Nanoparticles

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Direct Preparation of Sulfide Semiconductor Nanoparticles from the Corresponding Bulk Powders in an Ionic Liquid[**]

Borja Rodríguez-Cabo, Eva Rodil, Héctor Rodríguez, Ana Soto, and Alberto Arce[*]

The physicochemical properties of materials depend on their particle size. Appealing properties can be imparted to different materials at nanometric levels, thus generating a new range of interesting and promising products with different optical, electronic, magnetic, chemical, and mechanical properties from those of the bulk materials.[1] In particular, semiconductor nanoparticles, and more specifically chalcogenide nanoparticles, have been intensively studied because of their quantum confinement effects and size-dependent photoemission characteristics.[2] These semiconductor nanoparticles are widely used for biological labeling and diagnosis, light-emitting diodes, electroluminescent and photovoltaic devices, lasers, single-electron transistors, and catalysis.[3] Over the last decades, a great effort has been made in the development of approaches for the synthesis of nanoparticles with controlled size and shape, as well as on the study of their properties. Among these approaches, liquid-phase methods (which comprise both microemulsion and reaction techniques) are the most relevant because of their simplicity and ability to control the nanoparticles morphology according to the operation conditions.[4]

Ionic liquids are salts with low ($<100\,^{\circ}$C) melting temperatures. They typically exhibit properties such as extremely low vapor pressures, wide liquid ranges, ability to dissolve a broad variety of compounds, and good thermal and chemical stabilities.[5] Moreover, by judicious selection of the cation–anion combination ("design" of the ionic liquid), it is possible to adjust the properties of the ionic liquid to a considerable extent to match those required for a given application.[5b,6] These characteristics render them as interesting compounds for the development of more sustainable processes in a great variety of applications in different fields. Subsequent to a burgeoning in research on ionic liquids in the late 1990s, they were first used in a method for the preparation of nanoparticles about a decade ago.[7] Since then, it has been proposed that ionic liquids may provide both steric and electrostatic stabilization to nanoparticles,[8] and they have been used in a variety of roles (e.g., (co)solvents, reactants, templates) in a good number of methods for the synthesis of inorganic nanoparticles with novel morphologies and improved properties.[9]

Nanomaterials preparation methods involving ionic liquids have been mostly applied to the synthesis of metal nanoparticles,[9b] although the preparation of metal oxide nanoparticles is gaining increasing attention.[9d] Also, other nanoparticles of interest such as metal chalcogenides, in particular sulfides, have been synthesized using methods based on ionic liquids. For example, CdS and PbS nanoparticles were prepared in the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate, using ultrasonic irradiation, with thioacetamide and the corresponding metal acetate as precursors.[10] In another example, ZnS nanoparticles were prepared from zinc acetate in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, by a microwave-assisted method.[11]

In spite of the introduction of ionic liquids in liquid-phase methods for the preparation of nanoparticles, the utilization of organic solvents and/or solid precursors, which have associated undesired effects from a perspective of sustainability, has remained necessary. Herein, we present a novel method (Figure 1), in which only an ionic liquid and the bulk powder of the material of the target nanoparticle are used, thus avoiding the utilization of volatile solvents or solid precursors, which lead to by-products. The method is very simple: first, a mixture of the bulk solid material and the ionic liquid is heated, with stirring, then, the mixture is allowed to cool down, and it is centrifuged to remove any excess of the bulk material from the generated nanodispersion. The suitability of the method depends critically on the appropriate selection of the ionic liquid, which has to play a dual role as nanoparticle former and as a stabilizing agent.

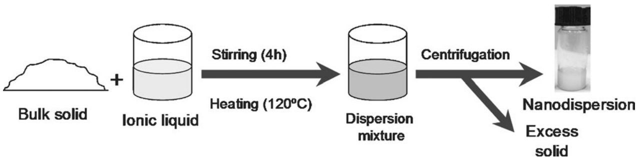

Figure 1. Method for the synthesis of nanoparticles directly from their bulk powder in an ionic liquid.

The viability of the method was tested for the synthesis of a series of semiconductor sulfide nanoparticles. Ionic liquids containing the bulky trihexyl(tetradecyl)phosphonium cation

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[*] B. Rodríguez-Cabo, Dr. E. Rodil, Dr. H. Rodríguez, Prof. A. Soto, Prof. A. Arce
Department of Chemical Engineering
University of Santiago de Compostela
15782 Santiago de Compostela (Spain)
E-mail: alberto.arce@usc.es

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($[P_{66614}]^+$) were initially selected, because the long alkyl chains enable coordination with the particle surface,[12] and they can efficiently self aggregate. In fact, the chloride salt, $[P_{66614}]Cl$, has already been used in the literature as a surfactant to form microemulsions in a liquid medium to obtain AgCl nanoparticles.[13] Thus, following the method in Figure 1, and starting with a powder/ionic liquid ratio of ca. 1 %, CdS and ZnS nanoparticles were formed in $[P_{66614}]Cl$, as phenomenologically evidenced by the change in color of the liquid medium; this color change is characteristic to the type of nanoparticle,[14] and is shown in Figure 2. X-ray fluorescence measurements, after the centrifugation step and removal of the remaining bulk solid, indicated a concentration of nanoparticles of approximately 0.8–0.9 % in the nanodispersion, therefore indicating that over 80 % of the initial bulk powder had been transformed into nanosized particles. The optimum time and temperature for the procedure were found to be 4 h and 120 °C, respectively, and stirring was necessary. Interestingly, when trying to form PbS nanoparticles from its bulk powder, in the same ionic liquid, $PbCl_2$ nanoparticles were obtained instead; these nanoparticles are a result of exchange with the chloride ions of the ionic liquid. PbS nanoparticles could be obtained, nonetheless, in trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide ($[P_{66614}][NTf_2]$). This ionic liquid was also used to produce MnS nanoparticles. The change of color of the liquid upon formation of the nanodispersions of PbS and MnS in $[P_{66614}][NTf_2]$ are also shown in Figure 2. UV/Vis absorption and photoluminescence measurements in the resulting dispersions were consistent with the presence and nature of the nanoparticles (see the Supporting Information). Also, UV/Vis absorption provided evidence of increased formation of nanoparticles with increasing time, through analysis of samples from experiments with different contact times (see the Supporting Information; exemplified for the case of CdS in $[P_{66614}]Cl$). The stability of all four nanodispersions was checked optically over a minimum storage period of two weeks, and no sign of agglomeration or sedimentation being observed.

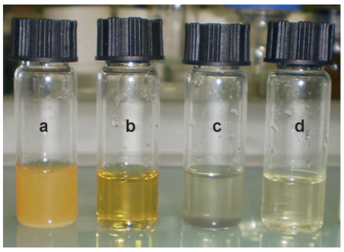

Figure 2. Dispersions of metal sulfide nanoparticles in ionic liquid, with their characteristic coloration (consistent with previous reports in the literature):[15] a) ZnS nanoparticles in $[P_{66614}]Cl$, off white particles; b) CdS nanoparticles in $[P_{66614}]Cl$, pale yellow particles; c) PbS nanoparticles in $[P_{66614}][NTf_2]$, gray particles; d) MnS nanoparticles in $[P_{66614}][NTf_2]$, pale green particles.

The stable nanodispersion can be the product of interest, although it may also be preferable or necessary to isolate and optionally redisperse (e.g., in a solvent such as toluene or isooctane) the nanoparticles obtained. In our case, it was possible to isolate the nanoparticles using the procedure in Figure 3. Ethanol and a capping agent (1-dodecanethiol) were added to cause the precipitation of the nanoparticles without agglomeration, then the solid nanoparticles and the liquid phase were separated by centrifugation. As a result of its negligible vapor pressure, the ionic liquid could be easily recovered by distillation of the liquid phase. X-ray fluorescence measurements confirmed the absence of metals (i.e., of nanoparticles) left in the liquid phase.

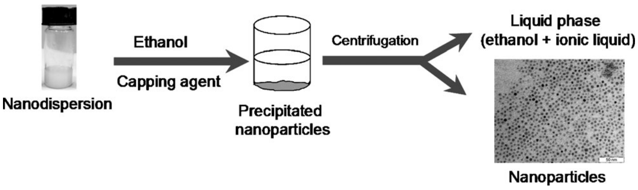

Figure 3. Procedure for precipitation of the nanoparticles.

The precipitated nanoparticles could be analyzed by powder X-ray diffraction, which confirmed the structures for all four cases included in Figure 2 (see the Supporting Information for details), face-centered cubic structure for ZnS, hexagonal for CdS, octahedrical for PbS, and cubic for MnS nanoparticles; these findings match diffraction patterns previously reported in the literature for these types of nanoparticles.[15d,16] Redispersion of the nanoparticles in toluene was carried out to prepare grids suitable for analysis by transmission electron microscopy (TEM). Nonagglomerated, spherical nanoparticles were observed in all four cases (see example in Figure 4 a,b for CdS nanoparticles—further examples in the Supporting Information), with relatively

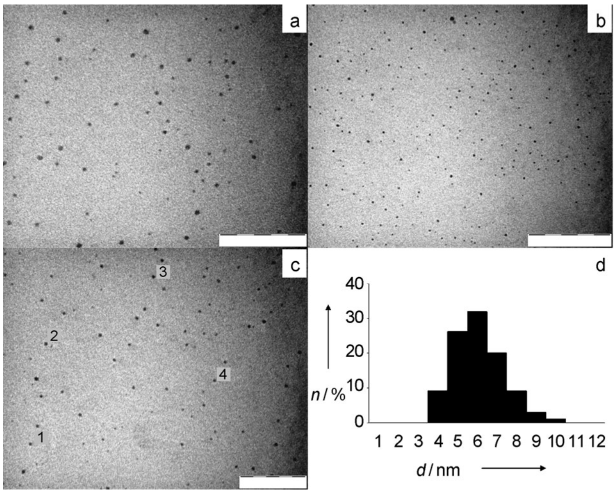

Figure 4. TEM micrographs at different degrees of magnification, for CdS nanoparticles: a) scale bar: 100 nm and b) scale bar: 200 nm. c) An example of size distribution determination with the TEM built-in software (scale bar: 100 nm). The diameters of the indicated particles are: 1) 5.94 nm, 2) 5.47nm, 3) 5.57 nm, 4) 4.29 nm. d) A histogram with the size distribution obtained by DLS for the CdS nanoparticles. d = diameter.

narrow size distributions. Their diameters were found to be in the ranges 4–8 nm, 3–7 nm, 3–7 nm, and 3–10 nm, for ZnS, CdS, PbS, and MnS nanoparticles, respectively, as determined directly from the micrographs by means of a built-in software (Figure 4c). The size distribution of the nanoparticles was additionally measured by dynamic light scattering (DLS) on the redispersion in toluene, and similar although in general slightly higher diameters were obtained (Figure 4d and the Supporting Information).

Analogous direct preparation of CdS nanoparticles from the bulk powder was attempted in common organic solvents (acetone, hexane, ethanol, dichloromethane) and in water. As expected, all the bulk material precipitated in its bulk form, and detailed analysis of the precipitate by TEM confirmed the absence of nanoparticles. Thus, the role of the ionic liquid is critical in the synthesis of nanoparticles from the bulk powder. In view of the ion exchange that occurs in the experiment in which $PbCl_2$ nanoparticles were obtained instead of PbS nanoparticles in $[P_{66614}]Cl$, and that much higher shear rates would have to be applied to reduce "directly" the particles size from the micro to the nano domain, we postulate that a mechanism based on dissolution–reprecipitation occurs. The observed influence of different reaction times and temperatures on the output of the experiments (the formation of nanoparticles increased as time and temperature were increased, up to a maximum plateau) is also compatible with the idea of solubilization phenomena governing the process. Therefore, the bulk powder is probably solubilized at high temperature, then nucleation is stimulated by supersaturation,[17] as a result of a decrease in solubility as the temperature of the medium is allowed to cool down, and finally the ionic liquid is able to stabilize the nanosized particles that are formed. To get a deeper insight on how this stabilization can be produced, ^{31}P NMR spectra were carried out for nanodispersions of CdS in $[P_{66614}]Cl$ and $[P_{66614}][NTf_2]$, and for the corresponding pure ionic liquids. The deuteriated solvent ($[D_6]$benzene) required for these experiments was placed in internal, coaxial tubes to prevent disturbance of interactions present in the ionic liquid media. A direct comparison of the spectra showed no evidence for interaction of the $[P_{66614}]^+$ cation (in either $[P_{66614}]Cl$ or $[P_{66614}][NTf_2]$) with the nanoparticles. Therefore, it is reasonable to think of a first layer of ionic liquid anions interacting directly with the partial positive charges on the surface of the particle, and a second layer of cations keeping the electrostatic balance and providing steric stabilization through interaction between the long alkyl chains. Thus, the overall stabilization would be a combination of electrostatic and steric stabilization. Further experiments carried out using dialkylimidazolium chloride ionic liquids gave results that are consistent with this hypothesis: when trying to form CdS nanoparticles from the bulk powder in 1-butyl-3-methylimidazolium chloride and in 1-methyl-3-octylimidazolium chloride, the presence of nanoparticles was verified by UV/Vis spectrophotometry and by TEM (see the Supporting Information), but the nanoparticles were in apparently lower concentration and with poorer stability as compared to the experiment in $[P_{66614}]Cl$. This can be interpreted in terms of an inferior steric stabilization by the imidazolium ionic liquids, as a result of the smaller contribution of their alkyl substituent chains.

In spite of these insights into the mechanism by which the nanoparticles are formed by the procedure described herein, some issues still remain unaddressed. One such issue is the role or influence of the metal in the sulfide. For example, it has been observed that the nanodispersion of CdS in $[P_{66614}][NTf_2]$ is less stable than those of ZnS, PbS, and MnS nanoparticles in the same ionic liquid, but no explanation has been identified for such behavior. Aspects such as the influence of the impurities in the phosphonium ionic liquid (produced at an industrial scale with a limited degree of purity), among others, should not be ruled out.

In summary, a simple route, based on ionic liquids, has been developed for the preparation of semiconductor chalcogenide nanoparticles directly from the corresponding bulk powders, and is exemplified for the case of several metal sulfides in two phosphonium ionic liquids. This method could lead to more environmentally friendly processes, because the ionic liquids, in contrast to the volatile organic solvents commonly used, do not produce atmospheric pollution and can be recovered after the process.

Experimental Section

Details on the materials used can be found in the Supporting Information. Nanodispersions were prepared in the ionic liquid media according to the procedure in Figure 1. The bulk powder (0.6 g) was added to the ionic liquid (6 g) in a round-bottomed flask at room temperature, and the reaction mixture was heated at 120 °C and vigorously stirred for 4 h in an argon atmosphere. The resulting colored mixture was allowed to cool down to room temperature, and then it was centrifuged at 4000 rpm for 15 min, to separate the excess bulk solid from the nanodispersion. Precipitation and isolation of the nanoparticles was carried out according to the procedure in Figure 3. Dodecanethiol ($50\,\mu L\,mL^{-1}$ of sample) was added to the nanodispersion, and the mixture was vortexed. Then, ethanol (20 mL) was added. The precipitated nanoparticles were isolated by centrifugation at 3000 rpm for ca. 10 min, and then allowed to dry under ambient conditions for 48 h. For some of the characterization analyses, redispersions of the nanoparticles in toluene were made. UV/Vis absorption spectra were produced by an Agilent 8543 UV/Vis spectrophotometer. Photoluminescence analyses were performed on a FluoroMax-3 spectrofluorimeter by Jobin Yvon Horiba. TEM images were recorded on a Philips CM-12 transmission electron microscope. Size distribution histograms by DLS were obtained on a Malvern Zetasizer Nano ZS. The concentration of nanoparticles in the ionic liquid medium was determined by X-ray fluorescence using an Oxford Instruments LabX3500S total sulfur analyzer. X-ray powder diffraction analyses were carried out on an X-ray powder diffractometer with Cu anode radiation. NMR spectra were recorded on a Bruker DRX-500 spectrometer.

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