

# Sonochemical reduction method for controlled synthesis of metal nanoparticles in aqueous solutions

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## ABSTRACT

Various types of methods for the synthesis of metal nanoparticles have been actively researched to obtain functional nanomaterials such as catalysts and sensors. In this study, sonochemical reduction methods for the synthesis of metal nanoparticles were investigated in aqueous solutions. The rates of sonochemical reduction of  $\text{MnO}_4^-$ ,  $\text{Au}^{3+}$ ,  $\text{Au}^+$  and  $\text{Pd}^{2+}$  were investigated under various irradiation conditions. To control the size and shape of metal nanoparticles, the control of the rates of reduction was found to be important. In the presence of an organic stabilizer such as citric acid, the size of the Au nanoparticles formed from the sonochemical reduction of  $\text{Au}^{3+}$  was able to be controlled. In the presence of cetyltrimethylammonium bromide (CTAB), Au nanorods with different aspect ratio were able to be synthesized by use of the sonochemical reduction of  $\text{Au}^+$ .

## INTRODUCTION

Sonochemical processes have been actively researched in the field of the synthesis of metal nanoparticles and nanostructured materials. It is important to control the reduction of metal ions, because the reduction processes can be often applied to the synthesis of various functional materials. There are a number of reports using sonochemical processes to synthesize various types of materials such as Fe nanoparticles [1], CdS nanoparticles [2],  $\text{TiO}_2$  nanoparticles [3], Pd-Sn nanoparticles [4], self-assembled  $\text{SrMoO}_4$  superstructures [5], hollow  $\text{PbWO}_4$  nanospindles [6], Pt-Ru bimetallic nanoparticles [7], meso- and macro-porous  $\text{TiO}_2$  [8], Pt nanoparticles on multi-walled carbon nanotubes [9],  $\text{Ag}_2\text{Se}$  nanocrystals [10] and hollow PbS nanospheres [11].

The synthesis of various types of metal nanoparticles has also been studied by use of the sonochemical reduction of the corresponding metal ions [12-15]. In this paper, the sonochemical reduction of  $\text{MnO}_4^-$ ,  $\text{Au}^{3+}$ ,  $\text{Au}^+$  and  $\text{Pd}^{2+}$  in the absence and presence of organic additives are investigated in relation to the synthesis of size and shape controlled metal nanoparticles.

## EXPERIMENTAL

Ultrasonic irradiation was performed using a 65 mm $\phi$  oscillator and a 200 kHz ultrasonic generator (Kaijo 4021 type, 200 W). The details of the irradiation set-up and the characteristics of the reaction vessel are described elsewhere [12]. An argon saturated aqueous solution containing a metal ion in the absence and presence of an organic stabilizer was irradiated in the water bath, which was maintained at a constant temperature by a cold water circulation system. The vessel was mounted at a constant position. The reaction vessel was closed from air during irradiation. When the effects of alcohols on the sonochemical reduction were investigated, alco-

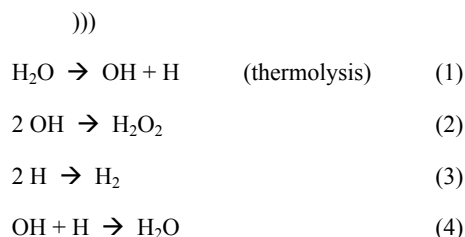
hols were injected into the solution with a microsyringe through a silicon rubber septum after Ar bubbling. After irradiation, the solution was taken by a syringe through the septum and then placed in a vial. The absorption spectra and extinction spectra of the irradiated solutions were measured by an UV-visible spectrophotometer. The synthesized metal nanoparticles were analysed by a transmission electron microscope.

## RESULTS AND DISCUSSION

### Sonochemical reduction of $\text{MnO}_4^-$ to $\text{MnO}_2$

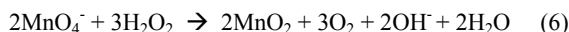
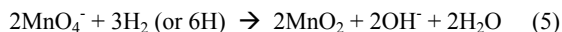
$\text{MnO}_2$  is one of the useful materials for the application to electrochemical capacitors, Li-batteries, sensors, catalysts, adsorbents, etc. It is important to control the size, shape and crystal structure of  $\text{MnO}_2$  nanoparticles, because it results in the changes in the physicochemical properties of  $\text{MnO}_2$  nanoparticles. Therefore, a number of preparation methods have been studied.

It has been reported that sonochemical processes provide unique reaction fields comprised of high temperature and high pressure cavitation bubbles: the following reactions occur, when an aqueous solution is sonicated under Ar atmosphere.



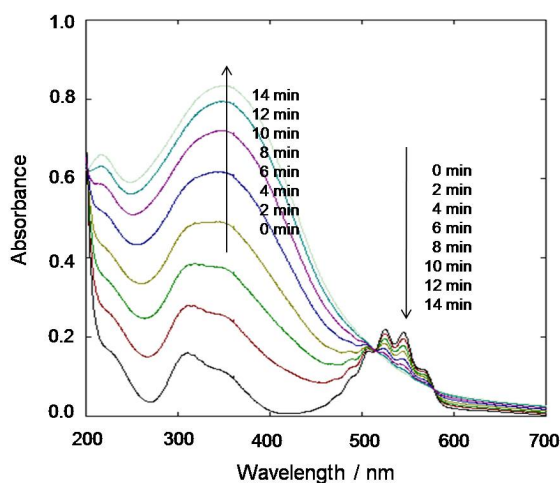
where the symbol ))) corresponds to the ultrasonic irradiation. The thermolysis of water molecules occurs due to high temperature and high pressure cavitation bubbles [16]. In pure water, OH radicals and H atoms that are formed rapidly recombine to form  $\text{H}_2\text{O}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$ .

To synthesize  $\text{MnO}_2$  nanoparticles, the reduction of  $\text{MnO}_4^-$  to  $\text{MnO}_2$  is effective. When an aqueous solution of  $\text{MnO}_4^-$  is sonicated in the absence of organic additives, the following reactions are suggested to occur [14].



where it should be noted that  $\text{H}_2\text{O}_2$  acts as a reductant for  $\text{MnO}_4^-$ . If the  $\text{MnO}_2$  solution was further irradiated, the reduction of  $\text{MnO}_2$  to  $\text{Mn}^{2+}$  progressed by the reaction with  $\text{H}_2\text{O}_2$ .

To understand the mechanism of the sonochemical reduction of  $\text{MnO}_4^-$  in more details, the effects of alcohols were investigated. Figure 1 shows the changes in the absorption spectra of 0.1 mM  $\text{MnO}_4^-$  aqueous solution containing 3.0 mM 1-butanol during ultrasonic irradiation. It can be seen that the absorption peaks corresponding to  $\text{MnO}_4^-$  at around 530 nm gradually disappear and a new broad peak at around 360 nm emerges. Based on the previous paper [14], this new peak at around 360 nm can be attributed to colloidal  $\text{MnO}_2$  particles. In Figure 1, two isosbestic points are also observed at around 510 nm and 580 nm, indicating that  $\text{MnO}_4^-$  is certainly reduced to form colloidal  $\text{MnO}_2$  particles by ultrasonic irradiation. As seen in Figure 1, the reduction of  $\text{MnO}_4^-$  to  $\text{MnO}_2$  finished at 14 min irradiation.



**Figure 1.** Changes in absorption spectra of  $\text{MnO}_4^-$  aqueous solution during ultrasonic irradiation under Ar atmosphere. Cell length: 1.0 cm.

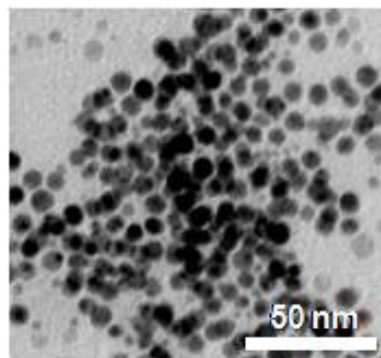
In the previous paper [14], we reported that the sonochemical reduction of  $\text{MnO}_4^-$  to  $\text{MnO}_2$  in pure water almost finished at 8 min irradiation under the same irradiation condition. Taking into account the previous result, the rate of  $\text{MnO}_4^-$  reduction is found to become slower by the addition of 1-butanol (3mM). When the concentration of 1-butanol was changed, unique reduction behaviour was observed: the rates of  $\text{MnO}_4^-$  reduction decreases as the concentration of 1-butanol increases and then starts to increase at higher concentration of 1-butanol. In the case of other alcohols, similar reduction behaviour was observed.

It is reported that organic radicals formed from the reaction of organic additives with OH radicals act as reducing species for the reduction of metal ions [12-15]. In addition, some

reducing radicals and unstable products are also formed from the pyrolysis reaction of organic additives and water [12-15]. Therefore, the amounts of the formed reducing species are strongly dependent on the concentrations of 1-butanol. At 100 mM of alcohols, the rates of  $\text{MnO}_4^-$  reduction was in the order methanol < ethanol < 1-propanol < 1-butanol. This order would be due to the difference of hydrophobicity of alcohol molecules. Higher hydrophobic molecules can accumulate easily at the interface of acoustic cavitation bubbles, resulting in that larger amounts of reductant are produced.

### Sonochemical reduction of $\text{Au}^{3+}$ to $\text{Au}^0$ and $\text{Pd}^{2+}$ to $\text{Pd}^0$

Au nanoparticles have been widely applied to various functional materials, such as analytical probes, catalysts, sensors, and nonlinear optics materials. There are many reports on the sonochemical reduction of  $\text{Au}^{3+}$  to  $\text{Au}^0$ . However, the mechanism of the sonochemical reduction is still unclear. In particular, the roles of organic radicals on the reduction of  $\text{Au}^{3+}$  are unclear. To discuss the effects of organic radicals, the rates of  $\text{Au}^{3+}$  reduction were investigated in the wide concentration range of organic additives. It was found that reducing radicals and unstable products formed from the pyrolysis reaction of organic additives and water mainly affect the reduction of  $\text{Au}^{3+}$ . In the presence of citric acid and 1-propanol, Au nanoparticles were formed as seen in Figure 2. The average size of the formed Au nanoparticles was 7.9 nm. The size of the formed Au nanoparticles increased with increasing initial concentration of  $\text{Au}^{3+}$ .



**Figure 2.** TEM image of sonochemically prepared Au nanoparticles in the presence of citric acid and 1-propanol.

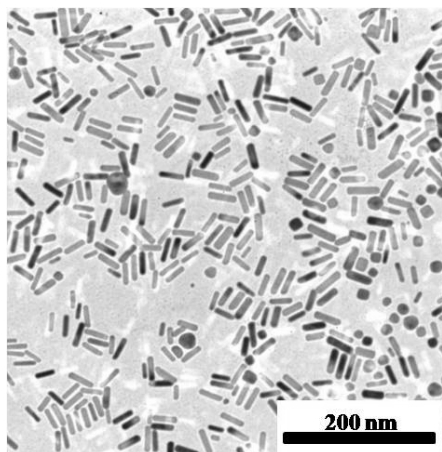
Pd is also used as catalysts and is expected as an alternative material of Pt, because Pd is cheaper than Pt and is 50 times more abundant than Pt. The size and shape of Pd nanoparticles affect the catalytic activity and selectivity of Pd. By use of the sonochemical reduction of  $\text{Pd}^{2+}$  in an aqueous solution, the size of the formed Pd nanoparticles can be controlled.

### Sonochemical reduction of $\text{Au}^+$ to $\text{Au}^0$ and synthesis of Au nanorods

When ascorbic acid was added into the solution of  $\text{Au}^{3+}$  ( $[\text{AuCl}_4]^-$ ), the color of solution changed from pale yellow to transparent. This color change is due to that the reduction of  $\text{Au}^{3+}$  to  $\text{Au}^0$  occurs. Appropriate amounts of CTAB and  $\text{AgNO}_3$  are added in this solution to prepare the sample solution. When ultrasonic irradiation was performed to this sample solution, the reduction of  $\text{Au}^+$  to  $\text{Au}^0$  occurred.

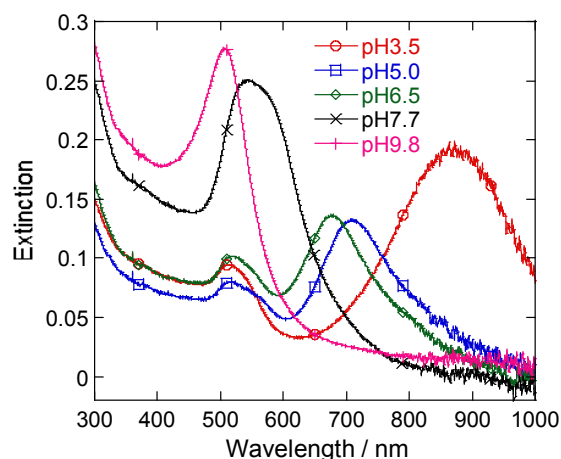
A representative TEM photograph of the sonochemically-formed Au nanoparticles is shown in Figure 3. It can be seen that most of the formed nanoparticles have a rod shape in the size range of 10 to 50 nm. It is suggested that CTAB and  $\text{AgNO}_3$  act as effective capping agents for the controlled growth

of Au nanoparticles, so that the formation of Au nanorods occurs during the sonochemical reduction of  $\text{Au}^+$ .



**Figure 3.** TEM image of Au nanorods and nanoparticles formed after ultrasonic irradiation of the sample solution of  $\text{Au}^+$  under Ar atmosphere at pH 3.5 [Source [13]].

Au nanorods show interesting physicochemical properties related to the size and aspect ratio of the nanorods. Therefore, Au nanorods have received much attention in a wide variety of applications such as contrast agents, sensors, surface enhanced Raman spectroscopy, photothermal therapy of cancer cells, and optical data storages. It is important to control the size and aspect ratio of Au nanorods. It was found that the pH value of the solution [13] and irradiation time strongly affect the size and aspect ratio of Au nanorods. Figure 4 shows the extinction spectra of the sonochemically prepared gold nanoparticles after 180 min irradiation for the different pH solution. It can be seen that the peak wavelength of the longitudinal plasmon band decreases as the pH of the solution increases. The change in the peak wavelength of the longitudinal plasmon band is closely related to the change in the aspect ratio of Au nanorods.



**Figure 4.** Effects of pH on the formation of Au nanorods and nanoparticles. Cell length: 0.5 cm [Source 13].

It is suggested that the sonochemical formation of Au seeds with an appropriate size for the formation of Au nanorods occurs: once the formation of Au seeds occurs, the reduction of  $\text{Au}^+$  ions with ascorbic acid should proceed catalytically on Au seeds as well as the sonochemical reduction of  $\text{Au}^+$  ions.

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