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ORIGINAL ARTICLE

Experimental study on effect of different parameters on size and shape of triangular silver nanoparticles prepared by a simple and rapid method in aqueous solution

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Abstract This paper continues our previous work on preparation of truncated triangular silver nanoparticles. The method proceeds with reaction of silver nitrate with hydrazine in the presence of sodium citrate in aqueous solution, in which triangular nanoparticles are formed in a few minutes with some spherical ones. In particular range of reactants, especially high reductant concentration, only spherical nanoparticles are formed. In further investigation we observed that spherical nanoparticles shape could change to triangular by aging. This means that controlled growth of nanoparticles could lead to the formation of triangular ones. Therefore, a method was devised to slow down the rate of reduction by adding Fe^{3+} to the reaction solution. The results show that in this case more triangular nanoparticles are formed compared to the original one. This result also confirms that with the increasing hydrazine concentration, growth becomes less important compared to nucleation and smaller triangles are formed.

1. Introduction

Research on metal nanoparticles has increased extensively in recent years due to their size and shape dependent optical (Kelly et al., 2003), physical (El-Sayed, 2001) and chemical properties (Kamat, 2002). Developing methods for tailoring metal nanoparticle size and shape enable us easy and large scale production and correlating the optimal properties to structure. Different shapes of silver nanoparticles have size and shape sensitive surface plasmon resonance bands and applications in optics (Kelly et al., 2003), electronics (El-Sayed, 2001), sensors (Haes and Van Duyne, 2002), surface enhanced Raman spectroscopy (SERS) (Nie and Emory, 1997), catalysts (Shiraishi and Toshima, 1999), biological detection and drug delivery (Nam et al., 2003).

Synthesis of triangular silver nanoparticles has become important since pioneering work of Jin et al. (2001) in photo-induced conversion of silver nanospheres to nanoprism in

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several hours. Subsequently, many methods for preparation of silver nanoprism have been reported. Callegari et al. (2003) could adjust size of triangular silver nanoplates by choosing the wavelength of light used to transform spherical nanoparticles to triangular nanoplates. Bastys et al. (2006) also modified Jin et al. (2001) method to form silver nanoprisms with surface plasmons at communication wavelengths. Jia et al. (2006) described synthesis of triangular silver nanoparticles by photoreducing silver ions by citrate. All photoinduced methods need several hours to prepare nanotriangles. Triangular silver nanoplates were also formed by reverse micelles of di(2-ethylhexyl)sulfosuccinate (AOT) (Maillard et al., 2003) and seed-mediated growth in the presence of cetyltrimethylammonium bromide (CTAB) micelles (Chen and Carroll, 2002).

Silver nanoprisms are also synthesized by boiling silver nitrate in dimethyl formamide (DMF) in the presence of poly(vinyl pyrrolidone) (PVP) (Pastoriza-Santos and Liz-Marzan, 2002) and shape transformation by refluxing spherical silver nanoparticles (Sun et al., 2003). Metraux and Mirkin (2005) developed thermal synthesis of silver nanoprism in 20–30 min with controllable thickness.

These methods for synthesis of triangular silver nanoparticles used photo, template, seed and thermal processing which were either time consuming or needed some steps and processings after initial synthesis of silver nanoparticles. No method is reported to produce silver nanotriangles directly as a product of a reaction in aqueous solution. Some methods are also reported in non-aqueous solutions; i.e., reducing silver perchlorate in formamide in the presence of polyethylene glycol (PEG) at room temperature (Sarkar et al., 2005) and shape transformation to triangular nanoplates by aging spherical silver nanoparticles prepared in pyridine in the presence of poly(vinyl pyrrolidone) (PVP) (Deivaraj et al., 2005).

In this paper we completed our previous work (Ghader et al., 2007) on synthesis of truncated triangular silver nanoparticles by improving the yield of triangular nanoparticles. In the previous study, spherical silver nanoparticles were formed in a special range of concentrations. In this study, we observed that these particles turned to triangular ones after two months. This means that after nucleation, when growth becomes a controlling factor the kinetic effects favors triangular nanoparticles formation. This hypothesis was confirmed by slowing down the rate of original synthesis method by introducing Fe^{3+} to the reaction solution. Shape change of triangular nanoparticles to smaller one with increasing concentration of hydrazine could also be justified by considering kinetics effects in shape evolution of particles.

2. Experimental

Silver nitrate, *tri*-sodium citrate dihydrate, hydrazine hydrate and ammonium iron sulfate were supplied by Merck. A solution of 100 mL silver nitrate 0.1 mM and 5 mL of sodium citrate 34 mM (1 wt%) is made. This solution is stirred by a magnet and 5 mL of 2 mM hydrazine is added to the solution drop by drop. Then, the sample exhibited two color changes. After about 3 min the solution color changed to yellow which turned to green in about 2 min indicating formation of truncated triangular silver triangular nanoparticles. The colloid was stable for months. A Zeiss transmission electron microscope (TEM) operating at 80 kV was used to observe the nanoparticles. The samples were prepared by dropping 10 μL of solution on the copper grid covered with amorphous carbon and let to dry in air. UV–vis absorption spectra were recorded with a Varian Cary 50 Conc spectrophotometer with 1-cm length optical cell.

3. Results and discussion

3.1. TEM images

Silver nanotriangles are the product of a reaction, which includes reducing silver nitrate with hydrazine in the presence of sodium citrate as a stabilizing agent. TEM images were taken from the product of the reaction and as Fig. 1 shows triangular nanoparticles are truncated in shape. TEM images indicate that the size of truncated triangular nanoparticles (maximum length of the base as defined by Brioude and Pileni (2005)) is 94 ± 8 nm. TEM images show a mixture of circular, hexagonal and triangular particles.

3.2. UV–vis absorption spectroscopy

The changes in the shape of the silver nanoparticles prepared by adding hydrazine was investigated by UV–vis spectra. Based on the theoretical calculations by Brioude and Pileni (2005) four peaks in absorption spectra of silver nanotriangles can be attributed to in-plane dipolar, in-plane quadrupolar, out-of-plane dipolar, and out-of-plane quadrupolar resonances. In-plane dipolar resonance, at the longest wavelength, is sensitive to the size of the triangle and red shifts with size. The out-of-plane quadrupolar peak appears at the lowest wavelength and is located around 340 nm (Brioude and Pileni, 2005). Fig. 2 shows the experimental UV–vis spectra of silver nanoparticles during the formation of nanotriangles.

Two peaks at the longest wavelengths and the lowest wavelength peak increase as the reaction proceeds, which implies that the amount of nanotriangles increases. Peaks gradually increase and the final absorption peak is observed after 5 min. Final UV–vis spectra exhibit four distinct peaks at 334, 404, 672 and 740 nm. The peak at 334 nm is assigned to out-of-plane quadrupolar resonance. The peaks at 740 and 672 nm are attributed to in-plane dipolar and in-plane quadrupolar resonances, respectively. An intense peak is observed at 404 nm. Since spherical nanoparticles have their absorption peak in this region it shows the existence of spherical nanoparticles in the solution – as observed in TEM images – which are more than triangular nanoparticles.

To examine the reproducibility of the nanotriangles preparation, usually more than 20 samples were prepared and the absorbance was recorded for each sample. Usually only two or three of these samples exhibited more than 5% deviation in the spectrum. Comparing the absorption of nanotriangles to nanospheres at 404 nm 22% of product is nanotriangles. Nanotriangles can be separated from spherical nanoparticles by centrifugation. This method is reported earlier in many references, for example, Maillard et al. (2003), Deivaraj et al. (2005) and Chen and Carroll (2004). The original solution was centrifuged at 6000 rpm for 20 min. Removing the supernatant, the precipitate was dispersed in water. This procedure was repeated once more and the UV–vis spectrum of triangular nanoparticles was obtained. The UV–vis spectrum after centrifugation is shown in Fig. 3 which is more similar to the theoretical calculations by Brioude and Pileni (2005). By

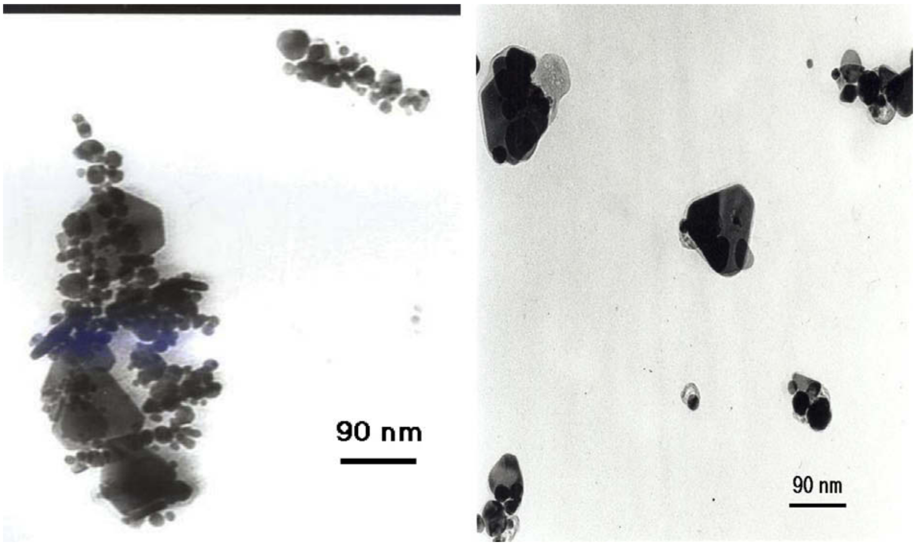

Figure 1 TEM images of truncated triangular silver nanoparticles synthesized by reduction of silver nitrate with hydrazine in the presence of sodium citrate (at different areas of TEM grid).

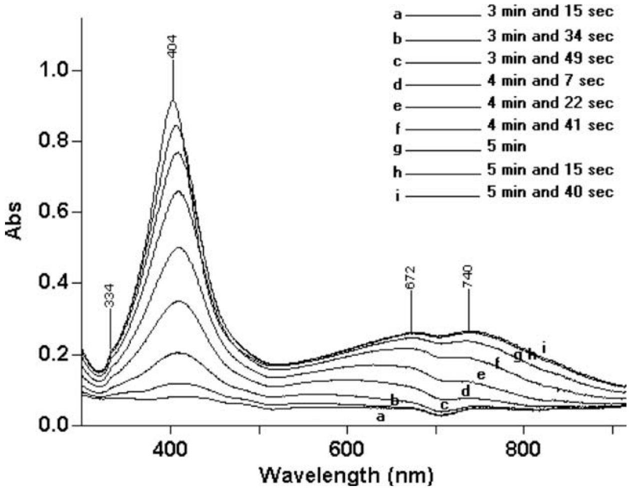

Figure 2 Time change of UV–vis absorption spectra during synthesis of truncated triangular nanoparticles.

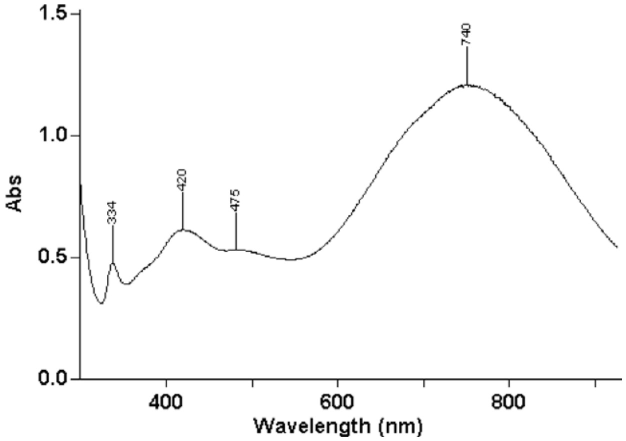

Figure 3 UV–vis spectrum of truncated triangular silver nanoparticles after centrifugation.

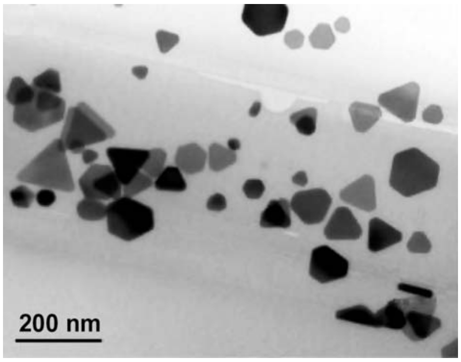

Figure 4 TEM image of truncated triangular silver nanoparticles after centrifugation.

collapsing the intense peak of spherical nanoparticles, a peak at 475 nm appears which is attributed to out-of-plane dipolar resonance. The weak peak at 420 nm relates to residual spherical nanoparticles. A TEM image (Fig. 4) was taken from nanoparticles after centrifugation which shows successful separation of triangular nanoparticles.

3.3. Effect of silver nitrate concentration and aging

Silver nitrate concentration was also an important parameter in triangles synthesis. When silver nitrate concentration was increased to 0.5 mM triangles did not form. The solution color was yellow and the UV–vis absorption spectra of colloid completely changed and a peak at 408 nm was observed (Fig. 5). TEM images of resulting nanoparticles show that spherical nanoparticles are produced (Fig. 6). Similar results on the changing of the shape with concentration of silver nitrate was reported by Pastoriza-Santos and Liz-Marzan (2002). Very small amount of tiny nanotriangles can be seen in the TEM image as shown in Fig. 6. When this solution was

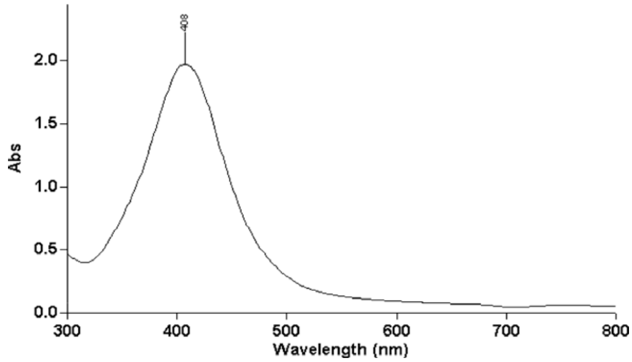

Figure 5 UV–vis spectrum of resulting nanoparticles when silver nitrate concentration increased to 0.5 mM.

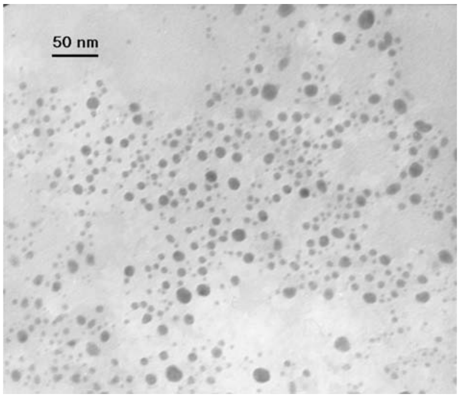

Figure 6 TEM image of resulting nanoparticles when silver nitrate concentration increased to 0.5 mM.

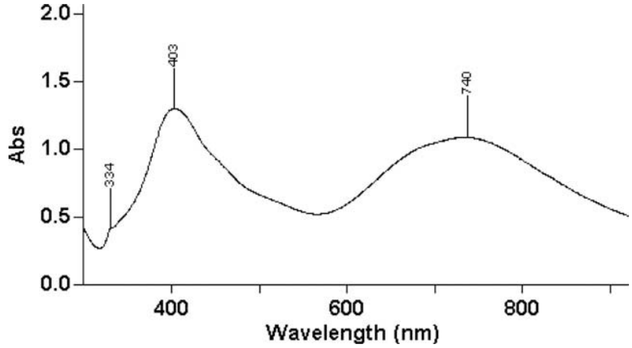

Figure 7 UV–vis spectrum of resulting nanoparticles after aging solution of Fig. 5 for two months (silver nitrate concentration 0.5 mM).

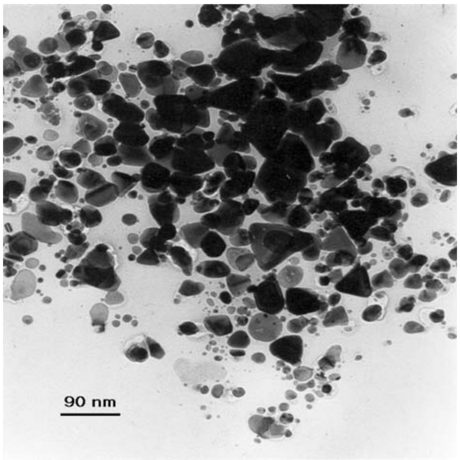

Figure 8 TEM image of resulting nanoparticles after aging solution of Fig. 5 for two months (silver nitrate concentration 0.5 mM).

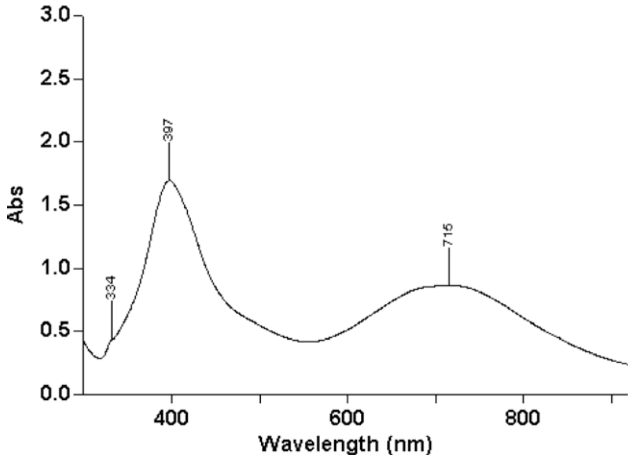

Figure 9 UV–vis spectrum of resulting nanoparticles after ageing solution of Fig. 5 for 45 days in darkness (silver nitrate concentration 0.5 mM).

remained unstirred for two months solution color changed from yellow to green. In this case nanotriangles were formed in the solution by aging – as UV–vis spectrum (Fig. 7) and TEM (Fig. 8) shows – indicating when the amount of silver nitrate is increased; hydrazine is not at sufficient amount to influence synthesis of nanotriangles. Effect of hydrazine is more discussed in the subsequent sections. Aging small spheres increased the yield of nanotriangles. Based on the UV–vis spectrum (Fig. 7) the yield of triangles after ageing increased to 44%.

In another experiment, the nanospheres were kept unstirred in darkness after formation. The nanotriangles were formed in this system too by aging and color of solution also changed to green. UV–vis spectrum (Fig. 9) was taken from this solution after aging it for 45 days which indicates formation of triangles. So it can be concluded that nanotriangles are also formed in darkness and the process is not affected by photo.

In summary, the reduction could be significantly slowed to induce anisotropic growth in the solution by aging. The initial product of such a synthesis was Ag nanoparticles. Once the supersaturation had been reduced to a certain level, the growth of Ag atoms would be switched to a highly anisotropic mode to form Ag nanotriangles. Since the Ag^+ existed in the solution at a low concentration for a long period of time, the Ag atoms could grow into triangles. Increasing yield of triangles and influence of slowing down reduction rate is more discussed in subsequent sections.

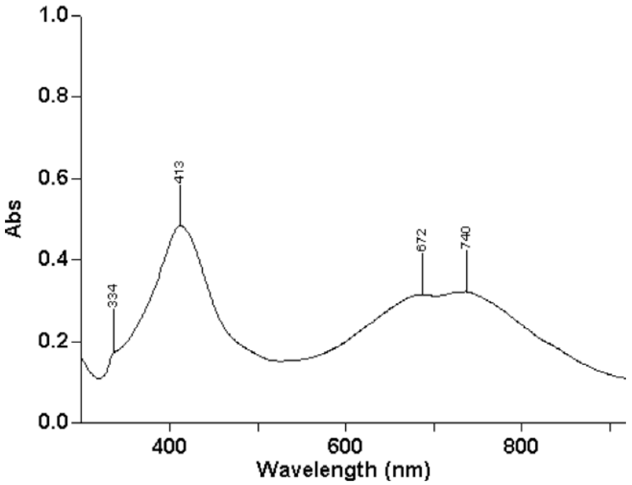

Figure 10 UV–vis spectrum of obtained truncated triangular nanoparticles with citrate concentration 0.3 mM.

3.4. Effect of sodium citrate concentration

Some other experiments were carried out to attain citrate effect on nanoparticles. It was found that triangular nanoparticles were formed at any citrate concentration. Fig. 10 shows the UV–vis absorption spectrum of on the product colloid at low citrate concentration (0.34 mM) as well as TEM image (Fig. 11).

Citrate likely effects face-selective growth by adsorbing more strongly to the Ag(1 1 1) surface to direct the final shape to be a triangle. Many studies have mentioned importance of citrate for preparation of silver triangular nanoparticles (Jin et al., 2001; Callegari et al., 2003; Bastys et al., 2006; Jia et al., 2006; Sun et al., 2003; Metraux and Mirkin, 2005).

3.5. Effect of pH

We also studied the effect of hydrazine solution pH on the synthesis of the triangular nanoparticles since it influences reducing power of hydrazine and formation of triangles. The pH of original hydrazine solution 9.2. Nitric acid and sodium hydroxide were added to hydrazine solution for pH 2–8 and 10–12, respectively. We tried to reveal the role of hydrazine by varying its effect; i.e., changing the pH. At pH 2 almost a clear solution obtained and UV–vis absorption spectra (Fig. 12a) shows weak peaks indicating very small amount of triangular nanoparticles is formed. This result also emphasizes critical role of hydrazine in formation of triangular nanoparticles. Since at low pH condition most of hydrazine is removed, nanotriangles are decreased dramatically. Thus, hydrazine may not just providing reducing power, but participate in shape control. Maillard et al. (2003) also indicated important role of hydrazine in nanotriangles formation. At pH 3.5 solution becomes green and four peaks in absorption spectra grow and become evident. As Fig. 12 represents from pH 4–8 plasmon resonance bands increase indicating formation and increase of triangular nanoparticles.

Nevertheless, further increasing pH results in blue shift of in-plane dipolar resonance band and at pH 12 in-plane dipolar resonance almost disappear and spherical nanoparticles are formed in a yellow color solution as TEM image of Fig. 13 shows. Similar change in absorption spectra with pH was observed by Chen and Carroll (2004). With the pH being 12 the stabilizing agent is most likely OH^- which adsorbs on the nanoparticle surface. Nickel et al. (2000) could also produce spherical nanoparticles by hydrazine pH above 10.

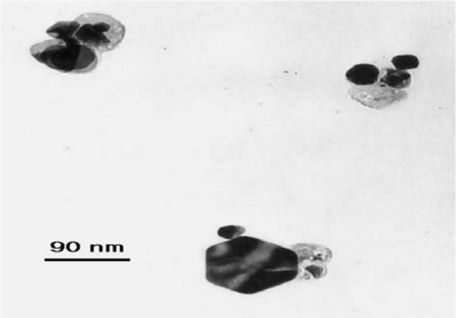

Figure 11 TEM image of obtained truncated triangular nanoparticles with citrate concentration 0.3 mM.

The reaction of hydrazine with silver nitrate produces Ag, N_2 and proton. With increasing pH protons are neutralized with sodium hydroxide and hydrazine does not remain partially protonated. Because of the high redox potential of protonated hydrazine, with increasing pH, the actual redox potential of reducing agent decreases. Therefore, the initial pH should be higher than 10 to see this effect. Furthermore, adsorbed OH^- on nanoparticles prevents triangles production. The peak for spheres also increases a little as triangles disappear. This set of experiments show that choosing proper pH is important for triangles synthesis and it can affect product shape. pH also accelerated the reduction time and even at pH 12 spheres are formed at 30 s.

3.6. Effect of hydrazine concentration and controlling rate of reduction

A study concerned the effect of hydrazine concentration on nanoparticles synthesis is being investigated. Interestingly, with increasing hydrazine concentration in-plane dipolar resonance blue shifts (Fig. 14) was occured. This effect is in accordance with the result observed with varying pH, as increasing pH has unfavorable effect on the production of truncated triangular nanoparticles and ultimately prevent their formation. As the theoretical calculations of Brioude and Pileni (2005) show for nanotriangles smaller than 60 nm two intermediate peaks almost disappear; only in-plane dipolar and out-of-plane quadrupolar resonances remains while smaller nanotriangles are formed as in-plane dipolar resonance blue shifts. TEM image shows that smaller nanotriangles are formed (Fig. 15 for the case c in Fig. 14) after increasing hydrazine. In order to justify why increasing hydrazine concentration leads to smaller triangles, an experimental study was conducted which is explained below.

Since a quasi-spherical nanoparticle has the lowest possible surface energy and is therefore favored by thermodynamics, the growth kinetics of a particle must be carefully controlled to obtain a shape that does not represent an energy minimum. Factors that influence the growth kinetics of a solution-phase synthesis include (i) the concentration of metal precursor, (ii) the rate of reduction (the concentration and power of the

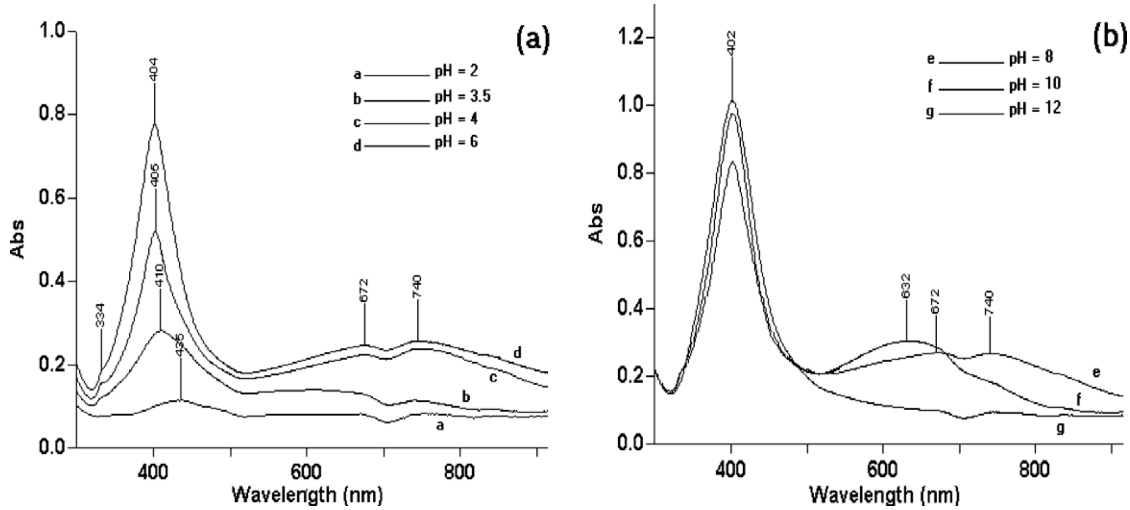

Figure 12 UV–vis spectra of resulting nanoparticles at different pH of hydrazine solution (a) pH 2, 3.5, 4, 6 and (b) pH 8, 10, 12.

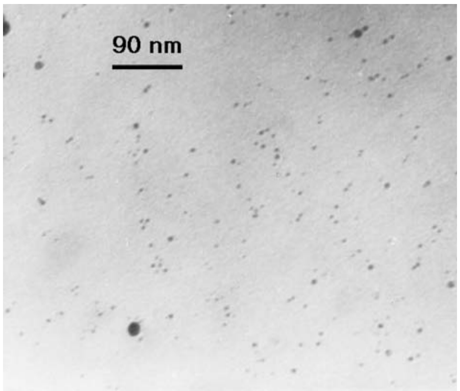

Figure 13 TEM image of resulting nanoparticles at pH of hydrazine solution pH 12.

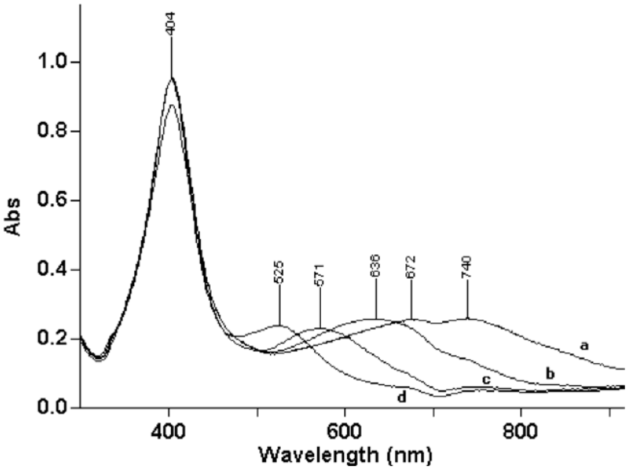

Figure 14 UV–vis spectra of nanoparticles at different hydrazine concentration: (a) 2 mM, (b) 3 mM, (c) 5 mM and (d) 10 mM.

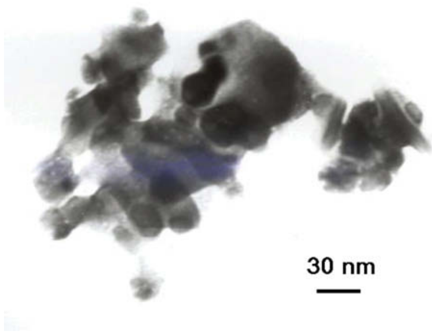

Figure 15 TEM image of truncated triangular nanoparticles at hydrazine concentration 5 mM.

reductant); (iii) the presence of a soft template or capping agent; and (iv) the specific adsorption of a capping agent to a particular crystallographic plane. Several research groups have employed such kinetic controls to generate triangular and circular nanoplates of silver in a number of different solvent systems (Jin et al., 2001; Chen and Carroll, 2002; Pastoriza-Santos and Liz-Marzan, 2002).

Therefore, we explored a way of controlling the rate of reduction to understand the effect of slower growth rate and thus a kinetically favored shape. Since reduction potential of Fe^{3+} is very close to Ag^{+}, the key strategy is the introduction of either Fe^{3+} or Fe^{2+} species to change the growth rate by slowing down the reduction reaction or change the level of supersaturation of Ag atoms, respectively. The addition of Fe^{3+} (0.1 mM) to the triangular silver synthesis slowed down the rate of reduction. This protocol produced results that were concentration dependent and with Fe^{3+} (0.01 M) nanoparticles did not form in the solution, unless excess hydrazine was added to the solution. The addition of Fe^{3+} (0.1 mM) increased the yield of triangular nanoparticles as UV–vis spectrum shows (Fig. 16) with increasing about 1 min the time previously required. The peak of nanospheres is almost reduced to one third of the original solution. The yield of triangular silver nanoparticles in this case was 74% based on absorptions in UV–vis spectrum.

Furthermore, the function of Fe^{2+} (0.1 mM) was not similar to Fe^{3+} and Fe^{2+} accelerated the rate of reduction. With

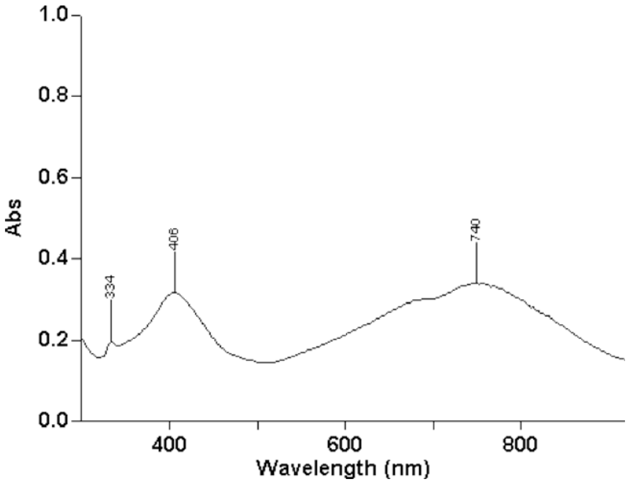

Figure 16 UV–vis spectrum of nanoparticles when adding Fe^{3+} (0.1 mM) to the solution (before adding hydrazine).

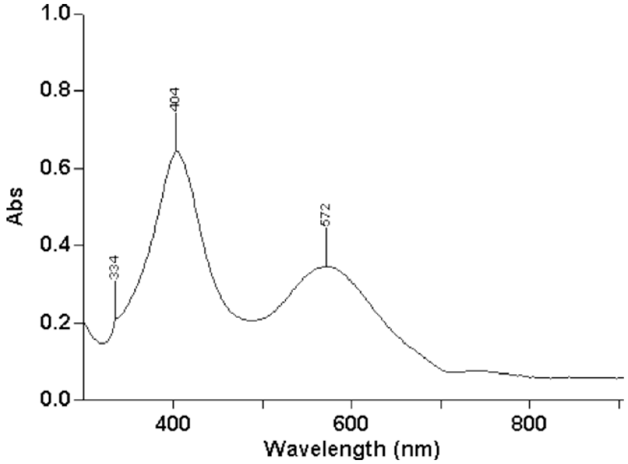

Figure 17 UV–vis spectrum of nanoparticles when adding Fe^{2+} (0.1 mM) to the solution (before adding hydrazine).

high reducing potential of hydrazine it may be concluded that Fe^{3+} is reduced to Fe^{2+} after addition which in turn changed the kinetics of the system to a slower growth which has led to nanotriangles synthesis which are to considered more favorable to be formed at slower growth. Nevertheless, adding Fe^{2+} to the synthesis has an effect similar to hydrazine since it could reduce more silver ions to Ag atoms. This procedure accelerates the formation of nanotriangles, in spite of Fe^{3+}, leading to increasing the growth rate and favors a shape that is not kinetically favored.

As a result smaller triangular nanoparticles are formed which are more similar to quasi-spherical nanoparticles (thermodynamically favored) as UV–vis spectrum shows (Fig. 17). With the increasing the hydrazine concentration in the original procedure, acceleration in reduction was observed. Considering the results of this experimental study, kinetics of the system at accelerated growth favors a shape more similar to quasi-spherical nanoparticles; i.e., smaller nanotriangles.

4. Conclusions

In this study we have continued our work on the synthesis of triangular silver nanoparticles. In previous work a simple method for the synthesis of truncated triangles was described at room temperature. The reaction occurs in aqueous solution between silver nitrate and hydrazine. Citrate is used to stabilize the nanoparticle formed. Concentration of reactants are important in formation of nanotriangles. When concentration of silver nitrate is increased to 0.5 mM triangular nanoparticles are not formed and the product is dominated by spherical nanoparticles.

Nevertheless, we observed that the shape of these spherical nanoparticles changed to a triangular after aging for two months. In other words, when growth becomes a controlling, factor low supersaturation for a long time provides space for shape change to a triangular in the presence of citrate and hydrazine. To confirm this hypothesis, Fe^{3+} was added to solution to slow down reduction rate. In this case more triangular nanoparticles were formed with a delay in formation time. Based on these observations, high concentration of hydrazine must favors smaller triangles, because it favors nucleation rather growth – which was observed experimentally.

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