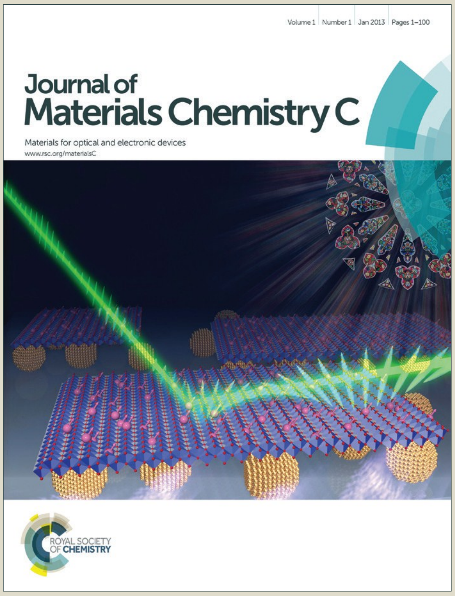
Journal of Materials Chemistry C

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

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Journal Name

ARTICLE

A two-step approach to realize size- and shape-selective separation of crude gold nanotriangles with high purification

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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In this work, a facile and effective two-step separated strategy combined both CTAB and CTAC has been proposed that enables the purification of gold nanotriangles in a large scale. The resulting nanotriangles exhibit straight edges and sharp corners, with a narrower size distribution. The separation of size or morphology could be achieved by utilizing different surfactant. It was found that CTAB served as a size separation agent and CTAC served as a shape separation agent in the separation process. The optimum concentrations of CTAB were found to be 0.167 M for size separation and CTAC 0.222 M for shape separation respectively. By simply adjusting the concentration and sequence of CTAB and CTAC, we were able to exquisitely separate nanotriangles from the crude gold nanoparticles. Furthermore, the separation mechanism has also been discussed based on surfactant depletion-induced aggregation on different contact areas of the nanoparticles. The proposed two-step separation strategy holds great potential to be extended to the separation of other nanoparticles with anisotropy shapes and different sizes, improving the high yield of anisotropy with great uniformity, which will eventually facilitate SERS-based application.

1. Introduction

Metal nanoparticles including gold and silver exhibit rich and fascinating optical properties that result from the free electron excitation induced localized surface plasmon resonance (LSPR).[1] Nanoparticles with various morphologies such as nanorod,[2-3] nanocube,[4] nanodumbbell,[5] nanotriangle,[6-7] nanobipyramid,[8] nanostar,[9] and nanowire[10] have been fabricated in the past decade. Among the numerous plasmonic anisotropic nanoparticles, nanotriangles are of particular interest. Nanotriangles exhibit an enhanced electromagnetic field due to the sharp vertices induced lighting rod effect or antenna effect, which makes them ideal candidates for biosensing and surface enhanced Raman scattering (SERS) applications.[11-16] Sajanlal et al. demonstrated the highest electromagnetic field enhancement of gold nanotriangles is the corner, and the next are edge and surface both theoretically and experimentally.[11] It is also reported that gold nanoprisms exhibit the enhanced field localization at the vertices of the nanoprisms.[12-15] Scarabelli et al. reported that self-assembled gold nanotriangles exhibited enhancement factor of 10^5 for thiophenol detection.[16]

A series of approaches including wet-chemical method[6-7], photochemical,[17] thermal process,[18] microwave polyol method,[19-20] and sonochemical methods have been reported for the preparation of nanotriangles.[21] Among them, wet-chemical synthesis is widely employed owing to its facile setup, relatively high yield as well as feasibility for large quantity production. Several examples of gold nanotriangles synthesized based on chemical method have been reported. In particular, an efficient production of gold nanotriangles was demonstrated via the seed-mediated approach. For instance, Millstone et al. synthesized gold nanotriangles through a seed-mediated method. The quadrupole plasmon mode of LSPR could be observed in the purified gold nanotriangles.[6] Later, Millstone et al. synthesized the gold nanotriangles with tailored edge length between 100 nm and 300 nm.[7] In a different approach, iodide anions were utilized to trigger the CTAC-coated gold seeds for the growth of nanotriangles.[16] Recently, Straney et al. proposed a one-pot seedless procedure to synthesis gold nanotriangles with the edge length ranging from 120 nm to over 700 nm.[22] Chen et al. synthesized gold nanotriangles with a smaller edge length and a high yield.[23] Shankar et al. demonstrated the biological method of large scale of gold nanotriangles by using the extract of the lemongrass as reducing agent.[24] Unfortunately, the yield of the nanotriangles is not high in which pseudospherical nanoparticles account for a higher percentage. In fact, the sharp tips of the nanotriangles tend to be truncated during the synthesis process, [25] leading to most of the synthesized gold nanotriangles face with the problem of nonuniform morphology and polydisperse with a quite broad size distribution, which greatly limits the plasmonic application ranging from biosensing to bioimaging.[26] For example, the uniformity of the size and morphology of nanoparticles plays

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x an essential role in self-assembly, especially for the nanotriangles assembled in the edge-to-edge fashion. The highly uniformed nanotriangles could be used as building block for self-assembly. The hot spot induced by six tips of the self-assembly nanotriangles exhibits an SERS enhancement factor of 10^7.[27] Therefore, it is imperative for us to design an effective separation approach for separating different morphology of nanoparticles mixture with improved homogeneity effectively.

Several separation attempts have been made to improve the unpurified nanoparticles. In general, centrifugation is routinely utilized to remove the unreacted ions in colloid science as well as molecular biology. Sharma et al. demonstrated the possibility of centrifugation to separate nanospheres and nanorods both theoretically and experimentally.[28] Nanospheres and longer nanorods have different size and mass, and larger mass of nanorods tend to aggregate in the presence of CTAB, which leads to the separation of these two nanoparticles.[29] Aluminum filter with certain pore size was utilized to separate the mixture of nanotriangles and nanospheres.[6] Liu et al. adopted density gradient centrifugation approach to purify Au nanobipyramids with a high yield. However, some impurity could be introduced in the process of the centrifugation.[30] In addition, gel electrophoresis and chromatography that were previously used extensively in biology and pharmacology have now been applied in nanoscience.[31-33] Novak et al. demonstrated the separation of gold nanoparticles from dimers and trimers through size exclusion chromatography.[33] However, these procedures are complicated and often call for more technical skills. Sodium chloride could induce the aggregation of nanotriangles via electrostatic effect. Therefore the separation of nanobipyramids and nanospheres could be realized.[34] Similarly, the separation of nanotriangles and nanospheres could also be achieved efficiently.[35] Park et al. reported the surfactant micelle induced size and shape separation of nanoparticles.[36] Liu et al. reported the surface area-based separation of nanotriangles from the mixture of nanoparticles with the same mass both theoretically and experimentally.[37]

The current work mostly focuses on the fabrication and separation of gold nanotriangles, however, little attention has been paid to the optimal separation of gold nanotriangles in a large scale. The selectivity between the size separation and shape separation was also seldom reported. In this work, we have carried out systematic studies and obtained the optimal condition for the separation of nanotriangles with high purity by combining the surfactant effect of CTAB and CTAC. The concentration and sequence of CTAB and CTAC could be adjusted to achieve nanotriangles with high uniformity. This two-step strategy allows us to develop in bulk volume of gold nanotriangles with reproducibility.

2. Experimental Section

2.1 Reagents and apparatus

Cetyltrimethyl ammonium bromide (CTAB) and Cetyltrimethyl ammonium chloride (CTAC) were purchased from Sigma-Aldrich. Gold chloride trihydrate ($HAuCl_4$, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) were used as received. Potassium chloride (KCl), potassium bromide (KBr), sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH), silver nitrate ($AgNO_3$), potassium iodide (KI) and ascorbic acid (AA) were obtained from Aladdin. Sodium chloride (NaCl) and sodium bromide (NaBr) were obtained from Tianli Chemical Reagent Co. Ltd (Tianjin, China). All the reagents were of analytical grade and were used without further purification. The ultrapure water used in all experiments had a resistivity of 18.2 MΩcm.

Ultrapure water was obtained from Millipore water purification system (Milli-Q, Millipore, USA). All the absorption spectra were recorded on a UV3600 absorption spectrometer (Shimadzu, Japan) with the wavelength range of 400 to 1350 nm. Transmission electron microscopy (TEM) images were obtained from JEM-200CX (JEOL Ltd., Japan) operating at an acceleration voltage of 120 kV. Scanning electron microscopy (SEM) images were acquired from JSM-7000F (JEOL Ltd., Japan).

2.2 Preparation of gold nanotriangles in a large scale

A large quantity of gold nanotriangles was prepared by previously reported method with slight modification with CTAC and KI as shape-control agents. [6, 23, 38] In a typical synthesis, 0.1 M 80 mL CTAC was prepared in a water bath (50 ⍰) with sonication. When it turned to transparent and cooled to room temperature of 30 ⍰, 0.01 M KI with a volume of 3.75 mL was injected into the solution and 400 mL ultrapure water was added to mix the solution thoroughly. And then the mixture of $HAuCl_4$ and NaOH mixed in the same proportion was added to provide Au^{3+} and an alkaline environment. AA was served as a reduction agent. The color from yellow to transparently colorless indicates the reduction of Au^{3+} to Au^+ after the introduction of 4 mL AA. The NaOH was added for the second time to deprotonate AA and initiates the anisotropy growth of gold nanoparticles.[35] The solution was continually stirred for 30 s and then left undisturbed for 12 h. The color of the colloid changes from colorless to pink-purple-blue within the first 30 min. This seedless method leads to the synthesized large scale of gold nanotriangles a relatively high polydispersity which contains different morphologies, including nanotriangles with two different size and nanospheres as well as some irregular morphology nanoparticles such as nanopentagons and nanotrapezoids.

2.3 Characterization of the as-prepared gold nanotriangles

It is calculated that the absorption spectrum of gold nanotriangles consists of three major bands, which are assigned to the in-plane dipole, in-plane quadrupole and out-of-plane dipole LSPR modes, respectively.[13, 35, 39] However, in terms of experimentally synthesized nanotriangles especially by chemical method, it is not easy for people to observe out-of-plane dipole LSPR mode. In-plane quadrupole could be observed in some circumstance.[6] And it is the in-plane dipole that takes the dominant. Therefore, here we mainly focus on the in-plane dipole LSPR mode.

In our experiment, the synthesized colloidal gold nanotriangles exhibit a color of dark blue, as shown in the inset of Fig. 1a. Fig. 1a is the absorption spectrum of gold nanotriangles. Two distinct absorption peaks can be observed, which are located at 630 nm and 1240 nm, respectively, as well as two less obvious shoulder peak centered at around 580 nm and 930 nm respectively. Absorption peaks located at 630 nm and 1240 nm assign to in-plane dipole LSPR mode of the smaller and larger size of the gold nanotriangles respectively, while the shoulder peak of 580 nm corresponds to dipole LSPR mode of the nanospheres and other irregular morphology of nanoparticles, and the shoulder peak of 930 nm corresponds to in-plane quadrupole LSPR mode of the larger size of the gold nanotriangles.[13] Fig. 1b is the typical TEM image of the synthesized colloidal gold nanotriangles. The yield of the nanotriangles is not high in which pseudospherical nanoparticles account for a higher percentage. Besides, nanotriangles have two different sizes. In fact, the product is typically a mixture of gold nanotriangles with small and large size as well as nanospheres and other irregular nanoparticles. Gold nanotriangles with two different sizes and nanospherical shape and other quasi-spherical shapes can be observed, which corresponds to the analyzed composition of the absorption spectrum. The small sized nanotriangles have an average length of 65 nm and the large sized nanotriangles have an average length of 170 nm. The one pot synthesized approach of gold nanotriangles is simple while it involves the problem of purification, of which different kinds of morphologies including nanotriangles with different size, pentagon and even hexagon in a small portion are produced. Then, how to purify the mixture and separate gold nanotriangles effectively with high yield?

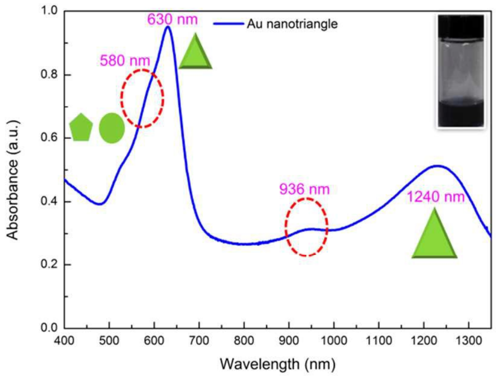


Fig. 1a: The absorption spectrum of the as-prepared gold nanotriangles.

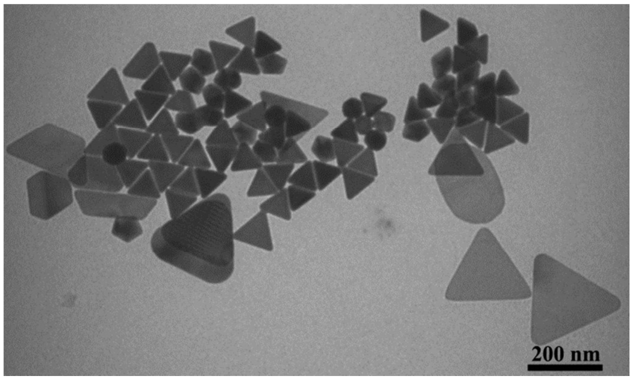


Fig. 1b: The typical TEM image of the as-prepared gold nanotriangles.

2.4 The surfactant induced the separation of as-prepared gold nanotriangles

In order to investigate the effect of CTAB on the separation of gold nanotriangles, we took the prepared crude gold nanotriangles with a volume of 60 mL, and divided into six portions with each portion of 10 mL. Different concentration of CTAB mother liquor was added, making the final concentration of CTAB 0.082 M, 0.124 M, 0.167 M, 0.206 M, 0.222 M and 0.248 M, respectively. The resulting solution was then kept undisturbed overnight for 12 h with a room temperature of 30 ℃. After that, the supernatant was poured into a new small bottle gently, and the rest of the precipitate was left at the bottom of the original bottle. Then we resuspended the precipitate in ultrapure water with the same volume of the origin. To guarantee the adequate dissolution of the purified precipitate, the violent shaking of the bottle is needed until the colloid is crystal clear.

The procedures of CTAC added to crude gold nanotriangles were the same with CTAB, with a final concentration of CTAC 0.082 M, 0.124 M, 0.167 M, 0.206 M, 0.222 M, 0.248 M and 0.333 M, respectively.

3. Results and Discussion

3.1 The effect of surfactant on the separation of gold nanotriangles

3.1.1 The effect of CTAB on the separation of gold nanotriangles

Fig. 2a and Fig. 2b are the absorption spectra of the supernatant and precipitate of gold nanotriangles after the addition of CTAB respectively. As can be seen in Fig. 2a, due to the separation effect of CTAB, the absorption peak located at 1240 nm which presents the large size of gold nanotriangles is disappear, while the absorption peak in 630 nm and shoulder peak at approximately 580 nm remain unchanged. When the concentration of CTAB is 0.222 M, the absorbance in 630 nm is decreased, which demonstrates the number of small size of nanotriangles is decreased. When the concentration of CTAB is increased to 0.248 M, the absorption peak of 580 nm emerges gradually. At the same time, the peak of 630 nm turns to a shoulder peak. This change reveals the supernatant contains both small size nanotriangles and nanospheres and other irrugular nanoparticles.

The absorption spectrum of the precipitate is depicted in Fig. 2b. A small concentration of CTAB can induce a distinct peak located at 1240 nm, implying the existence of larger sized gold nanotriangles. This absorption peak is increased as the increasing concentration of CTAB. When the CTAB concentration is 0.222 M, a weak peak located at 630 nm appears. As the concentration is increased continuously, the intensity of peak located at 630 nm is dramatically increased. It is noteworthy that compared with the absorption spectrum of the original gold nanotriangles, the shoulder peak at 580 nm is disappear and the peak at 630 nm exhibits a spectrum band with a narrower full width at half maximum. The vanished shoulder peak and the narrow full width half maximum of absorption peak at 630 nm both manifest a good monodispersity of gold nanotriangles with high purification.

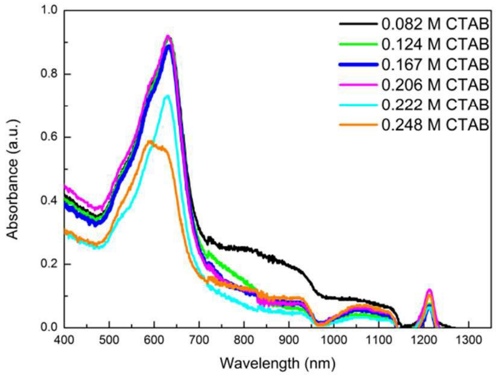


Fig. 2a: The absorption spectra of the supernatant of gold nanotriangles after the addition of different concentration of CTAB.

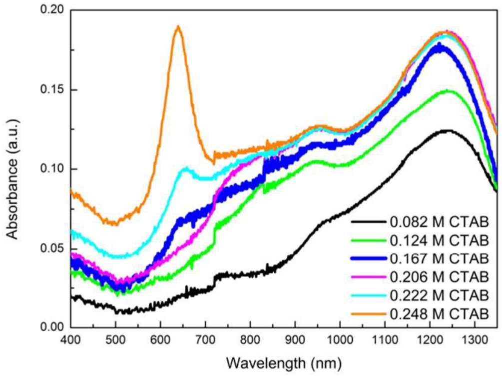


Fig. 2b: The absorption spectra of the precipitate of gold nanotriangles after the addition of different concentration of CTAB.

3.1.2 The effect of CTAC on the separation of gold nanotriangles

Fig. 2c and Fig. 2d are the absorption spectra of the supernatant and precipitate of gold nanotriangles after the addition of CTAC respectively. It can be observed in Fig. 2c that the absorption peak located at 1240 nm which presents the large size of gold nanotriangles is disappear due to the addition of CTAC, which is similar to CTAB. When the concentration of CTAC is increased to 0.206 M, the absorption peak located at 580 nm is prominent while the peak located at 630 nm turns to shoulder peak. This peak transformation means the proportion of small sized nanotriangles is increasing while the proportion of nanospheres and other irregular nanoparticles is decreasing. When the concentration of CTAC is further increased to 0.222 M, the shoulder peak at 630 nm is gradually disappear, which enventually merges with the band centered at 580 nm. This change demonstrates the missing of small sized nanotriangles, while nanospheres and other irregular nanoparticles are left in the supernatant. As the CTAC concentration is greater than 0.222 M, the peak position of 580 nm is kept unchanged with a slight decrease in intensity, which corresponds to the decreased number of nanospheres and irregular nanoparticles.

The absorption spectra of the precipitate are depicted in Fig. 2d. As the CTAC concentration is increased from 0.082 M to 0.167 M, there is only one distinct peak located at 1240 nm, which reveals that the nanotriangles with a larger size are separated from the mixture. Meanwhile, the absorbance of peak located at 1240 nm is increased as the increased concentration of CTAC. The new peak centered at 630 nm occurs when the CTAC concentration is increased to 0.206 M. This means the precipitate contains nanotriangles with both small and large size. The continuously increased CTAC concentration remains the peak centered at 1240 nm unchanged and a gradually increased intensity in peak centered at 630 nm.

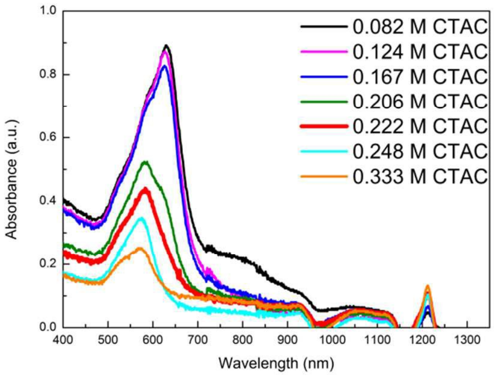


Fig. 2c: The absorption spectra of the supernatant of gold nanotriangles after the addition of different concentration of CTAC.

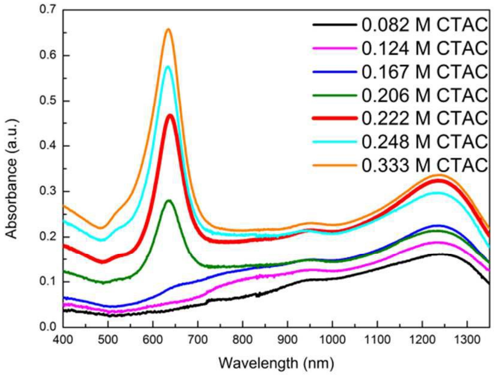


Fig. 2d: The absorption spectra of the precipitate of gold nanotriangles after the addition of different concentration of CTAC.

3.1.3 Optimize the concentration of CTAB and CTAC for the separation of gold nanotriangles from the mixture

Gold nanotriangles with large size were successfully separated from the mixture upon the addition of CTAB. The addition of CTAB to the as-prepared gold nanotriangles results in supernatant and precipitate due to the depletion effect of CTAB. Both the absorption spectrum and the TEM images reveal the separation of small and large sized nanoparticles is accomplished. The absorption spectra of supernatant and precipitate are shown in Fig. 3a. The color of the colloid before and after separation is distinctively different, as shown in the inset of Fig. 3a. The crude gold nanotriangles colloid exhibits a color of dark blue, while the supernatant and precipitate present a color of royal blue and green, respectively. The absorption peaks of the original absorption spectrum centered at 630 nm and 1240 nm become two separated absorption peak corresponding to supernatant (blue line) and precipitate (red line) respectively. The TEM images further confirm the morphology of separated nanoparticles. As can be seen in Fig. 3b, the supernatant contains small sized nanotriangles and nanospheres and other irregular nanoparticles such as pentagons and hexagons. Precipitate is mainly composed of the large size of the nanotriangles, as shown in Fig. 3c. The optimized CTAB concentration (0.167 M) made the size separation of nanotriangles successfully.

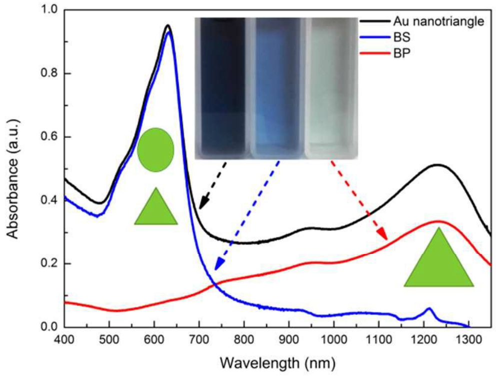


Fig. 3a: The absorption spectra of as-prepared gold nanotriangles before and after the addition of CTAB, the inset: the corresponding color. (BS denotes supernatant, BP denotes precipitate).

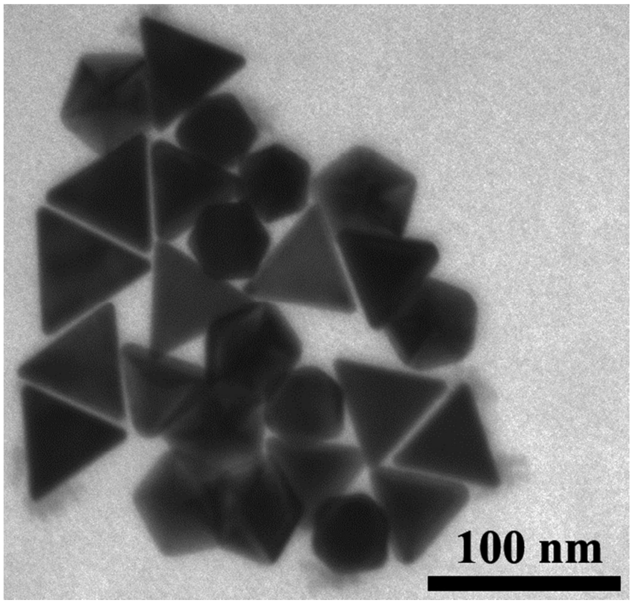


Fig. 3b: The TEM image of the separated supernatant upon the addition of CTAB.

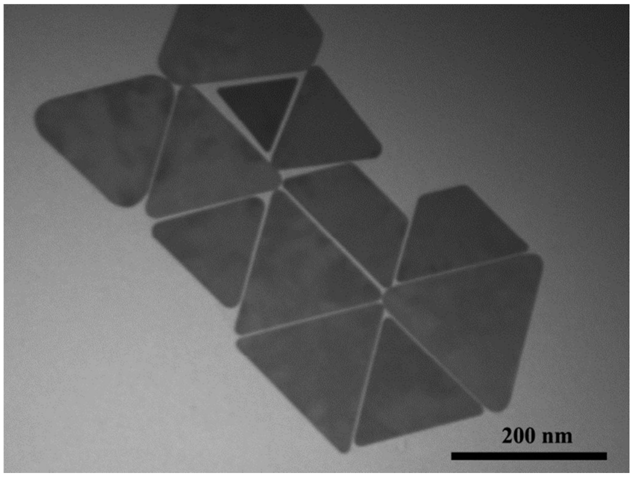


Fig. 3c: The TEM image of the separated precipitate upon the addition of CTAB.

CTAC plays a vital role in the shape separation of as-prepared gold nanotriangles. The addition of 0.222 M CTAC to the as-prepared gold nanotriangles results in supernatant and precipitate due to the depletion effect of CTAC. Both the absorption spectra and the TEM images reveal the separation of nanospheres and nanotriangles is accomplished. The absorption spectra of supernatant and precipitate are shown in Fig. 3d. As shown in the inset of Fig. 3d, the crude gold nanotriangles colloid exhibits a color of dark blue, while supernatant and precipitate present a color of orchid and dark cyan, respectively. The shoulder peak at 580 nm of the original absorption become separated (blue line). At the same time, the absorption of the precipitate shows the peaks of 630 nm and 1240 nm (red line). The TEM images further confirm the morphology of separated nanoparticles. As can be seen in Fig. 3e, the supernatant contains nanospheres and other irregular nanoparticles such as pentagons and hexagons. Precipitate is mainly composed of nanotriangles with two different sizes, as shown in Fig. 3f. Besides nanotriangles, however, one can find a small amount of trapezoid nanoparticles which might be attributed to the etching effect by bromide ions in the synthesized process. The separation of nanotriangles and nanospheres could be achieved by the introduction of CTAC.

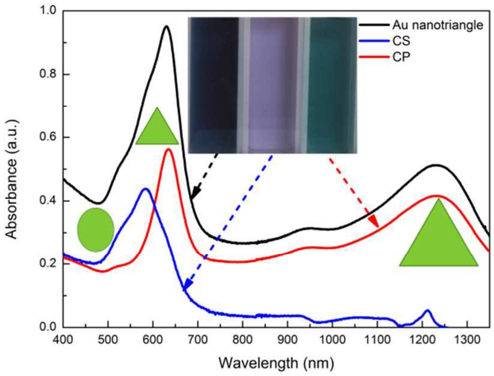


Fig. 3d: The absorption spectra of as-prepared gold nanotriangles before and after the addition of CTAC, the inset: the corresponding color. (CS denotes supernatant, CP denotes

precipitate).

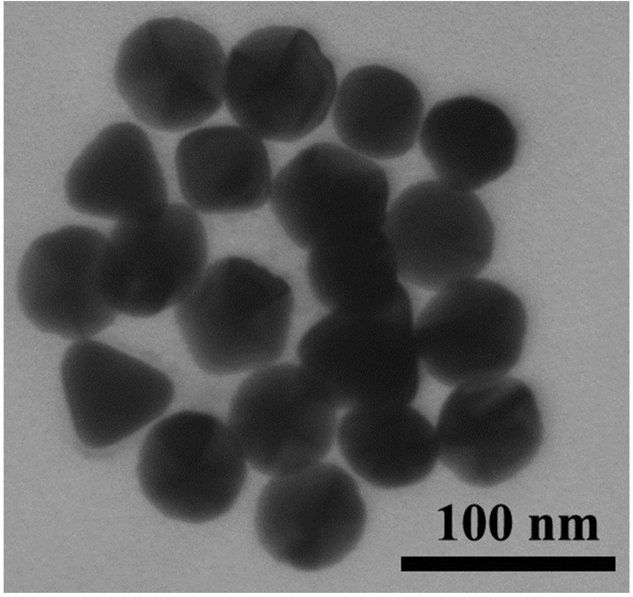


Fig. 3e: The TEM image of the separated supernatant upon the addition of CTAC.

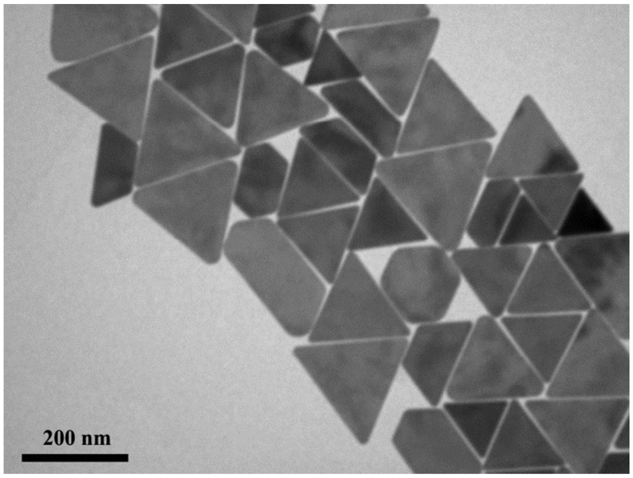


Fig. 3f: The TEM image of the separated precipitate upon the addition of CTAC.

3.2 A two-step strategy for the purification of gold nanotriangles

From the above chapter, we conclude that CTAB with certain concentration could serve as a size separation agent and CTAC serve as a shape separation agent. Since the as-prepared gold nanotriangles contain different sizes of nanotriangles as well as other shape of byproduct, could we combine the characteristic of CTAB and CTAC to achieve the purified nanotriangles in a large scale? We could separate different sizes of nanotriangles first and then separate other shapes of nanoparticles for further purification of nanotriangles. Similarly, we could separate different shapes of nanoparticles first and then separate different sizes of nanotriangles for further purification. Therefore, two kinds of two-step strategies were proposed.

In our proposed two-step strategy (Approach 1) combined with CTAB and CTAC, the separation of large and small sized nanotriangles as well as quasi-nanospheres with high purity can be achieved effectively. The schematic diagram of the two-step separation strategy (Approach 1) is summarized in Fig. 4a. As we know, the original prepared nanoparticles synthesized by one pot method are a mixture of large and small sized nanotriangles and other irregular morphology of nanoparticles. After depletion effect of CTAB, the separation of different size could be realized. The supernatant contains nanoparticles with small size including small sized nanotriangles and nanospheres, whereas the precipitate contains large sized nanotriangles. Take the supernatant for the secondary separation. Due to the shape selective separation induced by CTAC, the separation of nanoparticles with same mass but different shapes could be obtained. The supernatant predominantly contains quasi-nanospheres while the precipitate contains small sized nanotriangles. Without the introduction of other molecules, the separation of large and small sized nanotriangles as well as quasi-nanospheres can be achieved fast and efficiently with high uniformity.

Specifically, a typical separation procedure is performed as follows. In the first stage, the addition of CTAB to the as-prepared gold nanotriangles results in the size separation, with larger sized gold nanotriangles in the precipitate and small sized nanotriangles and irregular nanoparticles in the supernatant, as the above chapter mentioned in Fig. 3b and Fig. 3c. Subsequently, the CTAC is added to the supernatant separated in the first process for the secondary separation, with the purpose of achieving purified small sized nanotriangles. Being kept still one night, the supernatant was poured into a new bottle gently and the precipitate was resuspended in ultrapure water. The resulting supernatant shows a color of purple and the precipitate cadet blue, whose absorption spectrum is shown in Fig. 4b. The absorption spectrum of supernatant obtained in the first process shows a main absorption peak located at 630 nm and a shoulder peak located at 580 nm. After the separation, the absorption spectrum is split into two independent absorption peaks, one corresponds to the supernatant which peaks at 580 nm representing nanospheres and quasi-nanospheres; and the other corresponds to precipitate which peaks at 630 nm representing small sized nanotriangles. Fig. 4c and Fig. 4d are representative TEM images of the supernatant and the precipitate respectively. It can be seen that the supernatant contains nanospheres and other irregular morphology of nanoparticles such as the pentagon and hexagon, while the precipitate mainly contains the small nanotriangles with uniform size and fine morphology. It is observed that small sized nanotriangles exhibit straight edges and sharp corners, which is of great importance to the SERS based molecules detection. At this point, the nanotriangles with small size have been successfully separated with high purity.

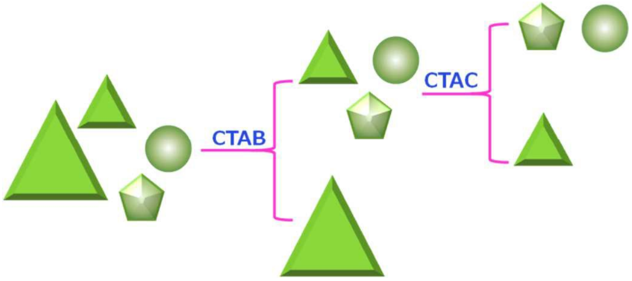


Fig. 4a: A schematic illustration of separation nanotriangles with high purification based on CTAB and CTAC through a two-

step strategy. (Approach 1)

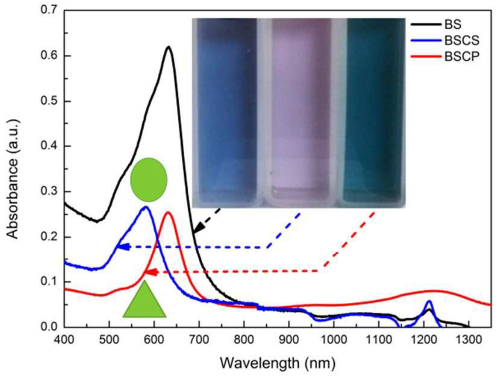


Fig. 4b: The absorption spectra of CTAB-separated supernatant before and after the addition of CTAC, the inset: the corresponding color. (BS denotes the CTAB-separated supernatant, BSCS denotes the supernatant of BS after the addition of CTAC, BSCP denotes the precipitate of BS after the addition of CTAC).

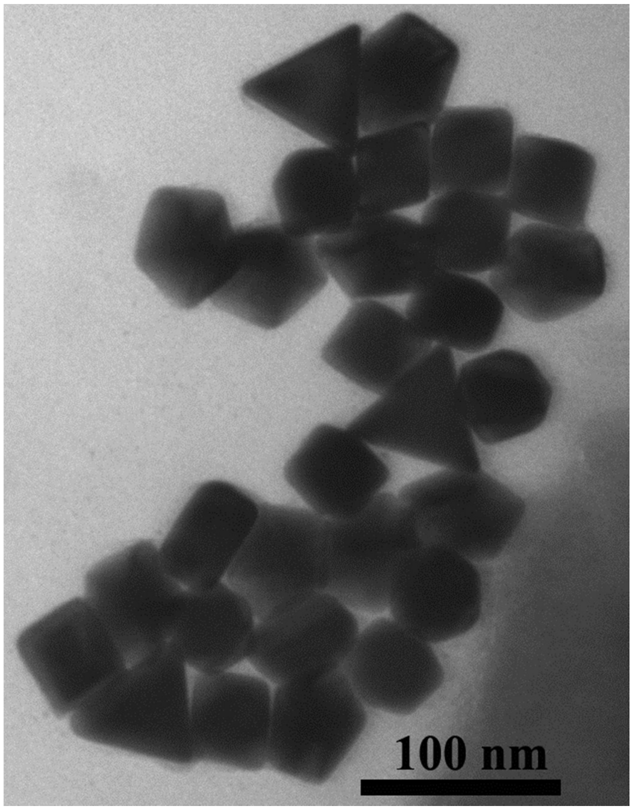


Fig. 4c: The TEM image of the separated supernatant upon the addition of CTAC in the secondary process.

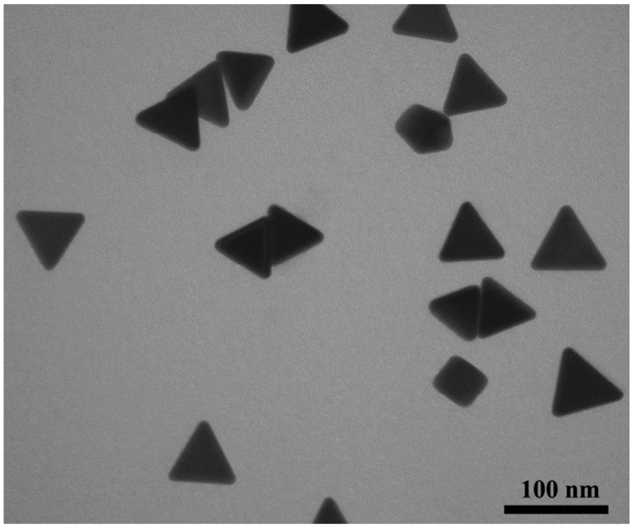


Fig. 4d: The TEM image of the separated precipitate upon the addition of CTAC in the secondary process.

Similarly, according to the CTAB- and CTAC-induced selectively size and shape separation, the as-prepared gold nanotriangles could be purified effectively in another way. The schematic diagram of the two-step separation strategy (Approach 2) is summarized in Fig. 5a. After depletion effect of CTAC, the separation of different shapes could be realized. The supernatant contains nanoparticles with nanospheres, whereas the precipitate contains nanotriangles with two different sizes, as can be seen in the above chapter in Fig. 3e and Fig. 3f. Then take the precipitate for the secondary separation. Due to the size selective separation induced by CTAB, the separation of nanoparticles with small and large size could be obtained in supernatant and participate respectively. The resulting supernatant shows a color of green and the precipitate light green, whose absorption spectra are shown in Fig. 5b. The absorption spectrum of supernatant obtained in the first CTAC process shows two distinct absorption peaks located at 630 nm and 1240 nm respectively. After the separation, the absorption spectrum is split into two independent absorption peaks. One corresponds to supernatant which peaks at 630 nm representing smaller sized nanotriangles, and the other corresponds to the precipitate which peaks at 1240 nm representing larger sized nanotriangles. Fig. 5c and Fig. 5d are representative TEM images of the supernatant and the precipitate respectively. The supernatant contains smaller sized nanotriangles with uniform size and fine morphology while the precipitate mainly contains nanotriangles with larger size. The SEM image of the separated small sized gold nanotriangles is shown in Fig. 5e. In spite of a small portion of large sized nanotriangles, the purified nanotriangles exhibit a good uniformity. The SEM image of the separated large sized gold nanotriangles is shown in Fig. 5f. In spite of a small portion of nanospheres, the purified nanotriangles exhibit a good uniformity. The nanotriangles with smaller size and larger size have been successfully separated with great uniformity.

In our experiment, the synthesized nanotriangles contain nanospheres, two different sizes of gold nanotriangles and other irregular nanoparticles. The small sized nanotriangles have an average length of about 65 nm and the large sized nanotriangles have an average length of about 170 nm. However, due to the difference of their thickness, the mass difference between these two sizes is not significant. Thus it is hard for them to separate by the traditional centrifugation. The proposed separated strategy is based on the difference of surface area and the aggregation induced by depletion of surfactant. Therefore, if the mixture contains nanoparticles with significant mass difference and it is recommend to use centrifugation for separation. If the mixture contains nanoparticles with different surface area, it is better for them to use this surfactant-induced separation strategy. Hence in this work, a two-step approach has been utilized for the separation of nanoparticles mixture, of which the large sized nanotriangles have an edge length more than twice as long as that of small sized nanotriangles. As for what different size it can be discerned, it depends on the option of what kind of surfactant and surfactant concentration. Although the accurate force analysis and numerical simulation have not been measured and calculated in detail, this strategy provides ideas for people to achieve shape separation from the mixture of nanoparticles. It is reported by the literature for separating nanoparticles with other morphology by utilizing CTAB, such as separation of nanorods from the binary mixture of nanorods and nanospheres [29] and purifying nanotriangels from nanospheres.[36] Therefore, it should be applied for the separation of the nanoparticles with different surface areas theoretically.

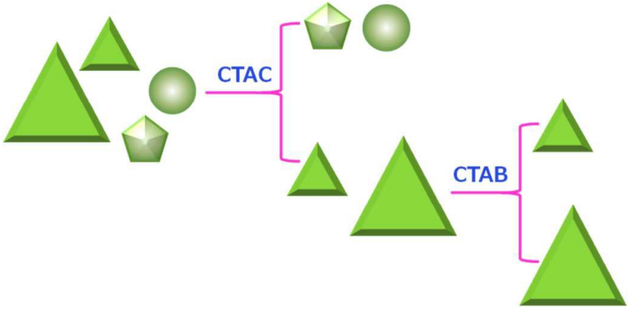


Fig. 5a: A schematic illustration of separation nanotriangles with high purification based on CTAB and CTAC through a two-step strategy. (Approach 2)

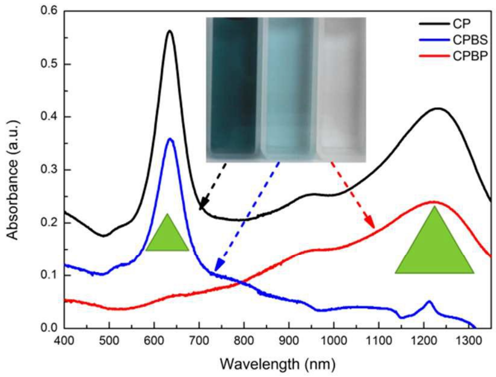


Fig. 5b: The absorption spectra of CTAC-separated precipitate before and after the addition of CTAB, the inset: the corresponding color. (CP denotes the CTAC-separated precipitate, CPBS denotes the supernatant of CP after the addition of CTAB, CPBP denotes the precipitate of CP after the addition of CTAB)

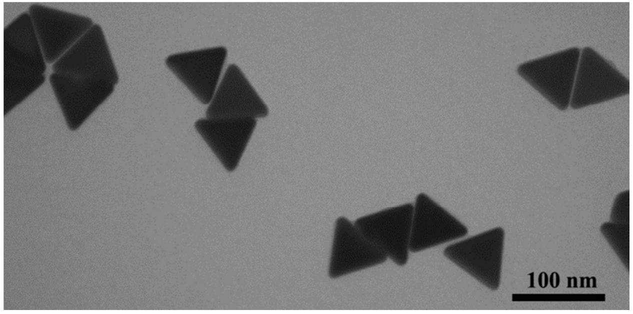


Fig. 5c: The TEM image of the separated supernatant upon the addition of CTAB in the secondary process.

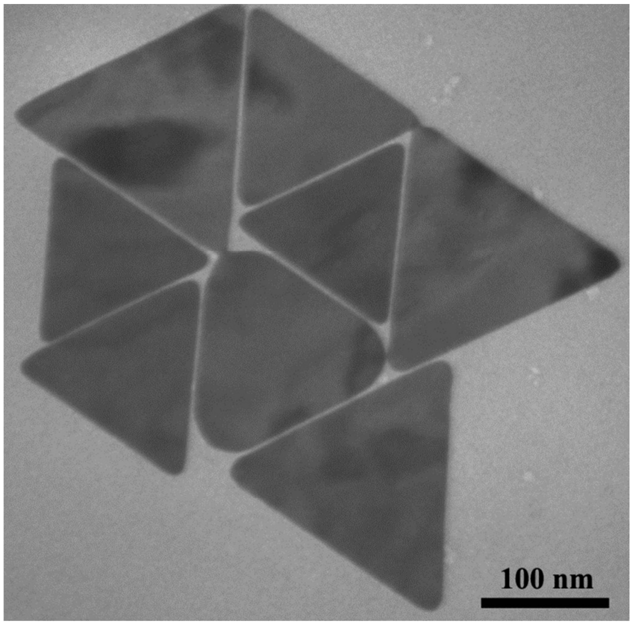


Fig. 5d: The TEM image of the separated precipitate upon the addition of CTAB in the secondary process.

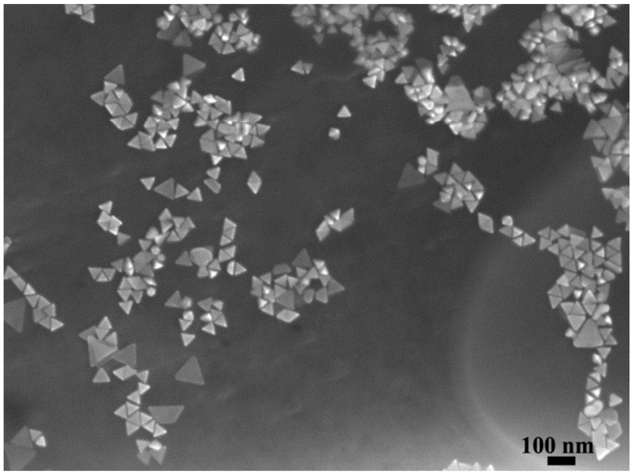


Fig. 5e: The SEM image of the separated gold nanotriangles with a small size.

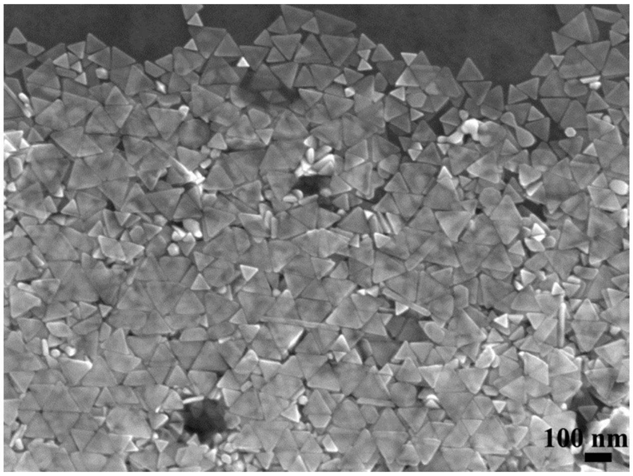


Fig. 5f: The SEM image of the separated gold nanotriangles with a large size.

3.3 The proposed mechanism of CTAB and CTAC induced size and shape separation from the mixture of the nanoparticles

To understand the possible mechanism of CTAB and CTAC induced size and shape separation from the mixture of the nanoparticles, we firstly investigated the effect of Cl^- and Br^- on gold nanotriangles. We compared the separation results of Cl^- with a concentration of 0.167 M introduced by NaCl, KCl and CTAC respectively. The absorption spectra of separated supernatant and precipitate are shown in Fig. 6a (the supernatant is in dotted line and precipitate is in solid line). The concentration of NaCl with 0.167 M leads to the synthesized nanotriangles completely aggregate and make the solution transparent. As is evidenced by the spectra, the absorbance of the supernatant is almost zero and the precipitate is only 0.2. In fact, NaCl with an even lower concentration could induce the separation of large sized nanotriangles in our experiment, which is consistent with the precious literature.[30] When the concentration of NaCl is ranging from 0.015 M to 0.08 M, it could also separate the large sized gold nanotriangles. Fig. 6b and Fig. 6c are the absorption spectra of separated supernatant and precipitate after the addition of different concentration of NaCl respectively. As the NaCl concentration is increased, the peak at 1240 nm is gradually reduced, demonstrating the decreased number of large sized nanotriangles in the supernatant, as shown in Fig. 6b. Accordingly, the peak at 1240 nm is gradually increased with the increasing concentration of NaCl, as is depicted in Fig. 6c. When the concentration of NaCl is 0.06 M, the absorption intensity of peak locating at 1240 nm reaches the highest, which demonstrates the separation of large sized nanotriangels effectively. When the concentration of NaCl is above 0.06 M, higher concentration begins to induce the aggregation of nanotriangles as is demonstrated by the orange line in Fig. 6c. Thus NaCl with a lower concentration could induce the separation of large sized nanotriangles in our experiment. Similarly, the separation results of Cl^- with a concentration of 0.222 M and 0.333 M introduced by NaCl, KCl and CTAC were also compared. The absorption spectra of separated supernatant and precipitate are shown in Fig. 6d and Fig. 6e (the supernatant is in dotted line and precipitate is in solid line). The aggregation of nanoparticles covered with carboxylate ligands can be induced by different monovalent cations and the critical K^+ concentrations required for nanoparticles aggregation is greater than that of Na^+.[40] When it comes to the difference effect of NaCl and KCl on nanoparticles, cations play an important role. Therefore, in the case of NaCl with a concentration of 0.167 M, we witnessed almost complete irreversible aggregation of nanoparticles. While for KCl with a higher concentration of 0.333 M, we only observed a little etching effect on nanotriangles and with no obvious aggregation at all. It is found that KCl could separate larger sized nanotriangles. However, it caused the etching of the nanotriangles as evidenced by the large blue shift of peak 1240 nm. The introduction of Br^- with concentrations of 0.167 M and 0.222 M by KBr and NaBr makes the peak of 1240 nm blue shift, demonstrating the etching effect of the nanotriangles to some degree. It is reported that Br^- could penetrate more deeply into the surface of the CTA^+ micelle.[41] Hence, when it comes to the difference effect of NaBr and KBr on nanoparticles, Br^- plays a far more major role than that of cations. Therefore it is found that both of NaBr and KBr induced the etching on nanotriangles and there is little difference between them, as depicted in Fig. 7a and Fig. 7b. When the concentration is 0.167 M, both of them could separate large sized nanotriangles with little etching to some extent. When the concentration is increased, both of them could separate nanospheres and severely etch large sized nanotriangles as evidenced by the drastic blue shift the peak wavelength at 1240 nm.[42] However, in terms of Br^- introduced by CTAB, the peak of 1240 nm keeps constant, indicating no etching of nanotriangles, as is shown in Fig. 7a and Fig. 7b. It is CTA^+ micelle that serves as a protecting agent that prevents the nanotriangles from etching by Br^- and Cl^-. Thus we could deduce that the micelle of CTA^+ play a vital role in the separation of nanotriangles. The CTAB- and CTAC-based separated process is a physical aggregation and do not involve chemical reaction.

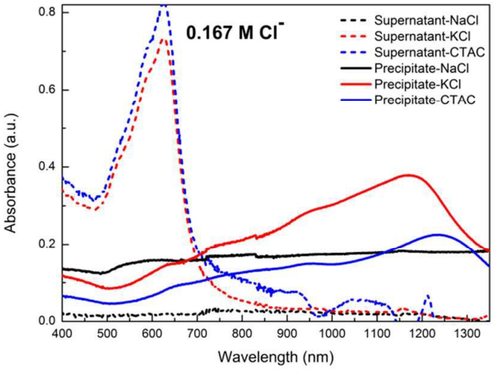


Fig. 6a: The absorption spectra of supernatant and precipitate separated by NaCl, KCl and CTAC. (0.167 M Cl^-)

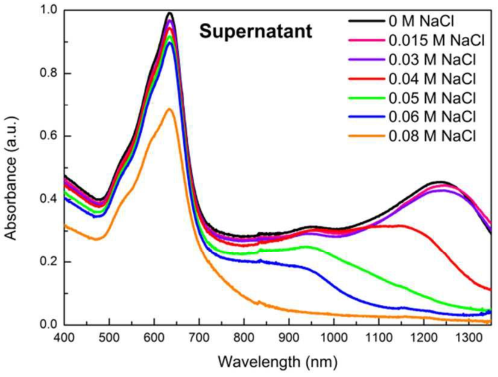


Fig. 6b: The absorption spectra of separated supernatant after the addition of different concentration of NaCl, the concentration of NaCl is ranging from 0.015 M to 0.08 M.

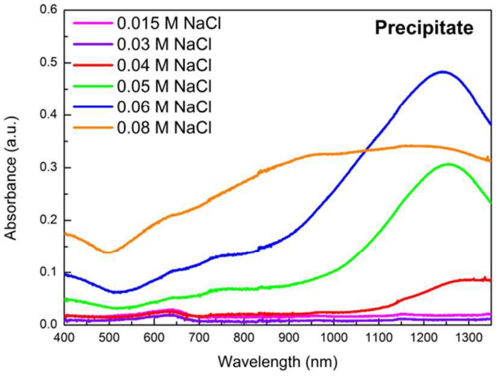


Fig. 6c: The absorption spectra of separated precipitate after the addition of different concentration of NaCl, the concentration of NaCl is ranging from 0.015 M to 0.08 M.

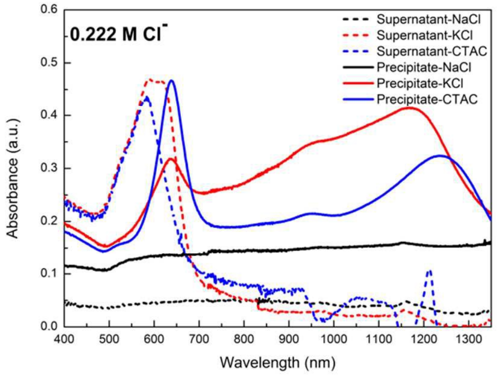


Fig. 6d: The absorption spectra of supernatant and precipitate separated by NaCl, KCl and CTAC. (0.222 M Cl$^-$).

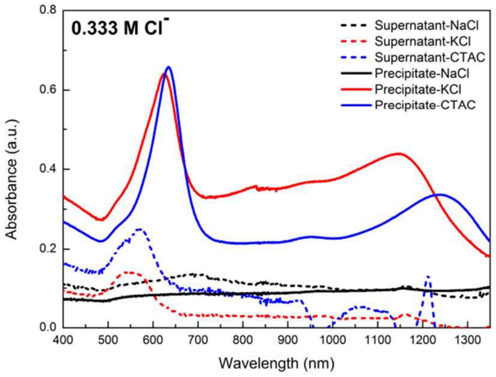


Fig. 6e: The absorption spectra of supernatant and precipitate separated by NaCl, KCl and CTAC. (0.333 M Cl$^-$).

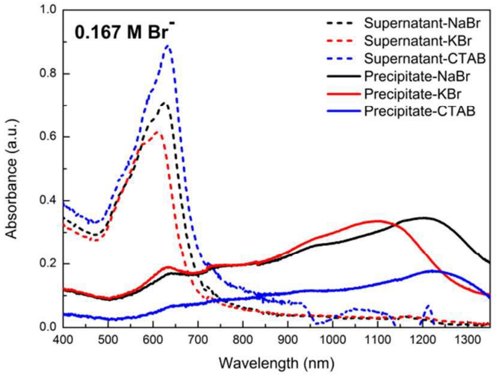


Fig. 7a: The absorption spectra of supernatant and precipitate separated by NaBr, KBr and CTAB. (0.167 M Br$^-$)

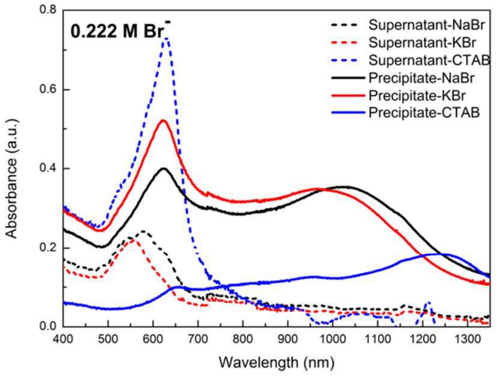


Fig. 7b: The absorption spectra of supernatant and precipitate separated by NaBr, KBr and CTAB. (0.222 M Br$^-$)

In addition, contact surface area between the adjacent nanoparticles may be another factor that accounts for this selectively separated process. As we know, traditional separation methods mainly use differences between the mass of nanoparticles, for the different morphology of nanoparticles with the same mass, the traditional separation methods no longer work. In spite of the same mass, these nanoparticles often have different contact area between the adjacent nanoparticles. The surfactant-induced attraction force is proportional to the possible contact surface area of the nanoparticles. According to Ahmad et al., a relatively flat surface with nearly zero curvature leads to larger overall interactions as compared with a surface with strong curvature.[43] The as-prepared gold nanotriangles contain nanospheres and two different sizes of nanotriangles, of which nanospheres and small sized nanotriangles have roughly the same size. As shown in Fig. 8, contact surface area between the adjacent nanospheres is the smallest, the following is small sized nanotriangles and the next is large sized nanotriangles. Jones et al. found that nanotriangles with flat and extended facets could support more DNA molecules due to the larger contact surface compared with nanospheres. Nanotriangles exhibit a higher association rate and lower dissociation rate compared with nanospheres.[44-46] In addition, Mason found that depletion force is particularly attractive for nanoparticles anisotropic shapes compared with their nanosphere counterparts because anisotropic nanoparticles incline to have the directionally dependent interaction.[47] Nanotriangles with both top surface and bottom surface tend to gain maximum depletion force compared with nanospheres.[48-49] When there is no external force added on the colloid, the as-prepared gold nanotriangles could keep stable for months. Therefore, the addition of low concentration of CTAB- and CTAC- induced depletion attraction force firstly bring large sized nanotriangles into proximity, with the gravity and attraction force altogether to reach a certain threshold and exceed the electrostatic repulsion, breaking the balance between the large sized nanotriangles, and then leads to the aggregation of large sized gold nanotriangles. The CTAB- and CTAC-induced nanotriangles aggregation is in the fashion of face-to-face rather than a random fashion, as demonstrated by the experimental results of the previous literatures.[47, 49] Large aggregation will cause the precipitate at the bottom of the bottle, while the small sized nanotriangles and nanospheres are still in the supernatant. This surfactant induced aggregation is reversible and the precipitate is easy to form colloid by resuspending in ultrapure water. Then the separation of nanoparticles with larger size could be achieved firstly. Thus, both CTAB and CTAC with a low concentration could realize this separation of larger sized nanoparticles. However, compared with both of the separated supernatant and precipitate obtained from different concentrations of CTAB and CTAC, an optimum concentration of CTAB is found for size separation when the separated nanoparticles could reach the highest absorption intensity, demonstrating the high purification yield of the nanoparticles. As the concentration of CTAB and CTAC is increased, besides large sized nanotriangles, small sized nanotriangles also experience an attractive force due to depletion interaction induced by surfactant, which flocculates gradually, leaving those nanospheres still in the supernatant. However, high concentration of CTAB solution is becoming viscous and hard to prepare.[36] It is found that CTAB and CTAC exhibit different micelle characteristic with the increasing of the surfactant concentration. CTAB becomes wormlike micelles while the micelles of CTAC remain spherical even at high surfactant concentrations.[50] CTAB with the as-prepared high concentration could no longer separated nanospheres while high concentration of CTAC leads to the aggregation of all the nanotriangles and leaves the nanospheres in the solution, thus nanoparticles with different shapes could be separated with a high yield. Therefore, an optimum concentration of CTAC is obtained for the shape separation from the mixture of the nanoparticles. As a consequence, two optimum concentrations of CTAB and CTAC are obtained for the size and shape separation of nanotriangles efficiently.

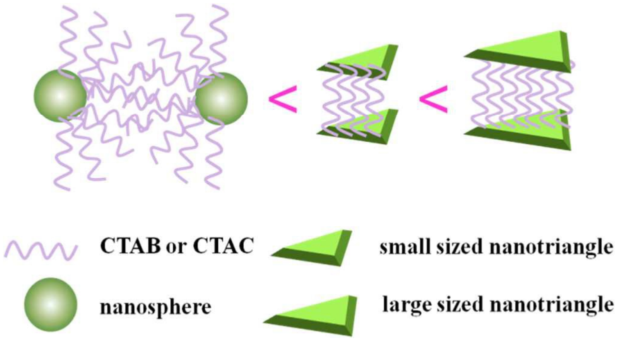


Fig. 8: The contact surface area between the adjacent nanospheres and two different sized nanotriangles upon the addition of CTAB or CTAC.

4. Conclusions

In conclusion, gold nanotriangles were synthesized in a large scale and the separation of as-prepared gold nanotriangles was achieved via a two-step strategy based on surfactant depletion effect. The effects of parameters including the concentrations of CTAB and CTAC were investigated in detail, and the optimum concentrations of CTAB were found to be 0.167 M for size separation and CTAC 0.222 M for shape separation respectively. Furthermore, the effect of chloride ions and bromide ions and the separation mechanism have also been investigated based on surfactant depletion-induced aggregation on different contact areas of the nanoparticles. The proposed two-step strategy could exquisitely separate nanotriangles from the crude gold nanoparticles, which gives an avenue for the separation of nanoparticles with different size and morphology effectively.

Acknowledgements

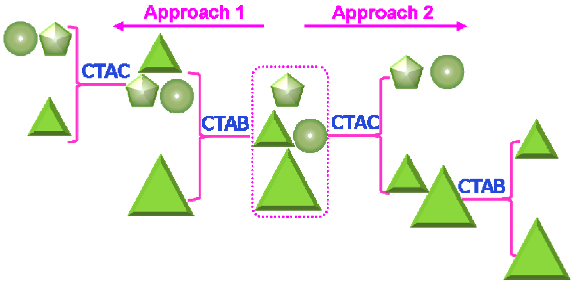
We acknowledge the financial supports of the Fundamental Research Funds for the Central Universities under grant No. 2011jdgz17 and the National Natural Science Foundation of China under grant No. 11174232 and 61178075.

Notes and references

1 P.K. Jain, X. Huang, I.H. El-Sayed and M.A. El-Sayed, *Acc. Chem. Res.*, 2008, **41**, 1578.
2 N.R. Jana, L. Gearheart and C.J. Murphy, *Adv. Mater.*, 2001, **13**, 1389.
3 T.K. Sau and C.J. Murphy, *Langmuir*, 2004, **20**, 6414.
4 X.S. Kou, Z.H. Sun, Z. Yang, H.J. Chen and J.F. Wang, *Langmuir*, 2008, **25**, 1692.

5 M.F. Cardinal, B. Rodríguez-González, R.A. Alvarez-Puebla, J. Pérez-Juste and L.M. Liz-Marzán, *J. Phys. Chem. C*, 2010, **114**, 10417.
6 J.E. Millstone, S. Park, K.L. Shuford, L. Qin, G.C. Schatz and C.A. Mirkin, *J. Am. Chem. Soc.*, 2005, **127**, 5312.
7 J.E. Millstone, G.S. Metraux and C.A. Mirkin, *Adv. Funct. Mater.*, 2006, **16**, 1209.
8 G.J. Zhou, Y. Yang, S.H. Han, W. Chen, Y.Z. Fu, C.Z. Zou, L.J. Zhang and S.M. Huang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 13340.
9 C.L. Nehl, H.W. Liao and J.H. Hafner, Nano Lett., 2006, **6**, 683.
10 A. Halder and N. Ravishankar, *Adv. Mater.*, 2007, **19**, 1854.
11 P.R. Sajanlal, C. Subramaniam, P. Sasanpour, B. Rashidian and T. Pradeep, *J. Mater. C*, 2010, **20**, 2108.
12 T. Kim, K.S. Jeon, K. Heo, H.M. Kim, J. Park, Y.D. Suh and S. Hong, *Analyst*, 2013, **138**, 5588.
13 Z.X. Li, Y. Yu, Z.Y. Chen, T.R. Liu, Z.K. Zhou, J.B. Han, J.T. Li, C.J. Jin and X.H. Wang, *J. Phys. Chem. C*, 2013, **117**, 20127.
14 G.K. Joshi, P.J. McClory, B.B. Muhoberac, A.K. Kimberly, A. Smith and R. Sardar, *J. Phys. Chem. C*, 2012, **116**, 20990.
15 E. Hao, R.C. Bailey, G.C. Schatz, J.T. Hupp and S.Y. Li, *Nano Lett.*, 2004, **4**, 327.
16 L. Scarabelli, M. Coronado-Puchau, J.J. Giner-Casares, J. Langer and L.M. Liz-Marzán, *ACS Nano*, 2014, **8**, 5833.
17 R.C. Jin, Y.W. Cao, C.A. Mirkin, K.L. Kelly, G.C. Schatz and J.G. Zheng, *Science*, 2001, **294**, 1901.
18 Y.G. Sun, B. Mayers and Y.N. Xia, *Nano Lett.*, 2003, **3**, 675.
19 M. Tsuji, M. Hashimoto, Y. Nishizawa and T. Tsuji, *Chem. Lett.*, 2003, **32**, 1114.
20 S. Kundu, L.H. Peng and H. Liang, Inorg. Chem., 2008, **47**, 6344.
21 C.C. Li, W.P. Cai, Y. Li, J.L. Hu and P.S. Liu, *J. Phys. Chem. B*, 2006, **110**, 1546.
22 P.J. Straney, C.M. Andolina and J.E. Millstone, *Langmuir*, 2013, **29**, 4396.
23 L. Chen, F. Ji, Y. Xu, L. He, Y.F. Mi, F. Bao, B.Q. Sun, X.H. Zhang and Q. Zhang, *Nano Lett.*, 2014, **14**, 7201.
24 S.S. Shankar, A. Rai, B. Ankamwar, A. Singh, A. Ahmad and M. Sastry, Nat. Mater., 2004, **3**, 482.
25 K.E. Lee, A.V. Hesketh and T.L. Kelly, *Phys. Chem. Chem. Phys.*, 2014, **16**, 12407.
26 Y.N. Xia, P.D. Yang, Y.G. Sun, Y.Y. Wu, B. Mayers, B. Gates, Y.D. Yin, F. Kim and H.Q. Yan, *Adv. Mater.*, 2003, **15**, 353.
27 B. Xue, D. Wang, J. Zuo, X.G. Kong, Y.L. Zhang, X.M. Liu, L.P. Tu, Y.L. Chang, C.X. Li, F. Wu, Q.H. Zeng, H.F. Zhao, H.Y. Zhao and H. Zhang, *Nanoscale*, 2015, **7**, 8048.
28 V. Sharma, K. Park and M. Srinivasarao, *Proc. Natl. Acad. Sci. USA*, 2009, **106**, 4981.
29 N.R. Jana, *Chem. Commun.*, 2003, 1950.
30 W.J. Liu, D. Liu, Z.N. Zhu, B. Han, Y. Gao and Z.Y. Tang, *Nanoscale*, 2014, **6**, 4498.
31 Y.M. Zheng, Y.L. Hong, W.W. Wu, D.H. Sun, Y.P. Wang, J.L. Huang and Q.B. Li, *Sep. Purif. Technol.*, 2015, **151**, 332.
32 M. Hanauer, S. Pierrat, I. Zins, A. Lotz and C. Sönnichsen, *Nano Lett.*, 2007, **7**, 2881.
33 J.P. Novak, C. Nickerson, S. Franzen and D.L. Feldheim, *Anal. Chem.*, 2001, **73**, 5758.
34 Z.R. Guo, Y. Wan, M. Wang, L.N. Xu, G. Yang, K. Fang and N. Gu, *Colloids Surf. A: Physicochem. Eng. Asp.*, 2012, **414**, 492.
35 Z.R. Guo, X. Fan, L.K. Liu, Z.P. Bian, C.R. Gu, N. Gu, Y. Zhang, D. Yang and J.N. Zhang, *J. Colloid Interf. Sci.*, 2010, **348**, 29.
36 K. Park, H. Koerner and R.A. Vaia, *Nano Lett.*, 2010, **10**, 1433.
37 R.M. Liu, J.H. Zhou, Z.K. Zhou, X.B. Jiang, J.M. Liu, G.H. Liu and X.H. Wang, *Nanoscale*, 2014, **6**, 13145.
38 T.H. Ha, H.J. Koo and B.H. Chung, *J. Phys. Chem. C*, 2007, **111**, 1123.
39 K.L. Kelly, E. Coronado, L.L. Zhao and G.C. Schatz, *J. Phys. Chem. B*, 2003, **107**, 668.
40 D. Wang, B. Tejerina, I. Lagzi, B. Kowalczyk and B.A. Grzybowski, *ACS Nano*, 2010, **5**, 530.
41 L.J. Magid, Z. Han, G.G. Warr, M.A. Cassidy, P.D. Butler and W.A. Hamilton, *J. Phys. Chem. B*, 1997, **101**, 7919.
42 J.S. DuChene, W.X. Niu, J.M. Abendroth, Q. Sun, W.B. Zhao, F.W. Huo and W.D. Wei, *Chem. Mater.*, 2012, **25**,1392.
43 I. Ahmad, H.J.W. Zandvliet and E.S. Kooij, *Langmuir*, 2014, **30**, 7953.
44 M.R. Jones, R.J. Macfarlane, A.E. Prigodich, P.C. Patel, and C.A. Mirkin, *J. Am. Chem. Soc.*, 2011, **133**, 18865.
45 M.R. Jones, R.J. Macfarlane, B. Lee, J. Zhang, K.L. Young, A.J. Senesi and C.A. Mirkin, *Nat. Mater.*, 2010, **9**, 913.
46 M.R. Jones and C.A. Mirkin, *Angew. Chem. Int. Edit.*, 2013, **52**, 2886.
47 T.G. Mason, *Phys. Rev. E*, 2002, **66**, 060402.
48 K. Zhao and T.G. Mason, *Phys. Rev. Lett.*, 2007, **99**, 268301.
49 K.L. Young, M.R. Jones, J. Zhang, R.J. Macfarlane, R. Esquivel-Sirvent, R.J. Nap, J.S. Wu, G.C. Schatz, B. Lee and C.A. Mirkin, *Proc. Natl. Acad. Sci. USA*, 2012, **109**, 2240.
50 V.K. Aswal and P.S. Goyal, *Chem. Phys. Lett.*, 2003, **368**, 59.

Table of Contents



A two-step separated strategy combined CTAB and CTAC has been proposed that enables the purification of gold nanotriangles effectively.