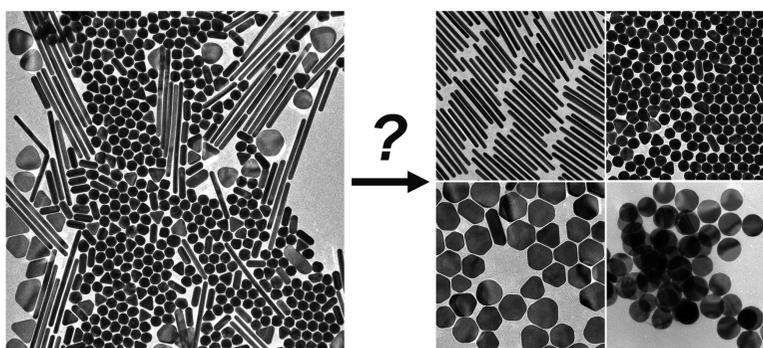


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Purification of High Aspect Ratio Gold Nanorods: Complete Removal of Platelets

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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 masses of platelets

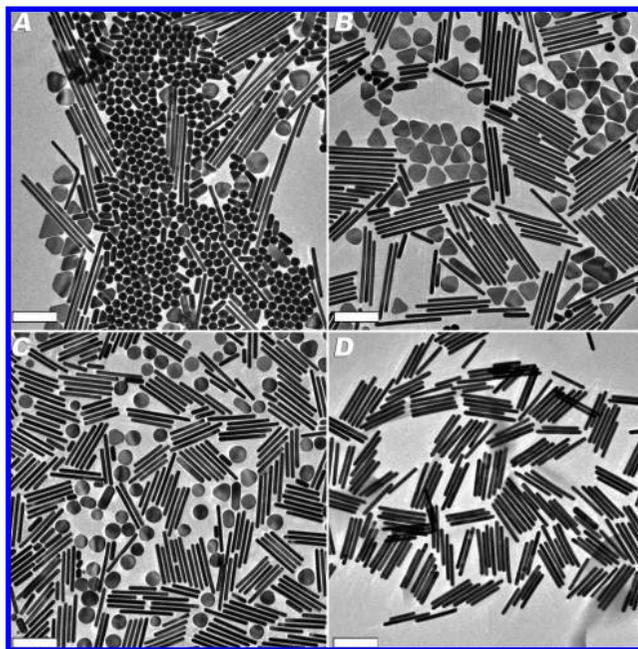


Figure 1. TEM images of gold nanostructures prepared by a three-step seed-mediated method: (A) as-synthesized mixture; (B) mixture of faceted platelets and rods after the removal of small spherical particles; (C) mixture of nanodisks and rods that was obtained by treating the mixture shown in panel B with Au(III)/CTAB complex; (D) nanorods precipitated from the solution of the mixture shown in panel C. All images are taken at 12000 magnification; all scale bars are 200 nm.

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 ± 2 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

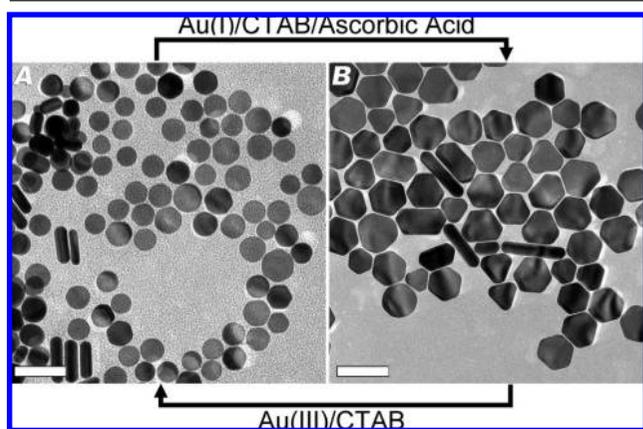


Figure 2. TEM images of isolated gold nanodisks (A) and faceted platelets (B). The two shapes can be repeatedly converted one into another under mild reducing (top) and oxidizing (bottom) conditions. Scale bars are 200 nm.

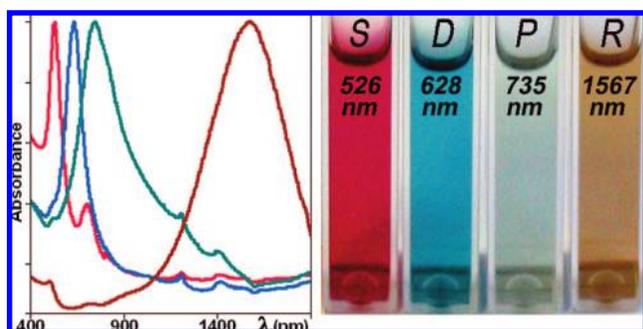


Figure 3. Normalized extinction spectra collected from D₂O solutions of isolated spheres (red), nanodisks (blue), platelets (turquoise), and nanorods (brown). The photograph on the right shows the corresponding solutions in deuterated water. S, D, P, and R stand for spheres, disks, platelets, and rods,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

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 an opportunity to synthesize larger nanodisks. Thus, the process is fully reversible and can be repeated multiple times with a great degree of reproducibility. Most importantly, the described combination of a gravity-driven sedimentation, dissolution, and amplification allowed us to separate the initial mixture of spheres, rods, and platelets into nearly pure components (see Supporting Information for more images).

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

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.

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

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