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Preparation of Gold Nanoparticles by Reduction-Oxidation Reaction of $HAuCl_4$

$HAuCl_4$ 의 산화-환원 반응에 의한 금 나노 입자 제군

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Abstract

We prepared gold nanoparticles (Au NPs) by reduction-oxidation reaction between $HAuCl_4$ and trisodium citrate and measured the size and morphology of Au NPs by TEM for various molar ratios of $HAuCl_4$ to citrate and for various concentrations of $HAuCl_4$. UV-vis spectroscopy was used to characterize the optical properties of Au NPs. Au NPs in the size range from 14.3 nm to 20.3 nm were prepared with monodisperse distribution.

키워드 : *금 나노 입자, 산화-환원 반응, 시트르산 나트륨*
Keywords : *gold nanoparticles, reduction-oxidation reaction, trisodium citrate.*

1. Introduction

Because of many promising properties of gold nanoparticles (Au NPs) such as high absorption and scattering coefficient, large surface area and high sensitivity, gold nanoparticles can be applied to catalysis, biological and chemical sensing, surface-enhanced Raman spectroscopy and electronics [1]~[3]. There are several methods to prepare Au NPs: photochemistry [4], reverse micelles [5], arc discharge [6], radiolysis [7] and reduction-oxidation method [8]~[10].

In the reduction-oxidation method, gold nanoparticles are routinely prepared by chemical reduction of gold precursor such as $AuCl_4^-$ ions with reducing agents. There are many reducing agents such as organic acids, sugars, aldehydes, alcohols and strong reducing agents (NH_2NH_2, BH_4^-). Citrate is well-known as one of the most widely used reducing agents to prepare monodisperse spherical gold nanoparticles [8] and can also be used to prepare branched gold nanocrystals [11], nanowires [12], tadpole-shaped gold particles [13], gold nanoplates [14], etc. The gold precursors are reduced to gold nanoparticles by the reaction with citrate. The gold nanoparticles grow by the coagulation with other particles and also by the deposition of gold precursor on their surface. The size and morphology of Au NPs depend on various process variables such as reactants concentration, temperature, pH and additives. There are some researches to discuss the effects of those process variables on the

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formation kinetics and the size and morphology of Au NPs [9],[10],[15]~[18].

In this study, we prepared Au NPs by reduction-oxidation reaction for various molar ratios of $HAuCl_4$ to trisodium citrate and for various concentrations of $HAuCl_4$ and investigated the optical properties and morphology of Au NPs.

2. Experiment

All equipments were cleaned in aqua regia solution (HCl : HNO_3 = 3:1), and washed out with deionized H_2O. We used hydrogen tetra-chloroaurate hydrate ($HAuCl_4.3.5H_2O$) as a gold precursor and trisodium citrate 2-hydrate ($Na_3C_6H_5O_7.2H_2O$) as a reducing agent. We prepared the $HAuCl_4$ solutions of 0.18 mM, 0.36 mM and 0.72 mM concentrations and the trisodium citrate solutions of 0.5%, 1% and 2 % concentrations.

We added trisodium citrate into the gold precursor solution at 65°C and kept the temperature of the mixed solution until the colour of the solution changed to red and then boiled the solution for 20 minutes. We changed the molar ratio of gold precursor to reducing agent and the concentration of gold precursor to investigate the effects of those process variables on the growth of Au NPs. The Au NPs were prepared for the molar ratio of gold precursor to citrate of 1:4, 1:8 and 1:12 by adding 4 mL, 8 mL and 12 mL of 1% trisodium citrate solution, respectively, into 100 mL of 0.36 mM $HAuCl_4$ solution.

8 mL of 0.5% and 2% trisodium citrate solutions were added into 100 mL of 0.18 mM and 0.72 mM $HAuCl_4$ solutions, respectively, to

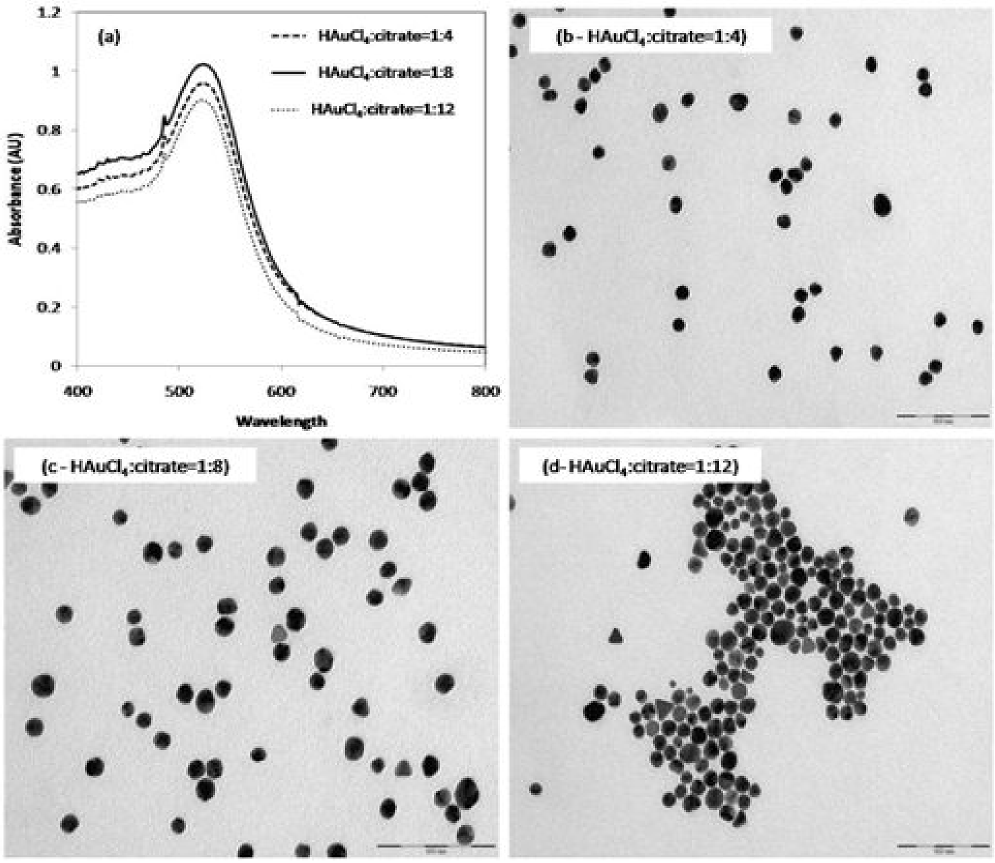

Fig. 1. UV-vis spectra (a) and TEM images of Au NPs prepared for the molar ratios of 1:4 (b), 1:8 (c) and 1:12 (d).

change the concentration of gold precursor with the same molar ratio of 1:8. UV-vis absorption spectroscopy has been used most widely to characterize the optical properties of Au NPs. The optical properties of Au NPs were measured by UV-visible spectrophotometer (UV-1600PC, Shimadzu). The size and morphology of Au NPs were examined by transmission electron microscope (TEM) (LEO 912AB Omega).

3. Results and discussions

Electron clouds can oscillate on the surface of nanoparticles by the absorption of electromagnetic radiation at a particular energy and thus solution of colloidal gold particles shows a distinctive red colour, correspondingly the absorption wavelength of 520 nm. This resonance known as surface plasmon resonance is a consequence of their small size but it can be influenced by numerous factors and in particular, solvent and surface functionalization are important contributors related with exact frequency and intensity of the band. Fig. 1 shows the UV-vis spectra (a) and TEM images of the gold nanoparticles prepared for the molar ratios of 1:4 (b), 1:8 (c) and 1:12 (d). The maximum absorption wavelengths of all samples are located at around 523 nm. With the same amount of supplied gold precursor, the particle size would be the same. In this case, trisodium citrate does not play an important role in UV-vis absorption. By TEM measurement, for the molar ratio of 1:4, 1:8 and 1:12, the average sizes of Au NPs are 15.0 nm, 15.6 nm and 15.3 nm, respectively. In the reduction-oxidation reaction between $HAuCl_4$ and citrate, citrate reduces Au precursor to Au NPs and surrounds

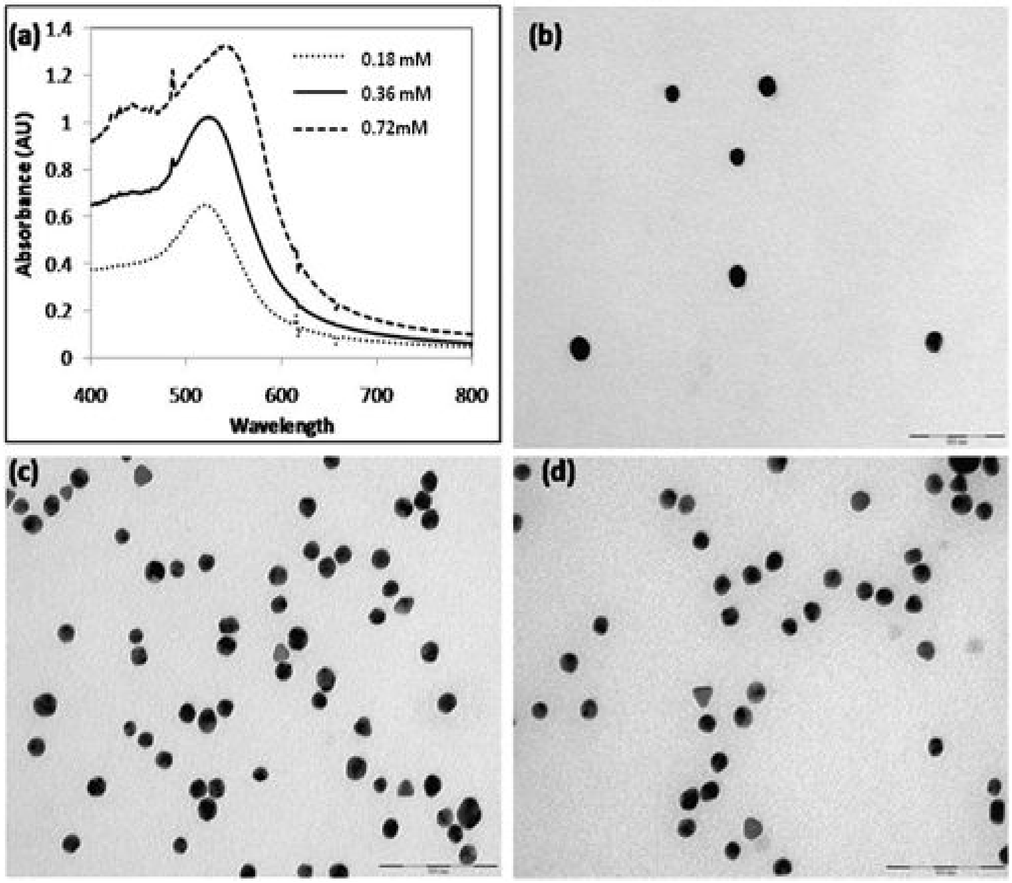

Fig. 2. UV-vis spectra (a) and TEM pictures of Au NPs prepared by 0.18 mM (b), 0.36 mM (c) and 0.72 mM (d) of $HAuCl_4$ solution.

those Au NPs to prevent the collision of those Au NPs with other particles and the monodisperse Au NPs can be prepared. The decrease in the molar ratio of gold precursor to citrate or the increase in amount of citrate not only promotes the nucleation of Au NPs by the faster reduction reaction and results in the smaller particle size but also enhances the dispersity of Au NPs and expedite the growth process by the diffusion of gold atoms into the Au NPs surface and tends to form bigger particles. The strong and narrow UV-vis absorption peaks in Fig. 1(a) indicate that monodisperse Au NPs were prepared, which can be seen in the TEM measurement.

Fig. 2. shows the UV-vis spectra (a) and TEM images of Au NPs prepared for the Au precursor concentrations of 0.18 mM (b), 0.36 mM (c) and 0.72 mM (d). For the $HAuCl_4$ concentrations of 0.18 mM, 0.36 mM and 0.72 mM, the maximum absorption wavelengths of the Au NPs colloidal solutions are 520 nm, 523 nm and 541 nm, respectively. The red-shift of absorption band indicates that the particle size increases with the increase of $HAuCl_4$ concentration. By TEM observation, the average particle sizes were measured as 14.3 nm, 15.6 nm and 20.3 nm, respectively with the narrow size distribution. As the concentration of Au precursor increases, nucleation rate becomes faster and the smaller Au NPs are generated. However, as the concentration of Au precursor increases, Au atom concentration becomes higher by reduction reaction and Au NPs become larger by the faster diffusion of Au atoms into the surface and growth process.

4. Conclusion

Gold nanoparticles were prepared by the reduction of $HAuCl_4$ with trisodium citrate for various molar ratios of $HAuCl_4$ to citrate and for various concentrations of $HAuCl_4$. Au NPs in the size range from 14.3 nm to 20.3 nm were prepared with monodisperse distribution. The increases in the amount of citrate and in the concentration of Au precursor enhance the nucleation rate of Au NPs and result in higher particle concentration. As the concentration of Au atom increases, the coagulation between particles and diffusion become faster and Au NPs grow more quickly, which results in formation of bigger particles.

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