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Fabrication of Gold Nanoparticles Using Luminol as a Reductive and Protective Reagent[1]

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Abstract—An easy and simple reaction is employed to synthesize ligand-protected gold nanoparticles. In this reaction, luminol is used as a reductive and protective reagent to prepare gold nanoparticles in aqueous solution. It includes two steps: chemiluminescence and formation of gold nanoparticles. The formation processes were monitored by resonance light scattering spectroscopy, and the results were observed by transmission electron microscopy and x-ray photoelectron spectroscopy. Highly stable gold nanoparticles about 110 ± 2 nm in size can be readily obtained. A new insight into the design of water-soluble ligand-protected gold nanoparticles for biomedical, analytical, and catalytic applications has been provided.

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INTRODUCTION

There has been much interest in the synthesis of dispersed gold nanoparticles for applications in catalysis [1], nanoelectronics [2], and sensing probes for biological systems [3, 4]. Gold is an excellent candidate by virtue of its facile reductive preparation, high chemical stability, and good biocompatibility. It has been well established that gold nanoparticle surfaces can be repeatedly functionalized with thiolated organic molecules. Ligand place-exchange is a key step in gold nanoparticle functionalization [5–7]. Functional groups on the outermost portion of the nanoparticles ligand sphere can undergo many synthetic transformations directly [8, 9], such as gold-thiol chemistry can be used as a platform for introducing ligands to manipulate aggregation, solubility, and reactivity—all the while maintaining the magnetic utility of the core, thus widening its applicability in the biomedical field significantly [10]. To date, relatively simple thiocyanuric acid [11] has been used to stabilize gold nanoparticles. To our knowledge, there has been no report on synthesizing ligand-protected gold nanoparticle using a simple luminol chemical reduction method at room temperature.

The formation of gold nanoparicles in aqueous solutions was always monitored by UV/vis spectra [12]. However, this method shows some interference to monitor the reductive process of gold nanoparticles, because some kinds of reductive chemicals have stronger UV/vis absorption. Solving this problem is to use a resonance light scattering (RLS) technique [13–18]. Though the RLS technique is proved to be an effective method to investigate nanoparticulate systems, the study on formation of gold nanoparticles using RLS remains an unexplored area.

In this article, we report the synthesis of ligand-protected gold nanoparticles in aqueous state with luminol by a simple two-step reaction. The formation processes were monitored by RLS spectroscopy. Then these nanoparticles were fully characterized by x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Since the reaction system only contains the gold precursor and luminol, it is helpful to have an insight into the formation of gold nanoparticles. Nanoparticles reduced by luminol offer high stability and good dispersion.

EXPERIMENTAL

Chemicals. Sodium tetrachloroaurate ($NaAuCl_4 \cdot 2H_2O$) and luminol were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All the chemicals were analytical grade and were used without further purification. All solutions were prepared with doubly deionized water.

Characterization. Chemiluminescence (CL) spectra were obtained with an F-4500 spectrofluorophotometer (Hitachi, Japan). CL was studied between 200 and 700 nm; the scan rate was 1200 nm/s.

The flow injection CL (FI-CL) system detection was conducted on a model IFFM-E flow injection system (Remex Electronic Science Co., Xi'an, China).

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[1] The text was submitted by the authors in English.

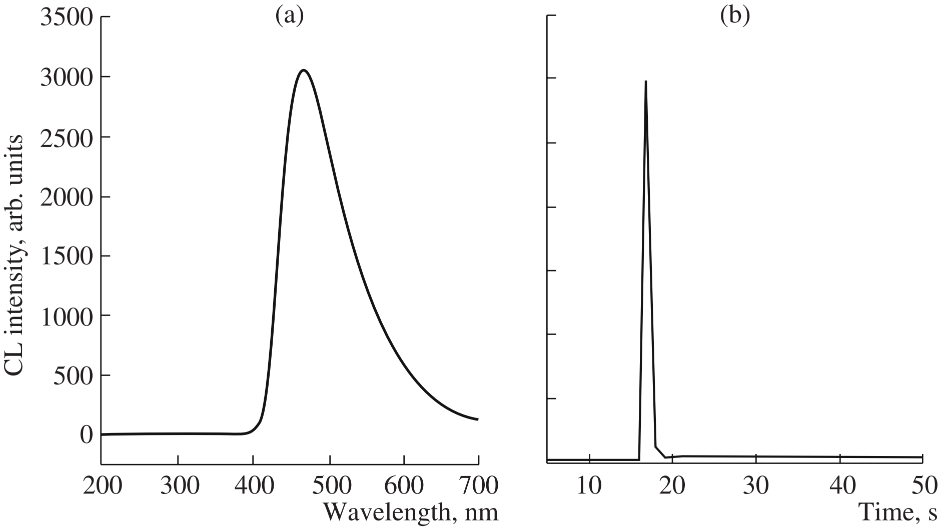

Fig. 1. CL spectra for luminol with aqueous $NaAuCl_4$: (a) wavelength scan, (b) time scan.

RLS spectra were recorded on an F-4500 spectrometer. In addition, RLS spectra were recorded with synchronous scanning at $\lambda_{ex} = \lambda_{em}$ (i.e., $\Delta\lambda = 0$), and the RLS intensities were measured successively by the spectrofluorophotometer. The intensities were plotted against the incident light wavelength to make RLS spectra.

The shape of the sample was observed by TEM on a JEOL JEM 200CX operating at 200 kV. TEM images were obtained from the solution without any purification or centrifugation. For the TEM observation, samples were obtained by dropping solutions onto carbon-coated copper grids placed on a filter paper for rapid removal of the liquid.

In the XPS measurement (Kratos X-SAM800 spectrometer) we used AlK_α (1486.6 eV) as the x-ray source, operated at 12 kV and 15 mA. The correction of the XPS measurement was done with the Au 4f peak at 84.0 eV and the Ag 3d at 386.3 eV. All measurements were performed in vacuum.

Synthesis of gold nanoparticles. The experimental method was a luminol reduction of $NaAuCl_4$ in aqueous solution. Luminol aqueous solution (5 ml, 3.0 mM) was added to 5 ml of a 1.0 mM aqueous solution of $NaAuCl_4$. After stirring for 30 s, the solution was put at room temperature. After the beginning of the reaction, the solution was taken out at specific time intervals for RLS spectroscopy.

Time-resolved measurement of procession of gold nanoparticles. The formation process of gold nanoparticles in the solution phase was determined by RLS. This was carried out by the following procedure: the solution was directly measured with RLS. The nanoparticles were confirmed from the absorption peak at 470 nm, which corresponds to the formation of gold nanoparticles.

RESULTS AND DISCUSSION

CL generation in luminol with $NaAuCl_4$ aqueous solution. Once mixing the solution of sodium tetrachloroaurate with basic luminol reagent at room temperature, intense blue CL is produced immediately from the reaction of tetrachloroaurate with luminol. Figure 1 shows a typical plot of the CL intensity vs. wavelength and time. The CL intensity decreased quickly, and the lifetime was kept for 1 s. The CL peak is at 470 nm. In aqueous solution, it is presumed that the luminescence results from the oxidation of luminol by the terachloroaurate complex. The slope of the plot obtained may be explained as the rate of formation of an excited intermediate which fluoresces when returning to its ground state.

CL method for the determination of $AuCl_4^-$ based on the luminol–$NaAuCl_4$ reaction. Because the CL of luminol–$NaAuCl_4$ reactions has a short lifetime, the FI configuration used for the determination of $AuCl_4^-$ was designed to provide the best conditions for reaction in order to measure the stable signals. The FI manifold finally adopted is not shown. The sample and luminol were injected simultaneously into the Y-confluence with the aid of two rotary valves while the sample zone was mixed in the Y-confluence over the PMT detector. The distance from the Y-confluence to the inlet point of the detector was set at about 6 cm, which is as short as possible. The reagents and tubing were covered with black box to prevent the loss of the feeble light produced by the reaction.

The proposed method provides a simple approach for the determination of $AuCl_4^-$ in aqueous solution. The dynamic range of the method is very wide, calibration curve for 1.92×10^{-7} to $1.21 \times 10^{-}$ M $AuCl_4^-$ ($R^2 = 0.9927$). To examine the possible interferences produced by foreign ions and some complexing agents, the concentration of $AuCl_4^-$ was fixed at 1.0×10^{-6}M, and the tolerable error was ≤±5.0%. The results were as follows. Foreign ions and some complexing agents (tolerance ratio in mass): K^+, Na^+, NO_2^-, Ba^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (1000). Therefore, we concluded that the proposed method has good selectivity. The method could use for determining $AuCl_4^-$ in some conditions.

The formation process of gold nanoparticles. The reaction of luminol with $NaAuCl_4$ in aqueous solution was readily monitored by RLS spectroscopy. Figure 2 shows the time-dependent RLS spectrum of solution containing luminol/$NaAuCl_4$ (the luminol/$NaAuCl_4$ molar ratio is 3.0), with a time interval 10 min in the first 50 min and 5 min in the later 10 min. When the reaction starts, we can observe an obvious scattering band at around 470 nm, which corresponds to the formation of gold nanoparticles. The scattering intensity in this wavelength range increased rapidly for one hour and then was almost constant. Besides, the color of the solution changed from colourless to pale black within several minutes with the addition of luminol to the $NaAuCl_4$ solution. Clearly, the formation of gold nanoparticles is due to the autoreduction of the luminol–$NaAuCl_4$ solution. To investigate the influence of the formation of gold nanoparticles, the molar ratio of luminol/$NaAuCl_4$ (denoted as R) 3.0 was selected. The introduction of microwave and ultrasound can speed up the autoreduction process. Because the molarity of luminol usually exceeds that of $NaAuCl_4$, and amine groups are known to interact with gold surfaces strongly, the amino ligands of luminol are expected to stabilize gold nanoparticles via external capping. The presumed formation mechanism of gold nanoparticles is depicted schematically in Fig. 3. There are two steps for the formation of gold nanoparticles. First, luminol-protected gold nanoparticles were prepared by simple rapid luminol reduction of partly $AuCl_4^-$ with strong CL. Second, the reduction of the remaining $AuCl_4^-$ leads to the growth of gold nanoparticles to make gold nuclei at the initial stage of the reaction. The amine group is known to form coordination compounds with Au(III) [19]. According to the above proposal, the remaining amine groups of luminol immediately cap the surface of the nucleating gold moieties, leading to a controlled growth of gold nanoparticles. The luminol capped on the surface of gold nanoparticles maintains its shape. The above discussion indicates that the dual role played by luminol is not only the formation but also the stabilization of gold nanoparticles.

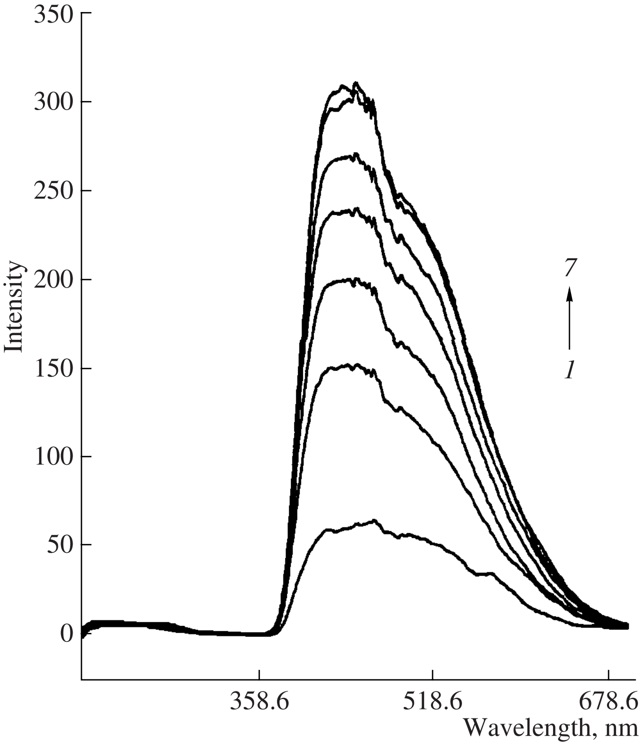

Fig. 2. RLS spectra of gold nanoparticles: (*1*) 10, (*2*) 20, (*3*) 30, (*4*) 40, (*5*) 50, (*6*) 55, (*7*) 60 min.

Figure 4 shows the TEM image of luminol-protected gold nanoparticles produced at room temperature. The gold nanoparticles have high dispersion. No distinct particle aggregation was observed, indicating that luminol can effectively stabilize gold nanoparticles. The size distribution reveals that the average size of the gold nanoparticles is 10 ± 2 nm for luminol/$NaAuCl_4$ = 3.0. Both morphologies and particle-size distributions may depend on the reduction rate and luminol content. In fact, the precipitate resulting from this aggregation was observed several weeks later. It should be pointed out that investigations are under way to further improve the control of gold particle sizes and shapes.

Gold nanoparticles were analyzed by XPS. We concluded from the XPS spectra (Fig. 5) that gold nanoparitcle had been prepared successfully. The appearance of N and Au peaks in the XPS data reveals that

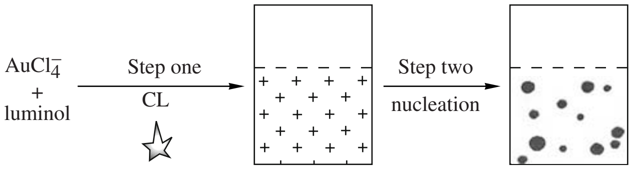

Fig. 3. Schematic illustration of the formation process of gold nanoparticles by luminol reduction of $NaAuCl_4$: step one, CL; step two, nucleation.

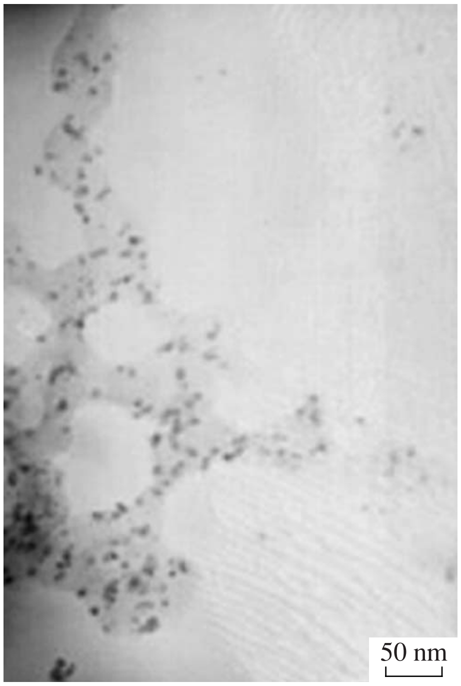

Fig. 4. TEM image of gold nanoparticles obtained using luminol reduction of $NaAuCl_4$.

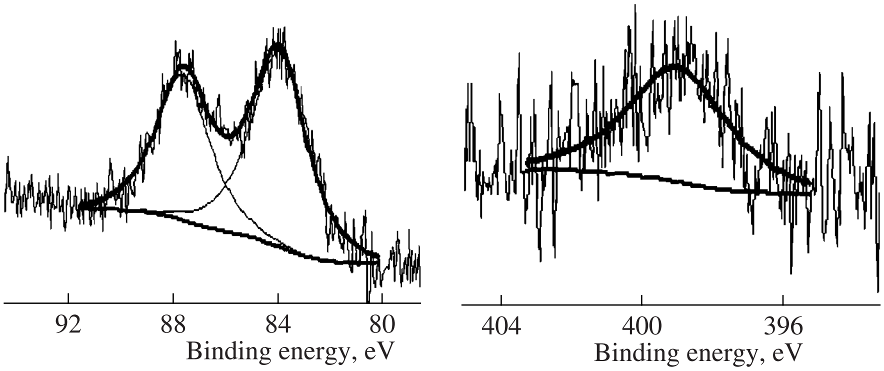

Fig. 5. XPS spectra in the Au 4*f* and N 1*s* regions.

NH_2 groups were adsorbed onto the gold nanoparticle surfaces. As expected, the binding energy at 83.8 eV of Au 4*f* is similar to pure Au (84.0 eV) (see Fig. 5). The N 1*s* signal from the Au nanoparticles shows the presence of chemical species with a binding energy of 398.98 eV. The decrease of the binding energy is due to the presence of nitrogen in the capped gold nanoparticles surfaces.

CONCLUSIONS

In this work, we have proposed a simple two-step reaction to synthesize ligand-protected gold nanoparticles. We demonstrate that luminol is used as a reductive and protective reagent for the reduction of $NaAuCl_4$ to prepare gold nanoparticles in aqueous solution. The gold nanoparticles have been characterized by various techniques. The results show that the gold nanoparticles have good dispersion and stability. Our ongoing work will focus on further exploring ligand-protected gold nanoparticle applications in various areas.

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