Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-Mediated Growth Method

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A method is used for preparing gold NRs with aspect ratios ranging from 1.5 to 10 for which the surface plasmon absorption maxima are between 600 and 1300 nm. This method has been adapted from a previously published seed-mediated growth method (Jana et al. *Adv. Mater.* **2001**, *13*, 1389). The disadvantages and limitations of the earlier method (i.e., formation of noncylindrical NRs, ϕ-shaped particles, and formation of a large fraction of spherical particles) have been overcome by use of a hexadecyltrimethylammonium bromide (CTAB)-capped seed instead of a citrate-capped one. In a single-component surfactant system, the silver content of the growth solution was used to grow NRs to a desired length. This results in reproducible formation of NRs with aspect ratios ranging from 1.5 to 4.5. To grow longer NRs with aspect ratios ranging from 4.6 to 10, a binary surfactant mixture composed of benzyldimethylhexadecylammoniumchloride (BDAC) and CTAB was used. NRs are grown in this mixture either by aging or by addition of a growth solution suitable to shorter NRs. Effects of the silver ion and the cosurfactant along with the growth mechanism of NRs are discussed.

Introduction

Nanoparticles show properties that are often different from those of their corresponding bulk materials[1–3]. Metal nanoparticles ranging from noble to transition elements have shown interesting properties in catalysis,[4] optics,[5] magnetism,[6,7] sensors,[8] etc. Significant progress in developing synthetic methods and understanding the optoelectronic properties of these nanoparticles has been carried out, but still a long list of unexplored subjects and ambiguous questions are present that ought to be addressed.

In the synthesis of metal nanoparticles, control over the shape and size has been one of the important and challenging tasks. The shape and crystallographic facets are the major factors in determining the catalytic and surface activity of the nanoparticles.[4] The size can influence the optical properties of metal nanoparticles. This is especially important when the particles have aspect ratios (length/width) larger than 1. In spheroidal or rod-shaped gold nanoparticles, the first distinct difference relative to spherical particles is the appearance of a surface plasmon band at lower energies.[9] In

these nanoparticles, a strong surface-enhanced Raman scattering (SERS) has been observed, which is sensitive to the shape and size of the particles.[10]

In general, rod-shaped metal nanoparticles can be synthesized in either rigid templates or in the presence of surfactants. In the former case, the metal ions are reduced inside cylindrical pores of oxide[11] or polymeric membranes.[12] In the latter method, neutral or charged surfactants are used for growth of the nanoparticles.[13] In nonaqueous media, surfactants such as tetraoctylphosphineoxide and oleic acid have been used to grow cobalt nanorods in the direction parallel to the {101} planes.[6] In aqueous media, hexadecyltrimethylammonium bromide (CTAB; Scheme 1) has been one of the most popular molecules in the synthesis of metals, although this has been limited to only gold[14–16] and silver[17] metals so far.

In preparing gold and silver nanorods (NRs) using surfactants two different approaches are available: the

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Scheme 1. Structures of Hexadecyltrimethylammoniumbromide (CTAB) and Benzyldimethylammoniumchloride (BDAC): the Latter Has a Bulkier Head Group
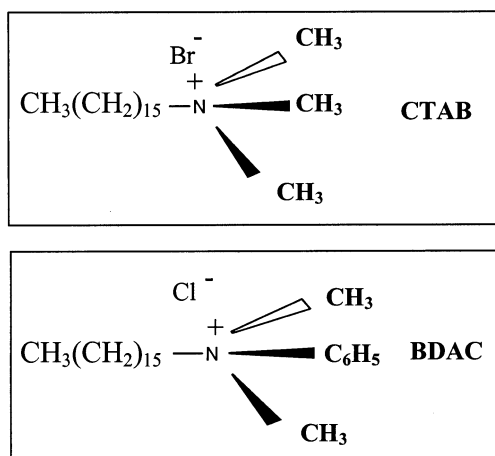
electrochemical[14] and seed-mediated[15] growth methods. In a single-batch synthesis, the former method produces more NRs than the latter approach. Both synthetic methods have weak points, which are the lack of control over the size and the formation of a large amount of spherical particles (NS) as a byproduct. For instance, our results show that in the electrochemical method, statistically, the formation of gold NRs is limited to those with plasmon bands shorter than 850 nm. The result is not reproducible and the fraction of the formed spheres could be significant.

In the seed-mediated growth, developed by Jana et al.,[15] cylindrical NRs are grown in a multistep process. In this method, the NR formation yield is so low that centrifugation is necessary to accumulate the number of NRs. More recently, this group reported an improved version of the above method,[16] in which different volumes of the seed were added to a growth solution. They changed the growth solution by adding a small amount of silver ions. On the basis of that report, the addition of different volumes of the seed solution produces NRs with different aspect ratios. The shape of the gold NRs produced using this method is no longer cylindrical, and the fraction of the formed spherical particles in the process is about 40−50%. This approach also results in the formation of ϕ-shaped particles as byproduct which alters the overall shape of the plasmon absorption bands of the NRs.

In this report, two strategies have been taken which could be considered as modifications of the seed-mediated growth method.[15] In the first approach, the following modifications have been applied for synthesizing NRs with aspect ratios of 1.5 to 5: (1) replacement of the citrate with CTAB molecules in the seed formation step; and (2) adjusting the silver content of the growth solution to grow NRs with controlled aspect ratios. The disadvantages associated with the original method have been overcome, and samples with 0−1% NSs and 0% ϕ-shaped nanoparticles are produced. In the second approach, in addition to the above changes, a binary surfactant mixture has been used to prepare NRs with longer aspect ratios. We have been able to grow long NRs either by increasing the growth time or by the gradual addition of the growth solution to a NR solution.

The growth mechanism of these gold nanorods is qualitatively discussed.

Experimental Section

Hexadecyltrimethylammoniumbromide (98%) and benzyldimethylammoniumchloride hydrate (98%) were purchased from Fluka. Sodium borohydride (99%) and L-ascorbic acid were purchased from Sigma-Aldrich. Deionized water (18 MΩ) was used in all the experiments. For preparation of NRs, seed and growth solutions were made as described below.

Seed Solution. CTAB solution (5 mL, 0.20 M) was mixed with 5.0 mL of 0.00050 M $HAuCl_4$. To the stirred solution, 0.60 mL of ice-cold 0.010 M $NaBH_4$ was added, which resulted in the formation of a brownish yellow solution. Vigorous stirring of the seed solution was continued for 2 min. After the solution was stirred, it was kept at 25 °C.

Growth of NRs with Plasmon Bands Less Than 850 nm. CTAB (5 mL, 0.20 M) was added to (0.050, 0.10, 0.15, 0.20, 0.25 mL) of 0.0040 M $AgNO_3$ solution at 25 °C. To this solution, 5.0 mL of 0.0010 M $HAuCl_4$ was added, and after gentle mixing of the solution 70 μL of 0.0788 M ascorbic acid was added. Ascorbic acid as a mild reducing agent changes the growth solution from dark yellow to colorless. It is worth noting that the five growth solutions above are identical except for their silver ion content.

The final step was the addition of 12 μL of the seed solution to the growth solution at 27−30 °C. The color of the solution gradually changed within 10−20 min. For longer NRs, the color change takes place more slowly. The temperature of the growth medium was kept constant at 27−30 °C in all the experiments. This pathway produces pure NR solutions with aspect ratios up to 4.7.

Growth of NRs with Plasmon Bands Longer Than 850 nm. Two strategies were used to grow longer NRs. In both cases a binary surfactant mixture of benzyldimethylhexadecylammoniumchloride (BDAC) and CTAB was used.

In the first approach the surfactant mixture was prepared by adding 5 mL of 0.15 M BDAC to 0.010, 0.030, 0.050, 0.080, 0.10, 0.12, and 0.20 g of CTAB for making surfactant mixtures with ratios of 27 to 1.3. After dissolving the mixtures by sonication (20 min at 40 °C), each solution was added to 200 μL of 0.0040 M $AgNO_3$. In these solutions the silver content was kept constant while the fraction of the cosurfactant (CTAB) was changed. To this solution, 5.0 mL of 0.0010 M $HAuCl_4$ was added, and after gentle mixing of the solution 70 μL of 0.0778 M ascorbic acid was added. The growth process completed 1 h after addition of a 12-μL seed. At this stage NRs with aspect ratios of 5−5.5 are formed. By aging the NR solution for 7 days, the aspect ratio increases to 9−10. It was found that the BDAC/CTAB ratios between 2 and 5.5 produce fewer spherical particles relative to the larger surfactant ratios. The color of the solution could change from red to light brown due to high or low concentration of NSs, respectively.

In the second approach, the growth solution with a BDAC/CTAB molar ratio of 2.7 was made as described above (called A). This ratio was selected because it favors the formation of fewer NSs relative to other ratios. The growth process was initiated after adding 12 μL of seed solution.

The growth solution (called B) was prepared by adding 5.0 mL of a mixture of 0.15 M BDAC and 0.10 g of CTAB to 200 μL of 0.0040 M $AgNO_3$. This solution was then added to 5.0 mL of 0.00050 M $HAuCl_4$ solution. To this solution, 36 μL of 0.0778 M ascorbic acid was added, which resulted in a colorless solution. The growth solution (B) was added to solution A at a rate of 1.0 mL per 20 min. Each addition of the growth solution redshifted the plasmon band by about 20−30 nm. This process can be continued until the desired NR length is obtained.

Size Distribution Measurements. TEM images of the prepared NRs were taken at 100 KV using JEOL100 and were used in the size distribution measurements. For each sample,

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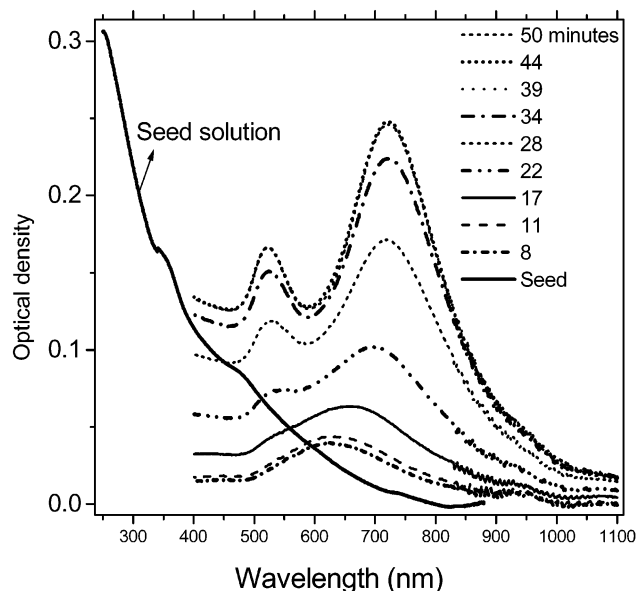
Figure 1. UV−visible spectrum of growth of a gold NR solution right after seed addition. The length and population of the NRs increase to a certain limit. The CTAB-capped seed spectrum (less than 4 nm in size) also is seen in the lower wavelength of the spectrum.

the size of 200 particles was measured to obtain the average size and the size distribution.

Results

Figure 1 (curve labeled as seed) shows the visible absorption of the seed solution a few min after preparation. Based on the TEM images, the particle size in this solution is less than 4 nm. By introducing 12 μL of the 5-min-aged seed solution to a growth solution, the NRs start to grow. Figure 1 shows the visible spectra at different stages of this process. Our results show that if the citrate-capped seed is used in a growth solution containing silver ions, ϕ and star-shaped nanoparticles are formed. In addition, the distorted NRs formed have a larger width in the middle than that at the ends, similar to the results reported in ref 16. When the CTAB-capped seed is used instead, these shapes are not formed. The NRs formed have the shape and structure that has been originally reported[10] and is shown later in Figure 6a−c.

In the case of citrate-capped seeds, upon increasing the silver ion content in the growth solution, the concentration of the nonrod-shaped particles increases drastically so that three plasmon bands associated with three different dimensions of these particles would dominate the overall shape of the spectrum. For surfactant-capped seeds, we have been able to decrease the amount of spherical particles almost to zero. More importantly, we have been able to control the length of the NRs by varying the silver ion content in the growth solution. Figure 2a shows the effect of adding identical growth solutions to 50−300 μL of 0.004 M AgNO$_3$ solution. It can be seen that by increasing the silver concentration, the longitudinal plasmon band redshifts and its intensity increases. Size distribution measurements confirm that the aspect ratio of NRs increases as shown in Figure 2b. In all the samples the fraction of the gold nanospheres is less than 1%.
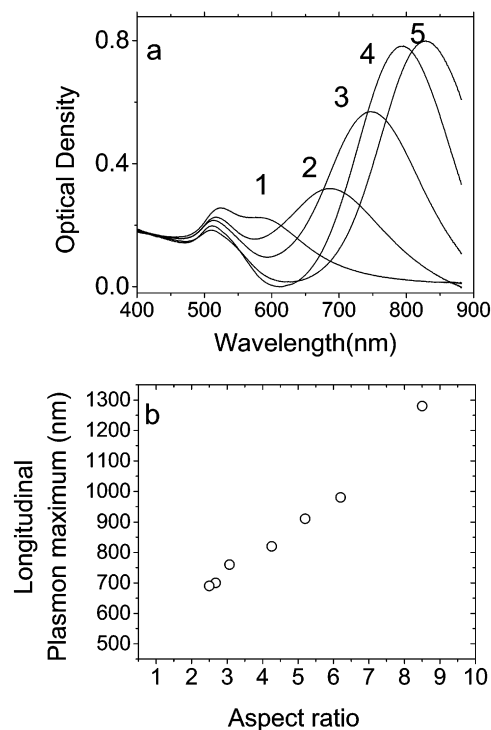
Figure 2. (a) Visible spectra of 5 identical growth solutions in which the silver content increases from sample no. 1 to 5. By controlling the Ag ion concentration, the length of the NRs can be adjusted. (b) The aspect ratios of NRs obtained from size measurements show an increase, which confirm the results of part (a).
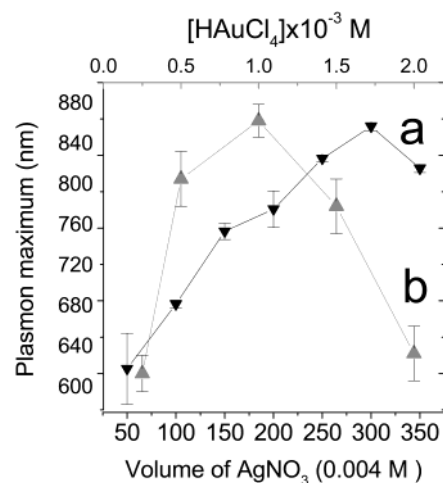
Figure 3. (a) Increase in the concentration of silver ions first increases then decreases the average aspect ratio of the NRs. (b) Similar effect is observed for HAuCl$_4$. At high concentration, the decrease in size could be related to the enhanced interaction of silver and gold ions with the surfactant counterions. The error bars represent the range that was obtained for each point after five trials.

The effect of the silver ion content is not always to increase the aspect ratio of NRs. Figure 3a shows that by increasing the concentration of the AgNO$_3$ in the growth solution to more than 0.00012 M (300 μL of 0.004 M), the length of the NRs starts to decrease. The negative effect of the silver ions in higher concentration is probably due to their interaction with the bromide counterion of the surfactant monomers, which will be discussed later. A similar effect on the growth of NRs is seen for gold ions, which is shown in Figure 3b. Our
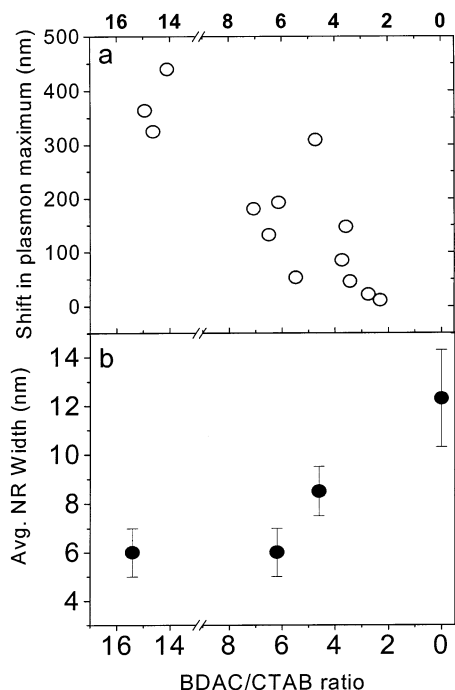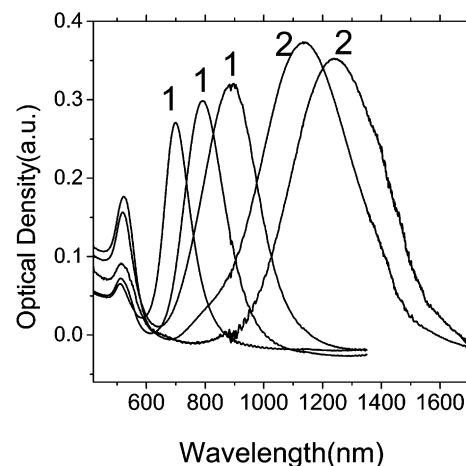
Figure 4. Effect of aging on growth solutions with different ratios of surfactant mixture. (a) Open circles show the shift in plasmon band maximum of the sample after 7−14 days of aging. It can be seen that as the CTAB fraction decreases the elongation of NRs increases. (b) There is a decrease in the average width of the NRs as the contribution of the BDAC increases. The width declines to 6±1 nm upon using BDAC/CTAB ratios of 6 or higher.

Figure 5. Visible NIR absorption spectra of the gold NRs prepared using single- and two-component surfactant mixtures shown by labels 1 and 2, respectively.

Figure 6. TEM images of gold NRs with plasmon band energies at (a) 700, (b) 760, (c) 790, (d) 880, (e) 1130, and (f) 1250 nm. The scale bar is 50 nm.
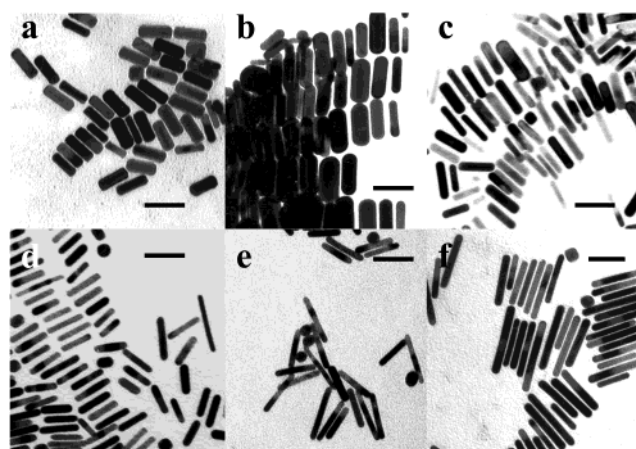
results show that in a single-component surfactant solution, by optimizing the silver and gold ion concentrations, the plasmon band maximum of NRs can be extended to 850 nm. This plasmon wavelength corresponds to NRs with aspect ratios of 4.5.

To grow NRs with longer aspect ratios, a binary surfactant mixture was used in which the CTAB and BDAC were the minor and major components, respectively. By changing the ratio of BDAC/CTAB from 16 to 2, NRs with plasmon bands from 900 to 1300 nm can be made. We found that the growth process in the binary system is made of a fast growth component and a slow one. The fast component slows down about 1 h after the addition of the seed solution. At this stage, the NRs formed are found to have plasmon bands between 880 and 940 nm. The contribution of the second growth process becomes apparent after aging the sample for 1 week. With aging, the plasmon band shifts to wavelengths of about 1100−1300 nm depending on the amount of the CTAB in the growth solution. Figure 4a shows the redshift in the longitudinal plasmon band due to changing the CTAB concentration. For higher ratios of BDAC/CTAB, there are two disadvantages associated with the aging of the growth solutions: one is the low reproducibility in size of the NRs, and the second is the formation of large amounts of NSs. Results show that the width of the NRs changes by changing the surfactant ratio of BDAC/CTAB. Figure 4b shows that as the BDAC/CTAB ratio increases to 15, the NR width decreases to 6 nm.

The aging period is independent of the surfactant ratio and is about 7−10 days. This process stops after the second week, and longer aging periods (more than

a month) do not increase the length of the NRs. Considering the growth solution has excess amount of surfactants, the reason for stop in the second growth process is most likely due to depletion of the gold supply of the growth solution. To stop the growth of the NRs after reaching the desired size, they need to be separated from the growth solution by centrifugation. The visible spectra and TEM images for samples prepared using the approaches above are shown in Figures 5 and 6, respectively.

The above observations led to a second pathway for growing NRs. In this approach, growth solution B (Experimental Section) was added gradually to growth solution A after the first stage of the NR growth was completed. Our results show that gold concentrations less than or equal to 0.00025 M result in a larger redshift of the longitudinal plasmon band. Growth solutions with higher gold content result in redshift of the transverse plasmon band and eventually deterioration of the particles. By continuing the gradual addition of the growth solution, the length of the NRs can be increased to the desired length. Figure 7 is an illustration of the elongation of the NRs. The intensity of the first plasmon band shows that the change in the concentration of NSs is not significant, though they grow along with NRs. This can be seen from the shift in the

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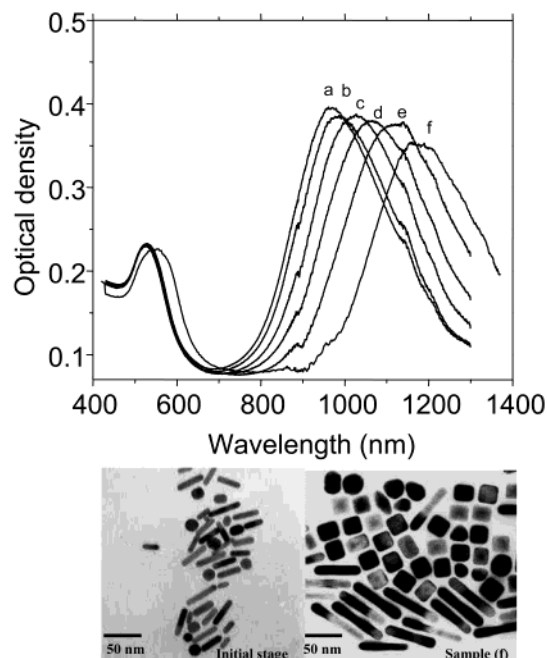
Figure 7. Growth of longer NRs by gradual addition of 15 mL of growth solution (B) containing 0.00025 M to 10 mL of a solution of shorter NRs with aspect ratio of 5. Redshift in the plasmon band is an indication of the increase in the average aspect ratio. Both NRs and NSs grow in dimensions.

band related to NSs. Figure 7 also shows the TEM images before and after growth of NRs. In NRs, the width increases from 6−7 nm to 10−12 nm and correspondingly the length increases as well. This approach can be used to grow NRs with aspect ratios of 7−10 or larger from shorter NRs. On the basis of the absorption intensity of NSs in Figure 6, it seems the number of spherical particles in the growth solution stays constant and only the size increases.

Discussion

There are at least two possible growth mechanisms. In one mechanism, the surfactants form a soft template in which the template has a certain size dependent on the surfactant concentration and the ionic strength of the solution. By introducing the seed to the growth solution, the surfactant-capped seed becomes part of the soft template and growth starts by diffusing the gold atoms into the template. The other possible mechanism is that the surfactant-capped seed starts growing and as the new atoms join the nanocrystal lattice, they are protected by the surfactant monomers coming from the solution.

An increase in the aspect ratio of NRs by increasing the gold atom content of the growth solution shows that NRs grow longer if the gold supply is greater. However, further increase in the concentration of the gold ions results in the decrease in the length of the NRs as can be seen in Figure 3b. The Au ions and the surfactant form a dark yellow complex (Au−Br−surfactant), which, by further increase in the gold concentration, precipitates. This interaction could result in a change in the size, charge density, and reactivity of the CTAB head-group toward gold surface. The effect of ion concentration (and ionic strength) on the size of the surfactants assembly has been the subject of several studies.[18,19]

To further study the gold ion effect, 1 mL of 0.005 M HAuCl$_4$ and 5 mL of 0.001M CTAB were added to two growth solutions so that the final concentrations of the gold and the surfactant remained equal in both solutions. The results show NRs with plasmon bands at 600 nm in the former and 800 nm in the latter, even though both solutions had similar gold content. As stated above, at high concentrations of gold ions, the decrease in the size of NRs may be due to the formation of new species of Au−X complexes (X: halogen), which do not have the same efficiency in producing gold NRs as the AuCl$_4$ anion. Figure 1 shows that NRs grow to a certain size, and only after this size is reached, the plasmon intensity increases. This could be an indication of a preformed soft template with a certain size distribution in the solution. Alternatively, it could be due to the homogeneous growth of the seed particles to rod-shaped particles, which is terminated upon depletion of the gold atom supply of the solution.

In explaining the role of silver in the growth process, Figure 3a shows that the silver ions could first increase and then decrease the length of the NRs, similar to what was observed for gold ions. The decrease in the size at the high concentration of silver ions could be due to the ionic strength effect, which was observed for gold ions. However, the cause of the increase in the NR size by increasing the number of silver ions still remains unanswered.

Silver is known to have a catalytic effect on the growth of gold film in electroless metal plating of the surfaces. For instance, in deposition of gold atoms in cylindrical pores of Al$_2$O$_3$ membrane,[20] silver ions are deposited on the walls of the cylinders and are reduced by exposing the whole membrane to Sn^{2+} ions. This reduces the silver ions attached to the walls to silver atoms (scattered islands inside the pore). Introducing the membrane to a solution of gold ions results in the galvanic displacement of silver atoms by gold atoms (reduction of gold ions). This results in the formation of metallic gold on the wall. These islands behave as nucleation sites for further growth of gold atoms inside the pores. The further reduction of gold by a mild reducing agent causes further growth and deposition of the gold atoms, and eventually filling out of the entire pore. This could form gold rods or gold tubes (depending on the initial gold content).

The above mechanism cannot be operative in the growth of NRs using a surfactant template, because the added silver ions are not reduced to atomic silver. The growth solution contains a mixture of silver and gold ions, and by addition of ascorbic acid as reducing agent only gold ions are reduced. Only in a basic pH, could ascorbic acid reduce the silver ion.[1,21] Jana et al.[16] have reported that NRs made in the absence of silver ions convert to NSs and suggested that the silver ions are adsorbed at the gold nanoparticle surface in the form of AgBr and restrict the growth and stabilize the NR surface.

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The TEM images show that the size of the seed particles is less than 4 nm, whereas the diameter of NRs is about 7−12 nm. The high-resolution images show that NRs have four {110} facets, but these facets are absent in gold NSs.[22] The surfactant binds to the {110} facet more strongly than to other facets.[23] The stronger affinity of this surfactant was also observed in multiply twined NRs,[24,25] which had a crystalline structure different from that of the single-crystal NRs prepared in our approach. A given seed needs to grow in the x and y directions to reach the observed NR width and length (assuming the long axis of the NR is the "z" axis). The results show that the structure and concentration of the surfactant monomers affect the width of the NRs. Figure 4b shows that in the binary system of BDAC/CTAB, the average NR width decreases from 12 to 6 nm upon changing the headgroup structure.

It seems the growth of a NR takes place simultaneously in all directions. Growth in the longitudinal direction takes place parallel to the {001} planes, which is accompanied by formation of four relatively unstable {110} facets and 4 {111} facets. Once the seed grows to a critical size, the facets become large enough for significant surfactant binding. The growth rate of different facets in the presence of the surfactant determines the final shape of the nanoparticle. The slower growth in the NR width is an example of better protection of {110} facets by CTAB. The fate of the growth and the final size of the NRs depend on the gold supply and the surfactant concentration. Because the surfactant is much higher in concentration, this process continues until the gold supply depletes. The idea of surfactant-assisted growth is also in agreement with what was concluded in the studies on growth mechanism of multiply twined NRs,[24,25] and is not consistent with the presence of a soft template in solution.

The question that remains unanswered is why the length of the NR increases by increasing the Ag^+ concentration. If the silver ion has catalytic activity and induces the rod shape, then the length should not be improved and only the number of NRs would increase. The silver ion could assist the template elongation with its ability to induce monolayer formation.[26] The monolayer formation was observed for 2-substituted benzimidazoles at the air/water interface. This effect has been attributed to the role of silver ions as a complexing agent between the monomers. In the case of CTAB assemblies, the Ag ions between the headgroups of the capping material could be considered as Ag−Br pairs. This combination may decrease the charge density on the bromide ions, and therefore result in less repulsion between the neighboring headgroups on the gold sur-face. Results of the surface-enhanced Raman scattering of the CTAB on the gold surface[11] show a low-frequency vibration at 174 cm^{-1}. Because Au−Br and Ag−Br have very similar vibrational frequencies, it is difficult to clearly assign this peak to a specific vibration, but it could be an overlap of both vibrations, which means the presence of both Ag−Br and Au−Br species at the surface of the gold NRs.

The elongation of NRs upon aging was observed only in the binary surfactant mixture of BDAC and CTAB. In a binary surfactant mixture, gradual addition of the growth solution to a NR solution also results in elongation of the NRs. This observation shows that the surfactant mixture is a more flexible template than the single-component system. Again, in the gradual growth of NRs, growth continues in all directions, however, it is faster in the longitudinal direction (Figure 7). Addition of growth solutions with larger gold content results in NRs with inflated ends, which appears to be due to the rush of gold atoms to join the ends of the nanocrystal.

The elongation effect of the silver ion was not observed in the case of pure BDAC or large ratios of BDAC/CTAB mixture. Indeed, using a growth solution containing BDAC, only NSs are formed and silver ions do not show any effect on elongation. This is an indication that CTAB monomers are required for growth of NRs and that these monomers are more influenced by the silver ions. This could be attributed to the fact that the chloride counterion has smaller size and polarizability than the bromide ion, thus a weaker bonding is expected in Ag−Cl relative to that in Ag−Br.

Because of the larger affinity of CTAB to the {110} facet, it is reasonable to assume there are larger numbers of CTAB monomers on these facets relative to BDAC. In addition, the fact that the largest redshift in the NR plasmon band was observed in the solutions with largest ratios of BDAC/CTAB suggests of having NRs with less protected ends. This is reminiscent of having more BDAC monomers at the ends of NRs.

Observations such as the dependence of the width of the NR on the ratio of the surfactant mixture, the elongation effect of silver on NRs in a single-component system, the absence of the silver effect on BDAC, and the elongation of NRs by aging or addition of gold atoms in the binary surfactant mixture are among the evidences that support the presence of some factors constraining the growth of the NR width. The selected types of surfactants provide a limited and slow growth in the x and y directions and faster growth in the z direction. Because elongation coincides with the formation of {110} facets, Ag ions most likely assist binding and packing of the CTAB monomers on these facets, which ultimately result in the slow growth of the NR width.

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