Localized Pd Overgrowth on Cubic Pt Nanocrystals for Enhanced Electrocatalytic Oxidation of Formic Acid

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Cubic Pt seeds and core-shell Pt/Pd nanocubes
The syntheses of cubic Pt seeds and core-shell Pt/Pd nanocubes were reported elsewhere [1,2]. Briefly, 1 mM aqueous K2PtCl4 in 100 mM TTAB (tetradecyltrimethylammonium bromide) was reduced by 30 mM NaBH4 at 50 °C. Excess H2 evolved from the reacting solution was released by inserting a needle into the septum. After 6 hrs, the reaction was allowed to cool to room temperature and left overnight to allow the remaining NaBH4 to decompose in water. The cubic Pt nanoparticles were collected and washed by repeated centrifugation and sonication.

The pH of the seed solution was decreased from ~9 to ~3 to ensure decomposition of residual NaBH4 by the addition of HCl, and then neutralized with NaOH. Conformal overgrowth of Pd on cubic Pt seeds was achieved by introducing Pt seeds (100 μl) and L-ascorbic acid (50 μl of 100 mM solution) into an aqueous solution (5 ml) containing 100 mM TTAB and 0.5 mM K2PdCl4 that had been heated at 50 °C for 5 min. The core-shell Pt/Pd nanocubes were removed from the heat after 1 hr.

Localized overgrowth of Pd on cubic Pt seeds
Overgrowth of Pd was localized in multiple positions on Pt nanocubes by adding Pt seeds (250 μL) that had not been acidified (pH~9) and L-ascorbic acid (25 μL of 100 μM L-ascorbic acid) to the reaction mixture.
mM) to an aqueous solution (5 mL) containing 100 mM TTAB and 0.25 mM K₂PdCl₄. The reduction of Pd occurred within minutes. Acidification and then neutralization of the seeds, under these conditions, decreased the rate of reduction and gave overgrowth of a conformal shell.

**Sample characterization**
The structure and composition of the samples was investigated by TEM (JEOL 200CX and Tecnai G2 S-Twin) and high resolution TEM (Philips, CM200). All TEM investigations, with the exception of those done on the Tecnai G2 S-Twin, were performed at the National Center for Electron Microscopy. Samples were centrifuged and washed with fresh TTAB solution and then water before re-suspending in water and drying on a carbon coated copper grid for TEM.

**Electro-oxidation of formic acid**
Electrochemical measurements were carried out in 0.25 M formic acid + 0.5 M H₂SO₄ solution at room temperature. A three-electrode cell was used with a standard calomel electrode (SCE) as a reference electrode (all potentials in this paper are quoted versus the RHE electrode) and a platinum wire as a counter electrode. The nanoparticles used in this study were washed and concentrated, then deposited on the surface of a gold disk (5 mm in diameter). The deposited nanoparticles were dried at room temperature. For CO stripping experiments, CO gas (Praxair, 99.99%) was bubbled at an open circuit through 0.5 M H₂SO₄ solution while the electrode with nanoparticles was immersed in the solution. Bubbling was stopped after full poisoning was confirmed by complete loss of the H₂ adsorption/desorption peak. Usually, CO gas was bubbled for 10 min. The electrode was quickly moved to a fresh solution and the stripping experiment was done at a sweep rate of 50 mV/s.
Figure S1. TEM images of (a) cubic Pt nanoparticles (12.3±1.4 nm diagonal, 79% cubes, 3% tetrahedra, and 18% irregular shapes), (b) core-shell Pt/Pd nanocubes (37.2±3.0 nm diagonal, ~75%), and (c) Pd nanoparticles synthesized without Pt seeds.

Figure S2. Cyclic voltammetric curves for (a) core-shell Pt/Pd nanocubes and (b) Pd nanoparticles synthesized without Pt seeds in 0.25 M HCOOH + 0.5 M H2SO4 solution at a scan rate of 50 mV/s. The insets are blank voltammograms for the same electrodes in 0.5 M H2SO4 at 50 mV/s taken without formic acid.
Figure S3. Voltammetric CO stripping experiments for (a) Pt nanocubes, (b) binary Pt/Pd nanoparticles, (c) core-shell Pt/Pd nanocubes, and (d) Pd nanoparticles synthesized without Pt seeds, performed in 0.5 M H₂SO₄ at the scan rate of 50 mV/s. CO gas was bubbled through the solution for 10 min at open circuit prior to stripping.

References