Supplementary Information

Synergistic Effects of NiPtCo/Ti $_{0.7}W_{0.3}O_2$ Hybrid Electrocatalysts

for Accelerating Formic Acid Electro-Oxidation Performance

EXPERIMENTAL DETAILS

Chemicals

Chloroplatinic acid hexahydrate (H₂PtCl₆.6H₂O, \geq 37.50% Pt), nickel(II) chloride hexahydrate (NiCl₂.6H₂O, 99.9%), and cobalt(II) chloride hexahydrate (CoCl₂.6H₂O, 98%) were purchased from Sigma-Aldrich, USA. Ethylene glycol (CH₂OH)₂, 99.0%), sodium hydroxide (NaOH, \geq 99.0%), and sodium borohydride (NaBH₄, 98.0%) were achieved by Merck, Germany.

Fabrication of ternary NiPtCo/Ti_{0.7}W_{0.3}O₂ hybrid electrocatalyst

A microwave-assisted chemical reduction method was used to anchor the NiPtCo ternary alloy on the non-carbon $Ti_{0.7}W_{0.3}O_2$ surface, being fabricated via the solvothermal process (200 °C, 10 h).^{1, 2} In this typical process, 100 mg of $Ti_{0.7}W_{0.3}O_2$ nanomaterial was homogeneously dispersed into a mixture of NaBH₄ (0.01 M) and ethylene glycol (1: 5 v/v%) under stirring for 5 min, which was then ultrasonicated for 15 min to achieve a homogeneous suspension. Next, $CoCl_2$ (0.02 M), NiCl_2 (0.02 M), and H_2PtCl_6 (0.02 M) were rapidly added into the above suspension according to the 1:1:3 molar ratio for Co:Ni:Pt, followed by adjusting pH value to 11 by NaOH (1M). Afterwards, the as-made mixture was put in a microwave oven (ELECTROLUXEMS2047X, 800 W, 2450 MHz) at 180 °C for 2.5 min. Finally, the resultant product was collected by centrifugation, washing, and drying overnight at 80 °C for further analysis.

Material Characterizations

The crystal structure of specimens was studied through X-ray diffraction analysis (XRD. D2 PHASER (Bruker), Germany) using a Cu K_{α} X-ray source in the 2-theta range of 20^o–80^o at a step size of 0.02^o. The chemical states of compositions were probed via an X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe (Ulvac-PHI), Japan) using a monochromator Al K_{α} X-ray source. The morphology of specimens was determined by high-resolution transmission

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electron microscopy (HR-TEM, JEM 2100F (JOEL), Japan) at 200 kV.

Calculation of the lattice parameters of specimens

The crystallite size of specimens was calculated by the Debye-Scherrer formula (Eq.(S1)):³⁻⁵

$$D_{(hkl)} = \frac{k\lambda}{\beta\cos\theta}$$
(S1)

where $D_{(hkl)}$ is crystallite size (nm), k denotes Scherrer constant (0.94), θ is the Bragg angle, λ and β present the X-ray wavelength (λ = 1.5406 Å), and line broadening at half the maximum intensity (FWHM), respectively.

The interplanar spacing of specimens was calculated by Bragg's law (Eq. (S2)):^{4, 5}

$$d_{(hkl)} = \frac{\lambda}{2\sin\theta}$$
(S2)

where: $d_{(hkl)}$ is lattice space (Å); λ and θ denote the X-ray wavelength (λ = 1.5406 Å) and Bragg angle, respectivelly.

The lattice strain of specimens was calculated by (Eqs. (S3) and (S4):⁶

$$L = 1/2d$$
 (S3)

$$L_2 \operatorname{strain} = (L_1 - L_2))/L_1$$
 (S4)

where *L* denotes the lattice parameter and *d* is the interplanar spacing of the selected crystal facet. L_2 % represents the percentage change of the lattice parameter of the as-obtained NiPtCo ternary alloy when compared to PtCo binary alloy. L_1 and L_2 are the lattice parameters of PtCo and NiPtCo alloys, respectively.

Electrochemical Tests

An Autolab potentiostat/galvanostat (PGSTAT302N) workstation (Metrohm Co., Ltd. Switzerland) coupled with a three-electrode cell (*i.e.*, glassy carbon (GCE), 3 mm), platinum wire, and Ag/AgCl/(sat.KCl)) was employed to determine the electrochemical behaviors of as-

made FAOR electrocatalysts. To ensure sufficient electronic conductivity, 20 wt% Vulcan XC-72 was added to the NiPtCo/Ti_{0.7}W_{0.3}O₂ catalyst. In catalyst ink preparation, 1.7 mg of the obtained catalyst was added into a mixture of Nafion and isopropyl alcohol (1:3 v/v%), and then was ultrasonicated for 30 min to form a homogeneous ink. Before the electrochemical test, 1.5 μ L of catalyst ink was covered on the polished GCE surface and dried naturally. The formic acid electro-oxidation (FAOR) performance of all studied electrocatalysts was tested via a linear sweep voltammetry (LSV) test in N₂-saturated 0.5 M H₂SO₄ + 0.5 M HCOOH electrolyte at a 50 mV s⁻¹ scan rate. The CO-tolerance ability of all investigated electrocatalysts was probed via a CO-stripping measurement in 0.5 M H₂SO₄ electrolyte, being purged with N₂ at 15 min, followed by CO bubbling for 45 min. Also, the chronoamperometry (CA) test was conducted in N₂-saturated 0.5 M H₂SO₄ + 0.5 M HCOOH solution at 0.4 V_{RHE} for 1 h in. All reported potentials were converted from Ag/AgCl to a reversible hydrogen electrode (RHE) scale.

Electrochemical surface area (ECSA) calculation

The electrochemically active surface area (ECSA) is calculated by Eq.(S5), and (S6):7-9

$$ECSA = \frac{Q_{\rm H}}{0.21*[Metal]}$$
(S5)

where Q_H (mC cm⁻²) is the coulomb charge for hydrogen adsorption; 0.21 (mC cm⁻²) and [Metal] denotes a charge required to oxidize an H₂ monolayer, and loaded catalyst metal onto the GCE surface (0.13 mg cm⁻²), respectively. Q_H is calculated by Eqs. (S6):^{10, 11}

$$Q_{\rm H} = \frac{1}{\nu A} \int I_{\rm (V)} dV \tag{S6}$$

where I (A) is a peak current, V (V) is a peak potential; ν (mV s⁻¹) and A (cm⁻²) denote a scan rate and GCE's geometric area, respectively.

Calculation of kinetic parameter

The kinetic parameter of all studied catalysts was determined by the Tafel equation (S7):¹²⁻¹⁵

$$\eta = b \log \frac{i}{i_0} = \frac{2.3 \text{ R T}}{\alpha \text{ F}}$$
(S7)

where R and T (K) denote the gas constant and the absolute temperature, respectively, α is the charge transfer coefficient, F is the Faraday constant, and i₀ (mA cm⁻²) is the exchange current density.

Calculation of the apparent activation energy

The activation energy (E_a) of the catalyst is calculated by the Arrhenius equation (S8):¹⁶⁻¹⁸

$$\mathbf{k}(\mathbf{T}) = \mathbf{A}\mathbf{e}^{-\mathbf{E}_{a}/\mathbf{R}\mathbf{T}}$$
(S8)

where k(T) is a rate constant, A denotes a pre-exponential factor, and T and R are temperature and gas constants, respectively. The apparent activation energy ($E_{a(app)}$) can be obtained from the measured currents at different temperatures through Eq. (S9):^{16, 18, 19}

$$E_{a(app)} = -2.303R \left[\frac{d\ln i}{d(1/T)} \right]$$
(S9)

The Arrhenius plots were achieved through plotting ln j against the reciprocal of T.^{16, 20}

Results and Discussion



Figure S1. EDX spectroscopy of the as-made NiPtCo/Ti_{0.7}W_{0.3}O₂ hybrid electrocatalysts.



Figure S2. LSV curves of all studied FAOR electrocatalysts in N₂-saturated 0.5 M H_2SO_4 + 0.5 M HCOOH electrolyte at a scan rate of 10 mV s⁻¹.



Figure S3. LSV curves at different scan rates in N_2 -saturated 0.5 M H_2SO_4 + 0.5 M HCOOH electrolyte of (a) NiPtCo/C, (b) PtCo/C, and (c) Pt/C (E-TEK) electrocatalysts.



Figure S4. LSV curves at 50 mV s⁻¹ scan rate at different temperatures in N₂-saturated 0.5 M $H_2SO_4 + 0.5$ M HCOOH solution of (a) NiPtCo/C, (b) PtCo/C, and (c) Pt/C (E-TEK) catalysts.

Figure S5. XRD patterns of the NiPtCo/Ti $_{0.7}W_{0.3}O_2$ catalyst before and after the ADT test.

Table S1. A summar	y of lattice	parameters of	⁼ NiPtCo/Ti _{0.} -	₇ W _{0.3} O ₂ catalyst.
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Catalyst	2θ / degree	Crystalline size	Interplanar spacing	Strain
	(111)	nm	nm	%
NiPtCo/Ti _{0.7} W _{0.3} O ₂	39.88	2.22	0.2260	0.168
$PtCo/Ti_{0.7}W_{0.3}O_2$	39.95	3.13	0.2256	-

Table S2. A summary of FAOR reactivity of all studied electrocatalysts in N_2 -saturated 0.5 M

 H_2SO_4 + 0.5 M HCOOH electrolyte at a scan rate of 50 mV s⁻¹.

Catalysts	ECSA	Mass activity	Specific activity	<i>ј</i> нсоон/ <i>ј</i> со
	$m^2 g_{Metal}^{-1}$	A mg _{Metal} ⁻¹	mA cm ⁻²	
NiPtCo/Ti _{0.7} W _{0.3} O ₂	40.18	0.45	1.25	0.82
NiPtCo/C	33.70	0.27	0.81	0.57
PtCo/C	57.75	0.19	0.33	0.29
Pt/C (E-TEK)	75.60	0.12	0.26	0.26

Table S3. Comparison of the FAOR activity of the as-made NiPtCo/Ti_{0.7}W_{0.3}O_2 catalyst with

Catalysta		Mass activity	Specific activity	Def
Catalysts	Electrolyte	A mg_{Metal} -1	mA cm ⁻²	Kel.
NiPtCo/Ti _{0.7} W _{0.3} O ₂	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	0.45	1.25	This work
PtCuCr h-NFs	0.5 M H ₂ SO ₄ + 0.25 M HCOOH	0.38	1.12	21
PtMnCu CNC	0.5 M H ₂ SO ₄ + 0.25 M HCOOH	0.19	1.87	22
PtAgCu@PtCu	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	0.31	1.65	23
PtPdRhAg NFs	0.5 M H ₂ SO ₄ + 0.25 M HCOOH	0.22	1.16	24
0.5%Sn/Pt₃Mn CNC	0.5 M H ₂ SO ₄ + 0.25 M HCOOH	0.13	1.58	25
Pt ₃ Zn ₁₀ /C-700	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	0.33	0.59	26
Au@Pt-graphene	0.1 M H ₂ SO ₄ + 0.1 M HCOOH	0.464	0.443	27
AgPt NWs	0.5 M H ₂ SO ₄ + 1.0 M HCOOH	0.152	1.03	28
HSCS Au_{100} @Pd $_{20}$ Pt $_{20}$ NPs	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	0.52	1.12	29
Commercial Pt/C	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	0.12	0.16	30
Pd ₃ Pt hafl-shells	0.5 M H ₂ SO ₄ + 0.5 M HCOOH	0.318	-	31
PtAu/CoNC-2	0.5 M H ₂ SO ₄ + 1.0 M HCOOH	0.29	0.8	32
Pt-Cu-Ni CNC	0.5 M H ₂ SO ₄ + 0.25 M HCOOH	0.07	1.50	33
PtFeMn CNC	0.5 M H ₂ SO ₄ + 0.25 M HCOOH	0.071	0.83	34

other reported Pt-based catalysts recently in the acidic electrolyte.

Catalysts	Tafel slopes	Exchange current density	Charge transfer	Apparent activation energy
	mV dec ⁻¹	mA cm ⁻²	coefficient	kJ mol ⁻¹
NiPtCo/Ti _{0.7} W _{0.3} O ₂	111.75	0.65	0.54	20.87
NiPtCo/C	224.92	0.52	0.27	23.50
PtCo/C	252.23	0.49	0.23	27.40
Pt/C (E-TEK)	303.93	0.43	0.19	30.64

 Table S4. A summary of FAOR kinetic parameters of all studied electrocatalysts.

Table S5. A summary of onset potential and CO oxidation peak potential of all studied FAOR

Catalvsts	Onset potential	CO oxidation peak potential	
	V _{RHE}	V _{RHE}	
NiPtCo/Ti _{0.7} W _{0.3} O ₂	0.53	0.67	
NiPtCo/C	0.65	0.79	
PtCo/C	0.79	0.87	
Pt/C (E-TEK)	0.83	0.89	

electrocatalysts in an acidic environment.

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