

Reactivity and resizing of gold nanorods in presence of Cu^{2+}

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Abstract. Due to the inherent anisotropy of the system, gold nanorods behave differently in comparison to their spherical counterparts. Reactivity of gold nanorods, in presence of cupric ions, was probed in an attempt to understand the chemistry of anisotropic particles. The reaction progresses through a series of intermediates. It can be arrested at any stage to get nanorods of desired dimension and therefore, can be used for their reshaping. The presence or absence of cetyltrimethylammonium bromide (CTAB) on the nanorod surface was found to be determining the site of initiation of the reaction. When a large concentration of CTAB is present in the system, selective etching of the tips of the nanorod occurs and when the nanorods are purified to reduce the amount of CTAB in the solution, the side faces of the nanorod also get reacted. Gold nanorods are converted to particles by further surface reconstructions in a systematic surface specific chemistry.

Keywords. Gold nanorods; anisotropic particles; Cu^{2+} .

1. Introduction

Scientific interest in the nano regime lies in the fact that it is considered as a bridge between the bulk and atomic or molecular structures. The size dependent properties of nanomaterials make them interesting and technologically important (Rao *et al* 2000). Quantum confinement in semiconductor particles (Norberg *et al* 2006) and characteristic surface plasmon resonances (SPR) in certain metal particles (Smith and Corn 2003; Jin and Friedman 2005) are some interesting examples of size dependent properties. Nanomaterials by virtue of their high surface to volume ratio exhibit very different chemical reactivity and properties, compared to their bulk counterparts (Zhan *et al* 2002; Prakash *et al* 2005). An example is the reactivity of Au and Ag nanoparticles towards halocarbons, which has been studied extensively (Nair and Pradeep 2003, 2004; Nair 2006). The reactions investigated can be extended for the degradation of some common pesticides present in surface waters. We devised an economical and efficient drinking water purifier based on this reaction in collaboration with Eureka Forbes Ltd. (Nair and Pradeep 2007).

Gold nanorods are excellent anisotropic nanostructures for a number of applications due to their size-dependent optical properties (Juste *et al* 2005). Nanorods can be prepared through several methods such as electrochemical deposition in hard templates (Foss Jr *et al* 1992) and at step edges (Martin 1996), electrochemical synthesis in solution (Yu *et al* 1997; Chang *et al* 1999), photochemical synthesis (Kim *et al* 2002), microwave heating (Liu *et al* 2004) and by the seed-mediated growth (Sau and Murphy

2004). Gold nanorods are characterized by two characteristic absorption maxima in the UV-vis spectrum. The first one, called the transverse surface plasmon resonance (TSP), is located around 520 nm. The other maximum, known as the longitudinal surface plasmon (LSP) resonance, appears at a longer wavelength. LSP is extremely sensitive to the nanorod aspect ratio (Juste *et al* 2005).

Nanorods have an edge over the spherical counterparts and that they can be assembled in different ways like end-to-end, side-by-side and parallel or perpendicular to the substrate. All of these are attractive for several applications such as surface-enhanced Raman spectroscopy or fluorescence sensing applications. Hexagonal patterns of gold nanorods were made by growing them on the surface of microgels and subsequently allowing the nanorod loaded microgels to self-organize. This opens up a new possibility for making patterns in high yield through solution phase methods (Rajeev Kumar *et al* 2007). Nanoparticle assemblies can be used as sensors. The generation of a potential difference, of the order of tens of millivolts, induced by the flow of polar liquids over an assembly of gold nanoparticles has been reported by our group (Subramaniam *et al* 2005). The potential generated is in transverse direction to the flow and is dependent on the nature of the flowing liquid. We proposed a simple theoretical model, based on coulomb interaction of the flowing dipole with surface charges on nanoparticles to account qualitatively for the generation of the flow induced transverse potential. This has been extended to anisotropic nanostructures such as nanorods also (Subramaniam *et al* 2007). Modifications in the theoretical model have been done to explain the non-linear dependence of the potential difference on flow rate.

Gold nanorod chemistry is found to be different from their spherical counterparts owing to the surface structure

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and the presence of the {110} facet which is absent in the spherical nanoparticles. The photothermal properties and electron dynamics (Song *et al* 2005), catalysis (Kline *et al* 2005) and biological applications (Salem *et al* 2003) of these systems have been investigated in great detail. Our group has recently investigated the electrostatic adsorption of hemoproteins on gold nanorods. The study suggested the retention of the molecular structure after immobilization on the nanoparticle surface. The biochemical activity of these electrostatically adsorbed hemoproteins was assessed using the selective affinity of prosthetic heme moiety towards metabolic inhibitor, azide ion (Tom *et al* 2007).

For any particular application, whether it involves individual particles or an assembly, the monodispersity and the size are two very important quantities that should be addressed with utmost care. Since the properties of nanorods are highly dependent on the dimension, researchers are interested in devising new methodologies for preparing monodisperse materials. One strategy is to devise various synthetic methodologies to prepare different sizes of rods. The second strategy is to make a monodisperse sample from a crude polydisperse sample post-synthetically (Link *et al* 2000; Jana *et al* 2002; Rodriguez-Fernandez *et al* 2005; Tsung *et al* 2006; Mohamed *et al* 2007). The latter has an added advantage that differently sized nanorods can be prepared from the same starting material, simply by adjusting the reaction parameters. In this paper, we describe the surface dependent chemical reactivity of gold nanorods in presence of cupric ions. Although the distribution of the particle sizes in the in-between stages of the reaction is large, this method may be developed further to yield particles of desired shape. This is a continuation of our earlier work on this problem (Sreeprasad *et al* 2007) and additional data are presented.

2. Experimental

2.1 Synthesis of gold nanorods

Nanorods were made as per the reported procedure which followed the well-established seed-mediated method (Sau and Murphy 2004). First, CTAB protected gold seeds were prepared by the reduction of the required quantity of gold ions by ice-cold NaBH_4 in presence of CTAB. After 3 h, a calculated amount of the seed solution was added to a growth solution containing specific amounts of CTAB, HAuCl_4 and ascorbic acid. The resultant solution was kept without disturbance for 24 h and examined using TEM to determine the monodispersity of the sample.

The as-prepared nanorod sample (R_1) was centrifuged at 11,100 rpm for 15 min. The supernatant was discarded and the residue was redispersed in an equal amount of triply distilled water. The sample was again centrifuged at 11,100 rpm. This was repeated twice, principally to remove

excess CTAB and other impurities present. The sample will be referred to as R_2 in the paper hereafter.

2.2 Reactivity study

The as-prepared (R_1) as well as the purified (R_2) samples were subjected to reaction separately. The chemical reactivity of nanorods with metal chlorides like CuCl_2 was studied. The nanorod solution was mixed with CuCl_2 solution and the mixture was heated in a water bath maintained at 70 °C. The UV-vis spectrum and TEM of the sample were analysed every 1 h. The reaction was done both with R_1 and R_2 as described by Sreeprasad *et al* (2007).

3. Instrumental

A Perkin-Elmer Lambda 25 UV-visible spectrophotometer was used to measure the UV-vis spectrum of the samples. Samples were drop casted on a carbon coated copper grid and dried in ambience. This was observed under a JEOL 3011, 300 kV Transmission Electron Microscope (TEM) with an ultra high resolution (UHR) pole piece.

4. Results and discussion

Figure 1 shows the UV-vis spectra acquired at various stages of the reaction between R_1 and CuCl_2 (1 mM). The position of plasmon gives us an idea about the aspect ratio of the gold nanorod. The LSP shifts linearly with aspect ratio of the nanorods (Juste *et al* 2005). As we can see the LSP blue shifts and decreases in intensity, while the TSP red

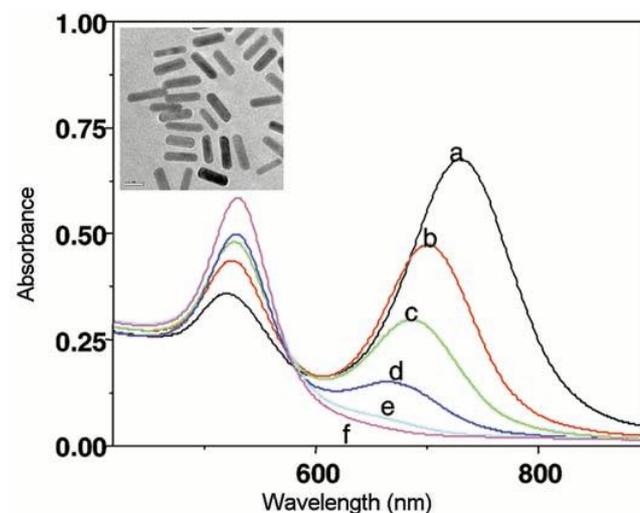


Figure 1. UV-vis spectra of the reaction between Au nanorods and CuCl_2 as a function of time. Spectra were acquired every 1 h of the reaction (a–f). Trace a corresponds to the parent nanorod sample and b is after 1 h of the reaction (Inset: TEM image of pristine nanorods).

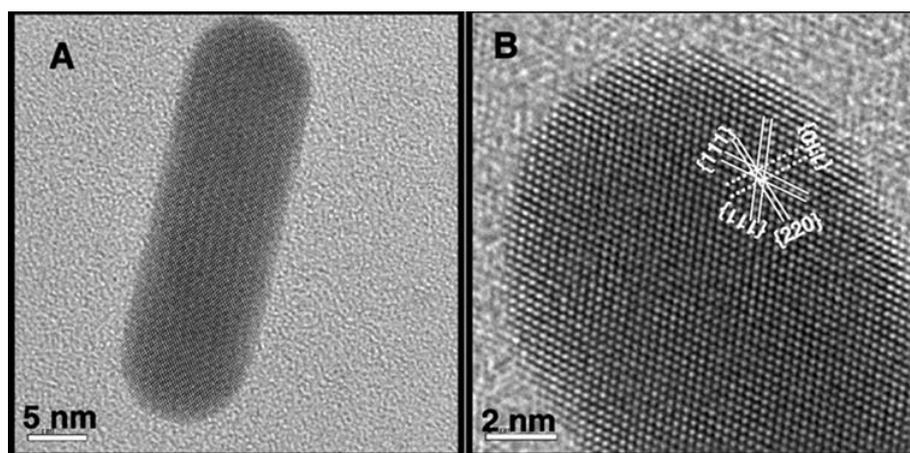


Figure 2. A. Lattice resolved image of a pristine nanorod showing the well defined tip and side devoid of any defects and B. a high magnification image of a nanorod tip.

shifts slightly and increases in intensity during the reaction. After 3 h of the reaction, only a hump is shown in place of LSP and finally after 4 h of the reaction, only TSP remains. All these spectral changes suggest the conversion of nanorods into spherical nanoparticles. The red shift in TSP from 518 nm to 531 nm indicates that the resultant particles formed have a larger diameter compared to the parent nanorods. The inset of figure 1 shows a large area image of pristine nanorods. We can see that they are highly monodisperse with a diameter of ~ 13 nm and a length of ~ 43 nm.

Figure 2A shows a lattice resolved image of a pristine nanorod showing well-defined tips and sides devoid of defects. Figure 2B shows a lattice resolved image of the tip of a nanorod before the reaction. All the rods seen are single crystalline and in majority of the cases examined, the rod axis is oriented along the [100] direction and the side faces are $\{110\}$. The tips are well structured with $\{111\}$ and $\{100\}$ facets (Wang *et al* 2000).

Figure 3 shows the TEM images of the nanorods at a few stages of the reaction of R_1 . We can see the truncated structures formed which gives an indication that the reaction starts from the tip of the rods. We can also detect a gradual decrease in the length of the rods during the course of the reaction and the end product is larger spherical particles. It is clear that specific and well-defined shapes can be created. Monodispersity of the samples in the in-between stages is not as good as the starting material or the end product. But we can see that the rods or particles produced during the reaction are similar in diameter in comparison to the parent material.

The difference in the surface energies of different planes present on the gold nanoparticle surface gives us a tool to selectively react with those planes and get the desired shape or size (Todd and Lynden-Bell 1993; Uppenbrink *et al* 1994). We found that when excess CTAB is present,

the edge faces of the nanorod comprising mainly of $\{111\}$ or $\{100\}$ are getting reacted. But when the nanorods are purified, the capping of the $\{110\}$ face becomes defective and the defects sites act as the reaction centres. So in the purified sample, the reactions get initiated at the defect sites and the rod body composed of $\{110\}$ facet is also getting reacted. This shows that the presence or absence of the surfactant can control the reaction. This is believed to be due to the extra stability offered to the otherwise unstable $\{110\}$ facet by the binding of CTAB.

Figure 4A shows an intermediate present in the case of reaction with R_1 . We can clearly see the tips are getting reacted. In R_2 , the rod body is also getting reacted (figure 4B). This is because when CTAB protects the $\{110\}$ surface, which constitutes the side faces, the reaction happens at the less protected rod tip composed of $\{111\}$ and $\{100\}$. But when the CTAB protection is defective, as a result of purification, the reaction happens in the exposed $\{110\}$ surface which is having the highest surface energy among the low index planes of gold. So when CTAB is present, due to the extra stability afforded to the $\{110\}$ surface by CTAB, the reaction deviates from path expected from surface energy calculations and in R_2 where most of the CTAB is removed, the reaction follows the expected path, i.e. according to the surface energy (Wang *et al* 2000). When nanoparticles are formed during the reaction, which are mainly composed of either $\{111\}$ or $\{100\}$ surfaces (Wang *et al* 2000), the system is stable (Todd and Lynden-Bell 1993) and no further reaction happens. In addition, the surfaces of the particles formed will be protected by CTAB in the medium.

The reaction can be quenched by removing the heating and we found that no reaction happens at room temperature. Thus, by controlling the reaction time and temperature, we can manipulate the size of the nanorods precisely. In the absence of the control, the reaction gives spherical

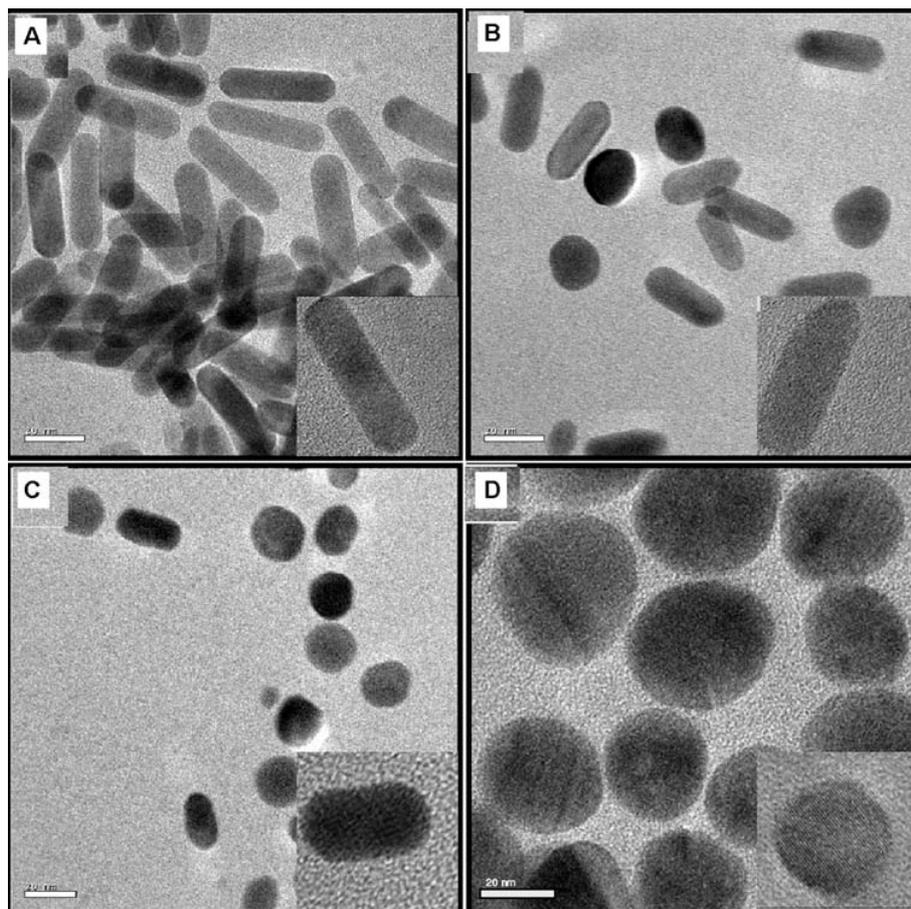


Figure 3. TEM images of R_1 during the course of transformation into particles. **A.** Pristine nanorods, **B.** after 1 h of reaction, **C.** after 4 h and **D.** the final spherical particles after 6 h of reaction. Insets show the lattice resolved images. Scale bars in all the images are 20 nm.

nanoparticles. The reaction product in R_1 (i.e. nanoparticles) are infinitely stable under the reaction conditions.

UV-vis and TEM data supported the conjecture that partial and selective etching happens to nanorods and the shape changes from rod to spherical particles. The reaction stops after the particles are formed. A concomitant increase in the intensity of TSP with the decrease in the intensity of the LSP shows that the conversion happens in a quantitative manner. This gives us a tool for manipulating the size and shape post-synthetically, from a single crude starting material. The reaction starts from the tip of the nanorods when they contain excess CTAB and when CTAB is removed, the reaction occurs on the rod body also. The surface which gets reacted is determined by the presence or absence of the protecting CTAB bilayer. The reaction showed a strong dependence on the Cu^{2+} concentration as well as the temperature of the reaction medium. Several control experiments were done to establish the mechanism of the reaction. We found that the purified nanorods did not show any reactivity with CuCl_2 when heated. We also found that when ascorbic acid was added

to R_2 , a reaction similar to R_1 took place and the nanorods got reshaped to particles. No reaction occurred in Ar atmosphere both with R_1 and R_2 . There are reports that Cu^{2+} in presence of ascorbic acid and O_2 can produce hydroxyl radical (Kadiiska *et al* 1992; Asplund *et al* 2002). The reduction potential of hydroxyl radical (Koppenol and Liebman 1984) is such that it can oxidize the $\text{Au}(0)$ to $\text{Au}(I)$ which in turn results in the shortening of nanorods. This reaction starts in the more exposed $\{111\}$ plane in R_1 , making the tips to get etched away. When the excess CTAB is removed and defects are produced in the CTAB capping, the reaction gets initiated on the thermodynamically less stable $\{110\}$ surface and the side faces get reacted. Since in R_2 , ascorbic acid is not present, the reaction does not happen. In presence of Na_2SO_3 , an oxygen scavenger (Carretero *et al* 1998), the reaction gets retarded. In presence of dimethyl sulphoxide, which acts as a hydroxyl radical scavenger (Bruck *et al* 2001), the reaction is retarded. All these observations made us to conclude that the reaction occurs as a result of the formation of hydroxyl radicals in presence of Cu^{2+} and ascorbic acid

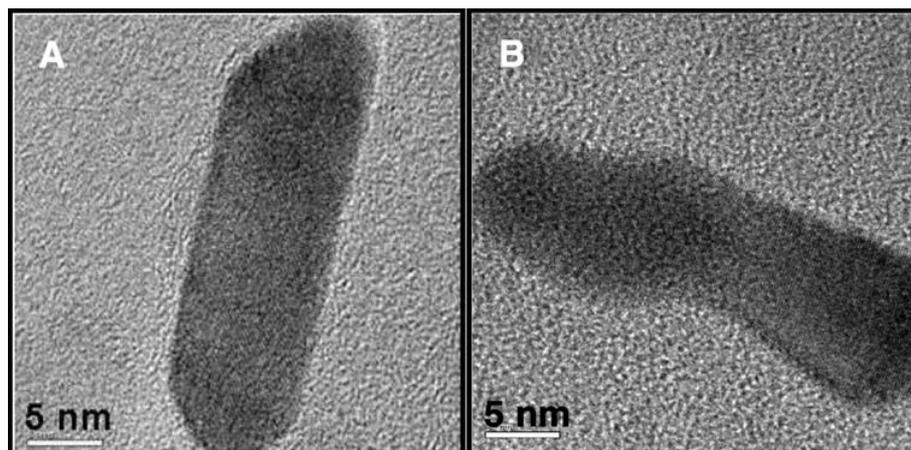


Figure 4. A. Reaction intermediate in R_1 , where excess CTAB is present and B. in R_2 , where the excess CTAB is removed by centrifugation.

(Sreeprasad *et al* 2007). As the final particles formed at the end of the reaction in figure 3D are larger and no gold ions are detected in the solution, it is concluded that the ions etched away from the tips are reduced on the nanoparticle surface.

5. Conclusions

The chemistry of anisotropic nanostructures such as nanorods is similar to spherical particles in several cases, but there are also significant differences. We found that using a simple reaction with CuCl_2 , nanorods can be resized within a range limited by the size of the starting sample. The reaction, if extended, results in reshaping and finally yields spherical nanoparticles. In presence of excess CTAB, reaction starts from the edge and when they are removed by centrifugation, rod body gets reacted preferentially. HRTEM and UV-vis data support the proposition. The preferential reactivity is believed to be due to the stabilizing ability of CTAB which adsorbs strongly on {110} and gives stability to this face and the reaction happens preferentially on other facets.

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