

Electronic Supplementary Information

Facile synthesis of highly active amorphous Pd-P nanoparticles for enhanced formic acid oxidation

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Experimental Procedure

1. Material Synthesis

1.1 Chemicals: All chemicals are analytical grade and used as received without further purification.

1.2 Synthesis and preparation of Pd-P NPs: The synthesis of Pd-P NPs by stepwise electroless deposition was according to literature.³¹ 0.2 M NaH₂PO₂ (Sigma-Aldrich) and 2 mM PdCl₂ (Sigma-Aldrich) were prepared and stored separately. A glassy carbon electrode (GCE) (3 mm diameter, Bioanalytical Systems, Inc.) was polished with a 0.05 μm alumina polish and wash thoroughly with deionized water (DI) (Millie-Q Gradient A10) after which it was sonicated for 5 mins before use. The stepwise electroless deposition process was machine automated. Firstly, the GCE was first dipped into the NaH₂PO₂ solution (reducing agent) for 10 s. It was then quickly air blown dry and dipped into PdCl₂ solution for another 10 s. It was then washed in DI water before air blown dry again. This constitutes one deposition cycle. This procedure can be repeated to achieve higher number of deposition cycles which changes the catalytic activity. After completing the desired number of deposition cycles, the GCE was tested using CV measurements.

1.3 Preparation of Pd/C: The Pd/C catalyst electrodes were prepared according to procedure described elsewhere.² Firstly, 1 mg of Pd/C powder (10% Pd, Sigma-Aldrich) was dispersed in 950 μL of DI water and 50 μL of Nafion (5% wt, Sigma-Aldrich) and ultrasonicated before use. Then using a microsyringe, 7.5 μL of this dispersion was cast onto the GCE. The GCE was then tested using CV measurements.

1.4 Annealing of Pd-P NPs: For the preparation of the Pd-P NPs for annealing, the above mentioned preparation method was used with the only exception that carbon cloth (CC) (7302001, Fuel Cell Store) was used instead of GCE as the rubber supporting structure of the GCE is unable to withstand the high temperature of heating (700 °C). The annealing process was conducted according to literature.⁴² The CC was put inside a porcelain crucible (High-Form Porcelain Crucible, CoorsTek) and heated at 700 °C for 1 hour in a furnace (BRF 14/5-2416, Elite Furnance).

2. Electrochemical Measurements: Electrochemical measurements were carried out in a typical three electrode cell with a working electrode (GCE), Pt wire counter electrode and a saturated silver/silver chloride (Ag/AgCl (KCl sat.)) reference electrode. The potentiostat used was Princeton Applied Research VersaSTAT3-200. All the CV measurements for FAO were conducted in N₂-saturated 0.5 M H₂SO₄ (Sigma-Aldrich) + 1 M HCOOH (Sigma-Aldrich) at 50 mV s⁻¹. Chronoamperometry was also conducted in N₂-saturated 0.5 M H₂SO₄ + 1 M HCOOH at a potential of 0.2 V vs Ag/AgCl (KCl sat.). For the measurement of the electrochemically active surface area (ECSA), the CV was conducted from -0.2 V to 1.2 V vs Ag/AgCl (KCl sat.) in N₂-saturated

0.5 M H₂SO₄ at 50 mV s⁻¹. For the calculation of the ECSA, the charge density (424 μC cm⁻²) for monolayer reduction of PdO was used.^{6, 18}

3. Preparation of inductively coupled plasma-mass spectroscopy (ICP-MS) samples: The amount of Pd-P NPs loaded onto the GCE was measured using ICP-MS. In order to extract the Pd-P NPs, 5 μL of concentrated HNO₃ solution (Merck) was dripped carefully onto the GCE for 5 mins. Next, 4 μL of HNO₃ was extracted carefully and dispersed into a plastic tube containing 496 μL of DI water. The sample was then analyzed with an ICP-MS (Agilent 7700) equipped with a 3rd generation He collision/reaction cell to minimize interferences. CV measurements were performed before and after the extraction to ensure that the Pd-P NPs were fully extracted (i.e., the CV obtained after the extraction was same as the blank GCE).

4. Characterization: SEM images were obtained from a JSM-7600F (JEOL Ltd.) microscope operated at 5.0 kV. X-ray diffraction (XRD) characterization was performed using a PANalytical Empyrean diffractometer equipped with a Cu Kα radiation source (λ = 1.54060 Å).

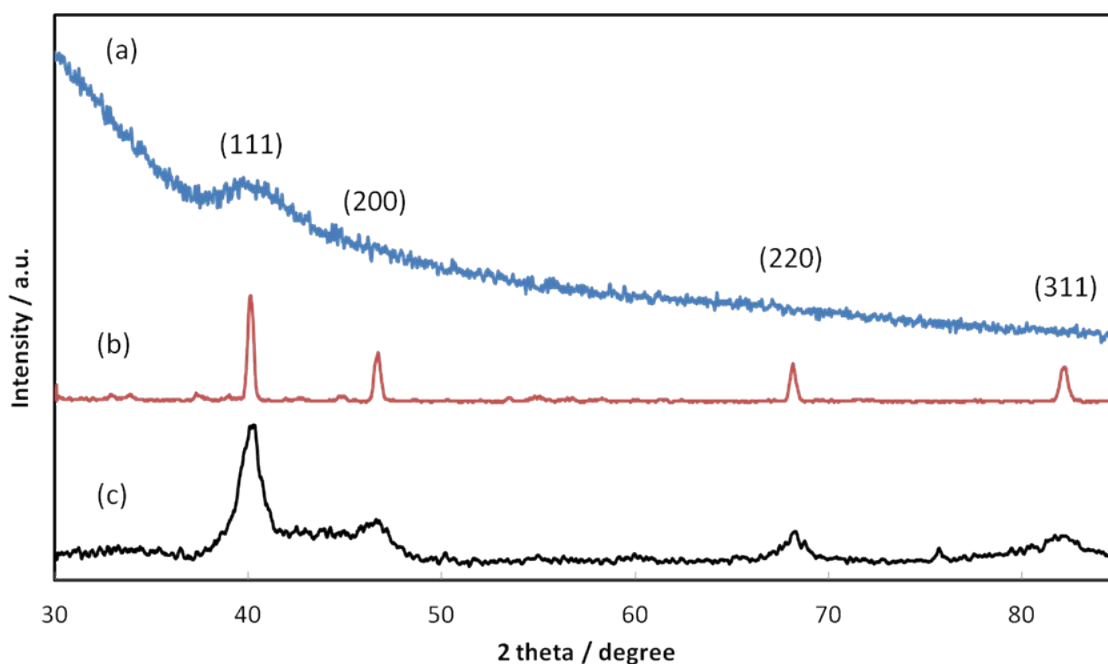


Figure S1. XRD profiles of (a) Pd-P, (b) Pd-P after annealing and (c) Pd/C.