Size-controllable Synthesis of Gold Nanoparticles via Carbonylation and Reduction of Hydrochloroauric Acid with CO and H_2O in Ionic Liquids

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The Au nanoparticles (AuNPs) with controllable sizes were successfully prepared through carbonylation and reduction of hydrochloroauric acid with CO and H_2O in $BMImBF_4$ ionic liquid. Transmission electron microscopy (TEM) and UV–vis absorption spectroscopy characterization indicated that the AuNPs with average diameters of 1.7–12.8 nm were obtained with different preparation conditions.

Various nanosized particles have attracted considerable interest as they exhibit particular physicochemical properties. Among the variety of the metal nanoparticles, Au is the most well studied and has been widely applied to various areas, e.g., catalysis,[1] optical materials,[2] and biosensors.[3] Continuous efforts in developing preparation strategy have always been an important requisite for the fabrication of the nanoparticles.

There are many established methods for synthesizing AuNPs, including chemical reduction,[4] photolytical,[5] radiolytic,[6] sonochemical,[7] and thermolytic[8] reaction. A survey of the synthetic methods reported in the previous literatures[9] clearly indicates that nanoparticle properties, such as stability and particle sizes, strongly rely on the experimental methodology and the employed conditions.

Room-temperature ionic liquids (RTILs) have unique physicochemical properties, such as no detectable vapor pressure, relatively high thermal stability, and high ionic conductivity. They have attracted increasing interest recently because of their promising roles as alternative media for reactions and separations.[10]

The previous researches showed that the adsorption of ions and their related counterions on the surface of nanoparticles with an electric double layer around the particles could generate the electrostatic stabilization and prevent particle aggregation,[11] and that the stabilization of metal nanoparticles in RTILs should be much more favored than those in conventional solvents, for example, the gold nanoparticles using tetraoctylammonium bromide (one of IL) as the stabilizing agent have been investigated.[12] A few papers have reported the synthesis and characterization of AuNPs in ionic liquids by reduction of sodium borohydride,[13] but the preparation process inevitably involved boric impurity. On the other hand, the potentialities of AuNPs as functional materials are mainly due to the quantum size effect; the precise control of nanoparticles size has been recognized as one of key research tasks. Therefore, to seek for a more convenient synthesis method in ionic liquid preparing size-controlled AuNPs with less impurity is highly desired.

In this letter, we report the synthesis of AuNPs via carbonylation and reduction of hydrochloroauric acid by CO and H_2O in ionic liquids. By regulating water proportion added in, the reduction rates are controlled and the AuNPs with the average size of 1.7–12.8 nm in diameter are obtained.

Using 2 mL of $BMImBF_4$ (1-butyl-3-methylimidazolium fluoroborate) as both solvent and stabilizer, we investigated the carbonylation and reduction of 20 mg (0.05 mmol) of $HAuCl_4\cdot 4H_2O$ by CO and H_2O. Altering experimental parameters, the results represented that the proper carbonylation conditions by CO were 1 MPa CO pressure and 180 °C for 1 h. Under this reaction conditions, the initial color of $BMImBF_4$ containing $HAuCl_4$ changed from yellow to colorless, suggesting that a new kind of gold complex might be formed. When a small amount of distilled water was added to the liquid mixture, it was found that the color of solution changed from colorless into violet, which indicated the formation of AuNPs. Decreasing the reaction temperature, $HAuCl_4$ could not be completely reduced to colorless compound; and that increasing the reaction temperature and prolonging the reaction time, metallic gold deposited directly. We discovered that the pressure of CO could not have an effect on formation of AuNPs. Under the optimized reaction conditions, nitrogen and hydrogen were also employed for the process and noted that no AuNPs were formed. N_2 is a noncoordinating and nonreducing reagent and does not involve in thermolysis of $HAuCl_4$. H_2 is a reducing agent like CO, but a noncoordinating agent. Also no AuNPs were formed, which confirmed that CO in reaction could serve both as a ligand to form some Au complex and as a reducing agent for facilitating the formation of the AuNPs. Further test proved that the IL also played an important role in the reaction process. Using other high boiling point solvent like dibutyl phthalate (bp 340 °C) under the identical reaction conditions, no AuNPs were obtained. It is possibly attributed to the polar environment of IL to accelerate the formation of Au complex. On the other hand, when the unknown complex was exposed to air for hours, we have not yet observed that any AuNPs were formed by adding water again. Therefore, it is possible that the complex is unstable in the presence of air.

The previous experimental results demonstrated clearly that the size of AuNPs could be controlled by varying the stabilizer/gold ratio (e.g., the trisodiumcitrate to gold ratio).[14] In our synthetic processes, with adjusting the amount of water added to, i.e. varying the IL stabilizer/gold ratio, the size of particles in a certain range could be controllable. We dissolved 20 mg of $HAuCl_4\cdot 4H_2O$ in 2 mL of $BMImBF_4$, which reacted with CO under the optimized reaction conditions. In order to obtain the AuNPs with average diameters of 1.7 ± 0.4 nm, 0.2 mL of water was employed to the system with drastic shaking at room temperature, and in a minute, 5 mL of benzene that dissolved 26 mg (0.12 mmol) of *n*-tetradecylamine was introduced to transferring AuNPs from $BMImBF_4$. Repeating above-mentioned steps and only increasing water amount to 2 mL and 10 mL, respectively (corresponding to decrease the stabilizer/

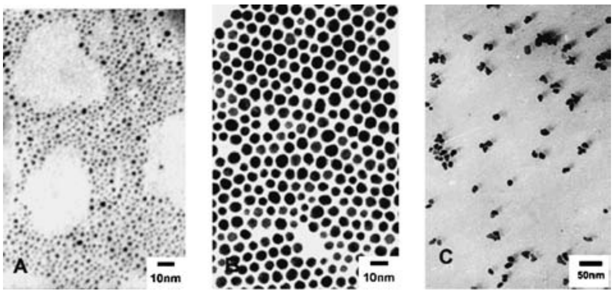

Figure 1. TEM images of AuNPs synthesized in ionic liquids (being empolyed to different amount of water, then transferring AuNPs from IL to benzene containing *n*-tetradecylamine as stabilizer) (A) 0.2 mL; (B) 2 mL; (C) 10 mL.

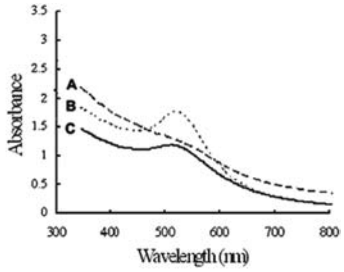

Figure 2. UV–vis spectra of a three-fold diluted solution of AuNPs in benzene.

gold ratio ten times and fifty times), we got the AuNPs with average diameters of 6.4 ± 0.8 nm and 12.8 ± 2.4 nm. The TEM pictures were given in sets A, B, and C of Figure 1, respectively. We can find that the nanoparticles are almost spherical in Figure 1, A and B. For the image of C, we can see that some few nonspherically shaped nanoparticles are formed.

In experiments we found that the electrostatic stabilization of $BMImBF_4$ was too weak to stabilize AuNPs for a long time. It was why alkylamine was introduced to preventing formed AuNPs from further aggregating, and at the same time, transferring AuNPs form IL phase to organic phase.

The UV–vis spectra of the differently sized AuNPs in benzene were recorded and showed in Figure 2. The AuNPs with average diameters of 1.7 nm have almost undetectable absorption band at 517 nm. The higher and sharper plasmon absorption at 521 nm is in agreement with the increase of the nanosizes to 6.4 nm. However, the plasmon absorption at 525 nm, being measured with the AuNPs of 12.8 nm average diameter, is lower and broader.

It is interesting that keeping the same reaction conditions as B and only replacing benzene by *n*-hexane; small areas of organization features of the AuNPs were observed (Figure 3). The nanoparticles exhibit a ring-structured ordering. The domain sizes of this type of ordering were found to range from 10 nm (a single ring) to 70 nm (many-ordered rings). A similar ring-type feature has been reported,[15] which was attributed to the charge balance between local electrostatic repulsion and dispersion forces among the particles.

The mechanism about this reaction is not clear. We conjecture that some gold complex could be formed with CO as a ligand. Water made the complex decomposed and finally produced the AuNPs. The research of mechanism on this reaction is in process.

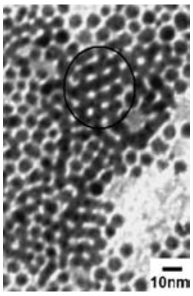

Figure 3. The organization features of AuNPs transferred to *n*-hexane.

In conclusion, the gold nanoparticles were prepared via carbonylation and reduction of $HAuCl_4$ with CO and H_2O in ionic liquid. With increasing amount of water added to, the AuNPs with average diameters of 1.7, 6.4, and 12.8 nm can be synthesized. Using *n*-hexane as a phase-transfer solution, a ring-structured ordering of AuNPs was observed. To our knowledge, this is the first report of preparing AuNPs with controllable sizes in ionic liquids.

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