Intermolecular Electron Modulating by P/O Bridging in IrO₂-CoPi Catalyst to Enhance Hydrogen Evolution Reaction

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Experimental Section

Preparation of CNTs-Modified Electrode

Prior to coating, bare glassy carbon electrodes (GCE, 3 mm diameter) were polished by 0.3 μ m and 0.05 μ m alumina slurry on a microcloth followed by rinse with ultrapure water. Subsequently, the electrodes were sonicated in ethanol and dried by mild nitrogen flow. 2 mg of carbon nanotubes (CNTs, purchased from Cnano Technology, Beijing) were dispersed in 500 μ L of the mixture of ethanol/ultrapure water (4:1, v/v) with the aid of ultrasonic agitation to form a homogeneous ink. 8 μ L of the ink (approximately 0.032 mg of catalyst) was dropped onto the GCE.

Synthesis of CoPi-CNTs Nanocomposites

The CoPi-CNTs hybrid catalyst were prepared through a cyclic voltammetry (CV) electrochemical deposition method. The CNTs-modified electrode as working electrode, a graphite as counter electrode, and a saturated calomel reference electrode (SCE) were firstly immersed in a 0.03 M $C_{10}H_{12}CoN_2Na_2O_8$ aqueous solution containing with NaH₂PO₂•H₂O and H₃BO₃, and then treated by a potential cycling range from -1.8 to +0.5 V at a scan rate of 50 mV s⁻¹. The obtained CoPi-CNTs modified electrode was gently rinsed with deionized water and dried under vacuum at room temperature. For comparison, the parallel experiments using various deposition cycles were also carried out under the same synthesis conditions.

Synthesis of IrO₂-CoPi-CNTs Nanocomposites

The IrO₂-CoPi-CNTs hybrid catalysts were prepared through a sacrificial counter electrode method. Typically, the electrodeposited experiments were performed in 0.5

M H₂SO₄ solution by a potential cycling from -0.6 to -1.2 V at a scan rate of 100 mV s^{-1} using a three-electrode system consisting of the CoPi-CNTs-modified working electrode, an iridium (Ir) wire counter electrode, and a saturated calomel reference electrode (SCE). After deposition, the obtained IrO₂-CoPi-CNTs-modified electrode was rinsed with deionized water and dried overnight at room temperature. The parallel experiments using various deposition cycles were synthesized under the same conditions. For comparison, the CNTs-modified GCE was used as the working electrode for the preparation of the IrO₂-CNTs hybrid catalyst by the same experimental conditions.

Characterization

X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ultra high-vacuum setup, equipped with a monochromatic Al Kα X-ray source (10 mA, 15 kV) and a high resolution Gammadata-Scienta SES 2002 analyzer. Scanning electron microscopy (SEM) images were obtained from a JSM-6700 (spot 3.0, 15 kV). Transmission electron microscopy (TEM), high resolution TEM (HRTEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray spectroscopy (EDS) elemental mapping were recorded with a JEOL-2100F instrument (200 kV). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed on VISTA-MPX.

Electrochemical Measurements

All of electrochemical measurements were performed in 0.5 M H₂SO₄ solutions on CHI760 electrochemical workstation (CH Instrument Inc.) at room temperature through a three-electrode system consisting of the catalysts-modified working electrode, a graphite counter electrode, and a KCl saturated calomel reference electrode (SCE). The SCE was calibrated with respect to reversible hydrogen electrode (RHE) for the measurements. In our work, the potentials were obtained versus the reversible hydrogen electrode (RHE) through the equation $E_{RHE} = E_{SCE} +$ 0.267 + 0.059 pH in 0.5 M H₂SO₄. Linear sweep voltammetry (LSV) was recorded at a scan rate of 5 mV s⁻¹. The chronoamperometry curve was recorded over 100 h at $\eta =$ 100 mV (vs. RHE). To estimate the double-layer capacitance, cyclic voltammetry (CV) was performed in the potential range from 0.1 to 0.3 V (vs. RHE) with various scan rates (20, 40, 80, 160, 200 mV s⁻¹). To assessment of the HER activities of hybrids catalysts, Tafel plots were obtained from LSV curves. According to the Tafel equation ($\eta = b \log (1 + a)$), the Tafel slope (b) can be obtained by fitting the linear portion of the Tafel plots.¹ Electrochemical impedance spectroscopy (EIS) measurements were carried over the frequency range from 100 kHz to 0.01 Hz at an open circuit potential with an amplitude potential of 5 mV. All data were reported without iR compensation.

TOF calculation

The turnover frequency (TOF) of the synthesized catalyst was estimated according to this equation: TOF = I/(2nF), where I represents the current density of the catalysts through LSV measurement obtained in 0.5 M H₂SO₄, F is the Faraday constant (C mol⁻¹), n is the number of the active sites (mol) of the catalysts.² To obtain the value of n, CV measurements were performed in 1.0 M PBS electrolyte (pH 7.0) within the

potential from -0.2 to 0.6 V (vs. RHE) at a scan rate of 50 mV s⁻¹. Assuming one electron redox process, the integrated charge over the whole potential range was divided by two. Then, the value was divided by the Faraday constant to get the number of active sites for different samples.

DFT calculation

All calculations were performed by utilizing the all-electron code Fritz-Haber Institute *ab initio* molecular simulations package (FHI-aims).³ The exchangecorrelation potentials were investigated using the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerholf (PBE).⁴ The "tight" species defaults for H, O, P, Co and Ir elements were selected in our work. To account for the weak non-covalent intermolecular interaction, these functionals were augmented by the van der Waals scheme of Tkatchenko and Scheffler.⁵ The IrO₂ (110) surface was modeled by a periodic stack of asymmetric slabs with adsorbates only on one side of the slab. The slab was a (1×2) surface model having the thickness of three O-Ir-O repeat units, equivalent to 9 atomic layers (Fig. S12a and b in Supporting Information). The upper five atomic layers were allowed to relax in all structural optimizations. A vacuum region of 20 Å was introduced to curtail interactions between the slabs along the [110] direction. A $(5 \times 5 \times 1)$ Monkhorst-Pack mesh of kpoints was adopted to sample the Brillouin zone of the (1×2) -IrO₂ (110) surface model. A larger supercell (3×4 slab model) was adopted to simulate the CoPi-IrO₂ complex. A schematic illustration of the CoPi cocatalyst was presented in Fig. S12c and d (Supporting Information), which suggested that phosphates was associated with

the Co-oxide fragments (containing 7 Co atoms). The convergence threshold was set to be 10^{-4} eV in energy and 10^{-2} eV·Å⁻¹ in force.

In acidic media, the key reaction steps of HER process were mainly composed of hydrogen intermediate formation and H₂ generation, which could be expressed as:

Volmer step:
$$H^+ + e^- + *cat \rightarrow H\text{-}cat$$
 (1)

Heyrovsky step: H-cat + H⁺ + e⁻
$$\rightarrow$$
 H₂ \uparrow + *cat (2)

Tafel step:
$$2H\text{-cat} \rightarrow H_2 \uparrow +2^*\text{cat}$$
 (3)

in which * denoted the active adsorption site in the catalyst.^{6,7} The binding energy (ΔE_b) of hydrogen was defined as the energy difference between catalyst with H adsorbed (E_{H-cat}) and the summation of the isolated H₂ molecules (E_{H^2}) and catalyst substrate (E_{*cat}):

$$\Delta E_b = E_{H-cat} - E_{*cat} - 1/2E_{H_2}$$
(4)

where, E_{H-cat} was the total energy of the adsorbed system, E_{H_2} and E_{*cat} were the total energy of an isolate hydrogen molecule in the gas phase and the catalyst computed in the work, respectively.

The free energy of $H^+ + e^-$ was almost equal to be half the formation energy of H_2 at standard conditions (pH 0, *p*=1 bar and T=298.15 K). The reaction free energy was then calculated following the equation:

$$\Delta G = \Delta E_b + \Delta Z P E - T \Delta S \tag{5}$$

where, ΔE_b was obtained from prior DFT calculations, the differences in zero point energies (ΔZPE) and the change in entropic contribution (ΔS) were calculated by using computed vibrational frequencies and standard tabulated values for the reactants and products (http://www.webbook.nist.gov/chemistry/).8



Fig. S1 Polarization curves (a) of CoPi-CNTs hybrids in various deposition cycles and the corresponding Tafel plots (b).



Fig. S2 Polarization curves (a) of IrO₂-CoPi-CNTs hybrids in various deposition cycles and the corresponding Tafel plots (b).



Fig. S3 SEM images of CoPi-CNTs hybrid catalyst of different deposition cycles. (a) CoPi_{20cyc}-CNTs hybrids catalyst. (b) CoPi_{30cyc}-CNTs hybrids catalyst. (c) CoPi_{40cyc}-CNTs hybrids catalyst.



Fig. S4 Characterizations of CoPi-CNTs hybrid catalyst: (a-b) TEM images.



Fig. S5 SEM images of IrO₂-CoPi-CNTs hybrid catalyst of different deposition cycles.
(a) IrO₂-CoPi-CNTs-10000cyc hybrids catalyst. (b) IrO₂-CoPi-CNTs-12000cyc hybrids catalyst. (c) IrO₂-CoPi-CNTs-14000cyc hybrids catalyst.



Fig. S6 SEM images of IrO₂-CNTs hybrid catalyst of different deposition cycles. (a) IrO₂-CNTs-10000cyc hybrids catalyst. (b) IrO₂-CNTs-12000cyc hybrids catalyst. (c) IrO₂-CNTs-14000cyc hybrids catalyst.



Fig. S7 Characterizations of IrO2-CNTs hybrid catalyst: (a-c) TEM images, (d) STEM

and the corresponding EDS element maps.



Fig. S8 Standard CV curves of different samples and corresponding C_{dl} with different scan rates. (a) and (b) CoPi-CNTs, (c) and (d) IrO₂-CNTs, (e) and (f) IrO₂-CoPi-CNTs hybrid catalyst.



Fig. S9 The Nyquist plots for the CoPi-CNTs, IrO₂-CNTs, and IrO₂-CoPi-CNTs hybrid catalysts(fitted curves as solid lines and experimental points as symbols). The inset shows the equivalent circuit diagram.



Fig. S10 Characterizations of IrO₂-CoPi-CNTs hybrid catalyst: (a) SEM images of IrO₂-CoPi-CNTs hybrid catalyst. (b) SEM and (c) TEM images of IrO₂-CoPi-CNTs hybrids catalyst after 100 h chronoamperometry i-t stability test.



Fig. S11 CVs obtained for CNTs, IrO_2 -CNTs, CoPi-CNTs, and IrO_2 -CoPi-CNTs hybrid catalysts in 1.0 M PBS (pH 7.0) at a scan rate of 50 mV s⁻¹.



Fig. S12 (a) Top and (b) front views of the (1×2) -IrO₂ (110) slab. The red and navy spheres were O and Ir atoms, respectively. (c) Top and (d) front views of CoPi polyhedral model. CoO₆ were presented as light blue octahedra, PO₄ were denoted as pink tetrahedra, and the sticks meant H-O bonds, respectively.



Fig. S13 Calculated free-energy diagram for hydrogen evolution of s-IrO₂ (110) surface (a) and CoPi cluster (b) at pH 0. Binding configurations for hydrogen ions at different adsorbed sites of s-IrO₂ (110) surface (c~e) and CoPi polyhedral cluster (f~h). The white, red, and navy spheres were H, O, and Ir atoms, the sticks meant H-O bonds, CoO₆ were presented as light blue octahedra, and PO₄ were denoted as pink tetrahedra, respectively.

Supplementary note 1:

The stoichiometric iridium dioxide (110) surface $[s-IrO_2 (110)]$ presented three different types of exposed atoms, 2-fold coordinated bridge oxygen (Obr), 3-fold coordinated surface oxygen (Osurf) and 5-fold coordinatively-unsaturated iridium (Ir_{cus}) .⁹⁻¹² The (110) crystal plane was one of the dominative facets of IrO₂, which had been characterized in recent studies. Fig. S12a and b displayed the atomic model of s- IrO_2 (110) surface. The hydrogen ions could attach to the surface via interacting with each O_{br} , O_{surf} and Ir_{cus} atoms, and the binding energy (ΔE_b) was -0.78, +0.34 and -0.45 eV, respectively. The weak chemical interaction between hydrogen adatoms and the Osurf sites could damage the surface lattice seriously, making them less prone to adsorption. The investigation also showed that the bindings between hydrogen and Obr/Ircus atoms on the surface dominated the dynamics for negative values of the pairing strength, resulted in an H-terminated surface at pH 0. The reaction free energy and geometric structures were summarized in Fig. S13a and c~e. The Ircus atoms showed as the mainly active sites with the value of $\Delta G_{\rm H}$ = -0.29 eV, which was close to the optimal Pt(111) value (ΔG_{H} =-0.08 eV) and was reactive to a certain degree. Unfortunately, the Obr sites exhibited large negative hydrogen adsorption free energies (ΔG_H) as low as -0.61 eV, which might hinder the diffusion of H intermediates and lead to sluggish HER kinetics.

Supplementary note 2:

In this work, we also calculated the adsorption of hydrogen on the CoPi nanoclusters for comparison, the possible structural motif for CoPi was showed in Fig. S12c and d, which the coordination number of CoPi was about 2.33 and the remaining terminal ligands of Co-oxide clusters might be water molecules and hydroxyls.¹³⁻¹⁵ The hydrogen ions could be anchored onto the cluster surface through locating at the O_{2c} , O_{3c} and hydroxyl sites, Fig. S13b and f~h listed the Gibbs free energies and optimized geometric structures of hydrogen adsorptions. And the binding energy (ΔE_b) was -0.57, -0.12 and -0.91 eV, respectively, most tended to adsorb at the hydroxyl sites, generating a H₂O molecule. Then we used Equations (5) to convert the data to Gibbs free energy, in turn, they were -0.26, +0.27 and -0.62 eV. On the other hand, the formed H₂O molecules would be decomposed since the Co-OH₂ tended to be oxidized and deprotonated to Co-OH and even to Co=O, its adjacent O_{2c} and O_{3c} sites could contribute to the migration of H* intermediates because of their moderate free energies. Hence, the CoPi nanoparticles acted as a water dissociation promoter, cleaved HO–H bonds and produced H* intermediates that then adsorbed on the neighboring catalytic active sites.

Sample	Overpotential @10mAcm ⁻² (mV)	Tafel slope (mV dec ⁻¹⁾	Loading (mg cm ⁻²⁾	Reference
17.7 wt % Ir/SiNW	22	20	0.339	ACS Nano 2019, 13 , 2786.
PtNi/Pt DNPs	21	23	0.05	J. Mater. Chem. A 2019, 7, 12800.
PtCo/CNFs	63	28	0.212	Chem. Commun. 2016, 52 , 990.
N-Co ₂ P/CC	27	45	5	ACS Catal. 2019, 9, 3744.
OsP2@NPC	46	43	0.285	Chem. Commun. 2019, 55, 4399.
PANI/CoP HNWs- CFs	57	34.5	4.5	J. Am. Chem. Soc. 2018, 140 , 5118.
CoP@NC	78	49	0.28	ACS Catal. 2017, 7, 3824.
Co ₂ P NP	103	58	0.5	Nano Lett. 2016, 16, 4691.
CoP/CC	38	51	5.7	J. Am. Chem. Soc. 2014, 136 , 7587.
CoS ₂ NW	145	51.6	0.25	J. Am. Chem. Soc. 2014, 136 , 10053.
$Zn_{0.1}Co_{0.9}Se_2$	140	49.9	0.285	J. Mater. Chem. A 2017, 5, 17982.
CoSAs/PTF-600	94	50	0.94	J. Mater. Chem. A 2019, 7, 1252.
CoP/NCNTs	79	49	0.199	J. Mater. Chem. A 2016, 4, 4745.
Mo-CoP	40	65	2.5	Nano Energy 2018, 48 , 73.
CoP@NPC	123	69	1.17	ACS Appl. Mater. Interfaces 2015, 7, 28369.
Co ₂ P Nanorod	134	71	1	Nano Energy 2014, 9, 373.
Urchin-like CoP	105	46	0.28	Nano Lett. 2015, 15, 7616.
Co-P@PC	72	49	1	Small 2018, 14, 1702895.
Co-NG	147	82	0.285	Nat. Commun. 2015, 6, 8668.
CoP@NC-NG	135	59.3	-	Small 2018, 14, 1702895.
1%Pd–MoS ₂	89	80	0.222	Nat. Commun. 2018, 9, 2120.
IrCoNi PHNCs	68	34.3	0.51	Adv. Mater. 2017, 29 , 1703798.
IrO2-CoPi-CNTs	29	27	0.45	This work

 Table S1. Comparision of HER performances of our sample with other reported
 electrocatalysts in acid media.

Sample	$\mathbf{R}_{s(\Omega)}$	$\mathbf{R}_{\mathrm{ct}(\Omega)}$	CPE _(µMho)
CoPi-CNTs	52.6	14.1	19.2
IrO ₂ - CNTs	57.1	8.2	27.5
IrO ₂ -CoPi-CNTs	52.8	5.68	52.2

Table S2. The impedance parameters derived by fitting the EIS responses on the different composites in $H_2SO_{4_{\circ}}$

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