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Single step morphology-controlled synthesis of silver nanoparticles

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ABSTRACT

Silver nanoparticles having different size and plasmon resonances were synthesized through a single step aqueous based method. The current procedure was based on the reduction of silver ions by ascorbic acid in the presence of sodiumborohydride and trisodium citrate. Triangular colloidal nanoparticles having different plasmon resonances (and hence different size and colours) were synthesized by varying only the concentration of ascorbic acid. These nanoparticles were found to be stable without using any surfactants or polymers. This study revealed a strong correlation between particle growth and concentration of constituent chemicals. Crystallinity and phase purity of the silver samples were investigated through powder X-ray diffraction studies (XRD). Absorption spectra of various silver particles were recorded using UV/Vis/NIR spectrometer. Morphological analysis was performed using transmission electron microscopy (TEM) and average edge lengths of nanoparticles were also calculated.

INTRODUCTION

Shape and size control of silver nanoparticles is a promising strategy to tailor their physical and chemical properties for various applications in the field of photonics [1], catalysis [2], medical research [3] and surface enhanced Raman spectroscopy (SERS) [4]. Superior physical and chemical properties were observed for the metal nanostructures with complex shapes. A typical example is the shape and size dependent optical properties exhibited by triangular silver nanoplates. Triangular plates show three surface plasmon resonance (SPR) bands corresponding to dipole and quadruple plasmon resonance, but only one SPR band is observed for spherical silver nanoparticles. A large number of aqueous and non-aqueous methods were reported in the past decade for the synthesis of silver nanoparticles having different size and shapes such as rods, prisms, cubes, wires and disks [5-7]. For some photochemical syntheses, reaction times can be longer ranging from several hours to days. Stability of nanoparticles and use of environmental friendly chemicals are other considerations for real life applications. Recently a two step seed –mediated methods are reported for the synthesis of triangular silver nanoparticles, which involve the synthesis of spherical silver seeds and their growth into triangular nanoplates using polyvinylpyrrolidone (PVP) as a stabilizing agent [8]. Reliability of this procedure is highly dependent on the structure of silver seeds and a range of morphologies were observed in the final sol. Extreme care was required while storing the silver seeds. Because of these reasons, there is still a necessity for a simple single step method. We are reporting an aqueous based rapid and surfactant-free simple single step method

for the synthesis of triangular silver nanoparticles having different sizes (and hence different colours and plasmon resonances).

EXPERIMENTAL DETAILS

Silver nitrate (Aldrich 99 %), sodium borohydride (Aldrich 99 %), trisodium citrate (SAFC 99 %) and ascorbic acid (Fluka 99 %) were used as received without further purification for the synthesis. Millipore water ($\rho = 18.2 \text{ M}\Omega$) was used throughout the experiment. In a typical synthesis of green sol, water (7 M) was mixed thoroughly with trisodium citrate (5 mM), ascorbic acid (50 mM), and sodium borohydride (0.1 mM). Silver nitrate solution (5 mM) was added dropwise to the above clear solution at room temperature, which causes a colour change to green through yellow red violet and blue. Silver colloids having other colours were also synthesized by varying the amounts of ascorbic acid (0 mM, 10 mM, 20 mM, 30 mM and 40 mM). Effect of Ag^+ ion on the growth of silver nanoparticles was studied by using various amounts of silver nitrate (1.25 mM, 2.5 mM and 5 mM).

The crystal phases of samples were analyzed by X-ray diffraction using a Siemens D 500 X-ray diffractometer ($2\theta = 10\text{-}70^\circ$) working with $\text{CuK}\alpha$ radiation ($\lambda=0.15418 \text{ nm}$). Average crystallite size of triangular silver nanoparticle was calculated using Scherrer equation [9] (Equation 1).

$$\Phi = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where Φ is the crystallite size, K is the shape factor, λ is the X-ray radiation wavelength, and β the full line width at half-maximum height of the main intensity peak after subtraction of equipment line broadening.

Absorbance spectra of the colloids were recorded using a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrometer. Stability of the colloid was investigated through a time dependant etching study of green sol using UV/Vis/NIR spectrometer. For transmission electron microscopy (TEM) analysis, as prepared colloids were dried on formvar-coated copper grids at room temperature. The particle-loaded grids were studied under JEOL 100 CX microscope operating at 100 kV.

DISCUSSION

Formation of silver nanoparticles

The colloidal silver nanoparticles formed were centrifuged and purified by washing with water, which was then dried on a glass plate at room temperature for X-ray analysis. X-ray diffraction (XRD) pattern (Figure 1) taken from a sample prepared (for *eg.* green sol) shows the peaks corresponding to pure metallic silver with a face-centred cubic (fcc) crystal structure (JCPDS, file no. 4-0783), which indicates the formation of silver nanoparticles.

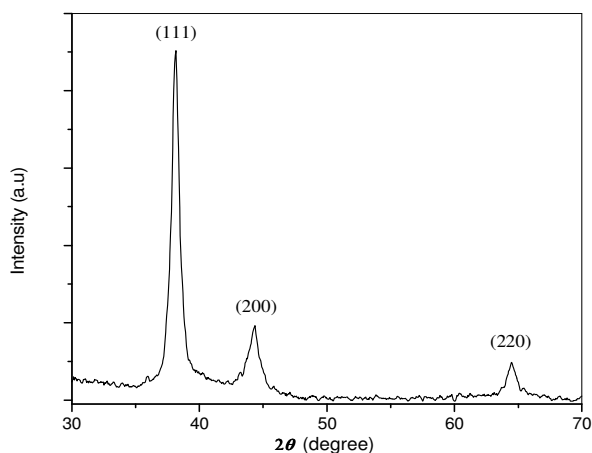


Figure 1. X-Ray diffraction pattern of triangular silver nanoparticles

Absence of any extra peaks shows the non-existence of unreacted silver nitrate or the formation of silver oxide. The average crystallite size obtained from Scherrer equation was 18.5 nm. Thus the XRD results verified the complete reduction of silver nitrate in to silver nanoparticles.

Growth of triangular silver nanoparticles

Growth of the nanoparticles was controlled by only varying the concentration of ascorbic acid (Figure 2). A single plasmon resonance (A) around 400 nm was formed without ascorbic acid which indicates the presence of only spherical nanoparticles [10] (18 nm size). Crystallization of triangular nanoparticles and a corresponding second plasmon resonance at a higher wavelength were observed as a result of increasing the amount of ascorbic acid. A gradual red shift of second plasmon resonances were also observed on increasing the concentration of ascorbic acid (B to F) and a green coloured sol containing biggest triangular particles were obtained using 50 mM ascorbic acid. Absorption band associated with spherical nanoparticles was also found in all other triangular nanoparticles colloids. Intensity ratios of these peaks were found to be highly dependent on the concentration of ascorbic acid. The red coloured sol containing 10 mM ascorbic acid was found to have a higher intensity peak around 400 nm and a lower one around 500 nm. On increasing the ascorbic acid concentration, the lower wavelength peak intensity decreases with a corresponding intensity increase of the higher wavelength peak. Shifting of the plasmon resonances to higher wavelength associated with a decrease in absorption intensity of spherical particles indicates the growth of triangular silver nanoparticles on the expense of spherical nanoparticles. Thus spherical and triangular nanoparticles were found to be stabilized at lower and higher ascorbic acid concentrations respectively. From these results it is clear that the concentration of ascorbic acid play an important role in the growth of triangular silver nanoparticles.

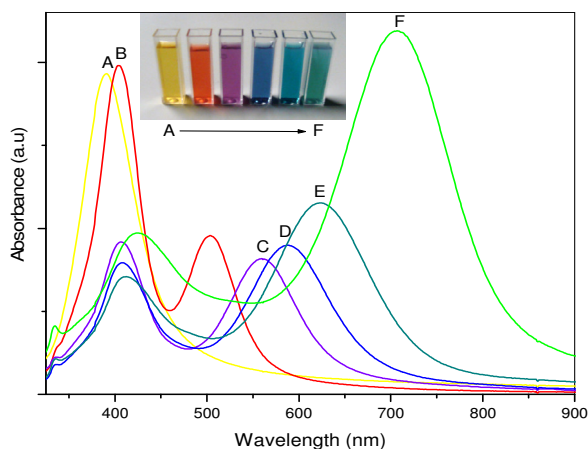


Figure 2. UV-vis spectra and photograph of different coloured sols prepared using various concentrations of ascorbic acid. A = 0 mM, B = 10 mM, C = 20 mM, D = 30 mM, E = 40 mM, F = 50 mM

Effect of Ag^+ concentration on further crystal growth has been studied under various Ag^+ concentrations. Lower concentrations of Ag^+ were found to be stabilizing spherical particles, whereas red shifts in plasmon resonances as a result of triangle particles stabilization were observed for higher concentration of Ag^+ (Figure 3). However, the concentration of silver nitrate was also found to have a significant effect on controlling the particle growth in a solution containing appropriate amount of ascorbic acid.

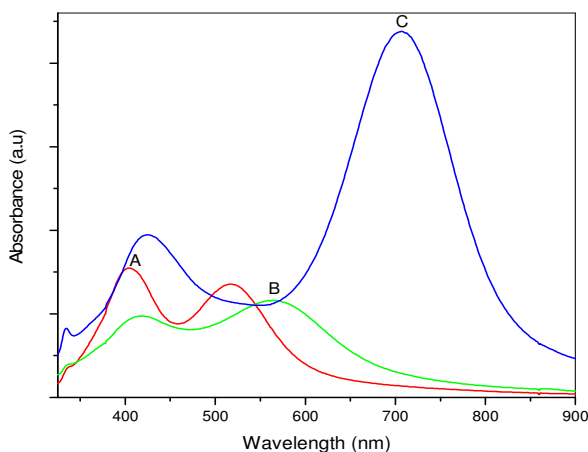


Figure 3. UV-vis spectra of different coloured sols prepared using various concentrations of silver nitrate. A = 1.25 mM, B = 2.5 mM, C = 5 mM.

TEM images of yellow sol having no ascorbic acid shows only spherical silver nanoparticles with an average particle size of 18 nm (Figure 4). A gradual increase in the amount and size of triangular silver nanoparticles were found on increasing the amount of ascorbic acid. Highest amount of well defined triangular nanoparticles (triangles and truncated triangles) were

found in the TEM images of green sol (Figure 5) with a highest average edge length of 115 nm. TEM analysis thus verified the size and shape variations under different synthetic conditions.

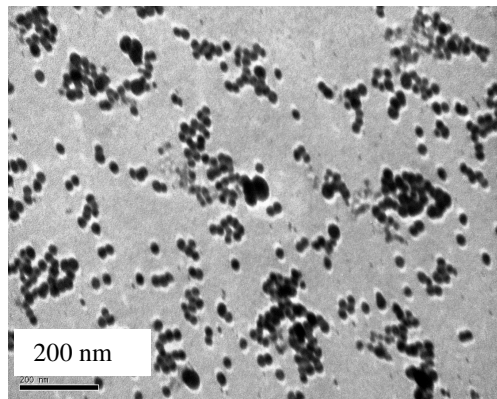


Figure 4. TEM images obtained by nanoparticles from the yellow sol

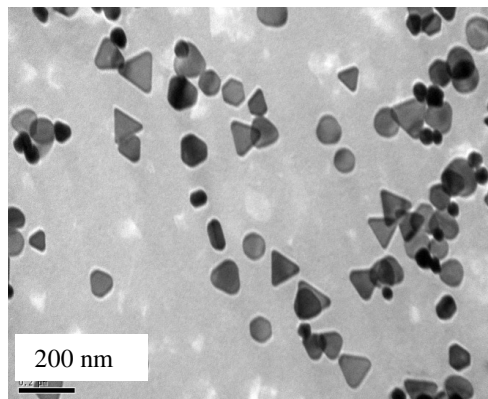
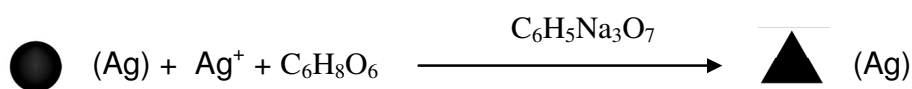
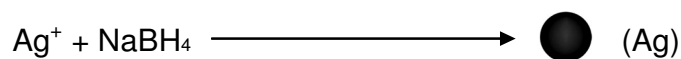


Figure 5. TEM images obtained by nanoparticles from the green sol

It is thus evident from these results that both the concentration of ascorbic acid and Ag^+ control the growth of triangular silver nanoparticles. So the formation of silver triangles can be explained as follows (Scheme 1).



Scheme 1: Formation of silver spheres and triangles

On adding the Ag^+ ions in to a solution containing small amount of a strong reducing agent sodium borohydride (NaBH_4) and a higher amount of mild reducing agent ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), a preferential formation of spherical silver seeds happens. Since we use the same amount of silver nitrate and NaBH_4 in all the synthesis, amount of spherical seeds formed should be the same. The spherical silver seeds formed can then react with unreacted Ag^+ ions in presence of ascorbic acid and citrate ions to form triangular silver nanoparticles. This mechanism explains the formation of large triangles (with plasmon resonances at higher wavelengths) while using higher amounts of ascorbic acid and Ag^+ ions.

Stability of nanoparticles

Stability of the silver nanoparticle formed in a solution is a highly challenging area when considering the size and shape dependant properties. Triangular nanoparticles undergo etching and finally convert to spherical particles resulting in a blue shift of the in-plane dipole resonance. The large blue shift, which can be up to 100 nm in magnitude is a direct measure of particle instability and a small blue shift value usually indicates higher particle stability [8]. An etching study of the green sol up to 1 hr after the final addition of Ag^+ has been performed to examine the stability of the formed nanoparticles, which is given below (Figure 6). In the present case, the blue shift observed for triangular nanoparticles were very small (5 nm), which clearly indicate the formation of stable silver nanoparticles.

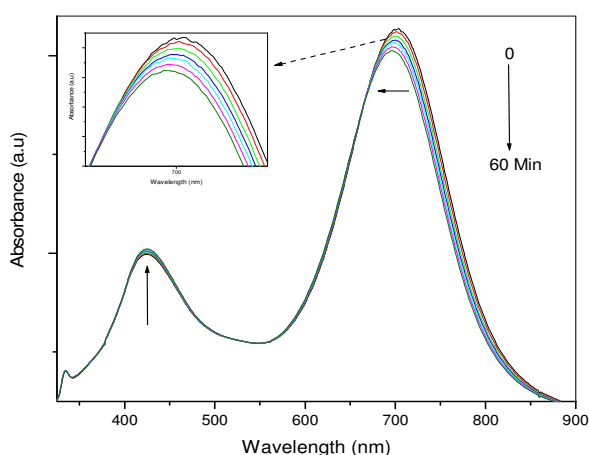


Figure 6. Longitudinal band blue shifting of green sol (up to 1 hr soon after synthesis).

CONCLUSIONS

A straight forward and single step aqueous method for the synthesis of triangular silver nanoparticles having different sizes and absorption was demonstrated. Colours of colloidal silver solutions were tuned from yellow to green by varying only the concentration of ascorbic acid. Time dependant etching study illustrated the stability of these nanoparticles. UV and TEM studies revealed a strong correlation between particle growth and concentration of the constituent chemicals. A possible mechanism for triangular silver particle formation has also been discussed.

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