Supporting information

Efficient CO$_2$ electroreduction to formate by Bi-Pb bimetallic catalysts with 2D vertically nanosheets

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Supplementary Notes

Experimental section

Carbon paper (CP, 99.8%) with 1.5 mm thickness was purchased from Shanghai Hesen Co., Ltd. Hydrochloric acid (HCl, 36.5%) and sulfuric acid (H_2SO_4, 98%) were obtained from Beijing Chemical Works. Lead acetate ($Pb(CH_3COO)_2$, 99.8%), sodium fluoride (NaF, 99.8%), potassium bicarbonate ($KHCO_3$, 99.8%), acetonitrile (AcN, 99.8%), bismuth nitrate ($Bi(NO_3)_3$, 99.8%) and acetone (CH_3COCH_3) were purchased from Shanghai Macklin Biochemical Co., Ltd. The 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid ([Bmim][BF_4], 98%) was purchased form Shanghai Chengjie Co., Ltd.

Characterizations

Scanning electron microscope (SEM, Hitachi SU8020) and Transmission electron microscope (TEM, JEOL JEM-2100 system) were employed to observe the morphologies of the catalysts. X-ray diffraction (XRD, Rigaku Smartlab diffractometer) and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi) were used to confirm the crystal structures and elemental compositions, respectively. Inductively coupled plasma spectrometry (ICP) was carried on an ICPE-9000 to determine the metal content.

Product analysis

The main products of CO_2 electroreduction are formate, CO, and H_2, respectively. Gas products were quantified by gas chromatography (GC, Agilent 7890A GC) with a thermal conductivity detector (TCD) and a flame ionization detector (FID). N_2 was

used as the carrier gas. The gases from the outlet of the cathodic compartment were collected by a gas bag, and then injected into the GC. Every gas sample was measured three times.

The concentration of liquid products was detected using a 600 MHz ^{1}H liquid NMR spectrometer (Bruker Advance). Phenol was used as an internal reference for the liquid products. The standard solution consisted of 0.5×10^{-3} M phenol and DMSO. Typically, NMR samples were prepared by mixing 300 μL of the product-containing electrolyte and 200 μL standard solution. Two electrons are needed to produce one CO, H_2 and formate molecule, so the FE of the CO_2 electroreduction products can be calculated as follows (Equation (1)):

$$FE = 2Fn/Q \tag{1}$$

Where F is the Faraday constant, 96485 C mol^{-1}; n is the molar amount of product, mol; and Q is the charge recorded by electrochemical workstation, C.

The formula for calculating the production rate of formate was as follow (Equation (2)).

$$The\ production\ of\ formate = \frac{n_{formate}}{t \times S} \tag{2}$$

Where $n_{formate}$ is the molar amount of formate (mol), quantified by NMR; t is the electroreduction reaction time (h); S is the geometric area of the catalyst.

DFT calculations

In order to investigate the origin of the high performance of Bi-Pb bimetallic catalysts, theoretical calculations were carried out using periodic DFT implemented in the Vienna Ab initio Simulation Package (VASP 5.4.4). The projector-augmented

method was applied to solve the ion-electron interaction in a periodic system. The generalized gradient approximation with Perdew-Burke-Ernzerh of functionals was used to treat the exchange-correlation interactions in the Kohn-Sham equations. Spin-polarized calculations were carried out with an energy cutoff for the plane waves of 520 eV. The convergence criteria for optimization of the atomic structure were set at 1×10^{-5} eV and a Hellmann-Feynman force of 0.02 eV Å^{-1}. A Monkforst-Pack k-point mesh of $5 \times 5 \times 1$ k-points was employed. The Pb(111) surface with four atomic layers and 5×5 unit cells was used as the model system. In order to simulate the role of Bi on this bimetallic catalyst, a Bi-Pb(111) surface was built by decorating Bi atom onto the surface of pure Pb(111) surface. A vacuum layer of 15 Å was added to separate neighbouring slabs to avoid possible interaction.
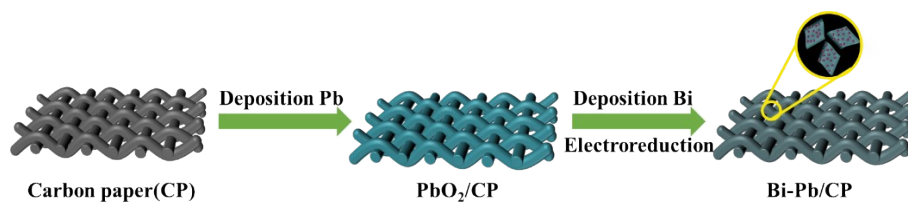
Fig. S1. The schematic of the synthesis process for the Bi-Pb bimetallic catalyst
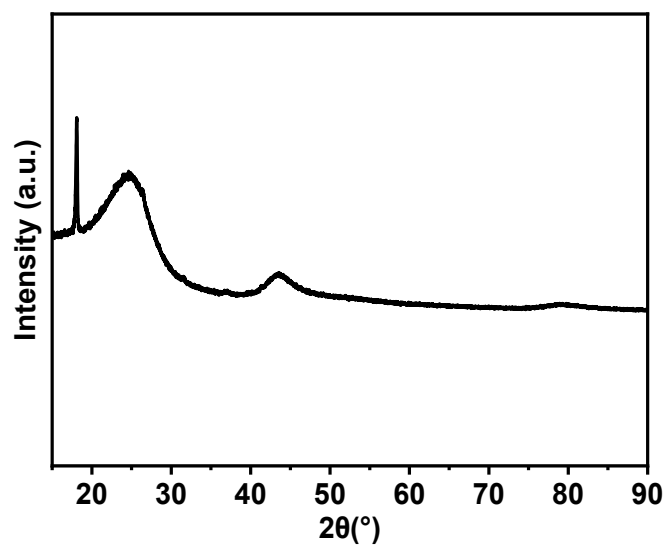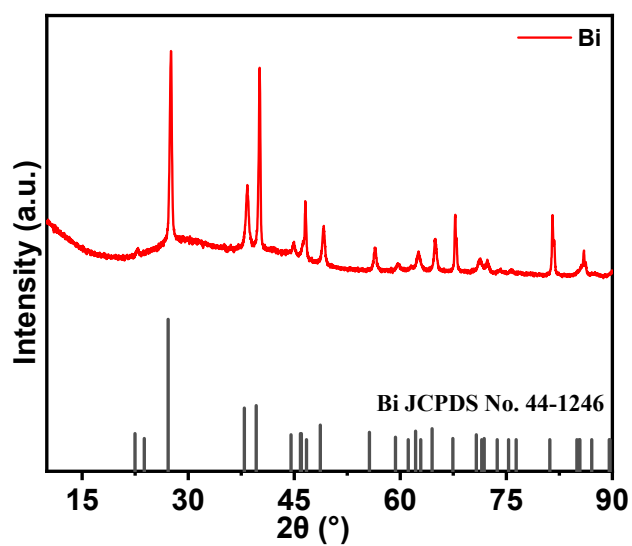

Fig. S2. XRD pattern of pure carbon paper
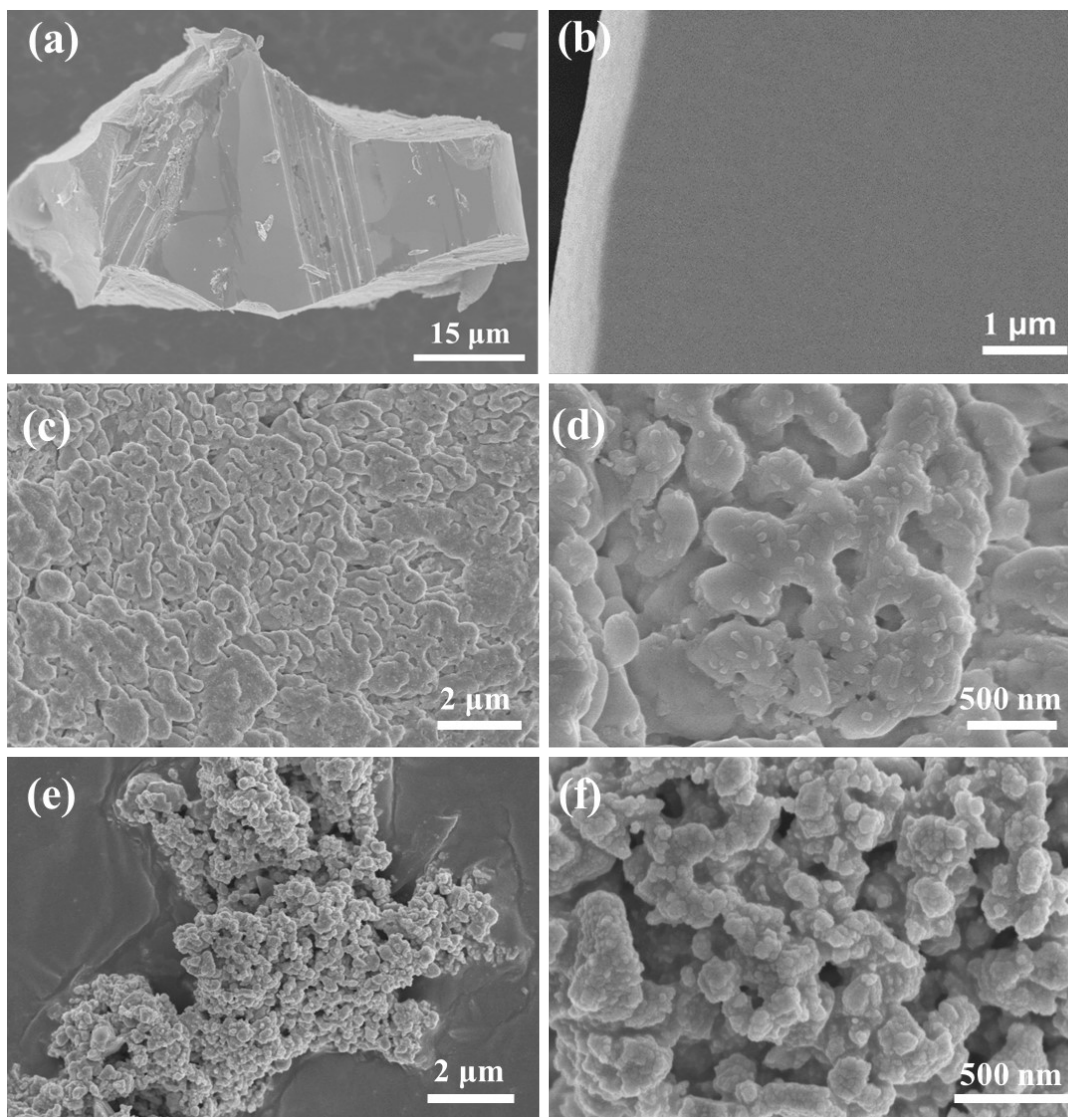

Fig. S3. XRD pattern of Bi/CP electrode

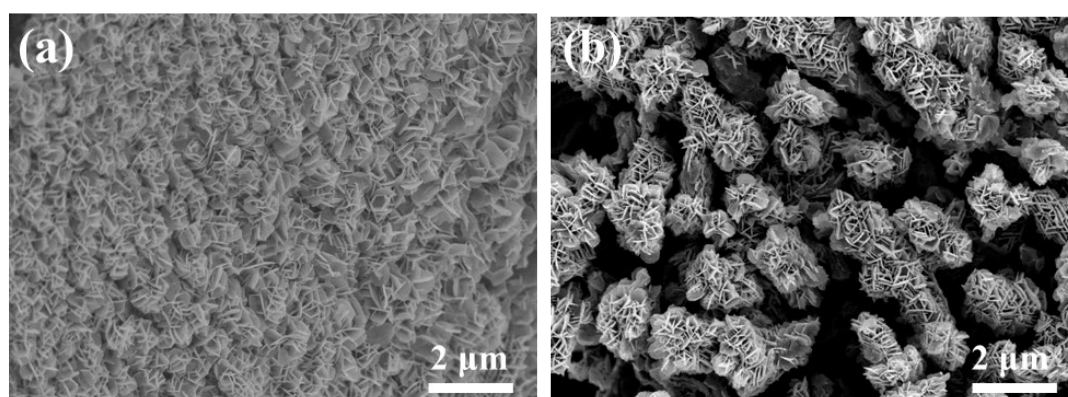Fig. S4. SEM images of PbO$_2$/CP (a, b), Bi-PbCl$_2$/CP (c, d), and Bi/CP (e-f)

Fig. S5. SEM images of PbO$_2$/CP (a) and Bi-PbCl$_2$/CP (b) after electroreduction
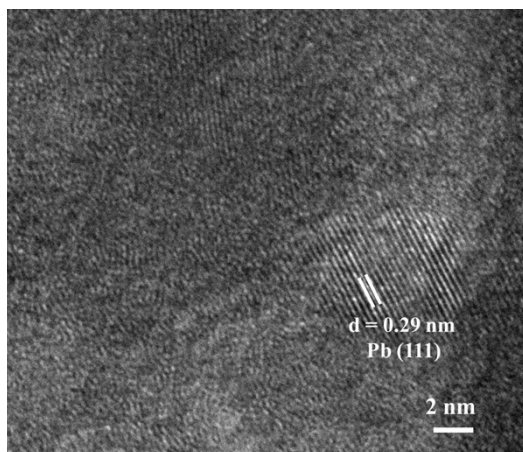
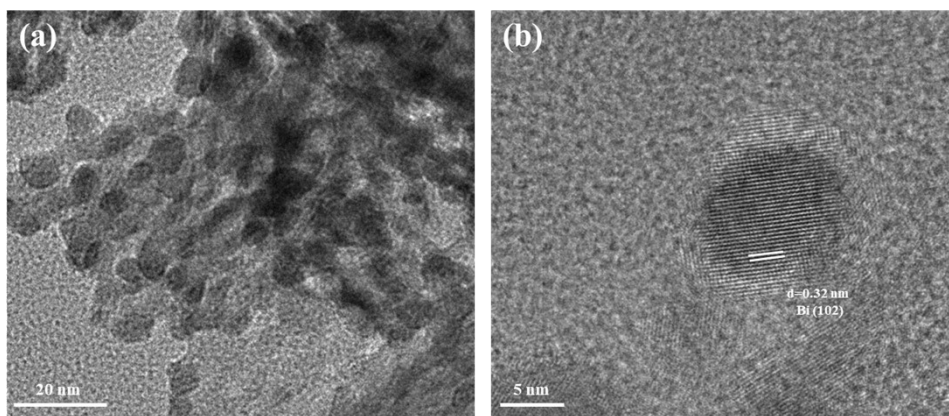Fig. S6. TEM image of PbO$_2$/CP after electroreduction

Fig. S7. TEM images of Bi/CP catalyst

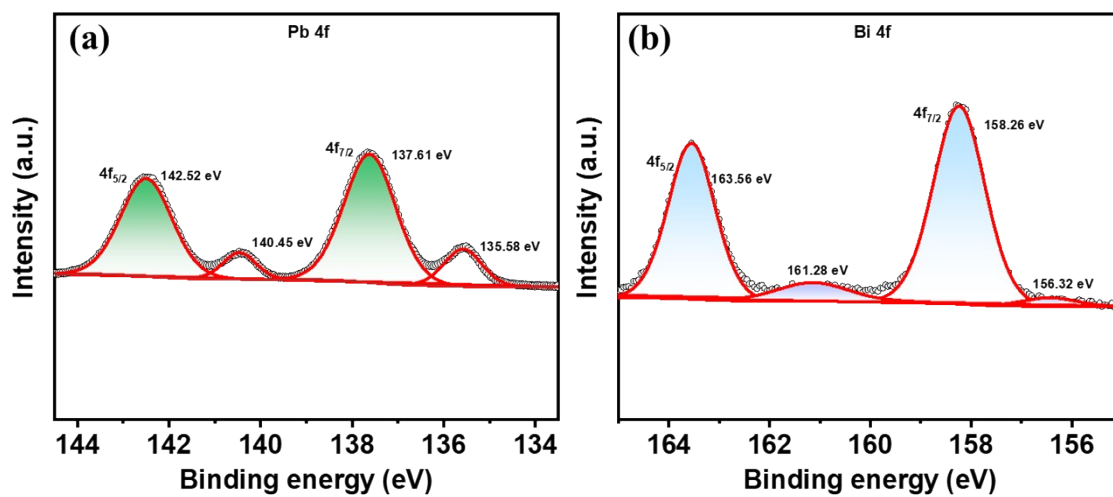Fig. S8. Pb 4f spectra of PbO$_2$/CP (a) after electroreduction and Bi 4f spectra of Bi/CP (b)
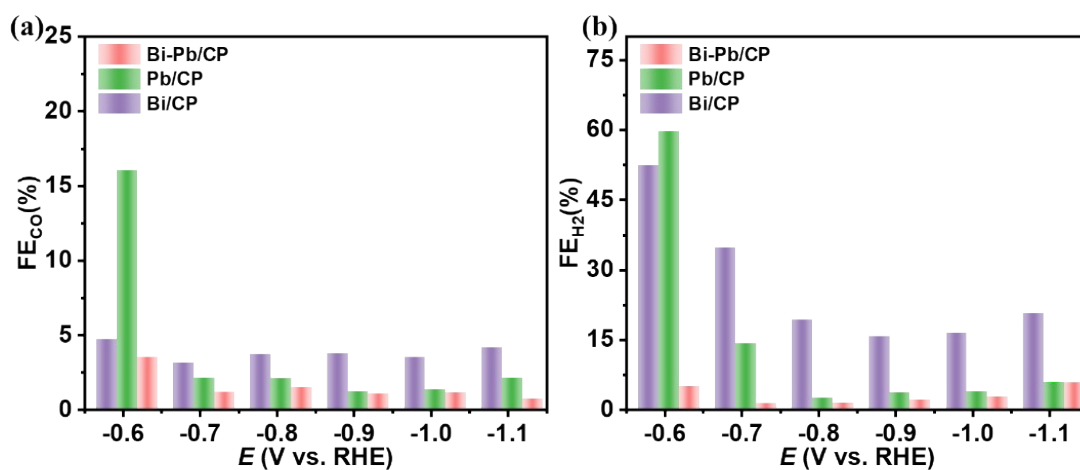
Fig. S9. The FE of CO (a) and H_2 (b) at various applied potentials for Pb/CP, Bi/CP, and Bi-Pb/CP in 0.5 M $KHCO_3$ solution

Fig. S10 The FE of formate (a), CO (b) and H_2 (c) at various applied potentials for Pb/CP, Bi/CP, and Bi-Pb/CP in 30 wt%[Bmim][BF_4]/AcN-H_2O (5 wt%) IL electrolyte

Fig. S11. XPS spectra of Pb 4f (a) and Bi 4f (b) and XRD pattern (c) of Bi-Pb/CP after 10 h electrolysis

Fig. S12. Cyclic voltammograms at the range of -0.55 to -0.65 V with different scan rates (10, 20, 40, 60, 80, 100 mV s^{-1}) for Pb/CP (a), Bi-Pb/CP (b) and Bi/CP (c); Charging current density differences plotted against scan rate (d)

Fig. S13. Nyquist plots for Pb/CP, Bi/CP and Bi-Pb/CP

Fig. S14. The DOS of Pb atom and O atom on Bi-Pb(111) and Pb(111) surfaces with adsorbed *OCHO

Table S1. Current density and FE of formate in CO_2 electrochemical reduction using various electrodes and catholytes in H-type cell

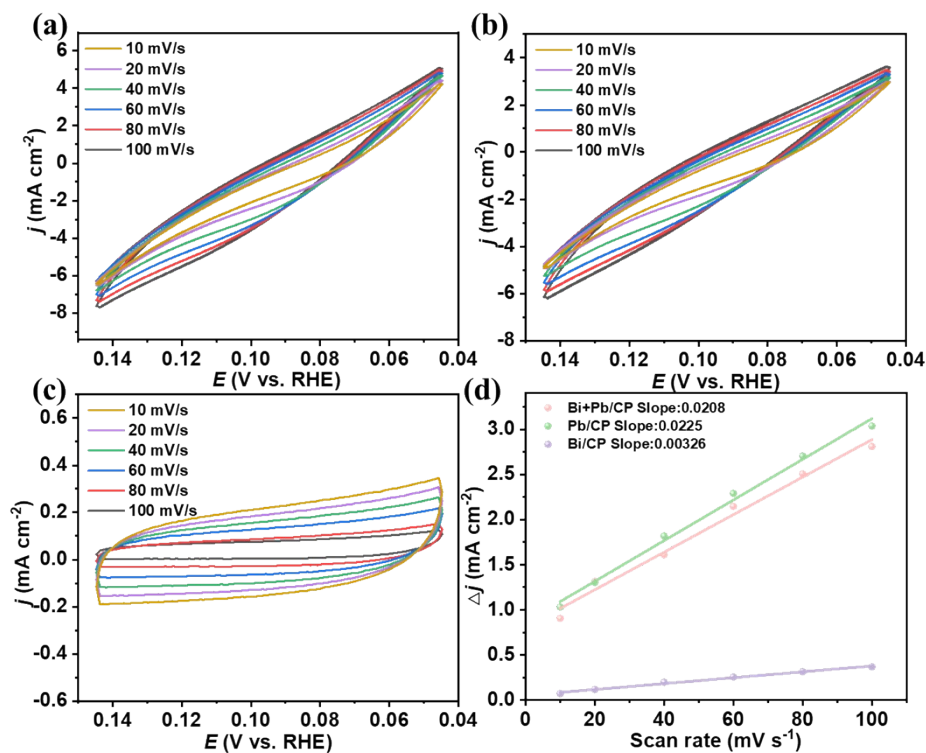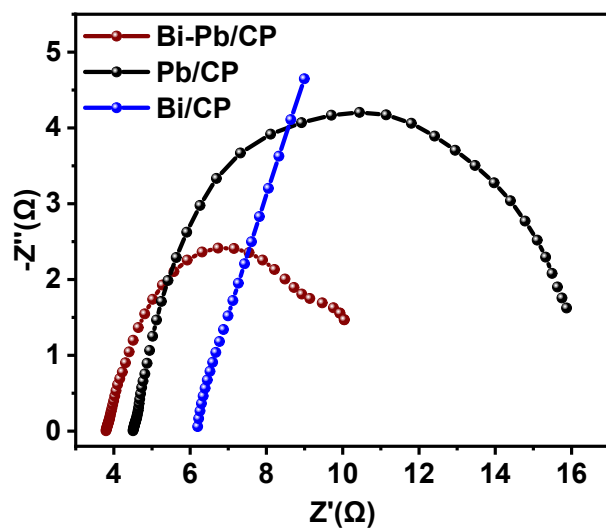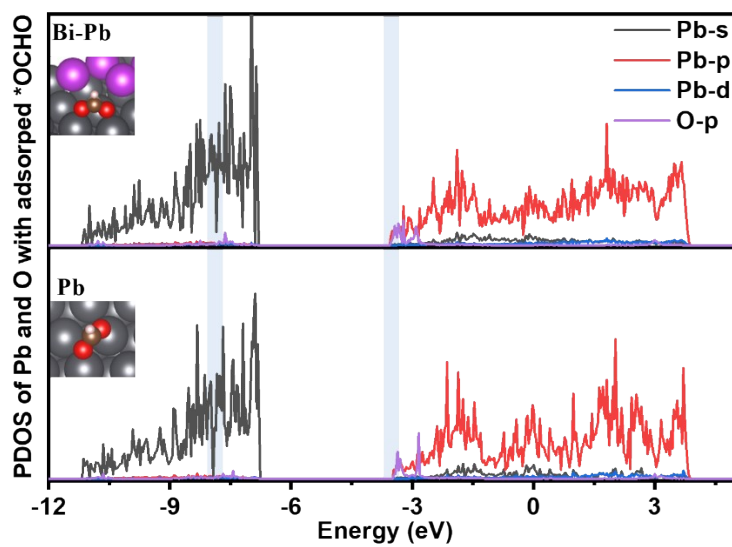| Catalysts	Electrolyte	Potential (V)	$FE_{formate}$(%)	$j_{foramte}$(mA cm^{-2})	Formate formation rate (μmol h^{-1} cm^{-2})	Ref.
Bi flake	0.1 M KHCO$_3$	-0.6 vs RHE	99	4	74.6	[1]
S-Bi$_2$O$_3$-CNT	0.5 M KHCO$_3$	-1.1 vs RHE	90	45	839.4	[2]
Bi-MOF	0.1 M KHCO$_3$	-0.9 vs RHE	92	4	74.6	[3]
Bi nanosheet with vacancies	0.1 M KHCO$_3$	-0.8 vs RHE	97	3.8	70.9	[4]
Bi nanotubes	0.5 M NaHCO$_3$	-1.0 vs RHE	97	25	466.3	[5]
Bi nanosheet	0.5 M KHCO$_3$	-0.8 vs RHE	93	30	599.6	[6]
Bi nanodendrites	0.5 M NaHCO$_3$	-1.8 vs SCE	96.4	15.2	283.5	[7]
S-Bi/Ag	0.5 M NaHCO$_3$	−1.0 vs. RHE	94.7	28.1	561.6	[8]
Bi$_2$O$_3$-NGQDs	0.5 M KHCO$_3$	-0.87 vs RHE	98	16.6	309.6	[9]
Helical Bi$_2$O$_3$ microfibers	0.1 M KHCO$_3$	-1.2 vs RHE	90	13	242.4	[10]
Eutectic Bi-Sn	0.1 M KHCO$_3$	-1.1 vs RHE	78	10.7	199.6	[11]
Bi@Bi$_2$O$_2$CO$_3$	0.5 M KHCO$_3$	-0.8 vs RHE	97	38	708.8	[12]
Nafion/Bi NSs@Cu foam	0.5 M KHCO$_3$	-0.97 vs RHE	97.3	36	671.5	[13]
Pd-Bi nanosheet	0.5 M KHCO$_3$	-1.0 vs RHE	91.9	25	466.3	[14]
CuBi	0.5 M KHCO$_3$	-1.2 vs RHE	90.8	33	615.5	[15]
Pb QDDCs	0.5 M KHCO$_3$	-0.2 vs RHE	95	16	298.4	[16]
Pb NP/MWCNT	0.5 M KHCO$_3$	-1.8 vs Ag/AgCl	70	30	559.6	[17]
Sulfide-derived Pb	0.1 M KHCO$_3$	-1.08 vs RHE	88	12	223.8	[18]
Bi@np-Cu	0.5 M KHCO$_3$	-0.97 vs RHE	97.7	82	1529.5	[19]

Ag-loaded $Bi_2O_2CO_3$	0.5 M KHCO$_3$	-1.1 vs RHE	95.8	15.3	285.4	[20]
$Bi_2O_2CO_2$ modified with iodine and pyrenyl-graphdiyne	0.5 M KSO$_4$ (pH: 3.5)	-1.4 vs RHE	94.84	~60	-	[21]
CuBi$_3$	0.1 M KHCO$_3$	-1.3 vs RHE	98.3	21.2	396.1	[22]
Ce leaching-derived Bi nanosheets	0.5 M KHCO$_3$	-1.4 vs RHE	95	46.4	865.5	[23]
Bi-MOFs	0.1 M KHCO$_3$	-1.1 vs RHE	90.4	20.8	-	[24]
3D bi-continuous nanoporous bismuth	0.1 M KHCO$_3$	-0.956 vs RHE	92.6	5	93.2	[26]
dendritic Bi film	0.1 M KHCO$_3$	-0.90 vs RHE	~80	8.6	160.4	[27]
2D Bi$_2$S$_3$ NSs	0.5 M KHCO$_3$	-0.93 vs RHE	~95	~30	559.6	[28]
Sb$_{2.5}$/Bi@C	0.5 M KHCO$_3$	-1.4 vs Ag/AgCl	94.8	~5	93.3	[29]
5% Bi-InOCl	0.5 M NaHCO$_3$	-0.9 vs RHE	89.9	14.89	277.7	[30]
$Bi_2O_2CO_3$ ultrathin nanosheets	0.5 M NaHCO$_3$	-0.9 vs RHE	96	25	466.3	[31]
Cu-doped Bi catalyst	0.1 M KHCO$_3$	-1.1 vs RHE	94	20	373.3	[32]
Bi-Cr$_2$O$_3$ nano-dendrites	1.0 M KHCO$_3$	-1.1 vs RHE	93.3	40.7	759.2	[33]
Bi-Pb	0.5 M KHCO$_3$	-1.1 vs RHE	93.0	53.1	990.5	This work

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