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# Synthesis of CuPt Nanorod Catalysts with Tunable Lengths

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Pt and Pt-containing alloys are important industrial catalysts and have many interesting properties and practical applications, particularly as nanoparticles.[1−5] For example, Pt nanoparticles are efficient catalysts for CO oxidation and steam reforming reactions. Pt−M alloys (M = Fe, Co, Ni) have also been found to exhibit useful magnetic properties.[6−8] From a catalysis perspective, Pt is expensive, and it is usually poisoned by CO, C, or S. This results in the blocking of active sites, reducing over time their catalytic efficacy. The ability to create bi- or trimetallic Pt-based nanomaterials may prove to be a useful route for reducing the overall cost of the catalyst while retaining desirable catalytic properties and also affording a decrease in susceptibility to poisoning.[9−13]

Facile, controllable syntheses of uniform, shape-controlled Pt alloy nanocrystals that incorporate inexpensive and readily available late-3d transition metals are important steps in this direction, but few examples are known. Recent examples include FePt spheres,[6] cubes,[14] and ultrathin rods;[15−17] $CoPt_3$ spheres and cubes;[18] NiPt spheres and faceted derivatives;[19] and PtPb nanorods.[20] The synthesis of one-dimensional (1D) nanostructures is particularly interesting, as anisotropic morphologies can dramatically influence the physical properties.[21,22] However, 1D Pt alloy nanostructures remain rare, presumably because of the synthetic challenges associated with inducing anisotropic growth while controlling multielement composition.

Here we report a colloidal method for the synthesis of uniform ultrathin CuPt nanorods with diameters of ~2.5 nm and aspect ratios that are tunable from approximately 5:1 to 25:1. Bimetallic CuPt alloys have extensive applications in catalytic hydrogenation and dehydration and in dechlorination of chlorinated hydrocarbons as well as potential for use as heterogeneous $NO_x$ reduction and CO oxidation catalysts.[23,24] While there have been some reports of methods for synthesizing CuPt nanoparticles, including coprecipitation and impregnation, reverse micelles, and polyol reduction,[24−26] there have been no reports of highly controllable 1D CuPt nanostructures. Here we describe a facile synthetic approach to the synthesis of 1D CuPt nanostructures with tunable size and detail the catalytic activity of these materials for CO oxidation.

CuPt nanorods were synthesized using standard air-free techniques. In a typical synthesis, 43 mg of $Pt(acac)_2$, 24 mg of $Cu(acac)_2$, 105 mg of 1,2-hexadecanediol, 0.6 mL of oleic acid, and 0.8 mL of oleylamine were mixed together with 5.0 mL of 1-octadecene in a 100 mL three-neck round-bottom flask. The flask was purged with Ar, heated to 120 °C for 20 min, and then heated to 225 °C at a rate of ~20 °C/min. After 30 min, the black-colored solution was cooled to room temperature. The as-synthesized samples often contained a mixture of spherical CuPt nanoparticles and CuPt nanorods, which were separated in high yield by precipitation and centrifugation (see the Supporting Information).

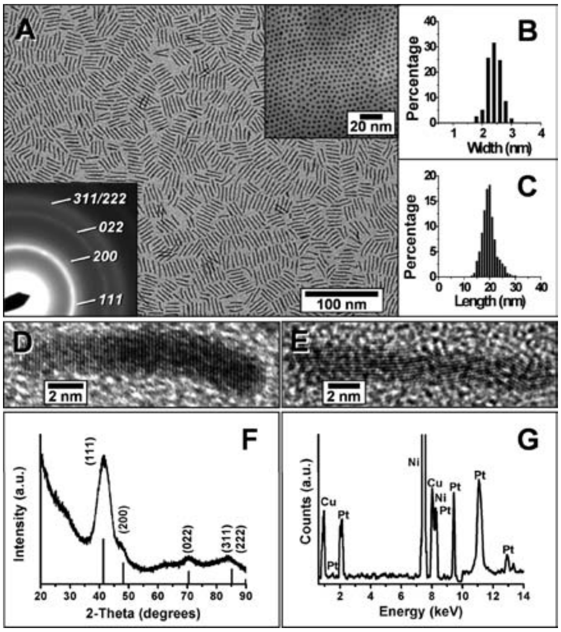

***Figure 1.*** CuPt nanorods. (A) Representative TEM image. Left inset: corresponding SAED pattern. Right inset: image of spherical CuPt nanoparticles. Histograms of (B) diameter and (C) length. HRTEM images of (D) a single-crystal nanorod and (E) stacking faults. (F) XRD pattern. (G) EDS analysis.

Figure 1A shows a transmission electron microscopy (TEM) image of a representative sample of CuPt nanorods with dimensions of 20.3 ± 2.7 nm × 2.3 ± 0.2 nm, corresponding to an aspect ratio of ~9:1. The inset shows the monodisperse CuPt spheres that were separated from the nanorods by centrifugation.

The size distribution histograms confirm the uniformity in both diameter (Figure 1B) and length (Figure 1C). The selected-area electron diffraction (SAED) pattern (Figure 1A, left inset) shows an fcc structure, which is consistent with a single-phase CuPt alloy. Most of the nanorods appeared to be either single-domain crystals (Figure 1D) or nanorods with twin boundaries (Figure S2 in the Supporting Information) and stacking faults (Figure 1E). The visible lattice fringes correspond to a spacing of 0.22 nm, which matches well with the expected *d*-spacing of the (111) plane of the CuPt alloy (0.218 nm). Lattice planes with a spacing of 0.19 nm were also present, and these are consistent with the (200) plane (0.189 nm).

The powder X-ray diffraction (XRD) pattern (Figure 1F) also shows an fcc structure, with peak positions that are intermediate between those of Cu and Pt. The XRD data yield a lattice constant of $a = 3.75$ Å, which suggests an approximate composition of $Cu_{55}Pt_{45}$ on the basis of Vegard's law ($a_{Cu} = 3.615$ Å, $a_{Pt} = 3.923$ Å). The energy-dispersive X-ray spectrum (EDS) in Figure 1G also

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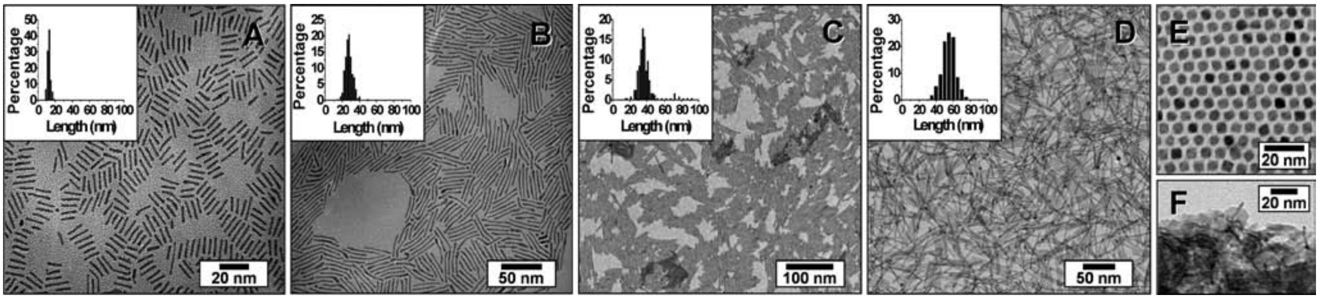

***Figure 2.*** TEM images of CuPt nanorods with average lengths of (A) 12.6 ± 1.9, (B) 27.8 ± 4.4, (C) 37.1 ± 10.1, and (D) 55.5 ± 7.8 nm (histograms of lengths are shown in the corresponding insets) and of (E) CuPt cubes and (F) the $\gamma$-$Al_2O_3$-supported CuPt nanorod catalyst prior to reaction.

indicates a Cu/Pt ratio of 55:45, matching the estimate from Vegard's law and consistent with a nearly 1:1 CuPt alloy. The XRD peaks are broad, with Scherrer analysis of the 111 peak indicating a grain size of ~3 nm. This is consistent with the average width of the nanorods (Figure 1D,E). The XRD data also show evidence of preferred orientation, with the 111 peak having a higher intensity relative to the 200 and other peaks than would be expected for an isotropic sample. Because of their uniformity, the nanorods tend to self-assemble into long chains (Figure S3).

Oleylamine is required to form CuPt nanorods, presumably to stabilize the (100) faces during growth. By variation of the oleylamine/oleic acid ratio as well as the reduction rate, solvent, and temperature, the morphology and nanorod length can be tuned. When 0.6 mL of oleylamine and 0.8 mL of oleic acid were used, average nanorod lengths of 12.6 ± 1.9 nm were obtained (Figure 2A). Increasing the amount of oleylamine to 1.2 mL yielded nanorods with an average length of 27.8 ± 4.4 nm (Figure 2B). The nanorod length could be increased to 37.1 ± 10.1 nm (Figure 2C) and 55.5 ± 7.8 nm (Figure 2D) by using diphenyl ether and dibenzyl ether, respectively, as the solvent. Monodisperse spherical CuPt nanocrystals formed at shorter heating times and lower temperatures, and CuPt nanocubes formed when larger amounts (210 mg) of 1,2-hexadecanediol were used (Figure 2E).

To investigate the catalytic properties of these materials, the CO oxidation activity was examined for the CuPt nanoparticles and nanorods supported on $\gamma$-$Al_2O_3$ and compared to that of a commercial $Pt/Al_2O_3$ catalyst. After the catalyst was cleaned by UV−ozone treatment at a $CO/O_2$ ratio of 2:1, the average light-off temperature for the CuPt nanorods (20 nm × 2 nm) supported on $\gamma$-$Al_2O_3$ (Figure 2F) was 556 K. Under the same reaction conditions, the light-off temperature obtained for the CuPt spherical nanoparticles (~2.5 nm diameter) was ~490 K. These light-off temperatures are significantly below the value of ~700 K obtained for the commercial $Pt/Al_2O_3$ catalyst, which employs ~2−3 nm Pt particles. These results are consistent with those of CO oxidation studies using Cu deposited on Pt(111) surfaces, which showed increased catalytic activity compared with pure Pt.[27] The increased activity for Cu alloyed with Pt in a nanoparticle form is likely the result of lowering the desorption temperature for CO from the reactive Pt sites. As such, these bimetallic nanomaterials offer a potential approach for reducing CO poisoning of Pt when used in polymer electrolyte membrane (PEM) fuel cells.

In summary, we have demonstrated a straightforward colloidal method for the synthesis of size- and shape-controlled CuPt nanoparticles and nanorods with tunable lengths and aspect ratios. These nanoparticles were found to be highly active for CO oxidation compared with a commercial supported Pt nanoparticle catalyst of comparable particle size. The ability of this method to tune the nanorod lengths over a wide range, coupled with the realistic possibility of extending this to other Pt alloy systems (e.g., CoPt, PtAg), makes the application of this strategy to other important magnetic and catalytic systems feasible.

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

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