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2011 Nanotechnology 22 025602

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# The controlled synthesis of stable gold nanoparticles in quaternary ammonium ionic liquids by simple heating

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Received 10 October 2010, in final form 17 November 2010

Published 7 December 2010

Online at [stacks.iop.org/Nano/22/025602](http://stacks.iop.org/Nano/22/025602)

## Abstract

Stable gold nanoparticle (AuNP) colloids were synthesized in a class of quaternary ammonium-based room-temperature ionic liquids (QAILs),  $[\text{Me}_3\text{NC}_2\text{H}_4\text{OH}]^+[\text{Zn}_n\text{Cl}_{2n+1}]^-$  ( $n = 1$  or  $2$ ), by heating in air at 135–145 °C. The QAIL was employed as a solvent, a reducing agent, and as a stabilizer. The size of the QAIL–AuNPs can be varied between 20 and 40 nm by changing the reaction temperature. A symproportionation reaction was employed to further decrease the size of the AuNPs by the addition of  $\text{Au}^{3+}$  ions. The surface covering of QAIL on the AuNPs had a significant impact on their surface plasmon resonance (SPR), which was red-shifted. The AuNPs synthesized by this simple and environmentally friendly reaction can be realized in several minutes and also exhibit high stability and good reproducibility, providing a new facile approach to metal nanoparticle preparation.

 Online supplementary data available from [stacks.iop.org/Nano/22/025602/mmedia](http://stacks.iop.org/Nano/22/025602/mmedia)

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Gold nanoparticles (AuNPs), also known as gold colloids, are relatively stable metal nanoparticles, and those ranging from 2.0 to 50.0 nm in diameter have attracted a great deal of attention due to their fascinating and desirable physicochemical and optoelectronic characteristics, including size-related electronic, magnetic and optical properties [1]. Numerous applications of AuNPs have been explored in chemical [2–4], optical [5–7], and biological research [8, 9]. Assorted conventional methods for the synthesis of AuNP colloidal solutions are known and have been investigated for a long time, including the reduction of  $\text{HAuCl}_4$  by citrate or  $\text{NaBH}_4$ , the seeding-growth method, and physical

methods (photochemistry, sonochemistry, radiolysis, thermolysis, etc) [10]. Since AuNPs grow into progressively larger clusters and eventually into precipitates [11, 12], this tendency can be hindered with cluster stabilizers. Up to now, several stabilizers and preparation methods have been reported for AuNPs, many of which are based on the reduction of Au(III) salts. For example, thermally stable and air stable AuNPs with a surface coating of thiol were prepared from the two-phase (water–toluene) reduction of  $\text{AuCl}_4^-$  by sodium borohydride in the presence of an alkanethiol [13]. Brust *et al* also developed a single-phase (methanol) reaction system for the synthesis of stable functionalized gold nanoparticles by organic thiol molecules [14]. Citrates have also been used as stabilizers in standard AuNP synthesis protocols for decades [15, 16], and even now this method is frequently used and modified [17]. Phosphine and amine-stabilized

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AuNPs were shown to be stable, while stabilizers, such as 4-(dimethylamino) pyridine (DMAP) and tetraoctylammonium bromide (TOAB), may be used in organic or aqueous solution [6]. Supramolecular assemblies (such as microemulsions, liquid crystals, vesicles, and so on) afford more unique conditions to control the composition and morphology of the AuNPs by radiolysis [18]. Macromolecules and polymers have also been applied to the synthesis of AuNPs, including polyethylene glycol [19], polyethylenimine [20, 21], poly[1-methyl-3-(4-vinylbenzyl)imidazolium chloride] [22], ascorbic acid [23], amino acid lysine [24] and plant tannin [25].

Room-temperature ionic liquids (RTILs) are excellent solvents. They can be considered as salts with a low melting temperature, good dissolution ability, high thermal stability and very low vapour pressure. In recent years, there have been a number of reports concerning the preparation of AuNPs using ionic liquids. Thiol-functionalized ionic liquids were described as capping agents for AuNPs in the one-phase synthesis process where the AuNPs' size and distribution were dependent on the number and position of thiol groups in the ionic liquid [26, 27]. Ionic liquids with cationic or anionic special functional groups act not only as reducing agents [28–30], but also as reaction media for the synthesis of AuNPs and polymer–AuNP composites [31, 32]. Nevertheless, either  $\text{NaBH}_4$  or citrate was used as a reducing agent or complex structured ionic liquids were employed.

Herein, we describe the use of a class of quaternary ammonium-based room-temperature ionic liquids (QAILs) as solvents, reducing agents and stabilizers to synthesize AuNPs by the solvent-thermal reduction method. We have previously used one of these QAILs in the synthesis of AuNPs by the radiation method. Their properties suggest that they may be used as ideal solvents and capping agents for the preparation of stable AuNPs [33]. In this study, AuNP colloids with good morphology and dispersion can be easily obtained by heating  $\text{Au}^{3+}$  imbued QAILs ( $[\text{Me}_3\text{NC}_2\text{H}_4\text{OH}]^+[\text{Zn}_n\text{Cl}_{2n+1}]^-$ ,  $n = 1, 2$ ), without any other additives. AuNP colloids were prepared in glass ampoules in air and at atmospheric pressure. The size of the colloidal AuNPs can be conveniently varied in a controlled manner. This process can be considered as an environmentally sound method for the synthesis of gold nanoparticles.

## 2. Experimental details

All chemicals used were of analytical grade and were purchased from SCRC (Shanghai, China) and used without further purification. The water was freshly deionized and distilled before use. The QAILs were prepared by mixing choline chloride and  $\text{ZnCl}_2$  in a molar ratio of 1:1 (QAIL-I) and 1:2 (QAIL-II), which have similar physical and chemical properties. Prior to use, the QAILs were kept under vacuum at  $90^\circ\text{C}$  overnight to remove moisture and volatile impurities. The liquids are at least as thermally stable as  $\text{AlCl}_3$ -based liquids, and can be heated to at least  $190^\circ\text{C}$  [34].

$\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$  was dissolved in deionized water to obtain a  $10.0 \text{ mmol l}^{-1} \text{ Au}^{3+}$  solution. Then  $0.2 \text{ ml}$  of  $\text{Au}^{3+}$  solution was added drop-wise into  $10.0 \text{ ml}$  of QAILs at different

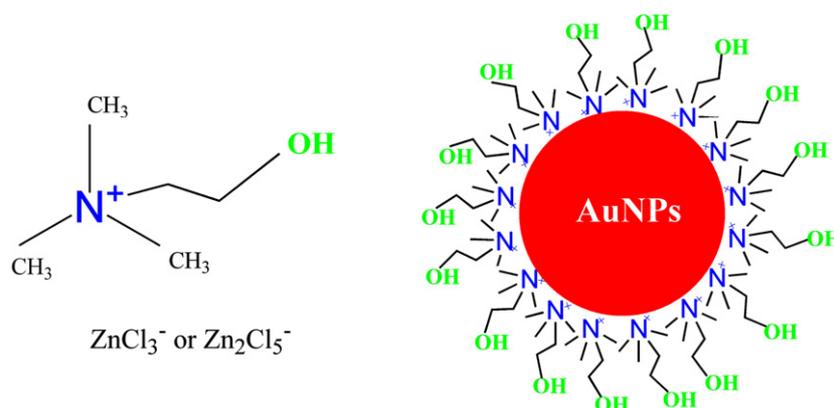
temperatures to prepare a series of QAIL stabilized AuNP colloids with the  $\text{Au}^{3+}$  concentration fixed at  $0.2 \text{ mmol l}^{-1}$ . Next, another  $0.2 \text{ ml}$  of  $\text{Au}^{3+}$  was immediately added drop-wise into these freshly prepared AuNP colloids while they were maintained at the same temperature. The QAILs and AuNP colloids were vigorously stirred in a glass beaker and heated by an oil-bath heating reactor for  $15 \text{ min}$  for each specimen. The QAIL–AuNP colloid specimens were separated and absterged with methanol, and the AuNPs were centrifuged to methanol with a dilution ratio of 1:4 for further measurements.

Transmission electron microscope (TEM) measurements on the AuNP colloids were carried out with a JEOL JEM-200cx operating at an accelerating voltage of  $200 \text{ kV}$  and a resolution of  $3 \text{ \AA}$ . The specimens used for the TEM measurements were prepared by depositing a drop of the colloid solution on carbon-coated copper grids, then allowing them to dry in ambient conditions. Wide-angle x-ray diffraction (XRD) patterns of the specimens were recorded by a Rigaku x-ray diffractometer (D\max-2550) at a voltage of  $40 \text{ kV}$  with  $\text{Cu K}\alpha$  radiation and the particle size was calculated from a  $2\theta$  range of  $10^\circ$ – $90^\circ$  at a scanning rate of  $8^\circ \text{ min}^{-1}$ . UV–Vis absorption spectra were obtained from  $300$  to  $900 \text{ nm}$  at room temperature with a UV-3010 spectrophotometer.

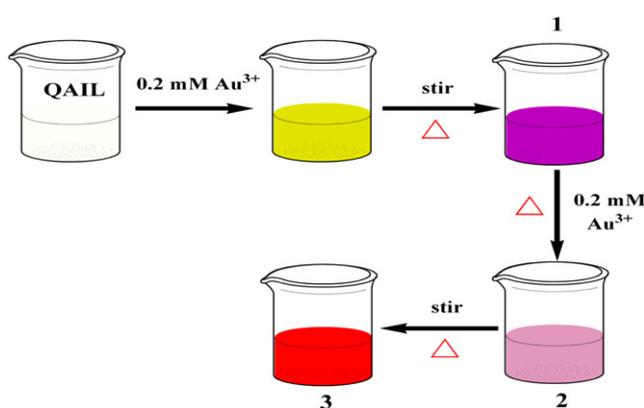
## 3. Results and discussion

The most accepted mechanism of metal nanoparticle synthesis involves a two-step process, i.e., nucleation and successive growth of the particles. Typically, some of the metal ions are reduced to zero valency metal nanoparticles by reducing agents and the metal cores are gradually accumulated by the newly reduced atoms, while cluster stabilizers occasionally participate in the process. The QAIL is organized by an organic cation and an inorganic anion (scheme 1). The organic cation consists of three methyl groups and one hydroxyethyl group. Reetz and co-workers have synthesized a series of palladium clusters stabilized by tetraalkylammonium salts [35], and the surface binding properties of tetraoctylammonium bromide-capped gold nanoparticles have been studied [36], just as the schematic representation exhibited in scheme 1 (anions are not displayed). 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 [37]. Therefore, the quaternary ammonium cation is able to combine with the surface of the gold nanoparticles to act as a stabilizer by strong electrostatic attraction and adsorbs on (111) faces for preventing the crystal growth [38], while the hydroxyl group can also be oxidized to the corresponding aldehyde and carboxyl by oxides [39], suggesting that QAIL can be used as a feasible reducing agent. On the other hand, as it possesses a high oxidation–reduction potential [29], the  $\text{Au}^{3+}$  ions may act as an oxidant when they come into contact with a QAIL under certain conditions, such as high temperature. Hence, we believe that  $\text{Au}^{3+}$  ions may be reduced to gold atoms in QAIL to form size-controllable AuNPs.

Figure 1 shows the TEM images and the particle size distribution of typical specimens of AuNPs prepared



**Scheme 1.** Molecular structures of QAILs and stabilized gold nanoparticles.



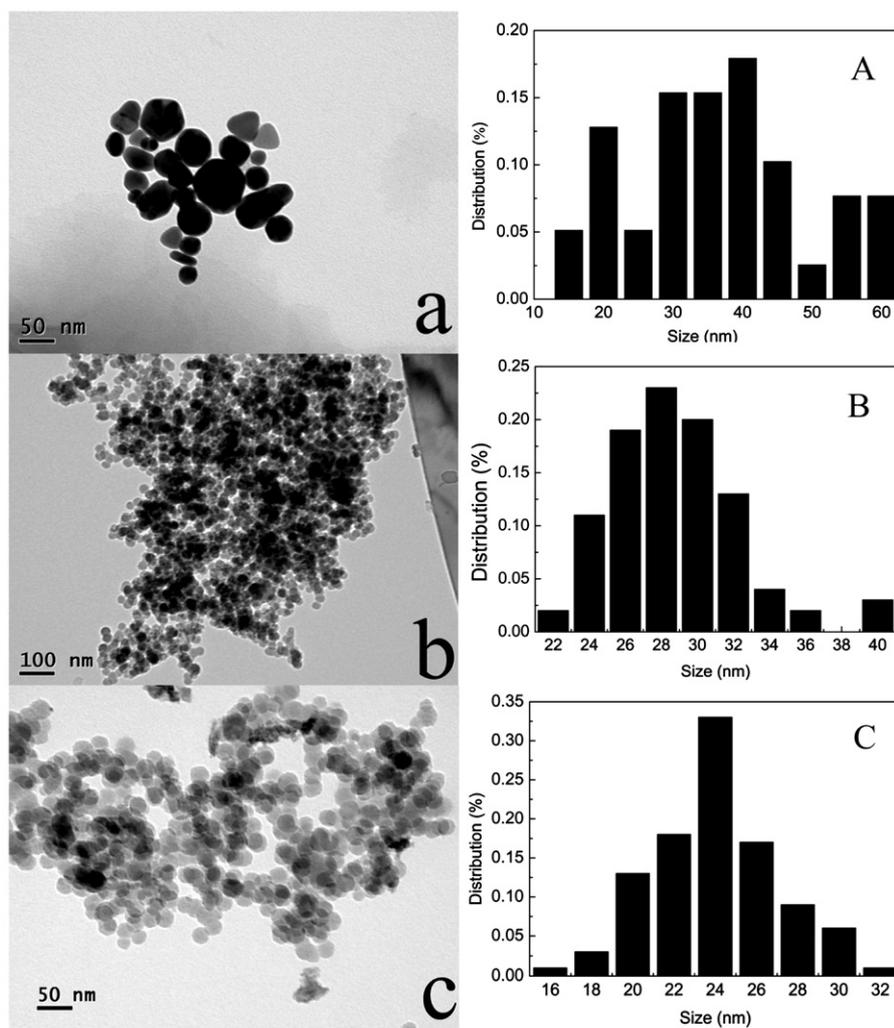
**Scheme 2.** Synthesis chart of gold nanoparticles prepared by the solvent-thermal method in QAILs.

at different temperatures in QAIL-II, following step 1 in scheme 2. The AuNPs obtained at 135 °C produced a more inhomogeneous size distribution than the other samples (figure 1(a)), while the 140 and 145 °C specimens displayed nearly the same length scale and good size uniformity without aggregates (figures 1(b) and (c)). Particle size distribution histograms indicate that the mean diameters of the AuNPs are  $35.2 \pm 12.2$ ,  $29.6 \pm 3.8$  and  $23.9 \pm 3.0$  nm, corresponding to temperatures of 135, 140 and 145 °C, respectively. The particle size and distribution of AuNPs in QAIL-II is highly relevant to the reaction temperature. Smaller and more even granular AuNPs are obtained at comparatively higher temperatures over a suitable range. However, according to previous studies [27, 28], the AuNPs prepared from imidazolium cation-based RTILs are usually smaller ( $<10$  nm). We speculate that there are two reasons for the larger AuNPs in our work, high viscosity and high temperature. The viscosity of the QAIL-II at 50 °C measured in our work is about 12.6 Pa s in a shear rate range of 1–25.1  $\text{s}^{-1}$ , which is much higher than that of water by four orders of magnitude [40]. Such high viscosity might baffle the distribution of the AuNPs. On the other hand, all of the reaction temperatures are above 100 °C, and at such relatively high temperatures, the newly created

particles synthesized in the QAILs easily aggregate into large clusters [41].

Figure 2 displays the XRD patterns of the same batch of AuNPs samples measured by TEM (as shown in figure 1). The peaks appearing at  $2\theta = 38.5^\circ$ ,  $44.7^\circ$ ,  $64.9^\circ$  and  $78.0^\circ$  are due to diffraction features from the (111), (200), (220) and (311) planes, respectively, of the standard face-centred cubic phase of gold. The XRD peaks of the nanocrystallites are considerably broader because of the finite size of the crystallites. The size of the AuNPs was further estimated from the peak width of the (111) Bragg reflection using the Debye–Scherrer formula. The estimated average diameters of the AuNPs for specimens *a*, *b*, and *c* are 37.0, 29.8 and 21.8 nm, respectively. These values are very similar to those measured by TEM.

The QAIL-II modified AuNPs synthesized at various temperatures were further investigated in the UV–Vis absorption spectrum through optical changes of the surface plasmon resonance (SPR), which result in a strong absorption of electromagnetic irradiation at the corresponding wavelength [42]. This wavelength depends on the size, shape and composition [43] and the refractive index of the surrounding medium [44]. In general, AuNPs with mean diameters of 22 and 48 nm often show an intense SPR band around 521 nm and 533 nm, respectively [45]. However, as shown in figure 3, AuNPs obtained at 135, 140 and 145 °C have SPR peaks at 574, 562 and 552 nm, respectively. Corresponding to the change tendency of AuNPs' average diameters, the spectral shift agrees well with the predictions by Mie theory [46]. These results demonstrate an obvious red-shift of the SPR, which is likely due to the strong electrostatic interaction of the QAILs and the AuNPs, or the refractive index change of the medium by adsorbed QAILs releasing from the surface of AuNPs [47]. Furthermore, the superfluous or residual QAIL molecules around AuNPs in the methanol probably stick to the nanoparticles and lead to agglomeration [27]. To verify this mechanism, we investigated the UV–Vis spectra of AuNPs obtained from different degrees of methanol rinsing. We observed that the quantity of QAILs encapsulating the AuNPs was decreased with an increase in rinse time. Figure 4 shows a series of UV–Vis spectra of one specific specimen of AuNPs

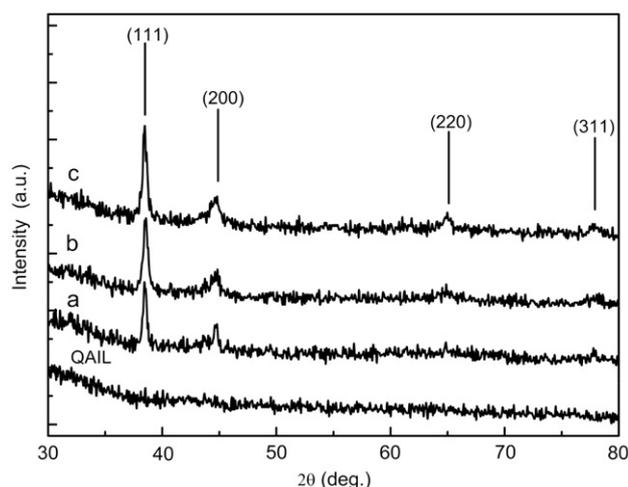


**Figure 1.** TEM images and size distributions of the QAIL-II stabilized Au nanoparticles. Reaction temperature: (a) and (A) 135 °C; (b) and (B) 140 °C; (c) and (C) 145 °C. The corresponding scale bars are 50, 100 and 50 nm, respectively.

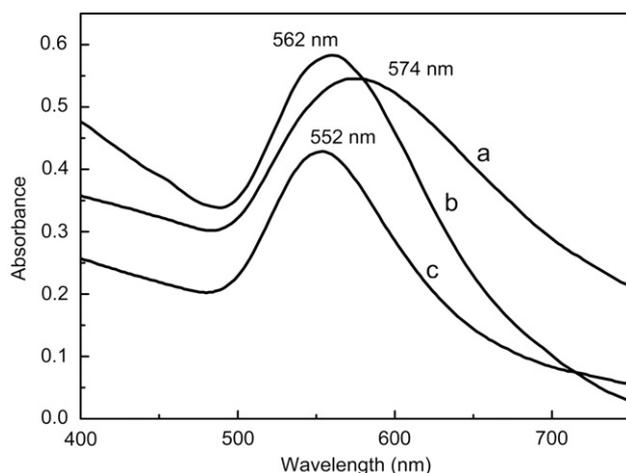
(synthesized in QAIL-I at 140 °C) undergoing a gradual rinse treatment. As the rinse times increases from 2 to 8, the maximum absorption peak drastically decreases from 562 to 540 nm. The existence of Zn and Cl elements in EDS and infrared signals in FT-IR spectra confirmed the presence of QAILs on the surface of AuNPs [48], and the rinse effect by methanol is also shown by the latter one (see figures 1 and 2 in the supporting information, available at [stacks.iop.org/Nano/22/025602/mmedia](http://stacks.iop.org/Nano/22/025602/mmedia)). This phenomenon validates the hypothesis of the influence of the AuNPs' surface properties on the UV-Vis absorption spectrum. Additionally, partial removal of the QAIL-stabilizer from the AuNP surface improved the dispersion stability of the nanoparticles in other dispersants. The AuNPs could be synthesized and kept stable in QAILs for more than half a year and the finally rinsed specimens remained unchanged in methanol after more than two weeks, indicating that the QAIL indeed acts as a good stabilizer for the nanoparticles.

We observed another interesting phenomenon when  $\text{Au}^{3+}$  ions at the same reaction temperature were added to the just-

synthesized QAIL-AuNP colloid wherein the colour of the colloid changed immediately from deep pink to colourless and transparent. The colour of the colloid subsequently changed gradually from colourless to dark red in the span of several minutes, as depicted in steps 2 and 3 of scheme 2. Figure 5 shows a picture of the experimental specimens, a typical TEM image and UV-Vis spectra of this fractional preparation process in QAIL-II at 145 °C. Specimens 1–3 (figure 5(A)) show a significant colour change and their corresponding UV absorption spectra further reveal a blue-shift of their SPR (figure 5(B)). Before the addition of  $\text{Au}^{3+}$ ,  $\lambda_{\text{max}}$  of the QAIL-AuNPs colloid was 552 nm. When  $\text{Au}^{3+}$  was injected into the liquid,  $\lambda_{\text{max}}$  immediately shifted to 534 nm and the absorption conspicuously decreased. Clearly, the final dark red AuNPs colloid (specimen 3) exhibits an absorption maximum at 542 nm, indicating a decrease in the average diameter of the AuNPs, as shown in the TEM image of figure 5(C). These AuNPs present an isolated distribution and a decreased average diameter, calculated to be  $16.4 \pm 4.8$  nm from the histogram in figure 5(D), which is much smaller than for specimen

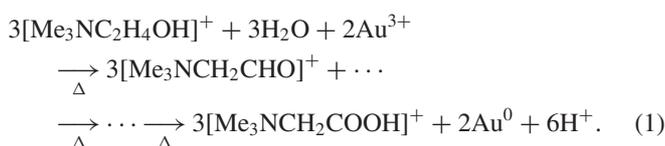


**Figure 2.** X-ray diffraction patterns of the QAIL-II stabilized Au nanoparticles. Reaction temperatures: (a) 135 °C, (b) 140 °C and (c) 145 °C.

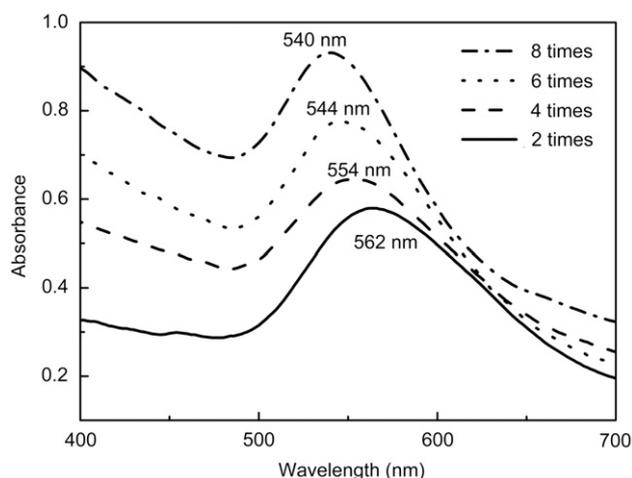


**Figure 3.** UV-Vis absorption spectra of the QAIL-II stabilized Au nanoparticles. Reaction temperatures: (a) 135 °C, (b) 140 °C and (c) 145 °C.

1 ( $23.9 \pm 3.0$  nm in figure 1(C)). These observations may suggest that a different reduction mechanism is responsible for AuNP regeneration in QAILs at high temperature. The possible mechanism for the formation and stabilization of QAIL-AuNPs is given as [25, 29, 49]:

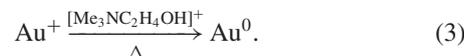
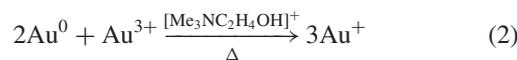


The activity of the hydroxyl group in QAILs is not large enough, so the reaction temperature must be raised to a suitable value. On account of the oxidation–reduction potential of the  $\text{Au}^{3+}$  ion, the reacted adjacent hydroxyl of the QAILs cation is inductively oxidized to the corresponding aldehyde and carboxyl groups. As a result, the  $\text{Au}^{3+}$  ions are reduced to  $\text{Au}^0$  atoms. These newly formed  $\text{Au}^0$  atoms are further



**Figure 4.** UV-Vis absorption spectra of the influence of the methanol rinse to QAIL-I stabilized Au nanoparticles at 140 °C.

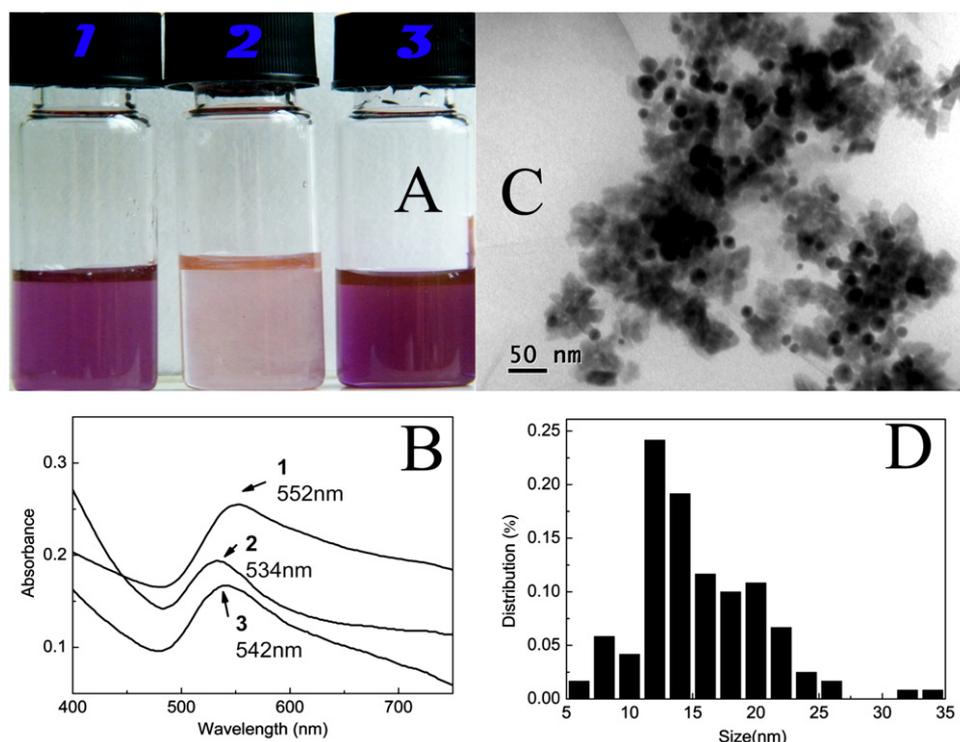
assembled with each other to form AuNPs. To contribute to the stabilization of the AuNPs, the QAILs' cation chelates with AuNPs through its midpoint nitrogen atom by binding to the surface of the AuNPs (scheme 1). However, when the completely grown AuNPs interact with the additional  $\text{Au}^{3+}$  ions at such a high reaction temperature, a symproportionation reaction occurs, when there is a sufficient quantity of  $\text{Au}^{3+}$ , as given by the stoichiometric relationship:



This symproportionation reaction decreases the particle size and leads to a more homogeneous distribution of the AuNPs [50]. Considering the QAILs as the reaction media in this work, the reduced and 're-reduced' AuNPs are well protected against aggregation by the quaternary ammonium cation. This two-step synthesis and size-decrease process leads to the increased interest in gold, and other metal, nanoparticle preparation.

#### 4. Conclusions

In this work, we described a novel, simple and effective means of synthesizing gold nanoparticles in room-temperature ionic liquids under atmospheric conditions using the solvent-thermal method. The QAILs can not only be used as the reducing agent due to the reactivity of its hydroxyl groups, but can also act as the stabilizing agent for its chelating ability. During the entire process, no other additional reagent or treatment is needed except for QAILs and simple calefaction. The nanoparticle size and uniformity are easily controlled by varying the reaction temperature. The interactions between the QAILs and the clusters markedly affect the absorption spectra of the nanoparticles and the particle aggregation. Considering the low cost of both the materials and the synthesis technique, as well as the environmentally friendly properties of RTILs,



**Figure 5.** The effect of additional  $\text{Au}^{3+}$  to QAIL-II stabilized Au nanoparticles at  $145^\circ\text{C}$ . (A) and (B): photographic and UV-Vis absorption spectra of specimens 1–3; (C) and (D): TEM image and size distribution of specimen 3. The scale bar is 50 nm.

metal nanoparticles prepared by this convenient and green approach have a bright future in their potential for practical applications in the fields of nano-materials, ionic liquids, chemical synthesis, functional materials, etc.

### Acknowledgments

The authors gratefully acknowledge the National Natural Science Foundation of China (Grant no. 20973192) for their financial support. The authors also give thanks to the Instrumental Analysis and Research Center of Shanghai University for the help of TEM and XRD tests.

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