Supporting Information
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69451 Weinheim, Germany

An Effective Pd–Ni$_2$P/C Anode Catalyst for Direct Formic Acid Fuel Cells**

Jinfa Chang, Ligang Feng, Changpeng Liu, Wei Xing,* and Xile Hu*

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EXPERIMENTAL

Chemicals and materials

Sodium hypophosphite (≥ 99.0%), Nickel chloride hexahydrate (≥ 98.0%), PdCl₂ and formic acid (≥ 95%) were purchased from Aldrich Chemical Co. (USA). Vulcan carbon powder XC-72 was purchased from Cabot Co. (USA). Nafion solution (5%) was purchased from Dupont Co. (USA). Sulfuric acid (≥ 95.0%) and ethanol (≥ 99.7%) were purchased from Beijing Chemical Co. (China). All the chemicals were of analytical grade and used as received. Highly purified nitrogen (≥ 99.99%), oxygen (≥ 99.99%) and carbon monoxide (≥ 99.99%) were supplied by Changchun Juyang Co Ltd. Ultrapure water (resistivity: $\rho \geq 18 \text{ M\Omega cm}^{-1}$) was used to prepare the solutions.

Preparation of Ni₂P, Ni₂P/C and Pd-Ni₂P/C

Ni₂P was prepared by a solid phase reaction method. A solid phase of 0.66 g NaH₂PO₂·H₂O and 0.3 g NiCl₂·6H₂O was mechanically mixed in a quartz boat at room temperature. The precursor was directly heated to 250 °C and kept for 1 h in a flowing 30 mL min⁻¹ N₂. Following cooling to room temperature in continued N₂ flow, the unsupported Ni₂P was passivated in a 1.0 mol % O₂/N₂ mixture at 20 mL min⁻¹ for 3 h. The synthesis is similar to that reported in Catalysis Communications, 2011, 12, 1157, except that NaH₂PO₂ rather than NaH₂PO₃ is used. The latter is not available to us.

A carbon-supported Ni₂P was prepared by a new route. Typically, 0.226 g Vulcan XC-72 was incipiently impregnated with an aqueous solution of 0.3 g NiCl₂, followed by drying at 120 °C for 3 h. Other steps are similar to prepare bulk Ni₂P to obtain Ni₂P/C-30% (30% representative wt. % of Ni₂P in the hybrid support). Other compositions of Ni₂P in hybrid support were also prepared.
and they were referred to as NiP/C-X% (X = 10, 20, 40, 50).

The palladium catalysts supported on NiP/C hybrid material with 20 wt. % Pd were prepared by microwave-assisted ethylene glycol reduction process. Briefly, 80 mg of NiP/C-X% support was ultrasonically dispersed in 50 ml of ethylene glycol to form a uniform suspension. Under stirring, a certain amount of H2PdCl4 solution (contain 20 mg Pd) was added to the suspension, and the pH of the suspension was adjusted to approximately 11.0 with 1.0 M NaOH solution. Then the suspension was placed and exposed in the middle of a microwave oven (LGMG-5021MW1, 2450 MHz) with 700 W with 90 s and cooled to room temperature naturally. At last, the suspension was filtered, washed and dried overnight at 80 °C in a vacuum oven to obtain the Pd-NiP/C-X% catalyst. The palladium catalyst supported on XC-72 (denoted as Pd/C-H) was prepared by the same method. The carbon supported PdNi catalyst (denoted as PdNi/C) was synthesized using a similar method except a certain amount of H2PdCl4 solution (containing 20 mg Pd) and NiCl2·6H2O (containing 20 mg Ni) was added to the suspension; Carbon supported PdP catalyst (denoted as PdP/C) was synthesized using a similar method except a certain amount of H2PdCl4 solution (contain 20 mg Pd) and NaH2PO2 (the mole ratios of Pd : H2PO2- = 1:60) was added to the suspension. A state-of-art commercial Pd/C catalyst (denoted as Pd/C-C, Sigma-Aldrich 407305-10G) was used for comparison as a baseline catalyst.

Physical characterizations

All transmission electron microscopy (TEM) and element mapping analysis were conducted on a TECNAI G2 operating at 200 kV. Metal deposited NiP/C samples were sonicated and dispersed in EtOH and placed dropwise onto a holey carbon support grid for TEM observation.

All scanning electron microscopy (SEM) and energy dispersive X-ray detector spectrum (EDS) measurements were performed with an XL30 ESEM FEG field emission scanning electron microscope to determine the morphology.

All Raman spectra were collected on a J-Y T64000 Raman spectrometer with 514.5 nm wavelength incident laser light. To ensure homogeneity of the samples, three spectra were recorded from different spots on the sample. Raman spectra were then normalized for the intensity of the G-band.

All X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos
XSAM-800 spectrometer with an Al Kα radiation source.

All X-Ray diffraction (XRD) measurements were performed with a PW1700 diffractometer (Philips Co.) using a Cu Kα (λ = 1.5405 Å) radiation source operating at 40 kV and 40 mA. A fine powder sample was grinded, then put into the glass slide and pressed to make a flat surface under the glass slide.

**Electrochemical measurements**

All the electrochemical measurements were performed with an EG & G PARSTAT 4000 potentiostat/galvanostat (Princeton Applied Research Co., USA). The cells used were a conventional three-compartment electrochemical cell. The saturated calomel electrode (SCE, Hg/Hg₂Cl₂) were used as the reference electrodes. All of the potentials are relative to the SCE electrode. A Pt disk was used as a counter electrode with a surface area of 0.0314 cm². A glassy carbon thin film electrode (diameter d = 4 mm) was used as a working electrode.

All Cyclic Voltammetry measurements were carried out with respect to SCE in a 0.5 M H₂SO₄ electrolyte and purged with high-purity N₂ to remove dissolved oxygen. Electrochemical experiments of formic acid oxidation were performed in 0.5M H₂SO₄ containing a 0.5 M HCOOH solution. All solution preparations were supplied by MilliQ water. All catalyst electrodes were cleaned by polishing with a 0.05 μm alumina powder suspension (water) followed by ultrasonic cleaning in deionised water before use.

**Electrochemical Pre-treatment**

The catalyst ink was prepared by ultrasonically dispersing a mixture containing 5 mg of catalyst, 950 μL of ethanol and 50 μL of a 5 wt. % Nafion solution. Next, 10 μL of the catalyst ink was pipetted onto a pre-cleaned working electrode.
Before electrochemical measurements, adsorption/desorption of hydrogen on metal nanoparticles surface were evaluated in 0.5 M H₂SO₄. The electrode potential was scanned between -0.2 V and 1.0 V vs. SCE at 50 mVs⁻¹ for surface cleaning. The cyclic voltammetry measurement was carried out until the steady voltammogram was obtained (about 10 cycles).

**Cyclic Voltammetry Measurements**

The activity of metal nanoparticles for formic acid electro-oxidation was measured. The measurements were carried out at room temperature in 0.5 M H₂SO₄ and 0.5 M solution of formic acid at potential range between -0.2 and 1.0 V vs SCE and at a potential sweep rate of 50 mV s⁻¹.

**CO stripping**

99.99% of CO was purged through the catalyst surface in the cells filled with 0.5 M H₂SO₄ electrolyte for 30 min while holding the working electrode at 0.2 V vs. SCE. Then the system was purged with N₂ for 30 min to remove non-adsorbed CO before the measurements were made. The CO stripping was performed in the potential of the range -0.2 ~ 1.0 V at a scan rate of 50 mV s⁻¹. The electrochemical surface areas (ECSA) and the tolerance to CO poisoning were estimated by the CO stripping test, assuming that the Coulombic charge required for the oxidation of the CO monolayer was 420 μC cm⁻².

**Chronoamperometry measurements**

To estimate the stability of the catalysts, the chronoamperometric (CA) experiments were performed in still 0.5 M H₂SO₄ and 0.5 M formic acid solution at 0.3 V or on the rotating disk
electrode to eliminate diffusion.

**Electrochemical Impedance Measurements**

The electrochemical impedance spectra (EIS) were recorded at the frequency range from 100 kHz to 10 mHz with 10 points per decade. The amplitude of the sinusoidal potential signal was 5 mV.

**Preparation of hot-pressed MEA and CCM**

Nafion 117 (DuPont) was used as the proton exchange membranes and the pre-treatment of the Nafion membrane was accomplished by successively treating it in a 5 wt. % H₂O₂ solution at 80 °C, distilled water at 80 °C, 8 wt.% H₂SO₄ solution at 80°C and then in distilled water at 80 °C again, for 30 min each step. Prior to the fabrication of hot-pressed Membrane electrode assemblies (MEAs) and catalyst-coated membrane (CCM), a carbon cloth was used as Gas diffusion layer (GDL) for current collector and it also assists in water management.

Membrane electrode assemblies (MEAs) with a 3*3 cm² active cell area were fabricated using a ‘direct paint’ technique applied to the catalyst layer. The ‘catalyst inks’ were prepared by dispersing the catalyst nanoparticles into appropriate amounts of Millipore® water and a 5% recast Nafion® solution. Anode and cathode ‘catalyst inks’ were directly painted onto either side of a Nafion® 117 membrane. For all MEAs in this study, the cathode consisted of unsupported platinum black nanoparticles (27 m² g⁻¹, Johnson Matthey) at a standard loading of 4 mg cm⁻². The anode consisted of carbon supported Pd catalysts. A carbon cloth diffusion layer (E-TeK) was placed on top of both the cathode and anode catalyst layers. Both sides of the cathode carbon cloth were Teflon® coated for water management. A single cell test fixture consisted of machined graphite flow fields with direct liquid feeds and gold plated copper plates as end plate to avoid corrosion (Fuel Cell Technologies Inc.). Hot-pressing was conducted at 140 °C and 10 MPa for 90 s.
Four different anode catalysts were investigated in this study: (I) 20 wt. % PdP on Vulcan XC-72 (PdP/C), (II) 20 wt. % PdNi on Vulcan XC-72 (PdNi/C), (III) 20 wt. % Pd on Ni$_2$P@Vulcan XC-72 (Pd-Ni$_2$P/C-30%), (IV) 20 wt. % commercial Pd/C (Pd/C-C). The anode catalyst loading of the Pd/C was 6 mg cm$^{-2}$ including the mass of the carbon support.

**Fuel cell performance test**

The MEA was fitted between two graphite plates in a punctual flow bed. The polarization curves were obtained using a Fuel Cell Test System (Arbin Instrument Corp.) under the operation conditions of 30 °C. High purity O$_2$ (99.99 %) is applied as the oxidant at 500 ml/min as the cathode atmosphere and 3 M formic acid as the reactant feed on the anode side at 200 ml/min. The potential range is from the open circuit potential to 0.1V, and one point is collected every 0.05V while it stays 1 minute to get the steady state plots. Both two sides are under ambient pressure.
Figure S1 Raman spectra of Ni$_2$P (a), Ni$_2$P/C-10% (b), Ni$_2$P/C-20% (c), Ni$_2$P/C-30% (d), Ni$_2$P/C-40% (e) and Ni$_2$P/C-50% (f).
Figure S2 XRD patterns of a) for Ni$_2$P/C-X% (X = 0, 10%, 20%, 30%, 40% and 50%) and b) for Pd-Ni$_2$P/C-X% (X = 10%, 20%, 30%, 40% and 50%), Pd/C-H, PdP/C and PdNi/C.
Figure S3 SEM (a), Elemental mapping images (b-f) analysis and EDS (g) of the Pd-Ni$_2$P/C-30% catalyst.
Figure S4 Typical TEM images and corresponding particle size distribution histograms of Pd-Ni$_2$P/C-10 % (a1 and a2), Pd-Ni$_2$P/C-20 % (b1 and b2) Pd-Ni$_2$P/C-40 % (c1 and c2) and Pd-Ni$_2$P/C-50 % (d1 and d2) catalysts; inset is HRTEM images for different catalysts.
Figure S5 Typical cyclic voltammograms of Ni$_2$P, Pd-Ni$_2$P/C-10%, Pd-Ni$_2$P/C-20%, Pd-Ni$_2$P/C-30%, Pd-Ni$_2$P/C-40% and Pd-Ni$_2$P/C-50% catalysts in 0.5 M H$_2$SO$_4$ supporting electrolyte.
The images show cyclic voltammetry (CV) plots for Pd-Ni$_2$P/C-30% and Pd-Ni$_2$P/C-40%. The plots compare the 1st cycle and the 2nd cycle for each composition.

- **Pd-Ni$_2$P/C-30%**
  - The 1st cycle shows a broad, asymmetric peak around 600 mV and a reduction peak around 800 mV.
  - The 2nd cycle shows a similar trend but with slightly reduced current.

- **Pd-Ni$_2$P/C-40%**
  - The 1st cycle demonstrates a more pronounced peak around 600 mV and a sharper reduction peak around 800 mV.
  - The 2nd cycle maintains a similar pattern but with notable changes in the peak shapes and currents.
Figure S6 Illustration of the CO tolerance of Palladium nanoparticles catalysts on different supports by stripping voltammetry of adsorbed CO. Exposure of the electrode to CO saturated solution at 0.20 V for 30 min was followed by purging the solution with N₂ for 20 min and a CV scan. Scanning rate was 50 mV s⁻¹ and 0.5 M H₂SO₄ as supporting electrolyte.
**Table S1** Electrochemical surface area estimation from hydrogen evolution and CO Stripping experiment and peak potential for CO stripping for the different catalysts

<table>
<thead>
<tr>
<th>sample</th>
<th>Pd/C-C</th>
<th>Pd-Ni₂P/C-10%</th>
<th>Pd-Ni₂P/C-20%</th>
<th>Pd-Ni₂P/C-30%</th>
<th>Pd-Ni₂P/C-40%</th>
<th>Pd-Ni₂P/C-50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECSA&lt;sup&gt;a&lt;/sup&gt; (m² g⁻¹)</td>
<td>71.68</td>
<td>61.88</td>
<td>85.31</td>
<td>90.00</td>
<td>65.63</td>
<td>62.52</td>
</tr>
<tr>
<td>ECSA&lt;sup&gt;b&lt;/sup&gt; (m² g⁻¹)</td>
<td>62.62</td>
<td>51.23</td>
<td>62.70</td>
<td>63.65</td>
<td>61.07</td>
<td>51.74</td>
</tr>
<tr>
<td>peak potential (mV)</td>
<td>687.05</td>
<td>766.13</td>
<td>763.33</td>
<td>687.50</td>
<td>780.90</td>
<td>759.03</td>
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</table>

<sup>a</sup> The ECSA of the catalysts integration from the H-evolution.

<sup>b</sup> The ECSA of the catalysts integration from the CO Stripping experiment.

**Table S2** Mass activity, specific activity and corresponding peak potential of Pd/C catalysts with different amounts of Ni₂P in 0.5 M HCOOH contain 0.5 M H₂SO₄.

<table>
<thead>
<tr>
<th>Catalysts on different supports</th>
<th>Mass Activity (A g⁻¹)</th>
<th>Specific Activity (A m⁻²)</th>
<th>peak potential (mV)</th>
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<tbody>
<tr>
<td>Ni₂P/C-10%</td>
<td>924.18</td>
<td>18.04</td>
<td>290</td>
</tr>
<tr>
<td>Ni₂P/C-20%</td>
<td>1162.08</td>
<td>18.53</td>
<td>295</td>
</tr>
<tr>
<td>Ni₂P/C-30%</td>
<td>1425.17</td>
<td>22.40</td>
<td>295</td>
</tr>
<tr>
<td>Ni₂P/C-40%</td>
<td>1217.65</td>
<td>19.94</td>
<td>301</td>
</tr>
<tr>
<td>Ni₂P/C-50%</td>
<td>611.18</td>
<td>11.81</td>
<td>270</td>
</tr>
</tbody>
</table>
Figure S7 Specific activity of Pd-Ni$_2$P/C catalysts with different amounts of Ni$_2$P. The surface area calculated from the CO stripping curves.
Figure S8 Chronoamperometric curves of Pd-Ni₂P/C catalysts in 0.5 M H₂SO₄ containing 0.5 M formic acid at 0.3 V. Insert figure: the magnified curves between 6000-7200s.
(a) Pd-Ni$_2$P/C-10%

(b) Pd-Ni$_2$P/C-20%
(c) Pd-Ni$_2$P/C-30%

(d) Pd-Ni$_2$P/C-40%
Figure S9 Comparative Nyquist plots (a)-(e) of the various electrodes, and (f) for the different catalysts at 0.3 V in 0.5 H₂SO₄ contain 0.5 M HCOOH solution.

For the Pd-Ni₂P catalysts, at the potential before 0.1 V, the loop in the first quadrant associated with a Faradic reaction due to the dehydrogenation of formic acid oxidation; After 0.1 V, the loop changed to the second quadrant indicated the negative charge-transfer resistance due to
the passivation originating from the chemisorbed hydroxyly species on the electrode surface.[1] And the loop diameter decrease with the potentials increase to 0.4 V (around the Peak potential) indicated the reactive resistance was reduced. Then, the strong hydroxyly species is increased with the increase of the potential and the resistance increase largely which caused the current reduced largely even to 0 after 0.8 V. From the EIS, it can be said more formic acid were oxidized around the peak potential due to the reduced Pd active sites passivation. Moreover, it is also evident that the lowest activity of the Pd-Ni$_2$P/C-50% could be attributed to the increased reactive resistance as compared at 0.3V (Fig.S9).
Figure S10 Typical XPS spectra. Pd 3d (a), Ni 2p (b) and P 2p (c) XPS spectra for Pd-Ni$_2$P/C-10%, Pd-Ni$_2$P/C-20%, Pd-Ni$_2$P/C-30%, Pd-Ni$_2$P/C-40% and Pd-Ni$_2$P/C-50% catalysts. The peaks of Ni and P elements became more obvious with the increase of the Ni$_3$P amounts but without obvious peak shift.
Figure S 11 Specific activity of Pd-Ni$_2$P/C-30%, PdNi/C, PdP/C, Pd/C-C and Pd/C-H catalysts.

The surface area calculated from the CO stripping curves (bottom) for PdP/C and PdNi/C catalysts and it is 65.81 and 53.39 m$^2$/g respectively.
Figure S12 Tafel slope for Pd-Ni$_2$P/C-30%, PdNi/C, PdP/C, Pd/C-C, Pd/C-H catalysts.
Figure S13 CA curves of the samples in the still state (A) and applied on the rotating disk electrode (B) with a rotary speed of 50 rpm at 0.3V.
Table S3 Tafel slope for Pd-Ni_{2}P/C-30%, PdNi/C, PdP/C, Pd/C-C and Pd/C-H samples calculated according to the Figure S12

<table>
<thead>
<tr>
<th>Samples</th>
<th>Slope</th>
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<tr>
<td>Pd-Ni_{2}P/C-30%</td>
<td>266</td>
</tr>
<tr>
<td>PdNi/C</td>
<td>315</td>
</tr>
<tr>
<td>PdP/C</td>
<td>273</td>
</tr>
<tr>
<td>Pd/C-C</td>
<td>338</td>
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<tr>
<td>Pd/C-H</td>
<td>306</td>
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</tbody>
</table>

Table S4 Specific activity of novel Pd-Ni_{2}P/C (30%) catalyst compared with others

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Specific Activity (A m^{-2})</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Ni_{2}P/C-30%</td>
<td>22.40</td>
<td>This work</td>
</tr>
<tr>
<td>Pd nanosheets</td>
<td>20.5</td>
<td>[2]</td>
</tr>
<tr>
<td>PdCo</td>
<td>13.2</td>
<td>[3]</td>
</tr>
<tr>
<td>Pd nanoparticles</td>
<td>12.5</td>
<td>[4]</td>
</tr>
<tr>
<td>PdAu/C</td>
<td>18.6</td>
<td>[5]</td>
</tr>
<tr>
<td>PdHoOx/C</td>
<td>12.3</td>
<td>[6]</td>
</tr>
<tr>
<td>Pd nanocrystals</td>
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<td>[7]</td>
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<tr>
<td>Pd-GO</td>
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<td>[8]</td>
</tr>
<tr>
<td>PdAu nanoparticles</td>
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</tr>
<tr>
<td>Pd-GN</td>
<td>7.5</td>
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<tr>
<td>Pt-on-Pd</td>
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<td>PdCo NPs</td>
<td>7.7</td>
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Reference:


