

Hydrogen-assisted fabrication of spherical gold nanoparticles through sonochemical reduction of tetrachloride gold(III) ions in water

Toshio Sakai,*¹ Hiroto Enomoto,² Hideki Sakai² and Masahiko Abe²

¹Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

²Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan.

* To whom correspondence should be addressed.

Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

Phone: +81-26-269-5405

Fax: +81-26-269-5424

E-mail: tsakai@shinshu-u.ac.jp

Abstract

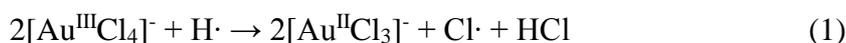
Spherical gold nanoparticles (AuNPs) were selectively synthesized through sonochemical reduction of tetrachloride gold(III) ions ($[\text{AuCl}_4]^-$) in an aqueous solution of hydrogen tetrachloroaurate (III) tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) with the aid of hydrogen (H_2) gas in the absence of any additional capping agents. On the other hand, various shaped-AuNPs such as spherical nanoparticles, triangular and hexagonal plates were formed from sonochemical reduction of $[\text{AuCl}_4]^-$ in argon (Ar)-, nitrogen (N_2)- or oxygen (O_2)-purged aqueous $[\text{AuCl}_4]^-$ solutions. The selective fabrication of spherical AuNPs assisted by H_2 gas is most likely attributed to the generation of hydrogen radicals ($\text{H}\cdot$) promoted by the reaction of H_2 introduced and hydrogen oxide radicals ($\cdot\text{OH}$) produced by sonolysis of water.

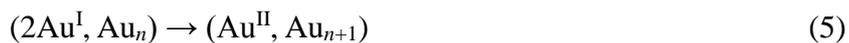
Key words: Gold nanoparticles; Ultrasonication; High-frequency ultrasound; Sonochemical reduction; Dissolved gas; Hydrogen gas.

1. Introduction

Unique properties of nanometer-scale metal particles (metal nanoparticles) such as size- and shape-dependent optical, catalytic, magnetic and electronic properties have led to the evolution of nanotechnology [1-12]. Methodology to selectively synthesize metal nanoparticles with a particular size and shape enables rational control the properties of metal nanoparticles. Thus, a number of works have focused on the development of synthetic methods for the preparation of metal nanoparticles in a size or shape-selected and -controlled manner [13-24]. In addition, the synthetic strategy of metal nanoparticles in view of environmental concerns (e.g., utilization of non-toxic chemicals, environmentally benign solvents, and renewable materials) is emerging an issue that merit important consideration [25, 26].

Conventional methods of metal nanoparticle synthesis from metal ion reduction in solutions require capping agents (e.g., alkylthiols, surfactants and amphiphilic polymers) and reducing agents (e.g., NaBH₄, hydrazine and citric acid) to achieve the controlled synthesis of metal nanoparticles [13-24]. Numerous reports have described the size- and shape-control of metal nanoparticles in terms of molecular characteristics of capping agents and kinetics of metal ion reduction by reducing agents [13-24]. On the other hand, we have recently investigated the synthesis of gold nanoparticles (AuNPs) through the sonochemical reduction of tetrachloride gold(III) ions ([AuCl₄]⁻) in aqueous solutions in the absence of any additional reducing and capping agents [27]. The AuNPs are formed through the reduction of [AuCl₄]⁻ by hydrogen radicals (H[·]) generated from sonolysis of water (H₂O → H[·] + ·OH) as follows [28-30]:





The AuNPs sonochemically synthesized in the absence of any additional reducing and capping agents should provide advantage for applications (e.g., electric device and catalyst) because of no byproduct afforded from reducing agents and no capping agent around AuNPs. However, the size and shape of the AuNPs are not well controlled in this sonochemical reduction method in the absence of reducing and capping agents. For example, triangular and hexagonal Au nanoplates are formed coexisting with spherical AuNPs through the sonochemical reduction of tetrachloride gold(III) ions ($[\text{AuCl}_4]^-$) in an argon (Ar)-purged aqueous hydrogen tetrachloroaurate (III) tetrahydrate ($0.1 \times 10^{-3} \text{ mol L}^{-1}$) solution in an ultrasonic bath (950 kHz, 300 W) at 25 °C (see **Figure 1a**). A bimodal absorption band centered at ~520 nm and ~720 nm is observed in the AuNP dispersion (see **Figure 2a**), which is originated from the surface plasmon resonance (SPR) of the spherical AuNPs and plate-like Au particles, respectively. Therefore, the development of the controlled synthesis of AuNPs using sonochemical reduction method is an important and challenging task. The size- and shape-controlled AuNPs should provide various opportunities for the various industrial fields such as catalyst, electronics and medical fields. Furthermore, the simplified system of metal nanoparticle synthesis (in the absence of any additional reducing and capping agents) should manifest the essential feature on size-, shape- and stability-control of metal nanoparticles synthesized in aqueous solutions.

In the present work, we examine the effect of the dissolved gas on the size and shape of AuNPs prepared using the sonochemical reduction method because the dissolved gas in aqueous solutions plays a critical role for sonochemical reaction [31]. In particular, we applied argon (Ar), nitrogen (N_2), oxygen (O_2) and hydrogen (H_2) gases as purged gases.

2. Experimental

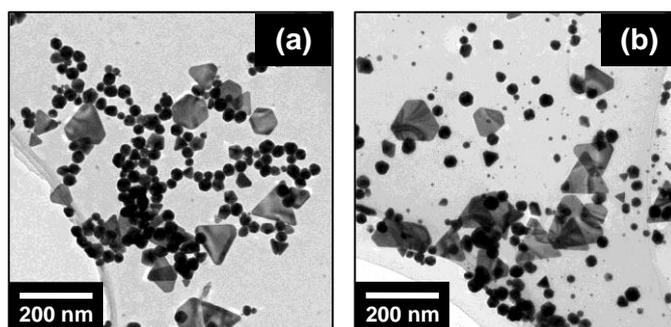
Gold nanoparticles (AuNPs) were prepared through the sonochemical reduction of tetrachloride gold(III) ions ($[\text{AuCl}_4]^-$) in a $0.1 \times 10^{-3} \text{ mol L}^{-1}$ aqueous hydrogen tetrachloroaurate (III) tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, Wako) solution in an ultrasonic bath with the frequency of 950 kHz (300 W, Mitsui Electric Co. Ltd.) for 8 min at 25 °C. The frequency of ultrasound (950 kHz) and the period of ultrasonication (8 min) that we applied in this experiment were determined following our previous work [27]. In order to elucidate the effect of gas on the size and shape of AuNPs, the AuNPs were sonochemically prepared from argon (Ar)-, nitrogen (N_2)-, oxygen (O_2)- and hydrogen (H_2)-purged aqueous hydrogen tetrachloroaurate (III) tetrahydrate solutions. Period of gas purging was 30 min. Note that gas purging alone (in the absence of ultrasonication) does not reduce $[\text{AuCl}_4]^-$ in aqueous solutions.

Formation of AuNPs was confirmed by monitoring the absorption spectra originating from surface plasmon resonance (SPR) of the AuNPs [32-35] using a UV-visible spectrometer (U-3310, Hitachi High Technologies Co.). The size and shape of the obtained AuNPs were observed by transmission electron microscopy (TEM) (H-7650, Hitachi High Technologies Co.) at an accelerating voltage of 120 kV under a low electron dose.

3. Results and Discussion

As shown in **Figure 1a**, triangular and hexagonal Au nanoplates were formed coexisting with spherical AuNPs through the sonochemical reduction of $[\text{AuCl}_4]^-$ in an Ar-purged aqueous $[\text{AuCl}_4]^-$ solution in an ultrasonic bath with the frequency of 950 kHz at 25 °C for 8 min. Correspondingly, bimodal absorption bands centered at ~520 nm and ~720 nm originated from the surface plasmon resonance (SPR) of the spherical AuNPs and plate-like particles [32-36], respectively, were observed in the AuNP dispersion (see **Figure 2a**). AuNPs formed in a N_2 -purged aqueous $[\text{AuCl}_4]^-$ solution were similar to those in the Ar-purged aqueous $[\text{AuCl}_4]^-$ solution, in which mixture of spherical nanoparticles, triangular

and hexagonal plates were observed in TEM image (see **Figure 1b**). Also bimodal absorption bands centered at ~ 520 nm and ~ 850 nm were observed (see **Figure 2b**). In the case of O_2 -purged aqueous $[AuCl_4]^-$ solution, larger particles were formed compared with those in Ar- and N_2 -purged aqueous $[AuCl_4]^-$ solutions (see **Figure 1c**). Absorption peak corresponding to SPR of AuNPs formed in the O_2 -purged aqueous $[AuCl_4]^-$ solution was shifted to longer wavelength (~ 570 nm) and became broader compared with those in Ar- and N_2 -purged aqueous $[AuCl_4]^-$ solutions (see **Figure 2c**). This supports the formation of larger-sized AuNPs in the O_2 -purged aqueous $[AuCl_4]^-$ solution observed in TEM image shown **Figure 1c**. On the other hand, spherical AuNPs with the diameter of ~ 20 nm were selectively formed from a H_2 -purged aqueous $[AuCl_4]^-$ solution by ultrasonication (see **Figure 1d**). At the same time, a single peak absorption band centered at ~ 520 nm was observed but a long-wavelength SPR band originating from the plate-like particles was not observed (see **Figure 2d**). Note here that the spherical AuNPs produced through sonochemical reduction of $[AuCl_4]^-$ in the H_2 -purged aqueous solution remained unchanged for more than one month. This is most likely due to the adsorption of chloride ions (Cl^-) onto surface of AuNPs. Since Cl^- ions prefer to adsorb onto gold surface [37, 38], Cl^- ions should affect strongly the crystal growth and stabilization. Indeed, we confirmed that plate-like particles were preferably formed rather than spherical AuNPs with the addition of HCl or NaCl in the sonochemical synthesis of AuNPs [27]. This means that Cl^- ions adsorb a certain crystal facet, and thereby $[AuCl_4]^-$ reduction occurs on other crystal facets [39, 40].



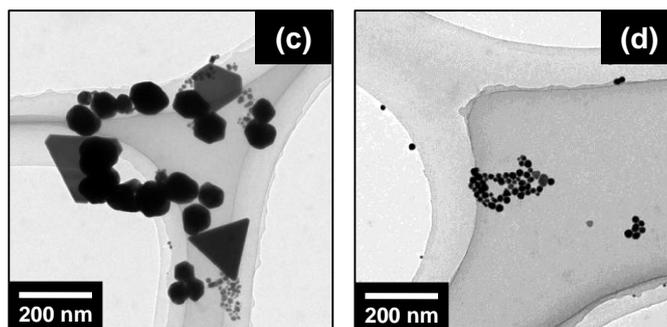


Figure 1. TEM images of AuNPs formed from an (a) Ar-, (b) N₂-, (c) O₂- and (d) H₂-purged aqueous 0.1 mM [AuCl₄]⁻ solution using 950 kHz ultrasound for 8 min at 25 °C. The aqueous [AuCl₄]⁻ solutions were purged by gas for 30 min.

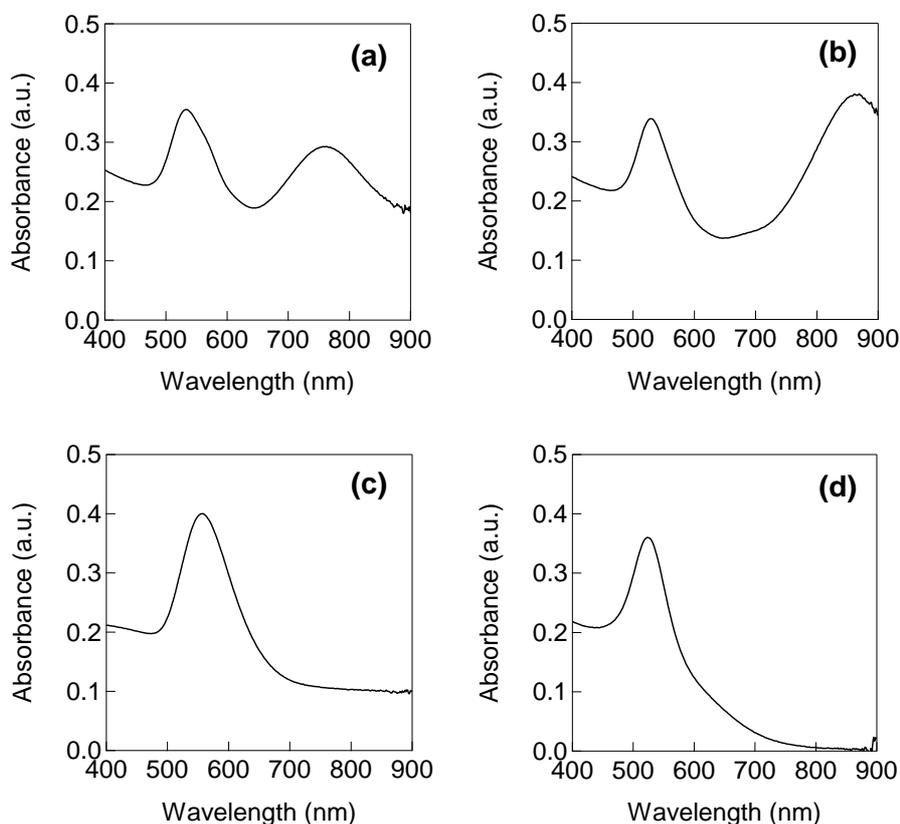
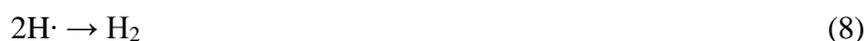
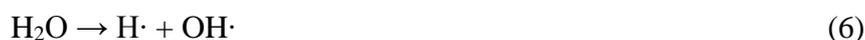


Figure 2. Absorption spectra originating from SPR of AuNPs formed from an (a) Ar-, (b) N₂-, (c) O₂- and (d) H₂-purged aqueous 0.1 mM [AuCl₄]⁻ solution using 950 kHz ultrasound for 8 min at 25 °C. The aqueous [AuCl₄]⁻ solutions were purged by gas for 30 min.

Size and shape of metal nanoparticles are typically determined by a competition

between nucleation (metal ion reduction in bulk) and growth (metal ion reduction on nuclei) processes [1, 29]. For a given initial concentration of metal ions, the average volume per metal particle formed (V_p) is inversely proportional to the number of particles (N_p): $V_p \propto 1/N_p$. Since the number of particles (N_p) is equal to that of the seeds (N_s), which is correlated to the initial reduction sites (N_r), the particle volume, V_p , can be controlled by the number of initial reduction sites: $V_p \propto 1/N_r$. Since the number of reduction sites (N_r) is proportional to the amount of reducing species (C_r): $N_r \propto C_r$, the amount of reducing species (C_r) determines the final volume (size) of particles formed: $V_p \propto 1/C_r$. Namely, the increase in the amount of reducing species such as $H\cdot$ should lead to the formation of smaller particles due to the increase of reduction sites. Then, we considered that the formation of smaller spherical AuNPs in the H_2 -purged aqueous $[AuCl_4]^-$ solution would be attributed to the increase in the amount of reducing species ($H\cdot$) due to the reaction of H_2 with $\cdot OH$ generated from sonolysis of water as follows [41-45].



The increase of reducing species ($H\cdot$) is expected to promote the nucleation process due to the increase of reduction sites (the amount of reducing species). Generally, hydrogen radicals ($H\cdot$) and hydrogen oxide radicals ($OH\cdot$) generated from sonolysis of water (see reaction 6) rebind with radical species ($H\cdot$, $OH\cdot$) and rebinding products (H_2 and H_2O_2) (see reactions 7-11) [41-45]. These rebinding of $H\cdot$ with radical species ($H\cdot$, $OH\cdot$) (reactions 7

and 8) and H_2O_2 (see reaction 10) would be competitive reactions for the reaction of $\text{H}\cdot$ with $[\text{AuCl}_4]^-$ (see reactions 1 and 3). On the other hand, the reaction 11 indicates the generation of $\text{H}\cdot$ by re-binding of $\text{OH}\cdot$ with H_2 . This implies that the generation of $\text{H}\cdot$ during the sonication is promoted in the presence of H_2 . Namely, the introduction of H_2 gas into an aqueous $[\text{AuCl}_4]^-$ solution would promote the reaction of $\text{OH}\cdot$ with H_2 and the resulting generation of $\text{H}\cdot$ (that acts as a reducing species for $[\text{AuCl}_4]^-$) [43]. As a result, smaller spherical AuNPs would be formed in the H_2 -purged aqueous $[\text{AuCl}_4]^-$ solution (see **Figure 1d**). In the presence of oxygen (O_2) in aqueous solutions, $\text{H}\cdot$ would be scavenged by O_2 (see reaction 12) [41-45] and $\text{O}\cdot$ (see reaction 14) so that the amount of $\text{H}\cdot$ should be smaller than that in the absence of O_2 in the solutions. This would result in the formation of larger particles. Indeed, larger AuNPs were formed in O_2 -purged aqueous solution (see **Figure 1c**).



Since argon (Ar), nitrogen (N_2) and its radical species ($\text{N}\cdot$) do not interact with hydrogen radical ($\text{H}\cdot$) (see reactions 15-19) [41-45], the size and shape of AuNPs formed would not be affected by the introduction of Ar and N_2 gas into aqueous $[\text{AuCl}_4]^-$ solutions. Consequently, AuNPs with similar size and shape would be formed in Ar- and N_2 -purged aqueous $[\text{AuCl}_4]^-$ solutions (see **Figure 1a and b**).





We also considered the influence of cavitation effects on the size and shape of AuNPs formed in sonochemical synthesis. The cavitation effects are known to be affected by the physical properties of atmospheric gases such as specific heats, $\gamma = C_p/C_v$, the thermal conductivity and the solubility of gas into medium [46]. The maximum temperature in the collapsing bubble, T_{\max} , is given by the following equation [46]:

$$T_{\max} = T_0 P_{\max}(\gamma - 1)/P \quad (20)$$

where T_0 is the temperature of the sample solution, P_{\max} is the maximal pressure in the liquid at the moment of transient collapse, and P is the sum of the vapor pressure of the solvent and the atmospheric gas pressure. Since the γ value of Ar, N₂, O₂ and H₂ gas is 1.664, 1.404, 1.393 and 1.384, respectively [47], the maximum temperature inside the collapsing bubbles, T_{\max} , should increase with the order of H₂ < O₂ < N₂ < Ar. Thermal conductivity of Ar, N₂, O₂ and H₂ gas is 17.4, 26, 26.3 and 186.9 (mW m⁻¹ K⁻¹) at 25 °C and 1 atm, respectively [47], suggesting that the maximum temperature inside the collapsing bubbles increases with the order of H₂ < O₂ < N₂ < Ar. The solubility of Ar, N₂, O₂ and H₂ gas into water is 3.42, 1.61, 3.12 and 1.92 (x 10⁻² m³ m⁻³) at 25 °C and 1 atm, respectively [47], which is related to the number of cavitation bubbles. Taking such atmospheric parameters into accounts, the cavitation effect and the resulting generation of reducing species (H \cdot) should be promoted with the order of H₂ < O₂ < N₂ < Ar. This suggests that the amount of reducing species (C_r) generated by cavitation effect in Ar, N₂, O₂ and H₂ atmosphere should increase with the order of H₂ < O₂ < N₂ < Ar. Namely, the final volume (size) of AuNPs formed should increase with the Ar < N₂ < O₂ < H₂.

From the above mentioned, it is realized the introduction of H₂ gas into aqueous [AuCl₄]⁻ solutions induces two opposing effects on the AuNP formation and size determination in sonochemical synthesis. So, it is concluded that the formation of smaller spherical AuNPs in H₂-purged aqueous [AuCl₄]⁻ solution that we observed in this work is most likely attributed to the promotion of H· generation due to the reaction of OH· with H₂.

4. Conclusions

We were successful to fabricate the spherical AuNPs from sonochemical reduction of [AuCl₄]⁻ with the aid of hydrogen gas (H₂). The introduction of H₂ gas into an aqueous [AuCl₄]⁻ solution would promote the generation of hydrogen radicals (H·) by the reaction of H₂ and hydrogen oxide radicals (·OH) produced by sonolysis of water. As a result, smaller spherical AuNPs would be formed because nucleation process would be more dominant than growth process due to the increase in the number of reduction sites. Utilization of hydrogen gas (H₂) should provide benefits in the production of the pure metal nanoparticles because H₂ produces only water (H₂O) after reaction while the conventional methods typically produce byproducts from the reaction of metal ions with reducing agents (e.g., NaBH₄, hydrazine and citric acid). These findings reported here should provide insights and offer further opportunities on the synthetic strategy in the sonochemical synthesis of metal nanoparticles in solutions.

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