

Synthesis of size controlled Ag nanoparticles

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Abstract

The parameters influencing the size of synthesized Ag nanoparticles are reported. The particles size decreased with increasing stabilizer: AgNO₃ molar ratio, decreased with increasing amount of methanolic NaOH added until an optimum amount was reached, and decreased with small amount of methanolic HCl added but increased rapidly on further addition. The reducing activity of the reducing agent influenced the particle size significantly. In addition, increasing the concentration of water in the reducing agent increased the particles size nearly linearly. PVP is a better stabilizer than β-CD to prevent aggregation of small particles. Microwave irradiation for 20 s at output power of 700 W produced smaller and more narrowly distributed Ag particles than conventional heating method.

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1. Introduction

Nanoparticles are intensively studied in recent years because of their potentials in catalysis, optical, mechanical and electronic devices [1]. For these nanoparticles, the catalytic activity as well as their electrical, thermodynamic and chemical properties are dependent on their size and shape [2]. The control over their morphology and size is thus an important goal. Specific control of shape and size is often difficult. Generally, this is achieved by varying the synthesis method, reducing agent, stabilizer and pH of the reaction system. However for Ag particles, diverse and sometime conflicting results have been reported. For examples, Henglein et al. [3] reported that the structure, shape, size and size distribution of Ag nanoparticles, reduced by γ-irradiation, could be controlled by varying the stabilizer (sodium citrate) concentration in the range from 5.0×10^{-5} to 1.5×10^{-3} M. Silvert et al. [4] found that the concentrations of AgNO₃ and stabilizing polymer, PVP, could affect the final particle size and size distribution by the polyol process. Zhou et al. [5] reported the for-

mation of Ag nanorod by the solid-liquid phase arc-discharge and ultraviolet irradiation-photoreduction methods. Braun et al. [6] utilized DNA as a template to grow nanometer Ag wire. Jiang et al. [7] successful synthesized Ag nanowire in a lamellar liquid crystalline alignment of oleate vesicles via UV irradiation under ambient condition. Esumi et al. [8] reported that very small Ag nanoparticles were obtained by using G3.5–G5.5 dendrimers with surface carboxyl group.

Although many chemical routes are available for the production of shape or size-controlled Ag nanoparticles, it is still desirable to design fast and large scale synthesis for these nanocrystals. The microwave synthesis, which is generally fast, simple and efficient in energy has been developed and is widely used in various fields of chemistry [9]. This technique has been increasingly applied in material science due to its unique reaction effects such as rapid volumetric heating and the consequent dramatic increase in reaction rate [9]. Its applications in the preparation of nanosized materials have been reported [10–13].

In this work, we have systematically examined the precursor and stabilizer concentrations, NaOH and HCl solution, reducing agent, water and also the synthesis method for the preparation of size-controlled Ag nanoparticles. PVP is a

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frequently used stabilizer for nanoparticles synthesis, while only a few papers reported the preparation of metal nanoparticles in β -CD [14,15]. These two stabilizers, PVP and β -CD, were examined and compared. The application of microwave irradiation in the preparation of Ag colloids was studied.

2. Experimental

The stabilizers, polyvinyl-pyrrolidone (PVP, MW = 40,000 Fisher, UK) and β -cyclodextrin (β -CD, Fluka, Switzerland), silver nitrate (Fluka, Switzerland) and sodium hydroxide (Fisher, UK) were used as received. Hydrochloric acid, *N,N*-dimethylformamide (DMF), ethylene glycol (EG), methanol (MeOH) and 2-propanol (IPA), all of AR grade, were purchased from Merck, Germany and used without treatment. The 95% ethanol (EtOH), AR grade, was obtained from R&M Chemical, UK.

The experiments were performed with freshly prepared solutions. All the glasswares were cleaned with chromic acid and repeatedly washed with distilled water obtained from a Millipore Milli-Q system.

The UV–vis spectrums were recorded using a Hitachi U2000 spectrophotometer. Before measurement, 0.20 ml of the colloidal solution was diluted to 5.20 ml with distilled water. TEM micrographs were recorded on a Phillip CM 12 transmission electron microscope. Four drops of the solution were placed on a carbon coated copper grid, followed by evaporation under vacuum for 25 min. The particle size and distribution were measured by Image Analyst Software (SIS Soft-Imaging software GmbH, Germany) from 300 particles.

In a typical preparation by the conventional heating method, 2 ml of AgNO_3 (2.945×10^{-2} M) was mixed with the required amount of stabilizer in 100 ml reducing agent in a two neck round bottom flask under vigorous stirring. After 5 min, 1 ml of methanolic NaOH (0.008–0.400 M) was added drop-wise for some preparations. The solution was refluxed under nitrogen on a silicon oil bath for 60 min. Other preparations using different reducing agent, with or without methanolic NaOH, were conducted similarly.

The microwave irradiation preparation was carried out in a commercial microwave oven. The required amount of stabilizer was mixed with 12.50 ml DMF in a 50 ml Pyrex beaker. Then 0.25 ml of AgNO_3 solution (2.945×10^{-2} to 2.356 M) was added. For some preparations, this was followed by drop-wise addition of 125 μ l methanolic NaOH (0.008–0.400 M) or methanolic HCl (8.000×10^{-6} to 8.000×10^{-4} M). The Ag colloid was obtained after irradiation for 20 s at output power of 700 W.

3. Results and discussion

3.1. Formation of nanosized Ag particles

In the preparation of the PVP stabilized Ag nanoparticles carried out in 97% MeOH + 2% H_2O + 1% methanolic

NaOH mixture by conventional heating, it was observed that the color changed as follow (Fig. 1A). At the initial state before the addition of methanolic NaOH solution but after refluxing for 3 min, the solution was pale yellow. The particles, which were of different sizes and shapes, were not well separated and stuck together to form many small groups with different shapes including round, rectangular and square. A clear yellow solution appeared immediately when the first drop of 0.08 M methanolic NaOH solution was added. The colour of the solution changed to yellowish dark brown as the final drop of 1.00 ml of the methanolic NaOH solution was added. The colour persisted after refluxing for 10 min. These solutions gave a low intensity broad absorption band from 350 to 500 nm with a maximum at 413 nm (Fig. 1B). TEM micrograph showed that the particles were small, spherical and well dispersed, with mean diameter of 4.2 nm. No small groups of particles could be seen. Apparently, the large particles have decomposed into smaller particles indicating that the bond between the particles and PVP is very weak. The large particles were thought to be physically linked with the hydrophobic main chains or branches of PVP at the initial state of the reaction, similar to what had been reported before [16].

In general, after the initial formation of the Ag^0 particles, which have mean diameter of 7.1 nm with large size dispersion, the mean diameter settled to 4.2 nm after refluxing for 10 min. The intensity of the absorption band increased gradually with time until a maximum was reached after 60 min. After which, only small fluctuations in mean particles size were observed (Fig. 1C). It has been confirmed that the intensity of the absorption maximum is correlated to the amount of Ag^0 present and that as the particles size increased, the absorption maximum was red shifted to higher wavelength [17–19]. Thus, we can infer that the reduction under the above conditions has been completed only after a period of about 1 h. Although the variation in particles size from 10 to 120 min is rather small after the initial particle formation, a weak correlation between the size and the small shifts in the absorption maximum is also perceptible.

In contrast to the above observation, Silvert et al. [17] reported that the formation process of Ag particles stabilized in PVP using ethylene glycol as the solvent and also as the reducing agent could be separated into three regions. At the initial state of the reaction, the majority of particles present are small with a few large one. As the reaction proceeded, the small particles grew in size. At the end of the reaction the system consisted mainly of larger particles. On the other hand, He et al. [16] reported that the 1-nonanethiol capped Ag nanoparticles were large at the beginning of the reduction. The particle size decreased slowly in mid-process and grew into larger particles at the end of the reduction.

3.2. Effect of reducing agent and water

The reductions of Ag colloids using EG, DMF, MeOH, EtOH and IPA as solvents and reducing agents with addition

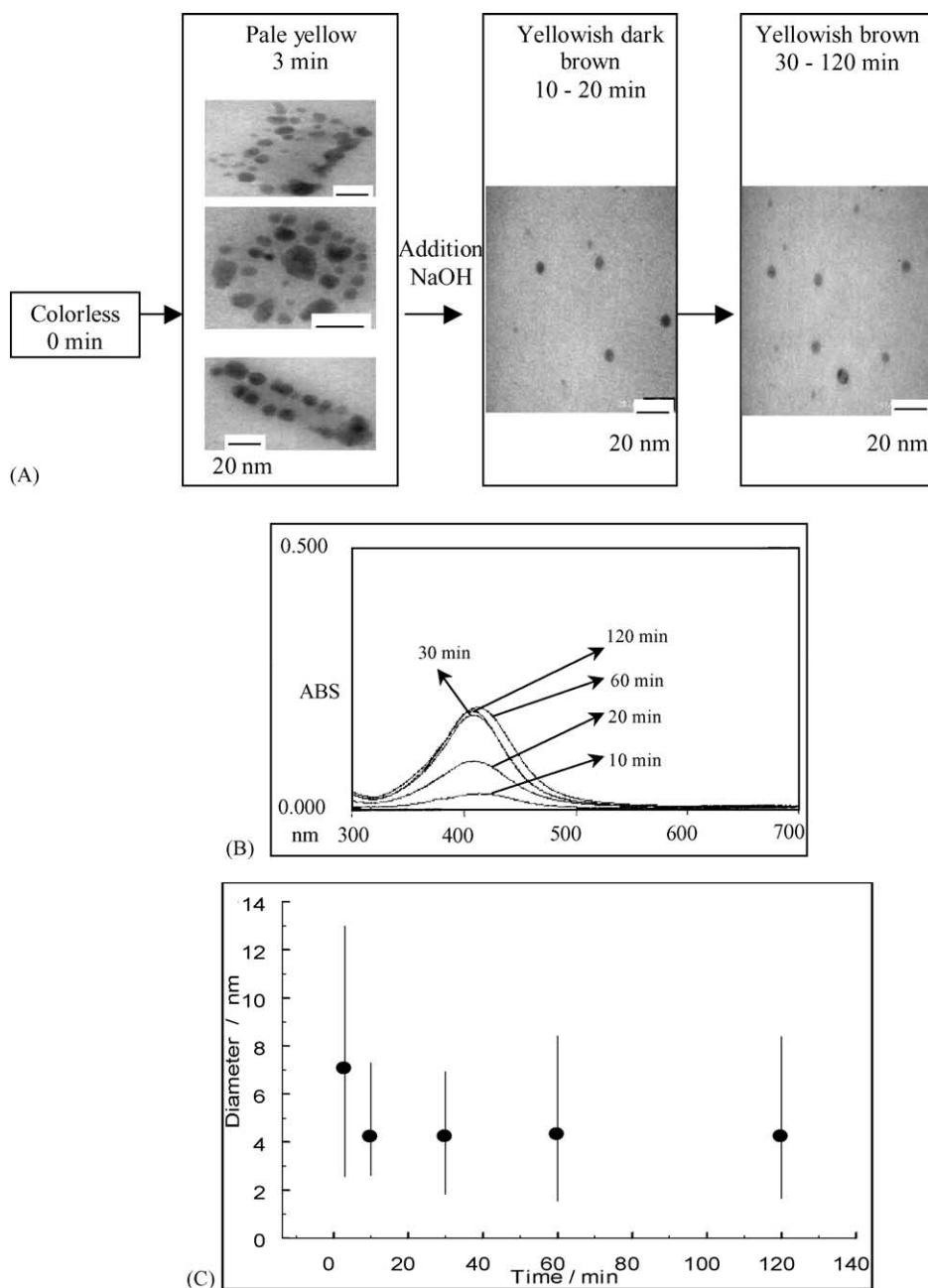


Fig. 1. Formation of Ag nanoparticles in 97% MeOH + 2% H₂O + 1% methanolic NaOH. (A) TEM micrograph and changes of color in the reaction solution, (B) UV-vis spectrum (dilution factor = 26×) and (C) particles size distribution. Conditions: [PVP]:[AgNO₃] = 150, [NaOH]:[AgNO₃] = 1.36, refluxed 120 min under N₂.

of 0.08 M methanolic NaOH were carried out. For all the preparation a small volume of water was needed to dissolve the precursor salt. Thus, the 97% reducing agent + 2% H₂O + 1% methanolic NaOH and 49% reducing agent + 50% H₂O + 1% methanolic NaOH solutions were prepared.

Fig. 2 shows the mean diameter and standard deviation of the particles obtained by different reducing agents at the two volume ratios. In the first solution, the particles were small, well dispersed and narrowly distributed in all preparations except with EG, from which large, broadly distributed particles although still spherical and well dispersed, were obtained.

On decreasing the concentration of the reducing agent, the particles size increased greatly with broad size ranges when reduced by DMF and MeOH. However, when reduced by EtOH and IPA, the mean diameter increased only slightly and a few of the larger particles were surrounded by small particles. The mean diameter of the particles varies in the order of DMF > IPA > EtOH > MeOH.

More detailed investigation on the effect of water using MeOH as the reducing agent was carried out. As shown in Fig. 3A, mean diameter of the particles increased from 3.5 to 11.5 nm with increasing volume of water in the solution.

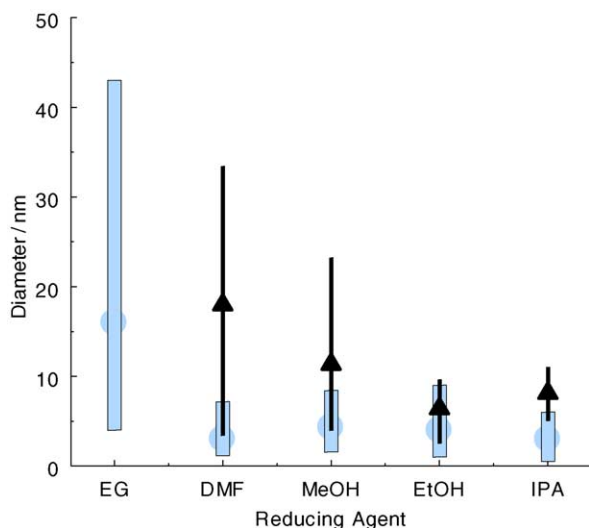


Fig. 2. Effect of reducing agent on particles size distribution. (●) 97% reducing agent + 2% H₂O + 1% methanolic NaOH and (▲) 49% reducing agent + 50% H₂O + 1% methanolic NaOH. Conditions: [PVP]:[AgNO₃] = 150, [NaOH]:[AgNO₃] = 1.36, refluxed 60 min under N₂.

From the TEM micrographs, the particles are spherical and well dispersed in all preparations except for the sample prepared in the 50% H₂O solution. In this solution, no spherical particles were observed. The small particles were joined together forming short rods and aggregated into chains, which is apparently the intermediate stage for the formation of nano-wire (Fig. 3B).

It is generally believed that the higher the reducing activity, the smaller the particles formed [18]. The increase in the mean diameter of particles as the water content in MeOH was increased thus means that its reducing activity had been reduced which is intuitively reasonable. It would also mean that increased in water content decreased the reducing activity of the more active reducing agents, DMF, more drastically than the less active reducing agents, EtOH, IPA and MeOH.

3.3. Effect of NaOH and HCl

The UV–vis spectrum of Ag colloids stabilized by PVP and reduced by different reducing agents without the addition of methanolic NaOH after refluxing for 60 min are presented in Fig. 4. The UV–vis spectrum of Ag colloids reduced by DMF has the highest intensity band followed by EtOH, IPA and MeOH corresponding to their decreasing reducing power. Further, stable Ag colloid was obtained when PVP was used as the stabilizer but precipitation was observed when β-CD was used. However, in the presence of methanolic NaOH, the intensities of the absorption bands with the different reducing agents were almost the same. This is consistent with the increase in reducing power by the addition of methanolic NaOH in all the reducing agents.

The mean diameter and standard deviation were shown in Table 1. It is seen that the mean diameter of the particles decreased with an increase in methanolic NaOH concentration

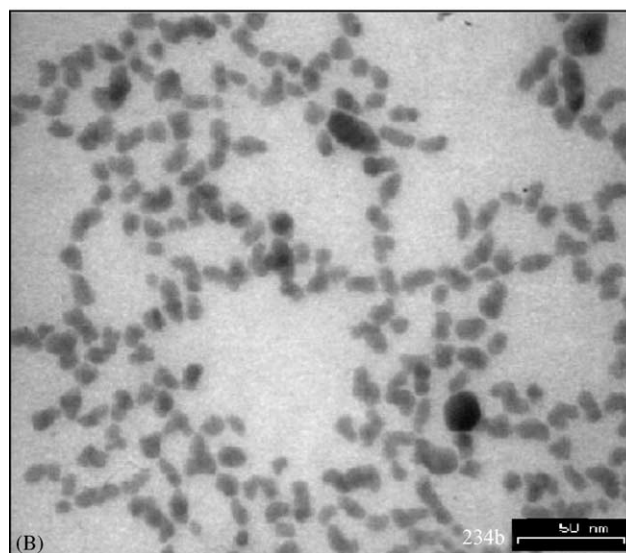
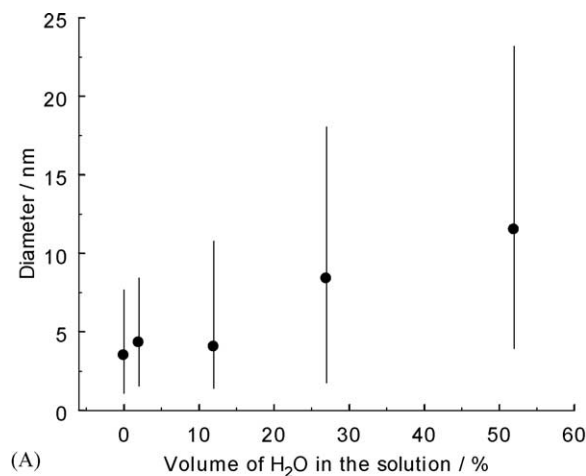


Fig. 3. Effect of water in PVP stabilized Ag colloids (A) particles size distribution and (B) TEM micrograph (scale bar = 50 nm) for 50% of water in the solution. Same conditions as in Fig. 2 reducing agent = MeOH.

then increased again at the highest methanolic NaOH concentration studied irrespective of the method of preparation or the stabilizer used. However, the conventional heating method produced larger particles and larger size distribution at the

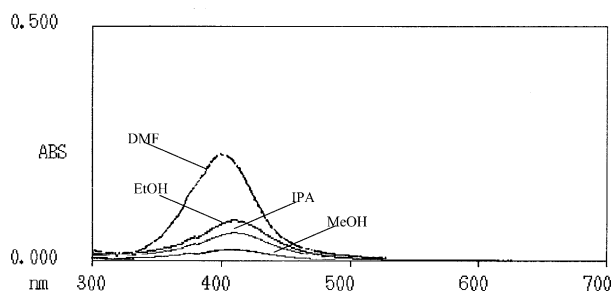


Fig. 4. UV–vis spectrum of Ag colloids reduced by 97% reducing agent + 2% H₂O + 1% MeOH in the absence of methanolic NaOH. Conditions: [PVP]:[AgNO₃] = 150, refluxed 60 min under N₂. Dilution factor = 26×.

Table 1
Effect of preparation conditions on particle size reduced by DMF

Run number	Stabilizer: [AgNO ₃] ^a	[NaOH] (M)	[HCl] (M)	Mean diameter ± standard deviation (nm)			
				Microwave irradiation ^b		Conventional heating ^c	
				PVP	β-CD	PVP	β-CD
1		0	0	6.6 ± 4.9	8.0 ± 5.6	11.5 ± 3.4	Precipitate
2		0	7.767 × 10 ⁻⁸	2.2 ± 3.0	3.4 ± 5.6		
3		0	7.767 × 10 ⁻⁷	4.6 ± 7.9	9.9 ± 7.0		
4		0	7.767 × 10 ⁻⁶	5.3 ± 9.3	20.0 ± 10.7		
5		7.767 × 10 ⁻⁵	0	10.6 ± 8.4	4.4 ± 2.6	14.7 ± 4.1	12.8 ± 5.5
6		3.883 × 10 ⁻⁴	0	3.1 ± 0.8	3.7 ± 2.0	8.5 ± 3.1	7.0 ± 2.6
7		7.767 × 10 ⁻⁴	0	2.6 ± 0.7	1.2 ± 0.2	3.2 ± 1.1	2.3 ± 1.0
8		3.883 × 10 ⁻³	0	6.9 ± 3.7	3.2 ± 2.3	5.8 ± 2.3	5.8 ± 1.7
9	1			5.4 ± 1.9	4.8 ± 2.9	11.0 ± 4.0	6.9 ± 3.3
10	2			5.5 ± 2.2	7.0 ± 7.8		
11	19			5.6 ± 1.8	4.0 ± 5.0		
12	50			3.5 ± 0.9	2.0 ± 0.3	4.4 ± 1.6	6.4 ± 1.8
13	100			2.6 ± 0.7	1.3 ± 0.3	3.8 ± 1.2	5.3 ± 1.6
14	150			2.6 ± 0.7	1.2 ± 0.2	3.2 ± 1.1	2.3 ± 1.0

^a For run 1–9, [AgNO₃] = 5.72 × 10⁻⁴ and [stabilizer]:[AgNO₃] = 150. For run 10–11, the stabilizer concentration was 8.572 × 10⁻² M (PVP as a monomeric unit). For run 9, 12, 13 and 14, the AgNO₃ concentration was 5.72 × 10⁻⁴ M.

^b Irradiation for 20 s at output power of 700 W.

^c Refluxed 60 min under N₂.

corresponding methanolic NaOH concentration whether stabilized by PVP or β-CD. It is further shown in Table 1 that smaller particles were produced in β-CD than in PVP at the corresponding methanolic NaOH concentration especially in the microwave irradiation method.

It has been reported by Chou et al. [20] that the Ag particle size could be controlled to the range of 10–100 nm by changing the pH of the reaction system by adjusting the concentration of Na₂CO₃ added to the solution containing 1:1 molar ratio of NaOH:AgNO₃. Furthermore, the Ag particles increased in size and precipitated when more NaOH was added. In contrast, we could control the particles sizes to within 1–50 nm by adding different methanolic NaOH concentration. The discrepancy may be due to the different synthesis condition used in the earlier work. In this work, Ag colloid was obtained from the PVP:Ag weight ratio of 100. In contrast, Chou et al. reported that the weight ratio of 9.27 and AgNO₃ solution concentration of 0.005 M was used, which was about 10 times higher than our AgNO₃ concentration.

A number of studies have been reported on the effect of alkaline solution on the particles size [12,13,20]. However, the effect of acidic solution is scarcely reported. In this study the effect of methanolic HCl on PVP and β-CD stabilized Ag colloids was carried out using microwave irradiation method. As shown in Table 1, the particle size is large in the absence of methanolic HCl. The addition of a low concentration of methanolic HCl decreased the particles sizes from 6.6 ± 4.9 to 2.2 ± 3.0 nm and 8.0 ± 5.6 to 3.4 ± 5.6 nm for PVP and β-CD stabilized Ag particles respectively. The particles became larger with further increases in the methanolic HCl concentration to 7.767 × 10⁻⁷ M. No further change in the colour of the solution was observed when the concentration of HCl was further increased.

3.4. Effect of stabilizer and precursor concentration

The particle size distributions of PVP and β-CD stabilized Ag colloids in the presence of methanolic NaOH under different synthesis method were presented in Table 1. The particle size decreased with increasing molar ratio of stabilizer: AgNO₃ from 1 to 150 in both the stabilizer and the synthesis method. When PVP was used as the stabilizer, the mean diameter of the particles decreased from 11.0 to 3.2 nm and 5.4–2.6 nm for conventional heating and microwave irradiation respectively. While with β-CD as the stabilizer, the mean diameter of the particles decreased from 6.9 to 2.3 nm and 4.8–1.2 nm for conventional heating and microwave irradiation, respectively. The size distribution of PVP and β-CD stabilized Ag colloids by microwave irradiation method are narrower than the conventional heating method at the same molar ratio. β-CD showed a lower effective protection for Ag particles at the lower molar ratio but at molar ratio above 50 no appreciable change in the particles size was observed.

The effect of the quantity of AgNO₃ between the molar ratio of AgNO₃: stabilizer from 6.7 × 10⁻³ to 0.520 in PVP and β-CD stabilized Ag colloids with addition of methanolic NaOH were studied by using microwave irradiation method. The mean diameter and standard deviation were shown in Table 2. The particles obtained were small and well distributed at low molar ratio of AgNO₃:stabilizer. The size of β-CD stabilized Ag particles increased from 4.0 ± 5.0 nm to 7.0 ± 7.8 nm corresponding to molar ratio of 0.052 and 0.520, respectively. In contrast, only negligible changes in the particles size were observed when stabilized by PVP.

The particle size increased with increasing stabilizer concentration and decreased with increasing precursor concentration. These observations can be understood as follow: at

low stabilizer or high precursor concentration, the stabilizer layer is not effectively built-up around the Ag^0 atoms, they will grow to become larger. At the same time, new nuclei are formed during the growth, resulting in wide size distribution. In the intermediate range and high stabilizer or low precursor concentration, stabilizer concentration is high enough to stabilize the Ag^0 atoms, preventing their aggregation hence smaller size and narrow distribution.

4. Conclusion

We have determined the parameters for the synthesis of size-controlled, well dispersed Ag nanoparticles. The particles size is small if the volume of water in the solution is less than 3%. However the mean diameter of particles would grow to 11.5 nm of short rod shape when the volume of water was increased to 50%. The particles size decreased with increasing methanolic NaOH concentration until an optimum amount, after which the particles size increased again. The presence of methanolic HCl, other than at very low concentration, does not favor the production of small nanosized Ag particles with narrow size distribution. The particles are large with broader size distribution.

Microwave irradiation method produces smaller and more narrowly distributed Ag particles than conventional heating method, most likely due to the much higher rate of reduction with microwave irradiation. Generally, the particle size decreased with increasing concentration of stabilizer in the reduction system. However, at the same precursor concentration, especially in the microwave irradiation method, β -CD stabilized Ag particles are smaller and more narrowly distributed than the PVP stabilized particles at the higher stabilizer concentration. At the same stabilizer concentration in the microwave irradiation, β -CD produces larger and more widely distributed particles than PVP at the higher precursor concentration.

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