Abstract. Triangular silver nanoparticles have special properties which increase their importance in chemistry, biology, physical and medical applications. This work concerns with fabrication of truncated nanotriangles, using a simple chemical method. The seed mediated growth method that is usually used to synthesize nanorods, is modified to create nanotriangles. By using this modified method, we successfully obtained silver truncated nanotriangles by adding low concentration of cetyltrimethylammonium bromide (CTAB) into seed solution. UV-visible spectroscopy (UV-Vis) was used to characterize the surface plasmon resonance of the formed nanoparticles. Also, the geometrical properties of nanoparticles were characterized by transmission electron microscopy (TEM) and scanning tunneling microscopy (STM). The average edge length of truncated nanotriangle is affected by varying the amount of seed added to the growth solution; it varies from 56 nm up to 75 nm according to the amount of seed used. The degree of truncation (T) for the produced nanotriangle edges has been estimated. Furthermore, the effect of CTAB concentration as well as the speed in which NaBH4 is added to the seed solution on the formed nanoparticles was investigated.

Keywords: Nanotriangles, degree of truncation, CTAB, surface plasmon resonance.

1. Introduction

In last decades, there are great interest in nanomaterials, particularly plasmonic nanoparticles because of their properties and applications in various fields, specially biosensor, nanoelectronics and nanophotonics [1, 2]. Plasmonics which are defined through the resonance of free electrons of metal nanoparticles and their quantum confinement lead to localized surface Plasmon resonance (LSPR). Triangular silver nanoparticles (TSN) as anisotropic nanoparticles have stronger plasmon resonance than nanorods and nanospheres. Consequently, they have a fundamental role in bioassay applications [3] as well as they are a key factor in surface enhanced spectroscopies [4]. Despite silver is of less stability than gold, LSPR of silver nanomaterials have superior sensitivity to local dielectric constant changes than gold. Also, enhancement factor and plasmonic property of Ag are better than other metals [5].

The optical properties of triangles nanoparticles with truncated edges have strong effect on the performance of LSPR sensor [6].

There are a various methods for synthesis of triangular silver nanoparticles such as photo-induced procedure and chemical reduction [7-10]. One of the most common chemical reduction methods is seed mediated growth method [11]. It is deemed basic protocol of synthesis anisotropic silver nanoparticles based on reduction of silver ions in the existence of CTAB and NaBH4. CTAB is usually used to induce the orientation growth of seeds to form anisotropic nanoparticles [12]. It plays an important role in determining the morphology and size of the nanoparticles [13]. In spite of the role of NaBH4 as strong reducing agent, it can increase stabilization, uniformity and monodispersity of silver nanoparticles [14]. Also, Jill E. Millstone et al. [15] studied the effect of NaBH4 concentration on nanoprin thickness and have shown change of optical spectra of the samples. Efforts are still needed to optimize methods of preparation of anisotropic nanoparticles, which depend on nature of chemical reaction, concentrations, speed of stirring, temperature, pH value and reducing agent [16].

In this work, we synthesized truncated TSN using a modified seed mediated method. The effect of adding various amounts of seed solution of low CTAB concentration to the growth solution has been studied through surface plasmon resonance, TEM and STM. Also, impacts of increasing CTAB concentration in the seed solution as well as the speed with which NaBH4 is added to it on the surface plasmon resonance of created nanoparticles have been investigated.
2. Experimental

The procedure of preparation followed that of seed mediated synthesis by C.R. Rekha et al. at room temperature [17]. This method is based on reduction of silver ions by ascorbic acid as weak reducing agent. Silver nitrate is used as precursor for the solutions, as it is dissolved into the deionized water; the silver ions (Ag⁺) are produced. Also, NaBH₄ is used as a strong reducing agent to create free metallic silver (Ag⁰) atoms by the reduction. However, CTAB is considered as capping agent in growth solution.

In our modified method, the seed solutions were prepared by mixing 20 mL of 0.01 M AgNO₃ and 80 μL of CTAB of molar concentration 0.034 M (lower than that used by C.R. Rekha et al. [17]) under slow stirring. 0.6 mL of 0.01 M NaBH₄ ice cooled aqueous solution was added all at once. With two minutes stirring the color was bright yellow. The 1 h aged seed solution added to the growth solution which prepared as a stated in reference [17]. Different amounts of seed colloidal solution (0.5, 0.25, 0.125, 0.1, 0.6, 0.3 mL) were added. The color of the colloid solution changed within 3 minutes depending upon the concentration of the seed colloidal solution added. The purification of the silver nanotriangles was carried out by centrifuging at 6500 rpm for 30 min.

UV–Vis spectrometer (Ocean optics USA) was used to record optical absorption of surface plasmon resonance of the formed TSN colloidal solution. Morphology, size distribution and aggregation of the TSN were determined using transmission electron microscope (TEM, JEM -1200EX) and UHV Omicron scanning tunneling microscope (STM).

3. Results and Discussion

3.1 The influence of seed amount

Figure 1 shows the UV-Vis absorption spectra of synthesized TSN colloids using different amount of seed solution as indicated in the figure. The spectra of the TSN showed the three apparent predominant peaks related to different modes of plasmon excitation. According to Mie theory, the surface plasmon bands of plasmonic nanoparticles are due to dipole and quadrupole modes [18]. At the largest seed amount (0.5 mL), a strong band located at 490 nm is ascribed to the in-plane dipole while the band at 390 nm is attributed to out-of-plane quadrupole plasmon resonance. As shown in the figure, the broad peaks around 420 which may include the in-plane quadrupole and out-of-plane dipole becomes more apparent at small amount of seed solution. Also, decreasing the amount of seed solution causes these absorption bands to shift toward longer wavelengths (visibly demonstrated by varying color of solutions). The highest energy resonance band at about 340 nm which is assigned to the out of plane quadrupole resonance, is nearly invariable. Also, the full width at half maximum (FWHM) increases with decreasing the seed amount, varying from 133.47± 0.81 nm at the largest seed amount to be 235.52 ± 0.84 nm at the least amount. This red shift and broadening of FWHM can be ascribed to the increased charge separation during Plasmon oscillation as enabled by the increase in size. It is cleared that by changing the amount of silver seeds added to silver ions, the size of the nanoparticles can be controlled [19].

![Figure 1 Color variations and UV–Vis spectra of TSN prepared with different amounts of seed solution.](image-url)
3.2 TEM and STM measurements

TEM and STM measurements display the uniformity and structural properties of the prepared TSN. Figure 2 shows two chosen TEM images of TSN prepared using 0.25 mL (a) and 0.03 mL (b) seed solution. The images display the creation of triangular silver nanoparticles with truncated edges. This truncation in the edges is formed because of the oxidation of silver nanoparticles during the preparation [20]. Figure 3 shows STM image that confirm the truncation of the prepared triangle silver nanoparticles.

![Figure 2 TEM images of TSN prepared at different amounts of seed solution (a) 0.25 mL and (b) 0.03 mL.](image)

![Figure 3 STM image of TSN at seed amount 0.03 mL.](image)

It is observed that the TSN have edges with different degrees of truncation. The average degree of truncation ($T$) can be calculated using TEM images according to the relation $T = b/a$, considering the particle is composed by an inner triangle of side length "b" included into a parent triangle of side length "a" [9]. Clearly, a perfect triangle shape of the particle will be at $T = 1$, while $T = 0$ is for circular shape. Histogram of Figure 4 shows the average degree of truncation is $0.48 \pm 0.0067$ for sample of larger seed amount. When the particle size increased for sample of lower seed amount, the degree of truncation decreased to $0.41 \pm 0.0068$. 
Side length of TSN is an important parameter affecting absorption efficiency and resonance frequencies of dipole and quadrupole bands [21]. Using up to 200 particles of nanotriangles, it was found that the average side length is 56 nm with standard deviation ± 9.4 nm for sample of 0.25 mL of seed amount. The side length increases to 75 nm with standard deviation ± 12.3 nm for sample of 0.03 mL seed amount as illustrated in Figure 5.

TEM images disclose the presence of other shapes of nanoparticles such as spheres, hexagons, rods, and others. Histogram of Figure 6 shows that most of the particles are nanotriangles and the minimum number of particles is nanorods. The nanotriangles occupy nearly 70% of nanoparticles in the colloids. The appearance of nano-hexagons may represent incomplete transformation to truncated nanotriangles.

3.3 The influence of CTAB in seed solution

Using CTAB in seed as capping surfactant contributes to improve the regularity of the particles [22]. Also, the formed capping surface helps to prevent the aggregation of seeds which means that CTAB can be used as stabilizer. In this experiment we study the effect of using various concentration of CTAB in the seed solution.
Figure 7 shows UV-Vis spectra of TSN prepared with different total concentrations of CTAB in the seed solution (as indicated in the figure). These values are larger than the total concentration of CTAB (0.13 mM) used before. The amount of the seed solution added to the growth was fixed at 0.25 mL. It is observed that, the intensity of the in-plane dipole resonance band slightly decreases with irregular shift of its frequency with increasing the CTAB concentration. Also, increasing CTAB concentration has no significant effect on other resonance bands of TSN. This indicates that increasing CTAB concentrations is not influential factor which agrees with the results in reference [23].

Figure 7 UV-Vis spectra of TSN prepared with different concentrations of CTAB.

3.4 The influence of sodium borohydride (NaBH₄)

How to add NaBH₄ is that significant? In this experiment we slowed down the speed of adding NaBH₄ to the seed solution, where 0.6 mL of 0.01 M NaBH₄ was added dropwise to the seed solution at rate of 0.018 mL for a total of 30 second with slow stirring. Figure 8 displays the absorption spectra of TNS prepared using three different amount of such seed solution (as indicated) of fixed CTAB concentration (0.13 mM). For fair comparison with the above results of UV-Vis spectra of TSN prepared via addition of NaBH₄ to the seed solution all at one shot, the three used amounts of the new seed solution in this case are similar to those used before with the same concentration of CTAB. With decreasing seed amount, the spectra show a larger red shift of the in-plane dipole band relative to that obtained for corresponding samples prepared by speedy addition of NaBH₄. This indicates that the particle size can be controlled by controlling the addition rate of NaBH₄ to the seed solution. Also, the intensity of in-plane quadrupole mode is significantly larger than that observed in the corresponding samples shown in figure 1, with a weak shoulder representing the out-of-plane dipole [10]. These observations can be attributed to the increase in thickness of nanotriangles with varying of charge density distribution [24]. These results imply that the speed of the addition of NaBH₄ significantly affects the particle size, thickness, and resonance modes of nanoparticles.

Figure 8 UV-Vis spectra and color variation of TSN prepared by addition of NaBH₄ drop by drop.
4. Conclusion

It is concluded that truncated triangle silver nanoparticles can be formed with seed mediate growth at low concentration of CTAB and low rate of stirring. Different degrees of truncation provide key control over many of the properties of nanoparticles and their applications. Also, rate of stirring and speed of adding NaBH₄ are effective parameters in tuning and enhancement of the surface plasmon resonance peaks of triangular nanoparticles which broaden their applications. Our results suggest that controlling the preparation conditions produces triangular nanoparticles appropriate to be used in various fields like surface enhance Raman scattering and as sensors in the environmental applications. Furthermore, the stability of the geometrical shape with tunable plasmonic properties suggests that truncated nanotriangles are a candidate to play an important role in biomedical imaging.

Reference

[1] Diantoro M, Suprayogi T, Sa’adah U, Mufid N, Fuad A, Hidayat A and Nur H 2018 Silver Nanoparticles: Fabrication, Characterization and Applications 233
[2] Liu S, Tao H, Zeng L, Liu Q, Xu Z, Liu Q and Luo J-L 2017 Journal of the American chemical society 139 (6) 2160-2163
[3] Kelly J, Keegan G and Brennan-Fournet M 2012 Acta Physica Polonica A 122 (2) 337-345
[4] Wu C, Chen E and Wei J 2016 Colloids and Surfaces A: Physicochemical and Engineering Aspects 506 450-456
[5] Yguerabide J and Yguerabide E E 1998 Analytical biochemistry 262 (2) 157-176
[6] Ma W, Yao J, Yang H, Liu J, Li F, Hilton J and Lin Q 2009 Optics Express 17 (17) 14967-14976
[7] Song H, Zhang H, Sun Z, Ren Z, Yang X and Wang Q 2019 AIP Advances 9 (8) 085307
[8] Zannotti M, Rossi A and Giovannetti R 2020 Coatings 10 (3) 288
[9] Chen S and Carroll D L 2002 Nano letters 2 (9) 1003-1007
[10] Jin R, Cao Y, Mirkin C A, Kelly K L, Schatz G C and Zheng J 2001 science 294 (5548) 1901-1903
[11] Zhong Y, Liang G, Jin W, Jian Z, Wu Z, Chen Q, Cai Y and Zhang W 2018 RSC advances 8 (51) 28934-28943
[12] Zhang W, Hu G, Zhang W, Qiao X, Wu K, Chen Q and Cai Y 2014 Physica E: Low-dimensional Systems and Nanostructures 64 211-217
[13] Törnblom M and Henriksson U 1997 The Journal of Physical Chemistry B 101 (31) 6028-6035
[14] Kruis F E, Fissian H and Rellinghaus B 2000 Materials Science and Engineering: B 69 329-334
[15] Millstone J E, Hurst S J, Metraux G S, Cutler J I and Mirkin C A 2009 small 5 (6) 646-664
[16] Khodashenas B and Ghorbani H R 2019 Arabian Journal of Chemistry 12 (8) 1823-1838
[17] Rekha C, Nayar V and Gopchandran K 2018 Journal of Science: Advanced Materials and Devices 3 (2) 196-205
[18] Zhang J, Li S, Wu J, Schatz G C and Mirkin C A 2009 Angewandte Chemie 121 (42) 7927-7931
[19] Raza M A, Kanwal Z, Rauf A, Sabri A N, Riaz S and Naseem S 2016 Nanomaterials 6 (4) 74
[20] Yang H, Owiti E O, Jiang X, Li S, Liu P and Sun X 2017 Nanoscale research letters 12 (1) 1-6
[21] Chen Q, Qi H, Ren Y-T, Sun J-P and Ruan L-M 2017 Aip Advances 7 (6) 065115
[22] Nikooabakht B and El-Sayed M A 2003 Chemistry of Materials 15 (10) 1957-1962
[23] Hu G, Liang G, Zhang W, Jin W, Zhang Y, Chen Q, Cai Y and Zhang W 2018 Journal of materials science 53 (7) 4768-4780
[24] Dreaden E C, Near R D, Abdallah T, Talaat M H and El-Sayed M A 2011 Applied Physics Letters 98 (18) 183115