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PREPARATION OF STABLE SUSPENSION OF GOLD NANOPARTICLES IN WATER BY SONOCHEMISTRY METHOD

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ABSTRACT : It had been reported that the sonochemical reduction of Au (III) in the presence of an organic additive proceeds via the following reaction: (i) formation of radical H (*H) from sonolysis of water (ii) formation of *R and H_2 from the abstraction reaction of organic additive with *OH or *H (iii) pyrolysis radicals and unstable products are formed by pyrolysis of organic additives and water (iv) the reduction of Au (III) proceeds by the reaction with various reducing species. In this work, stable suspension of gold nanoparticles were prepared using sonochemical synthesis by reduction of Au(III) in water without adding any reducing agent in the presence of a small amount of 2-propanol by using 20 KHz ultrasonic probe. 2-propanol had been used as an accelerator for the reduction of Au (III) and polyvinyl pyrrolidone (PVP) had been used in the aqueous solution to prevent clustering of the formed gold nanoparticles. The effects of different concentration of PVP on the size and shape of gold nanoparticles had been studied. As a comparison, solution containing PVP and trisodium citrate had been reported here. The formation of gold nanoparticles had been confirmed by using UV-Visible Spectroscopy. The morphology and size of gold nanoparticles were analyzed by using a Transmission Electron Microscope. Our results suggested that when we increased the concentration of PVP, the size of gold nanoparticles will decrease. When we add citrate into the solution, the particle size of gold nanoparticles will actually become smaller comparing to the solution without citrate.

KEYWORDS : Gold nanoparticles, sonochemical reduction, Transmission Electron Microscope

INTRODUCTION

Metal nano-sized particles of noble metals have attracted great interest in various fields of chemistry due to their unique properties such as size- and shape-dependent optical, magnetic, electronic and catalytic properties (Sakai *et al.*, 2008, Park *et al.*, 2006, Okitsu *et al.*, 1996). Due to this reason, extensive development on the simple and versatile methods of these nanoparticles was carried out in a size or shape-selected and controlled manner. Moreover, emerging issues that merit important consideration are environmental and economical concerns such as the utilization of non-toxic chemicals, environmentally benign solvents, and renewable materials (Sakai *et al.*, 2008, Okitsu *et al.*, 1996).

Recently, metal nanoparticles had been prepared by chemical reduction method by stirring process with the existence of stabilizers in order to control the morphology of nanoparticles. The examples of stabilizers used were tetra-n-octylammonium carboxylate, sodium dodecyl-sulfate, sodium polyacrylate, and poly ethylene glycol.

The other method to synthesize metal nanoparticles is by using sonochemistry method or ultrasound approach. The chemical effects of ultrasound do not come from a direct interaction between the sound field and molecular species. Sonochemistry will arise from acoustic cavitations. It involves the formation, growth and implosive collapse of bubbles within a liquid. When the bubbles collapse, localized hotspots will be generated. This local heating produces a wide range of high-temperature (5000 K) and high pressure (1800 atm). The high temperature and pressure are enough to dissociate water molecules into primary hydrogen radicals (*H) and hydroxyl radicals (*OH) (Park *et al.*, 2006).

In addition, the control of morphology and size distribution can be considered as the next target of preparation of metal nanoparticles, (Park *et al.*, 2006). Maeda *et al.* reported that stable and fine particles of noble metal are sonochemically produced from aqueous solutions of the corresponding metal ion in the presence of a stabilizer. Moreover, the advantages of sonochemical method include a rapid reaction rate compared with chemically synthesized method and the ability to form very small metal nanoparticles. However, metal nanoparticles prepared by sonochemical reduction generally have wide size distribution. Some efforts to control the particles size and shape using different initial metal concentration, different alcohols and surfactant type have been reported. Since the acoustic cavitation generated by ultrasound depends on not only the power of ultrasound but also on the concentration of stabilizer, the different ultrasonic power and different concentration of stabilizer might provide different reaction conditions for the formation of metal nanoparticles, (Park *et al.*, 2006)

In this study, we report the effect of concentration of stabilizer on the formation of gold nano-particles in the presence of constant ultrasonic power. For comparison purposes, the effect of citrate that act as reducing and stabilizers on the particles shape, size and distribution of gold nanoparticles had also been studied.

MATERIALS AND METHOD

Gold chloride hydrate 99.999 % ($HA_uCl_{4.x}H_2O$) and polyvinyl pyrollidone (PVP) were purchased from Sigma Aldrich. 2-propanol was purchased from Fisher Scientific. Tri-sodium citrate ≥98 % was purchased from Aldrich. Deionised water had been used throughout the experiments. All chemicals were laboratory reagent grade and used without further purification.

0.2 mmole HA_uCl_4 and 20 mmole 2-propanol was prepared in deionised water and used as stock solution for all experiments. PVP solution was also prepared according to different concentration by weight (1 %, 2 %, 3 % and 5 %).

21 ml PVP solution with different concentration was added into 105 ml of the gold solution. 3 ml propanol was then added into the solution. Ultrasonic irradiation was performed for 2 hours with a collimated 20 KHz beam from a ceramic transducer with a titanium amplifying horn (13 mm Ø, Sonic VCX750) directly immersed into the solution. The amplitude used throughout this experiment was 30 %.

As a comparison, samples containing (i) gold solution with PVP and tri-sodium citrate and (ii) gold solution containing only tri-sodium citrate have been used in this experiment. 5 ml (1 wt%) tri-sodium citrate and 5 ml (5 mM) PVP had been added into 25 ml (10 mM) gold solution. The solution had been irradiated by using ultrasound for 60 minutes at 30 % amplitude.

As the local heating produced by the cavitation also affect the solution temperature, the temperature of water bath was held at 283 K during sonication. The colloidal suspensions were analyzed using Shimadzu UV-2450 UV-vis spectrometer. Transmission Electron Microscopy (TEM) images were recorded with a TEM Philips CM12. Sample were prepared by placing a drop of the colloidal Au NPs solution onto a carbon-coated 400 mesh copper grid on an underlying paper, leaving behind a thin colloidal film.

RESULTS AND DISCUSSION

From our physical observation, aqueous HA_uCl_4 solution was observed as light yellow before the ultrasonic irradiation. During the ultrasonic irradiation, the color of HA_uCl_4 solution containing PVP changed from light yellow to pink, indicating the formation of gold nanoparticles. Solutions with various PVP concentrations were used to study its influence on the morphology and size distribution of gold nanoparticles. The color of noble metal nanoparticles such as Au, in terms of absorption in the visible region, is often referred to as the surface plasmon band (SPB). UV–vis spectrum offers a variety of information based on

the size and shape of nanoparticles due to this optical property of noble metal nanoparticles. Figure 1 shows the UV-vis absorption spectrum of gold nanoparticles solution. Gold nanoparticles show unique optical properties due to surface plasmon resonance. The surface plasmon resonance depends on the dielectric constant of the surrounding media. For spherical shape, the gold nanoparticles plasmon band generally appears between 520 nm and 550 nm. The characteristic surface plasmon band for the spherical particle is observed around λ_{max}= 535 nm, 532 nm, 528 nm and 531 nm for 1 % PVP, 2 % PVP, 3 % PVP and 5 % PVP respectively.

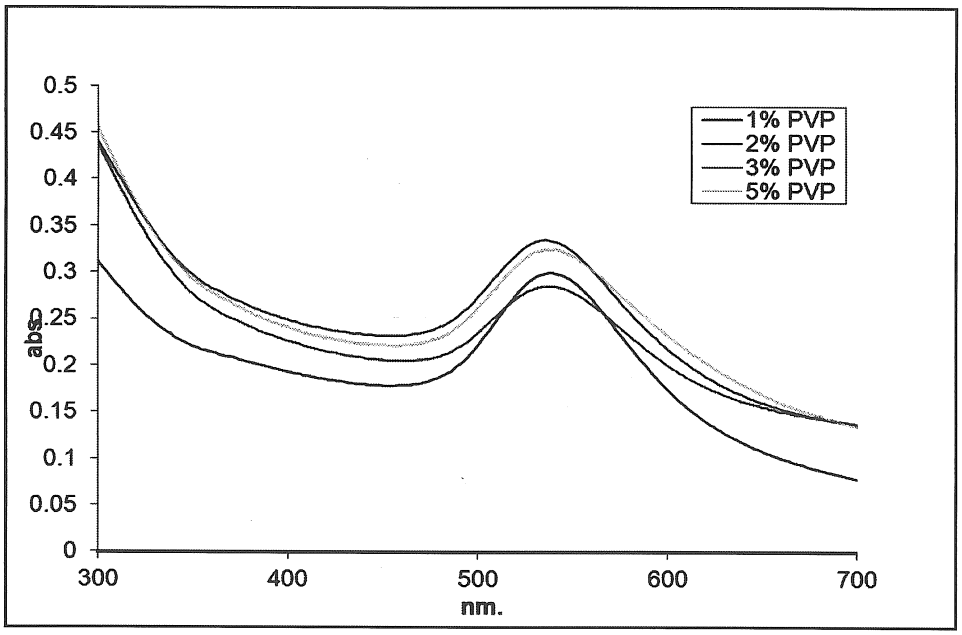
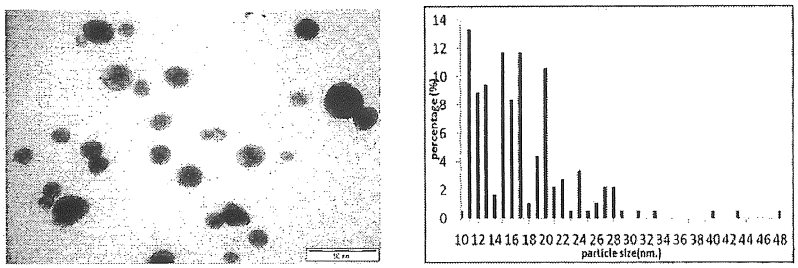
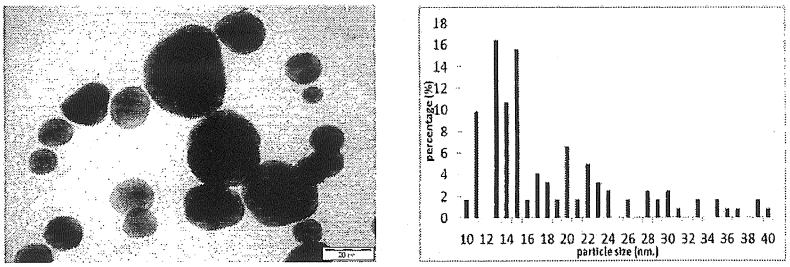


Figure 1. *UV-vis absorption spectrum for gold nanoparticles containing 1 % PVP, 2 % PVP, 3 % PVP and 5 % PVP.*

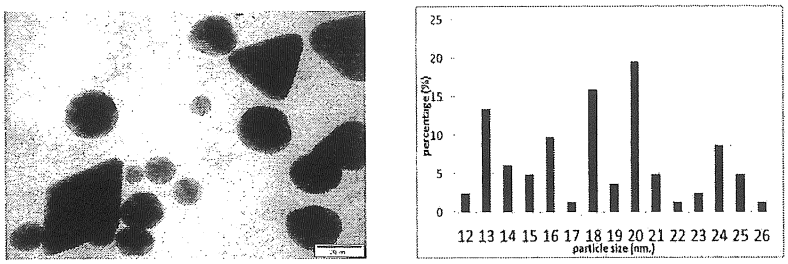
The TEM images in Figure 2 exhibit various types of gold nanoparticles for different concentration of PVP. For PVP = 1 % and PVP = 2 %, most of the particles exhibit spherical shape. The irradiated solution of gold solution containing 1 % PVP and 2 % PVP has an average size of 17 nm with size distribution of 10 – 48 nm and 10 – 40 nm respectively (Figure 2(a) and Figure 2(b)). On the other hand, sample containing 3 % PVP and 5 % PVP in gold solution has different shape and form compared with samples containing 1 % PVP and 2 % PVP. For samples containing 3 % PVP, the shape of nanoparticles were spherical, triangular and rhomboids that coexist as main products. The formation of this gold nanoparticles having an average size of 16 nm with size distribution of 12 – 26 nm. In the case PVP = 5 %, silver nanoparticles were obtained in spherical, triangular and also hexagonal that coexist as main products. It has an average size of 14 nm with size distribution of 7 – 20 nm when observed by using TEM.



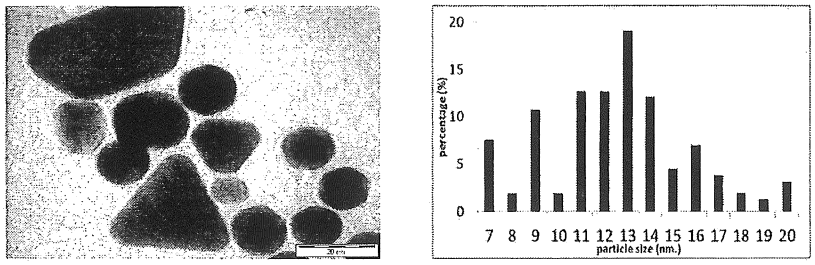
(a)



(b)



(c)



(d)

gure 2. *TEM micrograph and particle size analysis of gold nanoparticles containing several of PVP. a) 1 % PVP, PSD = 10-48 nm, b) 2 % PVP, PSD = 10-40 nm, c) 3 % PVP, PSD = ?-26 nm, d) 5 % PVP, PSD = 7-20 nm*

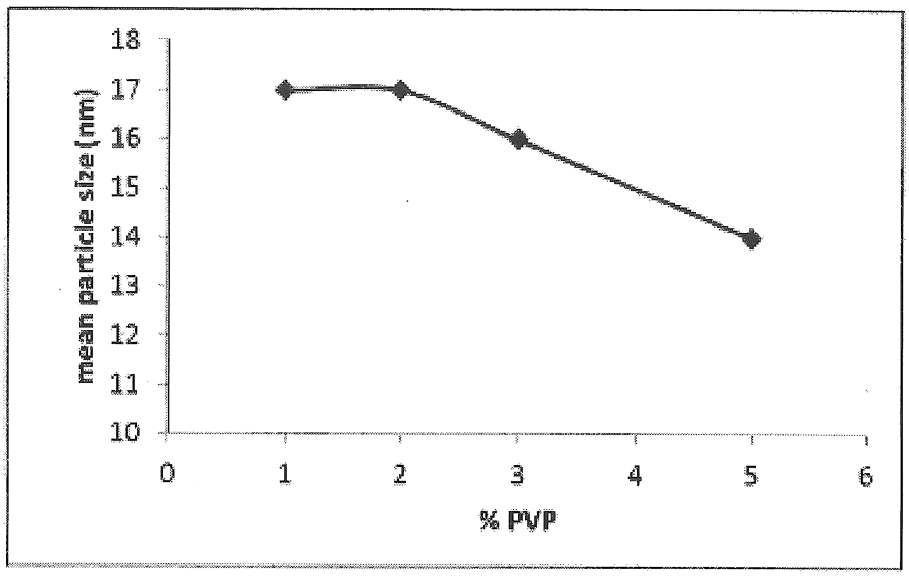


Figure 3. *Mean particle size of gold nanoparticles for various percentage of PVP*

When percentages of PVP were increased during the sonochemical reaction, the spherical shape of gold nanoparticles was changed from spherical to polygonal shape. Also, the average particle size were decreased (Figure 3) and the size distribution became narrower (Figure 2). The results indicated that the crystal growth process of gold nanoparticles was successfully limited by increasing the concentration of the PVP.

The main factors for the formation of nanoparticles are electrons. It had been reported that the reaction field for the synthesis of the gold nanoparticles was the interface between gas and liquid phases. The reduction reaction in the interface region was mainly related to electrons according to the reactions listed as follows (Kim *et al.*, 1998);

$$AuCl_4^- + 2e^- \; AuCl_2^- + 2Cl^- \quad (1)$$

$$AuCl_2^- + e- \; 2Au^0 + 2Cl^- \quad (2)$$

For comparison, gold nanoparticles synthesized with a) PVP and citrate and b) citrate had been studied. Figure 4 shows that the gold nanoparticles have characteristic of surface plasmon band for the spherical particles observed around λ_{max} = 522 nm for both samples.

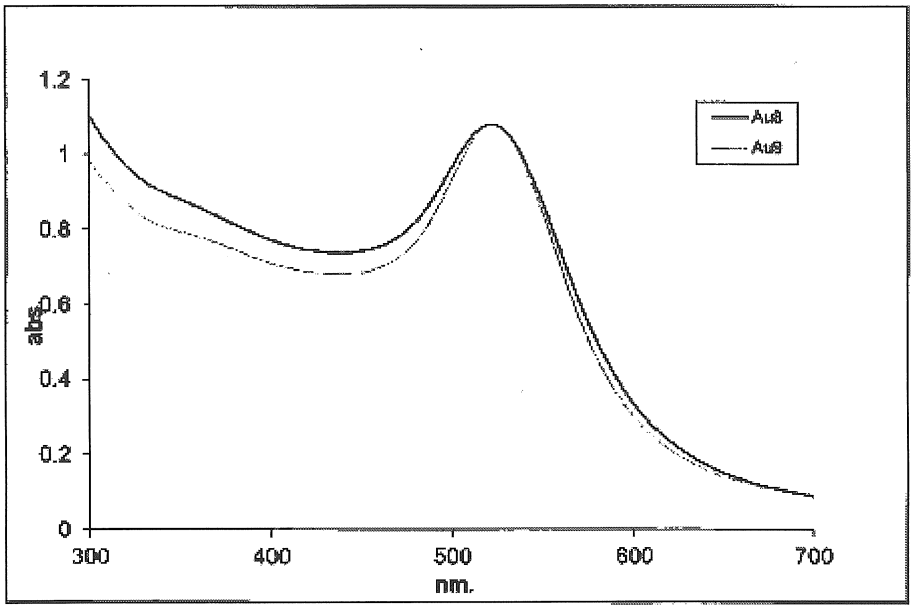
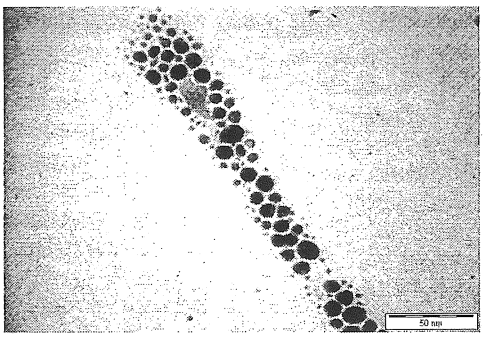
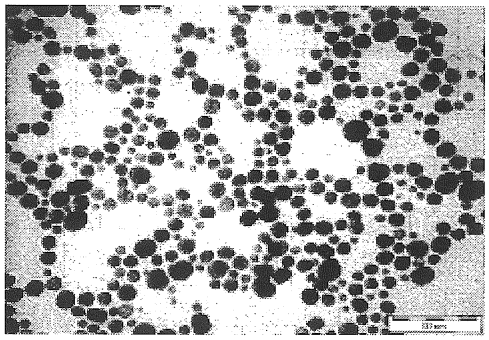


Figure 4. *UV-VIS absorption spectra for gold nanoparticles containing citrate and/or PVP*

From the physical observation, the color of the samples changes from light yellow to deep red indicating the formation of gold nanoparticles. As we can see from the TEM images in Figure 5, it is confirmed that gold nanoparticles have an average particle size of 6 nm and 7 nm with particle size distribution of 1 – 12 nm and 3 – 13 nm for sample containing PVP + citrate and citrate only respectively. We also can see that, both samples have narrower particle size distribution and more stable compared to samples containing only PVP (Table 1).



(a)



(b)

Figure 5. *TEM micrograph on gold nanoparticles. a) PVP + citrate, b) citrate*

Table 1. Mean particle size and particle size distribution of gold nanoparticles

Sample	Mean particle size, nm	Particle size distribution, nm
PVC + Citrate	6	1-12
Citrate	7	3-13

CONCLUSION

The sonochemical reduction methods of noble gold ions appear to be promising for the preparation of noble gold nanoparticles colloids in aqueous solution. In the presence of stabilizer, most of nanoparticles were stabilized and persisted for several months in the colloidal state. The shape and size of gold nanoparticles depend on the percentage of PVP. According to the study, 5 % PVP in the solution give the best mean particle size and narrow distribution compared to the other percentage. When we compared the samples containing PVP with samples containing citrate, we can see that samples containing citrate have smaller particle size and narrow size distribution. Moreover, the samples containing citrate are still stable and persisted even after 6 months while some sample containing only PVP settled down after 5 months.

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