

Electronic Supplementary Information (ESI)

Facile Synthesized Highly Active Pd Nanoparticle Electrocatalyst for Electroless Deposition Process

Desmond C. L. Tan, Bahareh Khezri, Wannipha Amatyakul, Richard D. Webster and Hirotaka Sato

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 nanoparticle (NP) electrocatalyst is the same stepwise deposition method mentioned in previous study¹ on glassy carbon (GC) electrode (3mm diameter, Bioanalytical Systems, Inc.). The GC was polished with Alumina slurry (0.05 μm , Bioanalytical Systems, Inc.), rinsed and sonicated in deionized (DI) water (Millie-Q Gradient A10) for 5 minutes. The GC was then air blow to dry the all surfaces before mounting onto the dipping machine. The solutions containing respective reducing agent, 0.2 M sodium hypophosphite (Sigma-Aldrich) for Pd-P, 0.2 M hydrazine hydrate (Sigma-Aldrich) for Pd-N₂H₄ or 0.2 M tin (II) chloride (Alfa Aesar) for Pd-Sn, and 2 mM palladium (II) chloride (Sigma-Aldrich) were separately prepared and poured into vials set for our custom manufactured dipping-machine. The machine sequentially run the stepwise electroless deposition procedures to deposit Pd NP catalyst on GC; (1) dip the electrode in the reducing agent solution for 20 s, (2) air blow to dry all surfaces, (3) transfer the electrode to dip in the PdCl₂ solution for 20 s, (4) wash the electrode in DI water to terminate the deposition reaction, and (4) air blow the electrode. There is an additional acceleration step for Pd-Sn after synthesis, where the Pd-Sn deposited on GC was immersed in 1.0 M NaOH for 3 minutes²⁻⁴. All synthesis steps are conducted in room temperature. Cyclic voltammetry (CV) and open circuit potential (OCP) was conducted to evaluate the Pd NPs electrocatalyst.

2. Electrochemical Measurements:

CV measurements were conducted in N₂-saturated nickel bath without nickel (nickel-less solution): 0.2 M sodium citrate (Sigma-Aldrich), 0.5 M boric acid (Strem Chemicals, Inc.), 0.24 M sodium hypophosphite (Sigma-Aldrich) and with its pH adjusted to 9.0 with 1.0 M sodium hydroxide. The scan rate for CV measurements was 50 mV s⁻¹. The OCP measurements were conducted in nickel bath: 0.2 M sodium citrate, 0.5 M boric acid, 0.06 M nickel(II) sulfate hexahydrate (BDH Prolabo Chemicals), 0.24 M sodium hypophosphite and with its pH adjusted to 9.0 with 1.0 M sodium hydroxide. The solution was preheated and maintained at 60°C before the OCP measurements.

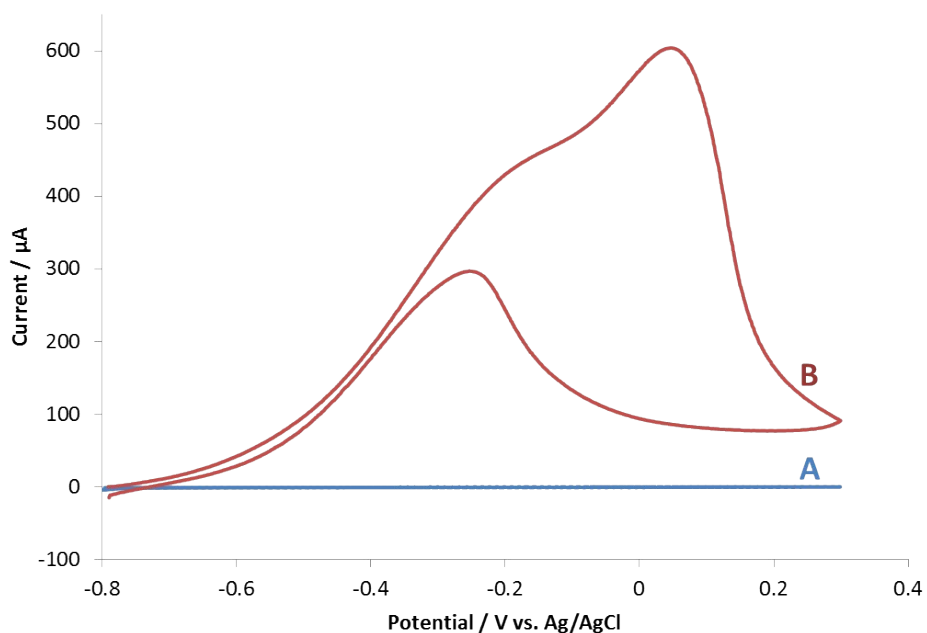


Fig. S1 CVs of (A) bare GC and (B) Pd-P in N_2 -saturated nickel-less solution. Scan rate 50 mV s^{-1} .

2. Electrochemical Active Surface Area Calculation^{1,5-7}:

The calculation of electrochemical active surface area (ECSA) can be evaluated from the cyclic voltammetry sweep of the catalyst in N_2 -saturated 0.5 M boric acid ($\text{pH} = 9$) solution. The charge for PdO reduction in each electrocatalyst was obtained by integrating the cathodic peak obtained in the cyclic voltammetry (e.g. Fig. S1B). The ECSA of Pd was then calculated by assuming that the monolayer PdO reduction charge is $405 \mu\text{C cm}^{-2}$ on the Pd surface.

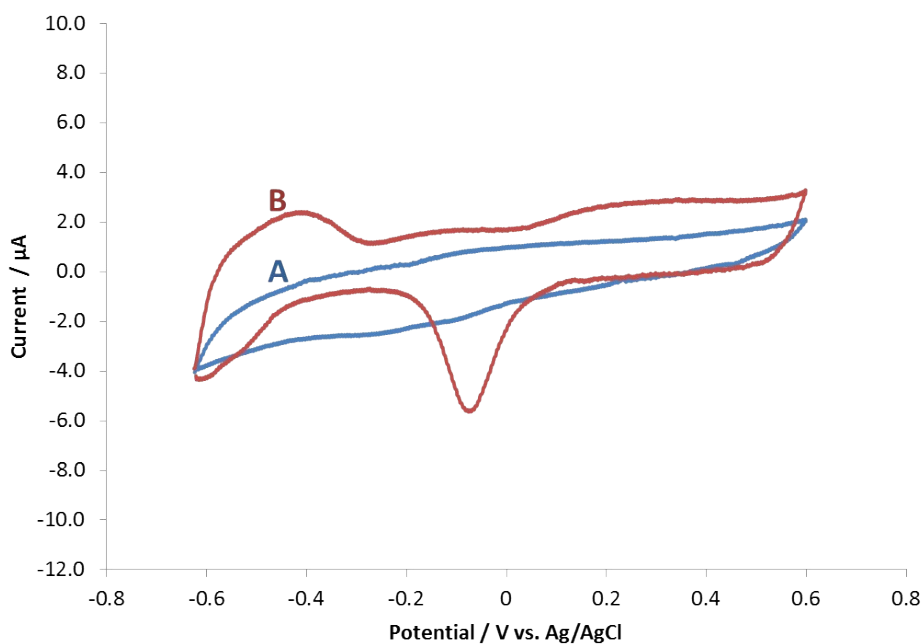


Fig. S2 CVs of Pd-Sn electrocatalysts (A) before acceleration and (B) after acceleration. Scan rate 50 mV s^{-1} .

3. Preparation of inductively coupled plasma-mass spectroscopy (ICP-MS) samples:

After the synthesis and testing of Pd electro-catalyst for the hypophosphite oxidation experiment, the GC surface was air blown dried, followed by dripping 5 μL of concentrated nitric acid (HNO_3 , Merck Millipore) and left for 5 minutes. Subsequently, 4 μL of HNO_3 from the electrode surface was extracted and diluted to 500 μL with DI water. The sample was then analyzed with inductively coupled plasma mass spectrometry, ICP-MS (Aligent 7700) with a 3rd generation He collision/ reaction cell equipped to minimize the interferences.

4. Characterization:

TEM 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 $\text{Cu K}\alpha$ radiation source ($\lambda = 1.54060 \text{ \AA}$). SEM-EDS measurements were obtained from a JEOL7600 microscope.

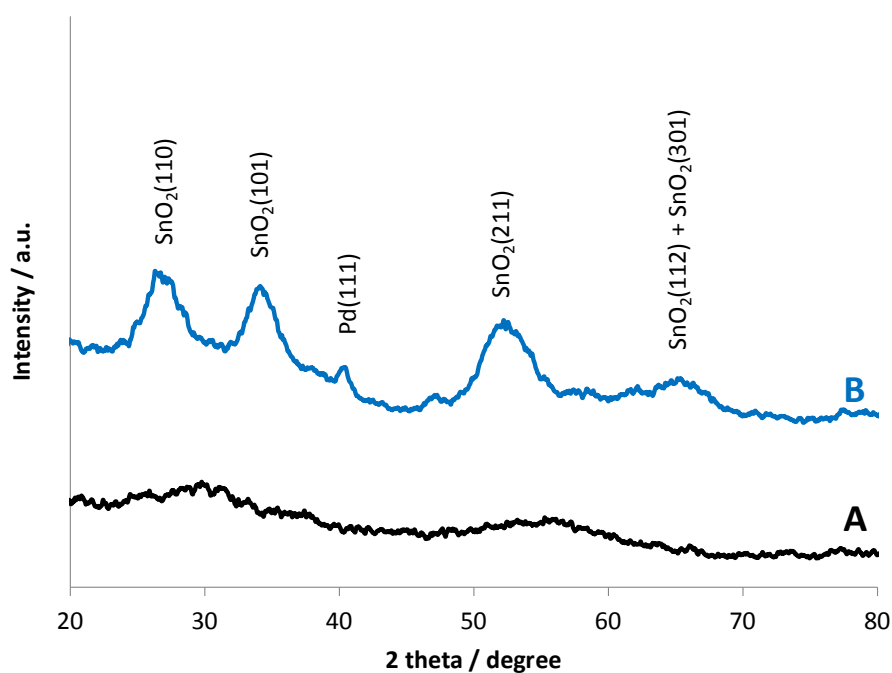


Fig. S3 XRD profiles of Pd-Sn (A) before and (B) after the acceleration treatment.

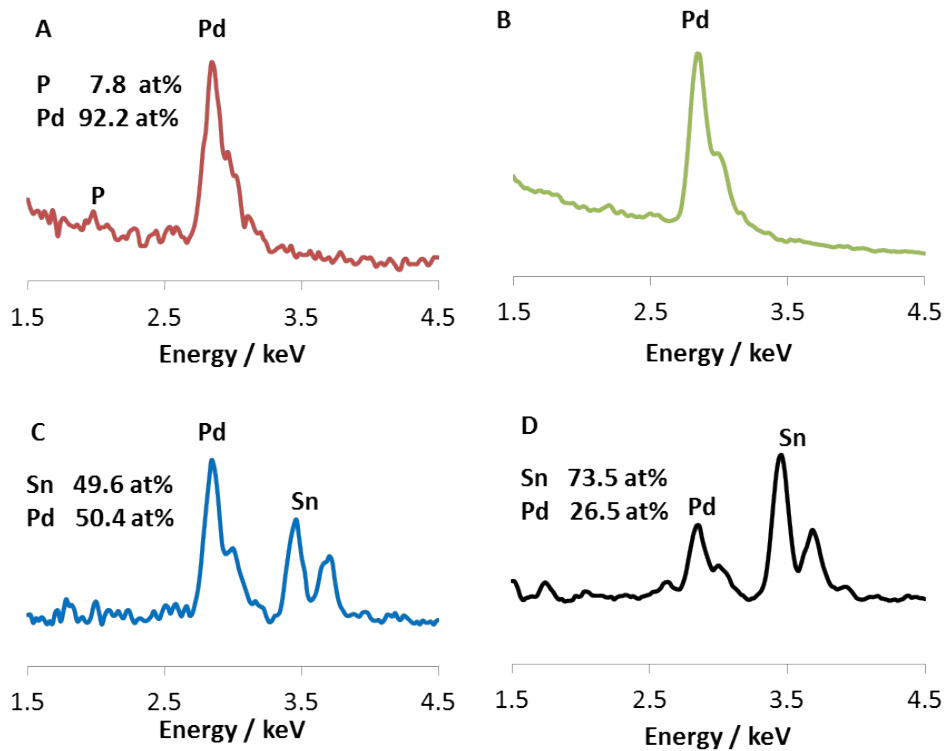


Fig. S4 EDS of (A) Pd-P , (B) Pd-N₂H₄, (C) Pd-Sn/AA and (D) Pd-Sn/BA.

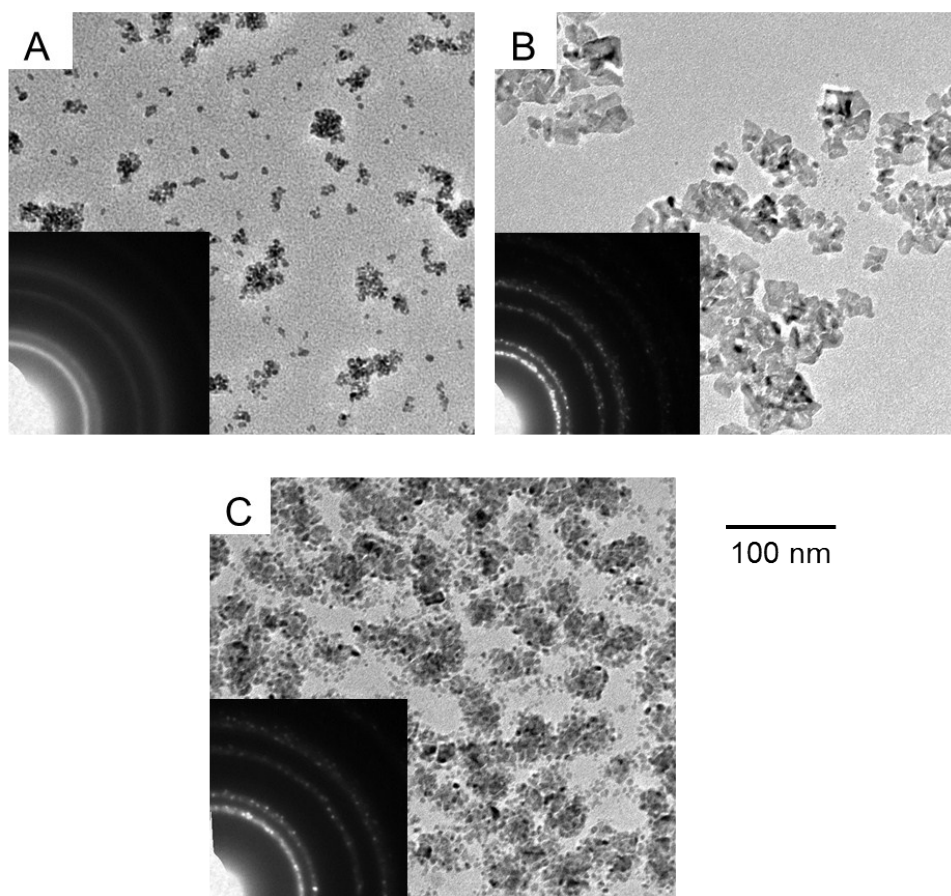


Fig. S5 TEM of (A) Pd-P , (B) Pd-N₂H₄ and (C) Pd-Sn/AA

References

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