One-pot synthesis of hierarchical concave tetrapod Pd nanocrystals and their electrocatalytic properties

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Experimental Details

Materials: palladium acetylacetonate, Pd(acac)₂ (99%) was purchased from Kunming Institute of Precious Metals (Kunming, China), PVP (MW=30000, AR), oleylamine (OAm), DMF, H₂SO₄, formic acid, acetone and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd.(Shanghai, China). All reagents were used as received without further purification.

Synthesis of hierarchical concave tetrapod Pd nanocrystals: In a typical synthesis, 25 mg of Pd(acac)₂, 80 mg of PVP were dissolved in 9 mL DMF to form a light-yellow solution in a 50-mL round-bottomed three-necked flask at room temperature. Then, 1 mL of OAm was added and the mixture became colorless. Under vigorously stirring, CO gas was bubbled continually into the solution at a flow rate of 0.2 mL·sec⁻¹. Following the exclusion of air, the flask was put into an oil bath with 140 °C for 3 h. After being cooled to room temperature, the resulting black colloids were
precipitated by acetone, separated by centrifugation and further purified by ethanol.

**Characterization:** Transmission electron microscopy (TEM) was conducted on a FEI Tecnai G² 20 transmission electron microscopy operated at 200 kV. HRTEM and SAED performed using a FEI Tecnai G² F30 field emission transmission electron microscope operating at 300 kV. The sample for TEM observation was prepared by placing a drop of the colloidal dispersion onto a copper grid coated with a perforated carbon film, followed by evaporating the solvent at ambient temperature. SEM images were taken on a SU8010 field-emission scanning electron microscope operated at 15 kV. X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer employing Cu Kα radiation with 40 kV and 50 mA. X-ray photoelectron spectroscopy (XPS) was performed on a VG Multilab 2000 X-ray photoelectron spectrometer using Mg Kα radiation under a vacuum of 8×10⁻⁷ Pa. All binding energy values were determined with reference to carbon, C₁s = 284.6 eV.

**Electrochemical Measurements:** Pd nanocrystals-modified working electrodes were fabricated by depositing ethanol dispersion of purified hierarchical concave tetrapod Pd nanocrystals onto a glassy-carbon electrode followed by natural drying. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrode, respectively. To investigate the CO adsorption on the freshly-prepared hierarchical concave tetrapod Pd nanocrystals, the CO stripping voltammetry was recorded in 0.1 M H₂SO₄ at a sweep rate of 2 mV·s⁻¹ without introducing any additional CO. Then a second potential scanning was followed at the same sweep rate. After that, CO gas (99.999%) was bubbled for 15 minutes through the 0.1 M H₂SO₄ solution in which the modified electrode was immersed before measurements. The modified electrode was quickly transferred into a fresh 0.1 M H₂SO₄ solution and the
third scan for CO stripping voltammetry was recorded once again.

For the electrooxidation of formic acid, the cyclic voltammograms were recorded at a sweep rate of 50 mV·s⁻¹ in 0.5 M H₂SO₄ + 0.5 M HCOOH. Before cyclic voltammetry measurements, six cycles of potential sweeps between -0.2V and 1.2V at a sweep rate of 50 mV·s⁻¹ were applied in order to clean the Pd surface in-situ. Both positive and negative CV scans were performed on each sample. The arrows in the CV curves indicate the direction of the scan. The same electrochemical experiment was conducted for commercial Pd black.
Fig. S1. SEM images of the hierarchical concave tetrahedral Pd nanocrystals.
Fig. S2. CO stripping voltammetry of the as-prepared Pd nanocrystals in 0.1 M H₂SO₄ solution. (a) the freshly-prepared hierarchical concave tetrahedral Pd nanocrystals without introducing any additional CO; (b) the second potential scanning; (c) after dosing CO for 15 minutes for clean Pd nanocrystals.
Fig. S3. XPS spectrogram of the hierarchical concave tetrahedral Pd nanocrystals, referring to C1s=284.6 eV.
**Fig. S4.** TEM images of the Pd nanocrystals prepared by using different amount of OAm. (a) 0 mL OAm; (b) 0.1 mL; (c) 0.3 mL OAm; (d) 0.5 mL Oam.
Fig. S5. TEM images of the hierarchical concave tetrahedral Pd nanocrystals prepared in the presence of dodecylamine.
Fig. S6. TEM images of Pd nanocrystals prepared at different CO flow rates. (a) 0.05 mL·sec⁻¹; (b) 0.1 mL·sec⁻¹.
Fig. S7. The effects of reaction temperature on the morphologies of Pd nanocrystals. (a) 80 °C; (b) 100 °C; (c) 120 °C; (d) 160 °C.
Fig. S8. Schematic illustrations for the formation process of the hierarchical concave tetrapod Pd nanocrystals with the increase of the amount of OAm.