Supporting Information

Carbon-loaded ultrafine fully crystalline phase palladium-based nanoalloy PdCoNi/C: facile synthesis and highly activity formic acid oxidation

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Experimental details

Chemicals and materials. Sodium tetrachloropalladate(II) (Na_2PdCl_4, A.R.), Nickel Chloride ($NiCl_2$, A.R.), cobaltous chloride ($CoCl_2$, A.R.), Sodium borohydride ($NaBH_4$, A.R.) used in this work were purchased from Titan (Shanghai, China). Carbon Black Vulcan XC-72 was obtained from Macklin (Shanghai, China). JM Pd/C was purchased from Johnsonmatthey Company.

Catalyst preparation. PdCoNi/C catalyst was synthesized by wet chemical reduction method. The specific synthetic process was as follows: three metal precursors, 7 mg $NaPdCl_4$, 6mg $CoCl_2$, and 6 mg $NiCl_2$ were all dissolved in 25mL distilled water, followed by adding 25mg Vulcan XC-72 into the above mixture with magnetic stirring, and stirring continued for the rest of 12 hours to form well-dispersed Vulcan XC-72 slurry. After that, 100mg $NaBH_4$ dissolved in 1mL distilled water was quickly injected at once into the above slurry and continued stirring at room temperature for another 2 hours to ensure the complete reduction and decompose of the reductant. The prepared PdCoNi alloy supported on carbon was separated through centrifuge and washed with distilled water and ethanol for twice, and dried under vacuum at 40 °C, and named as PdCoNi/C-Raw for further use. PdCo alloy supported on carbon and PdNi supported on carbon followed same protocol as above, expect without adding Ni metal precursor for preparing PdCo alloy supported on carbon and without adding Co metal precursor for preparing PdNi alloy supported on carbon and named as PdCo/C-Raw, PdNi/C-Raw, respectively. As prepared samples, PdCoNi/C-Raw, PdCo/C-Raw and PdNi/C-Raw were all annealed at 300°C under an Ar atmosphere for 1 h to improve crystallinity, samples were named as PdCoNi/C, PdCo/C and PdNi/C.

Electrochemical measurements. All electrochemical measurements were performed on a CHI 770E electrochemical workstation. Using three-electrode cell with Ag/AgCl and Carbon rod as the reference and counter electrodes, respectively. 2mg/ml catalyst ink was prepared as follows: mixed 2mg as prepared catalyst samples with 960 μL isopropanol and 40 μL 5 wt% Nafion solution, and followed by ultrasonication for 60 min. 8 μL of the catalyst ink was dropped onto a glass carbon (GC) electrode and dried.

Electrolytes were previously saturated with high-purity nitrogen for 15 min. Cyclic

voltammetry (CV) curves were measured in 0.1 M $HClO_4$ and 0.1 M $HClO_4$+ 0.5 M HCOOH electrolyte at scan rate 50 mV $s^{-1,}$ respectively. Chronoamperometry at a fixed potential of 0.25 V were obtained in 0.1 M $HClO_4$ + 0.5 M HCOOH electrolyte (vs. Ag/AgCl).

Characterizations. X-ray powder diffraction (XRD) patterns were recorded on an D8 ADVANCE X-ray polycrystalline diffractometer (Germany) at a scan rate of 5°/min. High-resolution TEM (HR-TEM) images and high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a Grand ARM 300F. The size distribution of the NCs was carried out by randomly measuring 100 NCs in different regions. X-ray photoelectron spectroscopic (XPS) measurement was carried out on Thermo Scientific ESCALAB 250 XI. The metal contents in the catalysts were measured by inductively coupled plasma mass spectrometry (ICP–AES, Agilent 725ES).

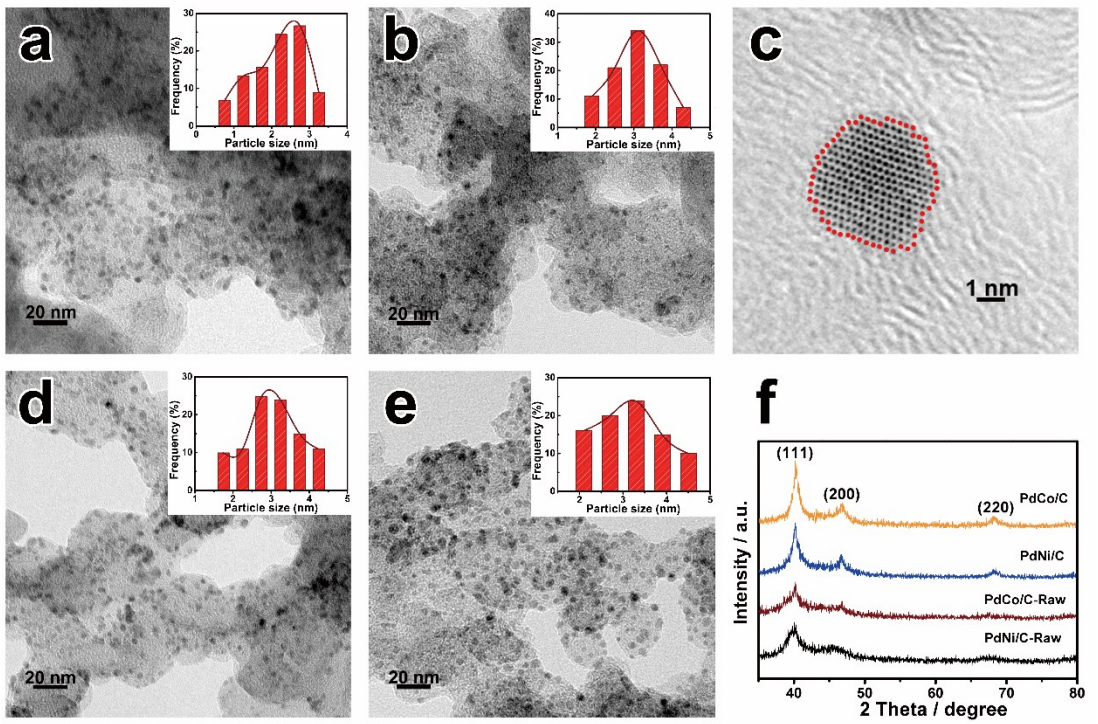

Figure S1. Characterization of as-synthesized Pd-based/C samples. (a,d) HR-TEM images of PdCo/C-Raw and PdNi/C-Raw samples (before thermal treatment), respectively. (b,e) HR-TEM images of PdCo/C and PdNi/C samples (after thermal treatment), respectively. (c) STEM-HAADF image of PdCoNi/C sample (after thermal treatment). (f) XRD patterns of as-synthesized Pd-based sample.

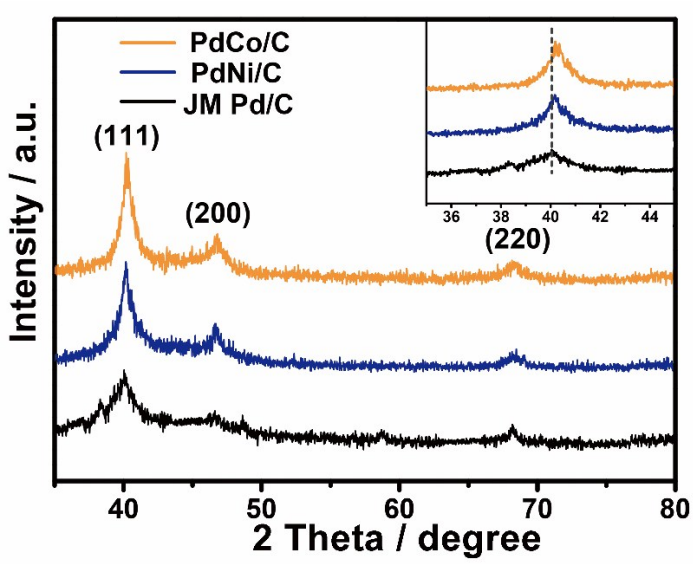

Figure S2. XRD patterns of PdCo/C, PdNi/C and JM Pd/C.

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