**Controlled synthesis of hierarchical tetrapod Pd nanocrystals and their enhanced electrocatalytic properties†**

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**Experimental Details**

**Reagents:** palladium acetylacetonate, Pd(acac)₂ (99%) was purchased from Acros Chemicals, PVP (MW=30000, AR), sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), Na₂SO₄, H₂SO₄, formic acid and DMF were purchased from Sinopharm Chemical Reagent Co., Ltd.(Shanghai, China). All reagents were used as received without further purification.

**Synthesis of hierarchical tetrapod Pd nanocrystals:** In a typical synthesis, 25 mg of Pd(acac)₂, 160 mg of PVP, 147 mg of SDS were dissolved in a mixed solvent of DMF (10 mL) and water (2 mL). After thorough mixing, the resulting homogeneous transparent yellow solution was transferred to a glass three-necked flask. 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 heated at 100 °C for 3 h under atmospheric pressure. After being cooled to room temperature, the resulting
black homogeneous Pd colloids were precipitated by acetone, separated by centrifugation and further purified by ethanol.

Under the same other conditions, the effects of SDS, CO flow rate, temperature and reaction time on morphological features were investigated, respectively.

**Characterization:** Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were conducted on a FEI Tecnai G² 20 transmission electron microscopy operated at 200 kV. Diffractograms of HRTEM were obtained by fast Fourier transformation. 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. 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:** Hierarchical Pd tetrapods-modified working electrodes were fabricated by depositing ethanolic dispersion of purified hierarchical 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. Firstly, to investigate the CO adsorption on the freshly-prepared hierarchical tetrapod Pd nanocrystals, the CO stripping voltammetry
was recorded in 0.1 M H₂SO₄ at a sweep rate of 2 mV/s 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 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 in 0.5 M H₂SO₄ + 0.5 M formic acid. Before cyclic voltammetry measurements, six cycles of potential sweeps between -0.2 V and 1.2 V at a sweep rate of 250 mV/s 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 The high-magnification TEM images (a, b) and HRTEM image (c) of the as-prepared hierarchical Pd tetrapod.
**Fig. S2** CO-stripping voltammetry of the hierarchical Pd tetrapods in 0.5 M H$_2$SO$_4$ solution. (a) the freshly-prepared products without introducing any additional CO; (b) the second potential scanning; (c) after dosing CO for 15 minutes for clean hierarchical Pd tetrapods.
Fig. S3 XRD pattern of the hierarchical tetrapod Pd nanocrystals.
Fig. S4 XPS spectrogram of the hierarchical tetrapod Pd nanocrystals.
Fig. S5 TEM images of Pd nanoparticles prepared without adding SDS.
Fig. S6 TEM images of Pd nanocrystals prepared at different reaction time at 100°C. (a) 15min; (b) 30min; (c) 60min; (d) 300min.
Fig. S7 Schematic illustrations for the formation process of the hierarchical tetrapod Pd nanocrystals.