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Photochemical Synthesis of Gold Nanorods

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Nanoscale materials are of great interest due to their unique optical, electrical, and magnetic properties. These properties are strongly dependent on the size and shape of the particle,[1,2] and therefore it is very important to be able to finely control the morphology of the nanomaterials. Current research has been focused on one-dimensional nanoparticles such as nanorods since the morphological anisotropy results in very complex physical properties and self-assembly behaviors compared to those of spherical nanoparticles.[3] Metal nanowires/rods have been synthesized by using various methods such as templating,[4,5] photochemistry,[6] seeding,[7,8] and electrochemistry.[9,10] The electrochemical synthesis of gold nanorods provides rods with fairly good uniformity and controlled aspect ratio although its growth mechanism remains elusive. For the growth of these nanorods, it has been noted that a small amount of silver addition is critical for the formation of rods instead of spherical particles, but there has not been much research done on the exact role of the silver. One reason is that the electrochemical process is highly complex and involves various effects such as sonication and electric field, making it difficult to verify the sole effect of silver. Here we were able to synthesize gold nanorods with controlled aspect ratio by using photochemistry in the presence of silver ions. This process itself is highly promising for producing uniform nanorods, and more importantly it will be useful in resolving the growth mechanism of anisotropic metal nanoparticles due to its simplicity and the relatively slow growth rate of the nanorods.

A quantity of 3 mL of an aqueous solution of 0.08 M hexadecyltrimethylammonium bromide (CTAB) and 0.42 mg/mL tetradodecylammonium bromide was used as the growth solution. Hydrogen tetracholoaurate (0.25 mL of 0.024 M, $HAuCl_4 \cdot 3H_2O$, Alfa Aeser) was added to the solution as the precursor of gold, and 0.065 mL of acetone and 0.045 mL of cyclohexane were added to loosen the micellar structure.[10] Different amounts of 0.01 M silver nitrate ($AgNO_3$) aqueous solution were added to the solution. The solution was irradiated with a 254-nm UV light (420 μW/cm^2) for about 30 h. The resulting solution was centrifuged at 3000 rpm for 10 min, and the supernatant was collected, which was centrifuged again at 10000 rpm for 10 min. The precipitate was collected and redispersed in deionized water. The color of the resulting solution varies with the amount of silver ions added, which is indicative of gold nanorods with different aspect ratios. Figure 1 shows various solutions prepared with different amounts of silver ion addition and their corresponding UV−vis spectra. The leftmost solution is produced when no silver ion solution is added and consists of mostly spherical particles with a very small amount of gold nanorods. Its UV−vis spectrum exhibits a single absorption peak at 530 nm. When silver ions are added, gold nanorods are formed which can be seen from the additional absorption peak due to the longitudinal surface plasmon in the UV−vis spectrum. Typically their UV−vis spectra show one transversal surface plasma peak at 520 nm and longitudinal ones at 600−800 nm.

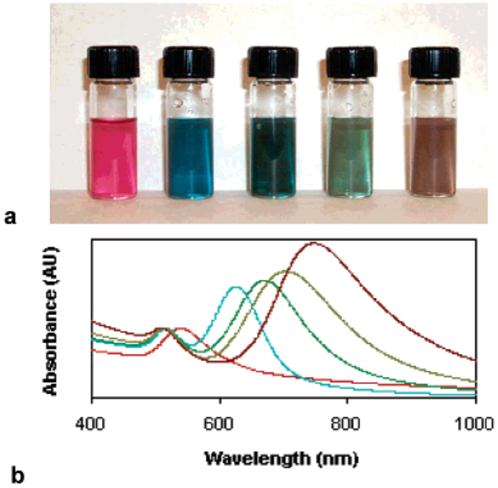

Figure 1. (a) Image of photochemically prepared gold nanorods solution, and (b) corresponding UV−vis spectrum. The leftmost solution was prepared with no silver ion addition. The other solutions were prepared with addition of 15.8, 31.5, 23.7, 31.5 μL of silver nitrate solution, respectively. The middle solution was prepared with longer irradiation time (54 h) compared to that for all other solutions (30 h), and the transformation into shorter rods can be seen.

Figure 2 shows transmission electron microscopy (TEM) images of gold nanorods produced by addition of 15.8, 23.7, and 31.5 μL of silver nitrate solution. The average aspect ratios for these rods are 2.8, 3.5, and 4.8, and the average diameter is 18, 15, and 12.6 nm, respectively. As can be seen, there is an apparent increase in the aspect ratio accompanied with a decrease in the diameter when more silver ion is added. However, there is a limitation to how much silver ion can be added, and with the current conditions the largest aspect ratio we were able to get was $\sim$5. However, by controlling the concentration of gold, we expect to obtain longer rods. Figure 2d shows a high-resolution TEM image of one of the nanorods. The crystallographic facets are the same as the electrochemically synthesized gold nanorods,[11] with the growth direction being [001] and the side mostly covered with {001} and {110} facets.

Irradiating the solution with UV light for an excess time produces shorter rods for a given silver ion concentration. This is possibly due to the transformation of the rods into the thermodynamically more stable spherical form.[12] It is also consistent with previous studies done on the electrochemically synthesized gold nanorods.[13] The degradation generally stops after a certain time ($\sim$40 h).

TEM studies at different points during the growth have been carried out. Preliminary results show that irregular polycrystalline

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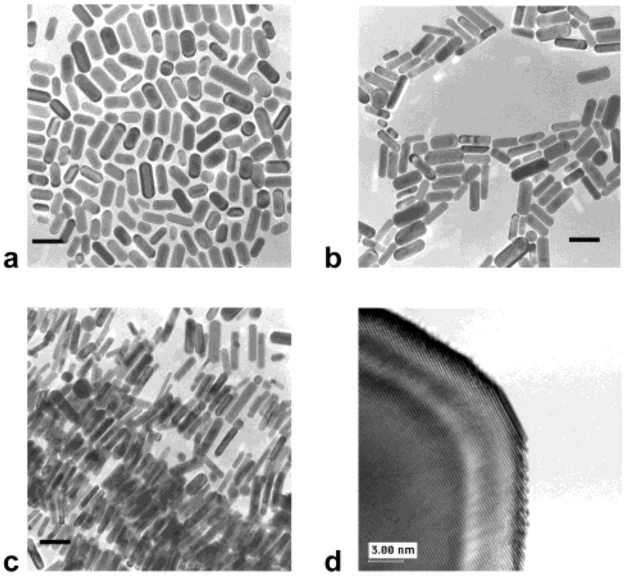

Figure 2. Transmission electron microscopy (TEM) images of gold nanorods prepared with (a) 15.8 μL, (b) 23.7 μL, (c) 31.5 μL of silver nitrate solution. The bar indicates 50 nm. (d) High-resolution image of a gold nanorod.

particles of gold and silver alloy are produced in the early stage right before the rod formation. This is quite surprising since elemental analysis using energy dispersive X-ray spectroscopy (EDS) confirms that there is little or no detectable amount of silver within the final gold nanorod products (see the Supporting Information). Time-resolved TEM studies on the electrochemical nanorod synthesis were also carried out for comparison, and we observed similar polycrystalline nanoparticles at initial stages.

Controlled experiments have been carried out to resolve the mechanism of the rod formation. It was found that Ag ions (in the form of AgBr) were photochemically reduced into Ag nanoclusters by the UV irradiation in the absence of $AuCl_4^-$ ions. These Ag clusters, however, can be oxidized back into AgBr when $AuCl_4^-$ ions are present, which explains the absence of Ag in the final nanorod products. Interestingly, when chemically synthesized Ag nanocrystals[14] were added to the photochemical process, nanorods with similar aspect ratios are obtained (see the Supporting Information). Since direct UV photo reduction of $AuCl_4^-$ ions in the absence of Ag results in mainly spherical particles, a rodlike micellar templating mechanism is less likely in the current process. The growth of Au nanorods in the presence of Ag ions or clusters indicates that silver is playing a critical role in regulating the nanocrystal shapes. Note that silver exists in either AgBr or neutral cluster form because of the competition between the photoreduction and chemical reactions with $AuCl_4^-$. This redox dynamics modulates the nascent surfaces of Au nanocrystals (produced by UV reduction) in an as yet-to-be-determined manner, and subsequently the growth rate along a particular direction ($\langle 001 \rangle$ in the current case) is enhanced. It is interesting to note that the previously reported electrochemical method[9] and seeding method[7] has also relied on silver ion addition for controlling the aspect ratio. We believe these processes share the same growth mechanism as our photochemical approach.

There have been studies on other photochemically synthesized nanowires suggesting that formation of one-dimensional gold nanostructures might occur through a combination of crystal aggregation and specific crystal face stabilization.[15−17] This aggregation-based particle formation has been also observed in other materials such as α-Fe_2O_3,[18] TiO_2,[19] and CdTe.[20] On the basis of our time-resolved UV−vis absorption and TEM studies, it is likely that the nanorod growth is based on a similar mechanism, where the role of silver (or AgBr) is to control/facilitate the aggregation of the particles and then be phase-separated from the final gold nanorods.

In conclusion, gold nanorods with controlled aspect ratios have been synthesized via a simple photochemical process. The amount of silver ions added to the system dictates the aspect ratio of the final rods. Ongoing efforts are being directed to resolve the details of the metal nanorod formation mechanism.

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Supporting Information Available: Figures showing the energy dispersive X-ray elemental analysis of the final Au nanorods and TEM image of Au nanorods prepared using Ag clusters as seeds during the photochemical reduction (PDF). This material is available free of charge via the Internet at http://pubs.acs.org

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