Supporting Information

1. Preparation of Pd electrode and electrochemical measurements

6 µl of suspension containing Pd arrow-headed tripods (1.43 mg/mL) or ultrafine Pd black (BASF) was pipetted onto a polished glass-carbon rotating disk electrode (d = 5 mm) and dried in air at room temperature. Then, 4 µl of Nafion solution (1 wt.%) was pipetted on it and the Pd working electrode was obtained. A conventional three-electrode cell was used, including a saturated calomel electrode (SCE) as the reference electrode, a platinum gauze as the counter electrode and the as-prepared Pd electrodes as the working electrode. The Pd loading was 44 µg cm⁻ ². Cyclic voltammeter (CV) with a scanning rate of 50 mV S⁻¹ and chronoamperometry (CA) experiments at 0.20 V were performed in a 0.5 M $H_2SO_4 + 0.5$ M HCOOH solution at room temperature. During the measurements, the rotating speed of the glass-carbon rotating disk electrode was controlled at 1000 rpm. The electrochemically active surface area (ECSA) of the Pd samples was measured by CO stripping experiments. CO stripping voltammograms began with bubbling CO (>99.9% purity) over the working electrode at -0.1 V for 20 min in a 0.5 M H₂SO₄. Subsequently, the dissolved CO was removed from the electrolyte by bubbling Ar for 30 min while maintaining the electrode potential at -0.1 V. Finally, the CO stripping voltammograms were obtained between -0.1 and 0.9 V at a scan rate of 50 mV s⁻¹. The ECSA of the Pd samples was calculated from the CO stripping peak area by assuming a charge of 420 µC cm⁻² for electrooxidation of the CO monolayer on Pd surface.



Fig. S1 TEM images of the Pd samples formed by using Pd(acac)₂ (a), Na₂PdCl₄ (b) and PdCl₂ (c) as the Pd(II) source.



Fig. S2 TEM images of the Pd samples formed without (a) and with stirring (b).



Fig. S3 TEM images of the Pd samples formed at 343 K (a) and 353 K (b).



Fig. S4 Cyclic voltammograms of Pd samples formed by different Pd(II) source in a 0.5 M HCOOH + 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹. (a) as-prepared Pd nanodendrites formed by using Na₂PdCl₄ as the Pd(II) source, (b) as-prepared Pd irregular nanoparticles formed by using PdCl₂ as the Pd(II) source, (C) electrochemically cleaned Pd nanodendrites formed by using Na₂PdCl₄ as the Pd(II) source, and (d) electrochemically cleaned Pd irregular nanoparticles formed by using PdCl₂ as the Pd(II) source, and (d) electrochemically cleaned Pd irregular nanoparticles formed by using PdCl₂ as the Pd(II) source.