Body- or Tip-Controlled Reactivity of Gold Nanorods and Their Conversion to Particles through Other Anisotropic Structures

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We report the shape transformation of gold nanorods to spherical nanoparticles, assisted by cupric ions. The reaction proceeds through a series of structures and could be arrested at any stage to produce particles of desired shape. In the presence of a larger concentration of cetyltrimethylammonium bromide (CTAB), selective etching of the tips of the nanorods occurs to a greater extent. The subsequent transformation is driven by the surface reconstruction of nanorods to generate more stable surfaces. As the stability of various surfaces depends on the protecting agent used, the reactivity is modified by controlling its presence at the surface. We show that the body of the rods is more susceptible for reaction at reduced CTAB concentrations. During the conversion to particles, several anisotropic transient structures were observed and were imaged using high-resolution transmission electron microscopy (HRTEM). The transformation occurs due to the hydroxyl radicals produced by Cu^{2+} in the presence of ascorbic acid (AA). A mechanism has been proposed and several control experiments were conducted to test it. The cupric ion induced shape transformations can be extended to other ions, and knowing the mechanism allows the control of the process to stabilize various anisotropic structures.

Introduction

Metals and semiconductors on the nanoscale exhibit properties that can be tailored by varying parameters such as size, shape, and dielectric constant, to mention a few.1 Photophysical properties of metal nanoparticles in the visible and near-infrared region can be varied by tuning their size, shape, aggregation state, and environment.² Controlling the size and shape of nanoparticles has been a challenge, and usually the size manipulations are done during the synthesis itself. Therefore, recent research is directed toward developing newer synthetic routes to achieve highly monodisperse structures.³ Several groups have used colloidal self-assemblies as templates for controlling the size and shape of nanocrystals.⁴ In these synthetic protocols, a variety of factors such as ionic concentration and temperature need to be controlled during the synthesis to ensure monodispersity. The surface structure of the nanoparticle is a critical property that determines the reactivity of the particles. However, this is difficult to study with spherical nanoparticles, because of their structural isotropy. Spherical metal nanoparticle surfaces are primarily composed of either {111} or {100}. Usually {110}

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facets will be absent owing to their inherent instability compared to the other two low index planes.⁵

Gold nanorods are versatile systems for diverse processes.⁶ The absorption spectrum of gold nanorods has two characteristic maxima.⁶ The first one, called the transverse surface plasmon resonance (TSP), is located around 520 nm. The TSP shifts to shorter wavelengths with increasing nanorod aspect ratio. The other maximum, known as the longitudinal surface plasmon (LSP) resonance, appears at a longer wavelength. This band exhibits a red-shift with increase in aspect ratio. Various aspects such as the chemistry,⁷ one- and two-dimensional assemblies as well as self-assembly on substrates,⁸ photothermal properties and electron dynamics,⁹ catalysis,¹⁰ and biological applications¹¹ of these systems have been investigated. For any specific application,

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size and shape control is vital. Significant research efforts have been made to evolve strategies for synthesizing nanorods of desired aspect ratio.⁶ An alternate strategy has been used to resize a given ensemble of nanorods, obtained from established procedures, using external stimuli such as thermal/laser heating¹² and chemical methods.¹³

Gold nanorods are different from their spherical counterparts, since their surface is considerably different. In a typical rod sample, the rod axis will be oriented along the [001] direction and the side faces are composed of $\{110\}$. The tips will be mainly composed of $\{111\}$ and $\{100\}$ facets.^{14d} It is understood that the presence of cetyltrimethylammonium bromide (CTAB), which is used as the capping agent, is responsible for the presence of {110} facets on the nanorod surface. Due to the larger interatomic distance in the {110} facet compared to other low index planes of gold, the bonding between surface gold atoms on the $\{110\}$ facet will be weaker compared to those on $\{111\}$ or $\{100\}$. This facilitates each atom on the $\{110\}$ facet to form stronger bonds with adsorbed or bonded atoms. So the {110} surface is preferentially stabilized by CTAB and this is the principal reason for the existence of this on the nanorod. The reconstructions happen where there is a disruption in the CTAB bilayer capping.

There exist subtle differences in surface energies of different planes of a nanocrystal that are related to the stability and hence reactivity of these surfaces. This gives a handle to manipulate and control reactions to occur preferentially on specific surfaces, leading to resizing and reshaping of the particles. Due to the higher surface energy of the {110} facet, it is prone to reconstructions. Reconstructions can be brought about by the addition of external stimuli also.

Recently, Stucky et al.^{13b} reported a method for the selective shortening of nanorods by oxidation. Selective oxidation happens, resulting in the shortening, as observed in the simultaneous decrease in the intensities of LSP and TSP. Laser irradiation^{12b} can be used for manipulating the aspect ratio of nanorods by melting. But the experimental setup requires sophistication. Thermal reshaping^{12a} of nanorods is another method for postsynthesis manipulation. But for the complete conversion of rods to particles, a comparatively higher temperature (~160 °C) is required. At 100 °C, the shift observed in the LSP was 60 nm and no reaction was observed further, even after prolonged heating.^{12b} Therefore, in-order to obtain different aspect ratio nanorods, different temperatures are required.

In this paper, we report a simple reaction between Au nanorods and cupric ions that induces surface reconstructions and results in a near-quantitative resizing of nanorods. The increase in the intensity of TSP occurs concomitantly with the decrease in LSP,

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indicating that the reshaping of rods to form spherical particles occurs in a more effective manner. The reaction can be stopped at any stage, resulting in a solution containing nanorods with desired aspect ratio. The reaction, if extended, results in spherical particles. With a careful control over the reaction conditions, it is possible to obtain a multitude of structures varying from truncated rods to fused multibranched structures. All these structures can be stabilized simply by cooling the reaction vessel to room temperature and separating the particles by centrifuging. The in-between structures were imaged using high-resolution transmission electron microscopy (HRTEM). The temperature of the reaction medium and concentration of the reagents were found to be critical factors that determine the shape of the nanoparticles formed. We have isolated the truncated rods and shown clearly that the reaction starts from the tips of a nanorod on specific surfaces in the presence of excess CTAB. The reaction deviates from this path when CTAB is not present in the purified rods, where the reaction happens on the rod body also. This emphasizes the fact that there is preferential reaction in the presence and absence of CTAB. We believe that the truncated rods, with corrugated edges, may show better surface enhanced Raman enhancement compared to the pristine rods. The experimental setup is simple and the reaction parameters are readily tunable. It is possible to obtain differently sized rods from a single starting material by stopping the reaction at different time intervals, but in our case, the range of sizes achievable is restricted by the aspect ratio of the starting material. The mechanism of this process has been established by a series of control experiments. The metal ion induced shape transformation can be expanded to other ions, opening up a prospect for future research.

Experimental Details

(i) Synthesis of Gold Nanorods. Au nanorods were synthesized by the seed-mediated method reported by Sau and Murphy.^{6f} Briefly, the method uses nanoparticle seeds of 4 nm diameter produced by NaBH₄ reduction of HAuCl₄. Subsequently, slow reduction of Au³⁺ ions was carried out using ascorbic acid (AA), in the presence of CTAB and Ag⁺, resulting in the formation of nanorods having an aspect ratio of 3.44 (with 11 nm diameter). In a typical synthesis, the LSP and TSP appeared at 730 and 518 nm, respectively. The LSP position varied depending on the synthesis. Transmission electron microscopy (TEM) was used to examine the quality of the sample. Optimization of the synthetic procedure yielded high-quality samples, and most of the frames in TEM showed only rods with uniform size. However, spherical particles were seen occasionally. Various experiments were conducted with this material, referred to as R_1 (4 × 10⁻⁵ M gold), which contained excess CTAB, AA, and ions present in the reaction medium. Experiments were also done with a sample without these impurities. To make this sample, R1 was stored at 4 °C until most of the excess CTAB in the solution settled down. It was filtered and again kept in the refrigerator for 24 h. The solution was filtered and centrifuged at 11 100 rpm for 15 min. The residue was taken and redispersed in triply distilled water. This process ensured effective removal of ionic impurities and excess CTAB and AA in the rod solution. We refer to this sample as R₂. The concentration of gold in this solution is less than 4×10^{-5} M, as there was some loss of gold during centrifugation.

(ii) Reaction between R_1 and CuCl₂. In a typical reaction, R_1 (4 mL, 4 × 10⁻⁵ M gold) was treated with 2 mL of 1 mM CuCl₂ in water. Six identical reactions were started simultaneously, and the test tubes were immersed in a water bath maintained at 70 °C. Every 1 h, a test tube was taken out from the water bath and the UV–vis spectrum was recorded with 4 mL of the reaction mixture using a Perkin-Elmer Lambda 25 UV–visible spectrophotometer. A small aliquot of the reaction mixture was dropped on a carbon-coated copper grid and dried in ambience. This was observed under

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a JEOL 3011, 300 kV TEM with a UHR polepiece. This was repeated every hour with different test tubes, and the reaction was found to be complete after 5 h. The reaction was stopped at various time intervals by cooling down the mixture to room temperature, and we found that the nanoparticles formed were stable.

(iii) Reaction between R_1 and $CuCl_2$ in Argon Atmosphere. The reaction was repeated in argon atmosphere and followed spectrophotometrically.

(iv) Reaction between R_1 and $CuCl_2$ in the Presence of Na_2SO_3 . The reaction was conducted as described in ii, except that the mixture contained 1 mL of 1 mM Na_2SO_3 in addition so that the total volume was 7 mL.

(v) Reaction between R_2 and CuCl₂ Solution. The purified nanorods were subjected to reaction as in (ii).

(vi) Reaction between R_2 and CuCl₂ with External Addition of CTAB. In six clean test tubes, 4 mL of R_2 ($^{4} \times 10^{-5}$ M gold), 2 mL of 1 mM CuCl₂, and 0.5 mL of 100 mM CTAB were taken. They were immersed in a water bath kept at 70 °C. After every hour, a test tube was withdrawn from the bath and UV–vis spectrum was analyzed. This was repeated for 6 h. After this, 0.1 mL of 100 mM solution of AA was added into the reaction mixture, heating was continued for 1 h, and UV–vis spectrum was taken.

(vii) Reaction between R_2 and CuCl₂ with External Addition of AA. The reactions were conducted as described in v, except that the mixture contained 1 mL of 100 mM AA in addition and the total volume was 7 mL.

Various other control experiments were conducted as described in Results and Discussion

Results and Discussion

Figure 1A shows TEM images of the starting nanorod sample. The nanorods, to begin with, were highly uniform. Figure 1B shows an expanded image of one of the nanorods showing the well-structured tip and body. The rod body was also devoid of any reconstruction. Figure 1C is an enlarged HRTEM image of a pristine nanorod body. Note that even the surface atoms at the edge could be imaged very well (see the dotted line).

Figure 2 shows the UV-vis spectra of the reaction between Au nanorod and CuCl₂, acquired every 1 h of the reaction (A–F). As we know, the LSP shifts linearly with the aspect ratio⁶ of the nanorod. The LSP blue-shifts and decreases in intensity with the progress of the reaction, while the TSP red-shifts slightly and increases in intensity. After 3 h of the reaction, the LSP becomes a hump and finally disappears completely at about 4 h of the reaction, suggesting the transformation of nanorods into nanospheres. The red-shift of the plasmon resonance from 518 to 531 nm indicates that the particles formed have a larger diameter than the parent nanorods.

Careful observation of the TEM images in Figure 2 shows that the reaction starts from the tip of the rods, giving rise to truncated structures. We can observe a gradual decrease in the length of the rod during the course of the reaction. Representative large area images are shown in the Supporting Information, indicating that images in Figure 2 are representative of the sample (S1). The transformation is believed to be facilitated by reconstructions. Different planes of a crystal have different surface energies.⁵ Depending on this, they have different stabilities and hence reactivity. For gold, the surface energies of the low index planes, $\{111\}, \{100\}, \text{ and } \{110\}, \text{ are } 0.58, 0.66, \text{ and } 0.70 \text{ J m}^{-2},$ respectively.⁵ On this basis, it is considered that $\{111\}$ is the most stable surface, and hence least reactive, and {110} is highly energetic and the most susceptible to reconstructions. So the rod body, which is mainly composed of {110} surfaces, is expected to reconstruct or react, but in the case of R_1 , we found that the reactions begin from the tips of the nanorods. This is due to the presence of excess CTAB, which stabilizes the {110} surface preferentially. As the reaction proceeds to form particles, more

{111} facets are formed, the structure stabilizes, and spherical particles are formed. TEM images shown in Figure 2 represent the changes in the course of the reaction; several other truncated shapes were also observed in a large area image. The color of the solution changed gradually during the course of the reaction. This reflects the changes in the aspect ratio of the rods. The photographs in Figure 2 show the color changes during the reaction. The transformation makes all the rods convert to particles ultimately and there is a uniform particle size distribution seen over a large area (Figure 2G). The particles formed were found to be single crystalline (see the inset of Figure 2F). Figure 2H is a plot of the aspect ratio as a function of reaction time. Aspect ratio of each sample was calculated from nearly 55 nanorods taken from different parts of the grid. The mean deviation is also given in the plot. We found that there is no reaction at room temperature (Supporting Information, S2) and reaction stops as soon as the reaction mixture is taken out of the water bath and cooled to room temperature. This way the reaction can be arrested at any given time to get the rods of desired aspect ratio. There was no further change in the rod geometry for weeks once the reaction was arrested.

Figure 3A is a lattice-resolved HRTEM of an unreacted pristine nanorod showing well-defined edges and the tip. Figure 3B is an image taken at an intermediate stage of the transformation showing the deformed tip of a gold nanorod, indicated by an arrow in the figure. The corrugations on the sides indicate the reaction sites were the CTAB micelle is absent or the capping is defective. Several depressions, which are the reconstructed planes, are seen and are marked with white lines in Figure 3B. We found that, to a lesser extent, the rod body is also getting etched. Figure 3C,D shows the etching in detail. It appears that the reconstructions may have started at the rod tip and extend to the rod body. Etching of the body leads to larger surface reconstructions. This is clearly visible in Figure 3C. The driving force of any lattice reconstruction is to lower the surface energy and attain more stability. The reconstruction of {110} to more stable {111} through the missing raw model in pure nanorods was reported by Wang et al.^{14d} It was reported that the shape transformations start from the $\{110\}$ surface^{14d} of the nanocrystal and by lattice reconstruction, it resulted in more stable {100} or {111} surfaces.¹⁴ When the reconstructions are induced externally by a reagent, and triggered by etching, their effect can be quite large and can lead to shape changes. This will continue until a stable structure is attained.

In order to investigate the kinetics of this transformation, we did several experiments where the concentration of the reacting species and temperature were varied. Figure 4 shows a plot of the LSP position as a function of the reaction time for two different reaction temperatures. Data corresponding to two different concentrations of CuCl₂ at the same temperature are also shown (the corresponding spectra are presented in Supporting Information, S3 and S4). The effect of these parameters on the rate is reflected in the slopes. From the plot, we can understand that the reaction does not follow a simple rate law and it probably involves more than one step. Temperature was found to be a crucial factor governing the transformation. The rate decreases with decrease in temperature and was found to stop at room temperature. The transformation was found to be dependent on the initial concentration of CuCl₂. Note that the experiment with reduced $CuCl_2$ concentration (data in S4) was done with a different nanorod sample with a slightly larger aspect ratio (as a result, the LSP occurs at a higher wavelength). Reactions occur in all the sizes investigated.





Figure 1. TEM images of the starting nanorod sample. (A) Lowmagnification image showing the high degree of monodispersity of the sample, (B) lattice-resolved image of a single nanorod showing well-defined tip, and (C) expanded image of the body of a nanorod showing that it is well-structured.

Figure 2. UV-visible spectra acquired every 1 h of reaction between gold nanorods and CuCl₂. R₁ (4 mL, 4×10^{-5} M) was treated with 2 mL of CuCl₂ (1 mM) and incubated at 70 °C: (A) 0 h, (B) 1 h, (C) 2 h, (D) 3 h, (E) 4 h, and (F) 5 h. Corresponding HRTEM images and photographs of the reaction mixture in the cuvette are given as insets. All scale bars in the TEM images (A-F) correspond to 5 nm. (G) TEM image of the sample after the reaction (5 h) showing monodisperse spherical particles over a large area. (H) Plot of the aspect ratio as a function of reaction time, with mean deviation.



Figure 3. HRTEM images of gold nanorod during the transformation. (A) An image of the unreacted rod with well-defined tip. The planes are indicated. (B and C) A rod during the reaction. Defects in the nanorod crystals along the $\{110\}$ surface due to the reaction are marked in B by a white line. Continued reaction leads to reconstructions shown in C. D is an enlarged view of the bottom portion of C indicated by the arrow.



Figure 4. The plot of LSP position against transformation time for R_1 : \blacksquare , 1 mM CuCl₂, 70 °C; \bullet , 1 mM CuCl₂, 60 °C; and \blacktriangle , 0.1 mM CuCl₂, 70 °C. \bullet - corresponds to a sample from a separate synthesis with a different LSP.

Various control experiments were conducted to know more about the nature of the reaction. To verify that this reaction is not due to the halide ions, 13d,14e and to know whether the reaction is specific to copper, we conducted the reaction with NiCl₂ and Cu(OOCCH₃)₂ under the same conditions. Figure 5A shows the UV-vis spectra measured during the reaction between R₁ and 1 mM NiCl₂. Even after prolonged heating for a period of 6 h, there was no transformation. In the case of cupric acetate, the nanorods underwent a similar transformation as in the case of CuCl₂ (Figure 5B), suggesting that the transformation is not due to chloride etching but due to some other pathway involving Cu²⁺ ion. To study whether oxygen is actively involved in the transformation, the same reaction was carried out in Ar atmosphere (Figure 5C). We saw that the rate of the reaction is lowered tremendously and only negligible reaction occurred. From this it was clear that oxygen is actively involved in the transformation. To further establish the involvement of oxygen in the transformation, we tried the reaction in presence of Na₂SO₃, which is a well-known oxygen scavenger.¹⁵ We found that in the presence of 1 mM solution of Na₂SO₃ the rate decreased (Figure 5D) and the reaction, which normally completed in 4 h in the absence of Na₂SO₃, took nearly 10 h for completion. This can be attributed to the reduced oxygen concentration available for the reaction. Increasing the concentration of Na₂SO₃ to 1 M quenched the reaction completely.

In order to understand the mechanism of the transformation, we performed the following experiments. The reaction was conducted with R2 and CuCl2 under identical conditions. Figure 6A shows the UV-vis spectra recorded. There was no significant change after 1 h of the reaction. From this we understood that some external agent, such as AA or CTAB, present in the as prepared nanorod solution, may be playing a key role in the transformation. Whatever minor blue-shift shown in the first hour of the reaction is due to traces of AA or CTAB left behind even after the purification. It is important to note that the changes in SP features never continued after the first hour, although the reaction mixture was examined for 6 h. In order to understand whether CTAB or AA is responsible for the transformation, we added these reagents externally into the purified rod solution, separately. Figure 6B is the UV-vis spectra obtained during the reaction in which CTAB was added externally to the reaction mixture containing R2 and CuCl2. Only negligible reaction

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Figure 5. UV–vis spectra of reaction between 4 mL of R_1 and 2 mL of 1 mM (A) NiCl₂, (B) Cu(OOCCH₃)₂, and (C) CuCl₂ in argon atmosphere. (D) CuCl₂ in the presence of 1 mM Na₂SO₃ in a total volume of 7 mL. All reactions were carried out at 70 °C and spectra were recorded every 1 h of the reaction till 6 h (for A–C). For D, the reaction was monitored till 10 h.

happened after the addition of CTAB, whereas the addition of AA to this mixture, which was done after 6 h of the reaction, produced a blue-shift immediately, indicated by the broken line trace. Therefore, it was concluded that CTAB was not involved in the transformation. The only possibility was a mechanism that involves Cu^{2+} and AA in the presence of oxygen. In order to explore this possibility, we did an experiment with R_2 and $CuCl_2$ with external addition of AA (Figure 6C). From the spectra, we see that as soon as AA was added to the reaction mixture, there was a change in the plasmon characteristics of the nanorods. Variations of the LSP position in the different conditions investigated are presented in Figure 6D.

Compared to R₁, the amount of AA present in the reaction mixture in the case of R2 (when AA was added externally) was in large excess. AA reduces Au(III) to Au(I) in the growth solution and Au(I) to Au(0) through surface electron transfer in the presence of seed.6d,6e The concentration of AA present in excess in R₁ is calculated to be 4.27×10^{-5} M in a total volume of 42.64 mL of rod solution (which is the total volume of rod solution in a synthesis, taking into account the added CTAB solution). In the case of reaction with R₂, the concentration was 1.43 \times 10^{-2} M in 7 mL, nearly 330 times of that present in R₁, so the reaction became faster. Since the excess CTAB was removed by repeated centrifuging and washing, there was no surfactant present in the reaction mixture to stabilize the resultant structure. Therefore, as the reaction of R_2 proceeds, a tendency for aggregation was shown by the mixture (Supporting Information S5). This can be observed when we examine the UV-vis spectra also (Figure 6C). The intensity decreases due to aggregation and resultant settling of the nanoparticles. Complete conversion to particles was not seen as a result of slow precipitation. Figure

6D reveals the role of oxygen and AA in the transformation process.

Figure 7 shows the TEM images taken from the sample (R_2) where AA was added externally. From these it is clear that the rod body is also getting reacted along with the rod tip, whereas in R_1 the rod tip is undergoing the transformation principally. It is well-known that CTAB micelles are not only confining the geometry of the Au nanorod growth but also stabilizing the unstable {110} facets on the nanorod surface.^{14d} In the case of the purified nanorod, most of the CTAB present in the rod solution is removed and only a thin layer remains on the rod surface. This layer of CTAB capping on the nanorod surface will most likely collapse at the elevated temperatures at which these reactions are carried out, making the unstable {110} facets more susceptible to reaction, so the reaction happens in the expected way, as suggested by the surface energy values. In the UV-vis spectrum of the reaction between R2 and CuCl2 with external addition of AA (Figure 6C), the important thing to be noted is that, even though there is a high degree of aggregation, in all the curves, both TSP and LSP are visible. This is because elongated particles are present throughout the reaction. The solution progressively developed a blue color due to aggregation.

It is clear that the transformation mechanism involves Cu^{2+} , AA, and oxygen. It has been reported that AA combined with Cu^{2+} , in presence of molecular oxygen, can produce hydroxyl radicals.¹⁶ On the basis of these reports and the experiments undertaken, we suggest the following mechanism:

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Figure 6. UV-vis spectra of reaction between (A) R_2 and CuCl₂ and (B) R_2 and CuCl₂ with external addition of CTAB, at 70 °C. Addition of AA after 6 h showed a shift in the LSP almost immediately (broken line in B). (C) R_2 and CuCl₂ with external addition of AA (1 mL 100 mM AA) and (D) the plot of LSP position against transformation time for the various conditions examined. CuCl₂ was present in all cases.

Cu(II) + ascorbate \rightarrow Cu(II)-ascorbate complex \rightarrow Cu(I) + ascorbyl (1)

$$Cu(I) + O_2 \rightarrow Cu(II) + O_2^{-}$$
(2)

$$\operatorname{Cu}(\mathrm{I}) + \operatorname{O}_2^{-} + 2\mathrm{H}^+ \to \mathrm{H}_2\mathrm{O}_2 + \operatorname{Cu}(\mathrm{II})$$
(3)

$$2O_2^- + 2H^+ \rightarrow H_2O_2 + O_2 \tag{4}$$

The reaction indicating the etching of gold atoms from the nanorod surface can be written as

$$\operatorname{Au(0)}_{\operatorname{rod}} + \operatorname{H}_2\operatorname{O}_2(\operatorname{aq}) + \operatorname{Cu(I)}_{\operatorname{aq}} \rightarrow \left[\operatorname{Au(OH)}_2\right]_{\operatorname{aq}}^- + \operatorname{Cu(II)}_{\operatorname{aq}}$$
(5)

The detailed stepwise mechanism of reaction 5 is given in the Supporting Information (S6). The reduction potential of $[Au(OH)_2]^-_{aq}$ is negative,¹⁷ but in a bromide-rich medium, there is a high probability that this species will be converted to the easily reducible AuBr₂⁻. The formed AuBr₂⁻ may be converted to Au(0) by AA.

Hydroxyl ions present in the growth solution, in basic medium, is known to make gold multipods and transform them subsequently to particles.¹⁷ Since our medium is acidic, the probability of hydroxyl ion induced transformations can be neglected. The reduction potential of •OH and Au(I) are 1.77 V [$E^{\circ}(\bullet OH_{aq})$] and 1.691 [$E^{\circ}(Au^+/Au)$], respectively.¹⁸ So the etching of Au(0) by •OH by reaction 5 is feasible. We note that the steps

1-4 are known in other situations¹⁶ and we invoke these in the reaction studied.

According to the mechanism, in presence of Cu(I) and H₂O₂ the reaction should proceed in the same fashion. We explored the changes in the reaction in the presence of added H₂O₂. The presence of peroxides such as hydrogen peroxide is known to increase the production of •OH radical.¹⁹ We added 1 mL of 20 vol % H₂O₂ into the reaction mixture containing R₁ and 1 mM CuCl₂. (Figure 8A). As H_2O_2 is involved actively in the mechanism proposed for the production of •OH (step 5), the presence of externally added H2O2 should increase the reaction rate. As expected, the rate was increased and the reaction occurred at room temperature. It was completed in 1.5 h. The final product turned out to be different and it gave a peak around 400 nm. It is unlikely to be due to Au(I), since it does not have a characteristic peak.^{12c} The reaction was tried between R₁ and H₂O₂ without Cu²⁺. Here also a similar reaction was found to occur, but the kinetics was visibly slower. It took nearly 9 h for the reaction to be complete. This also gave a peak around 400 nm, so the reaction in presence of excess H2O2 was giving distinctly different products. As the reaction occurred in the presence of H₂O₂ itself, the experiment was not repeated in presence of both Cu(I) and H₂O₂.

To further establish the mechanism, we added dimethyl sulfoxide (DMSO), a well-known scavenger for hydroxyl

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Figure 7. HRTEM images of gold nanorods during the transformation with external addition of AA clearly showing the rod body also getting reacted. Reacted parts are indicated with arrows in A. The sample was withdrawn after 2 h of the reaction. Various other structures observed are shown in B-D.

radical,²⁰ to the reaction mixture containing R₁ and CuCl₂. Figure 8B shows a UV-visible study of the reaction at 70 °C. The reaction rate was found to be decreased tremendously and it was completed only after 24 h. This suggests that hydroxyl radicals, formed in the reaction, are progressively scavenged by DMSO present in the system, retarding the reaction. It is likely that DMSO can scavenge other radicals such as O_2^{-} (superoxide radical), ascorbate radical, and HO₂• (hydroperoxide radical) that may be present in the system. It has been established that^{20d} the reduction of molecular oxygen in presence of Cu(II)ascorbate system can produce H₂O₂ to a larger extent compared to the above-mentioned radicals. Thus formed H_2O_2 can be converted to •OH in the medium in presence of Cu(I) (Supporting Information S6, eq a). Therefore, we believe that the major product in the reaction is •OH and the radical species scavenged by DMSO is •OH.

The fate of Au in the reaction after the conversion is not yet well understood. In order to check the presence of Au(I), we have added excess AA (0.25 mL, 10 mM) to the reaction mixture after 6 h of reaction and monitored the UV—vis spectra 1 h after addition. There was no change in the plasmon and it matched with the previous one (taken after 6 h of reaction). If there were Au(I), AA would have reduced it to Au(0) and thus should have produced an increase in intensity of the plasmon. This was taken as an indication of the conversion of Au(I) to Au(0), as we proposed. Thus, a quantitative transformation of rods to particles occurs. The same mixture (with more AA added) was further heated for 1 h more and the UV—vis spectrum was taken. There was no further reaction. This proved that the reaction is not

stopping because AA present in the reaction mixture was being used up but because all the rods got converted to more stable spherical particles and these are well-protected by the excess CTAB present in the medium.

We found that the particles formed after the reaction have higher diameter than the parent nanorods. The formation of particles of larger diameter occurs due to surface reconstructions initiated by the etching. In addition, as the CTAB layer protecting the rods in solution is increasingly disturbed at higher temperature, the nanorods are getting fused together, resulting in particles of larger diameter. This alternate suggestion for the formation of particles of larger diameter is supported by the TEM obtained during an intermediate stage of the reaction of R_1 (Supporting Information, S7). The fusion mentioned above was not electronbeam-induced. In addition, the reduction of Au(I) of nanorod/ nanoparticle surface during the transformation can also lead to larger particles.

The kind of branched structures (Supporting Information, S7) was not common in a normal reaction (and not a dominant reason for the formation of particles of larger diameter). Only in some part of the grid did we observed these features, but these structures and fusion were more common in the case of the reaction between R_1 and CuCl₂ in presence of Na₂SO₃, which was used as an oxygen scavenger. Therefore, this kind of branched structure may be a result of the deficiency of oxygen in the reaction mixture. It is not clear at this point whether Na₂SO₃ has any part in this kind of branching, other than oxygen scavenging. Since we got these kinds of structures even without Na₂SO₃, although to a lesser extent, we believe that it does not have any other role in this process.

From the results we suggest that AA used for the slow reduction of Au³⁺, present in excess in the as-prepared rod solution results in the formation of hydroxyl radicals in presence of molecular

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Figure 8. UV-vis spectra between R_1 and CuCl₂, in presence of (A) 1 mL of 20 vol % H₂O₂, carried out at room temperature. Spectra were measured every 5 min after the addition of H₂O₂. The first trace was recorded immediately after the addition of H₂O₂. (B). Reaction with 1 mL of DMSO, carried out at 70 °C. Spectra were measured every 1 h after the addition of DMSO. The first trace was recorded immediately after the addition of DMSO.

oxygen and Cu²⁺. The surface involved in the reaction is determined by the presence or absence of the protecting CTAB bilayer. Reconstruction finally leads to the shape transformation

of anisotropic nanorods to more stable spherical nanoparticles and results in concomitant spectral changes. The amount of hydroxyl radical produced depends upon the temperature of the reaction medium and the concentration of Cu^{2+} ion present in the solution, as indicated by the higher rate of transformation at higher temperature and higher concentrations of Cu^{2+} . The Au-(I) formed by hydroxyl ion induced etching is likely to be reduced in the presence of excess AA.

Summary and Conclusions

Surface specific shape transformation of gold nanorods was achieved, assisted by cupric ions in aqueous medium. The TEM and UV-vis observations showed shortening of the length of the nanorods as a function of time. TEM images showed truncated rods are the intermediate species during the shape transformation. The images confirmed that the reaction starts from the tips of nanorods, when the unstable {110} surfaces are stabilized by CTAB. The reaction, however, occurs on the $\{110\}$ surfaces when the protecting CTAB layer is removed. It was shown that the reaction involved the generation of hydroxyl radicals, the presence of which was confirmed by control experiments. Oxygen is an active participant in the transformation and plays a key role in the production of the radical. The reactant concentration and temperature have critical effects on the rate of the transformation. The methodology reported here may be extended to other metal ions and organometallic reagents, extending the scope of this research. Work along this line is in progress.

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Supporting Information Available: TEM images of R_1 during the reaction with CuCl₂ (large area images), UV-vis spectra for the reaction of R_1 and CuCl₂ at room temperature and 60 °C, UV-vis spectra for the reaction of R_1 at 70 °C with 10⁻⁴ M CuCl₂, TEM images of R_2 during reaction with external addition of AA without CTAB, steps involved in eq 5, TEM images showing branched structures formed during the reaction, UV-vis data, and TEM images for the reaction of R_2 with CuCl₂ with external addition of AA and CTAB. This material is available free of charge via the Internet at http://pubs.acs.org.

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