Purification of High Aspect Ratio Gold Nanorods: Complete Removal of Platelets

Bishnu P. Khanal and Eugene R. Zubarev*

Department of Chemistry, Rice University, Houston, Texas 77005

Received August 1, 2008; E-mail: zubarev@rice.edu

The properties of nanostructures are known to be dependent on their shape.1,2 Many literature reports describe the preparation of various nanostructures, but only few methods offer nearly quantitative yields of a targeted shape. In most cases mixtures of shapes are produced and the separation of a particular component may be the only way to obtain it in a pure state. Several techniques that can separate nanoparticles have been reported in the literature including HPLC, diafiltration, capillary electrophoresis, and gel electrophoresis.3 However, their applicability to CTAB-coated large nanostructures has not yet been demonstrated. A well-known example and long-standing challenge is given by high aspect ratio gold nanorods, which can only be prepared in solution by a three-step seed-mediated method.4 Unfortunately, the content of rods in the mixture that forms during that synthesis is very low (<20%), and two other components (spheres and platelets) are present in much higher quantities. Multiple rounds of centrifugation can remove the majority of spherical particles, but the remaining mixture of rods and platelets is known to be inseparable.4,5 Here we demonstrate that a partial dissolution of that mixture with Au(III)/CTAB complex transforms platelets into smaller nanodisks, which have much higher solubility and remain in the supernatant indefinitely while the pure nanorods slowly precipitate. This technique allows for the isolation of nearly all nanorods that were present in the initial mixture and brings the level of their purity to at least 99%. In addition, the separated nanodisks are ~90% pure and can be converted back to multifaceted platelets when treated with growth solution containing Au(I) ions and ascorbic acid. Therefore, the initial mixture can be separated into individual components, which is demonstrated by a combination of TEM, UV−vis, and NIR spectroscopy in deuterated water.

Figure 1A shows a representative TEM image of structures that form under standard conditions known as the three-step seed-mediated method introduced by Murphy et al.4 Three major components of the mixture are spherical nanoparticles (~50 nm), multifaceted platelets (100−150 nm), and high aspect ratio rods. The surface of all nanostructures is stabilized by a bilayer of CTAB molecules, which are present in high concentration (0.1 M). The solubility of nanostructures in CTAB-saturated aqueous solution is mainly dependent on their overall size and surface-to-volume ratio. Because of that spherical particles possess the highest solution stability and do not precipitate. This is in contrast to large platelets and nanorods which undergo gravitational sedimentation if the solution is left undisturbed for 10−12 h. At this point the supernatant containing nearly pure spheres (see Supporting Information, Figure S1) can be removed and the precipitate can be redispersed into CTAB solution (Figure 1B). Our initial attempts to separate platelets from rods using conventional centrifugation, membrane filtering, electrophoresis, and density gradient gel centrifugation have failed completely. This result may not be surprising considering the fact that the average mass of platelets and rods are very similar. For example, a 20 nm thick triangular prism (100 nm) has nearly the same mass as a 300 × 20 nm nanorod.

In a separate project we were investigating the oxidation of gold nanostructures by a complex that forms when Au(III) ions are added to CTAB aqueous solution. Interestingly, the rate of dissolution is strongly dependent not only on the size as was previously demonstrated,6 but also on the actual shape of nanostructures. We noticed, for example, that the treatment of the mixture of platelets and rods with Au(III)/CTAB complex results in a conversion of platelets into smooth disklike structures. More importantly, a nearly 40% reduction in the size of platelets occurs when the size of nanorods is decreased only by ~20% (Figure 1C). This difference in the rate of dissolution turned out to be critically important because the resulting nanodisks became fully soluble, whereas the shortened nanorods were still heavy enough to undergo gravitational sedimentation in 12 h. Examination of the precipitate by TEM revealed that the rods had a fairly narrow size distribution measuring 22 ± 3 nm in diameter and 247 ± 31 nm in length, and the content of impurities was found to be less than 1% (Figure 1D).

The dissolution of the platelets/rods mixture is accompanied by its continuous change from dark brown to green and further to blue...
strong absorption in the NIR region. Figure 3 shows the D2O color. The isolated blue supernatant contained ~90% of nanodisks (70 ± 15 nm in diameter) and a small amount of short rods that formed in the initial synthesis (Figure 2A). Remarkably, the nanodisks can be converted back into the original faceted platelets when a growth solution containing Au(I) ions, CTAB, and 10 mol % ascorbic acid is added. The observed amplification of disks proceeds without any new nucleation events, and no 3D shapes form during this process. The average size of the newly formed platelets is only dependent on the amount of the introduced growth solution, which allows one to control the size of the platelets within the range from 100 nm to few micrometers. Conversely, the dissolution of large platelets with Au(III)/CTAB complex offers the key element which allows for their complete removal from the isolated nanostructures we transferred them from aqueous solution spectra that cover both the visible and near IR ranges from 400 to 1900 nm. The spherical particles exhibit a large plasmon at 526 nm and a small peak at 695 nm corresponding to the longitudinal peak of low aspect ratio rods that are present in small quantity (~10% by TEM). Considering that the longitudinal peak of nanorods is at least an order of magnitude larger than that of transverse peak,7 one can conclude that the content of this impurity is fairly low. Similarly, nanodisks exhibit only one peak at 628 nm, and there is virtually no absorption around 526 nm which confirms the absence of spherical particles. The spectrum of platelets also shows one peak (735 nm), although it is much broader which is mainly due to their larger size. Importantly, the collection of the spectra from visible through the NIR region allows us to confirm that the isolated spheres, nanodisks, and platelets do not contain any appreciable amount of high aspect ratio nanorods. This is evidenced by little or no absorption near 1500 nm, where a very intense longitudinal peak of nanorods is located. The peak at 1567 nm is one of the highest values observed from a solution of nanorods or any other gold nanostructures (as opposed to solid films).5 The extinction of this peak is ~16 times higher than that of the transverse plasmon positioned at 492 nm. The purity of the nanorods is further confirmed by the absence of peaks corresponding to spheres, disks, and platelets at 526, 628, and 735 nm, respectively. The width of the nanorods peak is fairly large, which is expected because it strongly increases with the aspect ratio as predicted by theory.7 The size distribution of the nanorods is unlikely to be solely responsible for the broad width because the polydispersity of rods (~12%) is lower than that of nanodisks (~20%), which exhibit an extremely sharp peak. More importantly, when the extinction is plotted as a function of energy, the peak of nanorods becomes sharper than any other shape, (see Figure S5).

In conclusion, we demonstrated that partial dissolution of platelets is the key element which allows for their complete removal from high aspect ratio nanorods. In addition, the combination of dissolution and amplification offers an opportunity to separate mixtures of various shapes into nearly pure components.

Acknowledgment. Support for this work was provided by the NSF (DMR-0547399, CBET-0506832) and Welch Foundation (C-1703).

Supporting Information Available: Experimental procedures and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

References


Figure 2. TEM images of isolated gold nanodisks (A) and faceted platelets (B). The two shapes can be repeatedly converted one into another under mild reducing (top) and oxidizing (bottom) conditions. Scale bars are 200 nm.

Figure 3. Normalized extinction spectra collected from D2O solutions of isolated spheres (red), nanodisks (blue), platelets (turquoise), and nanorods (brown). The photograph on the right shows the corresponding solutions in deuterated water. S, D, P, and R stand for spheres, disks, platelets, and rods, respectively.

To study the optical properties and to better assess the purity of the isolated nanostructures we transferred them from aqueous solutions to deuterated water, which unlike H2O, does not have a strong absorption in the NIR region. Figure 3 shows the D2O solution spectra that cover both the visible and near IR ranges from 400 to 1900 nm. The spherical particles exhibit a large plasmon at 526 nm and a small peak at 695 nm corresponding to the
Purification of High Aspect Ratio Gold Nanorods: Complete Removal of Platelets

Bishnu P. Khanal and Eugene R. Zubarev*

Department of Chemistry, Rice University, Houston, Texas 77005

Supporting Information

General. Unless otherwise stated, all the starting materials were obtained from commercial suppliers and used without further purification. Cetyltrimethylammonium bromide (CTAB) was purchased from Acros Organics Inc. Hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O), gold (III) chloride, ascorbic acid, sodium borohydride, silver nitrate, and sodium citrate were purchased from Sigma-Aldrich. Deionized (DI) water was used for all the experiments. Optical extinction spectra were obtained with a Cary 5000 UV/Vis/NIR spectrophotometer using D₂O solutions of CTAB stabilized nanostructures. Transmission electron microscopy (TEM) was performed on JEOL 1230 (acceleration voltage 120 kV), JEM 2010 (acceleration voltage 200 kV) electron microscope using carbon-coated copper grid (Electron Microscopy Sciences). For the preparation of TEM samples 1.5 mL of nanostructures solution (~0.1 mg/mL) was centrifuged at 13,000 rpm for 10 min followed by removal of the supernatant containing excess CTAB. The procedure was repeated 2 times before the precipitate was redispersed in 100 µL of pure DI water upon brief sonication for 10-15 s. The resulting solution was then cast on a TEM grid and the drop was allowed to dry at room temperature.

Synthesis of high aspect ratio gold nanorods. High aspect ratio nanorods were synthesized by using seed mediated approach described by Murphy et al (ref. 4). Briefly, the synthesis begins with the preparation of citrate capped seed nanoparticles. In a typical experiment, 1.47 mg of sodium citrate and 1.97 mg of HAuCl₄·3H₂O was dissolved in 20 mL water. To this solution 0.6 mL of 0.1 M ice-cold NaBH₄ solution was added upon vigorous stirring (1200 rpm). The solution turned brownish-red, indicating the formation of 3-4 nm gold particles. These seed particles were used within 10 min after the preparation.

Preparation of the growth solution. In a 2 L flask, 64.06 g of CTAB was dissolved in 880 mL water upon gentle heating (~35°C). In a separate flask, 173.4 mg of HAuCl₄·3H₂O was dissolved in 880 mL water and mixed with CTAB solution. Three flasks with the capacity of 100, 250, and 2000 mL were labeled as A, B, and C, respectively. The prepared solution in the amount of 45, 140, 1575 mL was placed into flasks A, B, and C, respectively, and kept at 27°C. Next, 0.1 M ascorbic acid solution in water was prepared by dissolving 176 mg of ascorbic acid in 10 mL of water. After that, 0.25, 0.77, and 8.75 mL of ascorbic acid solution was added into flasks A, B, and C, respectively. All three flasks were hand shaken and the solutions became colorless. Then, 4 mL of seed solution was added to flask A and gently mixed. Immediately after that 12.4 mL of the resulting mixture was transferred from flask A to flask B within 3 seconds and gently mixed. This was immediately followed by transferring all of the
content of flask B into flask C within 3 seconds before quick mixing by shaking the flask. The flask C was then left undisturbed and the color of the resulting solution slowly changed to purple after 2-3 min and then to dark-red after 30 min. Flask C was then kept undisturbed for additional 14 h at 27°C. High aspect ratio nanorods along with significant amount of faceted 2D platelets precipitate from the solution and form a thin barely noticeable film at the bottom of the flask. The resulting supernatant, which contained mostly spherical nanoparticles (see Fig. S1 below), was carefully removed and the walls of the flask as well as the film on the bottom were carefully rinsed with a small portion of DI water to remove the residual amount of the supernatant. The film of nanorods and platelets was redispersed into 10 mL of 0.1 M CTAB solution upon brief sonication (30 sec).

**Partial dissolution of platelets.** Separately, an oxidizing Au(III)/CTAB complex for the partial dissolution of platelets was prepared by dissolving 364 mg of CTAB and 1.97 mg of HAuCl₄·3H₂O in 10 mL of DI water. Next, 1 mL of this solution was added to suspension of nanorods and platelets in CTAB aqueous solution upon stirring and left undisturbed for 14 h. Nanorods along with a small amount of large disks precipitated and formed a thin film on the bottom of the flask. The greenish-blue supernatant containing small nanodisks was carefully collected and the film of the precipitate was again redispersed in 10 mL of 0.1 M CTAB solution followed by addition of another 1 mL of the Au(III)/CTAB solution. This process of partial dissolution was repeated several times (typically 3-4) until the examination of the precipitate confirmed complete removal of platelets and the presence of pure nanorods. Importantly, the process can be accelerated if a larger amount of the oxidizing complex is added at once (4 mL instead of 4×1 mL). However, in that case the size distribution of the nanorods becomes much broader and low aspect ratio nanorods will be present in the supernatant. The Au(III)/CTAB complex dissolves the platelets from the sharp edges and slightly reduced the length (but not the width) of the nanorods.

**Amplification of nanodisks.** The collected supernatants were combined (~40 mL) and centrifuged at 13,000 rpm followed by removal of CTAB solution. The precipitate containing pure nanodisks was redispersed in 10 mL of 0.1 M CTAB aqueous solution and 3 mL of growth solution (see the preparation above) was added. The resulting mixture was kept undisturbed for 12 h at 27°C. The color of the solution was gradually changing from bright blue to turquoise to pale greenish. The platelets that formed were centrifuged at 6,000 rpm, redispersed into pure water twice, and analyzed by TEM.

**Transfer of nanostructures from water to D₂O.** Depending on the nature of nanostructures, slightly different conditions were used for the transfer. Aqueous solution of pure nanorods (0.1 M CTAB) was allowed to settle without any centrifugation. This is because centrifugation may cause the formation of bundles of nanorods and partial loss of solubility. After approximately 12 h the H₂O/CTAB supernatant was carefully removed and the precipitate of nanorods was redispersed into 10 mL of 0.1 CTAB solution in D₂O. The resulting solution contained 1-2 % of H₂O, which was enough to suppress or interfere with the plasmon peaks of nanorods (strong absorption at ~1500 nm). Therefore, it was critically important to reduce the amount of residual H₂O as much as possible. At least 3 rounds of centrifugation/redispersion in D₂O/CTAB solution were used before the spectra were collected. For all other shapes the use of centrifugation does not affect the solubility and that allows one to transfer the nanostructures much faster.
Solutions of spherical nanoparticles and nanodisks were centrifuged at 13,000 rpm for 10 min, whereas all platelets precipitate if centrifugation at 6,000 rpm is used for 15 min.

Figure S1. TEM image of isolated gold spheres.
Figure S2. TEM image of isolated high aspect ratio gold nanorods.
Figure S3. TEM image of isolated faceted platelets.
Figure S4. TEM image of isolated nanodisks.
Figure S5. Extinction spectra of D₂O solutions of isolated nanostructures plotted as a function of wavelength (left, see also Fig. 3 in the text) and as a function of energy (right). Letters S, D, P, and R stand for spheres, disks, platelets, and rods, respectively.