Fine-Tuning the Shape of Gold Nanorods

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Received March 8, 2005. Revised Manuscript Received May 10, 2005

Gold nanorods prepared by a seed-mediated growth approach use ∼4-nm gold nanospheres as the seeds and subsequent reduction of metal salt with a weak reducing agent (ascorbic acid) in the presence of a directing surfactant to produce nanorods. If insufficient ascorbic acid is added in the growth step, then metal salt remains. Additional input of ascorbic acid preferentially deposits more metal at the ends of the nanorods, to yield "dogbone"-like structures. Surprisingly, heat treatment of the unpurified gold nanorods (prepared with an insufficient amount of ascorbic acid) yielded fatter gold nanorods; the oxidation product of ascorbic acid appears to act as a reductant at higher temperature. These modified shapes of the gold nanorods directly influence their optical properties.

Introduction

One-dimensional gold nanostructures have received great attention due to their size-dependent optical properties,[1−5] their use as building blocks to form other nanostructures,[6−10] and biological applications such as gene delivery.[11] Several synthetic methods exist for preparing metallic nanorods, such as electrochemical deposition in hard templates[12] and at step edges,[13] electrochemical synthesis in solution,[1,14] photochemical synthesis,[15,16] microwave heating,[17−19] and the previous work of our group, a seed-mediated growth approach.[20−22] On the basis of this procedure, we can prepare gold nanorods, albeit in modest yield, with aspect ratios up to 25.[23] Recently, this method was modified whereby the introduction of silver ion produced shorter gold nanorods with controllable aspect ratio 2−5 in near-quantitative yield.[24,25]

However, the shape of metallic nanoparticles can also be modified after their preparation. It is known that femtosecond pulsed laser irradiation of gold nanorods can induce a rod-to-sphere shape transition, where a ϕ-shape particle (pointed ends, with a quasi-spherical middle) may form during the process.[14,26] The photoinduced conversion of silver nanospheres to prisms has been reported.[27] The optical, catalytic, and electronic properties of metallic nanostructures depend greatly on their size and shape, even for seemingly minor changes in shape.[28] In this work we demonstrate that by reducing additional gold ions in the presence of gold nanorods, we can modify the shape of gold nanorods in a controllable manner.

Experimental Section

Materials and Instruments. Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$, 99.99%) was purchased from Alfa Aesar. Ethanol (100%) was obtained from AAPER Alcohol and Chemical Co. Cetyltrimethylammonium bromide (CTAB, 99%) was obtained from Sigma. All other reagents were from Aldrich and were used as received. Ultrapure deionized water (Continental Water Systems) was used throughout the experiments. Transmission electron

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10.1021/cm050525w CCC: $30.25

microscopy (TEM) was performed with a Hitachi 8000 transmission electron microscope on carbon-coated copper grids at 200 kV. To prepare TEM grids, the samples were first purified by centrifugation at 10000 rpm for 15 min, twice, to remove excess surfactant. Precipitates were collected and redispersed in a small amount of DI water, and 1.2 μL of the suspension was deposited onto the copper grid and allowed to air-dry. UV−vis spectroscopy was performed on a Cary 500 Scan UV−vis−NIR spectrophotometer.

Synthesis of Gold Nanorods. Gold nanorods were prepared by a seed-mediated growth method[24] with slight modifications. Specifically, 9.5 mL of 0.1 M CTAB (cetyltrimethylammonium bromide) was mixed with various amounts (20, 40, 60, 80, and 100 μL) of 0.01 M silver nitrate aqueous solution, 0.5 mL of 0.01 M $HAuCl_4$ trihydrate (aq), and 55 μL of 0.10 M ascorbic acid (aq), respectively, with continuous stirring. An amount of 12 μL of the seed solution was finally injected into the mixture to initiate the growth of gold nanorods. The seed solution was prepared according to previous reports.[24] Since the aspect ratio (AR) of gold nanorods can be controlled by simply varying the amount of silver ion present in the solution, our experiments yielded five different gold nanorod samples with AR 2.2, 2.8, 3.9, 4.6, and 5.4 (samples A to E) for the silver nitrate amounts of 20−100 μL. These nanorod samples were aged for 24 h in air to ensure full formation of gold nanorods. A key feature of the gold nanorods prepared by this approach is that the ratio of ascorbic acid concentration to $HAuCl_4$ concentration is about 1:1, instead of the 1.5:1 necessary to reduce all the metal salt. Therefore, unreduced gold ions are still present in the solution.

Reduction of Gold Ions with Additional Ascorbic Acid To Yield “Dogbones”. From each aged sample from above, 1.0 mL of nanorod solution (unpurified, in the presence of the original reaction mixture) was transferred into a 1.5-mL Eppendorf tube. To each solution, 3−30 μL of a 0.10 M aqueous solution of ascorbic acid was added at room temperature. The samples were left undisturbed for 30 min. UV−vis spectroscopy was performed on each sample before and after the addition of ascorbic acid. Transmission electron microscopy was used to record the shape modification of gold nanorods.

Heat-Assisted Shape Changes of Gold Nanorods. Alternatively, we found that, even without introducing any additional reductant, the gold ions can be reduced by heating in the presence of the original reaction mixture. Specifically, 1.0 mL quantities of the unpurified gold nanorod solutions of various ARs were heated at 100 °C for different time intervals, from 5 to 60 min. Samples were subsequently removed from the heating stage and cooled to room temperature in air. UV−vis spectroscopy and TEM were performed on each sample before and after heating.

Results and Discussion

Unreduced Gold Ions Still Exist in Gold Nanorod Solutions. The stoichiometry of the reagents in the growth part of the synthesis is such that the amount of ascorbic acid (AA) is not enough to reduce all the gold salt in the solution. Theoretically, each ascorbic acid molecule loses two electrons upon oxidation,[29] and in order to reduce Au(III), three electrons are needed per gold ion. Therefore, the AA-to-gold salt ratio should be at least 3:2 to reduce the gold salt completely. Here, the AA-to-gold salt ratio is only ~1:1; thus, gold ions should be present even after the nanorod formation.

To quantitatively determine the presence of unreduced gold ions in solution, we separated the gold nanorods from solution by high-speed centrifugation (14000 rpm for 30 min). The nanorods precipitated as a pellet at the bottom of the centrifuge tubes. An amount of 30 μL of 0.1 M ascorbic acid was added into the colorless supernatant at room temperature, and the solution turned to purple-red in 10 min, indicating the formation of gold nanoparticles. The UV spectra and TEM images further confirmed this result (data not shown). The nanorods were digested with aqua regia to produce Au(III); the Au(III) was redox-titrated with iodide, using a standard starch−iodine test to quantitate ultimately the original amount of Au(III).[30] In a separate experiment, the supernatant from the gold nanorod solution was similarly titrated with iodide to quantitate the amount of gold ion. We found that ~60% of the original gold salt ended up in the gold nanorods, and ~40% was left over in solution, consistent with the initial gold salt/ascorbic acid stoichiometry.

Adding on to the Ends of Gold Nanorods: “Dogbones”. When the unpurified gold nanorod solutions were treated with ascorbic acid, the color of the solution changed from brownish to purple-red. After the samples were centrifuged and characterized under TEM, we found the original rodlike particles were now dogbone structures, having fatter ends and thinner middle sections. A typical TEM image is shown in Figure 1. The average length and width of these dogbones were ~75 ± 5 nm and 20 ± 3 nm, respectively, which are both larger than the original nanorods (57 ± 3 nm and 10.7 ± 0.5 nm, respectively), suggesting that the gold nanorods functioned as seeds and the subsequently reduced gold atoms were deposited onto them preferentially on the ends. The UV−vis specta (Figure 2) revealed that the plasmon bands of the dogbone structures were similar in the position but far broader in peak width than the original nanorods. However, if the same amount of ascorbic acid was added to the purified gold nanorod solutions (centrifuged and resuspended in DI water), there was no color or structural change. Therefore, purified rods are stable; only in the presence of additional metal salt and reducing agent does the reaction take place.

Heating-Assisted Reduction of Gold Ions. Our studies indicate that all nanorod samples (again, where nanorods were in solution with unreduced gold ions) changed color with heating, as shown in Figure 3. It is noteworthy that lower-aspect-ratio (AR) nanorods show optical changes faster than higher-AR nanorods. Since the color of each sample was stabilized after heating at 100 °C for 30 min, we took the TEM images at that point and found that their AR decreased (Table 1). Figure 4 shows the TEM images of nanoparticles of AR 2.2 and AR 5.4 before and after 30 min of heating, which clearly indicates that the length of nanorods does not change substantially, whereas the width increases significantly.

The kinetics of these shape changes were also monitored by UV−vis spectroscopy. For example, sample E contains

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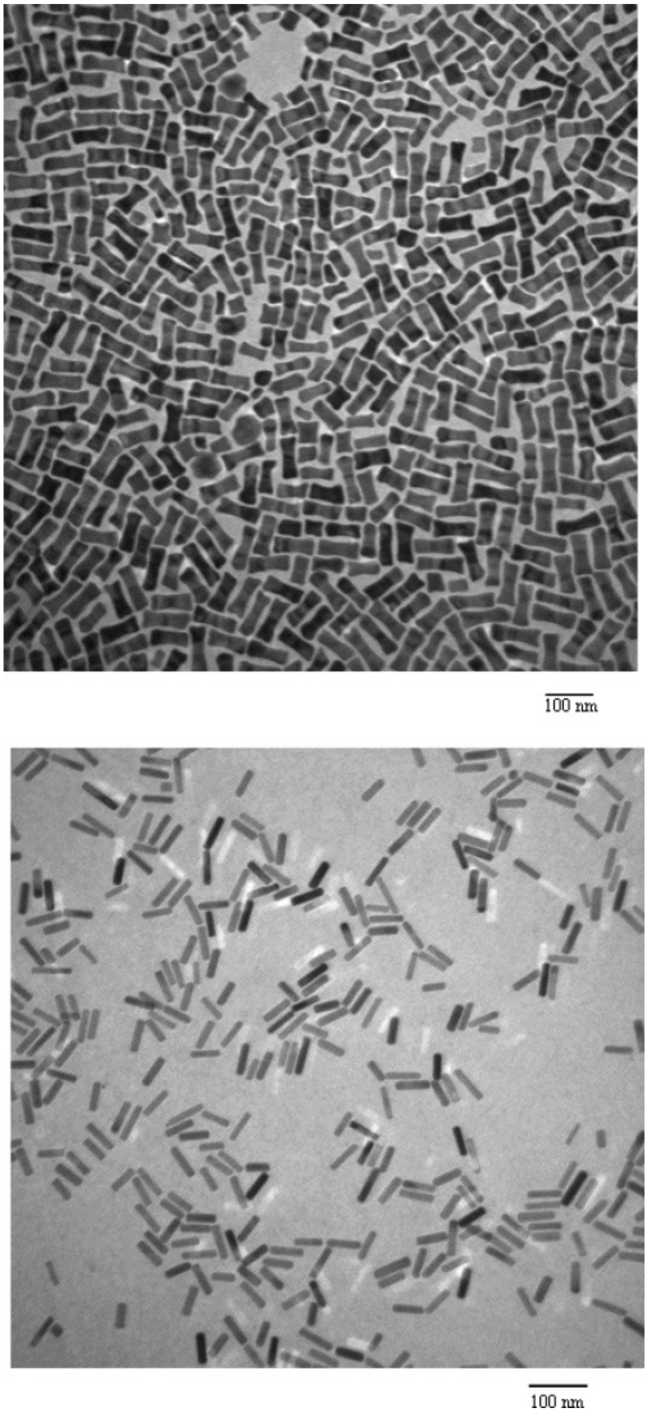

Figure 1. (top) Transmission electron micrograph of the dogbone-shaped nanoparticles formed by adding ascorbic acid into the gold nanorod reaction mixture, for sample D (Table 1). Scale bar is 100 nm. (bottom) Transmission electron micrograph of the original gold nanorods in Sample D (Table 1). Scale bar = 100 nm.

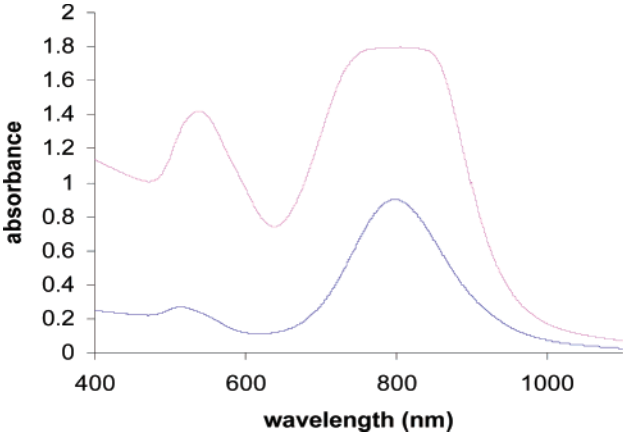

Figure 2. UV−vis spectra of “dogbones” (top, pink) compared to the original gold nanorod solution (bottom, blue) before the addition of ascorbic acid (sample D in Table 1).

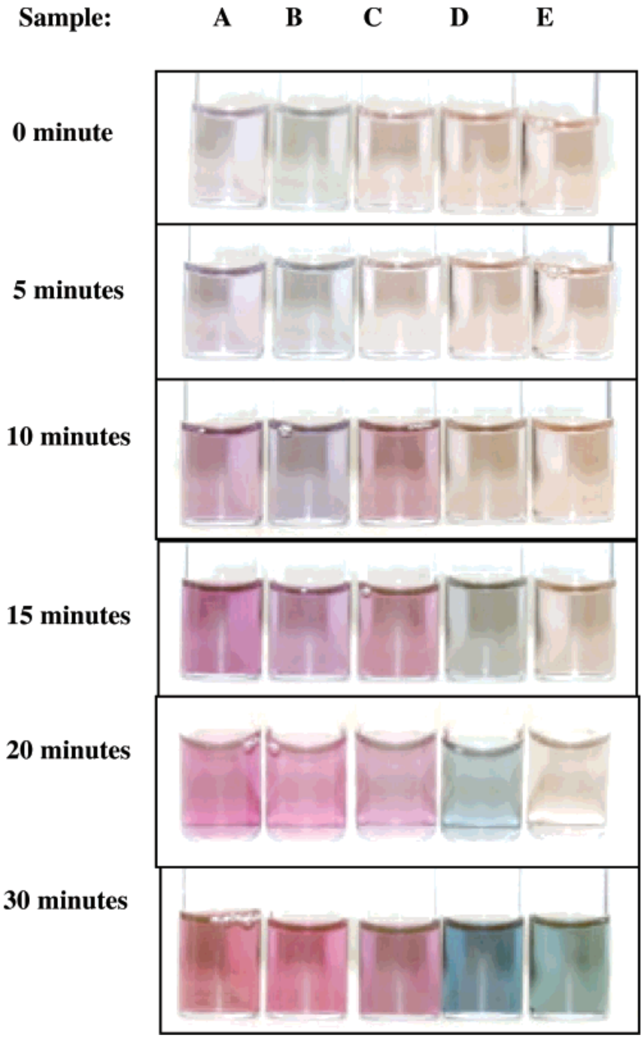

Figure 3. Photograph of gold nanorod solutions with different AR values when heated to 100 °C at various times. Samples are labeled according to Table 1.

gold nanorods with AR 5.4. These nanorods have two different plasmon bands: the transverse band at ∼520 nm and the longitudinal band at ∼840 nm. During the thermal treatment, the longitudinal peak blue-shifted with an increase in the heating time, while the transverse peak red-shifted slightly. The longitudinal peak could be eliminated with prolonged heating at 100 °C. Figure 5 shows the UV−vis spectra of nanorods with AR 5.4 during thermal treatment. Blue-shifts of longitudinal plasmon peak correspond to a decrease of the aspect ratio, in accordance with previous reports.[24,25] For fixed heating times and at various heating temperatures from 60 to 100 °C, similar results were found (Figure 6). Again, if gold nanorods are purified from the reaction mixture, no such shape changes by the same heating process are observed.

Proposed Mechanisms of Fine-Tuning Nanorod Shape. We propose that the addition of additional ascorbic acid to

Table 1. Dimensions and Aspect Ratios of Gold Nanorods before and after Heating at 100 °C for 30 min, As Measured by TEM

sample	initial length (nm)	final length (nm)	initial width (nm)	final width (nm)	initial AR	final AR
A	48 ± 5	47 ± 5	22 ± 5	47 ± 5.0	2.2	1
B	50.9 ± 5	45.4 ± 5	18 ± 0.5	21.6 ± 0.5	2.8	2.1
C	57.6 ± 3	58.5 ± 3	14.8 ± 0.5	19.6 ± 0.5	3.9	3
D	54.8 ± 3	55.5 ± 3	11.9 ± 0.5	16.7 ± 0.5	4.6	3.3
E	57.3 ± 3	54.4 ± 3	10.7 ± 0.5	16.5 ± 0.5	5.4	3.3

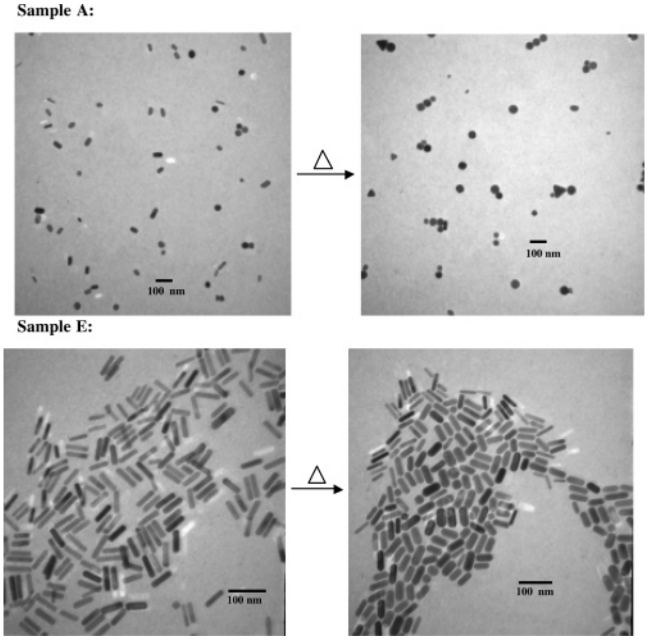

Figure 4. TEM images of AR 2.2 (A) and AR 5.4 (E) before and after 30 min of heating at 100 °C.

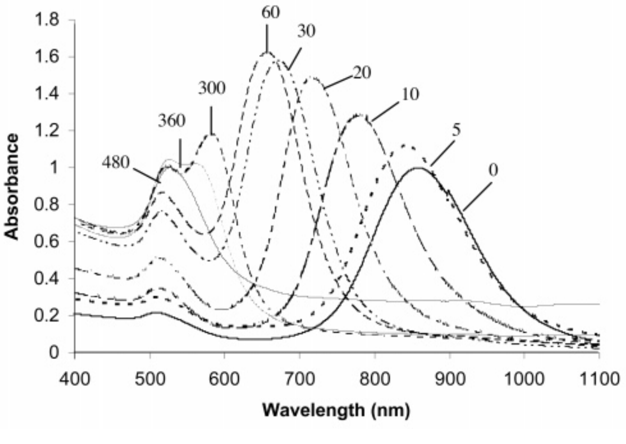

Figure 5. UV−vis spectra of gold nanorods, AR 5.4 (sample E in Table 1), heated to 100 °C for 0, 5, 10, 20, 30, 60, 300, 360, and 480 min.

the unpurified gold nanorod solution causes the reduction of the leftover gold ions. The gold nanorods that are present in solution serve as seeds in the reduction. The surfactant, CTAB, plays a crucial role here. Previous studies suggest that CTAB forms a bilayer on the nanorod surface; more importantly, different sections of the gold nanorod surface may have a different affinity with CTAB.[31,32] Specifically, the assembly of CTAB bilayers along the long gold nanorod faces is preferred, compared to the ends.[23,31] Therefore, the addition of ascorbic acid causes the reduction of the gold salt at the more accessible ends with some preference, leading to the dogbone structures.

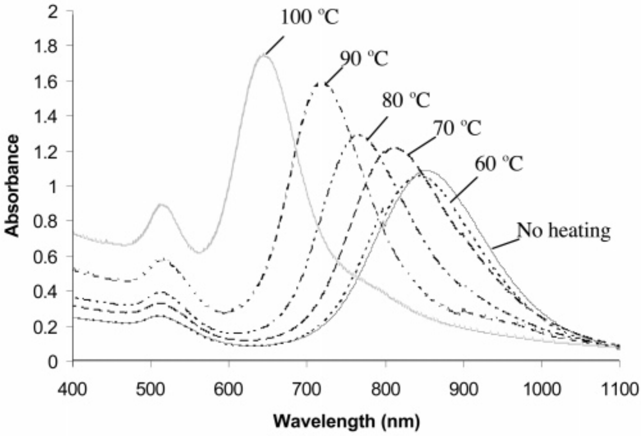

Figure 6. UV−vis spectra of gold nanorods (sample E) heated for 30 min at various temperatures.

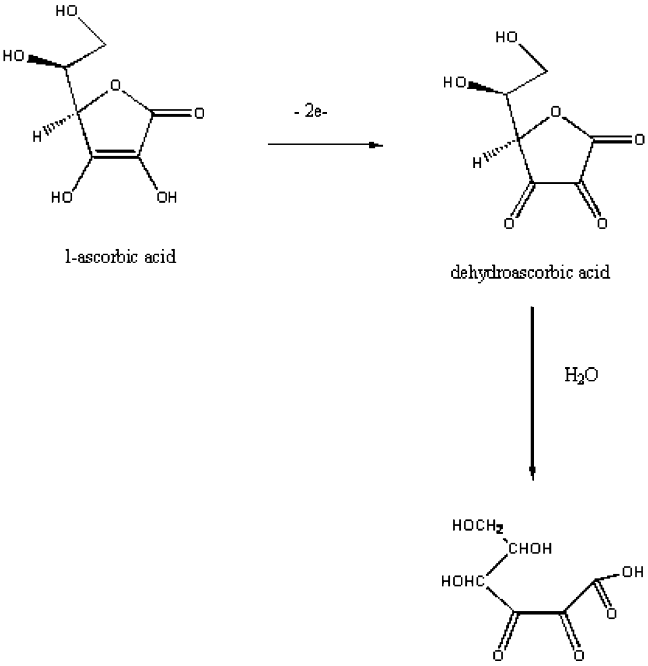

Figure 7. Chemical structures of the oxidation product of ascorbic acid (DHA) and its subsequent hydrolysis product (DGA).

The heating-induced shape changes were initially disturbing and implied that our gold nanorods were unstable, contrary to previous studies.[22] However, we hypothesized that the two-electron oxidized form of ascorbic acid, dehydroascorbic acid (DHA), upon heating, may reduce gold ions due to the presence of OH groups. DHA is quite unstable and is easily converted to 2,3-diketo-1-gulonic acid (DGA) with hydrolysis of the lactone ring[29] (Figure 7). Since both DHA and DGA have alcohol groups, which are known to have mild reducing abilities,[19,33] they might be able to reduce the rest of the gold ions upon heating. In a control experiment, we mixed 50 μL of 0.01 M DHA solution, 50 μL of 0.01 M $HAuCl_4$, and 12 μL of seeds in 0.9 mL of 0.1 M CTAB solution and heated the entire mixture at 100 °C.

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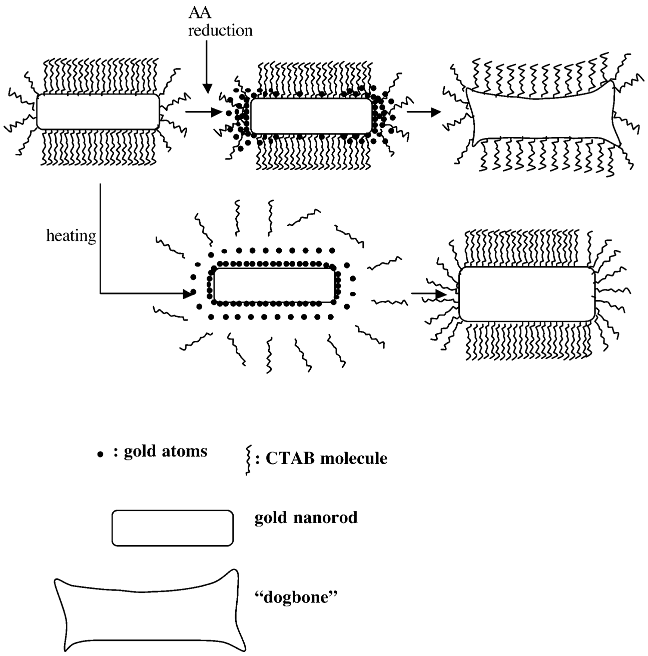
Scheme 1. Cartoon of the Proposed Mechanisms That Lead to Dogbone Structures from Gold Nanorods upon Additional Reduction of Gold Ions by Ascorbic Acid (top) and That Lead to Lower-Aspect Ratio Gold Nanorods upon Heating, in the Presence of Gold Ions



The bright-yellow mixture turned colorless and then purple-red within 10 min, which suggests that DHA does have the ability to reduce gold ions at higher temperatures. During the heating process, the CTAB bilayers are likely destabilized and no longer pack on the nanorod long-axis surface; therefore, reduction of gold salt by DHA or DGA occurs randomly all over the rods, and because there are more deposition sites on the sides, the rod width increases much more than their length increases. Therefore, CTAB played different roles in the two different fine-tuning strategies: in the case of additional AA reduction, the CTAB blocks the middle of the rods from reaction, while in the heating process, it dissociates and makes the deposition more homogeneous (Scheme 1).

The crystallography of both the short-nanorod starting material and the dogbone structures, as well as the heating-induced shape changes, needs to be examined carefully to derive a more complete mechanism of crystal growth than those proposed here. Such studies are in progress.

Conclusion

In conclusion, we demonstrate that gold nanorods prepared by the seed-mediated growth method, which still contain unreduced gold ions, can be used as substrates to fine-tune the structure and therefore the optical properties of gold nanorods. Also, our experiments indicate that the oxidized form of ascorbic acid is still able to reduce gold ions above room temperature. The structure-directing surfactant CTAB assists in the fine-tuning of the shape: for CTAB bound preferentially to the middle of the nanorods, deposition of more gold occurs preferentially at the ends, whereas if the CTAB bilayer is presumably removed upon heating, deposition of more gold occurs more uniformly over the nanorod surface to dial down the aspect ratio.

Acknowledgment. We thank USC and the National Science Foundation for funding.

CM050525W