

Preparation of silver nanoparticles with controlled particle size

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Abstract

Silver colloids show different colors due to light absorption and scattering in the visible region based on plasmon resonance. The resonance wavelength depends on particle size and shape. Here we report chemical reduction methods for preparation of silver nanoparticles exhibiting multicolor in aqueous solutions. Depending on chemical conditions the obtained nanoparticles are different regarding size and morphology. In order to investigate the relationship between size, stability and color of silver colloids we obtained silver nanoparticles in aqueous solutions using different reducing agents. The effect of polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA) on stabilization of obtained silver colloids was investigated. We have also studied the effect of silver precursor and its concentration on the formation of stable silver colloids. UV-VIS spectrum for silver colloids contains a strong plasmon band near 410 nm, which confirms silver ions reduction to Ag⁰ in the aqueous phase. The formation of metal silver was also confirmed by powder X-ray diffraction (XRD) analysis. The diameter size of silver nanoparticles was in the range from 5 nm to 100 nm

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1. Introduction

Silver particles having fine or ultrafine sizes have attracted scientific interest because of their unusual properties compared to bulk metal. Colloidal particles because of their quantum size effects and surface effects reveal excellent electrical conductivity, catalytic activity, chemical stability and antimicrobial activity.

These properties have led to tremendous range of applications of silver nanoparticles, such as antibacterial textiles and nanosilver-contained polymers used to make refrigerators, dish washers, rice cookers, plastic film, chopping boards, vacuum bottles, plastic pails, and garbage containers [1]. Silver nanoparticles can also be used in various near field optical microscopy applications. Silver colloids show different colors due to light absorption and scattering in the visible region based on plasmon resonance, the frequency at which conduction electrons oscillate in response to the alternating electric field of incident electromagnetic radiation. The color of metal nanoparticles depends on the shape and size of the nanoparticles and dielectric constant of the surrounding medium. However, only electrons with free electrons (essentially Au, Ag, Cu and the alkali metals) possess plasmon resonance in the visible spectrum, which give rise to such intense colors. Elongated nanoparticles (ellipsoids and nanorods) display two distinct Plasmon band related to transverse and longitudinal electron oscillations. The longitudinal oscillation is very sensitive to the aspect ratio of the particles, so that slight deviations from spherical geometry can lead to impressive color changes. The plasmon resonance and unique colors have significant potential for single molecule labeling based

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biological assays and biodiagnostic applications. In the past few years, nanoparticle production by a size-controlled or shape-controlled procedure has become a new and interesting research focus.

Due to the growth process of nanocrystallites controlled by the stabilizers, it is possible to manipulate the shape and size of silver nanoparticles by choosing different protecting agents. Thus, the stabilizer employed may be different with different shapes of silver nanoparticles required in the targeted application [2].

Shultz et al studied the effect of the size and shape on the spectral response of individual silver nanoparticles. They found that specific geometrical shapes give distinct spectral responses. The shape dependence of the optical spectra was obtained from controlled heating experiments on silver particles. The morphological and spectral changes of individual triangular particles were observed as a function of heat treatments [3].

The particle size and morphology can be modified due to changing the concentration of reducing agent and stabilizer. Pileni et al. [4] obtained silver colloids with different particle size and color by changing the concentration of reducing agent. By increasing the hydrazine content, the sizes of the silver nanoparticles increase, inducing drastic changes in the optical properties. They found that the color of the solution depends on the initial synthesis conditions, from red for the lowest reducing agent ratio to green and gray for the highest (see fig. 1)

Qian et al. [5] prepared silver nanoparticles by chemical reduction in different solvents under microwave irradiation. The influence of the solvent type on the optical properties and the morphologies of the silver particles were investigated. They reported that silver nanoparticles prepared in different solvents had different morphologies and sizes, for example in pyridine, spherical silver nanoparticles with an average size of 8 nm were formed. The solution was yellow and only one sharp symmetric absorption peak at ca. 403 nm was observed in the UV-Vis spectrum. In ethanol, most of the particles formed were spherical of 32 nm diameter. Nanoprisms were observed using DMF as the solvent [5].

In this study, we report the preparation method of silver colloids by aqueous solution phase routes. Depending on chemical conditions the obtained nanoparticles are different regarding size and morphology. The effect of stabilizers (polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA)) and type of reducing agents (hydrazine, sodium borohydride and ascorbic acid) on the particle size, shape and color of the colloid solution were investigated. We have also studied the effect of silver precursor and its concentration on the formation of stable silver colloids and the particle size.



Figure 1. Solutions of nanocrystals dispersed in reverse micelles and obtained at various hydrazine concentrations [Pileni, 2003]

2. Experimental procedure

Silver nitrate (pure p.a.) was provided by POCh, silver acetate and silver citrate were obtained, purified recrystallized and both were used as silver nanoparticles precursors. Hydrazine anhydrous, ascorbic acid (99%), sodium borohydride were purchased from Aldrich and used as the reducing agents. Polyvinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA) were provided by Aldrich and used as stabilizers. For the preparation of aqueous solutions, Milli-Q deionized water was used.

Ag colloids were prepared by the chemical reduction of AgNO_3 , $\text{C}_2\text{H}_3\text{AgO}_2$ or $\text{C}_6\text{H}_5\text{Ag}_3\text{O}_7$ with hydrazine, sodium borohydride or ascorbic acid in the presence of stabilizers such as PVP or PVA.

UV-visible spectra were recorded with a 1 cm path length quartz cell using an HP 8453 spectrophotometer. Deionized water was used as the reference sample to take the blank spectrum for all measurements. The size distribution of samples was measured on Malvern Instruments Zetasizer 3000. The crystal structures of the silver nanoparticles were examined by X-ray diffraction (XRD) analyses using a Philips Xpert PRO – MPD diffractometer. The diameter size of the silver nanoparticles was confirmed by XRD analysis. The average crystallite sizes of the doped samples were determined by analyzing the most intense XRD peaks and using the Scherrer's equation.

3. Results and discussion

3.1. Particle preparation and characterization

Silver nanoparticles of different morphology were prepared in aqueous solutions using wet chemical reduction methods. Application of various reducing agents led to colloids with different color, schematically represented in Fig. 1.

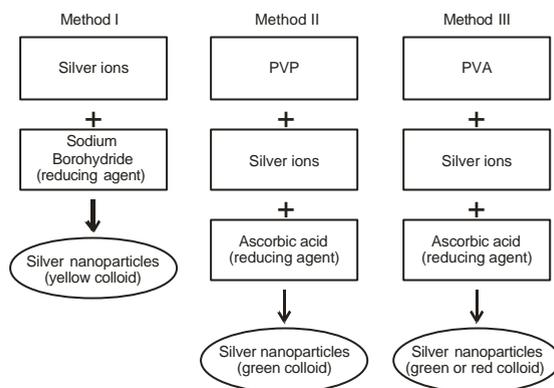


Fig 1 Diagram of preparation methods of silver nanoparticles obtained in aqueous solutions

3.1.1. Preparation of silver particles using NaBH_4 as reducing agent and stabilizer.

In the first method silver nanoparticles at the concentration of 250 and 500 mg/dm^3 were obtained by addition of silver precursor (silver citrate, silver nitrate or silver acetate) dropwise into an aqueous solution of sodium borohydride that had been chilled in an icebath. 2-fold molar excess of the reducing agent to silver ions was used. The reaction solution turned yellow characteristic for the spherical particles, when the entire silver precursor had been added (see fig. 2). The obtained colloids using silver citrate as precursor of silver were transparent and stable in time (for at least 3 months). When silver nitrate or silver acetate was used as precursors of silver particles the colloids were unstable and silver precipitated after 1 day. A spectrum of silver colloids using silver citrate as silver precursor contains a strong plasmon band close to 396 nm, which confirms that silver ions were reduced to Ag^0 in the aqueous phase (fig. 3).

Yellow color for spherical silver particles was also reported by Jin et al. [6]. They obtained spherical silver particles by injection of NaBH_4 solution to an aqueous solution of AgNO_3 in the presence of trisodium citrate followed by dropping of BSPP (as particles stabilizing agent. After 70 h irradiation of silver particles, they observed a decrease in intensity of the characteristic surface plasmon band in the UV-vis spectroscopy for the spherical particles at $\lambda_{\text{max}} = 400$ nm with a concomitant growth of three new bands of $\lambda_{\text{max}} = 335$ (weak), 470 (medium) and 670 nm (strong). Transmission electron microscopy shows that the initial spherical silver particles (8.0 + 1.7 nm) were converted to prismatic structures [6].



Fig. 2. Silver colloid prepared in aqueous solution using sodium borohydride as a reducing agent

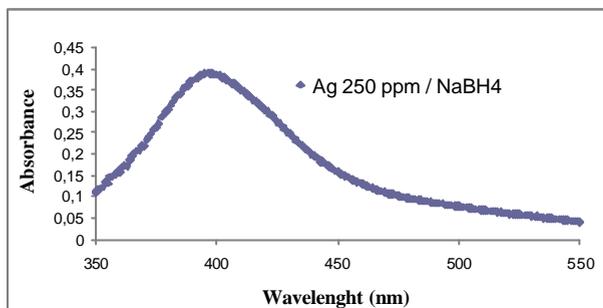


Fig. 3. UV- Vis absorption spectrum of yellow silver colloid

3.1.2. Preparation of silver particles using PVP as protecting agent

Silver nanocubes were obtained in aqueous solution using PVP as a protecting agent. Silver precursor was added into the 150 ml of deionized water containing 5g of PVP in order to obtain silver colloid in concentration 250 mg/dm^3 or 500 mg/dm^3 Ag. Then the aqueous solution of ascorbic acid in the molar ratio $\text{AgNO}_3/\text{C}_6\text{H}_8\text{O}_6 = 1.2$ or $\text{C}_6\text{H}_8\text{O}_6/\text{Ag}_2\text{C}_6\text{H}_5\text{O}_7 = 0.54$ were added dropwise into the silver nitrate or silver citrate solution and stirred for 1h.

The effect of silver precursor on color and stability of the obtained colloids using PVP as stabilizer was investigated. When silver nitrate or silver acetate were used as precursors of silver particles, greenish colloids were obtained (see fig. 4). These silver colloids were unstable in time and silver precipitated after 1 week. Colloids obtained using silver citrate as precursors of silver particles were transparent green and stable in time (fig. 5).



Fig. 4. Silver colloid prepared using silver nitrate as precursor of silver



Fig. 5. Silver colloids prepared using silver citrate as precursor of silver in aqueous solution, silver content: 1000 mg/dm^3

Spectra of silver colloids contain a strong plasmon band close to 410 nm, which confirms that silver ions were reduced to Ag^0 in the aqueous phase. We found that as the concentration of silver increased the absorption band became sharper (fig. 6). The maximum absorption gives rise to a red shift from 402 nm to 407 nm when the AgNO_3 concentration is increased from 250 mg/dm^3 to 1000 mg/dm^3 , meaning the particle size increased and large silver aggregates formed. These conclusions from the

absorption spectra have been confirmed by particle size distribution analysis. The particles size increased from 36 nm for silver colloid containing 250 mg/dm³ of silver to 82 nm for the silver colloid containing 1000 mg/dm³ of silver.

The formation of metal silver was also confirmed by powder X-ray diffraction (XRD) analysis. Fig. 7 shows typical XRD pattern of silver nanoparticles obtained in an aqueous solution using PVP as protecting agent and silver nitrate as a silver precursor. All the reflection peaks can be indexed to face-centered cubic silver. The crystallite size of the 250 ppm colloid of silver determined from XRD pattern using the Scherrer's equation average 40 nm. This result was confirmed by measuring particle size distribution (see table 1).

PVP was used to stabilize and complex silver ions by Pastoriza-Santos et al. [8]. They concluded that the use of PVP with different polymer chain lengths leads to particles with similar sizes though with a different degree of stability. Samples prepared using PVPK30 (MW 40000) are more stable than samples prepared in the presence of PVPK15 (MW 10000) [8].

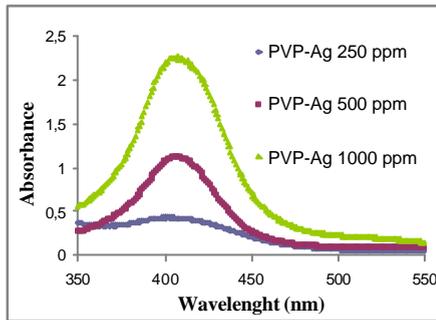


Fig. 6. UV-Vis absorption spectra of silver colloids containin different silver amount.

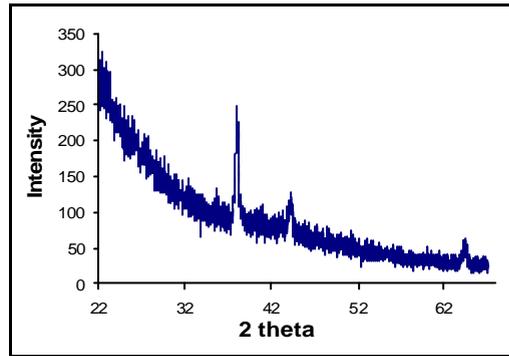


Fig. 7. Fig. 1. XRD pattern of silver nanoparticles prepared in aqueous solution using PVP as a protecting agent

3.1.3. Preparation of silver colloids using PVA as protecting agent

The effect of polyvinyl alcohol (PVA) on stabilization of silver colloids using different reducing agents (hydrazine, ascorbic acid) and silver precursors (silver nitrate, silver citrate, silver acetate) was investigated. Colloidal silver particles at the concentration of 250 and 500 mg/dm³ were obtained by addition by drop aqueous solution of reducing agent containing 0.5 g of PVA in 100 ml of water into the 100 ml of aqueous solution of silver precursor containing 0.5 g of PVA. The solution turned green after the addition of 10 ml of solution of ascorbic acid and red when all of reducing agent was added (see fig. 8). After one day the particles were aggregated and the color of the solution changed into transparent brown but the brown colloid were stable for several months without precipitation. We have also found that silver acetate does not stabilized silver nanoparticles in aqueous solutions using PVA as a protecting agent.

Fig. 9 shows that the absorption peak at approximately 410 nm corresponded well with that of silver nanoparticles and the UV-vis absorption spectra density for the silver formation depends on the silver ions concentration. Obviously, the absorption intensity increases with increasing silver ions concentration, which reflects the formation of more silver nanoparticles. However, the absorption maximum is little different when the AgNO₃ concentration is varied. When the silver ions concentration change from 250 mg/dm³ to 500 mg/dm³ the maximum absorption gives rise to a red shift from 410 to 414 nm. When the AgNO₃ concentration is further increased to 1000 mg/dm³ gives rise to a blue shift of the maximum absorption from 413 to 409 nm



Fig. 8. Observed colors of silver colloids prepared using PVA as stabilizer, silver content: 500

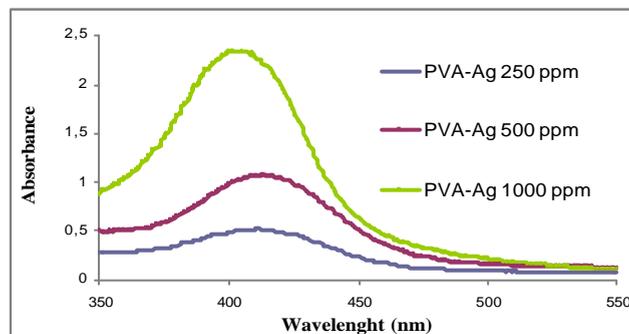


Fig. 9. UV-Vis absorption spectra of silver colloids containing different silver amount.

mg/dm³

3.2. Particles size distribution

Obtained silver nanoparticles had diameter in the range from 5 nm to 100 nm. It was found that the size of silver nanoparticles obtained in aqueous solutions using PVA as stabilizer did not depend on the concentration of silver in the range from 250-1000 ppm Ag. Preparation conditions and characterization of obtained silver colloids including relative abundance are presented in Table 1.

Table 1. Characteristics of silver particles obtained in from silver citrate

Silver amount [mg/dm ³]	Reducing agent	Protecting agent	Average particle size [nm]	pH	Relative abundance [%]				Color of the solution
					< 10 [nm]	10-50 [nm]	50-100 [nm]	> 100 [nm]	
250	Ascorbic acid	PVP	36	5.3	5	62	22	11	green
500	Ascorbic acid	PVP	58	5.3	2	44	30	24	light brown
1000	Ascorbic acid	PVP	82	5.6	1	27	40	32	light brown
250	Ascorbic acid	PVA	44	5.6	3	53	27	17	green
500	Ascorbic acid	PVA	45	5.8	3	53	27	17	light brown
1000	ascorbic acid	PVA	44	5.7	3	53	32	11	brown
500	Hydrazine	PVP	67	7.1	1	45	37	17	green
500	Hydrazine	PVA	48	7.6	3	51	30	16	green
250	Sodium borohydride	none	140	9.1	0	12	28	60	yellow

The particle size of the colloids obtained in the aqueous solution using PVP as the protecting agent increased with the increasing of silver concentration from 36 nm to 82 nm for initial Ag concentration equaled 250 ppm and 1000 ppm, respectively. Particle size distribution for colloids obtained in the presence of PVP are shown in Figure 10.

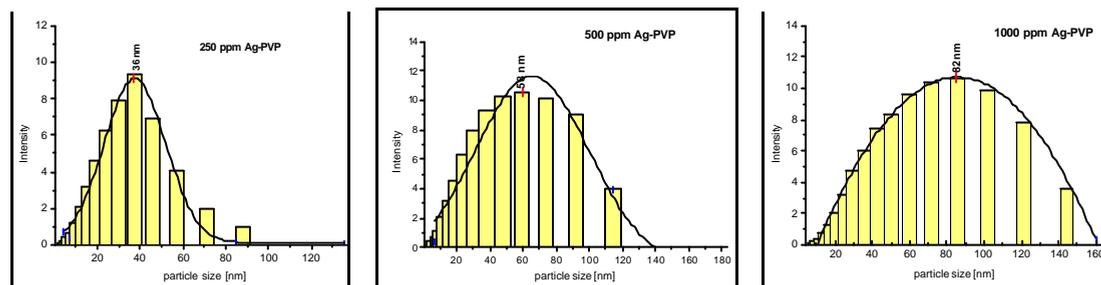


Fig. 10 Particle size distribution of silver nanoparticles with different silver concentration

The influence of reducing agent on stability and particle size was also investigated. We found that at the same concentration of silver ions the strongest reducing agent produced larger particles. When hydrazine was used as reducing agent in PVP aqueous solution the diameter of obtaining silver particles was larger (67 nm) than for ascorbic acid solution (58 nm). The reduction by hydrazine in PVA aqueous solution containing silver ions produced particles with diameter 48 nm while the reduction of silver ions using ascorbic acid in PVA solution results in average silver nanoparticles size around 45 nm (see Figure 11). The most narrow particles size distribution was obtained for system using 250mg/dm³ of silver citrate as Ag⁺ source, ascorbic acid as a reducing agent and PVP as a stabilizer. All samples had one pick on that score intensity, volume and numbers to give evidence about homogeneity of samples.

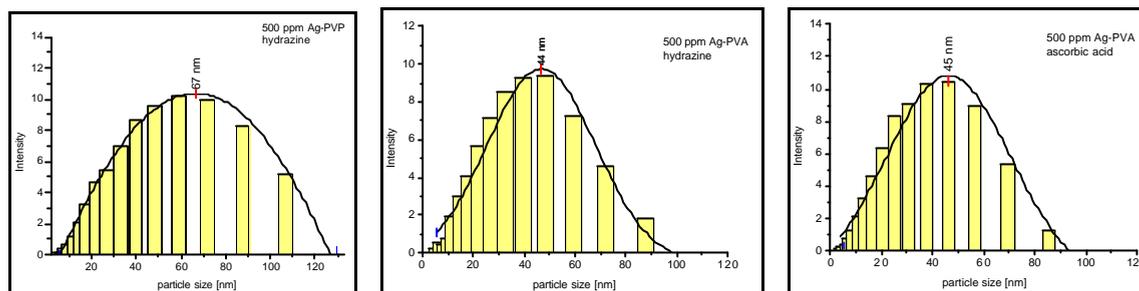


Fig. 11 Particle size distribution of silver nanoparticles using different reducing agents and stabilizers

4. Conclusions

Nanoparticles with different shapes and sizes can be prepared by controlling the reaction conditions. The color of metal nanoparticles depends on the shape and size of the nanoparticles and dielectric constant of the surrounding medium.

In this study we investigated the influence of different parameters such as, type of silver precursor, reducing agent and protecting agent on stability and optical properties of silver nanoparticles. We have found that the silver precursor had an important effect on the crystallinity of the silver nanoparticles. When silver citrate was used as precursor of silver particles in aqueous solution, all the obtained colloids were stable in time in the investigated range. When silver nitrate or silver acetate was used as precursor of silver particles in investigated conditions, silver particles were aggregated and precipitated from the solution.

Silver nanoparticles prepared using different reducing agents had different morphologies and sizes. At the same concentration of silver in solution smaller silver particles were obtained using ascorbic acid as reducing agent than for strong reducing agents such as hydrazine or sodium borohydride. We found that the size of silver nanoparticles obtained in aqueous solutions using PVA as stabilizer did not depend on the concentration of silver in the range from 250-1000 mg/dm³ Ag. The particle sizes of the colloids were around 44 nm. Silver nanoparticles obtained in the aqueous solution using PVP as the protecting agent increased with the increase of silver amount from 36 nm for 250 mg/dm³ Ag to 82 nm for 1000 mg/dm³ Ag.

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References

- [1] V. Pillai, P. Kumar, M. J. Hou, P. Ayyub and D. O. Shah, *Adv. Colloid Interf. Science* 55 (1995) 241-269.
- [2] W. Zhang, X. Qiao, J. Chen, *Mat. Sci. Engin. B*, 142 (2007) 1–15.
- [3] J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, and S. Schultz, *J. Chem. Phys.* 116 (2002) 6755-6759.
- [4] M. Maillard, S. Giorgio, M.P. Pileni, *J. Phys. Chem. B*, 107 (2003) 2466-2470.
- [5] R. He, X. Qian, J. Yin, Z. Zh, *J. Mater. Chem.* 12 (2002) 3783-3786.
- [6] R. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science* 294 (2001) 1901-1903.
- [7] I. Sondi, D.V. Goia, E. Matijevic, *J. Colloid Interface Sci.* 260 (2003) 75-81.
- [8] I. Pastoriza-Santos, L. M. Liz-Marzán, *Langmuir* 18 (2002) 2888-2894.