# **Electronic Supplementary Information**

## Enhancing electroreduction of CO<sub>2</sub> over Bi<sub>2</sub>WO<sub>6</sub> nanosheets by oxygen vacancies

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#### **Experimental Section**

**Materials:** Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and CTAB used in this paper were bought from Sinopharm Chemical Reagent Company (Shanghai, China). Ionic liquids: Tetrabutylammonium Perchlorate (TBAP) (purity>98.0%), 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF<sub>6</sub>, purity>99%), were purchased from the Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Toray carbon paper (CP, TGP-H-60, 19cm×19 cm), Nafion D-521 dispersion (5% w/w in water and1-propanol,  $\geq$ 0.92 meg g<sup>-1</sup> exchange capacity) and Nafion N-117 membrane (0.180 mm thick,  $\geq$ 0.90meg g<sup>-1</sup> exchange capacity) were purchased from Alfa Aesar China Co., Ltd. (USA). Poly (tetrafluoroethylene) 60 wt% dispersion in H<sub>2</sub>O (PTFE) was purchased from J&K. Silver nitrate (purity > 99%) were purchased from Alfa Aesar China Co., Ltd. Acetonitrile (MeCN, A. R. Grade), sulfuric acid, isopropanol (A. R. Grade) were bought from Beijing Chemical Works. All reagents employed in this work without further treated before used.

#### **Electrode Materials Synthesis**

**Synthesis of OV-rich Bi<sub>2</sub>WO<sub>6</sub>:** The procedures were similar to that reported by other authors.<sup>1,2</sup> In a typical experiment, 2 mmol Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, 0.5 g CTAB and 1mmol Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O were dissolved in 20 mL distilled water respectively. Firstly, 20 mL CTAB aqueous solution was added to Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O aqueous solution drop by drop and intensively stirred for 30 min. Then 20 mL Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O aqueous solution was added to the above solution and intensively stirred for 1 h at room temperature. Finally, the resulting solution was transferred to a 100 ml Teflon-line autoclave and heated at 120 °C for 24 hours. After the system cooled down to room temperature naturally, the products were collected by centrifugation, washed with distilled water (10 × 30 ml) and absolute ethanol (5 × 30 ml), and then dried in a vacuum oven overnight at 80 °C.

Synthesis of OV-poor Bi<sub>2</sub>WO<sub>6</sub>: The procedures were similar to the above, in addition to no CTAB assistances.

**Materials Characterization:** Power X-ray diffraction (XRD) pattern was implemented on X-ray diffractometer (Model D/MAX2500, Rigaka) with Cu-Kα radiation at a scan speed of 5°/min. X-ray photoelectron spectroscopy (XPS) analysis was performed using the

Thermo Scientific ESCA Lab 250Xi with a 200 W monochromated Al K $\alpha$  radiation. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

The morphologies of Bi<sub>2</sub>WO<sub>6</sub> electrodes were characterized by scanning electron microscopy (SEM) S-4800 and transmission electron microscopy TEM (JEOL-2100F). The adsorption isotherms of CO<sub>2</sub> for Bi<sub>2</sub>WO<sub>6</sub> simples were obtained at 298 K within the pressure range of 0-1 atm on a TriStar II 3020 device. Electron Spin Resonance (ESR) Spectra of Bi<sub>2</sub>WO<sub>6</sub> powder were performed at room tempreture using a JEOL JES-FA200 ESR spectrometer (300 K, 9.063 GHz). X-ray absorption fine structure (XAFS) experiments were operated at the 1W1B, 1W2B beamline at Beijing Synchrotron Radiation Facility (BSRF). All collected spectra were analyzed using Athena and Artemis program within the Ifeffit package.

**Electrochemical Study:** When it comes to the prepartion of the electrode, 5mg sample were dispersed in 1mL isopropanol and 20 uL 5% Nafion D-521 to form homogeneous ink with the help of ultrasound. Finally, the ink was spread onto carbon paper  $(1^{cm} \times 1^{cm})$  to investigate the performance of materials. In this work, all the electrode was manufactured by this way.

All the electrochemical experiments were carried out on the electrochemical workstation (CHI 660E, Shanghai CH Instruments Co., China). Linear sweep voltammetry (LSV) scans were conducted in a single compartment cell with a three electrodes configuration, which consisted of working electrode, a platinum gauze as counter electrode, and Ag/Ag<sup>+</sup> (0.01M AgNO<sub>3</sub> in 0.1M TBAP-MeCN) as reference electrode. Prior to experiment, the electrolyte was bubbled with N<sub>2</sub> or CO<sub>2</sub> at least 30 min to form N<sub>2</sub> or CO<sub>2</sub> saturated solution. LSV measurement was carried out within gas-saturated electrolytes in the potential range of -0.5 V to -2.5 V (vs Ag/Ag<sup>+</sup>) at a appropriate sweep rate of 20 mV S<sup>-1</sup> sweep rate. To obtain uniform electrolyte, slight magnetic stirring was allowed during the process of experiment.

The controlled potential electrolysis of  $CO_2$  experiments were conducted at 25 °C in a typical H-type cell.<sup>3</sup> In the experiments, Nafion-117 proton exchange membrane was used to separate the cathode and anode compartments and simultaneously permit H<sup>+</sup> to

transferred from anode compartment to cathode compartment.  $H_2SO_4$  aqueous solution (0.5 M) and [Bmim]PF<sub>6</sub>/MeCN solution (0.5 M) were used as anodic and cathodic electrolytes, respectively. It's worthy note that the catholyte was bubbled with CO<sub>2</sub> for 30 min before electrolysis and potentiostatic electrochemical reduction of CO<sub>2</sub> was performed under a steady stream of CO<sub>2</sub>.

**Double-layer capacitance** ( $C_{dl}$ ) measurements: The electrochemical active surface area is proportional to  $C_{dl}$  value.  $C_{dl}$  was determined in H-type electrolysis cell by measuring the capacitive current associated with double-layer charging from the scan-rate dependence of cyclic voltammogram (CV). The CV ranged from -1.35 V to -1.45 V (vs Ag/Ag<sup>+</sup>). The  $C_{dl}$  was estimated by plotting the  $\Delta j$  ( $j_a$ - $j_c$ ) at -1.40 V (vs Ag/Ag<sup>+</sup>) against the scan rates, in which the  $j_a$ and  $j_c$  were the anodic and cathodic current density, respectively. The scan rates were 20, 30, 50, 80, and 100 mV s<sup>-1</sup>.

**Electrochemical impedance spectroscopic (EIS):** The electrochemical impedance spectroscopic studies were executed in  $CO_2$  saturated 0.5M [Bmim]PF<sub>6</sub>/MeCN solution at an open circuit potential (OCP) within the frequency extent of 0.1 to 100,000 Hz and at a amplitude of 5 mV.

### **Product analysis:**

Gas chromatography (GC, HP 4890D) equipped with FID and TCD detectors was used to analyze the gaseous product which was collected using a gas sack during electrochemical experiments. The liquid product was detected by <sup>1</sup>H NMR (Bruker Avance III 400 HD spectrometer) in DMSO-d6 with TMS as an internal standard.

Calculations of Faradaic efficiencies of gasous and liquid products:

#### **Gasous products :**

$$FE = \frac{moles \ of \ products}{Q/nF} \times 100\%$$

(Q:electric quantity; F:Avogadro constant; n: transfer electron number)

The V % of gasous product can be obtained from the GC peak areas. Since the flow rate of the gas was constent, the amount of moles of  $H_2$  (or CO) could be calculated. The theoretical moles were obtained from current density and the amount of transfered electron in the process.

### liquid products:

After elecrolysis, the amount of liquid product can be calculated in NMR spectra, the C(2)-H on the [Bmim]<sup>+</sup> can be used as the internal standard. The Faradaic Efficiency of liquid products is:

$$FE = \frac{C \times V \times N_A \times n}{Q/nF}$$

(V: the volume of catholyte; NA: Avogadro constant; n: transfer electron number)

**Tafel analysis:** The partial current densities for CO under different potentials were measured. The overpotential was obtained from the difference between the equilibrium potential and the applied potential. Electrolysis experiments were performed at each potential to obtain the current density versus overpotential data in the H-type electrolysis cell as described above. Tafel plots were constructed from these data.



Figure S1 The SEM image of OV-poor  $Bi_2WO_6$ 



Figure S2 XPS survey spectra of OV-rich  $\mathrm{Bi}_2\mathrm{WO}_6$  (a) and OV-poor  $\mathrm{Bi}_2\mathrm{WO}_6$  (b)



Figure S3 Bi 4f XPS spectra of OV-rich  $Bi_2WO_6$  and OV-poor  $Bi_2WO_6$ 



Figure S4 The LSV curves for OV-rich  $Bi_2WO_6$  were determined in  $N_2$ - and  $CO_2$ -saturated 0.5 M [Bmim]PF<sub>6</sub>/MeCN solution.



Figure S5 The LSV curves for OV-poor  $Bi_2WO_6$  were determined in  $N_2$ - and  $CO_2$ -saturated 0.5 M [Bmim]PF<sub>6</sub>/MeCN solution.



Figure S6 The Faradaic efficiency of  $H_2$  on OV-rich  $Bi_2WO_6$  and OV-poor  $Bi_2WO_6$  electrodes at various applied potentials.



Figure S7 The partial current density of CO for OV-rich  $Bi_2WO_6$  and OV-poor  $Bi_2WO_6$  electrodes in  $CO_2$ -saturated electrolyte at different applied potentials.



Figure S8 The XRD pattern for OV-rich  $Bi_2WO_6$  electrode before and after electrolysis.



Figure S9 Comparison of Current density of CO over different electrodes.



**Figure S10** The plot of current densities for CO production on OV-rich  $Bi_2WO_6$  electrode versus different potentials which the equilibrium potential can be obtained by means of extrapolation method.



Figure S11 Nyquist plots for OV-rich  $Bi_2WO_6$  and OV-poor  $Bi_2WO_6$  electrodes when operated at -2.4 V vs Ag/Ag<sup>+</sup>.



Figure S12 Illustration of pathway for electrocatalytic  $CO_2$  reduction to CO on OV-rich  $Bi_2WO_6$  electrode.

Samples	Integral areas of lattice oxygen (530.2 eV)	Integral areas of vacancy oxygen		The content of vacancy	
		533.2 eV	531.8 eV	oxygen (%)	
OV-rich Bi <sub>2</sub> WO <sub>6</sub>	20236.72	20725.50	19869.19	66.7	
OV-poor Bi <sub>2</sub> WO <sub>6</sub>	20352.40	6498.97	4408.86	34.8	

Table S1 The calculated ratio of integral areas for vacancy oxygen and lattice oxygen in O 1s

Catalyst	Potential (V) vs RHE	Current Density (mA cm <sup>-2</sup> )	Electrolyte	Faradaic Efficiency	Ref
OV-rich	-2.4 V	43	0.5M [Bmim][PF <sub>6</sub> ]	91%	This
Bi <sub>2</sub> WO <sub>6</sub>	vs Ag/Ag <sup>+</sup>		/MeCN	5170	work
OV-poor	-2.4 V	34	0.5M [Bmim][pF <sub>6</sub> ]	80%	This
Bi <sub>2</sub> WO <sub>6</sub>	vs Ag/Ag+	54	/MeCN	00/0	work
Bi NPs	–2.0 V vs Ag/AgCl	16	0.1M [Bmim][OTf] /MeCN	96.1%	4
<b>Bi-CMEC</b>	-1.95 V vs SCE	15	20 mM [BMIM]PF <sub>6</sub>	85%	5
Au-CeOx/C	-0.89	12.9	0.1M KHCO <sub>3</sub>	89.1%	6
Pd NPs	-0.89	9.9	0.1 M KHCO <sub>3</sub>	91.2%	7
V <sub>o</sub> -rich ZnO	-1.1	16	0.1 M KHCO <sub>3</sub>	83%	8
Ni–N <sub>4</sub> –C	-0.81	28.6	0.5 M KHCO <sub>3</sub>	98%	9
Zn dendrite	-1.1	16	0.5 M KHCO <sub>3</sub>	79%	10
5 nm Ag/C	-0.75	<b>3.8</b> <sup><i>a</i></sup>	0.5 M KHCO <sub>3</sub>	79.2%	11
np-Cu-In	-0.95	4.5	0.1 M KHCO <sub>3</sub>	91%	12
NiSA-N-CNT	-0.7	23.5	0.5 M KHCO <sub>3</sub>	91.3%	13
In/Cu NWs	-0.6	1.7	0.1 M KHCO <sub>3</sub>	93%	14
Cu-Sn	-0.6	1.0	0.1 M KHCO <sub>3</sub>	> 90%	15
Cu-Pd alloy	-0.89	6.9	0.1 M KHCO <sub>3</sub>	86%	16
Nanoporous Ag	-0.6	18	0.5 M KHCO3	92%	17
Au NWs	-0.35	9~4	0.5 M KHCO3	94~85%	18
HNCM/CNT	-0.29	1	0.1 M KHCO <sub>3</sub>	80%	19
Pd icosahedra/C	-0.8	3	0.1 M KHCO <sub>3</sub>	90%	20
MoS <sub>2</sub>	-0.76	~43	96 mol% H <sub>2</sub> O / 4 mol% [EMIM]BF <sub>4</sub>	98%	21
Porous Cu fiber	-0.4	~	0.3 M KHCO₃	~70%	22

Table S2 The comparison of perfomence for  $CO_2$  electroreduction to CO over different electrodes.

<sup>a</sup>Partitial current density of CO.

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