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Design, synthesis, catalytic application, and strategic redispersion of plasmonic silver nanoparticles in ionic liquid media

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ABSTRACT

Silver nanoparticles synthesized in tetraalkylphosphonium ionic liquids are found to be excellent catalysts for borohydride-induced reductive degeneration of Eosin-Y, a dye that has been classified as a Class 3 carcinogen by the International Agency for Research on Cancer. TEM images indicated that the size of the Ag nanoparticles was significantly influenced by heat-induced sintering. A strategy was devised to redisperse smaller Ag nanoparticles from their aggregated/sintered counterparts via a two-step protocol that involved oxidative etching of Ag nanoparticles, followed by a re-reduction step. This protocol led to a reduction in the sintered Ag nanoparticle size from 15.7 ± 6.1 nm to 3.7 ± 0.8 nm, which was consistent with the size of the as-synthesized nanoparticles. The as-synthesized and the redispersed Ag nanoparticles were found to catalyze the bleaching of Eosin-Y with comparable efficiencies; first order rate constants for Eosin Y reduction were ~8 times higher for smaller Ag nanoparticles compared to their sintered counterparts. An examination of the kinetics of Ag nanoparticle etching was performed via temperature-controlled UV–vis spectroscopy. Changes in the oxidation state of Ag during this sequence of events were also followed by *in situ* X-ray absorption spectroscopy of Ag nanoparticles in the ionic liquid.

1. Introduction

Nanoparticles (NPs) dispersed in ionic liquids (ILs) or water are of interest as catalysts if they can be stabilized toward aggregation and particle sintering [1–5]. One of the several intriguing properties of ionic liquids is their well-documented capability to act both as solvents and as stabilizers when it comes to stable NP dispersions [6–8]. In imidazolium ILs, this is often due to functionalities deliberately appended to the substituents on the imidazolium cations, but there have been other examples where stabilization stems directly from the nature of the anions [9–12]. Tetraalkylphosphonium halides (PR_4X; X = Cl, Br) represent a class of ionic liquids with intrinsic NP stabilizing abilities [6,13–15]. While these ILs remain less studied for their applications in quasi-homogeneous nanocatalysis than their imidazolium counterparts, recent research indicates that NPs stabilized by these ILs are similar to traditional metal-surfactant combinations that have been used for nanoparticle stabilization for many years, such as CTAB-stabilized metal nanoparticles, which rely on strong halide absorption to the NP surface, along with steric stabilization by the charge balancing cation [16–19]. The exact nature of the forces that stabilize small NPs in tetraalkylphosphonium halide ILs have remained unidentified so far, although it has been suggested by us that a surfactant-like double layer, aided by the high viscosity coefficients of these systems, might contribute toward preventing NP coalescence in PR_4Cl ILs [6,20,21]. Others have suggested that this interaction originates in the well-ordered three-dimensional network structure of ionic liquids, which leads to the formation of well-defined hydrophobic and hydrophilic zones, with pockets where the NPs might find accommodation [14]. Presumably, the catalytic behavior of the NPs formed within these ILs would be influenced by the nature of both the metal used and the ILs [22]. It is essential, therefore, to examine NP/PR_4Cl IL systems in greater detail, which would give us valuable information not only about the individual systems under scrutiny, but also on the chemical and catalytic behaviors of this class of composite materials as a whole.

While Au, Pt, Pd, Ru and Rh NPs in tetraalkylphosphonium ILs have been studied by several groups in the recent past from the point of view of their catalytic behavior, Ag NPs in PR_4Cl ILs are yet to be explored as catalytic systems [13,14,23,24]. This is surprising, since Ag is one of the cheaper 'noble metals'; also, it also has various applications in areas as diverse as photography, anti-bacterial

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coatings and surface-enhanced Raman spectroscopy [25–27]. The presence of a well-characterized, intense surface plasmon resonance (SPR) band for silver nanoparticles in the visible region also makes them attractive candidates for morphological studies, since it is known that the size, shape and intensity of these bands depend upon the size and shape of the NPs being studied [28–30]. It has been recently been shown by us that Ag NPs can be synthesized in trihexyl(tetradecyl)phosphonium halides via a conventional borohydride reduction protocol. It has also been demonstrated that these NPs etch upon exposure to oxygen at high temperatures, presumably aided by the presence of a large excess of halide ions in the system [31].

For testing the catalytic behavior of these systems, we selected a well-studied reaction whose progress could be followed spectrophotometrically. The reaction chosen was the borohydride-induced degradation of Eosin-Y (EY), an organic dye used extensively in staining of histological tissue samples, in photoelectrochemical cells, and as a fluorescent pigment [32–34]. The addition of Ag NPs to this system leads to complete degradation of Eosin-Y. This is in accordance with previous reports, which indicate that coinage metal NPs serve as electron-transfer relays in borohydride-induced reductive degradation of dyes, with the nucleophilic borohydride ions transferring electron density onto the NP surface, which in turn injects those electrons into the dye molecule [35–39]. Most studies carried out in this context focus on the degradation of EY in water phase. Since ILs as solvents show behaviors drastically different from those of water as well as conventional organic solvents, it is worthwhile to examine such electron-transfer processes in these novel media [40].

In this paper, we show the synthesis of Ag NPs in tetraalkylphosphonium halide ILs via reduction of Ag(I) salts with lithium borohydride. The Ag NPs formed in tetraalkylphosphonium halide ILs remained stable for months. These Ag NPs were also able to catalyze the borohydride-induced degeneration of EY in non-aqueous media. It was found that over a large number of catalytic cycles and/or higher temperatures, Ag NPs sintered and aggregated in the IL media. We show that the resulting particles could then be etched via exposure to air or oxygen, which, followed by chemical reduction, can redisperse smaller Ag NPs. The kinetics of the oxidative etching of Ag NPs in P[6,6,6,14]Cl and P[6,6,6,14]Br were examined in this study by *in situ* UV–vis spectroscopy and X-ray absorption near edge spectroscopy. The catalytic activity of the redispersed Ag NPs was determined to be similar to freshly synthesized NPs.

2. Experimental

2.1. Materials

Unless otherwise mentioned, all chemicals were used as received. Silver nitrate (>99.7%) was purchased from Fisher Scientific. Eosin-Y and 2(M) $LiBH_4$ (in THF) were purchased from Sigma Aldrich. THF was purchased from EMD and used as received. The tri(hexyl)tetradecylphosphonium halide (P[6,6,6,14]X; X = Cl or Br) ILs were provided by Cytec Industries Ltd., and were dried under vacuum at 70 °C for 10–12 h with stirring before use. 18 MΩ cm Milli-Q water (Millipore, Bedford, MA) was used throughout.

2.2. Procedure for synthesis of Ag NPs in IL using lithium borohydride

In a representative synthesis of 5.0 mM Ag NPs in P[6,6,6,14]Cl, 8.5 mg of $AgNO_3$ (0.050 mmol) was added under nitrogen to a 10 mL sample of the IL at 80 °C (all the ILs studied are liquids at this temperature) in a Schlenk flask, and vigorously stirred. The solution was cooled to 50 °C, and a stoichiometric excess of $LiBH_4$ reagent (1.5 mL, 2.0 M in THF) was injected drop-wise into it over a period of 2–3 min. A brisk effervescence followed, and the entire solution turned deep yellowish-brown, indicating nanoparticle formation. After the addition of $LiBH_4$, volatile impurities were removed by vacuum-stripping the system at 80 °C. The Ag NP-IL composites thus obtained was stored under nitrogen in capped vials wrapped with foil until use.

2.3. Procedure for EY degradation

In a typical experiment, 0.2 mL of a 0.2 mM EY solution in THF was added to a 7 mL (5:2) mixture of IL:THF in a foil-wrapped vial under nitrogen. A stoichiometric excess of $LiBH_4$ (0.1 mL, 2.0 M in THF) was then added to the system, and stirring was commenced. After the desired time-interval, 200 μL of 5.0 mM Ag NPs in P[6,6,6,14]Cl was added to the system. UV–vis spectra of the ‘blank’ sample (i.e., without added Ag NPs) was also recorded. A quartz cuvette was then filled with the aliquot, and recording of spectra was initiated. Between successive readings, the cuvette was taken out of the spectrophotometer, wrapped in tinfoil to minimize exposure to ambient light, and manually shaken to ensure homogeneity of analyte. It has been noted by others that effervescence owing to the presence of borohydride in the reaction mixture also promotes thorough mixing, even in the absence of a magnetic stir-bar [41]. The recording of spectra was continued at suitable intervals of time, until the pink color of the solution faded to straw-yellow.

2.4. Procedure for Ag NP sintering

To bring about heat-induced growth in particle size, nitrogen was bubbled through Ag NPs in P[6,6,6,14]Cl at 135 °C for an hour, followed by overnight heating under a nitrogen atmosphere at the same temperature. In addition, the Ag NP size was monitored after repeated catalytic cycles; five portions of 0.2 mL, 0.2 mM EY solutions in THF were added to a single 7 mL (5:2) mixture of IL:THF, containing 500 μL of 5.0 mM Ag NP, in a foil-wrapped vial under nitrogen, with a gap of 1 h between each successive addition. 0.1 mL portions of $LiBH_4$ (2.0 M in THF) were also added to the system after each dye addition, and stirring was commenced. After five such cycles of EY degradation, a TEM sample was prepared from the reaction mixture, and Ag NP sizes were studied. We note that our reaction of choice is conducted at room temperature, rather than at elevated temperatures, where greater particle sintering might be expected after repeated reaction cycles as compared to a reaction that occurs under mild, ambient conditions.

2.5. Procedure for Ag NP oxidative etching and redispersion

The following procedure was adopted to redisperse the agglomerated Ag NPs back to ca. their initial sizes: oxygen was flushed through the Ag NP/P[6,6,6,14]Cl system at 65 °C until the characteristic yellow color of the NPs disappeared, followed by re-reduction of the redispersed precursor by drop-wise addition of 1.5 mL $LiBH_4$ solution in THF, followed by quenching of excess reductant and low-pressure removal of volatiles from the medium. The progress of the oxidative etching of Ag NPs in various tetraalkylphosphonium halide ILs was monitored spectrophotometrically by UV–vis spectroscopy. The kinetic studies were conducted in a Cary 6000i spectrophotometer. Ag NP/P[6,6,6,14]Cl samples were taken in quartz cuvettes and small Teflon®-coated magnetic stir-bars were immersed in them; they were then placed in a constant-temperature bath with a magnetic stirring base inside the spectrophotometer. Oxygen from a compressed gas cylinder was passed directly into the contents of the cuvettes at regular intervals using a gas regulator connected to a system of hoses, syringes and needles.