

# Ternary Pd-Ni-P Hybrid Electrocatalysts Derived from Pd-Ni Core-Shell Nanoparticles with Enhanced Formic Acid Oxidation Activity

**Xin Liang\*, Bo Liu, Juntao Zhang, Siqi Lu, Zhongbin Zhuang\***

State Key Lab of Organic-Inorganic Composites and College of Chemical  
Engineering, Beijing University of Chemical Technology, Beijing 100029, China.

Email: liangxin@mail.buct.edu.cn (X. L.), zhuangzb@mail.buct.edu.cn (Z. Z.)

## **Supporting Information**

## Experimental section

### 1. Materials

Analytical grade acetone, ethanol, benzyl alcohol, benzoic acid, palladium acetate,  $\text{Pd}(\text{ac})_2$ , nickel acetoacetate ( $\text{Ni}(\text{acac})_2$ ), sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ) and poly(vinylpyrrolidone) (PVP, MW = 58000). Technical grade multi walled carbon nanotubes (CNTs, XF Nano Cto.). All chemical reagents were used without any further purification.

### 2. Synthesis

For the typical synthesis of core-shell Pd-Ni nanoparticles (the Pd/Ni Atomic ratio is 20/80),  $\text{Pd}(\text{ac})_2$  (0.018 g),  $\text{Ni}(\text{acac})_2$  (0.082 g) benzoic acid (0.050 g) and PVP (0.08 g) were dissolved in benzyl alcohol (5 mL), followed by 30 min vigorous stirring. The resulting homogeneous green solution was transferred into a 35 mL pressure tube. The sealed vessel was then heated to 150 °C, and maintained at this temperature for 12 h before it was cooled down to room temperature. The products were precipitated and washed by acetone and ethanol mixture, separated via magnet.

For the synthesis of Pd-Ni-P/CNT hybrid catalyst, firstly, the prepared core-shell Pd-Ni nanoparticles and CNT (the mass ratio was 1 to 1) were dispersed in ethanol (30 mL) with the assistant of ultrasonic. The mixture was vigorously stirred for 12 h, and then the solvent was evaporated at 60 °C to get dry powder (Pd-Ni/CNT). Secondly, Pd-Ni/CNT and sodium hypophosphite were placed at two different positions at a quartz tube in the atmosphere of Ar, and sodium hypophosphite was place in the upstream side. The molar ratio for Ni to P is 1:3. Then the quartz tube was heated to 300 °C with a heating rate of 2 °C  $\text{min}^{-1}$ , and then maintained at this temperature for 2 h. The sample was collected after cooling to the room temperature under Ar flow and washed with deionized water and ethanol for several times to get the Pd-Ni-P/CNT hybrid catalysts.

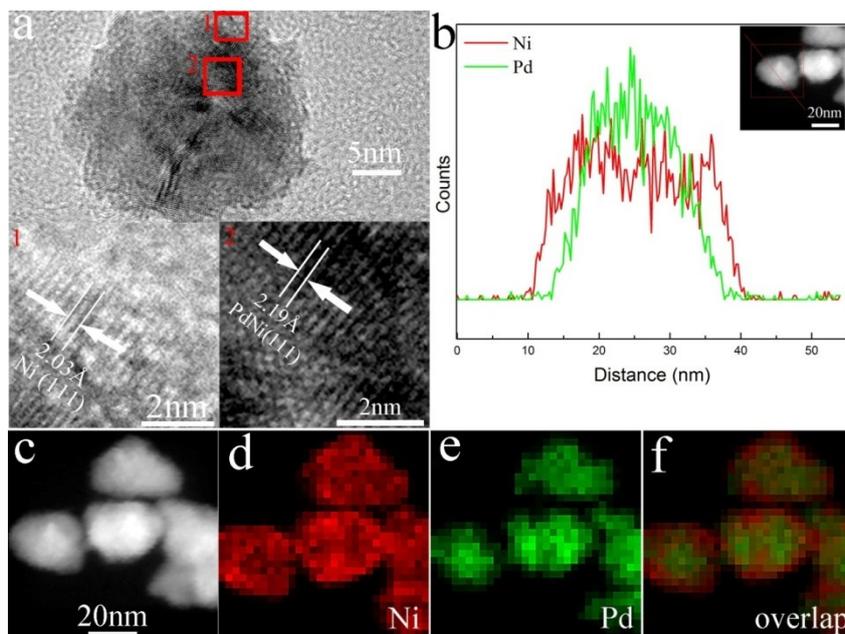
### 3. Physical characterization

The phases of the products were analyzed by X-ray powder diffraction (XRD) measurements, which were using a Bruker D8 diffractometer with Cu  $K\alpha$  as the radiation source ( $\lambda=0.15406$  nm).The morphologies of the samples were observed by transmission electron microscope (TEM) measurements, which were acquired by JEOL JEM-1230 transmission electron microscope with an accelerating voltage of 200 kV. STEM images were made on a FEI Tecnai G2 F20 S-TWIN transmission electron microscope with an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) spectra were

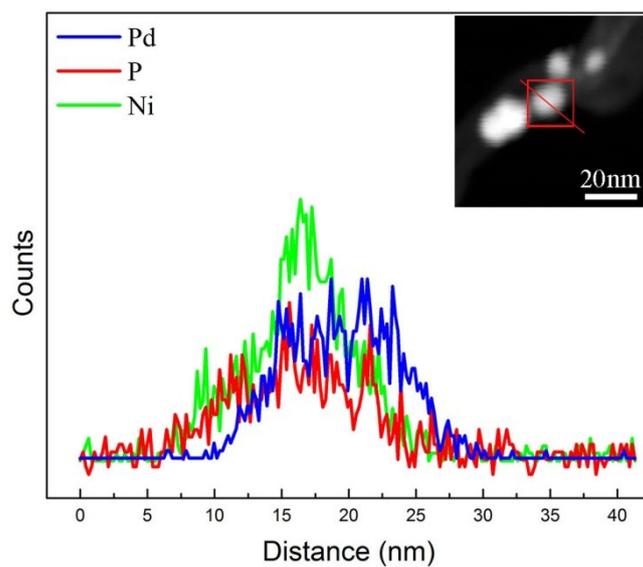
recorded on Thermo Fisher ESCALAB 250 XPS system with a monochromatic Al K $\alpha$  X-ray source. The high resolution scans were conducted at a pass energy of 30 eV using a step size of 0.05 eV.

#### **4. Electrochemical measurements.**

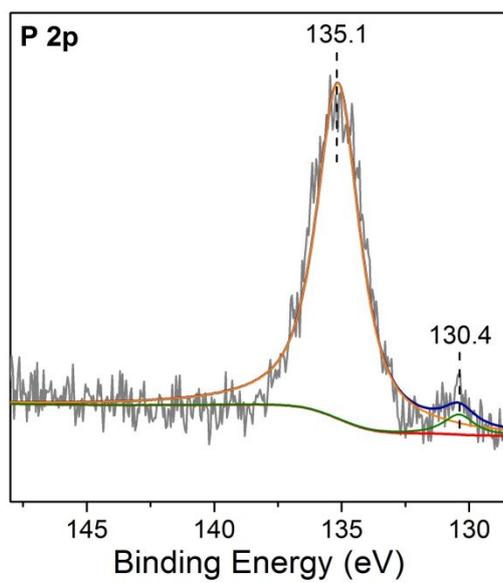
For the preparation of working electrodes, 2 mg of catalyst powder was dispersed in isopropanol (1 mL) with 0.05 wt% Nafion. The mixture was then ultrasonicated for at least 30 min to generate a homogeneous ink. Next, 5  $\mu$ L of the dispersion was transferred onto the glassy carbon electrode (5 mm in diameter), and repeated 3 times to cast a total volume of 20  $\mu$ L catalyst ink on electrode. Electrochemical measurements were performed at room temperature by using a potentiostat (CHI 660E) and three-electrode setup with a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. The electrolyte was 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The formic acid oxidation activities were measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte with 0.5 M formic acid added. Polarization data were collected at a sweep rate of 50 mV s<sup>-1</sup> and the potentials in our work are reported vs. the reversible hydrogen electrode (RHE). The RHE potential was determined by the HOR/HER equilibrium potential of a platinum disk electrode in the H<sub>2</sub>-saturated electrolyte.



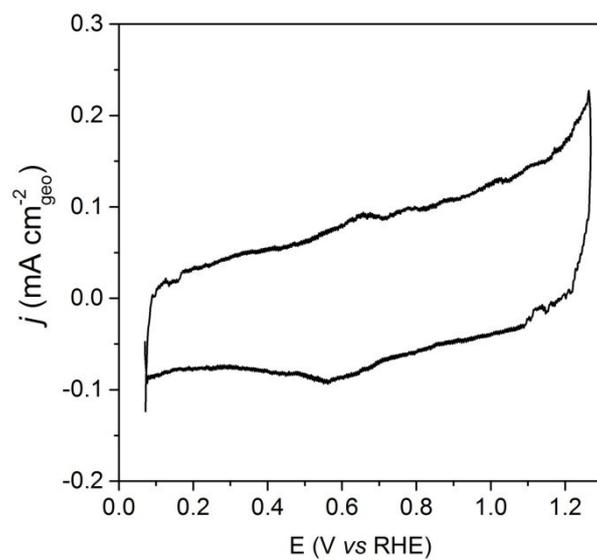
**Figure S1.** (a) HRTEM of Pd-Ni nanoparticle, (b) EDX elemental line scanning of Pd-Ni nanoparticle, (c-f) STEM image and EDX elemental mapping of Pd-Ni nanoparticles.



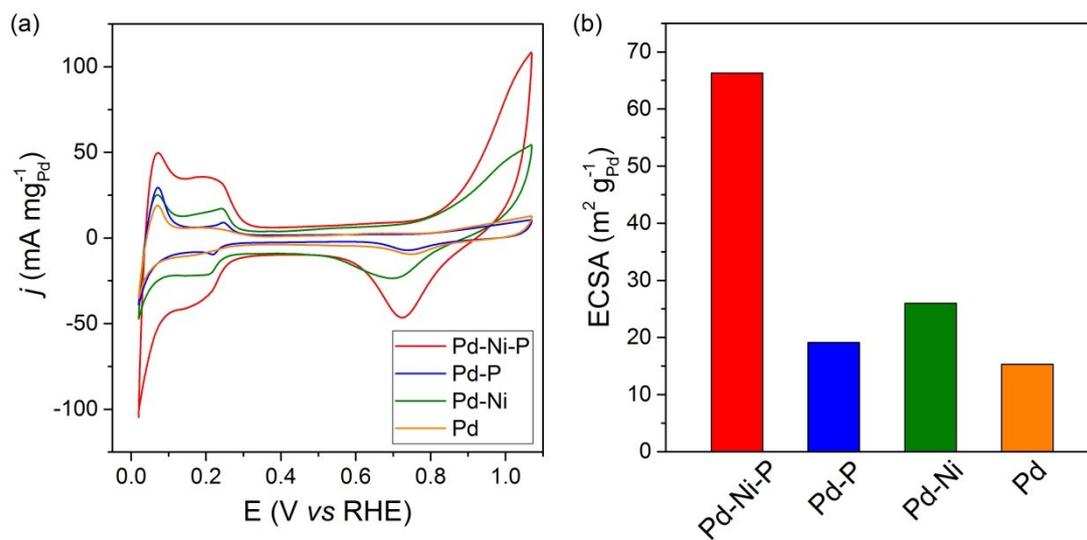
**Figure S2.** EDX elemental line scanning of a Pd-Ni-P nanoparticle. Inset is the corresponding STEM image to indicating the scanned line.



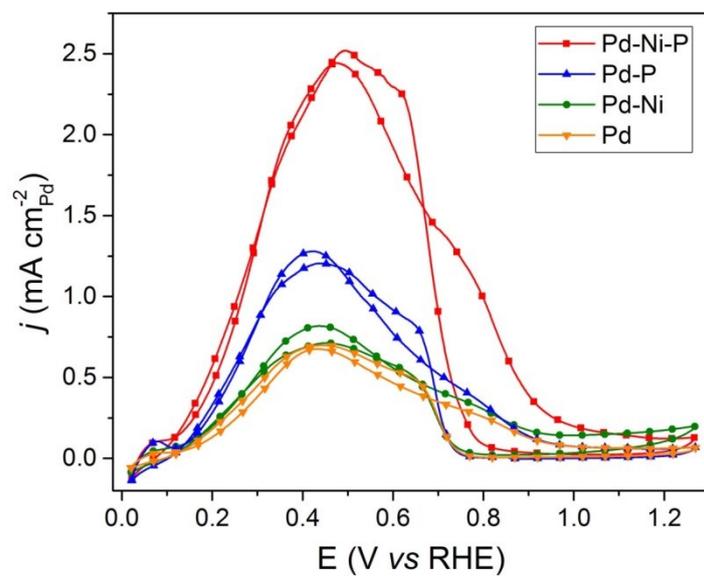
**Figure S3.** XPS spectra of P 2p for Pd-Ni-P/CNT.



**Figure S4.** CV for Ni<sub>2</sub>P in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte with 0.5 M HCOOH.



**Figure S5.** (a) CVs of the catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte. (b) Pd mass normalized ECSA of the catalysts.



**Figure S6.** ECSA normalized CVs of the catalysts in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte with 0.5 M  $\text{HCOOH}$ .