Rh particles induced by radiation. The laser excitation can constitute a complementary method for the generation of stable metal colloids in ionic liquids and also for the regeneration of small-size nanoparticles that may result from their agglomeration after different applications such as catalysis.

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Supporting Information Available: Experimental procedure, TEM micrographs, EDS, XRD and XPS spectra of the nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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