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Growth and Stabilization of Silver Nanoplates in Aqueous Solvent Monitored Through UV-Vis Spectra

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Sliver nanoplates were prepared through a visible light induced reduction process by a reaction between sodium citrate and silver nitrate in an aqueous solvent at room temperature. UV-Vis spectra were employed to monitor the growth of the silver nanoplates. The resulting spectra indicated that, at an early stage, the products were spherical particles with planar nanoparticles appearing and growing subsequently. In the last stages of the process, some spherical particles were consumed by the growth of the nanoparticles, through an Ostwald ripening mechanism. Furthermore, it was found that the addition of either Poly(Vinyl Pyrrolidone) (PVP) or excessive citrate could stabilize the colloidal system effectively, and that rigorous stirring was necessary for the anticipant products. Introduction of a large quantities of sodium hydroxide can dramatically accelerate the reactive rate of the photoreduction process.

Key words: Silver, Nanoplates, Surface plasmon resonance, Stabilization, Stirring

I. INTRODUCTION

A UV-Visible spectrophotometer is a very convenient tool for monitoring the evolution of metal nanoparticles in solution-phase system, due to their specific surface plasmon resonance (SPR) excitation of various morphologies. SPR is an optical phenomenon which occurs in the interaction between incoming light and the free conduction of electrons of metal nanoparticles. It arises when the wavelength of light couples with the oscillation frequency of the conductions [1], such resonance frequencies are always in the UV-Visible wavelength range. The absorption spectrum of spherical particles exhibits only one SPR peak, while that of nanorods exhibits two peaks, corresponding to the longitudinal and transverse plasmon modes [2,3]. Triangular nanoplates might have four SPR peaks, corresponding to two quadrupole and two dipole plasmon excitation modes, and the intense in-plane dipole peak and the sharp out-of-plane quadrupole peak are apt to be observed [4,5]. Even for the spherical nanoparticles, the absorption spectrum would change markedly if an aggregated structure formed [6].

Recently, silver nanoplates have attracted intense interest due to their unique optical properties, potential applications in biological diagnosis, and multiple labels [7]. Many synthetic methods have been used to prepare silver nanoplates, such as sonochemical technique [8], seed-mediated growth [9,10], soft template-directing growth [11], thermal-reduction in organic solvent [5] and photoinduced conversion of small silver

nanospheres to nanoplates [4,12]. We had found that silver nanoplates could be prepared through a direct photoreduction method in aqueous solvent at room temperature, and this method didn't require any seeds or soft-templates to induce the growth process. In a solution-phase system, nanoparticles tend to aggregate due to their large surface energy, caused by the large surface-volume ratio, and then their physical and chemical properties may be affected remarkably. So it is important to ensure the stabilization of the colloid system [13]. As we mentioned above, the absorption spectrum of the nanoparticles depends on their shape and can be altered by the aggregated structure. In this research, we used a UV-Vis spectrophotometer to investigate the growth process of silver nanoplates and surveyed various experimental conditions for preparing colloid products with good stability. In addition, we examined the influence of alkali on the reaction system.

II. EXPERIMENTAL SECTION

A. Materials

Silver nitrate($AgNO_3$), PVP(M_W=40,000), trisodium Citrate dehydrated ($Na_3Cit \cdot 2H_2O$) and sodium hydroxide (NaOH) were purchased from Shanghai Chemical Reagents Company. All chemicals were of analytical grade.

B. Basic experimental process

1 mL $AgNO_3$ (5 mmol/L), 1 mL Na_3Cit (30 mmol/L) and 48 mL de-ionized (DI) water were mixed in a 100 mL conical flask, and the neck of the flask was covered with an inverted 50 mL beaker. The system was

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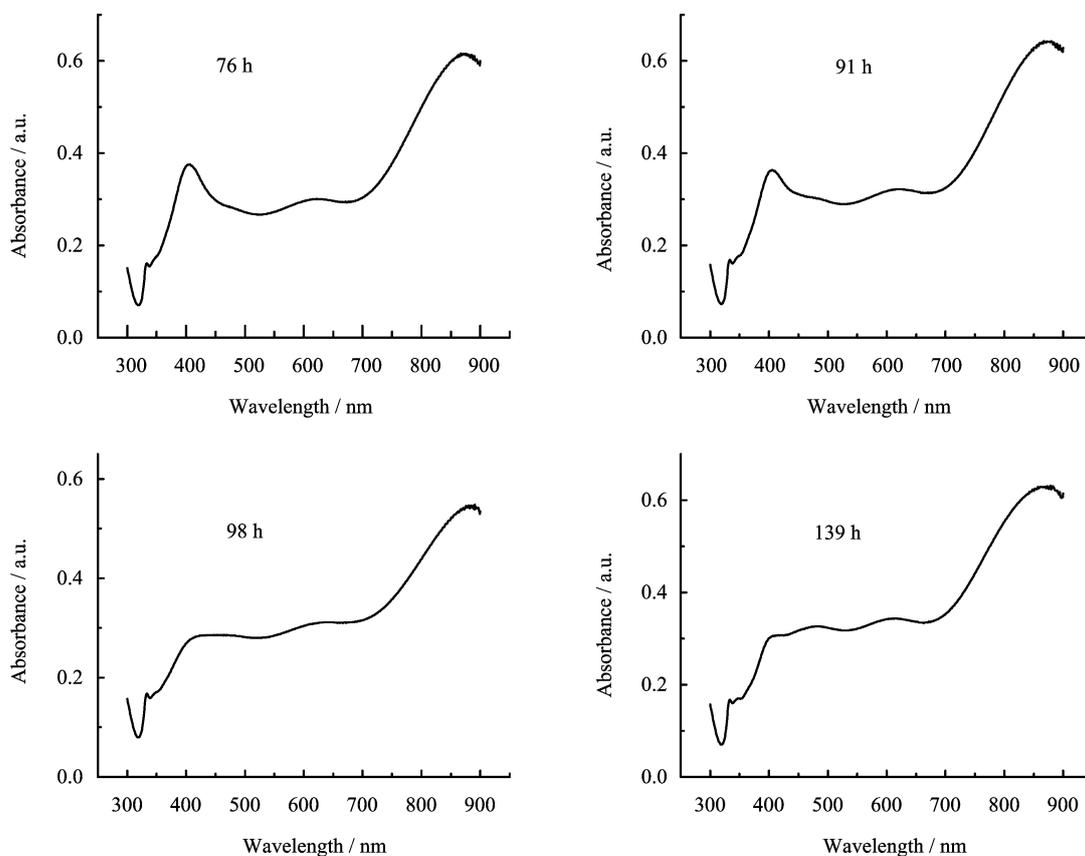
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FIG. 1 UV-Vis spectra of the silver nanoparticles when using additional sodium citrate (4 mL).

then irradiated with a conventional 40 W tungsten lamp (the distance between the lamp and the solution being about 13 cm). It was at the room temperature and the temperature of the solution was never higher than 25 °C, so the thermal effect of the irradiation could not be significant.

Other experimental conditions were as follows: use of more solution of Na$_3$Cit (4 mL); addition of aqueous solution of PVP (2 mL, 45 mmol/L (repeat unit)) before irradiation; application of magnetic stirring; introduction of an alkali to the reaction system.

C. Characterization

The reacting solution was monitored using a UV-2401PC spectrophotometer (Shimadzu), sampling 3 mL with a pipet each time. The products were characterized by transmission electron microscope (TEM) (JEM-100SX, Japan) and X-ray diffraction pattern (XRD) (Philips X' Pert Pro Super X, Holland).

III. RESULTS AND DISCUSSION

Under initial experimental conditions, the solution appeared to be green and cloudy after being irradiated

about 70 h. Further irradiation led to a cloudier solution, in which little precipitation could be observed on the bottom of the flask. These phenomena indicated that the colloid solution, at that point, had poor stabilization, and that the particles were apt to aggregate. In order to produce the desired products, we explored changing experimental parameters, such as the use of more citrate, introduction of PVP to the system, and use of magnetic stirring to improve the stabilization of the colloid system. UV-Visible spectra were used to monitor the influence of different experimental approaches. Citrate acted as a reducing agent in our experiments, as it could be oxidized into acetone-1,3-dicarboxylate and carbon dioxide [14].

A. The effect of more citrate

Citrate proved to be a good stabilizer for silver nanoparticles in a dimethylsulfoxide solvent [13], and it was also used as a stabilizer in an aqueous solution [15]. Based on this finding, we increased the quantity of citrate to test its effect in our experiment. The quantity of citrate was increased from 1 mL to 4 mL, while other experimental conditions were unaltered. Figure 1 shows the time-dependent absorption spectra of the reacting system in the late stages.

The absorption spectrum at 76 h exhibited three peaks at 335, 410 and 870 nm. The peak at 410 nm can be attributed to the SPR excitation of the spherical nanoparticles, and the other two demonstrate the formation of planar nanoparticles, the 335 nm peak being the out-of-plane quadrupole resonance and the 870 nm peak being the in-plane dipole resonance of the nanoplates [4]. This spectra indicate that the spherical particles and planar ones coexisted in the solution. It can be seen that the absorbance of the 410 nm peak began to drop at 91 h, this may result from the aggregation of the nanoparticles or the transformation of spherical particles to nanoplates. From the absorption spectrum at 98 and 139 h, it can be seen that the peak at 410 nm disappeared, the spectra became irregular and the absorbance between 400 and 700 nm showed a flat configuration with few waves. These features are very similar to the absorption spectrum of the aggregated silver nanoparticles [6], so it can be concluded the aggregation phenomenon had happened in the last stage of the reaction. From the above results, we know that increasing the quantity of citrate does not facilitate a well stabilized colloid solution.

B. Influence of PVP on the stabilization of the colloid system

As a water-soluble macromolecule, PVP could be chemically absorbed by the surfaces of silver nanoparticles and prevent them from aggregating into larger ones [16]. So it was tested as a stabilizer in our experiment. An aqueous solution of PVP (2 mL, 45 mmol/L) was added to the original mixed solution with the other components unchanged. The mixture was then irradiated with the tungsten lamp. The resultant colloid solution was more transparent and bright compared to that of the initial experiment under similar conditions. Figure 2 shows the time-dependent absorption spectra of the reacting system.
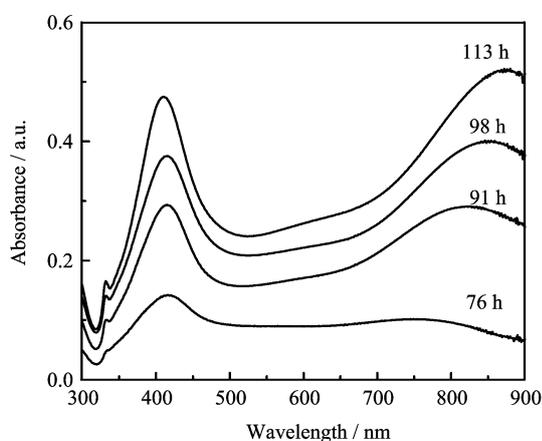
The spectrum at 76 h show an obvious peak at around 410 nm and other two weak peaks located at about 335 and 770 nm. It can be concluded that the products were mostly spherical nanoparticles at the early stage, with a few planar particles also existing in the system. Introduction of PVP reduced the growth rate of the nanoplates due to its capption effect, so the SPR peaks relative to the planar particles were very weak. As the reaction proceeded from 91 h to 113 h, the peak at 410 nm gradually increased in intensity, indicating the formation of more spherical nanoparticles. Concurrently, the other peaks became more and more intensive, indicating a significant increase in the formation of nanoplates. The absorption spectra beyond 113 h showed no obvious extra change. This might indicate that the silver ions were all reduced by the citrate and the spherical particles were in equilibrium with the nanoplates. From Fig.2, we can see that the peaks at 410 nm were always symmetrical and no irregular absorption spectrum appeared as in Fig.1. Furthermore, the absorption spectra of the resultant colloid solution showed little or no change even after being stored in darkness for one week. All these features demonstrate the stabilization effect of PVP on the colloid system.

C. Influence of stirring

Magnetic stirring can improve the homogeneity of the solution-phase reacting system and prevent the enrichment of particles in partial regions, so it favors the obtaining of a stable colloid solution. We investigated the evolution of the absorption spectra of the reacting system with magnetic stirring, without changing the concentration of mixture component or introducing any macromolecules (Fig.3). We discuss, at great length, the growth of the nanoparticles.

The absorption spectrum at 76 h shows only one peak at around 410 nm, indicating that the spherical

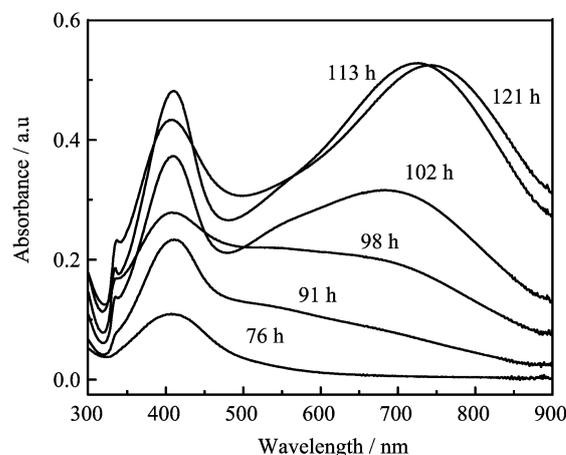FIG. 2 UV-Vis spectra of the colloid solution when adding 2 mL of PVP solution (45 mmol/L).

FIG. 3 UV-Vis spectra of the solution under rigorous magnetic stirring condition.

nanoparticles were the only products in this early stage. As the reaction proceeded to 91 h, the number of spherical particles increased, and a weak peak at 335 nm relative to the out-of-plane quadrupole resonance of planar particles appeared. This weak peak suggests the nanoplates were growing. When the reaction had proceeded for 98 h, this peak became more obvious, and another peak in the longer wavelength zone, relative to the in-plane dipole resonance of the planar particles, appeared. In the period from 102 h to 113 h, the intensity of the in-plane dipole resonance peak increased more and more, indicating the formation of more nanoplates. The position of the peak red shifted stage by stage, indicating an increase in the size of the nanoplates. As the reaction proceeded to 121 h, the intensity of the peak at 410 nm decreased substantially, and the peak in the longer wavelength zone showed a slight red-shift. These changes in the optical spectra imply that the silver ions had been all reduced and that the nanoplates were growing at the expense of the spherical particles through an Ostwald ripening process.

Compared to Fig.1, Figure 3 lacked any similar spectral character, indicitive of the aggregative structure, and the peaks at 410 nm were always symmetrical. These features demonstrated that the magnetic stirring promoted homogeneity in the reacting system and facilitating production of the desired colloid solution.

Figure 4 shows TEM image of the products (sampled from the solution without any purification). It can be observed that the spherical particles and the nanoplates coexisted in the colloid system. The particles were well dispersed, and no aggregate structures appeared, corroborating the UV-Vis spectral results. Moreover, most of the particles were triangular nanoplates or truncated nanoplates, which could explain the out-of-plane quadrupole resonance and the in-plane dipole resonance peaks shown in the above absorption spectra. It was reported [4] that the in-plane dipole resonance peak was at 770 or 670 nm for triangular nanoplates and truncated nanoplates with edge length of 100 nm. This peak in our experiment clearly red shifted; this could
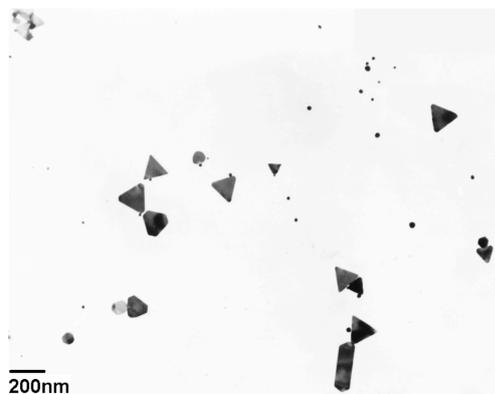
be attributed to the larger size of the nanoplates (edge length of the nanoplates was up to 120 nm even 130 nm). XRD pattern (unshown here due to article length limitations) affirmed the crystallization of the nanoparticles. The cell parameter calculated from the XRD result was 4.084 Å, coinciding with previous reports in the literature (e.g. PCPDF No.04-0783).

D. Influence of alkali on the reaction

We investigated the influence of alkali on the reaction system. Under rigorous magnetic stirring, we found that the introduction of a large quantities of sodium hydroxide could accelerate the reaction dramatically. Figure 5 is the time-dependent absorption spectra of the reacting solution with introduction of 10 mL aqueous solution of sodium hydroxide into the initial mixture. It was found that the reaction had proceeded sufficiently in 70 h, further irradiation did not further enhance the in-plane resonance absorption of the nanoplates, and, in fact, led to a slight decrease of the SPR peak of spherical particles due to the Ostwald ripening process. In the absence of additional alkali, the photoreduction reaction would progress sufficiently in about 110 h (Fig.3). The reason for acceleration of the reaction is not yet confirmed, but may be due to the fact that an alkaline environment favors the photooxydation of citrate.
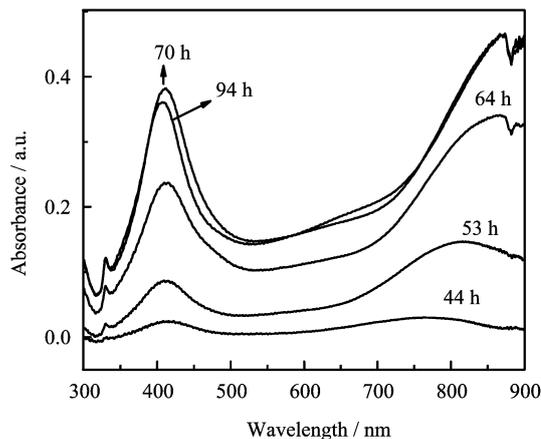

FIG. 5 UV-Vis spectra of the solution when adding 10 mL NaOH (1 mmol/L) under magnetic stirring condition.

IV. CONCLUSION

UV-Vis spectra were used to investigate the growth and stabilization of the colloid solution of silver nanoparticles under different experimental conditions. Under rigorous stirring conditions, the spectra indicated that the products were all spherical particles at the early stage, and that planar nanoparticles appeared

FIG. 4 TEM image of the products.

and grew subsequently. In the final stage of the reaction, some spherical particles were be consumed by the growth of the nanoplates through an Ostwald ripening process. Both magnetic stirring and introduction of appropriate PVP can promote the stabilization of the colloid system effectively. Moreover, we found that adding of a large quantity of sodium hydroxide to the initial mixture can also accelerate the photochemistry process.

[1] U. Kreibig and M. Vollmer, *Optical Properties of Metal Clusters*, Berlin: Springer-Verlag, (1995).

[2] B. Nikoobakht and M. A. El-Sayed, Chem. Mater. **15**, 1957 (2003).

[3] M. Maillard, S. Giorgio and M. Pileni, J. Phys. Chem. B **107**, 2466 (2003).

[4] R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J G. Zheng, Science **294**, 1901 (2001).

[5] I. Pastoriza-Santos and L. M. Liz-Marzn, Nano Lett. **2**, 903 (2002).

[6] T. Yonezawa, S. Onoue and N. Kimizuka, Adv. Mater. **13**, 140 (2001).

[7] R. Elghanian, J. J. Storhoff, R. C. Mucic, R. L. Letsinger and C. A. Mirkin, Science **277**, 1078 (1997).

[8] M. Maillard, S. Giorgio and M. Pileni, Adv. Mater. **14**, 1084 (2003).

[9] S. Chen and D. L. Carroll, Nano Lett. **2**, 1003 (2002).

[10] M. Maillard, P. Huang and L. Brus, Nano Lett. **3**, 1611 (2003).

[11] D. O. Yener, J. Sindel, C. A. Randall and J. H. Adair, Langmuir **18**, 8692 (2002).

[12] Y. G. Sun and Y. N. Xia, Adv. Mater. **15**, 695 (2003).

[13] G. Rodriguez-Gattorno, D. Diaz and G. O. Hernandez-Segura, J. Phys. Chem. B **106**, 2482 (2002).

[14] A. M. Ahern and R. L. Garrell, Anal. Chem. **59**, 2813 (1987).

[15] K. K. Caswell, C. M. Bender and J. Murphy, Nano Lett. **3**, 667 (2003).

[16] X. Zhang, B. Zhao and L. Hu, J. Solid State Chem. **121**, 105 (1996).