

## Aqueous–Organic Phase Transfer of Gold Nanoparticles and Gold Nanorods Using an Ionic Liquid

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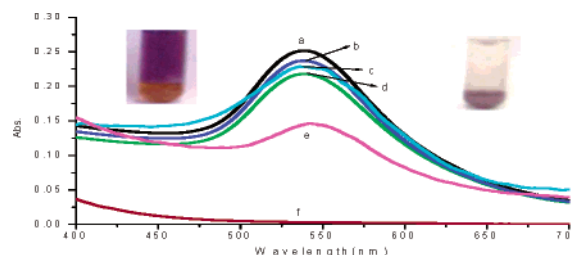
Because ionic liquids (ILs) have unique physicochemical properties, such as no detectable vapor pressure and relatively high thermal stability,<sup>1</sup> they continue to attract an increasing amount of interest for their promising roles as alternative media for reactions and separations.<sup>2,3</sup> ILs do not lose solvent through evaporation, and so their use circumvents the environmental and safety problems that result from traditional volatile organic compounds (VOCs). As a result, ILs are regarded as potential “green solvents”.<sup>4</sup>

Metal nanoparticles have also attracted considerable interest, in fields such as optics and catalysis, because of their size- and shape-dependent physicochemical properties.<sup>5</sup> Various procedures have been developed for preparing nanoparticles with controlled sizes and shapes.<sup>5,6</sup> Among such procedures, those that require an aqueous medium are the most convenient to develop because of water’s ability to solubilize a variety of ions and stabilizing molecules. On the other hand, nanoparticles prepared in organic media are interesting for, among other things, applications to catalytic processes and for further surface modifications with organic functional groups to fine-tune their properties.<sup>5d,7</sup>

Differently sized and shaped metal nanoparticles can be obtained in organic media either by preparing them directly in those media<sup>6f</sup> or by transferring nanoparticles from aqueous phases to organic phases.<sup>8</sup> The first approach is a very sensitive one that requires considerable effort to develop convenient size- and shape-controllable processes. The second approach has the advantage that there are many well-developed procedures available for the preparation of well-defined metal nanoparticles in aqueous media. Phase transfer of metal nanoparticles from an aqueous phase to an organic phase can be achieved by capping the nanoparticles with thiols and amines,<sup>8a</sup> or by using phase-transfer reagents, such as surfactants, to improve the solubility of nanoparticles in organic media. The efficiency of the latter approach, however, is limited.<sup>8b</sup> When thiols are absent from a metal nanoparticle’s surface, active sites on that surface remain accessible to substrates undergoing catalytic reactions, which enhances catalytic activity.<sup>9</sup>

In this paper, we present a process, which does not require the use of a thiol, for the phase transfer of gold nanoparticles (GNPs) from an aqueous medium to an ionic liquid (IL). This process is a simple one for obtaining solutions of well-defined GNPs in ILs, such that further reactions (catalysis or modification) of these nanoparticles can be performed in this novel medium. ILs are known to have the potential to enhance certain properties of metal nanoparticles, and they have also been used as stabilized agents to prepare metal nanoparticles.<sup>10</sup> We employed a typical water-immiscible IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([C<sub>4</sub>MIM][PF<sub>6</sub>]), to demonstrate the capability of phase transfer of metal nanoparticles.

An aqueous solution of GNPs formed upon the reduction of a solution of HAuCl<sub>4</sub> with citrate was added to the organic phase. A photograph of the test tube containing this aqueous/IL biphasic



**Figure 1.** The UV–vis spectrum of the aqueous layer of a GNP solution (a) before and after phase transfer with (b) benzene, (c) hexane, (d) chloroform, (e) 10-undecen-1-ol, and (f) [C<sub>4</sub>MIM][PF<sub>6</sub>]. The inset displays the test tubes containing the GNPs before (left) and after (right) phase transfer with the IL.

mixture is displayed in the inset of Figure 1 (left-hand test tube). Vigorous shaking of this biphasic mixture results in the complete transfer of the GNPs from the aqueous layer to the IL layer, but we observed that precipitation of the GNPs occurred in the IL as a result of severe aggregation of GNPs. Adding a cationic surfactant, tetradecyltrimethylammonium bromide (TTAB; ca. 30 mM), however, to the aqueous phase reduced this precipitation problem, because TTAB is also transferred from the aqueous phase to the IL phase and prevents the aggregation of the GNPs in the IL. The dissolution and solvation behavior of surfactants in ILs has been reported recently.<sup>11</sup> With the addition of TTAB, the GNPs become transferred and evenly suspended in the IL phase, as indicated from the distribution of color in the right-hand test tube in Figure 1.

Next, we compared the phase transfer of GNPs from the aqueous solution using the IL and some water-immiscible solvents under a constant set of conditions, that is, adding 30 mM TTAB to each organic solvent. Figure 1 presents the UV–vis spectra of the aqueous layer recorded before (curve a) and after phase transfer with (b) benzene, (c) hexane, (d) chloroform, (e) 10-undecen-1-ol, and (f) [C<sub>4</sub>MIM][PF<sub>6</sub>]. With traditional solvents (b–d), we observe little change in the absorbance of the aqueous layer after phase transfer, but curve f indicates that the GNPs can be transferred efficiently from an aqueous phase to an IL phase without requiring the use of capping reagents such as thiols. This phase transfer can be quantified by considering the distribution of the GNPs between the aqueous and organic phases. Although the distribution of different species between ILs and other media has been described recently,<sup>12</sup> the distribution of nanoparticles or colloids between ILs and other immiscible media has yet to be described.

The empirical solvent polarity scales that have been developed to assess the strength of interactions between an analyte and a solvent can be used to explain distribution coefficients. ILs have been characterized by various approaches to have polarities that are close to those of alcohols.<sup>13</sup> A water-immiscible alcohol, 10-undecen-1-ol, was employed to examine the efficiency of using an alcoholic solvent for this phase-transfer process (curve e in Figure

1). The reduction in the intensity of the signal of the GNPs indicates that ca. 42% of the GNPs have been transferred to the organic phase. This observation implies that this alcohol is a moderately effective solvent for the phase transfer of GNPs. A possible reason for the complete phase transfer of GNPs when using the IL is its alcohol-like polarity, but the highly salt-like character of the IL may also play an important role in this process. We added *N*-tetrabutylammonium bromide (TBABr) to the organic solvents in an attempt to mimic the salt effect on the phase transfer of GNPs. A small concentration of salt (1000 ppm) in 10-undecen-1-ol has a dramatic effect (ca. 5% increase) on the phase transfer of GNPs, and the efficiency of the phase-transfer process increases upon increasing the salt concentration (ca. 22% at 6000 ppm). In contrast, the effect of salt concentration on the phase transfer of GNPs into benzene is marginal (only ca. 8% at 8000 ppm; see Supporting Information). It seems reasonable to assume that the effectiveness of ILs toward the phase transfer of GNPs may be attributed to a combination of their alcoholic-like polarity and their ionic properties. Other interactions between the GNPs and IL may also contribute, to a certain extent, to the efficiency of this phase-transfer process, because ILs are the most complex solvents known.<sup>12a,14</sup>

From transmission electron microscopy (TEM) images of the gold nanoparticles before and after phase transfer (see Supporting Information), we estimate that their diameters are  $48.1 \pm 9.0$  and  $49.9 \pm 9.3$  nm, respectively; that is, the size of the gold nanoparticles is preserved upon phase transfer. Aggregation of gold nanoparticles in IL may still exist, however, as evidenced by the TEM and UV-vis spectroscopy measurements. Nevertheless, the nanoparticles can be suspended in the IL for several weeks without precipitation occurring. To prove that this phase-transfer process is also successful when using differently shaped GNPs, we applied the same procedure to an aqueous solution of gold nanorods (GNRs). UV-vis spectroscopy and TEM images indicate that the GNRs were completely transferred into the IL and their shapes were preserved (see Supporting Information).

In conclusion, we have demonstrated that an IL can be employed as a medium to transfer GNPs and GNRs from aqueous solutions to an organic phase without the requirement of capping with thiols or amines. The size and shape of the GNPs and GNRs seem to be preserved when using this phase-transfer process. The significance of this work is that it offers a relatively simple process by which differently sized and shaped GNPs/GNRs can be obtained in an IL after using the facile procedures developed for the preparation of well-defined GNPs/GNRs in aqueous phases. Preliminary experiments (not described here) indicate that this process can be applied also to the phase transfer of other metal nanoparticles. Our findings open up new avenues for further investigations toward the modifications and applications of differently sized and shaped metal nanoparticles in ILs, which are solvents known to have the potential to enhance chemical selectivity and activity.<sup>1a,b</sup>

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**Supporting Information Available:** Experimental procedures, TEM images, histograms displaying the range of sizes of the gold

nanoparticles and nanorods, and an analysis of the effect of salt concentration on the phase-transfer process (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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