Front. Chem. China (2006) 4: 418–422
DOI 10.1007/s11458-006-0067-0

RESEARCH ARTICLE

Cheng Jingquan, Yao Suwei, Zhang Weiguo, Zou Yi

Preparation and characterization of silver colloids with different morphologies under ultrasonic field

Abstract In the ultrasonic field, stable silver colloids were produced by the reduction of $AgNO_3$ with the protection of PVP using KBH_4 or $N_2H_4{\cdot}H_2O$ as reductant. The main factors affecting the morphology of silver nanoparticles, such as distribution of the ultrasonic field, ultrasonic time, ultrasonic power, and the species of reductant, were studied. The silver colloids were identified by TEM and spectrophotometry. The results indicate that the factors such as distribution of the ultrasonic field, ultrasonic time, ultrasonic power, and the species of reductant have a great impact on the morphology of the silver nanoparticles. The size of the silver nanoparticles decreases with the ultrasonic power and ultrasonic time increasing. Ag nanoparticles prepared in standing wave field preferentially grow in a certain direction, which is propitious for forming hexagonal- and spherical-like silver nanoparticles. Monodispersed spherical silver nanoparticles are easily synthesized in the diffusion field. The stability of silver colloid becomes improved by ultrasonic treatment. For example, precipitate is not found after several weeks for the silver colloid prepared with an ultrasonic treatment time of 180 min. The silver nanoparticles prepared without ultrasonic treatment are large spherical-like and hexagonal. Well-dispersed spherical silver particles with a mean size of about 20 nm have been prepared under ultrasonic treatment. Spherical, spherical-like, and hexagonal silver nanoparticles can be obtained by changing the reductants..

Keywords ultrasonic, standing wave field, diffusion field, silver colloid

Translated from *Journal of Tianjin University,* 2006, 39(1) (in Chinese)

Cheng Jingquan (✉)
Department of Applied Chemistry, Hengshui University, Hengshui 053000, China
E-mail: cjq217@eyou.com

Yao Suwei, Zhang Weiguo, Zou Yi
SUGIYAMA Laboratory of Surface Technology, Department of Applied Chemistry, School of Chemical Engineering, Tianjin University, Tianjin 300072, China

Colloidal precious metals refer to the dispersion of precious metal particles with sizes ranging from 1 to 100 nm in fluids. These colloidal particles are small in radius, but big in surface area, so they present many unique properties, like special conductive, antistatic, photographic, antimagnetism, and catalytic behaviors [1]. The colloids have wide applications in a variety of industrial fields, such as, optical material, precious metal slurry, biological engineering, medicine, catalyst and micro-electronics [2]. The preparation and application of the precious metal nanoparticles with macromolecular protection has been an attractive research area. The dispersion of the nanosized particles is a colloidal solution. When utilized for catalytic oxidization of ethylene, dispersion of silver nanoparticles exhibits higher catalytic activity and selectivity than conventional silver powder [3]. The conductivity and uniform dispersity of silver colloids are used in developing antistatic coating, conductive coating, and additives in emerging materials with new functions, showing a broad application prospect in the future.

Silver colloid with macromolecule protection can be prepared by chemical reduction [4–7] or light radiation [8–9]. However, no literature is available on its preparation in ultrasonic field. This paper describes the preparation of individually dispersed silver colloids with various morphological features through reduction by either hydrazine hydrate or potassium borohydride, with silver nitrate as stating compound and PVP as protecting agent. The main part will include the effects of ultrasonic field distribution, ultrasonic time, ultrasonic power, and reducing agent types on the morphologies of the silver nanoparticles and their colloidal stability.

1 Experimental

1.1 Raw materials

$AgNO_3$, AR, was from Tianjin Wenda Rare-Agents Chemical

Plant. PVP, K30, at 360 degree of polymerization, was obtained from Tianjin Bodi Chemical Co. $N_2H_4{\cdot}H_2O$, AR, was manufactured in Tianjin Kemiou Technical Ltd. KBH_4, AR, was taken from Zhongdao Company of Tianjin Development Area.

1.2 Experimental devices

The KQ-250DB digital ultrasonic cleaning device was produced by Kunshan Ultrasonic Devices Ltd. A Hitachi H-300 TEM and A 722 spectrometer were used to characterize the nanoparticles.

1.3 Experimental process

In ultrasonic field, with PVP being the protecting agent, $AgNO_3$ reacts with $N_2H_4{\cdot}H_2O$ or KBH_4 to produce the colloid. Then TEM and the spectrometer are used to observe the particle morphology and absorption spectrum.

2 Results and discussion

The morphological features of the silver nanoparticles show remarkable variation under different preparation conditions. This paper focuses on evaluating the effects of ultrasonic distribution, ultrasonic time, and ultrasonic power, and reducing agent types.

2.1 Influence of ultrasonic field distribution

Figure 1 shows the schematic diagram of the ultrasonic distribution reported by Deng et al. [10], which indicates that a standing wave field is formed in a flat-bottomed vessel and a diffusion field is formed in a round-bottomed flask.

The silver colloids were prepared in the above two vessels with PVP as protecting agent and $N_2H_4{\cdot}H_2O$ as reducing agent for silver nitrate. Figure 2 shows the TEM pictures of the silver colloids prepared in the two ultrasonic fields with an ultrasonic treatment time of 30 min. It is evident that in standing wave field the silver colloidal particles are spherical, hexagonal or irregularly shaped (Fig. 2a) while in diffusion field they are spherical (Fig. 2b). Apparently, this is associated with the ultrasonic field distribution in the reaction vessel. Specifically, a standing wave is a stack of two same-amplitude coherent waves traveling along a straight line but in reverse directions. After stacking, the standing wave only fluctuates in a limited area, but does not propagate outwards. Therefore, in a standing wave field, the particles can grow along some directions into a regular shape, from a sphere to a sphere-like or irregular shape until they

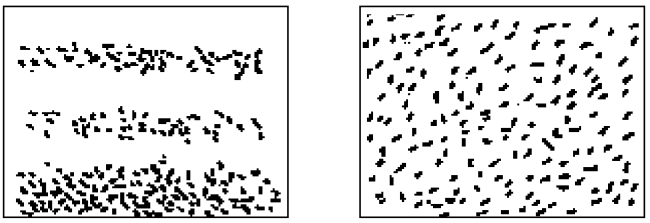

Fig. 1 The schematic diagram of ultrasonic field distribution, from Ref. [10] courtesy of Deng Shiyan
a) Standing wave field, b) Diffusion field

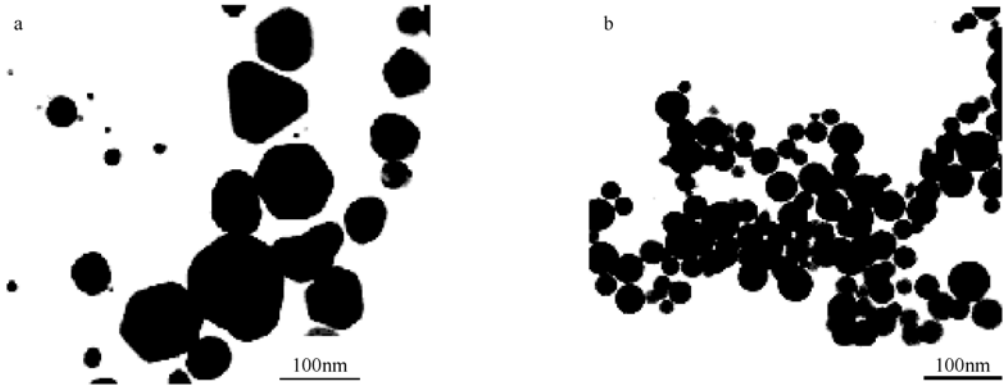

Fig. 2 The TEM images of silver colloids prepared by ultrasonic irradiation
a) Standing wave field, b) Diffusion field

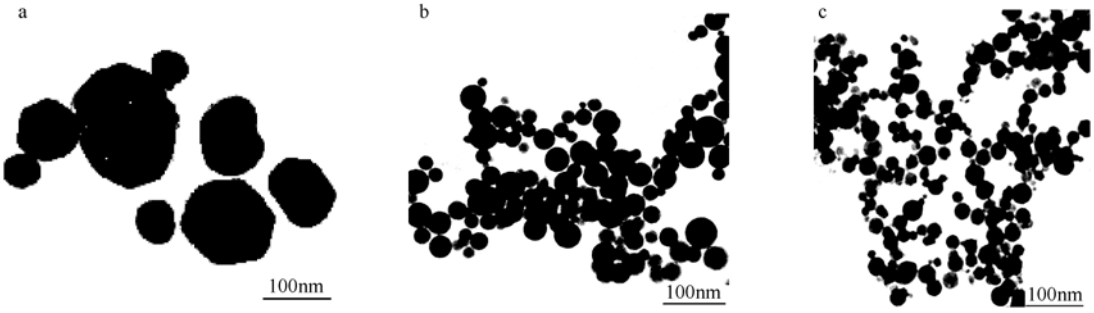

Fig. 3 TEM images of silver colloids prepared with different treatment time prepared in diffusion field
a) $t = 0$, b) $t = 30$ min, c) $t = 180$ min

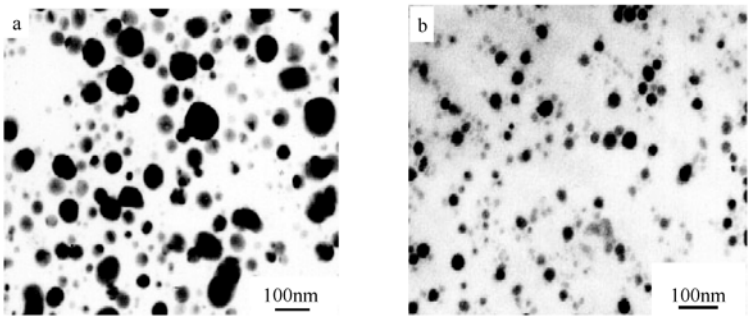

Fig. 4 TEM images of silver colloids prepared with different ultrasonic powers
a) $P = 100$ W, b) $P = 150$ W

form hexagons with 60 nm side length. In a diffusion field, the possibilities of ultrasonic waves passing any locations are the same. But on one location, when the waves meet, their phases are incoherent, so the average energy density is evenly distributed, leading to an even field in which particles grow in all directions with the same possibility into 20–30 nm spheres. Lots of tests verified that in a diffusion field, the produced silver particles are spherical even though other test conditions are changed, while in a standing wave field, the silver particles grow in a preferred direction. Further investigation is still needed to understand the detail mechanism.

2.2 Influence of ultrasonic time

Figure 3 shows the TEM pictures of silver colloids prepared with various ultrasonic times. Figure 3a shows the larger particles in spherical, normal hexagon or irregular shapes prepared without ultrasonic treatment. In a diffusion field with a treatment time of 30 min, the silver nanoparticles prepared are spherical with a 30 nm mean diameter. As the treatment time increases, the silver particles become smaller, more uniform and stability is improved. After standing for 2 days, the silver colloid prepared without ultrasonic treatment will precipitate. The silver colloid prepared in a diffusion field with a treatment time of 30 min will precipitate in 2 weeks while the colloid formed in ultrasonic field with a treatment time of 180 min are uniform spherical nanoparticles having a mean diameter of 20 nm and no precipitate was observed after standing for several weeks.

2.3 Influence of ultrasonic power

Ultrasonic intensity related to the ultrasonic power, influences aggregation of particles. Therefore, the silver colloids prepared with KBH_4 as reducing agent under ultrasonic power of 100 and 150 W at 40 kHz frequency for 30 min were investigated. Figure 4 shows that higher ultrasonic power produces smaller colloidal particles. The mean acoustical power of a sonic wave in media is derived by the following equation [11],

$$W = 1/2\ p\ CV^2S = 1/2P_AV_OS,$$

where W is the mean acoustical power of sonic waves traveling in the media in w, p is the media density in $kg \cdot m^{-3}$, C is sonic traveling velocity in $m \cdot s^{-1}$, V is the vibration rate of media particles in $m \cdot s^{-1}$, S is the media area perpendicular to the sonic traveling direction, P_A is the alternating acoustic pressure in Pa and V_O is the media volume in m^3.

It is understood from the above equation that with increasing power the alternating acoustic pressure P_A increases and the intensity of cavitation will be enhanced. Thus, the diameters of the silver particles decrease due to the enhanced cavitation effect.

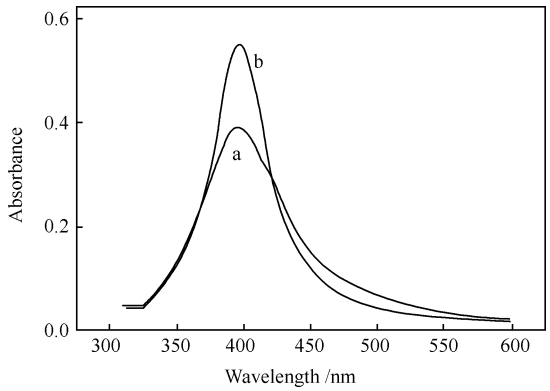

Fig. 5 UV-vis absorption spectra of silver colloids prepared with different ultrasonic powers
a) p = 100 W, b) p = 150 W

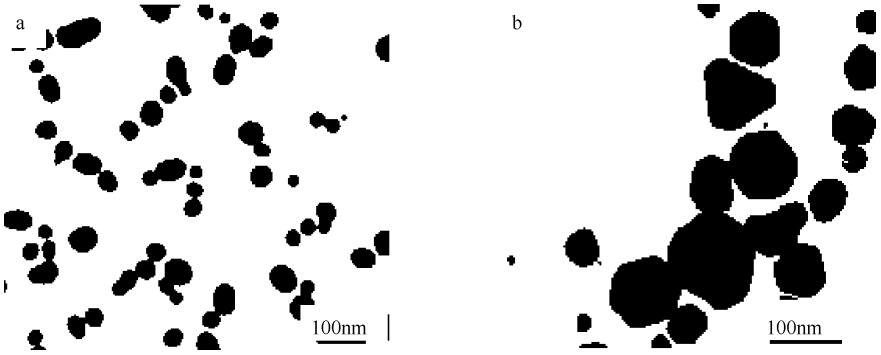

Fig. 6 The TEM images of silver colloids prepared with different reductants in diffusion field
a) KBH_4, b) $N_2H_4{\cdot}H_2O$

In Figure 5 curves 5a and 5b show the absorption spectra of the silver colloids in Figs. 4a and 4b, respectively. Under higher ultrasonic power, the absorption peak of prepared silver colloid is higher and shows a better symmetry and a less half-peak width. These imply that the size distribution of the particles become narrower, which is consistent with TEM results.

2.4 Influence of reducing agents

Figure 6 shows pictures of silver colloids prepared in a standing wave field but using different reducing agents. When KBH_4 is used as the reducing agent, prepared silver particles are spherical or sphere-like with diameters of 20–30 nm. When $N_2H_4{\cdot}H_2O$ is used as the reducing agent, hexagonal particles are produced. The reasons may be as follows. KBH_4 is a strong reducing agent, which in an ultrasonic field reduces Ag^+ into Ag quickly. Due to the protection of PVP, the formed primary Ag particles are not liable to aggregate and grow up and thus present as smaller spherical or sphere-like particles with a better dispersity (Fig. 6a). When $N_2H_4{\cdot}H_2O$ is the reducing agent, it takes a longer time for Ag^+ to be reduced into Ag in an ultrasonic field. This may be beneficial for Ag to aggregate and grow into silver particles with regular shapes (Fig. 6b).

3 Conclusions

In ultrasonic field, stable silver colloids can be prepared with $AgNO_3$ as starting material, PVP as protecting agent, and KBH_4 and $N_2H_4{\cdot}H_2O$ as reducing agents.

Ultrasonic field distribution, ultrasonic treatment time, ultrasonic power, and reducing agents are the main factors affecting the morphological features of silver nanoparticles. A standing wave field facilitates the formation of hexagonal nanoparticles while a diffusion field is favorable for the formation of spherical silver nanoparticles with uniform particle size. As ultrasonic time and power increase, silver nanoparticles become smaller, and their aggregation stability is enhanced. The silver colloid prepared in diffusion field with a treatment time of 180 min consists of uniform spherical particles with a mean diameter of 20 nm, and does not precipitate after being left standing for weeks. By changing the reducing agents silver nanoparticles with various shapes like sphere or sphere-like and hexagons can be produced.

References

1. Zhao Bin, Yao Mingyi, Zhang Zongtao, Hu Liming, Research on controlling the silver particle size in colloidal dispersions of ultrafine silver particles, Petroleum Chemical Technology, 1996, 25: 159–163 (in Chinese)
2. Huang Lizhong, Wang Ying, Wang Yongli, Colloidal precious metals and its application, Precious Metals, 1997, 18(3): 58–62 (in Chinese)
3. Zhao Bin, Yao Mingyi, Wen Dong, Hu Liming, Preparation and electric conductivity of ultrafine silver particles with polymer-protected colloidal dispersions, Journal of East China University of Science and Technology, 1995, 21: 428–434 (in Chinese)
4. Guo Lijun, Yu Juanjuan, Li Yuncai, Gu Yuzong, Huang Yabin, Mo Yujun, Absorption tropism of PNBA on silver nanoparticles surface, Chinese Science Bulletin, 2000, 45: 571–574 (in Chinese)
5. Li Degang, Chen Shenhao, Zhao Shiyong, Wang Chuntao, Production of the monolayer of Ag nanoparticles by phase transfer ring, Acta Chemica Sinica, 2002, 60: 408–412 (in Chinese)
6. Chou Kansen, Ren Chiangyuh, Synthesis of nanosized silver particles by chemical reduction method, Material Chemistry and Physics, 2000, 64: 241–246
7. Tan Yiwei, Li Yongfang, Zhu Daoben, Preparation of silver nanocrystals in the presence of anline, Journal of Colloid and Interface Science, 2002, 258: 244–251
8. Zhou Yong, Yu Shu H, Wang Cui Y, Li X. G., Zhu Y. R., Chen Y. C., A novel ultraviolet irradiation photoreduction technique for the preparation of single-crystal Ag nanorods and Ag dendrites, Adv. Mater., 1999,10:850–852
9. Jin Rongchao, Cao Yunwei, Mirkin, Chad A., Kelly K.L., Schatz, George C., Zheng J.G., Photoinduced conversion of silver nanospheres to nanoprisms, Science, 2001, 294(30): 1901–1903
10. Deng Shiyan, Xing Weihong, Xu Nanping. Influence of ultrasonic field on the zirconium sol preparation, Journal of Nanjing University of Technology, 2003, 25: 80–83 (in Chinese)
11. Li Tingsheng, Yin Qiguang. Sonochemistry, Beijing: Science Press, 1995, 38–39 (in Chinese)