Supporting Information

High-Performance Alcohol Electrooxidation on Pt₃Sn-SnO₂

Nanocatalysts through Transformation of PtSn Nanoparticles

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EXPERIMENTAL SECTION

1. Synthesis of Pt₃Sn-SnO₂/NG and Pt₃Sn/NG catalysts

The graphene oxide (GO) is prepared by a modified Hummers methods previously reported by our group.¹ The N-doped GO (NG) was synthesized by pyrolysis of the mixture of GO and urea in an N₂ atmosphere at 600°C for 30 minutes. Pt-Sn/NG was prepared using H₂PtCl₆•6H₂O and SnCl₂•2H₂O as precursors by the polyol method². Pt₃Sn-SnO₂/NG catalyst were obtained by direct heat treatment of Pt-Sn/NG at 300°C for 1 h under air condition. For comparison, the ordered Pt₃Sn/NG catalysts prepared by heating treatment of the disordered Pt₃Sn/NG catalysts (prepared by above polyol method) at 300°C for 1 h under 10%H₂/90% N₂ atmosphere.

2. Materials characterization

The Scanning electron microscopy (SEM, SUPRA 55), transmission electron microscopy (TEM, TECNAL G2F2O) and X-ray powder diffraction (XRD, ULTIMA III) were carried out to characterize the morphology and structure of the obtained samples. X-ray photoelectron spectroscopy (XPS) characterization was examined using a K-Alpha.

3. Electrochemical characterization

All electrochemical measurements were characterized using an Autolab electrochemistry station in a standard three-electrode cell at room temperature. A catalyst coated glassy carbon electrode was used as the working electrode while Ag/AgCl (sat. KCl) and platinum wire were used as reference and counter electrodes, respectively. The potentials presented in this study are referred with respect to reversible hydrogen electrode (RHE). The working electrodes were prepared by

deposition of 5 uL uniform catalyst ink prepared by ultrasonicated mixing 4 mg of catalyst in 1 mL deionized water and 1 mL isopropyl alcohol and 20 μ L Nafion (5 wt. %). Cyclic voltammetry (CV) measurements were performed at a scan rate of 50 mV s⁻¹ within a potential range from 0.05 V to 1.2 V (vs. RHE) in 0.5 M H₂SO₄. The ethanol oxidation reaction or methanol oxidation reaction was performed in 0.5 M H₂SO₄ + 1 M ethanol or 0.5 M H₂SO₄ + 1 M ethanol between 0.05 V and 1.2 V at a scan of 50 mV s⁻¹. For CO stripping experiment, CO was bubbled through the 0.5 M H₂SO₄ electrolyte for 20 mins when the electrode potential was held at 0.05 V vs. RHE. N₂ was then bubbled to remove the free CO in the electrolyte. Then, the CO stripping voltammetry was performed between 0.05 V and 1.2 V at a scan of 50 mV s⁻¹.



Figure S1. (a) TEM and (b) HRTEM of Pt-Sn/NG catalyst.



Figure S2. (a) TEM and (b) HRTEM of ordered Pt_3Sn/NG catalyst prepared by annealing of disordered Pt_3Sn alloy on NG at the $10\%H_2/90\%N_2$ atmosphere.



Figure S3. XPS survey spectrum of $Pt_3Sn-SnO_2/NG$, Pt-Sn/NG, Pt_3Sn/NG and Pt/C catalysts.



Figure S4. (a) The specific activity towards EOR on $Pt_3Sn-SnO_2/NG$, Pt-Sn/NG, Pt_3Sn/NG and Pt/C catalysts. (b) Chronoamperometric curves of different catalysts in N_2 -saturated 0.5 M $H_2SO_4 + 1$ M CH_3CH_2OH solution at constant voltage 0.7 V for 3600 s.



Figure S5. (a) The mass activity and (b) specific activity towards EOR on $Pt_3Sn-SnO_2/NG$, Pt-Sn/NG, Pt_3Sn/NG and Pt/C catalysts at different potential.



Figure S6. The forward peak current density of EOR for Pt₃Sn-SnO₂/NG, Pt-Sn/NG, Pt₃Sn/NG and Pt/C catalysts.



Figure S7. (a) EOR curves and (b) XRD patterns of catalysts prepared by different heat treatment temperatures for 1 h under air condition. (c)TEM and (d)HRTEM of catalyst prepared by direct heat treatment of Pt-Sn/NG at 200°C for 1 h under air condition. (e) TEM and (f) HRTEM of catalyst prepared by direct heat treatment of Pt-Sn/NG at 400°C for 1 h under air condition.



Figure S8. Cyclic voltammogram of (a) Pt_3Sn/NG , (b) Pt-Sn/NG and (c) Pt/C catalysts in N₂-saturated 0.5 M $H_2SO_4 + 1$ M CH_3CH_2OH solution at scan rate of 50 mV s⁻¹ during the durability tests.



Figure S9. TEM of Pt/C catalyst (a) before and (b) after ADT.



Figure S10. (a) TEM and (b) HRTEM of $Pt_3Sn-SnO_2/NG$ catalyst after the durability tests for 5000 cycles in N₂-saturated 0.5 M $H_2SO_4 + 1$ M CH₃CH₂OH solution.



Figure S11. Linear sweep voltammograms of different catalysts in 0.5 M $H_2SO_4 + 1$ M CH₃OH solution with a sweep rate of 50 mV s⁻¹.



Figure S12. (a) The specific activity towards MOR on $Pt_3Sn-SnO_2/NG$, Pt-Sn/NG, Pt_3Sn/NG and Pt/C catalysts. (b) Chronoamperometric curves of different catalysts in N_2 -saturated 0.5 M $H_2SO_4 + 1$ M CH₃OH solution at constant voltage 0.7 V for 3600 s.



Figure S13. (a) The mass activity and (b) specific activity towards MOR on $Pt_3Sn-SnO_2/NG$, Pt-Sn/NG, Pt_3Sn/NG and Pt/C catalysts at different potential.



Figure S14. The forward peak current density of MOR for $Pt_3Sn-SnO_2/NG$, Pt-Sn/NG, Pt_3Sn/NG and Pt/C catalysts.



Figure S15. The current density of different catalysts at 0.7 V at 3600 s obtained from Figure 6c.



Figure S16. Cyclic voltammogram of (a) $Pt_3Sn-SnO_2/NG$, (b) Pt-Sn/NG, (c) Pt_3Sn/NG and (d) Pt/C catalysts in N_2 -saturated 0.5 M $H_2SO_4 + 1$ M CH₃OH solution at scan rate of 50 mV s⁻¹ during the durability tests.

Samples	Pt ⁰ 4f _{7/2}	$Pt^{2+}4f_{7/2}$	$Pt^{4+}4f_{7/2}$	Pt ⁰ 4f _{5/2}	$Pt^{2+}4f_{5/2}$	Pt ⁴⁺ 4f _{5/2}
Pt ₃ Sn-SnO ₂ /NG	71.55	72.65	73.83	74.79	76.02	77.97
Pt ₃ Sn/NG	71.45	72.74	/	74.79	76.02	/
Pt-Sn/NG	71.51	72.72	/	74.79	76.06	/
Pt /C	71.71	72.97	/	75.08	76.29	/

 Table S1. XPS spectra of different catalysts with Pt 4f.

Table S2. XPS spectra of different catalysts with Sn 3d.

Samples	${\rm Sn}^{4+}{\rm 3d}_{5/2}$	Snº3d _{5/2}	${\rm Sn^{4+}3d_{3/2}}$	$Sn^03d_{3/2}$
Pt ₃ Sn-SnO ₂ /NG	486.9	485.68	495.36	494.33
Pt ₃ Sn/NG	486.81	485.68	495.23	494.18
Pt-Sn/NG	487.08	485.56	495.5	494.09

Table S3. Electrochemically active surface area (ECSA) of different catalysts estimated from CO stripping experiments, the onset potential and the peak potential for CO oxidation for the relevant catalysts.

Samples	ECSA (m ² g ⁻¹)	Onset	Small Peak	Main Peak
		potential	potential	potential
		(V)	(V)	(V)
Pt ₃ Sn-SnO ₂ /NG	54	0.33	0.47	0.71
Pt ₃ Sn/NG	36	0.38	0.49	0.72
Pt-Sn/NG	41	0.43	/	0.73
Pt/C	67	0.83	/	0.89

Catalysts	Onset Potential (V	Peak currents	Electrolytes	Ref.
	vs. RHE) from	MA (mA mg _{Pt} ⁻¹)		
	СО			
Pt ₃ Sn-SnO ₂ /NG	0.33	1365	0.5 M H ₂ SO ₄ + 1 M CH ₃ CH ₂ OH	This
				work
PtSn	/	764.1	0.5 M H ₂ SO ₄ + 1 M CH ₃ CH ₂ OH	3
$L1_0$ -Co ₄₁ Pt ₄ Au ₁₅	/	1550	0.1 M HClO ₄ + 2 M CH ₃ CH ₂ OH	4
Pt1Mo1/C	~0.4	1000.0	0.1 M KOH + 0.5 M CH ₃ CH ₂ OH	5
Pt49Ru51/C	/	~630	0.1 M HClO ₄ + 0.5 M CH ₃ CH ₂ OH	6
Pt ₃ Co@Pt/PC	/	~830	0.1 M H ₂ SO ₄ + 0.1 M CH ₃ CH ₂ OH	7
Pt-Ni NFs/C	/	1040	0.1 M HClO ₄ + 0.2 M CH ₃ CH ₂ OH	8
PtRu/C	0.75	771	1 M HClO ₄ + 1 M CH ₃ CH ₂ OH	9
Pt-Ce _{0.6} Zr _{0.4} /C	0.42	272	1 M HClO ₄ + 1 M CH ₃ CH ₂ OH	9
Pt ₆ Sn ₃ NWs	/	1080	0.1 M HClO ₄ + 0.5 M CH ₃ CH ₂ OH	10
$Pt/C + TiO_2$	~0.67	648	1 M HClO ₄ + 1 M CH ₃ CH ₂ OH	11
Pt/SnO ₂ /graphene	/	713	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{CH}_2\text{OH}$	12
SnO ₂ /Pt/G ₃₀	/	454	$0.5 \text{ M H}_2\text{SO}_4 + 0.25 \text{ M CH}_3\text{CH}_2\text{OH}$	13
PZCNT (1:1)	0.52	660	1 M HClO ₄ + 1 M CH ₃ CH ₂ OH	14
Pt-CoSn/C	/	~454	0.5 M H ₂ SO ₄ + 0.5 M CH ₃ CH ₂ OH	15
$Pt_{69}Ni_{16}Rh_{15}$	0.4	1530	0.1 M HClO ₄ + 0.5 M CH ₃ CH ₂ OH	16
Pt-0.5SnOx/NCNC	0.3	1187	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{CH}_2\text{OH}$	17
Pt3Fe NWs	/	1300	0.1 M HClO ₄ + 0.5 M CH ₃ CH ₂ OH	18

Table S4. EOR Electrochemical activity of the catalysts reported in the literaturecurrently and compared with our $Pt_3Sn-SnO_2/NG$ catalyst.

Catalysts	Onset Potential (V	Peak currents	Electrolytes	Ref.
	vs. RHE) from CO	MA (mA mg_{Pt}^{-1})		
Pt ₃ Sn-SnO ₂ /NG	0.33	1345	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	This
				work
Pt/CeO ₂ -P	/	714	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	19
Pt ₃ Au/N-G	/	417	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$	20
PZCNT (1:1)	0.52	847	1 M HClO ₄ + 1 M CH ₃ OH	14
porous PtRu NCs	/	384	0.1 M HClO ₄ + 1 M CH ₃ OH	21
Pt ₃₂ Cu ₆₈ alloy	0.48	707	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$	22
Pt _{3.5} Pb NNWs	/	1180	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	23
Pt/rGO NCs	/	333	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$	24
Pd@PtNi NPs	~0.65	782	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$	25
PtFe@PtRuFe	0.39	690	0.1 M HClO ₄ + 0.5 M CH ₃ OH	26
Pt/Pd NSLs-WPAS	/	952	$0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$	27
PtRuCu/C	~0.6	1350	0.1 M HClO ₄ + 1 M CH ₃ OH	28
Pt ₉₄ Zn ₆ NWs	~0.65	511.3	0.1 M HClO ₄ + 0.2 M CH3OH	29
PtRu NWs	/	820	0.1 M HClO ₄ + 0.5 M CH ₃ OH	30
Pt-CoSn/C	/	970	0.1 M HClO ₄ + 0.5 M CH ₃ OH	31
Pt/ATO-200-3h	0.36	1520	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	32
Pt ₆₉ Ni ₁₆ Rh ₁₅	0.4	1720	0.1 M HClO ₄ + 0.5 M CH ₃ OH	16
Pt3Fe NWs	/	1500	0.1 M HClO ₄ + 0.5 M CH ₃ OH	18
20%Pt-Ni ₂ P-G	/	1554.6	0.5 M H ₂ SO ₄ + 1 M CH ₃ OH	33

 Table S5. MOR Electrochemical activity of the catalysts reported in the literature

 currently and compared with our Pt₃Sn-SnO₂/NG catalyst.

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