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Seed-Mediated Synthesis of High Aspect Ratio Gold Nanorods with Nitric Acid

Hsiang-Yang Wu, Hsin-Cheng Chu, Tz-Jun Kuo, Chi-Liang Kuo, and Michael H. Huang*

Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan

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We report a new approach for the seed-mediated synthesis of gold nanorods with high aspect ratios by the addition of nitric acid. Various amounts of nitric acid were added during nanorod growth to significantly enhance the production of high aspect ratio nanorods. The resulting nanorods have uniform diameters of 19−20 nm and can reach lengths of 400−500 nm to yield nanorods with average aspect ratios of 21−23. The nanorods represent a large fraction of the gold nanostructures synthesized, with triangular, truncated triangular, and hexagonal nanoplates about 120−200 nm in width making up rest of the gold nanostructures formed. These nanorods spontaneously self-assemble into a high-density three-dimensional packing structure with the nanorods arranged side-by-side and end-to-end. These nanorods possess a 5-fold twinned structure with ten {111} end faces and five {100} side faces. UV−vis absorption spectrum shows a transverse plasmon absorption band at 508 nm. The longitudinal plasmon absorption band should appear beyond 2500 nm due to the extremely long length of these nanorods. The presence of nitrate ions, rather than the slight pH change caused by nitric acid, is believed to have a greater effect on the formation of these nanorods.

Introduction

Gold and silver nanorods are of great interest to study because of their shape-dependent optical properties and potentially wide ranges of applications.[1−9] A wide variety of molecules can also be attached to these nanorods for various applications including chemical analysis and biological assays as have been demonstrated for spherical gold nanoparticles.[10−12] Recently, interesting superstructures formed by the end-to-end linkages of gold nanorods into chainlike structures via covalent bonding and hydrogen bonding have been reported.[13−15] Strategies for the side-by-side self-assembly of gold nanorods have also been examined.[16,17] Metal nanorods with high aspect ratios may also find applications in the fabrication of nanoscale devices if they can be properly positioned on substrates. Although several different approaches such as electrochemical,[2] photochemical,[4,5] and seed-mediated methods[3] have been used to grow gold nanorods, only the seed-mediated synthesis approach developed by Murphy et al. has produced nanorods with aspect ratios above 20.[18−21] In one report, it was suggested that addition of NaOH to increase the solution pH during the seed-mediated growth of gold nanorods is critical to the formation of nanorods with aspect ratios greater than 20.[18] However, this procedure is accompanied by increased polydispersity. Several other reports on the preparation of gold nanorods with lower aspect ratios (that is, 1.5−10) have shown that addition of a trace amount of $AgNO_3$ can increase the length of nanorods formed, but high aspect ratio gold nanorods have not been produced.[3−6,22] Good methods for the preparation of ultrahigh aspect ratio gold nanorods is very desirable because many research ideas can be tested and the applications of gold nanostructures can be greatly extended.

Here seed-mediated synthesis of gold nanorods with high aspect ratios and monodisperse size distribution by the addition of nitric acid is presented. The amount of nitric acid

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* To whom correspondence should be addressed. E-mail: hyhuang@mx.nthu.edu.tw.

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used was varied with the aim to prepare nanorods with the highest aspect ratio possible. The crystal structure was analyzed, and UV−vis absorption spectra were taken to characterize these nanorods. The effects of acid and nitrate ions were investigated to determine which species promotes the growth of these nanorods.

Experimental Section

The procedure for making high aspect ratio gold nanorods is based on the work of Murphy et al. with some modifications.[18,20,21]

Preparation of Gold Seeds. A volume of 0.2 mL of 0.025 M sodium citrate solution was added to 19.8 mL of aqueous solution containing 2.5×10^{-4} M $HAuCl_4$ and stirred for 3 min. Concurrently, 10 mL of 0.01 M $NaBH_4$ solution was prepared by adding $NaBH_4$ to 10 mL of ice-cold 0.025 M sodium citrate solution. When 0.6 mL of the $NaBH_4$ solution was added to the $HAuCl_4$ solution, the resulting solution immediately turned orange-red, indicating the formation of gold particles. The particle size was approximately 2.5 nm.[23]

Preparation of Growth Solution. A volume of 100 mL of 2.5×10^{-4} M $HAuCl_4$ aqueous solution was prepared. Then 1×10^{-2} mol of cetyltrimethylammonium bromide (CTAB) surfactant was added to the solution with stirring until the CTAB powder was completely dissolved. This solution was used as the growth solution.

Synthesis of High Aspect Ratio Gold Nanorods. Two 25-mL and one 100-mL conical flasks were labeled A, B, and C. In flasks A and B, 25 μL of 0.1 M ascorbic acid was added to 4.5 mL of growth solution. In flask C, 250 μL of 0.1 M ascorbic acid and 100−400 μL of nitric acid were added to 45 mL of growth solution. Next, 400 μL of the gold seed solution was added to the solution in flask A and stirred slightly for 3 s. Then 400 μL of the solution in flask A was immediately added to flask B and stirred for 5 s. Finally, 4 mL of the solution in flask B was transferred to flask C and stirred for 5 s. Flask C was left undisturbed for 12 h for the reaction to go to completion. The solution contained mostly spherical nanoparticles and was removed, leaving only high aspect ratio nanorods and some triangular nanoplates settled to the bottom of the flask as a precipitate. Then 10 mL of deionized water was added to redisperse the precipitate, and the solution color was brown. The nanorods can be concentrated by centrifugation at 2000 rpm for 20 min (Hermle Z323 centrifuge).

Instrumentation. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6330F scanning electron microscope. A drop of the nanorod sample was added to a silicon substrate and dried for SEM images. Transmission electron microscopy (TEM) characterization was performed on a JEOL 2000FX electron microscope operating at 200 kV. UV−vis absorption spectra were taken using a JASCO V-570 spectrophotometer. To obtain absorption spectra of the nanorods in the near-infrared (near-IR) region, the concentrated nanorod precipitate after centrifugation was transferred to a microscope cover glass and dried. The cover glass was mounted on a sample holder for measurements with a background subtraction.

Results and Discussion

The seed-mediated synthesis approach has been successfully used to prepare high aspect ratio gold nanorods and branched gold nanocrystals.[24] In the present study, spherical gold nanoparticles were used as seeds to grow into nanorod shape by a fast and successive addition of growth solutions containing more gold source, CTAB surfactant, and ascorbic acid as a weak reducing agent. Long nanorods were eventually formed by allowing the nanorods sufficient time to grow. This method for the synthesis of high aspect ratio gold nanorods was developed by Murphy et al. and is adopted in the present study.[18,20,21] As shown in Figure 1a, long gold nanorods with lengths around 400 nm were synthesized without adding any nitric acid. However, the yield was low, and many triangular and hexagonal nanoplates and spherical nanoparticles were produced. This sample was prepared the same way as the other nitric acid-added samples by waiting 12 h before collecting and resuspending the precipitate for direct comparison.

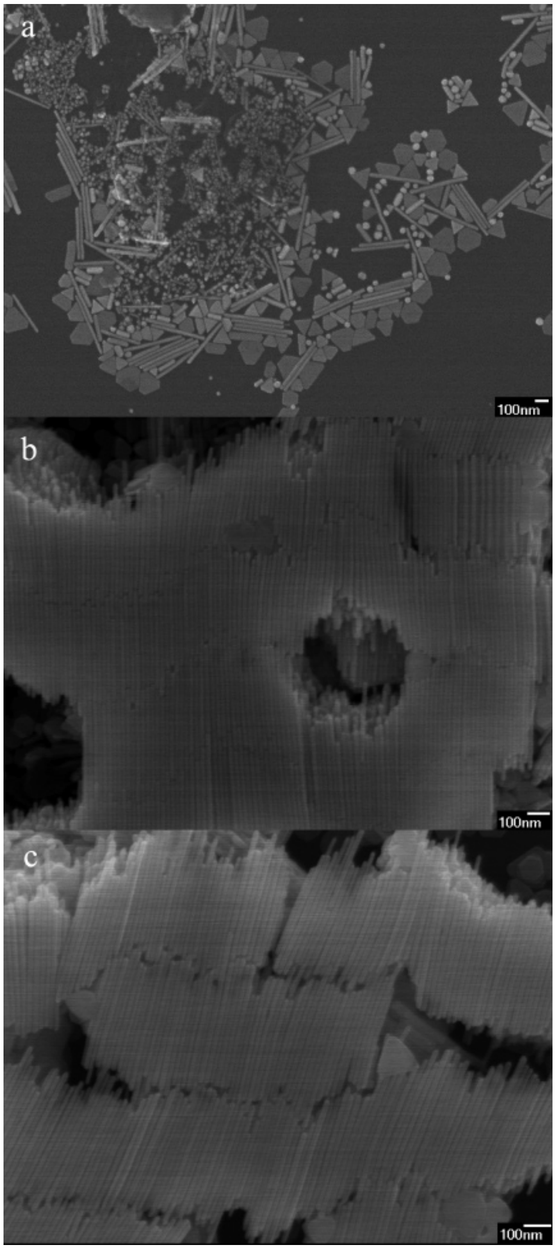

Figure 1. (a) SEM image of a mixture of gold nanorods, nanoplates, and spherical nanoparticles produced without the addition of nitric acid during the growth process. (b) SEM image of high aspect ratio gold nanorods synthesized with the addition of 200 and (c) 400 μL of nitric acid.

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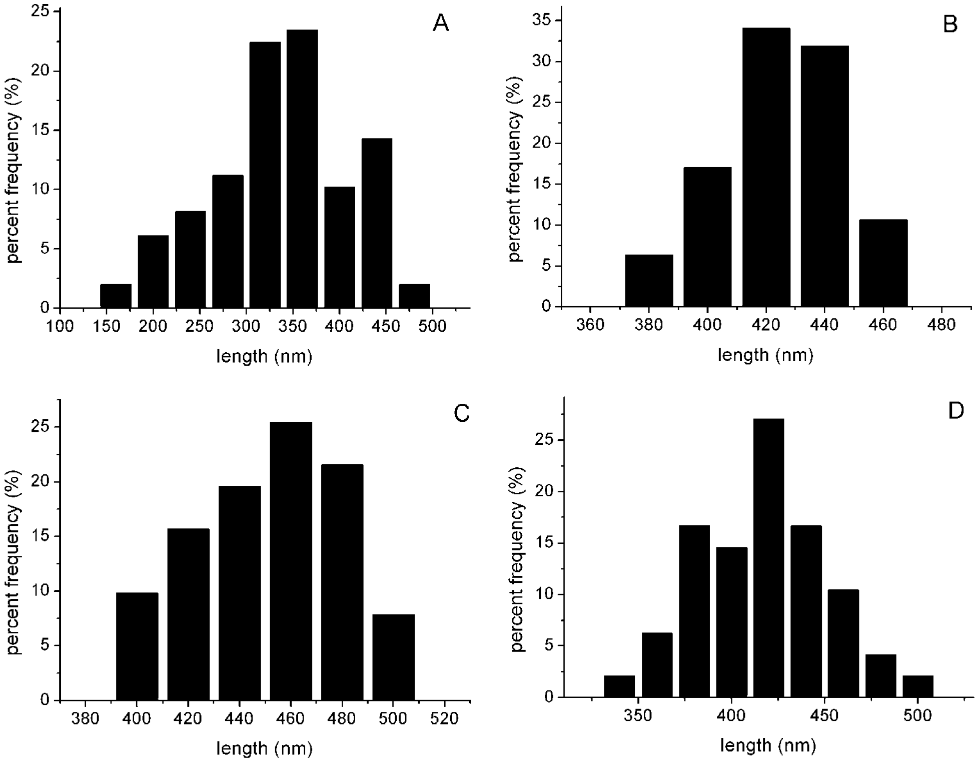

Figure 2. Length distribution histograms of the gold nanorods prepared with the addition of (a) 100, (b) 200, (c) 300, and (d) 400 μL of nitric acid.

To improve the yield of gold nanorods, we discovered that the addition of nitric acid during nanorod growth can significantly increase the amount of gold nanorods formed. Figure 1b shows a SEM image of the sample obtained by adding 200 μL of nitric acid in flask C. A large quantity of rods was produced. These nanorods are straight and very uniform in dimensions with an average length of 424 ± 20 nm and an average diameter of 19.4 nm (70 nanorods were counted for the determination of nanorod diameter), giving them an average aspect ratio of ~22. Upon evaporation of water, these nanorods spontaneously self-assembled into a high-density three-dimensional packing order with the nanorods aligned side-by-side and end-to-end. Nanorods consist of a large fraction of the gold nanostructures observed (without counting the spherical nanoparticles left in the solution that have to be removed), with triangular, truncated triangular, and hexagonal nanoplates (~120−200 nm in width) accounting for the majority of other gold nanostructures formed. Few spherical nanoparticles were observed. Figure 1c gives a SEM image of gold nanorods prepared by adding 400 μL of nitric acid in flask C. Similar high-density arrangement of long nanorods was observed. These nanorods also appear to be straight and uniform in dimension with an average length of 410 ± 33 nm and an average diameter of 19.6 nm (75 nanorods were counted for the nanorod diameter), giving them an average aspect ratio of ~21. Figure 2 shows the histograms of lengths of nanorods prepared by adding 100−400 μL of nitric acid in flask C. Except a wider size distribution observed for nanorods formed by adding just 100 μL of nitric acid (with an average length of 330 ± 72 nm), nanorods synthesized with the addition of 200−400 μL of nitric acid exhibited narrow distributions of lengths. In particular, nanorods prepared with the addition of 300 μL of nitric acid showed the longest average length of 453 ± 29 nm, giving these nanorods an average aspect ratio of ~23. Some nanorods with aspect ratios greater than 25 have been found in the sample. Addition of more nitric acid (that is, greater than 400 μL) generated shorter nanorods.

Figure 3 shows a TEM image of some representative gold nanorods with aspect ratios of 20−22 to reveal detailed structural information. The nanorods exhibit twin boundaries along their long axes and contain faceted ends. The nanorods grow along the [110] direction, as determined by the selected-area electron diffraction (SAED) pattern taken over a single nanorod (see inset of Figure 3). Consistent with the findings of Mann and Murphy, our gold nanorods appear to be penta-tetrahedral in shape with the rods bounded by five {100} side faces and ten {111} end faces.[25] Interestingly, this surface structure is somewhat different from two other reports on gold nanorod structure characterization in which growth of nanorod along the [100] direction with side faces bounded by {110} faces have been determined.[26,27] A high-magnification TEM image of the end face region of a nanorod is also shown in Figure 3. Lattice fringes parallel to the long axis of the nanorod can be discerned with *d*-spacings of 2.35 Å corresponding to the (111) lattice planes, a result consistent with a previous report.[25]

The optical property of these high aspect ratio gold nanorods was characterized by UV−vis absorption spectroscopy. Figure 4 shows the UV−vis absorption spectra of gold nanorods prepared with the addition of 300 μL of nitric acid. Gold nanorods typically exhibit a transverse surface plasmon resonance (SPR) absorption band at around 510−

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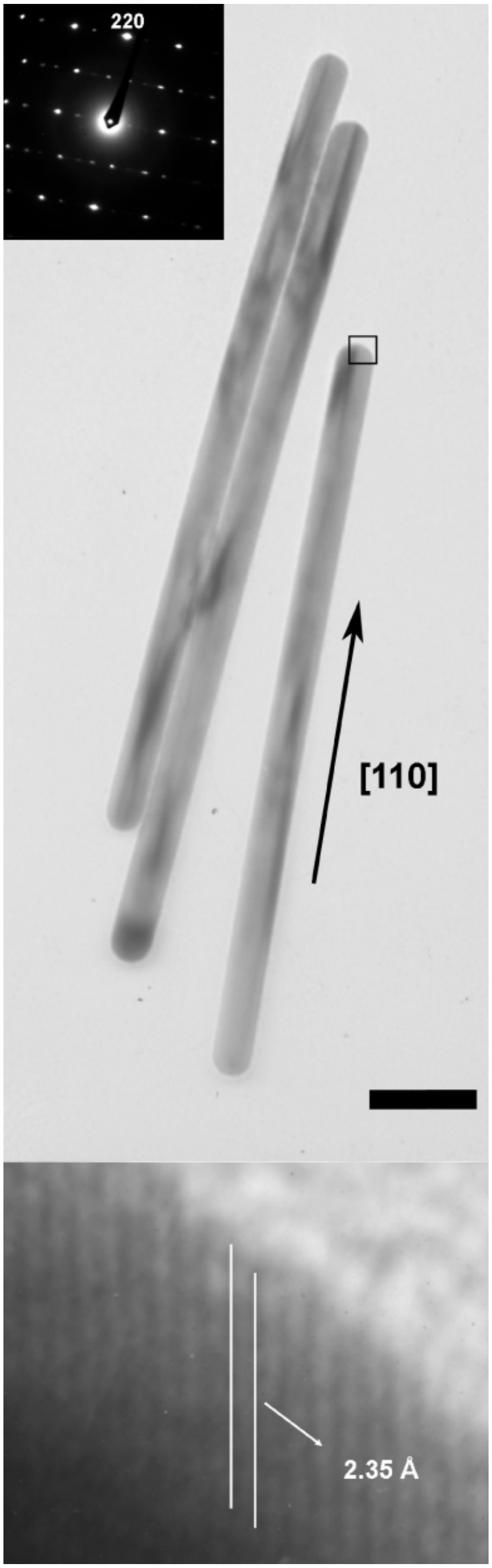

Figure 3. (Top) TEM image of some representative high aspect ratio gold nanorods. Scale bar = 50 nm. Inset shows the SAED pattern of a single gold nanorod. (Bottom) High-resolution TEM image of one end of a nanorod. The square area in the top figure indicates the region of the nanorod the image was taken, although a different nanorod was imaged. Lattice fringes from the (111) planes are observed. The lattice fringes are aligned parallel to the direction of the long axis of the gold nanorod.

520 nm and a longitudinal SPR band that is red-shifted to the near-IR region when the nanorods have high aspect ratios.[2,10,20] To overcome the strong absorption interference from water, dried nanorod sample was used for the optical characterization in the near-IR region from 1300 to 2500 nm. The spectra show an absorption band at 508 nm which should correspond to the transverse SPR band of the nanorods. The progressively increasing absorption in the near-IR region is due to the longitudinal SPR absorption. The band maximum should appear beyond 2500 nm, out of the scanning range of the spectrophotometer used, due to the very high aspect ratios of the nanorods produced. This result is reasonable, as gold nanorods with aspect ratio of 13 have been shown to display a strong longitudinal SPR absorption band at 1700 nm.[28] It is also in agreement with a recent report using the discrete dipole approximation method for the determination of the position of the longitudinal SPR band of gold nanorods (that is, $\lambda_{\max} = 96\mathrm{AR} + 418$, where AR refers to aspect ratio).[29] With an average aspect ratio of 23, the predicted position of the longitudinal SPR band is at 2626 nm. No multiple absorption bands are present in the near-IR region of 1300−2500 nm, suggesting that the nanorods examined have high aspect ratios. The strong and broad absorption band centered at 920 nm and a shoulder band to its lower wavelength side are attributed to absorption by mainly triangular and truncated triangular nanoplates as they are the major byproducts formed.[30] Light absorption by these nanoplates is so strong because there are still many nanoplates present in the solution. Many nanoplates can be found underneath the stack of nanorods shown in Figure 1. The absorbance of the transverse SPR band for gold nanorods is very low compared with that of the longitudinal SPR band.[19b] On the other hand, gold nanoplates absorb light strongly. A direct determination of the relative amounts of long nanorods and nanoplates in the solution by an examination of their UV−vis absorption spectra (Figure 4a) may not be accurate. It is clearly more desirable to reduce the absorption from the nanoplates by removing these products from the long nanorods. Future efforts should address methods of separating high aspect ratio gold nanorods from other nanostructures or seek to improve the yield of nanorods for greater applications of these nanorods.

The effects of acid and nitrate ions on nanorod formation have been investigated to determine why nitric acid can promote the growth of high aspect ratio gold nanorods. The solution pH in flask C before the addition of nitric acid was 3.25. Addition of 300 μL of nitric acid only caused a slight change to pH 2.91. When HCl, H_2SO_4, or H_3PO_4 was added to flask C instead of HNO_3 (300 μL used in each case), shorter nanorods and more nanoplates and spherical nanoparticles were produced. These results suggest that nitric acid is superior to other acids in producing high aspect ratio gold nanorods, and the minor change in solution pH upon the addition of nitric acid may not be the major factor for the significant increase in the formation of long nanorods. The ability to prepare long nanorods at this low pH is contrary to a previous report in which the addition of NaOH to raise

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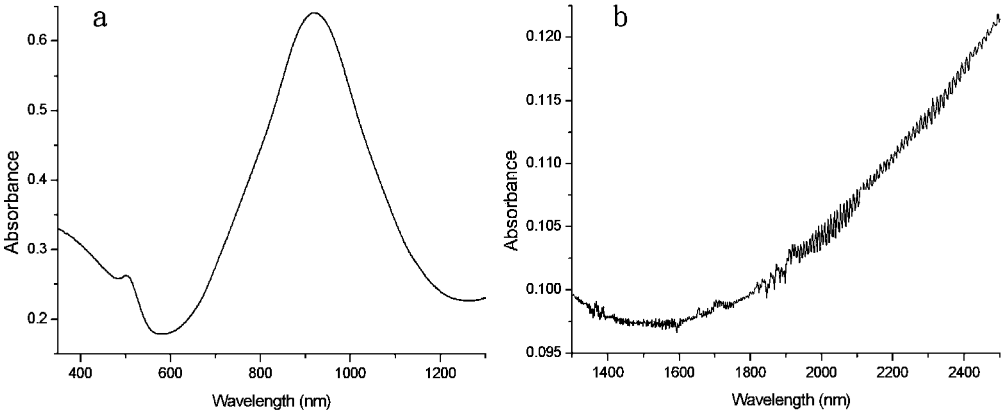

Figure 4. (a and b) UV−vis absorption spectra of the gold nanorods made with the addition of 300 μL of nitric acid. Absorbance value in panel b cannot be directly compared with that in panel a. This is because panel a is the absorption spectrum of nanorods in solution using 1 cm × 1 cm cuvette; in panel b nanorods were placed on a microscope cover glass. There is no absorption band at 1300 nm.

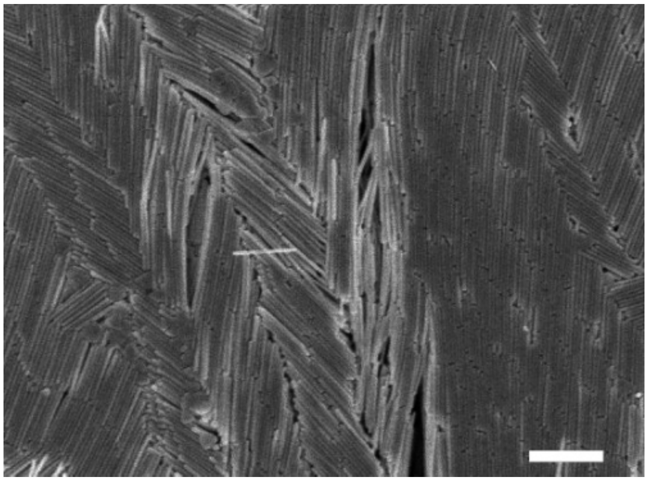

Figure 5. SEM image of gold nanorods prepared with the addition of 300 μL of sodium nitrate in flask C. Scale bar = 500 nm.

the solution pH from 2.8 to 3.5−5.6 and increase the fraction of ascorbate was considered critical for preparing gold nanorods with aspect ratios of 20−25.[18]

Since a slight change in solution pH is likely not the reason for the pronounced increase in the production of long nanorods, the presence of nitrate ions on nanorod formation was examined. Figure 5 shows a SEM image of gold nanorods prepared with the addition of 300 μL of sodium nitrate. Similar high-density packing arrangement of long gold nanorods to those observed with the addition of 200−400 μL of nitric acid was revealed. The nanorods also appear to be straight and uniform in dimensions with lengths of mostly 350−400 nm, giving them high aspect ratios of ∼18−21. The results suggest that nitrate ions play a key role in the growth of nanorods to exceptionally long lengths. It is still not clear why nitrate ions can significantly increase the amount of high aspect ratio gold nanorods synthesized, but sulfate and phosphate ions are not as effective even though they have similar structures. The molar ratios of nitrate to gold salt are 0.82, 1.63, 2.45, and 3.27 for the solutions in flask C with addition of 100, 200, 300, and 400 μL of nitric acid, respectively, so the concentrations of nitrate in all the solutions are very high. Several reports on gold nanorods have discussed the role of silver ions in promoting the formation of gold nanorods by adding a trace amount of $AgNO_3$ to the reaction mixture.[3−6,22] However, the effect of the accompanying nitrate ions was not studied. El-Sayed et al. have shown that by increasing the concentration of $AgNO_3$ in the reaction medium, the average aspect ratio of gold nanorods first increases and then decreases.[3] This result is similar to our observation in this work in which the average aspect ratio of the nanorods increases to a maximum of 23 with the addition of 300 μL of nitric acid and then decreases with further addition beyond 400 μL. This direct relationship is interesting and points to the possibility of nitrate ions as a key factor in regulating the growth of both low and high aspect ratio gold nanorods. Of course, the possibility of the hindrance of nanoplate formation with the addition of nitric acid also needs to be considered, as nanorod yield can be enhanced by reducing the production of nanoplates. Further work is necessary to clarify the mechanism by which nitrate ions assist the formation of high aspect ratio gold nanorods.

Conclusion

A new synthetic approach for the preparation of high aspect ratio gold nanorods by a seed-mediated growth mechanism with the addition of various amounts of nitric acid is presented. The nanorods generally have very uniform dimensions with an average diameter of around 19−20 nm and aspect ratios of 20 to over 25. They spontaneously self-assemble into a high-density packing order with side-by-side and end-to-end alignments. The nanorods possess pentatwinned structure with surfaces bounded by {111} end faces and {100} side faces. These nanorods show a transverse SPR band at 508 nm; the longitudinal SPR band is expected to appear beyond 2500 nm due to their extremely long lengths. It was found that nitrate ions, rather than the slight pH change produced with the introduction of acid, exert a greater influence on the formation of these high aspect ratio nanorods. This simple synthetic method should open up more opportunities for the demonstration of unique physical properties of gold nanorods, preparation of hierarchical structures constructed from these long nanorods, and applications in nanoelectronics and molecular sensing.

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