Synthesis of Thioethyl Pendant Ligand-Stabilized Colloidal Gold Nanoparticles

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A general synthetic method capable of producing a kind of water-soluble gold nanoparticles possessing single-phase synthetic route, high concentration, small size under control, easy store, and excellent thermal, pH and salt stability, was demonstrated. The combined studies with transmission electron microscopy (TEM), Energy dispersive X-rayspectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and UV-visible spectra clearly show that the gold nanoparticles modified by thioethyl-pendant ligand exist.

Keywords: Gold nanoparticles, Thioethyl Pendant Ligand, Transmission Electron Microscopy, X-ray Photoelectron Spectroscopy, UV-Visible Spectra.

1. INTRODUCTION

Gold nanoparticles (Au NPs) present fascinating aspects such as their assembly of multiple types involving materials science, the behavior of the individual particles, size-related electronic, magnetic and optical properties (quantum size effect), and their applications to catalysis and biology.1–8 There are a large variety of techniques available now for preparing Au NPs.6–25 Ligand-stabilized metal nanoparticles have been extensively investigated due to interest in their unique physical properties, chemical reactivity, and possible applications (e.g., as bio-/chemosensors, nanoelectronic components, biological tags, and catalysts/catalyst supports).17

To date, a general synthetic method capable of producing a kind of water-soluble gold nanoparticles possessing single-phase synthetic route, high concentration, small size under control, easy store, and excellent thermal, pH and salt stability, has not been reported yet. Such nanoparticles are needed for applications in aqueous media (e.g., as biochemical supports and probes). In this case, a new thiol, thioethyl pendant ligand (TPL, 1-thioethyl-4,8,11-trimethylcyclam) was served as stabilizer for Au NPs with many advantages (see Fig. 1). The details of synthesis and characterization of Au NPs are presented.

2. MATERIALS AND METHODS

2.1. Materials

Hydrogen tetrachloroaureate (III) hydrate (HAuCl4·3H2O) was obtained from Sigma-Aldrich, other compounds were used as received. All aqueous solutions were made with ultra-high-purity water purified with an ultrapure water system Mill-Q Plus (Millipore Co.).

2.2. Synthesis of Thioethyl Pendant Ligand

A new thiol, thioethyl pendant ligand (TPL, 1-thioethyl-4,8,11-trimethylcyclam) served as the stabilizer for Au NPs (see Scheme 1) was synthesized according to the literature.26

2.3. Synthesis of TPL-Stabilized Aqueous Colloidal Au NPs

Here we describe the single step to prepare stable Au NPs aqueous solution. Au NPs were prepared by the reduction of HAuCl4 in an aqueous TPL solution using NaBH4 as reducing agent. Typically, 10 mL of 0.45 M TPL aqueous solution and 10 mL of 0.3 M HauCl4 aqueous solution were mixed together and stirred vigorously, and then 10 mL of 0.9 M NaBH4 aqueous solution was added into the above solution. The solution turned dark-red color.
immediately, indicating that the oxidation-reduction reaction occurred with the formation of Au NPs. After further stirring for 30 min the solvent was purified by dialysis (Spectra/Por CE, MWCO = 10,000) in water over a 7-day period to remove possible un-reacted reagents thoroughly. Then solvent was removed by freeze drying to get the pure product as a dark-red solid. 0.1 M of Au aqueous colloid was obtained by dissolving the powder in water with appropriate volume. Actually, higher concentration of Au NPs can also be obtained easily in this way.

2.4. Characterization

TEM was conducted on a JEOL-2000F (JEOL Co. Ltd Japan) at 200 kV. Specimens for inspection with TEM were prepared by slowly evaporating one drop of prepared gold nanoparticle solutions at room temperature on a 200 mesh copper grid which was covered by a carbon-supported film. The size distributions of the AuNPs were determined by measuring the diameter of nanoparticles viewed in the images. X-ray photoelectron spectra (XPS) were obtained on an ESCA Lab MK II (VG Scientific Co. Ltd, UK) spectrometer using AlKα radiation. UV-vis absorbance spectrometric of gold nanoparticles was collected using a UV-visible spectrophotometer (Agilent 8453, Agilent Technologies Co. Ltd, USA) with a slit width of 2.0 nm.
3. RESULTS AND DISCUSSION

A typical TEM image obtained from the material, along with the corresponding selected area diffraction pattern, is shown in Figure 2. The characteristic rings in the polycrystalline diffraction pattern can be indexed to the {111}, {200}, {220}, {311}, {222} and {400} allowed reflecting planes expected from fcc Au. The diffuse nature of the rings is a simple manifestation of the crystal shape effect due to the nanoscale size of the particles. Discrete Au NPs were observed in electron micrographs. A particle size distribution investigation was carried out using a sample of 150 particles with a mean diameter of 3.24 nm. TEM photographs of the nanoparticles (Fig. 2) show that their diameters are in the range of 3.24 ± 0.7 nm. In contrast with many other preparations of gold aqueous solution, the size is very smaller. It is proposed that this could result from the conditions of stabilizer employed, where a self-assembled thiol layer was formed on the growing nuclei.

To confirm the composition of the particles, EDS spectra were collected from single particle during TEM imaging (see Fig. 3). This spectrum confirms the presence of Au, N and S in the particles. It is a simple but significant experiment showing that TPL has indeed been grafted to the surface of the gold nanoparticles.

The oxidation state of gold in the nanoparticles was determined by X-ray photoelectron spectroscopy (see Fig. 4). Au 4f7/2 and Au 4f5/2 peaks observed at 83.8 and 87.4 eV, respectively, were also identified with Au0. The absence of a band at 84.9 eV as found for Au1 in a gold thiol complex indicates that the gold atoms in the clusters must be present largely as Au0. Consequently, it is suggested that the gold-thiol bond does not have the characteristic of gold sulfide. As expected, weak sulfur signals were observed in the XPS spectrum. The S binding energies at 163.2 and 164.6 eV correspond to S 2p3/2 peaks of thiolates and free –SH species, respectively. There are two other major peaks at 167.8 and 169.2 eV, which could be attributed to the formation of oxidized species.

Figure 5 shows the UV-vis spectra of Au NPs prepared under aqueous conditions at different concentration, respectively. The maximum at around 521 nm is a peculiar characteristic of the gold surface plasmon band. However, for the higher concentration of Au NPs, the surface plasmon band doesn’t appear at 521 nm. We can’t offer any rational explication. However, it is not attributed to agglomeration of Au NPs.
Stability under a wide range of environmental conditions is necessary if nanoparticles are to be employed in biological or nanoelectronic applications. The colloidal solutions obtained were very stable and did not show signs of decomposition or aggregation over a period of several months (see Fig. 5 inset). We also evaluated the stability of the nanoparticles with elevated temperature, extremes of pH and high salt concentrations. The stability can be monitored by UV-vis spectroscopy because aggregation, precipitation, and decomposition each will lead to distinctive changes in the spectra. There were no changes in the spectra of nanoparticles over 6 h at 75 °C, suggesting that both are thermally stable. Au NPs are stable through a broad pH range (pH 1–13) without aggregation, whereas there is a little red-shift (ca. 5 nm) under slightly basic (pH 7–8) conditions. Au NPs were stable for weeks in solution in the presence of 0.1 M NaCl with no evidence of aggregation or decomposition.

In general, the size of the Au NPs is controlled in the stipulated range by maintaining a HAuCl₄/TPL ratio. For example, Au (TPL 0.15 M) with an average core size of 3.24 ± 0.7 nm, shows a smaller size compared with the gold nanoparticles prepared with lower TPL concentration (TPL 0.10 M, 4.08 ± 1.1 nm), as shown in Figure 6. At present, it seems that there is apparently a simple correlation between the TPL concentration and particle size, i.e. the particle size increases with the decrease in the concentration of the TPL molecules.

Through the TPL stabilizer Au NPs were synthesized in water, but they are easily separated from solution in the form of a powder that would be readily re-dispersible in water after storage. The product was dissolved instantly in water with dark-red color, and still dissolved partially in methanol, and ethanol with the help of ultrasonic, but insoluble in chloroform, acetonitrile, 2-propanol, N,N-Dimethylformamide and acetone.

4. CONCLUSIONS

In summary, we have demonstrated a novel one-step synthetic route to prepare TPL-stabilized aqueous colloidal gold nanoparticles with many advantages including single-phase synthetic route, high concentration, small size under control, easy store, and excellent thermal, pH and salt stability. This method also offers the potential for Au NPs with application in biology and catalysis in aqueous media. For example, TPL is a valuable precursor for the preparation of chelates of potential utility in synthetic inorganic and medicinal chemistry investigations.26
So possible methods of introducing metal ions (such as Cr$^{3+}$, Fe$^{3+}$, Ni$^{2+}$, etc.) to TPL that grafting onto the surface of Au NPs (see Fig. 7), and then for preparation of catalyst are being attempted at our group.

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References and Notes


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