\textbf{\textgamma-IRRADIATION-INDUCED PREPARATION OF AG AND AU NANOPARTICLES AND THEIR CHARACTERIZATIONS}

Taihua Li\textsuperscript{a}, Hyun Gyu Park\textsuperscript{a,}\textsuperscript{*}, Seong-Ho Choi\textsuperscript{b}

\textsuperscript{a} Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science & Technology (KAIST), Daejeon, 305-701, Republic of Korea

\textsuperscript{b} Department of Chemistry, Hannam University, Daejeon, 306-901, Republic of Korea

*Corresponding author: Tel: +82-42-869-3932;
Fax: +82-42-869-3910.
E-mail address: hgpark@kaist.ac.kr (H.G. Park)

\textbf{Abstract}

Using \textgamma-irradiation-induced reduction in the field of a \textsuperscript{60}Co \textgamma-ray source, colloidal silver and gold nanoparticles were prepared from their corresponding metal salts in aqueous solution and compared with those by chemical reduction. The radiation-based method provided silver nanoparticles with higher concentration and narrower size-distribution than those obtained by chemical reduction method while there was no significant difference between the two strategies for the preparation of gold nanoparticles. \textgamma-irradiation of 1.0×10\textsuperscript{-3} M AgNO\textsubscript{3} solution resulted in nearly 100 times more highly concentrated silver colloids than those by citrate reduction. Furthermore, the radiation method could lead to more highly concentrated silver colloids by simply increasing the concentration of AgNO\textsubscript{3} solution up to 2.0×10\textsuperscript{-2} M. The two metal nanoparticles prepared by the two different methods were characterized by UV-vis spectrophotometry and transmission electron microscopy (TEM), and compared regarding to their respective attainable concentrations and size distribution.

\textbf{Keywords:} \textgamma-irradiation; chemical reduction; silver/gold nanoparticle.
1. Introduction

A number of production techniques have been reported for preparation of metallic colloids using metal salts as starting materials, such as chemical [1-3], photochemical [4], electrochemical [5], radiolytic [6-8], and sonochemical [9] reduction. Of these techniques, the radiation-induced synthesis is one of the most promising strategies because there are some important advantages to the use of the irradiation techniques [10], as compared to conventional chemical and photochemical methods: (1) the process is simple and clean, (2) the γ-ray irradiation has harmless feature, (3) controlled reduction of metal ions can be carried out without using excess reducing agent or producing undesired oxidation products of the reductant, (4) the method provides metal nanoparticles in fully reduced, highly pure and highly stable state, (5) no disturbing impurities like metal oxide are introduced.

Radiolytic reduction generally involves radiolysis of aqueous solutions that provides an efficient method to reduce metal ions and form homo- and heteronuclear clusters of transition metals. In the radiolytic method, aqueous solutions are exposed to γ-rays creating solvated electrons, $e_{aq}$:\ These solvated electrons, in turn, reduce the metal ions and the metal atoms eventually coalesce to form aggregates as depicted by following reactions [11].

$$\begin{align*}
\text{H}_2\text{O} \xrightarrow{\text{Radiation}} & e_{aq}^-, \text{H}_3\text{O}^+, \text{H}^+, \text{H}_2, \text{OH}^-, \text{H}_2\text{O}_2 \\
& e_{aq}^- + M^{n+} \rightarrow M^{(n-1)+} \\
& e_{aq}^- + M^{n+} \rightarrow M^n \\
& nM^n \rightarrow M_2 \rightarrow \ldots \rightarrow M_{agg}
\end{align*}$$

Due to its unique advantages, the irradiation-based strategy, as a worthful tool, has been extensively used to prepare nanoscale particles and materials during the past twenty years. The nanoscale materials are receiving considerable attention since they can offer highly promising and novel options for a wide range of applications such as bio and chemical sensors [12-14], nanoscale electronics [15, 16], catalysis [17, 18] and optics [19]. For example, due to their nanosized dimensions, metal nanoparticles can show peculiar optical, magnetic and electronic properties that bulk solid or isolated molecules do not usually exhibit [20], which may find important applications in material technologies like microelectronics, catalytic systems and nanobiosensors.

Silver and gold nanoparticles in particular, are of great interest because of their ability to efficiently interact with light by virtue of plasmon resonance, which are the collective oscillations of the conduction electrons in the metal [21-25]. Silver and gold nanoparticles certainly have the potential to be the building blocks of future photonic and plasmonic devices as the field of nanotechnology matures. Furthermore, since silver and gold colloids exhibit interesting optical properties, they have been widely studied to develop a novel detection strategy for biomolecular interactions [26-28] and therefore, received the most attention in connection with biomolecular conjugates [23, 29 and 30]. They have also been widely employed as nanostructured substrates for surface enhanced Raman spectroscopy (SERS) [31].
In relation to \(\gamma\)-irradiation-based synthesis of silver or gold nanoparticles, Bertino et al. \[32\], Choi et al. \[23\], and Kang et al. \[33\] synthesized alloy metal clusters (Ag-Pd), silver nanoparticles, and magnetic nanoparticles, respectively. In their papers, they have just presented structural characterization and their morphological features. Another research group, Henglein team \[21\] reported radiolytic control of the size of colloidal gold nanoparticles. They prepared ultrafine gold particles (~2 nm) by using \(\gamma\)-irradiation of deaerated solutions containing hydrolyzed AuCl\(_4^-\) and poly (vinyl alcohol) (PVA) or poly (vinylpyrrolidone) (PVP), and used the particles as seeds in the subsequent radiolytic reduction of added Au(CN)\(^{-}\) to yield larger particles of any desired size and improved monodispersity. The radiolytic method was also employed by Bertino et al. to synthesize high aspect ratio bimetallic Ag-Pt core-shell nanostructures. In their work, they found out that key parameters for nanowire formation are the molar ratio between the two metals, the counterions (such as metal ions), and the degree of hydrolysis of the PVA capping polymer \[34\]. Other radiation sources such as electron and UV beams have been also employed to prepare TiO\(_2\) nanoparticles \[35\] or aqueous Ti/Ag bimetallic clusters \[36\].

Even though several papers have been published about the irradiation-induced synthesis of silver and gold nanoparticles as described above, there has little been studied about the systematic comparison of the two metal nanoparticles prepared by \(\gamma\)-irradiation method and conventional chemical method (especially citrate reduction method). Therefore, we describe herein, \(\gamma\)-irradiation-induced preparation of silver and gold nanoparticles and their comparisons with those obtained by chemical reduction. Since one of the major challenges in the preparation of nanoparticles is large-scale synthesis with a high concentration and a narrow size distribution, characterization of the nanoparticles was mainly focused on attainable concentration and monodispersity.

2. Experimental

2.1. Chemicals

Silver nitrate (AgNO\(_3\)) was purchased from Kojima Chemicals Co. Ltd. (Japan). Hydrogen tetrachloroaurate (\(\text{III}\)) (HAuCl\(_4\)) and a polyvinylpyrrolidone (PVP, Mw.=10,000) were obtained from Aldrich Chemical (USA). Sodium citrate was purchased from Sigma (USA). 2-propanol was purchased from Junsei (Japan). Hydrogen gas was provided by Special gas Co. (Korea). All chemicals were used without further purification. Purified and deionized water was acquired from Millipore Milli-Q system (Millipore).

2.2. Sample preparation

2.2.1. Preparation of silver and gold colloids by \(\gamma\)-irradiation

Silver nitrate or hydrogen tetrachloroaurate (\(\text{III}\)) was dissolved in water with 2-propanol and PVP to form primary solution with predetermined concentration of the metal salts (AgNO\(_3\): \(2\times10^{-4}\) M ~ \(2\times10^{-2}\) M; HAuCl\(_4\): \(2\times10^{-4}\) M ~ \(2\times10^{-3}\) M). The mixture solution was bubbled with pure nitrogen for about 20 min to
remove oxygen and then irradiated in the field of Co-60 $\gamma$-ray source at irradiation dose rate of 20 KGY/h for 2 hr in Korea Radiation Research Group of Korea Atomic Energy Research Institute (KAERI). Dark brownish silver colloids or reddish gold colloids were prepared as homogenous solution. The addition of PVP and a small amount of 2-propanol did not lead to any thermal reduction of the Ag or Au salt [8].

2.2.2. Preparation of silver and gold colloids by chemical reduction
Silver and gold colloids were synthesized by citrate reduction of AgNO$_3$ (1.0 x 10$^{-3}$ M and 2.0 x 10$^{-3}$ M) and H$_2$AuCl$_4$ (2.0 x 10$^{-4}$ M~2.0 x 10$^{-3}$ M), respectively, in the aqueous solution. For silver colloids, the aqueous AgNO$_3$ solution (containing surfactant PVP (MW. 10,000) as a colloidal stabilizer) was reduced by vigorously stirring with 1% sodium citrate for about 20 min at near-boiling temperature [1]. For gold colloids, the similar procedures were employed using H$_2$AuCl$_4$ instead of AgNO$_3$, but without the surfactant PVP [2].

2.3. Characterization of metal colloids
2.3.1. Ultraviolet-visible (UV-vis) absorbance spectroscopy measurement
The UV spectra of the prepared silver or gold colloids were recorded at a resolution of 2 nm on a Varian Cary 100 Conc. Deionized water was used as reference.

2.3.2. Transmission Electron Microscopy (TEM) measurement
Size distributions and shape of the metal nanoparticles were obtained from TEM photographs. TEM measurements were performed on a TECNI F20 model 1300 KX instrument operated at an accelerating voltage of 131 eV. Samples for TEM studies were prepared by placing a drop of the silver or gold colloidal solution on a TEM copper grid (200 mesh, carbon-coated, colloidon-covered). The films on the TEM grids were allowed to dry for several hours after the extra solution was removed using blotting paper.

3. Results and Discussion
Using two different methods, $\gamma$-irradiation-based reduction and conventional chemical reduction, we prepared silver and gold colloids from their respective salt solutions at various concentrations. For radiation method, 2-propanol and PVP were used as a radical scavenger and colloidal stabilizer, respectively, and sodium citrate was employed as a reducing agent for chemical reduction because citrate reduction is the most widely used method. Reducing agent, citrate, also acts as a stabilizer for the metal colloids, preventing their rapid aggregation. Furthermore, the ratio of initial concentrations of citrate to gold or silver ions plays an important role in the formation of the gold or silver nanoparticle and has a great effect on the size of the resulting nanoparticles [37].

Since nanometer-sized metal clusters usually exhibit unique optical properties with their specific
absorption and scattering [38], the resulted silver and gold colloids were characterized with UV-visible spectrometer and their quantitative aspects were summarized in Table 1 and 2.

Figure 1 shows the UV–vis spectra of silver colloids prepared with various AgNO₃ concentrations. With chemical reduction method, silver nanoparticles were generated only from two specific concentrations, 1.0×10⁻³ M and 2.0×10⁻³ M of salt solution while radiation-based reduction led to a successful generation of silver nanoparticles from all the concentrations in the tested range from 2.0×10⁻⁴ M to 2.0×10⁻² M. The chemically synthesized silver colloids showed surface plasmon absorption bands with maximum around 420 nm (curve b₁ in Figure 1) and 445 nm (curve b₂ in Figure 1), and these absorption bands were rather broad and red-shifted compared with those from silver colloids prepared by radiation method (spectra a₁ - a₅). The irradiation-induced silver colloids from the lowest AgNO₃ concentration of 2.0×10⁻⁴ M had a light yellow color with maximum plasmon band at 416 nm (curve a₁ in Figure 1). As the concentration of the precursor salt solution increased up to 1.0×10⁻² M, the color of the silver colloidal solution changed to dark yellow and the absorbance accordingly increased (curve a₄ in Figure 1). By increasing the concentration from 1.0×10⁻² M to 2.0×10⁻² M, however, there was no further enhancement of the absorbance and 1.0×10⁻² M appeared to be maximum salt concentration from which the most highly concentrated silver colloidal solution could be obtained by irradiation-induced reduction in this study (Table 1).

Since the magnitudes of the absorbance at maximum wavelength reflect concentrations of the corresponding materials, the irradiation-induced method is considered to be superior to the chemical reduction method in the aspect of the preparation of concentrated colloidal product (Table 1). When a same starting AgNO₃ solution of 1.0×10⁻³ M was used for the both methods, the absorbance of silver colloid by irradiation method was nearly 100 times higher than that by chemical method. Furthermore, the irradiation method can lead to more highly concentrated silver colloids by simply increasing the concentration of the starting salt solution. For example, by using irradiation-induced reduction of a salt solution of 1.0×10⁻² M, it was possible to obtain silver colloids with a concentration 200 times higher than that attainable by chemical reduction.

Figure 2 illustrates the UV-visible spectra of gold nanoparticles generated by γ-irradiation or chemical reduction using various HAuCl₄ solutions with different concentrations. Both chemical reduction and γ-irradiation method resulted in gold nanoparticles with several different concentration of HAuCl₄, but not with higher concentrations of HAuCl₄ than 2.0×10⁻³ M (Table 2). It is interesting and noticeable that the generation of silver nanoparticles from various concentrations was only possible with γ-irradiation. Increasing the concentration from 1.0×10⁻³ M to 2.0×10⁻³ M did not further increase the absorbance of the resulted gold nanoparticles and the absorbance, on the contrary, decreased. Therefore, it is considered that 1.0×10⁻³ M HAuCl₄ is the optimal concentration for both preparation strategies to achieve highly concentrated gold nanoparticles. The absorbance of gold colloids prepared by γ-irradiation of 1.0×10⁻³ M HAuCl₄ was approximately two times larger than that by chemical reduction even though
the other concentrations generated gold colloids with similar absorbance in the same order between the two methods.

As we explained in the introduction section, the generated hydrogen atoms H\(^+\) and hydrated electrons e\(_{aq}^-\) from the water radiolysis and 2-propanol radiolysis are strong reductants capable of reducing metal ions Mn\(^+\) to lower valences and finally to metallic state. The secondarily generated radical of (CH\(_3\))\(_2\)COH also efficiently reduces the noble metal ions. These \textit{in situ} generated reductants transform the noble metal ions Mn\(^n+\) to M\(^{(m-1)+}\), leading to the formation of noble metal nanoparticles. Above results indicate that the \(\gamma\)-irradiation method has more opportunities to synthesize silver nanoparticles than chemical reduction. For a specific AgNO\(_3\) solution of 1.0\(\times\)10\(^{-3}\) M, \(\gamma\)-irradiation has nearly 100 times more powerful reducing efficiency than the conventional chemical reducing strategy while there are no big advantages of the \(\gamma\)-irradiation method for the preparation of concentrated gold nanoparticles over chemical reduction method. From the data of the UV-vis spectra for silver nanoparticles (Table 1), it is clear that the \(\gamma\)-irradiation-based strategy has excellent merit for preparing highly concentrated silver colloids.

To determine the sizes of the silver and gold nanoparticles, transmission electron micrographs (TEM) were performed (Figure 3 and Figure 4) and their sizes were presented in Table 1 and 2. The size of silver nanoparticle prepared by chemical reduction of 1.0\(\times\)10\(^{-3}\) M AgNO\(_3\) was 23 nm, which is larger than that by \(\gamma\)-irradiation-based method which was 13 nm. Moreover, the size of silver colloid formed by citrate reduction of 2.0\(\times\)10\(^{-3}\) M AgNO\(_3\) was much bigger (ca. 84 nm), and the colloids were very unstable at the room temperature. Upon increasing the concentration of starting AgNO\(_3\) solution in \(\gamma\)-irradiation-based reduction, the size of the resulted silver nanoparticles increased (except highest AgNO\(_3\) concentration of 2.0\(\times\)10\(^{-2}\) M, shown in Table 1). The correlations of nanoparticle size and starting salt concentration can be different depending on following three different situations described by Chen and Wu [39]. (1) If the number nuclei increased faster than that of total ions, smaller particles would be obtained. (2) If the increase of nucleus number was proportional to that of total ion number, the particle size might remain unchanged. (3) When the number of nuclei remained constant or increased slower than that of total ions, the particle size would become larger with the increase of ion concentration. Based on the above observation, our case appears to belong to the third situation. According to this correlation, silver nanoparticle can be efficiently prepared with controlled size. Gold nanoparticles prepared by \(\gamma\)-irradiation strategy had smaller sizes than their corresponding gold nanoparticles prepared by chemical reduction (Table 2). The size of gold nanoparticles also increased upon increasing the concentration of starting H\(\text{AuCl}_4\) solution indicating the conditions for gold nanoparticles also belong to the third situation. As mentioned above, in chemical reduction, the average size of the colloidal gold can be controlled to some extent by adjusting the ratio of concentration of the citrate ion to that of the metal salt. The use of stronger reducing agents such as sodium borohydride can be another way to extend the range of accessible sizes but their control is difficult [40].

One of the key issues for the preparation of metal nanoparticles is size distribution that was
represented with TEM images (Figure 3 and 4) and CV (coefficient of variation) value for size (Table 1 and 2). Generally, the narrower distribution is the more desirable. The CV for the size of silver nanoparticle prepared by $\gamma$-irradiation using $1.0 \times 10^{-3}$ M AgNO$_3$ solution was 26.6% and much smaller than that (45.3%) by chemical reduction using the same concentration (Table 1). Furthermore, $\gamma$-irradiation-based strategy resulted in silver nanoparticles with smaller size distribution upon increasing the starting concentration of AgNO$_3$. $\gamma$-irradiation method, however, is seemed not to have any advantage for the preparation of gold nanoparticles over conventional chemical reduction method in the aspect of size distribution.

4. Conclusion

In summary, we prepared silver and gold colloids by using both $\gamma$-irradiation-induced reduction and chemical reduction, and compared the two nanoparticles made by the two different methods with respect to their concentrations and size distributions. With $\gamma$-irradiation-induced method, highly concentrated silver nanoparticle could be achieved simply by increasing the concentration of starting AgNO$_3$ solution whereas citrate-based chemical reduction strategy was possible only for two specific concentrations of AgNO$_3$ solution. Upon increasing the AgNO$_3$ concentration, the size of the nanoparticles resulted from $\gamma$-irradiation increased and this correlation could be efficiently used for the preparation of silver nanoparticles with controlled size simply by changing the starting AgNO$_3$ concentration in the tested range. $\gamma$-irradiation-induced strategy also offered silver nanoparticles with narrower sized distribution. We demonstrated that $\gamma$-irradiation-based strategy has remarkable merits for preparing highly concentrated silver colloids with small size distribution while there are no noticeable advantages for the preparation of gold nanoparticles, compared to the conventional chemical reduction methods. This work would greatly help widen the application of $\gamma$-irradiation-based strategy for the preparation of metal nanoparticles with favorable features.
Acknowledgment

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References

List of Tables

Table 1. Physical properties of silver nanoparticles prepared by γ-irradiation or chemical reduction using different concentrations of AgNO₃

Table 2. Physical properties of gold nanoparticles prepared by γ-irradiation or chemical reduction using different concentrations of HAuCl₄

List of Figures

Figure 1. UV-vis spectra of silver nanoparticles prepared by γ-irradiation (labeled a₁ - a₅) at various AgNO₃ concentrations (a₁: 2.0×10⁻⁴ M; a₂: 1.0×10⁻³ M; a₃: 2.0×10⁻³ M; a₄: 1.0×10⁻² M; a₅: 2.0×10⁻² M) and chemical reduction of 1.0×10⁻³ M (labeled b₁) and 2.0×10⁻³ M (labeled b₂) AgNO₃. The a₁~a₅ were obtained after 100 times dilution and b₂ was obtained after 10 times dilution of the corresponding samples, but original sample was directly used for b₁.

Figure 2. UV-vis spectra of gold nanoparticles prepared by γ-irradiation (a₁, a₂ and a₃) at various HAuCl₄ concentrations (a₁: 2.0×10⁻⁴ M; a₂: 1.0×10⁻³ M; a₃: 2.0×10⁻³ M) and chemical reduction (labeled b₁, b₂, b₃) at various HAuCl₄ concentrations (b₁: 2.0×10⁻⁴ M; b₂: 1.0×10⁻³ M; b₃: 2.0×10⁻³ M). All samples were diluted 10 times before analyzing UV-vis spectra.

Figure 3. TEM images of silver nanoparticles prepared by γ-irradiation (a₁ - a₅) and chemical reduction (b₁ and b₂) using different AgNO₃ concentrations (more details shown in Table 1)

Figure 4. TEM images of gold nanoparticles prepared by γ-irradiation (a₁, a₂ and a₃) and chemical reduction (b₁, b₂ and b₃) using different HAuCl₄ concentrations (more details shown in Table 2.)
Table 1. Physical properties of silver nanoparticles prepared by $\gamma$-irradiation or chemical reduction using different concentrations of AgNO$_3$\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>AgNO$_3$ Concentration</th>
<th>$\lambda_m$ (nm)</th>
<th>Abs.$^b$</th>
<th>Coefficient of variation (CV)</th>
<th>Ag particle size$^c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a$_1$</td>
<td>$2.0 \times 10^{-4}$ M ($\gamma$-irradiation)</td>
<td>416</td>
<td>3.9</td>
<td>52.4%</td>
<td>7 ± 4</td>
</tr>
<tr>
<td>a$_2$</td>
<td>$1.0 \times 10^{-3}$ M ($\gamma$-irradiation)</td>
<td>402</td>
<td>12.9</td>
<td>26.6%</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>a$_3$</td>
<td>$2.0 \times 10^{-3}$ M ($\gamma$-irradiation)</td>
<td>417</td>
<td>20.0</td>
<td>18.5%</td>
<td>19 ± 3</td>
</tr>
<tr>
<td>a$_4$</td>
<td>$1.0 \times 10^{-2}$ M ($\gamma$-irradiation)</td>
<td>417</td>
<td>28.4</td>
<td>13.7%</td>
<td>17 ± 3</td>
</tr>
<tr>
<td>a$_5$</td>
<td>$2.0 \times 10^{-2}$ M ($\gamma$-irradiation)</td>
<td>416</td>
<td>24.3</td>
<td>15.2%</td>
<td>17 ± 3</td>
</tr>
<tr>
<td>b$_1$</td>
<td>$1.0 \times 10^{-3}$ M (chemical reduction)</td>
<td>420</td>
<td>0.14</td>
<td>45.3%</td>
<td>23 ± 6</td>
</tr>
<tr>
<td>b$_2$</td>
<td>$2.0 \times 10^{-3}$ M (chemical reduction)</td>
<td>445</td>
<td>1.13</td>
<td>30.2%</td>
<td>84 ± 10</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The experiments were repeated at least three times and they were averaged to give the data in Table 1 and Table 2.

\textsuperscript{b} The data were obtained by multiplying the absorbance of the corresponding diluted solutions by their dilution factors when diluted solutions were used for the data.

\textsuperscript{c} The size of Ag nanoparticles was determined by measuring diameters of about 100 nanoparticles in TEM image and by averaging them.

Table 2. Physical properties of gold nanoparticles prepared by $\gamma$-irradiation or chemical reduction using different concentrations of HAuCl$_4$\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>HAuCl$_4$ Concentration</th>
<th>$\lambda_m$ (nm)</th>
<th>Abs.$^b$</th>
<th>Coefficient of variation (CV)</th>
<th>Au particle size$^c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a$_1$</td>
<td>$2.0 \times 10^{-4}$ M ($\gamma$-irradiation)</td>
<td>522</td>
<td>0.71</td>
<td>12.3%</td>
<td>7 ± 3</td>
</tr>
<tr>
<td>a$_2$</td>
<td>$1.0 \times 10^{-3}$ M ($\gamma$-irradiation)</td>
<td>524</td>
<td>2.37</td>
<td>13.6%</td>
<td>10 ± 3</td>
</tr>
<tr>
<td>a$_3$</td>
<td>$2.0 \times 10^{-3}$ M ($\gamma$-irradiation)</td>
<td>524</td>
<td>1.24</td>
<td>43.2%</td>
<td>15 ± 5</td>
</tr>
<tr>
<td>b$_1$</td>
<td>$2.0 \times 10^{-3}$ M (chemical reduction)</td>
<td>520</td>
<td>1.12</td>
<td>16.4%</td>
<td>13 ± 3</td>
</tr>
<tr>
<td>b$_2$</td>
<td>$1.0 \times 10^{-2}$ M (chemical reduction)</td>
<td>530</td>
<td>1.25</td>
<td>23.6%</td>
<td>35 ± 7</td>
</tr>
<tr>
<td>b$_3$</td>
<td>$2.0 \times 10^{-3}$ M (chemical reduction)</td>
<td>546</td>
<td>0.92</td>
<td>19.5%</td>
<td>45 ± 6</td>
</tr>
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</table>

\textsuperscript{a} The experiments were repeated at least three times and they were averaged to give the data in Table 1 and Table 2.

\textsuperscript{b} The data were obtained by multiplying the absorbance of the corresponding diluted solutions by their dilution factors when diluted solutions were used for the data.

\textsuperscript{c} The size of Au nanoparticles was determined by measuring diameters of about 100 nanoparticles in TEM image and by averaging them.
Figure 1.
Figure 2.
Figure 3.
Figure 4.