[Supplementary Information]

Shaping Pd Nanocatalysts through the Control of Reaction Sequence

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Experimental

In a typical synthesis of Pd nanocubes, 1 mL of 5 mM aqueous solution of K$_2$PdCl$_4$ (Aldrich) was added to 47 mL deionized water and then 1 mL of 30 mM aqueous solution of cetyltrimethylammonium bromide (CTAB, Aldrich) was added to this solution with vigorous stirring. After 10 sec, 1 mL of 100 mM aqueous solution of ascorbic acid was injected into the reaction mixture via syringe within few seconds. After additional stirring for 5 min, the reaction solution was stored under dark. Pd nanodendrites were prepared by just changing the injection sequence of CTAB and ascorbic acid into the reaction solution under otherwise identical synthetic conditions. Multi-armed Pd nanoparticles were synthesized by simultaneous addition of CTAB and ascorbic acid. The resultant Pd hydrosols were centrifuged (10,000 rpm) and re-dispersed in water three times to remove excess reactants in the solution.

The extinction spectra were recorded with a UV-vis absorption spectrometer (Agilent 8453). Scanning electron microscopy (SEM) images of the samples were taken with field-emission scanning electron microscopes (FEI Sirion 600 and Phillips Model XL30 S FEG). Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2010 transmission electron microscope operating at 200 kV. High-resolution TEM (HRTEM) characterizations were performed with a FEI Technai G2 F30 Super-Twin transmission electron microscope operating at 300 kV. X-ray diffraction (XRD) patterns were obtained with a Bruker AXS D8 DISCOVER diffractometer using Cu Kα (0.1542 nm) radiation. Cyclic voltammetry (CV) measurements were carried out in a three-electrode cell using a CH Instrument Model 600C potentiostat. The drop-casting films of nanoparticles on indium–tin oxide (ITO) substrates served as working electrodes. Before CV measurements, the nanoparticles-modified substrates were cleaned by washing with acetone and ethanol. Pt wire and Ag/AgCl (in saturated KCl) were used as the counter and reference electrodes, respectively. All cyclic voltammograms were obtained at room temperature. The electrolyte solutions were purged with high-purity N$_2$ gas before use for about 30-40 min.
**Fig. S1.** HRTEM images of the (a) cubic, (c) multi-armed, and (e) dendritic Pd nanoparticles. High-magnification HRTEM images of the square regions in the HRTEM images (a, c, and e) are shown in (b), (d), and (f), respectively. The $d$-spacing for adjacent lattice fringes measured from several different points on a single nanoparticle was 1.94 Å (Fig. S1b) and 2.24 Å (Figs. S1d and f), which correspond to \{200\} and \{111\} planes of fcc Pd, respectively.
**Fig. S2.** Successive UV-vis absorption spectra (1 min interval) of the reduction of (a) K₂PdCl₄ and (b) K₂PdBr₄ by ascorbic acid. Final concentrations of metal precursors and ascorbic acid were 0.1 and 1 mM. All the experiments were performed under ambient conditions at room temperature. As the reduction reaction proceeds, the ~250 nm peak associated with ascorbic acid decreases. Comparison between spectral changes of different metal precursors clearly shows that the reduction rate of PdBr₄²⁻ was much slower than that of PdCl₄²⁻.

**Fig. S3.** Cyclic voltammograms of indium–tin oxide (ITO) electrodes modified with Pd nanoparticles obtained in 0.1 M HClO₄ at a scan rate of 50 mV s⁻¹. Typical redox peaks associated with the oxidation/reduction of Pd as well as hydrogen adsorption/desorption were observed. The current densities are normalized to the electrochemically active surface areas, which were calculated by measuring the coulombic charge for oxygen desorption with peak potential of around 0.4 V.