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Nanocrystals

# Selective Placement of Faceted Metal Tips on Semiconductor Nanorods**

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There is strong interest in the sequential synthesis of multicomponent nanostructures where there are segregated regions of different materials within one particle.[1] To this end, there have been many reports on core–shell nanostructures[2] as well as metal-semiconductor hybrids.[3] Very recently, synthetic routes have even achieved the selective placement of one component onto another component of complex shape with a high degree of reproducibility.[4] As an example, a metal (or semiconductor[5]) can be selectively grown on the tips of semiconductor nanorods or onto semiconductor tetrapod arms.[4,6] The potential utility of such structures was recently demonstrated in two different applications exhibiting the flexibility of such hybrid materials. In one study, the single particle conductivity was enhanced by many orders of magnitude when Au nanoparticles were selectively grown onto the ends of CdSe nanorods, compared with CdSe nanorods that did not have Au tips.[7] In a second study, platinum tips were grown onto nanorods which had a CdSe seed embedded within a CdS nanorod. The catalytic activity of these particles with respect to hydrogen reduction in the overall water splitting reaction was then examined. It was demonstrated that the catalytic activity of the structure could be affected by either altering the length of the nanorod or by controlling the size of the CdSe seed.[8]

In prior work, the metal tips selectively deposited on the ends of semiconductor rods have been of undefined shape and faceting. Yet the catalytic activity and selectivity of the metal particles is strongly related to the crystal shape and specific surface facet on which the chemical reaction occurs.[9] Herein, we demonstrate that it is possible to specifically control the faceting of metallic nanocrystals grown in colloidal solution on the tips of semiconductor nanorods by depositing cube-shaped Pt nanoparticles at the tips of both CdS and CdS/CdSe seeded nanorods.

The cube-like particles were formed in two steps: an intitial deposition of Pt without shape control, followed by further growth in the presence of a molecule that favors defined facets. To initially grow platinum tips on the nanorods, a calculated quantity of nanorods was mixed with platinum acetylacetonate (Pt(acac)$_2$), 1,2-hexadecanediol (HDD), oleic acid (OAC), and oleylamine (OAM) in a solution of diphenyl ether (see Supporting Information for experimental details). The procedure is similar to that reported by Habas et al., with slight modifications.[10]

This reaction yields small, Pt-metal particles of mostly undefined shapes on the rod tip. The metal particles were formed preferentially on either one or both tips ({0001} facets) of the nanorods (Figure 1, middle column), depending on the initial nanorod concentration. For our experiment we chose an initial rod concentration of 2.9 nmol (the amount of the Pt-precursor and a detailed description are given in the Supporting Information). This method achieved a high yield of nanorods having either one or two Pt-tips. HRTEM analysis of the as-synthesized samples did not show specific faceting of the small Pt tips (Supporting Information, Figure S4).

To grow faceted, cube-like tips, we used carbon monoxide as both the metal-reducing and shape-directing agent. It has been well established that CO adsorbs preferentially to specific metal surfaces.[11] In some cases, this selective binding[12] can lead to directed growth of Pt atoms onto specific facets of the Pt nanoparticle. Carbon monoxide can also undergo oxidation to $CO_2$ on selected Pt facets.[13] The behavior of CO molecules bound to Pt is also contingent on which facet the molecule is bound to. For example, CO molecules bound to the {100} surface of Pt are slightly more stretched and closer to the particle surface than CO molecules bound to the {111} facet of Pt.[13] This is a result of the stronger binding of CO on the {100} Pt surface with respect to the {111} surface. In the case of platinum, these different binding

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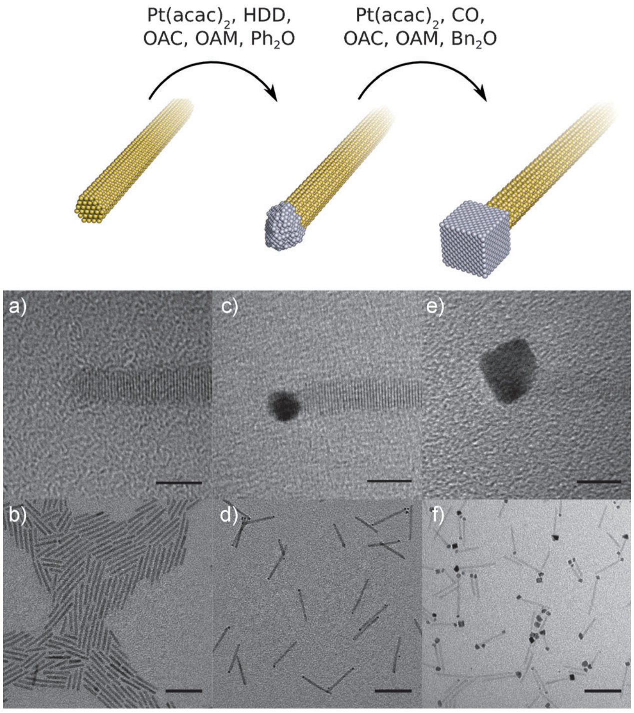

***Figure 1.*** Scheme of the three-step synthetic process leading to faceted Pt-tipped semiconductor nanorods. HRTEM images of a,b) CdS nanorods, c,d) pre-tipped nanorods, and e,f) faceted-tipped nanorods. Scale bars: a,c,e) 5 nm and b,d,f) 50 nm.

strengths of CO to the {100} facets with respect to the {111} facets might lead to the unique shape-directing effects shown earlier for free-standing particles,[14] manifesting in cubic Pt structures attached to the semiconductor nanorods. Also, recent reports have suggested that CO is an adequate reducing agent[14,12] and can be used to form Pt cubes, Pd spheres, and Au nanowires.[14]

We exploited the coupled effects of CO as both a reducing agent and a shape-directing agent to manipulate the Pt tips to transform from unfaceted and undefined shapes to faceted cube-like particles. To obtain cube-like, faceted Pt tips, the pre-tipped nanorods were dispersed in a solution of 3.68 mL oleylamine (OAM), 0.63 mL of oleic acid (OAC), and 40 mg of platinum acetylacetonate in benzyl ether. Carbon monoxide gas was then introduced from a tank 30 minutes before and during the reaction. These reaction conditions are similar to those present in previous free-standing Pt-nanocube synthesis. In our synthesis, the growth to faceted metal particles starts with small Pt-nuclei that are already formed on the rod tips, and addition of CO promotes the transformation to cube-like, faceted Pt tips.

Under vigorous stirring, the reaction flask was immersed into an oil bath (200 °C) for 4–5 minutes and then quickly quenched using a water bath at room temperature. This method enabled reproducible heating profiles during the relatively short reaction time. Our method leads to faceted Pt tips attached to the nanorods as shown in Figure 1. We also synthesized cadmium selenide seeded CdS-nanorods (CdSe@CdS) and grew faceted, cube-like Pt tips onto the seeded rods demonstrating that this method is robust and can be applied to varying rod materials. The UV/Vis absorption and emission spectra of the CdSe@CdS-semiconductor rods, as well as of the CdSe-seeds can be found in the Supporting Information (Figure S2).

During preliminary experiments we found that the yield of tipped rods could be significantly increased by pre-tipping the semiconductor nanorods, so we chose to grow the faceted Pt tips from small Pt-seeds placed on the tip of the semiconductor nanorods. We attribute the higher yields following this approach to the relatively high ligand concentration in the common CO-based Pt-cube synthesis,[14,15] compared to the Pt-tipping process[10] leading to the initial, unshaped tips. We assume that the higher ligand concentration increases the probability of homogeneous nucleation events and therefore makes the faceted-growth reactions unsuitable for the initial tipping step.

Figure 2b shows the X-ray diffraction pattern of CdS-nanorods, which confirms the wurtzite crystal structure of the nanorods. High-resolution transmission electron micrographs (Figure S3) clearly show lattice fringes along the ⟨0001⟩ axis of the CdS-nanorods, which represents the unique *c*-axis of the nanorod. The wurtzite crystal structure of the nanorods leads to dissimilar (0001) and (000$\bar{1}$) facets of the nanorod terminal ends.[16] Several lines of evidence suggest that the terminal facets have a lower ligand density than the rod sidewalls. Terminating atoms on the (000-1) facet show either three (000-1Cd) or one (000-1S) dangling bonds, while terminating cadmium atoms on the (0001) facet have one and terminating sulfur atoms three dangling bonds. These dangling bonds increase the reactivity of the terminal facets and the lower ligand density allows for facile access to the nanorod surface resulting in the preferential growth of Pt on the nanorod tips in the first step. The reduction of platinum in the presence of the CO containing solution during the second

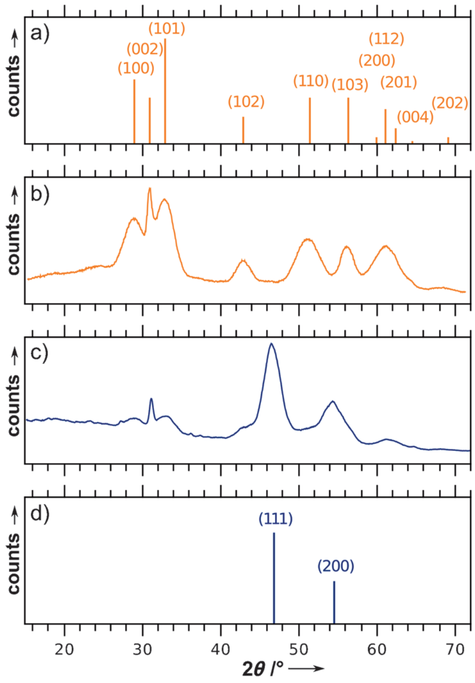

***Figure 2.*** X-ray diffraction patterns of b) CdS nanorods and c) faceted Pt-tipped CdSe@CdS nanorods. For comparison, reference diffractograms are given for a) CdS and d) Pt.

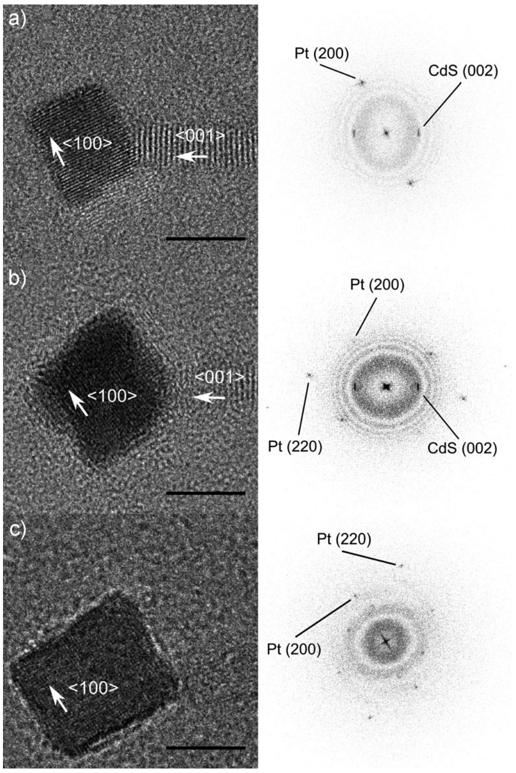

***Figure 3.*** a,b,c) HRTEM micrographs of faceted Pt tips on the tips of CdSe@CdS nanorods (left column) with corresponding FFTs (right column). Scale bar: 5 nm.

step led to faceted tip growth. Figure 2c shows the X-ray diffraction pattern of the faceted Pt-tipped nanorod structures. Reflections of the face-centered cubic (fcc) Pt tips as well as reflections originated from the wurtzite–CdS@CdSe nanorods are clearly visible and confirm the crystallinity of both compounds.

Figure 3 shows different HRTEM-micrographs depicting cubic Pt tips on CdSe@CdS nanorods and their corresponding fast Fourier transform patterns (FFTs). The orientation of the $\langle 100\rangle$ zone axis towards the edges of the tips is clearly visible and confirms the $\{100\}$ faceting of the Pt tips. Orientation of the Pt tip with respect to the CdSe@CdS rod indicates a preferential alignment of the Pt $\langle 110\rangle$ axis with the $\langle 0001\rangle$ axis of the rod with a misorientation angle of approximately 5°. The method of growing faceted-Pt-tipped semiconductor-metal heterostructures proposed in this paper is not limited to nanorod shaped particles. For example, tetrapod shaped structures, which were obtained as a byproduct in the semiconductor nanorod synthesis could be found in the final reaction product, having cubic Pt tips attached to the arms of the tetrapods. However, a definitive and careful study on how the semiconductor shape effects the growth of the metal tip is still required.

In summary we present a method to achieve $\{100\}$ faceting of Pt tips on different semiconductor nanorod structures. This demonstrates both selective placement and shape control of a metal component onto a semiconductor nanostructure. These novel particles open the possibility of examining facet effects on the catalytic activity of hybrid semiconductor-metal nanostructures.

## Experimental Section

A solution of platinum acetylacetonate was formed by dissolving 40 mg Pt(acac)$_2$ in 5.00 mL benzyl ether, 3.68 mL oleylamine, and 0.63 mL oleic acid. Isopropyl alcohol was added to a calculated amount of pre-tipped nanorod solution, followed by centrifugation at 4000 rpm (2576 × g). The precipitate was dried and redissolved in the previously prepared platinum precursor solution. The resulting mixture was transferred to a 25 mL three-neck flask. After bubbling CO into the stirred reaction mixture for 30 min (approximately 10 mL min$^{-1}$), the flask was immersed into a preheated oil bath (approximately 200 °C). After 4–5 min the reaction was quenched by immersing the flask in cold water. The product was isolated by adding approximately 6 mL isopropyl alcohol and centrifuging at 4000 rpm (2576 × g).

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