

Facile synthesis of PdFe alloy tetrahedrons for boosting electrocatalytic property towards formic acid oxidation

Binfeng Cai[†], Yanrong Ma[†], Shangzhi Wang, Na Yi, Yang Zheng,
Xiaoyu Qiu^{*}, Yawen Tang^{*}, Jiangchun Bao

[†] *Binfeng Cai and Yanrong Ma contributed equally to this work*

Jiangsu Key Laboratory of New Power Batteries, Jiangsu Collaborative
Innovation Center of Biomedical Functional Materials, School of
Chemistry and Materials Science, Nanjing Normal University, Nanjing
210023, P. R. China

* To whom all correspondence should be addressed.

E-mail addresses: qxy18251813615@163.com (X. Qiu);
tangyawen@nynu.edu.cn (Y. Tang);

Experimental Section

1. Reagents and Chemicals.

Palladium(II) acetone ($\text{Pd}(\text{acac})_2$), iron(II) acetate ($\text{Fe}(\text{Ac})_2$) were purchased from Aladdin Ltd. (Shanghai, P. R. China). Poly(vinyl pyrrolidone) (PVP, $M_w=30\ 000$), N, N-dimethyl formamide (DMF), and formaldehyde solution (HCHO, 40%) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, P. R. China). (S)-(-)-2,2'-Diamino-1,1'-binaphthalene ($\text{C}_{20}\text{H}_{16}\text{N}_2$, molecular structure shown in Fig. S1, supplementary data) was obtained from Yuanye Bio-Technology Co. Ltd. (Shanghai, P. R. China). Commercial Pd black was supplied by Johnson Matthey Corporation. All the reagents were of analytical reagent grade and used without further purification.

2. Synthesis of the PdFe alloy tetrahedrons.

In a typical synthesis, 0.5 mL of 0.05 M $\text{Pd}(\text{acac})_2$ aqueous solution, 0.5 mL of 0.50 M $\text{Fe}(\text{Ac})_2$ aqueous solution and 8 mL DMF solution were dispersed in a 20 mL vial with continued stirring. After adding 35 mg of PVP and 35.5 mg of $\text{C}_{20}\text{H}_{16}\text{N}_2$, 0.1 mL of HCHO solution (40 %) was added into the above solution. Then the vial was heated at 120 °C for 3 h in oil bath. After cooling down to room temperature, the obtained products were separated by centrifugation at 15000 rpm for 5 min, washed with water for several times, and then dried at 60 °C for 5 h in a vacuum dryer. For the synthesis of single-component Pd tetrahedrons, the synthetic protocol was under the similar experimental conditions, only using $\text{Pd}(\text{acac})_2$ as the metal precursor.

3. Characterization.

The morphology and structure of the products were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) with model of JEOL JEM-2100F. The composition of the products were analyzed by X-ray diffraction (XRD) at Model D/max-rC X-ray diffractometer. X-ray elemental mapping measurements and energy dispersive X-ray analysis (EDX) of the products were carried out on a JSM-2010 SEM. High-resolution X-ray photoelectron spectroscopy (XPS) was acquired on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al $K\alpha$ radiator with the vacuum in the analysis chamber maintained at about 10^{-9}

mbar. The binding energy was calibrated by means of the C 1 s peak energy of 284.6 eV. Fourier transform infrared (FT-IR) spectrum was performed with a Nicolet 520 SXFTIR spectrometer. Ultraviolet and visible spectroscopy (UV-vis) analysis was recorded on a Shimadzu UV3600 spectrophotometer equipped with an optical path length of 1 cm at room temperature.

4. Electrochemical measurement.

All electrochemical experiments were performed on a CHI 660 C electrochemical analyzer at 25 °C by using a standard three-electrode system. The standard three-electrode construction was consisted of a Pt wire as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode, and a catalyst-modified glassy carbon electrode (GCE, 3 mm in diameter, 0.07 cm²) as the working electrode. For the immobilization of catalyst on the surface of working electrode, 2 mg of the as-prepared catalyst powder and 1 mL of ethyl alcohol were mixed and sonicated for 10 min to obtain a homogeneous catalyst suspension. Afterwards, 6 μL of the newly-formed suspension was uniformly dispersed on the surface of the GCE. After drying, 3 μL of Nafion solution (5 wt%) was dropped on the catalyst-modified GCE and dried again. Electrochemical measurements were carried out in a 0.5 M N₂-purged H₂SO₄ solution with and without 0.5 M HCOOH at a scan rate of 50 mV s⁻¹. The electrochemically active surface areas (ECSAs) of the catalysts were calculated by using the following equation:

$$\text{ECSA} = Q / (0.424 * \text{Pd}_m)$$

where Pd_m was the mass of Pd located on the electrode and the charges(Q) were associated with the peak from the reduction of Pd oxide, assuming 0.424 mC cm⁻² was required for reducing the Pd(II) oxide monolayer.

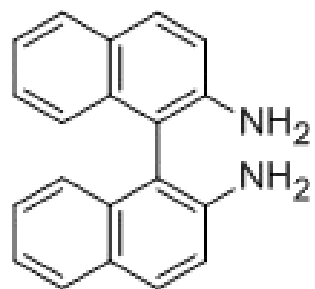
The turnover frequency (TOF) represents the number of formic acid molecules formed per second per Pd surface site, assuming that all surface Pd atoms are active, which was calculated by using the following equation:

$$\text{TOF} = i_k / neN_s$$

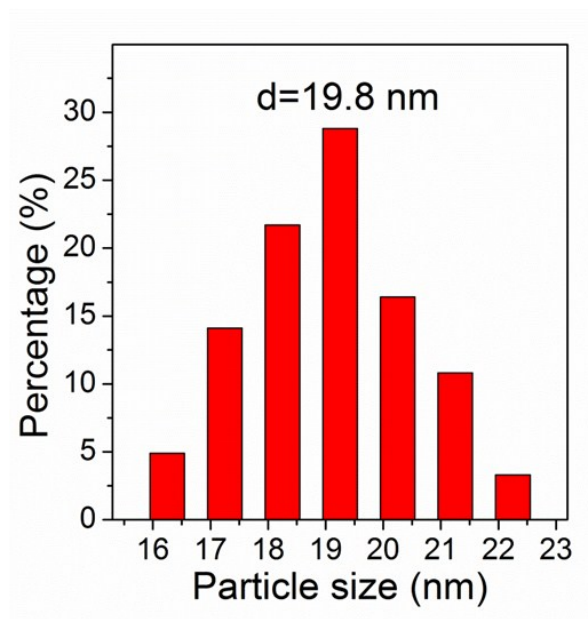
where i_k was the specific current density at 0.1 V, n was the number of electrons transferred, e was elementary charge, and N_s was the atomic surface density.

Chronoamperometry (CA) curves were tested in the N₂-saturated 0.5 M HCOOH + 0.5 M H₂SO₄ solution for 3000 s at 0.1 V. The accelerated durability tests (ADTs) measurements were performed in the N₂-saturated 0.5 M H₂SO₄ solution with and without 0.5 M HCOOH for 1000 cycles.

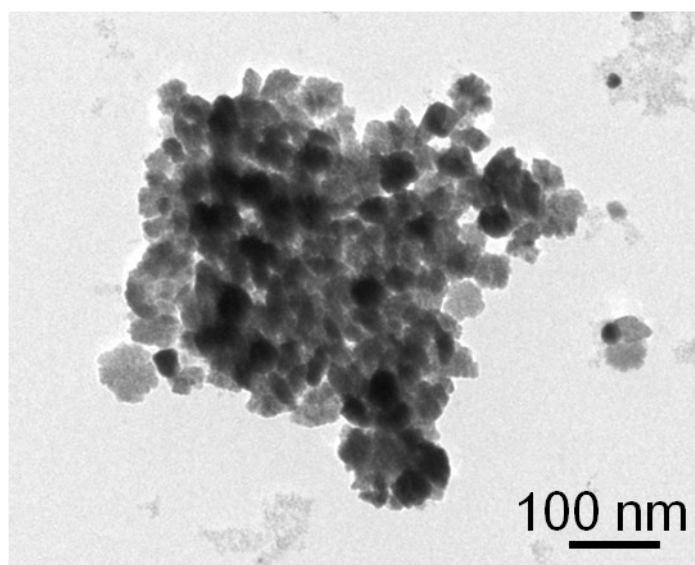
Figures



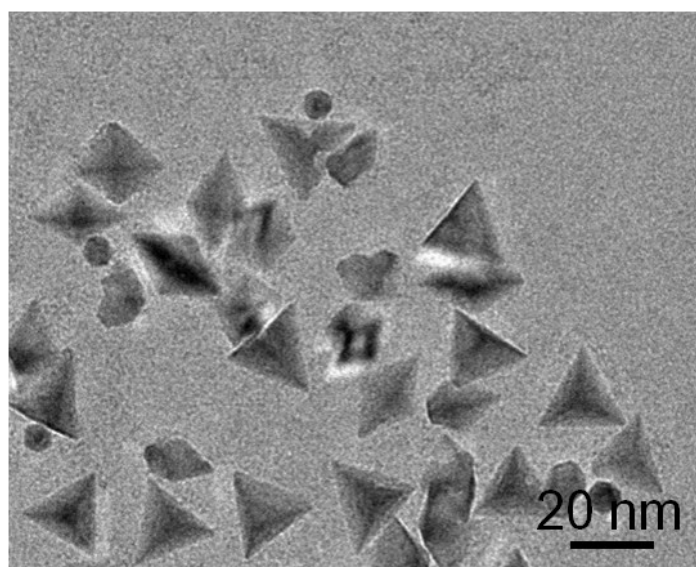
S1. Structure of (S)-(-)-2,2'-Diamino-1,1'-binaphthalene.



S2. Histogram of particle size distribution.



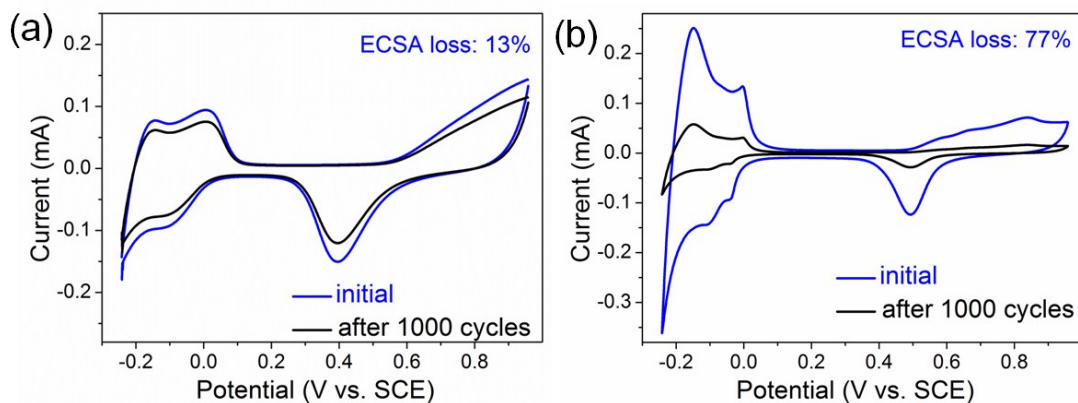
S3. TEM images of the products produced without the demand of (S)-(-)-2,2'-Diamino-1,1'-binaphthalene.



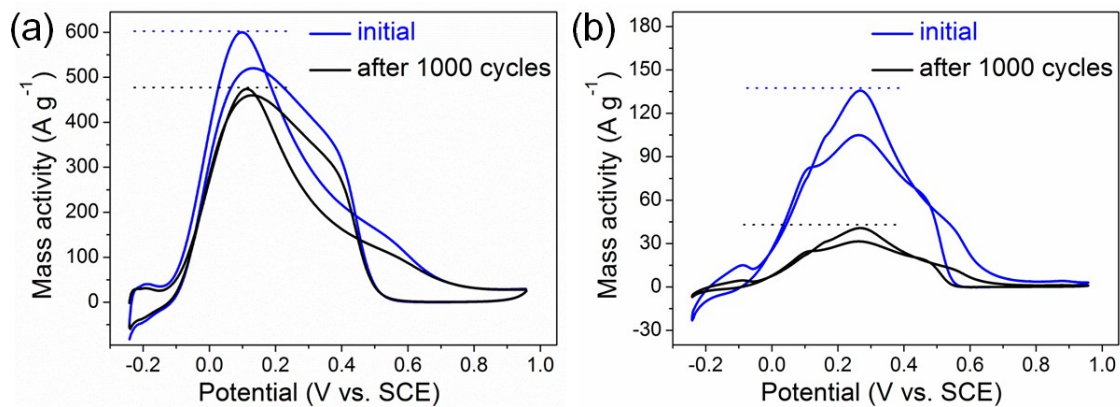
S4. Typical TEM images of pure Pd tetrahedron achieved through a similar synthetic protocol without the addition of $\text{Fe}(\text{Ac})_2$.

Table S1. Comparison of PdFe alloy tetrahedron catalyst with other catalysts for HCOOH oxidation.

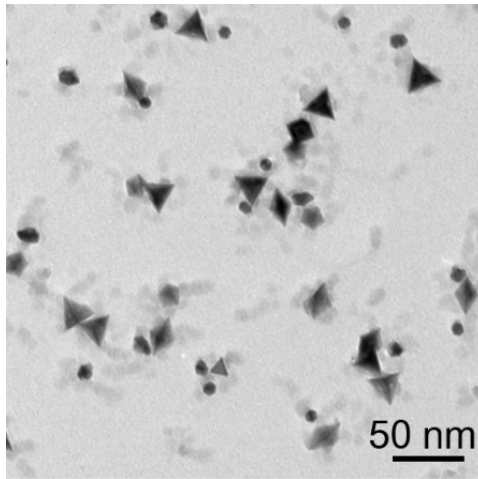
Catalyst	Initial oxidation potential (V)	Peak potential (V)	Mass activity ($A\ g^{-1}$)	Ref
PdFe tetrahedron	-0.15	0.10	595.8	This work
Pd-Ag 0.317	0.12	0.30	525.1	<i>Nano Res.</i> , 2016 , 9(6), 1590-1599.
Pd₅₁Cu₄₉	-0.08	0.27	517.0	<i>Int. J. Hydrogen Energ.</i> , 2016 , 41, 6773-6780.
Core-shell CuPd@Pd tetrahedra	-0.13	0.17	501.8	<i>J. Mater. Chem. A</i> , 2018 , 6, 10632-10638.
Single crystalline Pd arrow-headed tripods	-0.10	0.24	401.0	<i>Chem. Commun.</i> , 2015 , 51, 7195-7198.
Pd₃Pt half-shells	-0.15	0.30	318.0	<i>Small</i> , 2018 , 14, 1703940.
Pd₃Cu multipods	-0.12	0.22	230.0	<i>RSC Adv.</i> , 2016 , 6, 43980-43984.
Branched Pd nanoparticles (BNPs)	0.10	0.40	28	<i>J. Mater. Chem. A</i> , 2017 , 5, 11582-11585.



S5. Long-term stability comparisons of the as-prepared PdFe alloy tetrahedron and commercial Pd black performed in N_2 -saturated 0.5 M H_2SO_4 solution.



S6. Long-term stability comparisons of the as-prepared PdFe alloy tetrahedron and commercial Pd black performed in N_2 -saturated 0.5 M H_2SO_4 + 0.5 M $HCOOH$ solution.



S7. TEM images of the PdFe alloy tetrahedrons after the stability test.