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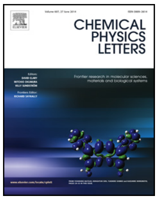

Editor's Choice

A novel gold nanoparticle stabilization and its muon chemistry

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ABSTRACT

We report a novel one-pot synthesis of gold nanoparticles (AuNPs) non-covalently stabilized by ionic liquid benzyldimethyltetradecylammonium chloride (Bac-14). Bac-14 demonstrates unprecedented long-term stabilization for its class of long-chain alkylated quaternary ammonium halides; the AuNP size remained constant for months. The mechanism of stabilization of similar surfactants has not been thoroughly explored in the literature. We elucidate the conformational mechanism of Bac-14 stabilization of the AuNP. Our proposed conformation suggests that these AuNPs are promising catalytic oxidization agents. This is suggestive of their ultra-fast electron capture behavior investigated by muon chemistry, which pioneers the field of muon chemistry of nanostructures.

1. Introduction

The Brust–Schriffin *in situ* biphasic gold nanoparticle (AuNP) synthesis published in 1994 introduced the use of tetraoctylammonium bromide (TOABr)—a quaternary ammonium ion stabilized by a bromide anion—as a stabilizing agent, and phase transfer catalyst in the production of colloidal gold from chloroauric acid ($HAuCl_4$). When reducing $HAuCl_4$ with sodium borohydride, TAOBR stabilizes the precipitating colloidal gold in the aqueous phase. This stabilizing interaction allows the AuNPs to solvate into an organic phase, with TOABr effectively acting as a phase transfer catalyst. However, TOABr does not bind gold particularly strongly and thus only provides temporary stabilization, with gold aggregating in the long term. Thus, usually a subsequent covalent stabilizer such as a thiol is added [1]. Ionic liquids (ILs) are a viable option as stabilizing agents because of their ionic character and can be easily made task-specific as phase transfer catalysts due to their tunable nature. However, ILs are generally used as temporary stabilizing agents. They are used to halt aggregation of Au(0) produced in the reduction of $HAuCl_4$, thus limiting the size of the gold aggregates that form nanoparticles (NPs) [2]. Several studies, as far back as 2002, have reported the synthesis of transition metal NPs using ILs as the media and stabilizers [3–5]. The earliest mention in the literature of an IL with a nitrogen cation used as the capping agent for AuNPs was an imidazolium-based cation IL reported by Itoh et al. [6]. Several other imidazolium ILs followed, however these ILs (along with those by Itoh et al.) contained sulfur functional groups which provided permanent covalent stabilization of the gold; these were effectively task-specific ILs that combined the phase transfer catalyst and permanent stabilizer into one molecule by functionalizing the IL with an aurophilic capping agent (sulfur) [7–9].

In this Letter, we present for the first time AuNPs stabilized by an IL-surfactant in solution for weeks without aggregation. The IL used—benzyldimethyltetradecylammonium chloride (Bac-14)—stabilizes the NPs non-covalently *via* electrostatic interactions. Long-term stabilization of AuNPs by a quaternary ammonium IL has not been described in the literature to our knowledge [1,10] (Figure 1).

Astruc et al. proposed a model based on differential anion stabilization of iridium NPs in the following order: polyoxometallate > citrate > polyacrylate ~ chloride. They argue that the anion must be at the surface of the metal, because the stabilization of the NPs correlates with the sterics of the anion [1].

However, some mechanistic descriptions of AuNP stabilization by imidazolium chloride ILs posit that the cation is at the surface of the metal (Figure 2) [11].

In this Letter, we propose a stabilization similar to what was proposed by Thomas et al. which was based on the strong association of photo-responsive molecules on the surface of AuNPs (Figure 3) [10,12]. Our proposed mechanism of stabilization is outlined in Figure 4.

Formation of AuNPs was determined by UV–vis and TEM. Conformational assignment of the Bac-14-stabilized AuNPs was based on FT-IR, ^1H and ^{13}C NMR, and computational study.

Elucidation of the stabilization mode of these NPs can provide information on the viability of these particles as catalysts for

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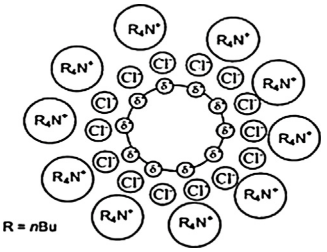

Figure 1. Metal nanoparticle stabilization by an alkyl ammonium chloride mechanism as proposed by Astruc et al. [1].

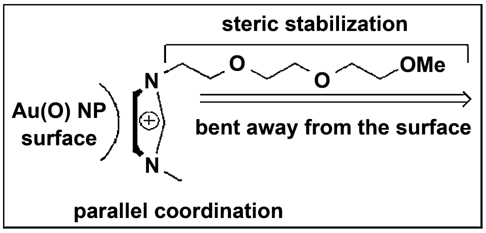

Figure 2. Imidazolium cation coordination and stabilization.

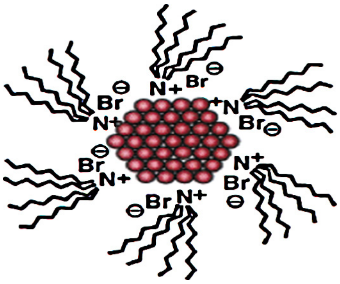

Figure 3. Proposed schematic for a gold nanoparticle stabilized by TOABr.

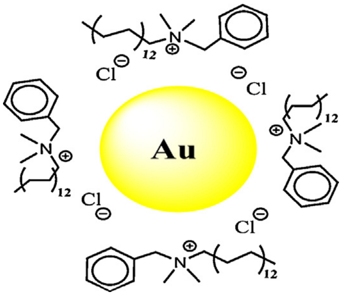

Figure 4. Proposed schematic for a gold nanoparticle stabilized by Bac-14.

oxidation reactions. There have been numerous studies demonstrating the promise of Au(0) as a catalyst, whether in varying NP size, one-dimensional sheet form or simply as gold powder [13–17].

2. Experimental

2.1. Materials and methods

Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4{\cdot}3H_2O$) was purchased from Alfa Aesar. Benzyldimethyltetradecylammonium chloride (Bac-14) was purchased from TCI. Sodium borohydride was purchased from Sigma. All chemicals were purchased and used without further treatment. All reagents used were spectroscopic grade or better. Deionized water was used in all syntheses and was obtained from a Millipore Milli-Q, with resistivity of 18.2 MΩ cm at 25 °C.

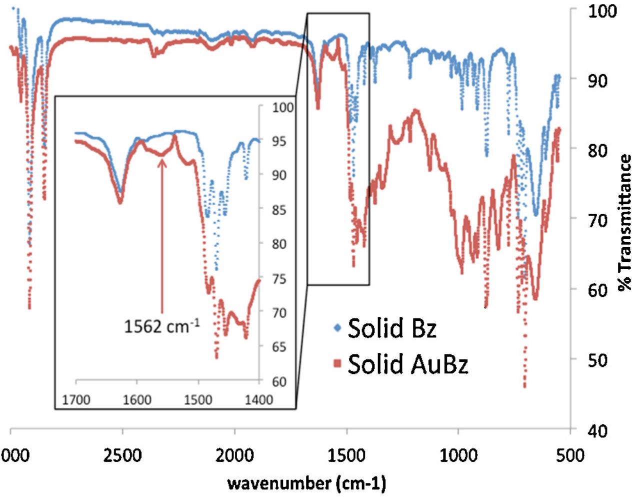

Figure 5. FT-IR spectra of Bac-14 and AuNP.

2.2. Synthesis

The AuNPs were synthesized as follows: a stock solution of 0.01 M $HAuCl_4{\cdot}3H_2O$ (30 mL) was placed under reflux with mild heat for several minutes with stirring. Then 80 mL of concentrated Bac-14 (2.94 g) in water was added and stirred vigorously. Sodium borohydride (0.38 g, 10 mmol) was then added to 25 mL of water and combined with the reaction mixture. The mixture was allowed to stir under mild heat for 2–3 h.

2.3. Characterization

The NPs were characterized (Figures S1 to S5) by UV–vis, scanning and transmission electron microscopy (S/TEM), energy-dispersive X-ray spectroscopy, IR, and ^1H and ^{13}C NMR spectroscopy in D_2O. The reduction of Au(III) to Au(0) was assumed when a solution of 25 mL deionized water (Milli-Q 18.2 MΩ·cm) and $NaBH_4$ (0.38 g, 1 mol eq.) was added drop wise. Chemical reduction was observed in the appearance of a surface plasmon band, λ_{max} = 522 nm, using UV-vis spectroscopy.

3. Results and discussion

The ^1H and ^{13}C NMR demonstrated that Bac-14 remains virtually chemically identical when stabilizing the AuNPs (Figures S9–S12); therefore, there is no NMR-detectable covalent interaction between Bac-14 and the Au(0).

The IR spectra, however, showed some significant differences between pure Bac-14 and the dried stabilized AuNPs. The most significant change outside the fingerprint region was a new peak at 1562 cm^{-1} in the AuNP IR (Figure 5). A computational assessment was performed on a single Bac-14 molecule stabilizing one Au(0) and one Cl^- atom using the density functional theory (DFT) UB3LYP method and the LANL2DZ basis set [18–20]. This basis set is widely used in studying compounds and clusters containing heavy elements and is routinely used in the framework of DFT calculations [21]. The optimized structure depicted in Figure 6 yielded a vibration (1547 cm^{-1}) in good correspondence with the new signal in the IR spectrum.

The changes seen in the fingerprint region have been attributed to the lengthy alkyl chain gaining more vibrational freedom while in a stabilizing conformation. If Bac-14 IL molecules are surrounding the AuNP in a radial arrangement similar to a micelle (with the alkyl tails pointing outwards as seen in Figure 3), then they have