

Photochemical synthesis of polygonal gold nanoparticles

Wei-Chieh Huang · Yu-Chie Chen

Received: 15 April 2007 / Accepted: 26 August 2007 / Published online: 19 September 2007
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Abstract In this paper, we propose a method to generate gold nanoparticles capable of absorbing near infrared light (NIR) radiation through a photochemical reaction. This approach does not require the use of either surfactants or polymers, reducing the difficulties that may arise in further chemical modifications for the gold nanoparticles. The gold nanoparticles with either triangular or hexagonal shapes were generated using the photo-reduction method, mixing hydrogen tetrachloroaurate with sodium oxalate, a reducing agent, in aqueous solution under illumination of a mercury lamp ($\lambda_{\text{max}} = 306$ nm) for more than 10 min. The size of the gold nanoparticles varies from 25 to 200 nm, which mainly depends on the duration of light illumination and the concentration of sodium oxalate. Furthermore, we demonstrate that the presence of the gold nanoparticles in aqueous solutions can effectively elevate the temperature of the solutions under irradiation of NIR light (808 nm) within a few minutes. The gold nanoparticles can be potentially used as suitable photothermal agents for hyperthermia.

Keywords Gold nanoparticles · Near infrared · Photochemical reaction · Photothermal · Hyperthermia

Introduction

Gold nanoparticles with size-dependent optical properties have been widely used in various fields. Particularly, spherical gold nanoparticles have good absorption capacities in the visible region. Thus, a number of chemical/biochemical sensors have been developed using gold nanoparticles as the reporter probes (Kuong et al. 2007; Lin et al. 2002, 2006; Mirkin 2000) which are based on the change in the color of gold nanoparticles as they change from a dispersed state to an aggregated state. These changes result from molecular interactions between the probe molecules adhering to the surface of gold nanoparticles and their target species. The optical resonances of non-spherical gold nanoparticles such as gold nanorods (Kim et al. 2002) and gold nanoparticles with polygonal shapes (Chu et al. 2006; Malikova et al. 2002; Millstone et al. 2005) can be tuned to the near-infrared (NIR) region of the electromagnetic spectrum. Many methods have been developed to generate gold nanoparticles with polygonal shapes including chemical (Ah et al. 2005; Chu et al. 2006; Malikova et al. 2002; Millstone et al. 2005; Sau and Murphy 2004), biological (Esumi et al. 1995; Shankar et al. 2004, 2005; Singh et al. 2006), and photo-reduction

W.-C. Huang · Y.-C. Chen
Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan

Y.-C. Chen (✉)
Institute of Molecular Science, National Chiao Tung University, Hsinchu 300, Taiwan
e-mail: yuchie@mail.nctu.edu.tw

methods (Esumi et al. 1995; Eustis et al. 2005; Mallick et al. 2005; Pucci et al. 2006; Sau et al. 2001; Zhou et al. 1999). When employing photo-reduction methods to generate gold nanoparticles, gold seeds combined with the use of surfactants (Esumi et al. 1995; Sau et al. 2001) are generally employed to control the sizes and shapes of gold nanoparticles. However, when introducing gold nanoparticles as imaging agents or hyperthermia medium for animal testing, the presence of surfactants in the particle solution may induce adverse effects for the animals. Polymers such as polyvinyl alcohol (Zhou et al. 1999; Pucci et al. 2006) and poly(vinylpyrrolidone) (Eustis et al. 2005) are also added in the reaction to control the sizes and shapes of gold nanoparticles. However, the presence of polymers and surfactants on the shell of gold nanoparticles may cause difficulties in further modifications for the surfaces of the nanoparticles. Thus, developing a new method to eliminate the use of these chemicals may solve this problem. Additionally, low-pressure mercury lamps ($\lambda_{\text{max}} = 254.3 \text{ nm}$, $\geq 30 \text{ W}$) (Esumi et al. 1995; Zhou et al. 1999) were commonly used as the light source for photochemical reaction to generate gold nanoparticles with polygonal shapes. However, the reaction time generally takes several hours to more than 1 day (Esumi et al. 1995; Eustis et al. 2005; Mallick et al. 2005; Pucci et al. 2006; Sau et al. 2001; Zhou et al. 1999). In this paper, we propose a method, which can generate gold nanoparticles capable of absorbing NIR radiation through a photochemical reduction in a short time.

Experimental

Reagents and materials

Hydrogen tetrachloroaurate (III) tetrahydrate was obtained from Showa (Tokyo, Japan), while tris (hydroxymethyl) aminomethane (tris) was obtained from Sigma (St. Louis, MO). Sodium oxalate and thymol blue were obtained from Riedel-de Hen (Seelze, Germany).

Preparation of gold nanoparticles via photochemical reduction

Aqueous sodium oxalate (0.1 M, 62 μL , 65 μL , or 68 μL) was diluted to 9.7 mL by deionized water

with shaking in a quartz vial, which was wrapped with aluminum foil. Aqueous tetrachloroaurate (0.01 M, 0.3 mL) was added to the vial. The mixture was shaken at 200 rpm under the irradiation of UV light, which was illuminated from an 8 W, column like, low-pressure mercury lamp ($\lambda_{\text{max}} = 306 \text{ nm}$), for 10–120 min at room temperature. An electric fan was used to prevent the reaction from overheating. The generated gold nanoparticle suspension was centrifuged at 3,500 rpm for 15 min and the supernatant was removed by pipette. The remaining particles were re-suspended in deionized water (0.2 mL).

Illumination of the nanoparticle suspension under NIR light

To examine the photothermal effect of the gold nanoparticles, aqueous sample solutions containing gold nanoparticle were irradiated by a diode laser (808 nm), 4.5 cm distant from the top of the sample solution for 3–5 min. The power of the laser, measured from 4.5 cm distance from the laser, was $\sim 200 \text{ mW/cm}^2$. Thymol blue (10 mM) dissolved in tris buffer (15 mM) was used as the thermoindicator for monitoring the temperature change of the sample solutions. The sample solutions were prepared by mixing the aqueous gold nanoparticle suspension (0.2 mL) with thymol blue (10 mM, 0.3 mL), followed by dilution with an equal volume of tris buffer (15 mM, 0.5 mL). The absorption spectra of the sample solution (0.2 mL) were obtained as the temperature increased from 21 to 65 $^{\circ}\text{C}$. The absorption spectra of another set of sample solutions were also obtained after illumination by a diode laser (808 nm) for 0–5 min.

Instruments

The TEM images were obtained using either a Hitachi H-7500 (Japan) transmission electron microscope (TEM) or a JEOL 2000FX (Japan) TEM. The absorption spectra were obtained using a Varian Cary 50 spectrophotometer (Melbourne, Australia). The XRD pattern was obtained from a Bruker X-Ray Powder Diffractometer (D8 Advance, Germany).

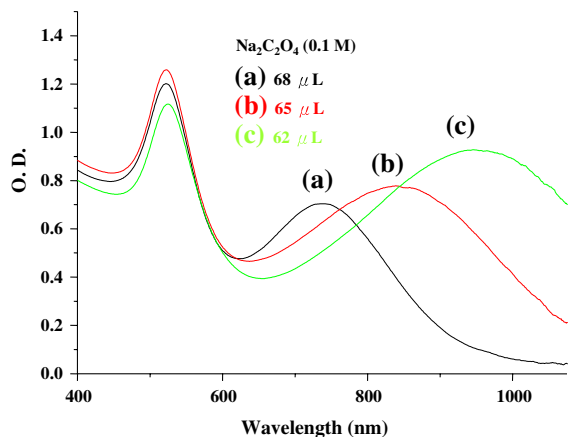


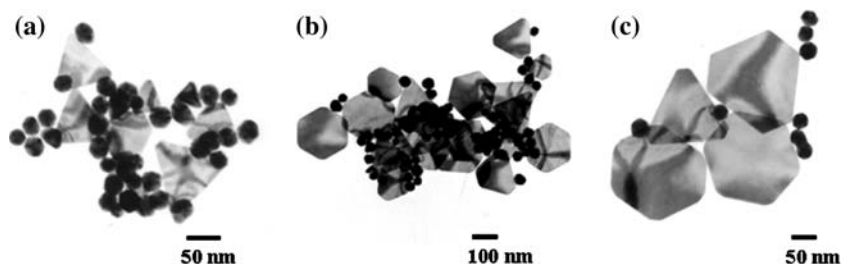
Fig. 1 Absorption spectra of the gold nanoparticles obtained by adding (a) 68 μL , (b) 65 μL , and (c) 62 μL of aqueous sodium oxalate (0.1 M) in tetrachloroaurate solution (0.01 M, 0.3 mL) under irradiation by a mercury lamp ($\lambda_{\text{max}} = 306 \text{ nm}$) for 50 min

Results and discussion

Figure 1 presents the absorption spectra of the gold nanoparticles marked with letters a, b, and c, which were obtained by varying the concentration of sodium oxalate in the reaction solution. The absorption band at 522 nm indicates the generation of spherical gold nanoparticles in the photochemical reduction. The other absorption band appearing at $>700 \text{ nm}$ in the near infrared (NIR) region indicates the presence of gold nanoparticles with shapes other than spherical. Furthermore, this broad absorption band shifts to a longer wavelength ($>1,000 \text{ nm}$) with the decrease of sodium oxalate in the reaction solution.

Figure 2a–c present the TEM images corresponding to the same solutions in Fig. 1 for obtaining the absorption spectra marked with letters a, b, and c, respectively. The gold nanoparticles with sizes varying from 25 to 80 nm give rise to band a in Fig. 1 (Fig. 2a). With the decrease of sodium oxalate, the size of the particle becomes larger to particle sizes of

Fig. 2 TEM images (a–c) corresponding to the solutions for obtaining the absorption spectra in Fig. 1a–c



50–200 nm (Fig. 2b and c), and hexagonal and truncated triangular gold nanoparticles contribute to the morphology. The duration of the light irradiation required for the photochemical reduction herein was much shorter than that reported previously (Zhou et al. 1999), which required 48 h of light irradiation by a mercury lamp ($\lambda_{\text{max}} = 253.7 \text{ nm}$, 30 W). In our approach, a lower power mercury lamp ($\lambda_{\text{max}} = 306 \text{ nm}$, 8 W) is sufficient to carry out the reaction.

We also investigate the effect of the duration of light irradiation in the photochemical reaction. Figure 3 shows the absorption bands obtained by irradiating the reaction solution with 10 min (band a), 30 min (band b), 50 min (band c), and 120 min (band d). After light irradiation for 10 min, the absorption spectrum (band a) of the reaction product presents an absorption band at $\sim 520 \text{ nm}$, representing the presence of spherical gold nanoparticles. The other band appearing at $\sim 670 \text{ nm}$ indicates the generation of gold nanoparticles with non-spherical shapes. As the illumination time increases, the absorption band at $\sim 520 \text{ nm}$ remains unchanged, while there is a red shift arising at the maximum absorption of the second band at the NIR region. Furthermore, the intensity of the absorption band at the NIR region increases with the increase of illumination time. The results indicate that the reaction tends to result in the generation of polygonal gold nanoparticles with increasing particle sizes as the extensions of illumination time. Figure 4 presents the X-ray diffraction (XRD) pattern of the generated gold nanoparticles. This pattern indicates that the nanoparticles are the fcc gold.

To examine the photothermal effect of our gold nanoparticles, a pH thermoindicator system (thymol blue (10 mM), in tris buffer (15 mM)) was employed. The ionization constant of tris buffers varies with the temperature. That is to say, tris buffers are temperature dependent. The pH of the tris buffer decreased with the elevation of the temperature. Thymol blue is an acid–base indicator. There are three levels of pH dependent

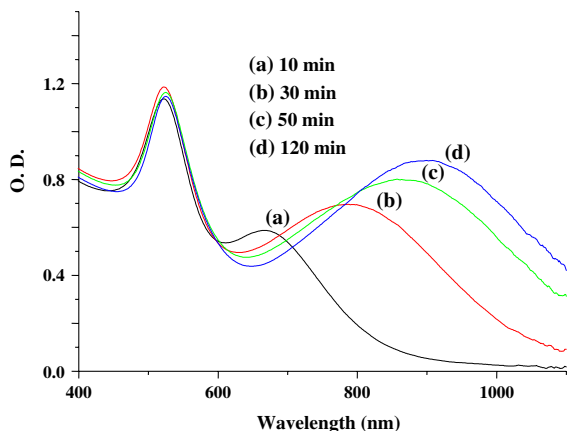


Fig. 3 Absorption spectra of the gold nanoparticles obtained by adding 65 μL of aqueous sodium oxalate (0.1 M) in tetrachloroaurate solution (0.01 M, 0.3 mL) under irradiation by a mercury lamp ($\lambda_{\text{max}} = 306 \text{ nm}$) for (a) 10 min, (b) 30 min, (c) 50 min, and (d) 120 min

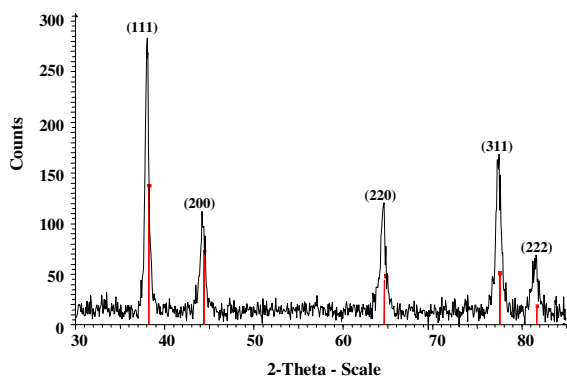
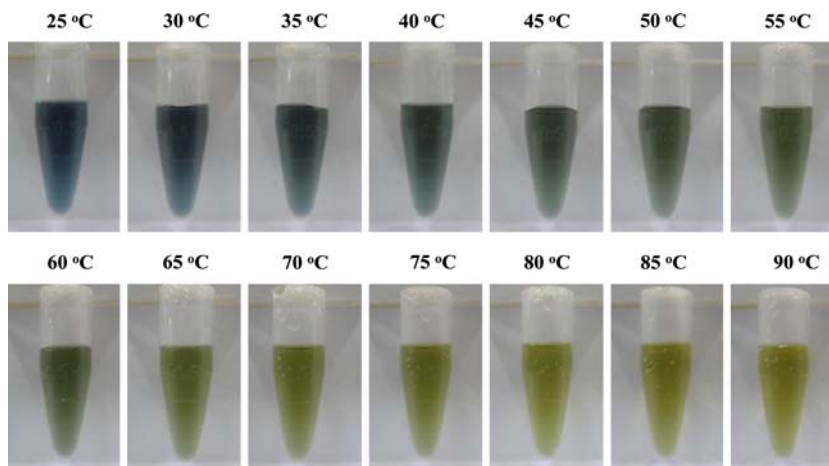


Fig. 4 XRD pattern of gold nanoparticles

Fig. 5 Photographs of the thymol blue solutions (10 mM in tris buffer (15 mM)) obtained with the temperature varying from 25 to 90 $^{\circ}\text{C}$



color-change intervals in thymol blue. That is, the color of thymol blue change from red, to yellow, to blue corresponding to the intervals of pH 1.2–2.8, 2.8–7.8, and 7.8–9.5, respectively. With the elevation of the temperature, both the pH and the intensity of the absorption band at 600 nm of the thymol blue solutions decrease. The color of thymol blue changes from blue to yellowish green as the temperature varies from 25 to 90 $^{\circ}\text{C}$ (Fig. 5). The optical density (O.D.) at the wavelength of 490 nm (A_{490}) in the absorption spectra of thymol blue is unaffected by the temperature change, while the O.D. at the wavelength of 600 nm (A_{600}) decreases as the elevation of the temperature (Fig. 6). On these bases, the ratio of A_{600} to A_{490} is generally used to monitor the temperature change in sample solutions (Aslan and Geddes 2007). Figure 7a displays the absorption spectra of the gold nanoparticle suspension containing thymol blue with the increase of the temperature from 21 to 65 $^{\circ}\text{C}$ by heating. A_{490} remains unchanged with the elevation of the temperature, but A_{600} gradually decays with the raising of the temperature. Figure 7b shows the absorption spectra of the gold nanoparticle suspension containing thymol blue under illumination of NIR light for 0–5 min. Figure 8a displays the plot of the ratio of A_{600}/A_{490} as a function of the temperature based on the absorption spectra in Fig. 7a. It is apparent that the ratio of A_{600}/A_{490} decreases with the elevation in temperature. Figure 8b shows the plot of the ratio of A_{600}/A_{490} as a function of the illumination time by NIR light based on the absorption spectra in Fig. 7b. As illumination time is increased, the ratio of A_{600}/A_{490} gradually decays. We estimated the temperatures in the samples are ~ 33 , ~ 42 , and ~ 50 $^{\circ}\text{C}$ corresponding to the

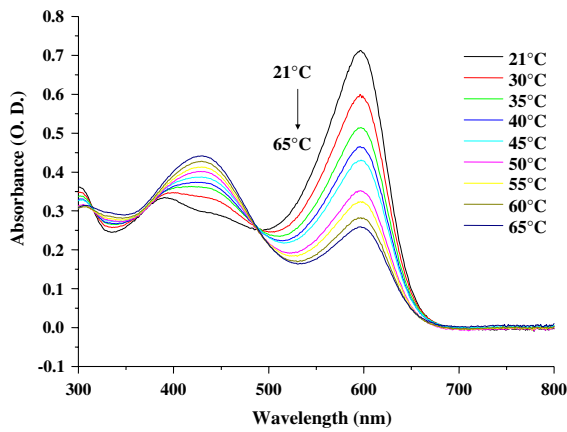


Fig. 6 Absorption spectra of the thymol blue solutions (10 mM in tris buffer (15 mM)) obtained with the temperate varying from 21 to 65 °C

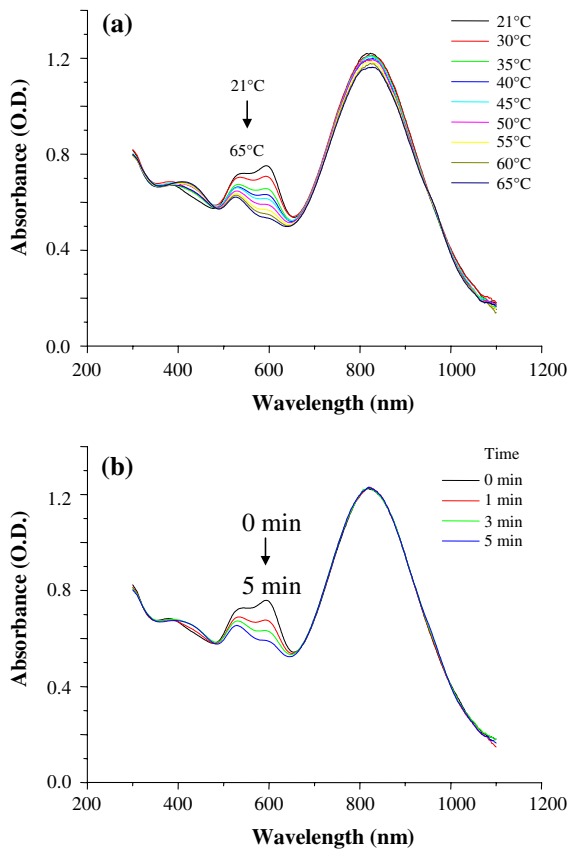


Fig. 7 (a) Absorption spectra of the gold nanoparticle suspensions containing thymol blue obtained with the temperate varying from 21 to 65 °C. (b) Absorption spectra of the gold nanoparticle suspensions containing thymol blue obtained by irradiating the suspensions by a diode laser (808 nm) for 0–5 min

illumination time of 1, 3, and 5 min, respectively. The results indicate that our gold nanoparticles have the capacity of absorbing NIR light and therefore raising the temperature of the sample solutions within a few minutes.

Conclusions

We have demonstrated that using a low power mercury lamp as the light source to irradiate a mixture of aqueous hydrogen tetrachloroaurate and sodium oxalate for more than 10 min can successfully generate polygonal gold nanoparticles, which have the capacity

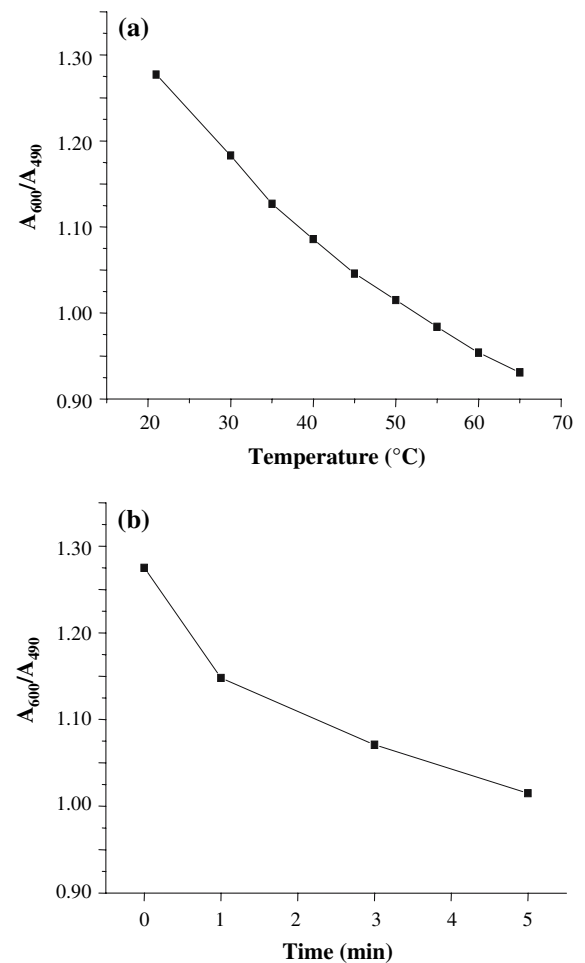


Fig. 8 (a) Plot of the ratio of A_{600}/A_{490} as a function of the temperature based on the absorption spectra in Fig. 7a. (b) Plot of the ratio of A_{600}/A_{490} as a function of the irradiation time under NIR light (808 nm) based on the absorption spectra in Fig. 7b

of absorbing NIR light. To the best of our knowledge, this approach proposes the shortest time required for generation of polygonal gold nanoparticles via photochemical reduction that has ever been reported. Another feature of this approach is that no additional reagents such as surfactants and polymers are added for generation of the polygonal gold nanoparticles. Because surfactants may cause adverse effects for animal cells, the nanoparticles should have better biocompatibility with biological systems without the presence of surfactants in the gold nanoparticle solution than those generated from other photochemical approaches. Furthermore, the presence of surfactants on the surfaces of the nanoparticles may cause some difficulties in further modification of the surfaces. Our approach eliminates the use of these unpleasant chemicals and avoids this potential problem. Additionally, it is quite economical in terms of time-saved and energy-reduced. Furthermore, we have demonstrated that the aqueous gold nanoparticles can be rapidly heated to ~ 50 °C under illumination of NIR light within 5 min. Thus, these gold nanoparticles are potentially suitable to be used as photothermal agents in hyperthermia for animal testing in vivo.

Acknowledgments We thank the National Science Council (NSC) of Taiwan for financially supporting this research. We also thank Dr. Chi-Shen Lee's group and Mr. Cheng-Tai Chen for their assistance in obtaining XRD pattern and TEM images, respectively.

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