Supplementary Information

## Pt<sub>3</sub>Sn Nanoparticles Enriched with SnO<sub>2</sub>/Pt<sub>3</sub>Sn Interface for Highly Efficient Alcohol Electrooxidation

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## **Electrochemical Measurements**

The electrochemical measurements were tested on an Autolab electrochemistry station with a standard three-electrode cell. Platinum wire, a glassy carbon electrode coated with catalyst and Ag/AgCl (sat. KCl) were used as a counter electrode, working electrode and reference electrode, respectively. The potentials in this study were converted to reversible hydrogen electrode (RHE). The working electrodes were modified by deposition of 5 uL uniform catalyst ink on a glassy carbon electrode. The uniform catalyst ink synthesized through ultrasonicated mixing 4 mg of catalyst in 1 mL deionized water 20  $\mu$ L Nafion (5 wt.%) and 1 mL isopropyl alcohol and. Cyclic voltammetry (CV) measurements were carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 50 mV s<sup>-1</sup>. The ethanol oxidation reaction or methanol oxidation reaction was performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M ethanol or 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M methanol at a scan of 50 mV s<sup>-1</sup>. The CO stripping voltammetry was performed in 0.5 M CO-free H<sub>2</sub>SO<sub>4</sub> electrolyte at a scan of 50 mV s<sup>-1</sup> after the electrode was held at 0.05 V vs. RHE in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution bubbled with CO for 30 min.



Fig. S1 (a) TEM and (b) HRTEM of  $Pt_2Sn/NG$  catalyst.



Fig. S2 (a) TEM and (b) HRTEM of  $Pt_2Sn-H/NG$  catalyst.



Fig. S3 The selected diffraction pattern of  $Pt_3Sn@u-SnO_2/NG$  catalyst.



**Fig. S4** (a) CV curves of different catalysts in 0.5 M  $H_2SO_4$  solution with a sweep rate of 50 mV s-1. (b) Linear sweep voltammograms of different catalysts in 0.5 M  $H_2SO_4$  + 1 M CH<sub>3</sub>CH<sub>2</sub>OH solution with a sweep rate of 50 mV s<sup>-1</sup>.



Fig. S5 The mass activity towards EOR on  $Pt_2Sn/NG$ ,  $Pt_2Sn-H/NG$ ,  $Pt_3Sn@u-SnO_2/NG$  and Pt/C catalysts at different potential.



**Fig. S6** Cyclic voltammogram of (a)  $Pt_3Sn@u-SnO_2/NG$ , (b)  $Pt_2Sn-H/NG$ , (c)  $Pt_2Sn/NG$  and (d) Pt/C catalysts in  $N_2$ -saturated 0.5 M  $H_2SO_4$  + 1 M  $CH_3CH_2OH$  solution at scan rate of 50 mV s<sup>-1</sup> during the durability tests.



Fig. S7 (a) TEM and (b) HRTEM of  $Pt_3Sn@u-SnO_2/NG$  catalyst after the durability tests for 1000 cycles in N<sub>2</sub>-saturated 0.5 M  $H_2SO_4 + 1$  M  $CH_3CH_2OH$  solution.



Fig. S8 The mass activity towards MOR on  $Pt_2Sn/NG$ ,  $Pt_2Sn-H/NG$ ,  $Pt_3Sn@u-SnO_2/NG$  and Pt/C catalysts at different potential.



Fig. S9 Corresponding Tafel plots for MOR on  $Pt_2Sn/NG$ ,  $Pt_2Sn-H/NG$ ,  $Pt_3Sn@u-SnO_2/NG$  and Pt/C catalysts.



**Fig. S10** Cyclic voltammogram of (a)  $Pt_3Sn@u-SnO_2/NG$ , (b)  $Pt_2Sn-H/NG$ , (c)  $Pt_2Sn/NG$  and (d) Pt/C catalysts in  $N_2$ -saturated 0.5 M  $H_2SO_4 + 1$  M CH<sub>3</sub>OH solution at scan rate of 50 mV s<sup>-1</sup> during the durability tests.



**Fig. S11** Cyclic voltammogram of (a)  $Pt_3Sn@u-SnO_2/NG$ , (b)  $Pt_2Sn-H/NG$ , (c)  $Pt_2Sn/NG$  catalysts in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at scan rate of 50 mV s<sup>-1</sup> during the durability tests.

	(111)	(200)
Standard Pt <sub>3</sub> Sn	100	39
Standard Pt	100	53
Pt <sub>3</sub> Sn	100	40.6

 Table S1. The peak height ratio of crystal plane.

**Table S2.** XPS spectra of different catalysts with Pt 4f.

Samples	$Pt^{0}4f_{7/2}$	$Pt^{2+}4f_{7/2}$	$Pt^{0}4f_{5/2}$	$Pt^{2+}4f_{5/2}$
Pt <sub>2</sub> Sn/NG	71.49	72.69	74.77	76.08
Pt <sub>2</sub> Sn-H/NG	71.23	72.42	74.59	75.77
Pt <sub>3</sub> Sn@u-SnO <sub>2</sub> /NG	71.32	72.50	74.61	75.90
Pt/C	71.76	72.96	75.10	76.27

Samples	${\rm Sn}^{4+}{\rm 3d}_{5/2}$	$Sn^03d_{5/2}$	$Sn^{4+}3d_{3/2}$	$Sn^03d_{3/2}$
Pt <sub>2</sub> Sn/NG	486.98	485.51	495.41	494.04
Pt <sub>2</sub> Sn-H/NG	486.88	485.53	495.34	494.01
Pt <sub>3</sub> Sn@u-SnO <sub>2</sub> /NG	486.93	485.51	495.34	494.06

Table S3. XPS spectra of different catalysts with Sn 3d.

**Table S4.** The valent state mass percent of  $Sn^0$  and  $Sn^{4+}$  for different samples.

Samples	Sn <sup>0</sup>	Sn <sup>4+</sup>
Pt <sub>2</sub> Sn/NG	2.1	97.9
Pt <sub>2</sub> Sn-H/NG	8.5	91.5
Pt <sub>3</sub> Sn@u-SnO <sub>2</sub> /NG	2.4	97.6

Catalysts	Onset Potential (V vs. RHE) from CO	Peak currents MA (mA mg <sup>-</sup> <sup>1</sup> Pt)	Electrolytes	Ref.
Pt <sub>3</sub> Sn@u-SnO <sub>2</sub> /NG	0.36	1322	0.5 M H <sub>2</sub> SO <sub>4</sub> + 1 M CH <sub>3</sub> CH <sub>2</sub> OH	This work
PtSn	/	764.1	0.5 M H <sub>2</sub> SO <sub>4</sub> + 1 M CH <sub>3</sub> CH <sub>2</sub> OH	[1]
L1 <sub>0</sub> -Co <sub>41</sub> Pt <sub>4</sub> Au <sub>15</sub>	/	1550	0.1 M HClO <sub>4</sub> + 2 M CH <sub>3</sub> CH <sub>2</sub> OH	[2]
PtRu@FeP	~0.5	660	0.5 M H <sub>2</sub> SO <sub>4</sub> + 1 M CH <sub>3</sub> CH <sub>2</sub> OH	[3]
Pt49Ru51/C	/	~630	0.1 M HClO <sub>4</sub> + 0.5 M CH <sub>3</sub> CH <sub>2</sub> OH	[4]
Pt <sub>3</sub> Co@Pt/PC	/	~830	$0.1 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M CH}_3\text{CH}_2\text{OH}$	[5]
Pt-Ni NFs/C	/	1040	$0.1 \text{ M HClO}_4 + 0.2 \text{ M CH}_3\text{CH}_2\text{OH}$	[6]
PtRu/C	0.75	771	1 M HClO <sub>4</sub> + 1 M CH <sub>3</sub> CH <sub>2</sub> OH	[7]
Pt-Ce <sub>0.6</sub> Zr <sub>0.4</sub> /C	0.42	272	1 M HClO <sub>4</sub> + 1 M CH <sub>3</sub> CH <sub>2</sub> OH	[7]
Pt <sub>6</sub> Sn <sub>3</sub> NWs	/	1080	0.1 M HClO <sub>4</sub> + 0.5 M CH <sub>3</sub> CH <sub>2</sub> OH	[8]
$Pt/C + TiO_2$	~0.67	648	1 M HClO <sub>4</sub> + 1 M CH <sub>3</sub> CH <sub>2</sub> OH	[9]
Pt/SnO <sub>2</sub> /graphene	/	713	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{CH}_2\text{OH}$	[10]
SnO <sub>2</sub> /Pt/G <sub>30</sub>	/	454	$0.5 \text{ M H}_2\text{SO}_4 + 0.25 \text{ M CH}_3\text{CH}_2\text{OH}$	[11]
PZCNT (1:1)	0.52	660	1 M HClO <sub>4</sub> + 1 M CH <sub>3</sub> CH <sub>2</sub> OH	[12]
Pt-CoSn/C	/	~454	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{CH}_2\text{OH}$	[13]

**Table S5.** EOR Electrochemical activity of the catalysts reported in the literaturecurrently and compared with our  $Pt_3Sn@u-SnO_2/NG$  catalyst.

Catalysts	Onset Potential (V vs. RHE) from CO	Peak currents MA (mA mg <sup>-1</sup> Pt)	Electrolytes	Ref.
Pt <sub>3</sub> Sn@u-SnO <sub>2</sub> /NG	0.36	1377	0.5 M H <sub>2</sub> SO <sub>4</sub> + 1 M CH <sub>3</sub> OH	This work
Pt <sub>3</sub> CoRu/C@NC	0.35	970	0.1 M HClO <sub>4</sub> + 0.5 M CH <sub>3</sub> OH	[14]
PtRu@FeP	~0.5	700	0.5 M H <sub>2</sub> SO <sub>4</sub> + 1 M CH <sub>3</sub> OH	[3]
PZCNT (1:1)	0.52	847	1 M HClO <sub>4</sub> + 1 M CH <sub>3</sub> OH	[12]
Pt/H-TiO2@N- HPCN-800	0.465	695	0.5 M H <sub>2</sub> SO <sub>4</sub> + 1 M CH <sub>3</sub> OH	[15]
Pt <sub>32</sub> Cu <sub>68</sub> alloy	0.48	707	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M CH <sub>3</sub> OH	[16]
Pt <sub>3.5</sub> Pb NNWs	/	1180	0.5 M H <sub>2</sub> SO <sub>4</sub> + 1 M CH <sub>3</sub> OH	[17]
Pt-Fe-Mn UCNC	0.43	950	0.5 M H <sub>2</sub> SO <sub>4</sub> + 2 M CH <sub>3</sub> OH	[18]
Pd@PtNi NPs	~0.65	782	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$	[19]
PtFe@PtRuFe	0.39	690	0.1 M HClO <sub>4</sub> + 0.5 M CH <sub>3</sub> OH	[20]
Pt/Pd NSLs-WPAS	/	952	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$	[21]
PtRuCu/C	~0.6	1350	0.1 M HClO <sub>4</sub> + 1 M CH <sub>3</sub> OH	[22]
Pt94Zn6 NWs	~0.65	511.3	0.1 M HClO <sub>4</sub> + 0.2 M CH <sub>3</sub> OH	[23]
PtRu NWs	/	820	0.1 M HClO <sub>4</sub> + 0.5 M CH <sub>3</sub> OH	[24]
Pt-CoSn/C	/	970	0.1 M HClO <sub>4</sub> + 0.5 M CH <sub>3</sub> OH	[25]

**Table S6.** MOR Electrochemical activity of the catalysts reported in the literaturecurrently and compared with our  $Pt_3Sn@u-SnO_2/NG$  catalyst.

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