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Stabilized and size-tunable gold nanoparticles formed in a quaternary ammonium-based room-temperature ionic liquid under γ -irradiation

Shimou Chen^{1,2}, Yaodong Liu¹ and Guozhong Wu^{1,3}

¹ Shanghai Institute of Applied Physics, Chinese Academy of Sciences, PO Box 800-204, Shanghai 201800, People's Republic of China

² Graduate School of the Chinese Academy of Sciences, Beijing 10039, People's Republic of China

E-mail: wuguozhong@sinap.ac.cn

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Abstract

Colloidal gold nanoparticles were synthesized in a quaternary ammonium-based room-temperature ionic liquid (QAIL) by γ -radiation for the first time. Transmission electron microscopy, x-ray diffraction and optical techniques were used to characterize the colloidal nanoparticles. By changing the experimental conditions, the size of the gold nanoparticles can be varied between 10 and 50 nm. It was found that gold nanoparticles coated by QAIL are very stable in dispersion.

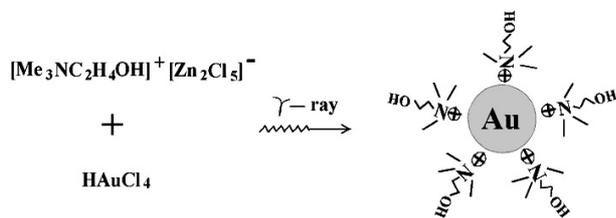
1. Introduction

The synthesis and processing of nanoparticles consisting of metal cores and stabilizer shells promise interesting technological applications in that they can be repeatedly isolated from and redissolved in common solvents without irreversible aggregation or decomposition [1, 2]. Surfactants, polymers, micelles, and ligands have been widely used as stabilizers in order to generate certain characteristic properties of nanoparticles [3]. On the other hand, the control of nanoparticle size and a better understanding of their chemical behaviour have attracted considerable interest because of their size- and shape-dependent physicochemical properties [3, 4].

Room-temperature ionic liquids (RTILs) have received growing attention for various applications such as catalysis, electrochemistry, extraction and supporting of nanoparticles [5, 6]. In particular, since RTILs are liquids that entirely consist of ions, the solvation and stabilization of metal ionic species in RTILs should be much more favoured than in conventional solvents [7]. Many studies have been reported on the synthesis of metal nanoparticles using ionic liquids as the media and stabilizers [7–13]. The unique

structure and properties of RTILs present a new strategy for the preparation of nanoparticles in a controlled manner. On the other hand, radiation has been extensively used to prepare nanomaterials, and the radiolysis technique has proven to be a convenient method of preparing size-controllable metal nanoparticles [14–16], because hydrated electrons (e_{aq}^-) generated from water radiolysis have very strong reduction capability. However, it has been suggested that metal atoms formed by irradiation or any other method tend to coalesce into oligomers, which themselves progressively grow into larger clusters and eventually into precipitates [17, 18]. A cluster stabilizer should be introduced during the formation of nanoparticles in water or common organic solvents, whereas in RTILs this becomes unnecessary as some moieties of RTILs can effectively act as a stabilizer. A combination of the use of radiation and an RTIL may have advantages in preparing metal nanoparticles over the use of either radiation or an RTIL. To our knowledge, there is no report yet on the synthesis of metal nanoparticles in RTILs by applying the radiation method. Pulse radiolysis work has demonstrated the formation of solvated electrons in some alkylimidazolium cation-based RTILs upon irradiation [19, 20]. It is believed that this type of solvated electron, acting like the hydrated electrons in water,

³ Author to whom any correspondence should be addressed.



Scheme 1. Stabilized gold nanoparticles formed in RTILs under γ -irradiation.

Table 1. Conditions for the preparation of gold nanoparticles.

Sample no.	HAuCl ₄ ^a concentration (mmol l ⁻¹)	QAIL content (v/v)	2-PrOH content (v/v)	H ₂ O content (v/v)
1	0.1	99%	—	—
2	0.1	94%	5%	—
3	0.1	50%	—	49%
4	0.1	—	5%	94%

^a 0.1 ml aqueous HAuCl₄ (0.01 mol l⁻¹) was added to 9.9 ml solution.

can reduce transient metal ions to atoms that further aggregate into nanoparticles.

Here we present a simple way of preparing gold nanoparticles under γ -radiation in a quaternary ammonium-based ionic liquid (QAIL) [Me₃NC₂H₄OH]⁺ [Zn₂Cl₅]⁻. Gold was selected since it is relatively easy to be reduced and the preparation of gold nanoparticles has been studied widely, due to its potential use in different fields. By combining the advantages of both the RTIL and the radiation technique we have developed a new approach to prepare stabilized gold nanoparticles of different sizes. In the course of irradiation, HAuCl₄ is reduced to gold atoms by the solvated electrons generated from γ -radiolysis of the QAIL, and nitrogen moieties of the QAIL act as a stabilizer by binding to the surface of gold nanoparticles (scheme 1). We also outline how the size of the colloidal particles can be conveniently varied in a controlled manner.

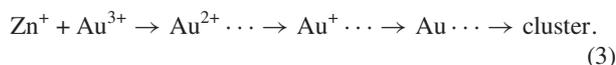
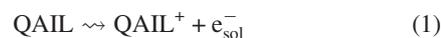
2. Experimental section

All chemicals used were of analytical grade and were purchased from Acros Corp. The QAIL was prepared by mixing choline chloride and ZnCl₂ in a molar ratio of 1:2, according to the literature method [21]. Prior to use, the QAIL was kept in vacuum at 100° overnight to remove moisture and volatile impurities. As described previously, this ionic liquid is relatively stable under γ -radiation up to a dose of 100 kGy [22]. Aqueous hydrogen tetrachloroaurate (HAuCl₄, 0.01 mol l⁻¹) was added to the ionic liquid and its concentration was fixed at 0.1 mmol l⁻¹ for each reaction mixture. To tune the size of the gold nanoparticles, different amounts of QAIL, H₂O and 2-propanol (2-PrOH) were added (table 1). The mixture was vigorously stirred to form a transparent solution and then sealed in a glass ampoule after N₂ bubbling. The γ -irradiation was carried out in the ⁶⁰Co source of Shanghai Institute of Applied Physics; all the samples were exposed at room temperature for 8.5 h to a total dose of 10.0 kGy (dose rate: 19.6 Gy min⁻¹).

Transmission electron microscopy (TEM) observations were performed with a Philips EM400 microscope at an accelerating voltage of 80 kV. The samples for TEM observation were prepared by depositing a drop of the colloid solution on carbon-coated copper grids, then allowing them to dry in a desiccator. The x-ray diffraction (XRD) measurements were carried out in the diffraction mode on a X'Pert Pro diffractometer operated at a voltage of 40 kV and a current of 40 mA with Cu K α radiation. Particle size distributions were measured on a NANOPHOX (Sympatec GmbH) particle analyser based on photon cross correlation spectroscopy (PCCS) [23]. UV-vis absorption spectra were recorded by scanning from 300 to 800 nm at room temperature. Each colloidal solution was diluted (1:5) with distilled water for PCCS and absorption measurements.

3. Result and discussion

For the synthesis of metal nanoparticles by radiation, the most accepted mechanism involves a two-step process, i.e. nucleation and successive growth of the particles. In the first step, a part of the metal ions in solution is reduced by a suitable reducing agent. In the second stage the atoms produced act as nucleation centres and catalyse the reduction of the remaining metal ions present in the bulk solution; this stage has an autocatalytic nature. Gachard and co-workers have investigated the reduction of AuCl₄⁻ in water under γ -irradiation, and they made a careful examination of the mechanism of gold nanoparticle formation [24]. Based on Gachard's conclusion, the final size of the gold clusters depends markedly on the conditions of the reduction of the ionic precursors and even on the strongly reducing radiolytic radicals; the low valency Au^I ions are somewhat protected by the more concentrated Au^{III} ions from reduction unless a cluster or 2-propanol catalyses their disproportionation. However, since the QAIL is a complex organized by an organic cation and an inorganic anion, the radiation-induced transient species are different from those in water. The possible reactions responsible for the reduction of Au^{III} in the QAIL are proposed as follows:



Since the anion of the QAIL is Zn₂Cl₅⁻, Zn²⁺ can be reduced by a solvated electron to form Zn⁺, and we speculate that the main reducing species in the QAIL is Zn⁺. In water, however, the main reducing species is a hydrated electron, e_{aq}⁻. When 2-propanol is present, the hydroxyl radical (oxidizing species) is transformed into a reducing radical via H abstraction.

The dispersion and the particle size of gold nanoparticles formed in the QAIL were characterized by TEM, as shown in figure 1. The images indicate well-isolated nanoparticles without aggregates for samples 1–3 as they are generated in the presence of the QAIL (figures 1(a)–(c)). However, the particles synthesized in water were joined together, forming short rods, and aggregated into chains (figure 1(d)). It is

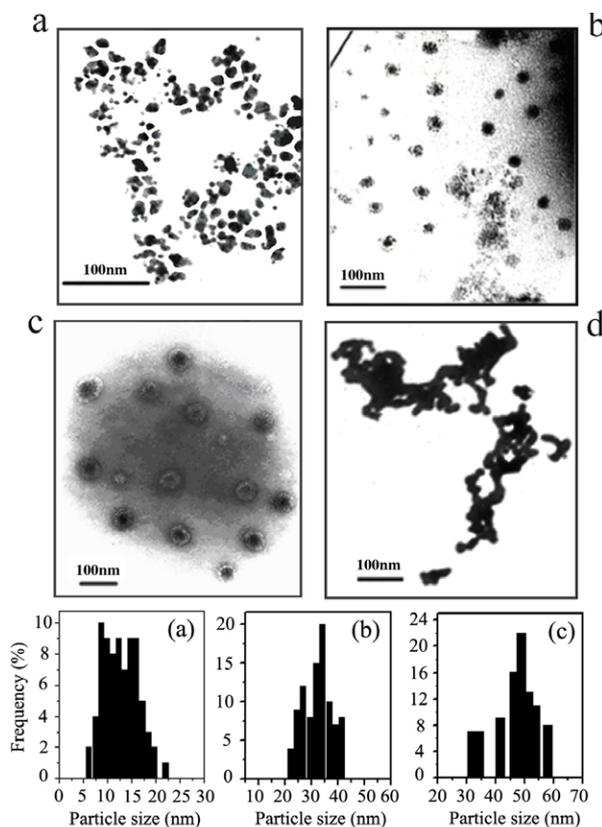


Figure 1. TEM images of gold nanoparticles formed in (a) QAIL (sample 1); (b) QAIL + 2-PrOH (sample 2); (c) QAIL + H₂O (sample 3); (d) H₂O (sample 4).

suggested that the QAIL bound to the nanoparticle surface prevents cluster coalescence. Owing to the presence of ZnCl₂ in the QAIL, the background of the TEM image becomes somewhat obscure as compared to that of the sample in water. The particle size histograms are also plotted in figure 1. Analysis of the TEM data indicates that the average diameters of gold nanoparticles for samples 1–3 are 12, 35, and 50 nm, respectively. However, one can see in figure 1(b) some small aggregates of smaller particles instead of isolated nanoparticles for sample 2, as was further proved by x-ray diffraction and described later in the text. The increase of the mean diameter of nanoparticles with the addition of 2-PrOH or water means that interactions between the gold clusters, solvent and ionic liquid are complicated and significantly affect the particle size. It should be mentioned that the gold nanoparticles prepared from imidazolium cation-based RTILs at relatively higher temperature usually have smaller size (< 10 nm), according to previous studies [7, 11]. This difference may be mainly due to the high viscosity of the QAIL. In this work the synthesis of gold nanoparticles was carried out at 25 °C and the viscosity of the QAIL measured at this temperature is about 10 Pa s at a shear rate of 10 s⁻¹, higher than that of water by four orders of magnitude.

In order to confirm the crystal phase and calculate the mean size of the gold nanoparticles, XRD analysis was performed. Figure 2 shows the XRD patterns of the nanoparticles obtained by different experimental conditions. The diffraction features

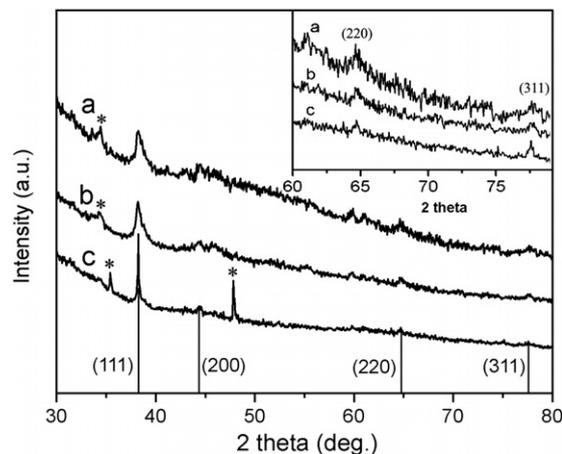


Figure 2. X-ray diffraction patterns of (a) sample 1, (b) sample 2, and (c) sample 3. (* The peaks may be due to the zinc components of the QAIL.)

appearing at $2\theta = 38.2^\circ, 44.5^\circ, 64.6^\circ,$ and 77.6° correspond to the (111), (200), (220), and (311) planes of the standard face-centred cubic phase of Au, respectively. As expected, the XRD peaks of the nanocrystallites were considerably broadened because of the finite size of the crystallites. The size of the gold particles was further estimated from the peak width of the (111) Bragg reflection using the Debye–Scherrer formula [25]. The estimated average diameters of the gold nanoparticles for samples 1–3 are 10.6, 16.8, and 42.7 nm, respectively. The sizes of samples 1 and 3 are close to those of the TEM observation. However, the average size of sample 2 analysed by XRD is about half of that observed by TEM, indicating that the spherical aggregates may consist of smaller particles, as confirmed by TEM (figure 1(b)).

It is well known that, due to the high density charge on the surface of gold nanoparticle, organic molecules containing functional groups such as amines and thiols can cap the nanoparticles easily [3]. Kamat and co-workers have studied the surface binding properties of tetraoctylammonium bromide-capped gold nanoparticles [26]. Pradeep and co-workers demonstrated that the nitrogen atom of the piperazine group could bind strongly to gold nanoparticles, as confirmed by voltammetric and spectroscopic studies [27]. It has also been suggested that the combined intrinsic high charge plus the steric bulk of ionic liquid can create an electrostatic and steric colloid-type stabilization of transition-metal nanoparticles, similar to the proposed model for the stabilization of nanoclusters by polyoxo-anions or by tetraalkylammonium salts [9]. Therefore, the strong electrostatic attraction of quaternary ammonium to gold can stabilize the gold nanoparticles during the formation process. Suspensions (diluted by water or ethanol) of these QAIL-coated gold nanoparticles are quite stable and can be stored at room temperature for more than two months without obvious deterioration, and little change was observed in the UV–vis absorption of the upper layer of the aqueous solution for samples 1–3 after a centrifugation treatment (at 4000 rpm for 20 min). The high stability of colloidal gold nanoparticles in an RTIL makes them useful in applications such as catalysts and biosensors.

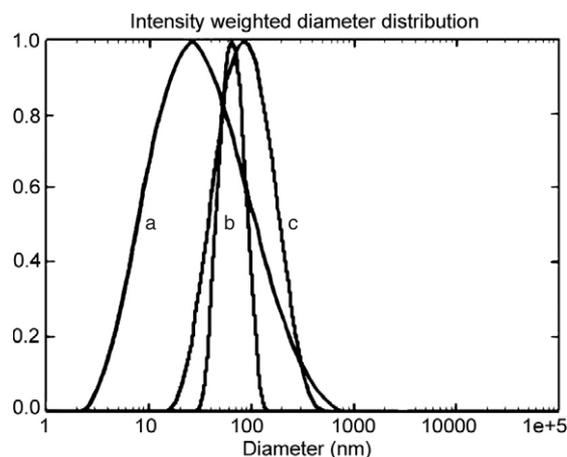


Figure 3. Intensity weighted average diameter distributions of (a) sample 1, (b) sample 2 and (c) sample 3.

The particle size and intensity weighted distribution of Au colloid were further measured by PCCS (figure 3). The average hydrodynamic diameters of samples 1, 2, and 3 were measured to be 34, 65, and 85 nm, respectively, higher than the values obtained by TEM and XRD. This implies that the QAIL was coated or adsorbed on the surface of gold nanoparticles, since the stabilized QAIL shell cannot be detected in the solid state by TEM but is taken as a part of nanoparticle in solution when recorded by PCCS.

It has been suggested that the colour of colloidal gold depends both on the size and the shape of clusters, as well as the surrounding medium [28, 29]. In general, a colloidal solution of gold nanoparticles with diameters of 5–20 nm exhibits a red colour, because such nanoparticles have an optical absorption peak around 520 nm caused by surface plasmon resonance. Aggregation of the nanoparticles shifts the peak toward longer wavelength and changes the colour of the colloidal solution to purple [30]. In the present study, we also observed the colour change of colloid gold from reddish orange to purple to bluish purple as a result of the increase in particle size (figure 4(a)). This shift may be attributed to the difference in the surface plasmon band (SPB). It should be noted that the gold nanoparticles prepared in pure water (figure 4(a)–(d)) precipitate in three days whereas the particles prepared in the presence of the QAIL are stable even after two months of storage. The UV–vis absorption spectra for the colloidal solutions are shown in figure 4(b). The positions of the SPB maxima for samples 1–4 are 525, 541, 546, 562 nm, respectively. The spectral shift agrees well with the predictions by Mie theory [31]. The SPB maximum and bandwidth are also influenced by the particle shape, medium dielectric constant, and chemical interactions with the surrounding ligands [28, 32, 33], which are all responsible for the red shift observed in the present study. In addition, sample 4 shows a weak band at 700–780 nm, which is usually taken as an indication of either particle elongation or aggregation [29], also as confirmed by TEM image (figure 1(d)).

4. Conclusion

We demonstrated for the first time a simple way of synthesizing gold nanoparticles in an RTIL by the radiation technique.

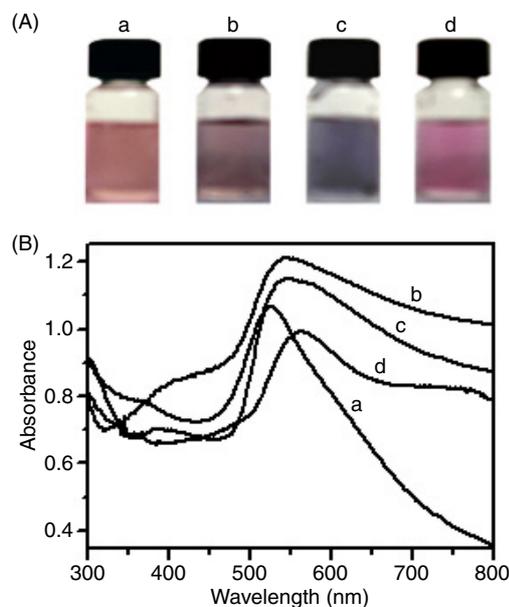


Figure 4. (A) Photographs of the gold nanoparticles obtained from the solutions of (a) sample 1, (b) sample 2, (c) sample 3 and (d) sample 4. (B) UV–vis absorption spectra corresponding to (a)–(d) in photographs.

(This figure is in colour only in the electronic version)

The QAIL surrounding the nanoparticle surface can act as an effective stabilizer of gold nanoparticles, and the nanoparticle size and uniformity are affected by the interactions between the QAIL and clusters during the formation of the nanoparticles. The medium composition can also be used as selective gates to control the size of the stabilized particles. Considering the cost advantages of the radiation technique and the unique properties of RTILs, there is promise for a convenient strategy for the controlled preparation of metal nanoparticles using this combinatorial approach.

Acknowledgments

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