

Photoinduced shape transformation from nanospheres to silver triangular nanoprisms and nanodisks: citrate ion concentration and stirring effects

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Silver nanospheres were transformed into triangular nanoprisms and nanodisks via a photoinduced growth process. In order to show the citrate ion concentration effect, the silver nanospheres were prepared in three different silver/citrate ratios (1:1, 1:2 and 1:3). The photoinduced shape transformation was carried out under magnetic or ultrasonic stirring with the purpose of showing the stirring effect. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) images of the obtained nanoplates show nanoprisms and nanodisks of 50 and 30 nm, respectively. The formation of silver nanoplates is very sensitive to the citrate ion concentration, which is confirmed by the UV-Vis spectra. Higher concentrations of citrate ion produce triangular nanoprisms with more sharp vertices. The ultrasonic stirring limits and controls the nanoplate growth.

Keywords: Silver nanoprisms; ultrasonic stirring; localized surface plasmon resonance.

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1. Introduction

In the last years, silver and gold nanoparticles have been of great interest because of their unique chemical and physical properties [1-3]. These nanoparticles have potential applications including surface plasmon resonance [4], surface-enhanced Raman scattering [5], biosensing [6], and optoelectronic devices [7]. The localized surface plasmon resonance highly depends on the particle shape and size, and surface modifications. Silver nanoparticles are easily to use in the design of plasmonic materials and nanodevices [7,8]. Therefore, great efforts have been made to control the shape and size of silver nanoparticles. Nowadays, there are some reports about the truncation of the vertices of triangular nanoprisms in order to obtain nanodisks [9-12]. In contrast, we report the study of the citrate ion concentration and stirring effects in the photoinduced growth of nanoplates, with the purpose of controlling the nanoplate morphology.

2. Experimental section

All chemical reagents used in this work were of analytical grade and were used without any further purification. A Perkin-Elmer lambda 12 spectrophotometer was employed for the UV-Vis analysis of the silver nanocrystals. SEM and STEM images of the silver nanoplates were recorded using a Hitachi S5500 microscope.

Silver nanoplates were obtained via a photoinduced growth method reported by Xu *et al.*, [10]. Firstly, silver nanospheres were synthesized by dropwise addition of 1 mL of 8.0 mM NaBH₄ solution to 100 mL of a 0.1 mM AgNO₃ and 0.1, 0.2 or 0.3 mM trisodium citrate aqueous solution under vigorous magnetic stirring. Then, the nanosphere dispersion was irradiated by a conventional sodium lamp (70 W) under magnetic or ultrasonic stirring.

3. Results and Discussion

A set of color changes for the preparation of silver nanoplates was observed during the course of the reaction under magnetic stirring. The time required for the color change in each experiment is related with the citrate ion concentration of the aqueous dispersion; while higher is the citrate ion concentration, longer time is required for the color change. In general, the initial silver dispersions were yellow, after few hours they turned green and then finally blue. The dispersion with silver/citrate ratio of 1:1 only showed a color change from yellow to light green. Similarly, the dispersion with silver/citrate

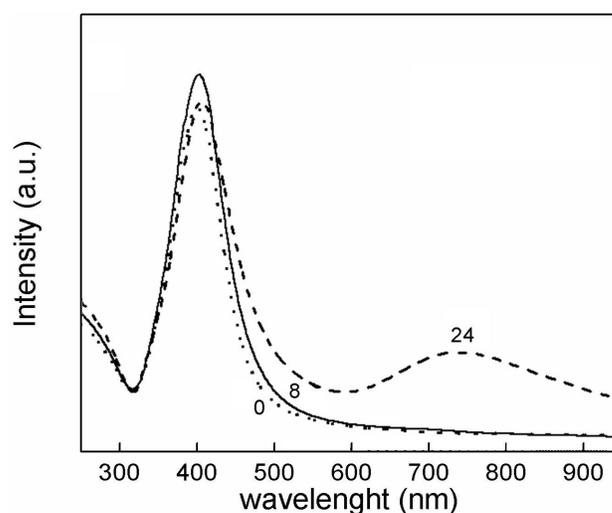


FIGURE 1. UV-Vis absorption spectra of the dispersion with silver/citrate ratio of 1:1, under magnetic stirring, at irradiation times of 0, 8 and 24 h.

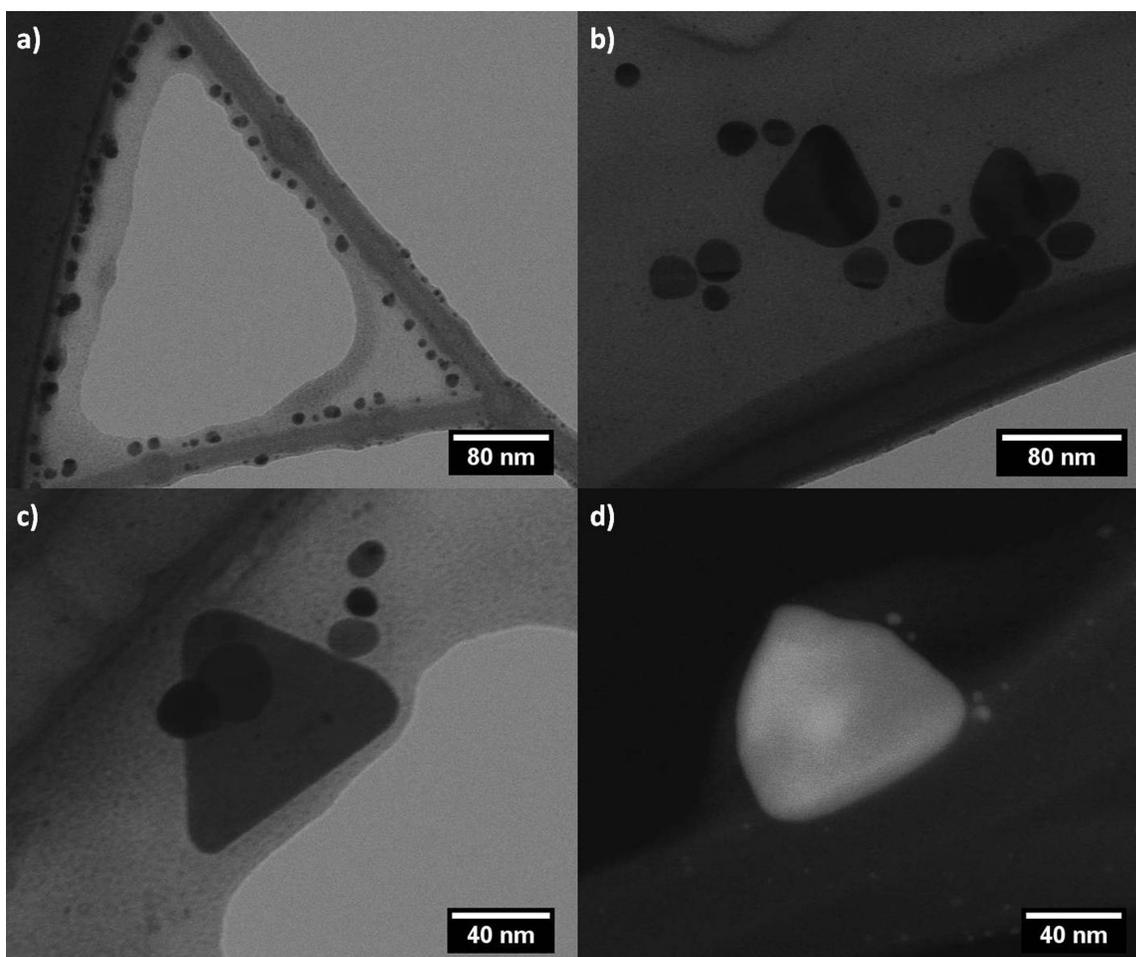


FIGURE 2. STEM (a, b and c) and SEM (d) images of the dispersion with silver/citrate ratio of 1:1, under magnetic stirring, at irradiation times of a) 0, b) 5 and c) 24 h. d) Intermediate state between nanodisks and triangular nanoprism morphologies.

ratio of 1:2 showed a color change from yellow to dark green. The dispersion with silver/citrate ratio of 1:3 was the only one to achieve the blue color. The yellow color is characteristic of the silver nanosphere dispersions, the blue color is characteristic of the silver triangular nanoprism dispersions, and the green color is observed for intermediate states between nanosphere and triangular nanoprism morphologies [13].

UV-Vis absorption spectra of the dispersion with silver/citrate ratio of 1:1, under magnetic stirring, at different irradiation times are shown in Fig. 1. The absorption spectra recorded at 0 and 8 h of sodium lamp irradiation show only a single surface plasmon resonance band at 400 nm, which is according with Mie's theory [14]. This theory predicts that anisotropic particles could show two or more surface plasmon resonance bands depending on their shape. The anisotropy of the triangular nanoprisms leads them to exhibit four surface plasmon resonance bands [13]. The in-plane dipole resonance band is the highest of these absorptions. The spectrum of the silver nanoparticle dispersion recorded after 24 h of sodium lamp irradiation confirms the growth and shape transformation of the nanospheres into anisotropic nanoplates.

Figure 2 shows SEM images of the dispersion with silver/citrate ratio of 1:1, under magnetic stirring, at different irradiation times. As illustrated in Fig. 2(a), silver nanospheres synthesized have an average diameter of 10 nm with a narrow size distribution. After 5 h of sodium lamp irradiation, the nanospheres were transformed into nanodisks with an average diameter of 30 nm, as is shown in Fig. 2(b). Besides, Fig. 2(c) shows that after 24 h one silver triangular nanoprism can be appreciated, however, there are some nanodisks that have not been transformed into nanoprisms. An intermediate state between nanodisks and triangular nanoprism morphologies is shown in Fig. 2 (d). These SEM images are consistent with the UV-Vis spectra of Fig. 1.

Figure 3 shows UV-Vis absorption spectra of the dispersion with silver/citrate ratio of 1:2, under magnetic stirring, at different irradiation times. The absorption spectra recorded at 0 and 4 h of irradiation show only a single surface plasmon resonance band around 400 nm. In contrast, the spectra recorded at 8 and 24 h of irradiation show multiple surface plasmon resonance bands. In the case of the spectrum recorded at 24 h, three distinctive bands appeared at 330 (weak), 400 (medium), and 787 nm (strong) which corre-

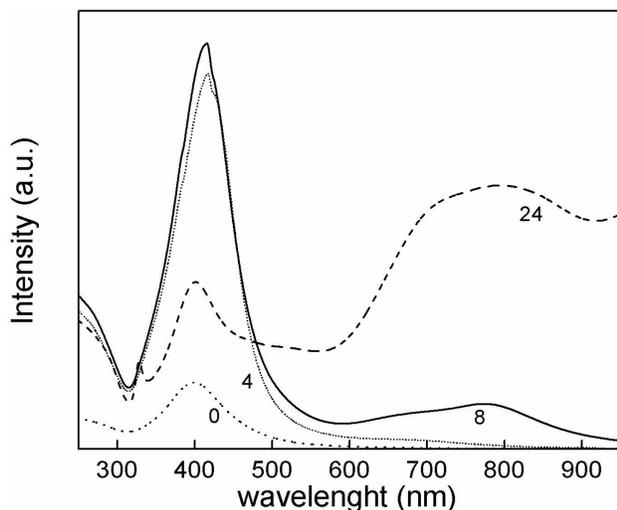


FIGURE 3. UV-Vis absorption spectra of the dispersion with silver/citrate ratio of 1:2, under magnetic stirring, at irradiation times of 0, 4, 8 and 24 h.

spond to the out-of-plane quadrupole, in-plane quadrupole, and in-plane dipole resonances, respectively. The out-of-plane dipole resonance is sufficiently weak that it is not resolved in this absorption spectrum.

UV-Vis absorption spectra of the dispersion with silver/citrate ratio of 1:3, under magnetic stirring, at different irradiation times are shown in Fig. 4. Similarly to the Fig. 3, the absorption spectra recorded at 0 and 4 h of irradiation show only a single surface plasmon resonance band around 400 nm, and the spectra recorded at 8 and 24 h of irradiation show multiple surface plasmon resonance bands. Besides, the spectrum recorded at 24 h shows three distinctive bands appeared at 328 (weak), 400 (medium), and 783 nm (strong) which correspond to the out-of-plane quadrupole, in-plane quadrupole, and in-plane dipole resonances, respectively. In this case, the in-plane dipole resonance band is better defined and narrow than in the spectrum of the dispersion with silver/citrate ratio of 1:2.

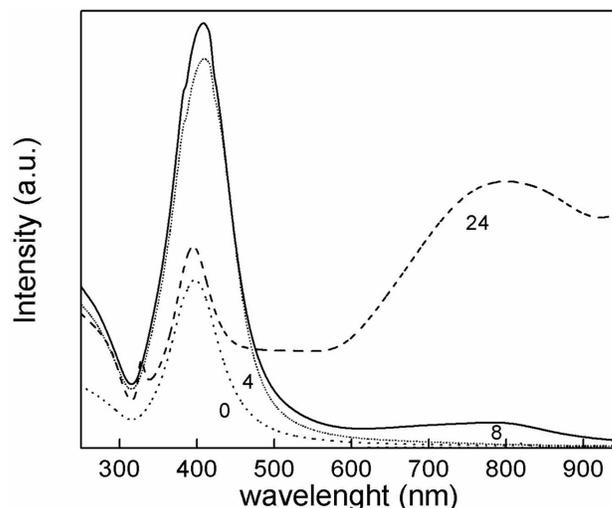


FIGURE 4. UV-Vis absorption spectra of the dispersion with silver/citrate ratio of 1:3, under magnetic stirring, at irradiation times of 0, 4, 8 and 24 h.

Theoretical calculations indicate that the in-plane dipole plasmon resonance band is very sensitive to the sharpness of the triangle vertices [13]. Therefore silver triangular nanoprisms, obtained from the dispersion with silver/citrate ratio of 1:3, under magnetic stirring, have a narrower edge size distribution than the other experiments. Furthermore, the position of their in-plane resonance band indicates that these silver triangular nanoprisms have sharp vertices.

Figure 5 shows SEM images of the dispersion with silver/citrate ratio of 1:3, under magnetic stirring, after 24 h of sodium lamp irradiation. As illustrated in Fig. 5(a), the silver triangular nanoprisms have edges between 50 and 180 nm. The average thickness of the silver triangular nanoprisms is less than 10 nm, as is shown in Fig. 5(b)

By comparing, Fig. 2 (c) and Fig. 5 (b), we observe that the STEM image of the dispersion with silver/citrate ratio of 1:1 shows nanodisks, even at 24 h of sodium lamp irradiation, while the SEM image of the dispersion with silver/citrate

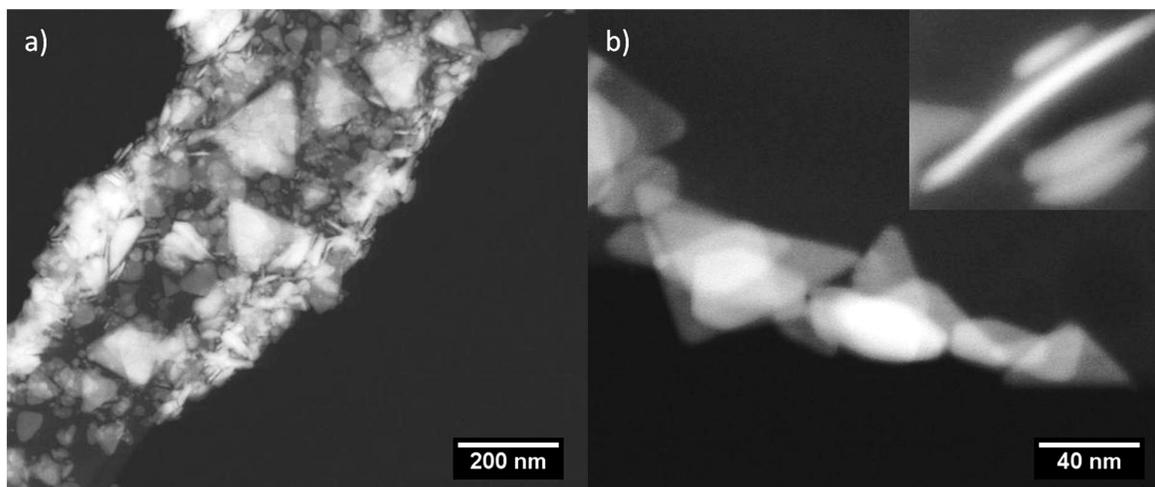


FIGURE 5. SEM images of the dispersion with silver/citrate ratio of 1:3, under magnetic stirring, after 24 h of sodium lamp irradiation.

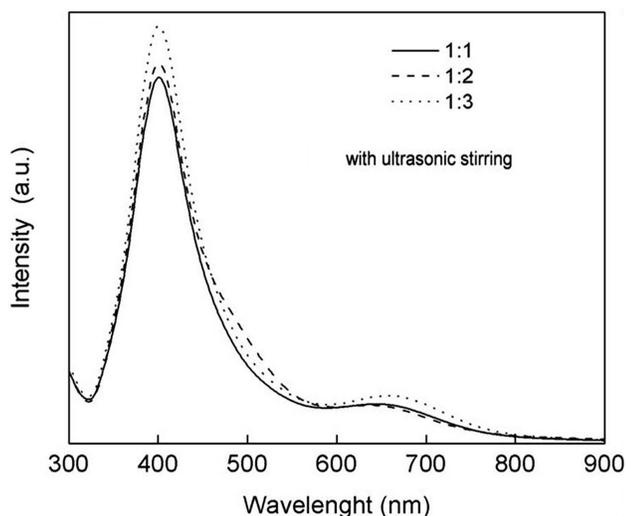


FIGURE 6. UV-Vis absorption spectra of the dispersion with different silver/citrate ratios after 24 h irradiation under ultrasonic stirring.

ratio of 1:3 shows nanoprisms bigger and with more sharp vertices than it showed in Fig. 2(c). The difference between these morphologies is attributed to the stabilizing effect of the citrate ions

In summary, under magnetic stirring, the citrate ion concentration determines the morphology of the silver nanoplates. A higher ion concentration leads to the formation of silver triangular nanoprisms with more sharp vertices. The citrate ions enhance the photoinduced growth process and stabilize the nanoplates. The *ab initio* electronic structure calculations indicate that citrate ions are much more likely to bind to the silver (111) planes than to the (100) planes [15]. Therefore, the (111) planes are not changed during the photoinduced growth process.

Figure 6 shows UV-Vis absorption spectra of the dispersion with silver/citrate ratios of 1:1, 1:2, and 1:3 after 24 h of sodium lamp irradiation under ultrasonic stirring. The three spectra are similar to each other, they show a strong band at 400 nm related to the dipole resonance of the silver nanospheres, and a wide band at 600-700 nm related to the in-plane dipole resonance of the silver nanoplates. This band indicates that the nanoplates have an irregular morphology and size distribution. Therefore, the shape transformation of the nanospheres into nanodisks is not carried out under ultrasonic stirring.

It can be asserted that the ultrasonic stirring limits the growth of the nanospheres and the formation of the nanoplates. The ultrasonic waves avoid the diffusion of the solvated silver ions towards a nanosphere or nanoplate and their subsequent reduction, stopping the growth and shape transformation of the nanospheres into nanoprisms.

4. Conclusions

Silver nanodisks and triangular nanoprisms have been successfully obtained by using a photoinduced growth process. In this method silver nanospheres grow in the presence of citrate ions under sodium lamp irradiation. The citrate ions enhance the photoinduced growth process and stabilize the nanoplates. We can assert that a higher citrate ion concentration leads to the formation of silver triangular nanoprisms with more sharp vertices. The ultrasonic stirring limits the growth of the nanospheres, and therefore the formation of the nanoplates. In addition, the ultrasonic stirring promotes the agglomeration of the nanoparticles.

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