Electronic supplementary information

One-step Synthesis of Three-dimensional Pd polyhedronNetworks with Enhanced Electrocatalytic Performance

You Xu, Rui Xu, Jianhua Cui, Yang Liu and Bin Zhang*

1. Experimental Section

1.1 Chemicals: All chemicals were of analytical grade and were used as received without further purification. Aqueous solutions were prepared by using Milli-Q water.

1.2 Synthesis of Pd PNs: In our typical synthesis, 0.0446 mmol H_2PdCl_4 and 0.0134 mmol $Cu(NO_3)_2 \cdot 2H_2O$ were added to a 20 mL Teflon-lined autoclave, to which 20 mg (0.0065 mmol) dodecyl trimethylammonia bromide (DTAB) and 10 mL ethylene glycol (EG) were added under vigorous magnetic stirring to form homogeneous solution. Subsequently, 0.1 mL formaldehyde solution was injected into the resulting mixture rapidly. The mixture solution was then transferred into a 25mL Teflon-lined stainless steel autoclave and sealed. The sealed vessel was then maintained at 150 ºC for 8h. After reaction, the samples were collected and washed through centrifugation and ultrasound six times with ethanol, acetone, and water, respectively.

1.3 Characterization: The morphology and the composition of the products were characterized by scanning electron microscopy (SEM) using Hitachi S-4800 scanning electron microscope (SEM, 5 kV) equipped with the Thermo Scientific energy-dispersion X-ray fluorescence analyzer. Transmission electron microscopy (TEM) images were obtained with JEOL-2100F system. Specimens for TEM measurements were prepared via dropcasting a droplet of ethanol suspension onto a copper grid, coated with a thin layer of amorphous carbon film, and allowed to dry in air. The X-ray diffraction patterns (XRD) of the products were recorded with Bruker D8 Focus Diffraction System using a Cu Kα source (λ= 0.154178 nm).

1.4 Electrochemical Measurements: The relative electrochemical performance of 3D Pd PNs was tested by three-electrode system using a three-compartment glass cell on an electrochemical workstation (CHI 660, CH Instruments, Austin, TX). The working electrode was obtained by dropcasting a drop of concentrated sample of Pd PNs on glassy carbon (GC) electrode. A platinum wire ring and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. All potentials, if not specified, were recorded according to saturated calomel electrode (SCE) in this work. The Pd catalysts were assembled on the working electrode by drop-coating to obtain the working electrode. In a typical preparing process of working electrode, 2 mg of Pd catalyst was dispersed in 2 mL of a mixture solvent (the volume ratio of H_2O: isopropanol: 5% Nafion is 4:1:0.025), and the mixture was sonicated for 5 min to get a dispersed suspension. Then 10μL of the suspension was dropped onto the working electrode and

dried in flowing argon. So the Pt loading on the working electrode was 10 μg. In order to produce a clean electrode surface, the working electrode was cleaned in 0.1M H_2SO_4 by potential cycling between -0.20 and +0.75V at 100 mV s^{-1}until stable voltammogram was obtained. Specifically, cyclic voltammetrys (CVs) were performed in a deoxygenated 0.1 M H_2SO_4 solution at a scan rate of 50 mV s^{-1}. For formic acid oxidation, CVs were performed in 0.1 M H_2SO_4+0.1 M formic acid at a scan rate of 50 mV s^{-1}, respectively. Chronoamperometry was test in 0.1 M H_2SO_4 + 0.1 M formic acid at 0.1V (vs.SCE) for 500s. All the experiments were carried out at room temperature.

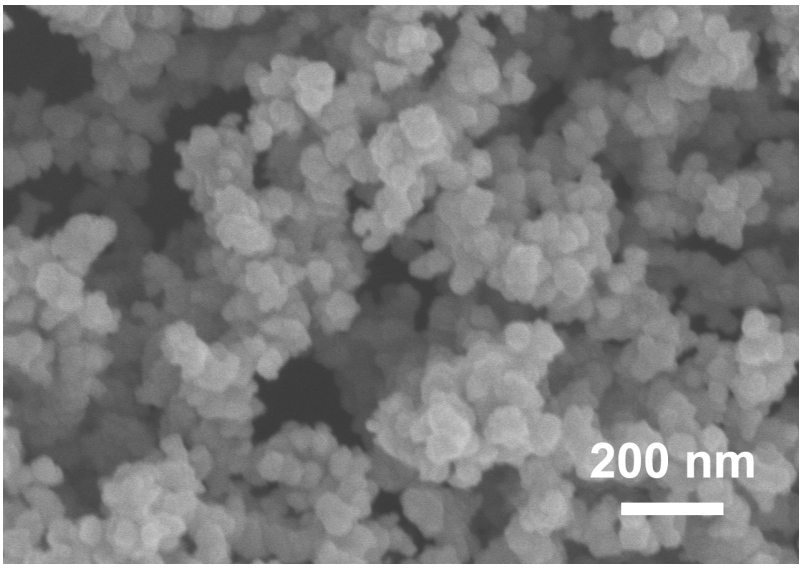

Fig. S1 SEM image of Pd nanoparticle networks prepared in the absence of Cu^{2+}. It was found that Pd porous network structure composed of nanoparticles with an average size of 50 nm was obtained in the absence of Cu^{2+} and other conditions kept unchanged.

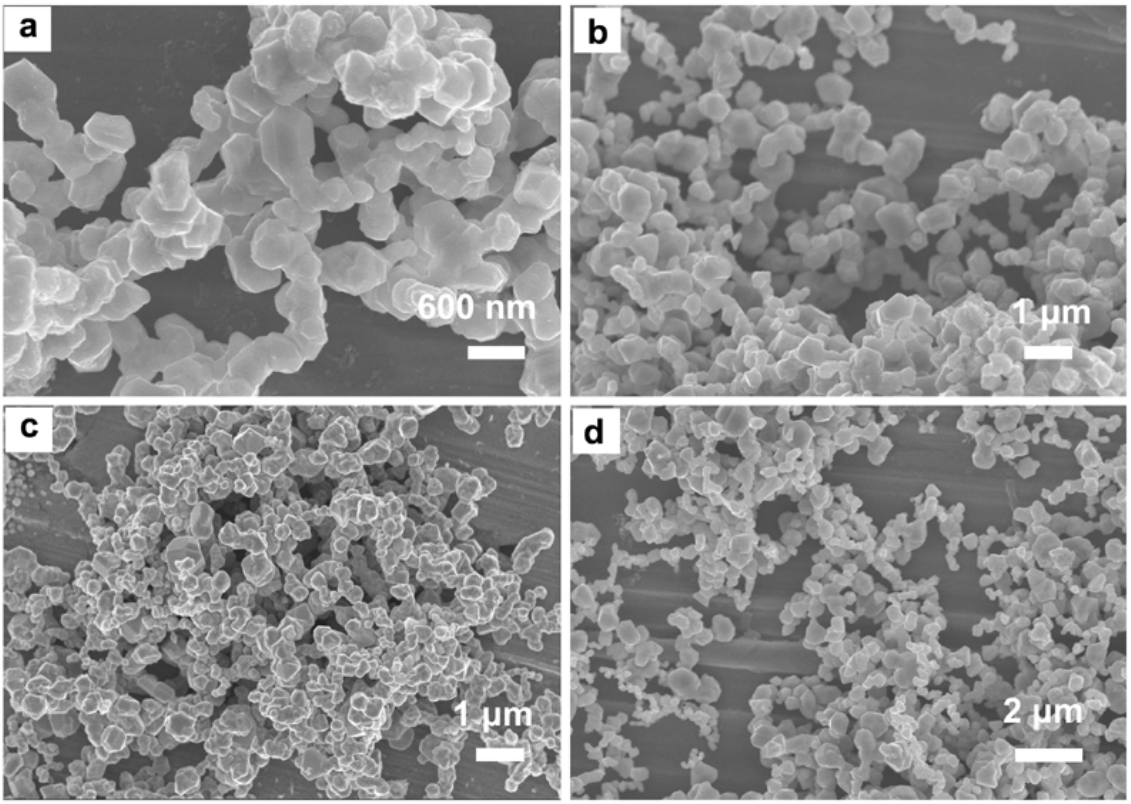

Fig. S2 SEM images (a-d) of Pd PNs obtained by adding different amounts of copper ions: 0.009mmol (a); 0.0178mmol (b); 0.0268mmol(c) and 0.0357mmol (d). It was found that when the Cu^{2+} adding amounts are less than 0.0134mmol (e.g. 0.009mmol) or more than 0.0134mmol (e.g. 0.0178, 0.0268, and 0.0357mmol), the yield of the Pd polyhedron decreases along with poor 3D network structures generate. These results suggested that the introduction of an appropriate amount of $Cu(NO_3)_2$ would not only facilitate the formation of the Pd polyhedra, but also promote the generation of interconnected network structure.

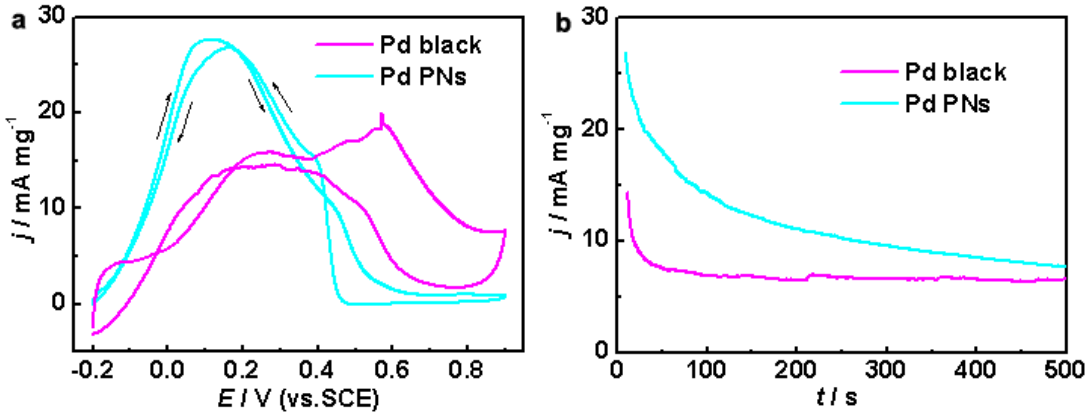

Fig. S3 CV curves at a scan rate of 0.05V/s (a) and chronoamperometric curve at 0.1V (vs. SCE) (b) of Pd black and Pd PNs in 0.1 M HCOOH + 0.1M H_2SO_4. The currents were normalized to the amount of Pd catalysts. The arrows in CVs (a) indicate the potential scan direction.