# **Electronic Supplementary Information**

Sustainable 2,5-furandicarboxylic synthesis by direct 5-hydroxymethylfurfural fuel cell based on bifunctional PtNiS<sub>x</sub> catalyst

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#### **Experimental Section**

#### Chemicals and materials

Hydrochloric acid (HCl, 36.0-38.0%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95.0-98.0%), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%) and potassium hydroxide (KOH), nickel chloride (NiCl<sub>2</sub>·6H<sub>2</sub>O), chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), commercial carbon black (CB), 1-dodecanethiol and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. Nafion (5.0 wt.%) were purchased from Sigma-Aldrich. Commercial Pt/C catalyst (20 wt.% Pt supported on Vulcan XC-72 carbon) was obtained from Johnson Matthey. Carbon paper was purchased from Shanghai Hesen Electrical Co. Ltd. Deionized water (18.2 MΩ) was used in all experiments.

#### Synthesis of PtNiS<sub>x</sub>/CB

The PtNiS<sub>x</sub>/CB catalyst was synthesized with the modified carbon black (CB) as support. Firstly, the commercial CB was washed by piranha solution to form functional groups on the surface. In detail, 70 mL of  $H_2SO_4$  and 30 mL of  $H_2O_2$  were mixed slowly, followed by adding 1.0 g commercial CB powder. After aging for several hours, the mixture was filtered with deionized water until the supernatant was neutral and dried in the oven for overnight to get modified CB powder. Metal ions adsorption on the support was obtained *via* a simple impregnant method. In detail, 0.018 mmol NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in 15 mL of deionized water, then 0.1 g modified CB and 3.0 mL of 0.06 MH<sub>2</sub>PtCl<sub>6</sub> were added to the solution and stirred for 12 hours. Afterwards, the mixture was filtered with deionized water and ethanol for 3 times, and dried in oven for 6 hours. Then self-assembly process was conducted by a facile mercaptan vapor reaction approach. The as-prepared sample was heated to 50 °C for 12 hours with 1.0 mL of 1-dodecanethiol by the side. Finally, the sample was thermal-reduced at 400 °C for 2 hours under argon atmosphere.

### Synthesis of Pt/CB, NiS<sub>x</sub>/CB and PtNi/CB

The Pt/CB and NiS<sub>x</sub>/CB were prepared as the similar method without addition of NiCl<sub>2</sub>·6H<sub>2</sub>O or H<sub>2</sub>PtCl<sub>6</sub>. The PtNi/CB was also prepared without the sulfur source assembly process. In detail, 0.1 g modified CB and 3.0 mL of 0.06 MH<sub>2</sub>PtCl<sub>6</sub> were added to 15 mL of deionized water and stirred for 12 hours. Afterwards, the mixture was filtered with deionized water and ethanol for 3 times, and dried in oven for 6 hours. Finally, the sample was annealed at 400 °C for 2 hours under argon atmosphere, and the Pt/CB was obtained; For the NiSx/CB catalyst, 0.018 mmol NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in 15 mL of deionized water, then 0.1 g modified CB was added to the solution and stirred for 12 hours. Afterwards, the mixture was filtered with deionized water and ethanol for 3 times, and dried in oven for 6 hours. The as-prepared sample was heated to 50 °C for 12 hours with 1.0 mL of 1-dodecanethiol by the side. Finally, the sample was annealed at 400 °C for 2 hours under argon atmosphere; For the PtNi/CB catalyst, 0.018 mmol NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in 15 mL of deionized water, then 0.1 g modified CB and 3.0 mL of 0.06 MH<sub>2</sub>PtCl<sub>6</sub> were added to the solution and stirred for 12 hours. Afterwards, the mixture was filtered with deionized water and ethanol for 3 times, and dried in oven for 6 hours. Finally, the sample was annealed at 400 °C for 2 hours under flowing argon atmosphere.

#### **Characterization**

Field emission scanning electron microscope (FE-SEM, SU8020, Hitachi, Japan) with an acceleration voltage of 5.0 kV and transmission electron microscope (TEM, JEOL-2010, Japan) with acceleration of 200 kV was used to attain morphology and highresolution images. The elemental mapping images of the samples were also obtained on the TEM. XRD patterns of the materials were measured with Philips X-Pert Pro Xray diffractometer with Cu-K $\alpha$  ( $\lambda_{K\alpha l}$ =0.15418 nm) radiation at 40 kV and 40 mA. Raman spectra of the samples were recorded on a confocal microscope Raman system (LabRAMHR800, Horiba Jobin Yvon, Japan) using an Ar ion laser operating at 532 nm. The chemical compositions of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB250) equipped with Al K $\alpha$ 1, 2 monochromatized radiations at 1486.6 eV X-ray source. The Pt and Ni element content in the samples were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICP-6300, Thermo Fisher Scientific) after microwave digestion of the sample.

#### Electrochemical measurements

The electrochemical performance of samples was investigated by the cyclic voltammetry (CV), linear sweep voltammetry (LSV), open circuit potential-time (OCPT), chronopotentiometry with current ramp (CPCR), chronopotentiometry (CP) on a rotating ring-disk or a two-apartment cell with an electrochemistry workstation (CHI660, China). When testing ORR performance of the samples on rotate disk electrode (RDE), 0.1 M KOH solution was applied as the electrolyte, and a calibrated Hg/HgO reference electrode was applied as the reference electrode. All potentials in

this work were reported versus applied potential (*vs.* RHE), and the current densities were normalized using the geometric surface area. The result is E(RHE) = E(Hg/HgO)+ 0.866 V in 0.1 M KOH electrolyte at room temperature. When test was performed at the reaction temperature higher than 40°Cin 1.0 M KOH, *E* was further calibrated with the temperature coefficient (**Fig. S1**). What's more, we carried out H<sub>2</sub>-saturated calibrate experiment to confirm the potential versus RHE exactly<sup>1</sup>. In detail, the calibration was performed in a H<sub>2</sub>-saturated electrolyte with a Pt wire as the working electrode. The current-potential curve was run at a scan rate of 1.0 mV s<sup>-1</sup>, and the potential at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reaction. All potentials in this paper were calibrated with these values.



Fig. S1 Potentials when current densities are zero in  $H_2$ -saturated 1.0 M KOH at a scan rate of 1.0 mV s<sup>-1</sup>.

The catalyst ink was prepared as follows: 5.0 mg samples and 5.0  $\mu$ L of Nafion

solution was added into 1.0 mL of ethanol and 0.5 mL of DI water, and then ultrasonicated for 3 min to gain a homogenous suspension. Then 12  $\mu$ L of mixture was cast on the glassy carbon electrode with a geometric area of 0.196 cm<sup>2</sup>.

When testing the whole fuel cell performance, 0.4 mL of the above suspension was uniformly deposited on the carbon paper (CP) with 2.0 cm<sup>2</sup> (~2.0 mgcm<sup>-2</sup>) and dried in air. Then, two same pieces of sample supporting carbon paper were used as cathodic electrode and anodic electrode in the two-apartment cell, respectively, to construct a two-electrode system. 5-HMF was added into anodic cell with 1.0M KOH to obtain an HMF concentration of 10 mM and continuously purged N<sub>2</sub>, while the KOH solution in cathodic cell was purged O<sub>2</sub>. During the conversion of the as-added 5-HMF, the electric quantity needed is:

$$Q = 6nF = It \tag{1}$$

where Q is the electric quantity, 6 is the number of electrons transferred per HMF molecule, n is HMF mole involved in conversion, F is the Faraday constant (96485C mol<sup>-1</sup>), I is the constant current, and t is completely conversion time. Different temperatures were obtained with water bath for cells, and all the measurements were conducted after the temperature was stable. The OER activity was also measured with the two-apartment cell, while two pieces of material supporting carbon paper with electrode holders and the Hg/HgO reference electrode construct a three-electrode system.

The active surface area (ECSA) of catalysts was determined by H-UPDmethod<sup>2</sup>. CV curves were first measured under saturated  $N_2$  atmosphere. Then, the hydrogen desorption area of CV curve was integrated from 0.1 to 0.55 V to acquire the hydrogen area charge. ECSA was calculated according to the formula:

$$=\frac{Q_{\rm H}}{m \times q_{\rm H}}$$

(2)

where  $Q_{\rm H}$  is hydrogen area charge,  $q_{\rm H}$  is the charge need of hydrogen desorption in Pt surface (210  $\mu$ Ccm<sup>-2</sup>), and *m* is metal mass loading in the electrode.

The overall electron transfer numbers per oxygen molecule involved in the typical ORR process were calculated from the slopes of the Koutecky-Levich plots using the following equation:

$$\frac{1}{J} = \frac{1}{J_{\rm L}} + \frac{1}{J_{\rm k}} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_{\rm k}}$$

(3)

$$B = 0.2nFC_o(D_o)^{2/3}v^{-1/6}$$

$$J_k = nFkC_o$$
(5)
(4)

where *J* is the measured current density,  $J_k$  and  $J_L$  are the kinetic and mass-transport limiting current densities,  $\omega$  is the electrode rotating speed in rpm, *B* is the reciprocal of the slope, *n* is the number of electrons transferred per oxygen molecule, *F* is the Faraday constant (96485C mol<sup>-1</sup>),  $D_o$  is the diffusion coefficient of O<sub>2</sub> in 0.1 M KOH  $(1.9 \times 10^{-5} \text{ cm s}^{-1})$ , *v* is the kinetic viscosity (0.01 cm<sup>2</sup> s<sup>-1</sup>), and *C*<sub>o</sub> is the concentration of O<sub>2</sub> (1.2×10<sup>-3</sup>mol L<sup>-1</sup>). The constant 0.2 is adopted when the rotating speed is in rpm, and *k* is the electron transfer rate constant.

### **Product analysis**

The oxidation products were determined by high performance liquid chromatography (HPLC). The calibration of HMF, DFF, FFCA, HMFCA, FDCA was executed by an eluent of 5.0 mM ammonium formate solution and methanol (volume ratio=7:3). 10  $\mu$ L of electrolyte during the reaction was diluted with 490  $\mu$ L of deionized water, and injected into the HPLC system.

## Theoretical calculations

All spin-polarized calculations were carried out in Vienna ab-initio simulation package (VASP). The exchange-correlation interaction among electrons was described *via* a generalized gradient approximation (GGA), and the projector augmented wave (PAW) method. In the interaction, the van der Waals (vdW) correction with the Grimme approach (DFT-D3) was included. For PtNiS<sub>x</sub> slab, a four layer Pt(111) with p(4\*4) unit cell was adopted. The top two layers were relaxed. The force convergence's criterion was set to 0.02 eV/Å.

The binding energy  $E_b$ , describing not only the NiS<sub>x</sub>-PtNPs interaction but also the stability of oxygen, was defined as follows:

$$E_b = E_{total} - \left( E_{(composite)substrate} + E_{adsorbate} \right)$$
(6)

where  $E_{total}$  is the total energy of the adsorbate-substrate system,

 $E_{(composite)substrate}$  and  $E_{adsorbate}$  are the energies of the (pre-adsorbed or pure) substrate and the free adsorbate, respectively. The calculated binding energies of O and OH on Pt(111) were -3.82 eV and -1.91 eV, respectively.



**Fig.S2** Schematic of the synthesis of  $PtNiS_x/CB$  catalyst.



Fig. S3 FT-IR spectra of  $PtNiS_x/CB$ , Pt/Ni-dodecanethiol complex/CB, PtNi/CB and piranha solution-modified CB.



**Fig. S4** Schematic diagram of saturated dodecanethiol vapor reaction, and reaction scheme of the adsorbed Pt<sup>4+</sup>and alkanethiol.



Fig. S5 HRTEM images of PtNiS<sub>x</sub>/CB catalyst.



**Fig. S6** EDS spectra of PtNiS<sub>x</sub>/CB catalyst.



Fig. S7 High resolution Pt 4f (a) and Ni 2p (b) XPS spectra of  $PtNiS_x/CB$  catalyst.



Fig. S8 Polarization curves of LSVs at different rotating speeds for  $PtNiS_x/CB$  conducted in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 10 mV s<sup>-1</sup> (inset shows the corresponding *K-L* spots).

The results show that the calculated transferred electron number by *K-L* equation is  $\sim$ 3.7 using the PtNiS<sub>x</sub>/CB ORR catalyst, demonstrating an approximate fourelectron ORR process.



Fig. S9 Tafel curves of commercial Pt/C, Pt/CB, PtNi/CB and PtNiS<sub>x</sub>/CB catalysts.



Fig. S10 ORR polarization curves of  $PtNiS_x/CB$  before and after 5,000 cycles between 0.6 and 1.0V.



**Fig. S11** The DFT computational model: (a) Adsorption of O on the hollow site of  $NiS_x/Pt(111)$ . (b) Adsorption of OH on the hollow site of  $NiS_x/Pt(111)$ . (c) Difference charge density analysis of  $NiS_x/Pt(111)$ . (d) The calculated binding energy of O and OH on Pt(111) and  $NiS_x/Pt(111)$ .



**Fig. S12** (a) LSV curves of  $PtNiS_x/CB$ ,  $NiS_x/CB$ , PtNi/CB and commercial Pt/C catalyst in 1.0 M KOH solution with HMF. (b) Corresponding calculated Tafel slopes of prepared catalyst.



Fig. S13 (a) HRTEM image, (b) XRD patterns (the sample was examined in the carbon paper directly after long-time test), (c) High resolution Pt 4f and (d) Ni 2p XPS spectra of the  $PtNiS_x/CB$  after long-time HMF oxidation test.



Fig. S14 Schematic diagram of direct HMF fuel cell (DHMF-FC).



Fig. S15 Onset potential of  $PtNiS_x/CB$  for ORR and over-potential (10 mA cm<sup>-2</sup>) of

 $PtNiS_x/CB$  for OER at various temperatures.



Fig. S16 Polarization and power curves of DHMF-FC with different catalysts.



Fig. S17 Long-time discharge stability test of DHMF-FC assembled by  $PtNiS_x/CB$  catalyst.



Fig. S18 Reaction pathways of HMF oxidation.



Fig. S19 The calculated FE for five-cycle FDCA production.

Elements	С	S	0	Pt	Ni	Ni at.% to
	at.%	at.%	at.%	at.%	at.%	Pt at.%
Before test	95.19	1.41	1.32	0.42	1.66	3.95
After test	95.78	1.30	1.26	0.33	1.33	4.03

**Table S1.**  $PtNiS_x/CB$  catalyst composition before and after use determined by XPS.

**Table S2.** Comparison of the FDCA electrosynthesis from HMF activity with other catalysts.

Catalyst	Potential and current	Electrolyte	<i>C</i> <sub>HMF</sub>	FE for FDCA	Ref.
PtNiS <sub>x</sub> /CB	Driven by DHMF-FC	1.0 M KOH	10 mM	99%	this work
Ni <sub>x</sub> B	1.45 V (100 mA cm <sup>-2</sup> )	1.0 M KOH	10 mM	98.5%	[3]
CoP	1.38 V (20 mA cm <sup>-2</sup> )	1.0 M KOH	50 mM	90%	[4]
Ni <sub>2</sub> P/NF	1.423 V (>200 mA cm <sup>-2</sup> )	1.0 M KOH	10 mM	98%	[5]
Ni <sub>3</sub> N@C	1.38 V (50 mA cm <sup>-2</sup> )	1.0 M KOH	10 mM	98%	[6]
NiCo <sub>2</sub> O <sub>4</sub>	1.43 V (14.83 mA cm <sup>-2</sup> )	1.0 M KOH	10 mM	87.5%	[7]
NiFe LDH	1.43 V (100 mA cm <sup>-2</sup> )	1.0 M KOH	10 mM	97%	[8]
hp-Ni	1.423 V (>200 mA cm <sup>-2</sup> )	1.0 M KOH	10 mM	95%	[9]
CoNiFe LDH	1.55 V (30 mA cm <sup>-2</sup> )	1.0 M NaOH	10 mM	90%	[10]
Cu <sub>x</sub> S@ NiCo LDH	1.3V (87 mA cm <sup>-2</sup> )	1.0 M KOH	10 mM	99%	[11]
Ru <sub>(III)</sub> - PEI@MWCN Ts	1.34V (0.5 mA cm <sup>-2</sup> )	1.0 M KOH	10 mM	94%	[12]
Ni <sub>3</sub> S <sub>2</sub> /NF	1.423 V (>200 mA cm <sup>-2</sup> )	1.0 M KOH	10 mM	100%	[13]

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