

Preparation and characterization of size controllable spherical silver nanoparticles*

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By adjusting pH values of reactant system, the mass ratio of stabilizer/water and aging temperature, size controllable spherical silver nanoparticles (NPs) were synthesized. The properties of silver NPs are characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and ultraviolet visible (UV-VIS) absorption spectra. Within the pH values of 7.0—11.0, the aging temperature of 80 °C is better to improve silver NPs in shape to nearly sphere, concentrate size distribution and reduce aggregation than the aging temperature of 25 °C. The shape and dispersibility of silver NPs are the best when the pH of the reactant system is within 7.0—8.0. With pH of 7.5, aging at 80 °C, and stabilizer/water mass ratio of 1%, the spherical silver NPs with sizes of 50—70 nm were synthesized. The results are promising to be used to synthesize core/shell NPs when silver NPs are as core.

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Silver nanoparticles (NPs) have been widely investigated for their special properties and wide applications^[1-8]. Many synthetic routes have been reported for the preparation of silver NPs^[9-11]. Chemical reduction methods are the most popular. Usually, reductants, such as citrate^[12], borohydrate^[13], formaldehyde^[9] or ascorbic acid^[13], were used to prepare silver NPs in water. The balance between nucleation and growth processes of silver NPs is poor in a citrate reduction system because sodium citrate has three roles in synthesis system: reducing reagent, protection ligand and pH mediator^[12]. The spherical silver NPs were difficult to obtain by one-step citrate reduction method as pH in the range of 5.7—11.1^[12]. The sizes of silver NPs prepared by borohydrate^[13] or formaldehyde reduction^[9] are small (<10 nm) for high reactivity and quick nucleation process. Nanoparticles with different morphologies will present new physicochemical properties, which will have new potential applications. So shape controllable synthesis of NPs has attracted great attention and become hot research spot. In some cases, large sizes and spherical silver NPs are needed. For example, in order to tune the absorption spectra of silver NPs to visible range, core-shell NPs are synthesized^[14,15]. For surface plasma effect, silver NPs are often as core. To control the sizes and shapes of silver NPs, the nucleation and growth processes should be controllable, which can be done by changing the experimental conditions, such as molar ratio of silver precursor/reductant, mass ratio of stabilizer/water, pH values of the reactant system and

reactive temperature. In this paper, ascorbic acid is used to reduce AgNO₃ and polyvinylpyrrolidone (PVP) as stabilizer. By adjusting pH values of reactants, aging temperature, and mass ratio of stabilizer/water, the size controllable spherical silver NPs are prepared and corresponding properties are characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and ultraviolet visible (UV-VIS) absorption spectra.

AgNO₃ (content 99.8%), ascorbic acid (C₆H₈O₆), sodium hydroxide (NaOH) and PVP were bought from Aladdin. All of the reactants are analytical grade and are used without further purification. The molecular weight (MW) of PVP is 58000. The solvent is deionized water.

Silver NPs were synthesized by using ascorbic acid as reductant and PVP as stabilizer. Typically, 0.8 g PVP was added into 80 mL ascorbic acid solution (6×10⁻⁴ mol/L) and stirred homogeneously. By adding 0.2 mol/L solution of NaOH, the pH values of above solutions were adjusted to different values of 7.0, 8.0, 9.0 and 11.0. Then 0.8 mL AgNO₃ (0.1 mol/L) was added into the above solution under vigorous stirring in a 30 °C water bath for 15 min. Then the solutions were aged at 25 °C or 80 °C for 30 min. After cooling down to room temperature, the solution was centrifuged three times to separate silver NPs. The final products were dispersed in ethanol and preserved in a refrigerator at 4 °C.

The crystalline structure of silver NPs is characterized by X-ray diffraction (XRD, Bruker D8 ADVANCE). Fig.1 shows the XRD pattern of silver NPs. The peaks

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positioned at 38.08° , 44.18° , 64.25° and 77.46° match well with (111), (200), (220) and (311) planes of the standard data for the face-centered cubic (fcc) structure of silver (JCPDS No. 04-0783).

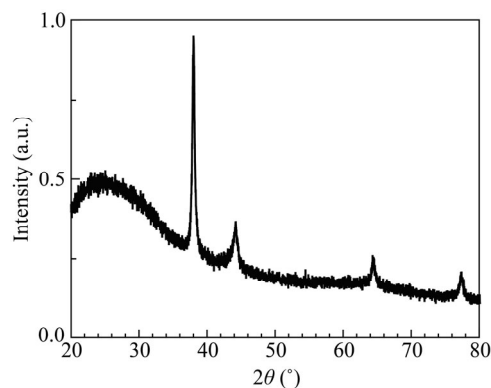


Fig.1 XRD pattern of silver NPs (JCPDS No. 045-0783)

In order to observe morphologies and sizes of silver NPs, TEM (H-7650, Japan) analysis of silver NPs is conducted. Fig.2 shows the TEM images of silver NPs after aging at 25°C for 30 min and at different pH values of 7.0, 8.0, 9.0 and 11.0. One can see that the sizes, shapes and dispersibility of silver NPs are closely related to the pH values of reaction solutions. As pH is 7.0, there are two groups of silver NPs with sizes of 60–100 nm and 150–200 nm, respectively. The former is dominant. The shape of silver NPs is polygon. When the pH is 8.0, the sizes of silver NPs drop to 30–60 nm. And the shape of silver NPs is quasi-sphere. But when the pH increases to 9.0, slight aggregation begins. And serious aggregation appears when pH is 11.0.

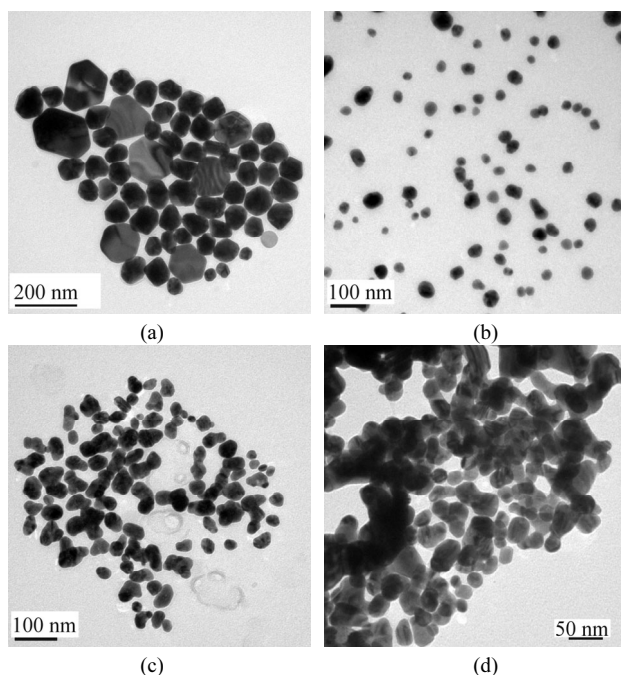


Fig.2 TEM images of silver NPs synthesized at different pH values of (a) 7.0, (b) 8.0, (c) 9.0 and (d) 11.0 and aged at 25°C for 30 min

A Cary-50 UV-VIS spectrophotometer is used to measure the absorption spectra. Fig.3 shows the UV-VIS absorption spectra of the silver NPs after aging at 25°C for 30 min. One can see that for the pH values of 7.0, 8.0, 9.0 and 11.0, the main absorption peaks of silver NPs are at 416 nm, 413 nm, 412 nm and 406 nm, respectively. When the pH is 7.0, except for the absorption peak localized at 416 nm, there is another absorption peak positioned at 600 nm. The two peaks coincide with the two groups of silver NPs with sizes of 60–100 nm and 150–200 nm (Fig.2(a)). The full width of half maximum (FWHM) values of the UV-VIS absorption for the pH values of 9.0 and 11.0 are 211 nm and 166 nm, respectively. But the FWHMs are more than 472 nm and 355 nm for the pH values of 7.0 and 8.0, respectively. The wide FWHMs of the absorption spectra indicate the size distribution of the silver NPs is also wide.

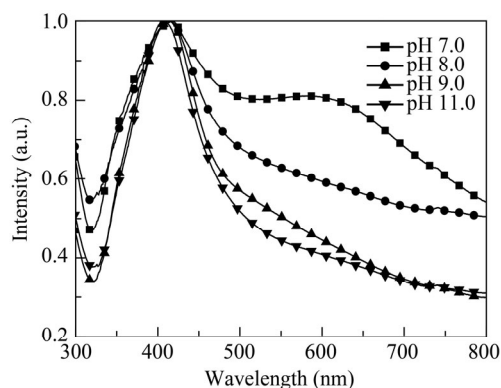
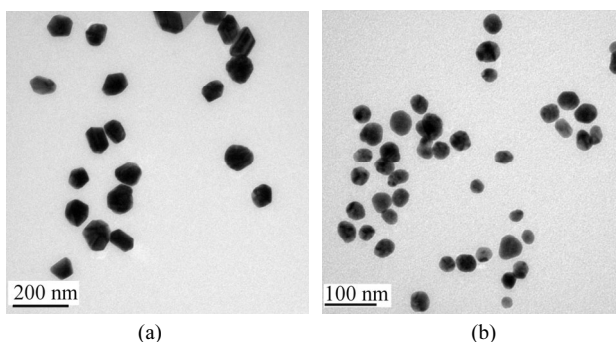


Fig.3 UV-VIS absorption spectra of silver NPs synthesized at different pH values (7.0–11.0) and aged at 25°C for 30 min

Except for aging at 25°C , the samples after water bath at 30°C were also aged at 80°C . Fig.4 shows the TEM images of silver NPs after aging at 80°C for 30 min and at pH values of 7.0, 8.0, 9.0 and 11.0. As the pH values are 7.0, 8.0 and 9.0, the sizes of silver NPs are in the range of 60–100 nm, 25–50 nm, 30–55 nm, respectively. Compared with those aged at 25°C , at the same pH values, the shape of silver NPs is more close to spherical-like and the sizes of silver NPs decrease and are well distributed. The aggregation of silver NPs disappears as the pH is 9.0. And the aggregation becomes weaker at pH of 11.0.



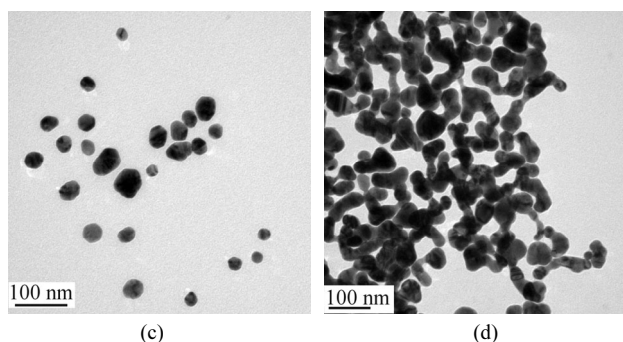


Fig.4 TEM images of silver NPs synthesized at different pH values of (a) 7.0, (b) 8.0, (c) 9.0 and (d) 11.0 and aged at 80 °C for 30 min

Fig.5 indicates the absorption spectra of silver NPs aged at 80 °C for 30 min. One can see that for the pH values of 7.0, 8.0, 9.0 and 11.0, the main absorption peaks of silver NPs are at 471 nm, 423 nm, 422 nm and 404 nm, respectively. The FWHMs are 273 nm, 122 nm, 158 nm and 312 nm, respectively. Compared with those aged at 25 °C, there is only one absorption peak as the pH value is 7.0, which indicates that the number of silver NPs with sizes of 150—200 nm decreases greatly. Most silver NPs are with sizes of 60—100 nm. That is to say, it is effective to concentrate the size distribution when the aging temperature increases. After aging at 80 °C, the FWHMs of absorption spectra of silver NPs as pH values of 8.0 and 9.0 are less than those aged at 25 °C, which also shows that it is better to narrow the size distribution of silver NPs as the aging temperature increases. The results coincide with the TEM results.

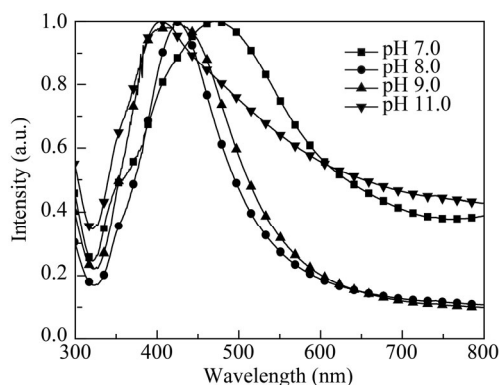


Fig.5 UV-VIS absorption spectra of silver NPs synthesized at different pH values (7.0—11.0) and aged at 80 °C for 30 min

When the pH values are in the range of 7.0—8.0 and aging at 80 °C, the size distribution of silver NPs is narrower, the shape is spherical-like and the NPs have good dispersibility. So when we investigate the effect of mass ratio of stabilizer/water on silver NPs, the pH value of the reactant is adjusted to 7.5. And the aging temperature and time are the same. The silver NPs are synthesized as the mass ratio of stabi-

lizer/water is adjusted within 0.5%—1.5%. Fig.6 shows the TEM images when the mass ratios of PVP/water are 0.5%, 0.75%, 1%, 1.25% and 1.5%, respectively. The corresponding sizes of silver NPs are mainly in the ranges of 40—100 nm, 50—80 nm, 50—70 nm, 40—80 nm and 40—120 nm, respectively. Except for the mass ratio of 1.5%, the silver NPs have good dispersibility. When the mass ratio of PVP/water is 1%, the silver NPs have the narrowest size distribution and the shape is spherical-like.

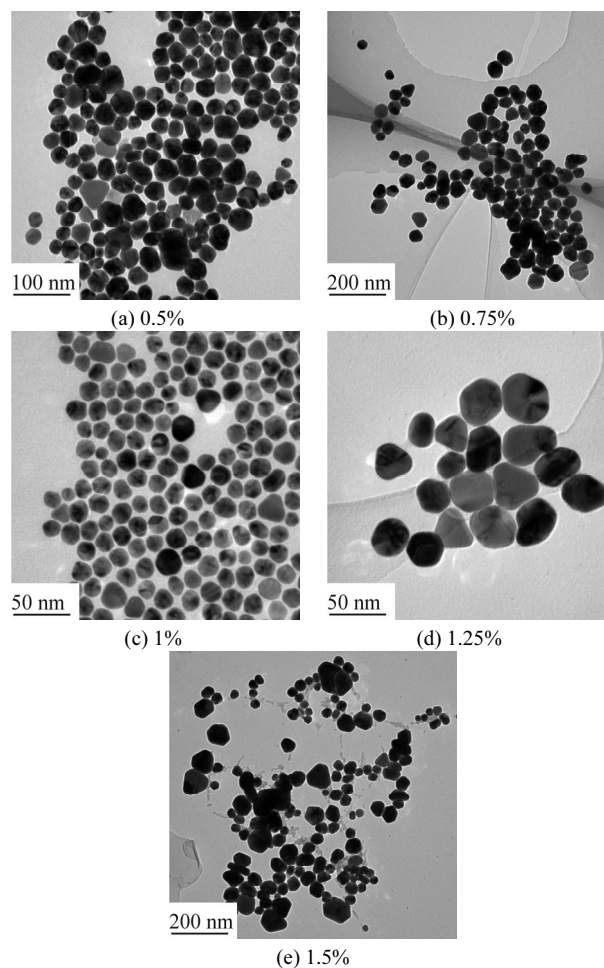
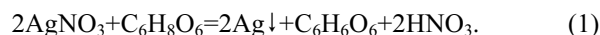


Fig.6 TEM images for different mass ratios between stabilizer and water with pH value of 7.5 and aging temperature of 80 °C for 30 min

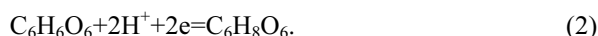
Fig.7 shows the UV-VIS absorption spectra of the silver NPs when the mass ratios of PVP/water are 0.5%, 0.75%, 1%, 1.25% and 1.5%, respectively. The absorption peaks are at 434 nm, 434 nm, 433 nm, 429 nm and 438 nm, respectively. The FWHMs are 166 nm, 156 nm, 173 nm, 323 nm and >484 nm, respectively.

The reactive process between AgNO_3 and ascorbic acid is as follows



When the reaction happens, the molar ratio of AgNO_3 to ascorbic acid is 2:1. In the real experiment, the ratio is

2:1.2. But when the pH value increases, $C_6H_6O_6$ will be changed into ascorbic acid,



The reduction activity of ascorbic acid will be improved. The nucleation and growth process will be quicker. The size of silver NPs tends to decrease. But at the same time, the stability of $AgNO_3$ will decrease when the pH value increases. $AgNO_3$ will be changed into $AgOH$ or Ag_2O as the pH value increases, which will decrease the nucleation and growth process and thus increase sizes of the silver NPs. So there is a best pH value in the reaction system. In this paper, the best pH value is within 7.0—8.0.

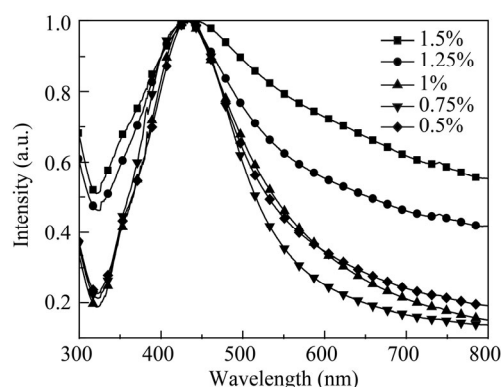


Fig.7 UV-VIS absorption spectra of the silver NPs aged at 80 °C as the mass ratios of PVP/water are 0.5%, 0.75%, 1%, 1.25% and 1.5%, respectively (The pH value of the reactant system is 7.5)

It is known that silver NPs will undergo intraparticle ripening after complete consumption of the monomer. As the aging temperature increases, the intraparticle ripening will be violent, which will make the silver NPs become more spherical-like in shape and with better size distribution. So the shape and size distribution of silver NPs are better after aging at 80 °C than those after aging at 25 °C.

Spherical silver NPs were synthesized by using ascorbic acid as reductant and PVP as stabilizer. By adjusting the pH value of reactant system, the ratio of stabilizer/water and aging temperature, the sizes and shape

of silver NPs are controllable. Within pH values of 7.0—11.0, aging at 80 °C is better to improve the silver NPs in shape, narrow size distribution and decrease aggregation than those aged at 25 °C. The shape and dispersibility of silver NPs are the best when the pH value is within 7.0—8.0. As the pH of 7.5, aging at 80 °C, and stabilizer/water ratio of 1%, spherical silver NPs with size of 50—70 nm were synthesized and have good dispersibility. The results are promising to be used to synthesize core/shell NPs with silver NPs as core. The related experiment is also conducted.

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