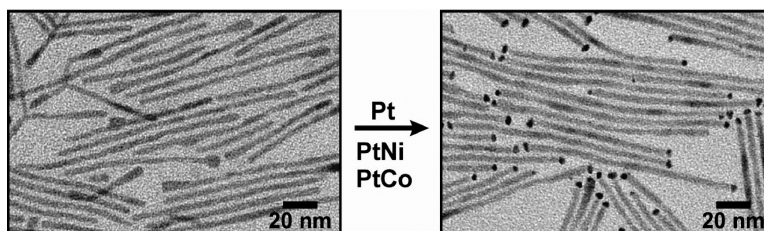


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Selective Growth of Metal and Binary Metal Tips on CdS Nanorods

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Advances in the size¹ and shape² control of solution-grown nanocrystals have driven recent interest in the development of well-defined multicomponent nanostructures. Composition control, through the incorporation of two or more distinct nanostructured components, represents an effective approach to tailoring the chemical and physical properties of nanocrystals. The resulting hybrid structures often have multifunctional capabilities with tunable or enhanced properties.

Alloy and core/shell structures are two of the most fundamental types of hybrid nanomaterials. These structures have been prepared for various materials with distinctive properties. For example, metal alloy and core/shell nanoparticles have been demonstrated for systems such as FePt and CoPt₃ alloys³ and Pt/Pd core-shell particles.⁴ Analogous systems have also been shown for semiconductor nanocrystals, including PbSe_xS_{1-x} alloys,⁵ CdSe/ZnS core-shell particles,⁶ and other compositions. Recently, one of the coauthors demonstrated a novel route to form heterostructures by the selective growth of metals on semiconductors.⁸ This type of metal-semiconductor composite combines two materials with different properties to yield a unique hybrid nanostructure with new properties and functionalities. Various approaches have been used to selectively grow metals on semiconductors through reduction, physical deposition, or photochemistry. Some of the materials that have been developed include Au-CdSe,⁷ Au-CdS,⁸ Au or Ag on ZnO,⁹ Co and Au on TiO₂,¹⁰ and other systems.¹¹

Recently, Weller and co-workers demonstrated an organometallic approach to prepare Ni_xPt_{1-x} nanocrystals¹² with magnetic properties that are of interest for high-density data storage and other applications. Additionally, bimetallic materials often exhibit properties distinct from their constituent metals. For example, NiPt nanoparticles have potential application as catalysts, where they show enhanced activity for oxygen reduction relative to pure Pt.¹³

Herein, we demonstrate the synthesis of three systems: Pt-CdS, PtNi-CdS, and PtCo-CdS hybrid nanostructures with controllable size and composition. A mixture of Pt precursor and CdS rods was injected into diphenyl ether containing oleylamine and oleic acid at 200 °C. The reaction was quenched after several minutes, and the Pt-CdS composite separated from free metal particles by centrifugation. Ni or Co precursors could be added to the diphenyl ether prior to heating to promote bimetallic PtNi or PtCo formation (see Supporting Information for experimental details).

Figure 1 shows the selective growth of Pt nanoparticles (4.3 nm) on CdS nanorods (120 nm × 4 nm). The anisotropic wurtzite crystalline structure of the CdS allows for selective chemistry on different facets. The reactivity of the nanorods is higher at the tips than along the body of the rod due to the increased surface energy, which also leads to preferential growth along the <001> axis of the CdS rods, as can be seen in the transmission electron microscopy

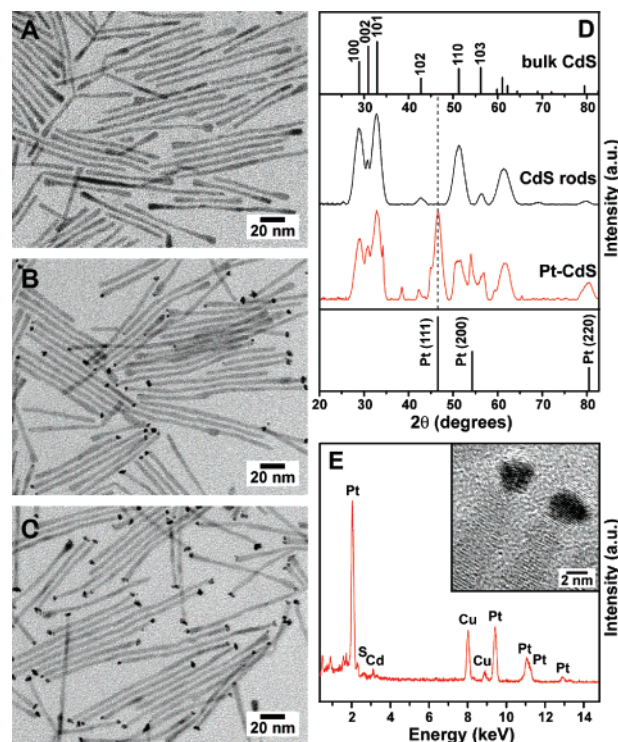


Figure 1. Selective growth of Pt nanoparticles with different sizes on CdS nanorods, (A) CdS rods (120 nm × 4 nm), (B) CdS with small single Pt tips (4.3 nm), (C) CdS with larger double Pt tips (5.7 nm), (D) XRD patterns of CdS rods and Pt-CdS hybrid structures with corresponding CdS and Pt bulk patterns (stick patterns shown above and below, respectively), and (E) selected area EDS spectrum of a single Pt tip, with inset HRTEM image of two Pt-CdS hybrids.

(TEM) image in Figure 1A. During the early stages of Pt growth, or at a low Pt concentration, Pt deposition appears to occur preferentially on one tip of the rods (Figure 1B). This can be understood by considering the distribution of Cd and S along the <001> axis. The lattice planes along the axis are alternately composed of either Cd or S atoms, which makes growth at earlier stages more favorable on the S rich facets. Alternatively, due to the considerable length of the CdS rods relative to the metal particles, each tip may act as an isolated nucleation site independent of the opposite tip. Therefore, if the concentration of metal precursors is low enough that some of the rods do not experience metal growth on either tip, then, statistically, the remainder of metal nucleation will occur on only one of the tips. Increasing the amount of Pt relative to the concentration of CdS rods leads to two sided growth (5.7 nm), as shown in Figure 1C.

The XRD patterns in Figure 1D for pure CdS rods and the Pt-CdS heterostructures agree well with the bulk CdS wurtzite crystal structure and face-centered cubic Pt. Selected area energy dispersive X-ray spectroscopy (EDS) performed on a single metallic tip (Figure

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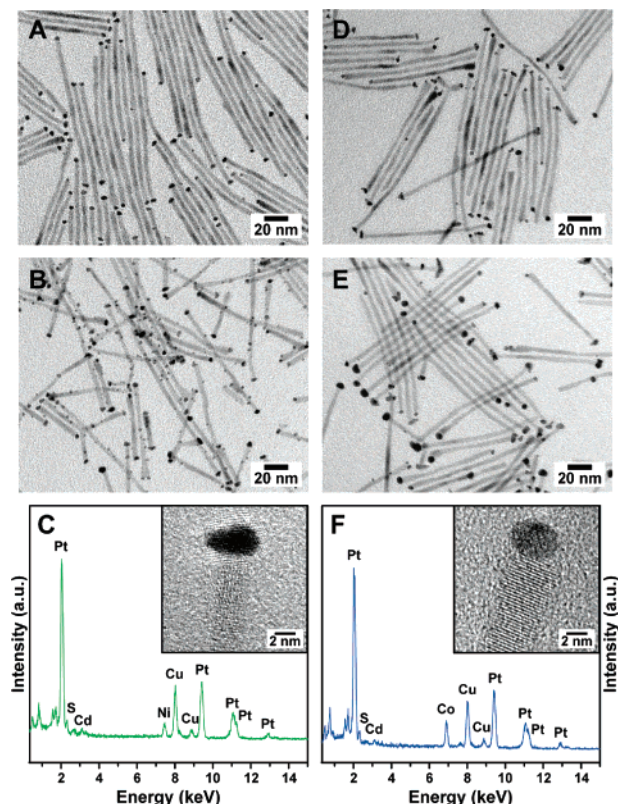


Figure 2. TEM images of binary-CdS heterostructure nanoparticles with different sizes and compositions: (A) PtNi-CdS (4.7 nm), (B) PtNi-CdS prepared with increased metal concentration showing a loss of selectivity, (C) selected area EDS spectrum taken on the tip of a PtNi-CdS hybrid structure, (D) PtCo-CdS (5.2 nm), (E) larger PtCo-CdS (7.2 nm), and (F) selected area EDS spectrum of a PtCo-CdS heterostructure.

1E) indicates that the tip contains Pt. High-resolution TEM (HRTEM, Figure 1E inset; see Figure S1A for enlarged image) confirms that both the CdS rod and the Pt tip are crystalline. The growth axis of the CdS nanorods is along the $\langle 001 \rangle$ direction, although the metal tips do not appear to have any preferential orientation with the rods.

Growth of binary metals on semiconductors may be of particular interest for photocatalytic and photovoltaic applications. Figure 2 shows the selective growth of PtNi and PtCo on CdS nanorods. As described earlier for Pt, selective growth of the binary material can be achieved by adding the desired metal precursor to the growth solution prior to heating. Small PtNi nanoparticles (4.7 nm) were grown with high selectivity on the tips of the CdS rods (Figure 2A). At lower metal concentrations, PtNi also exhibits growth on only one of the tips. As the amount of PtNi is increased relative to the CdS rod concentration, however, growth occurred along the body of the rod as well as at the tips (Figure 2B). Selected area EDS shows the presence of both Pt and Ni in the tip (Figure 2C, representative HRTEM inset; see Figure S1B for enlarged image). Analysis on a larger sampling of tips gives an average of 25% Ni relative to Pt.

Hybrid structures of PtCo-CdS were prepared in the same manner. Unlike the PtNi-CdS system, however, PtCo exhibited a high degree of selectivity for nanocrystal tips of sizes 5.2 and 7.2 nm shown here in Figure 2D and E. Selected area EDS performed on one of the smaller tips shows the presence of both Pt and Co (Figure 2F, representative HRTEM inset; see Figure S1C for enlarged image). The size variation in the PtCo tips from 5.2 to 7.2 nm was accompanied by a change in composition (determined by EDS on a larger sampling of tips) from 30% to 50% Co relative

to Pt, respectively. Altering the composition of the tips could have a direct effect on the catalytic activity of these materials. The XRD measurements performed on the binary metal structures (Figure S2) provide evidence for the presence of crystalline CdS and Pt. There was no evidence for pure Ni or Co phases or their respective oxides. Analysis by selected area EDS clearly indicates the presence of Ni (Figure 2C) or Co (Figure 2F) in the tips of the PtNi-CdS and PtCo-CdS hybrid structures, respectively.

The synthesis described here differs from the previous approach used to grow Au on CdSe.⁷ Attempts to grow Pt onto CdSe at room temperature with didodecyltrimethylammonium bromide and dodecylamine in toluene resulted in no reduction. Also, the attempts to grow Au on CdS resulted in growth of metal clusters over the entire rod, with less selectivity for the tips. The advantages of the approach used here, include high growth selectivity, retention of the rod size because of the absence of etching, and control over the composition of the metal tips.

The development of Pt-CdS, PtNi-CdS, and PtCo-CdS multicomponent heterostructures, and multicomponent nanostructures in general, is an emerging field in nanoscience. Systems like these represent a new class of materials, where catalytic metals are paired with a semiconductor material within the same structure. These heterostructures are of special interest for a variety of applications including photocatalysis, water splitting, and magnetic applications.

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Supporting Information Available: Experimental details of the synthesis, enlarged HRTEM images of the three materials, and XRD patterns of the bimetallic heterostructures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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