Electronic Supplementary Information (ESI) for:

A novel photoelectrocatalytic approach for water splitting by an I-BiOCl/bipolar membrane sandwich structure

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1. Chemical reagents

All chemicals used for the following investigations were of analytical grade. Chitosan (CS) with an *N*-deacetylation degree of 90%, Carboxymethylcellulose (CMC) with Na-content degree of 6.5-8.5%, PVA (molecular weight of 105,000 g mol^{-1}, 98.5±0.5% hydrolyzed), glutaraldehyde (GA, 25% by weight in water), iron trichloride($FeCl_3$), Sodium bismuthate ($NaBiO_3$•$2H_2O$), potassium iodide (KI) were all purchased from Guoyao Chemicals Co. Ltd. hydrochloric acid (HCl, 36.0~38.0 wt.% solution in water, Beijing Chemical Works).

2. Instrumentation

Powder X-ray diffraction (XRD) patterns were recorded on a DX-2700 diffractometer using Cu Kα radiation under 40 kV and 30 mA. The morphology and microstructure were observeded by using TEM (JEM-2010). The surface electronic states were analyzed by XPS (ES-CALAB 250). The UV-Vis diffuse reflectance spectrum (DRS) was recorded on a PerkinElmer Lambda 35 spectrophotometer. The current-voltage curve was measured using a direct current source (HB171501SL 5A, Hongbao Electric Group Co., Ltd. in China). An electrochemical workstation (CHI660C; Shanghai Chenhua Instrument Company, China) was used to perform AC impedance spectroscopy of the BPM.

3. Preparation of I-BiOCl/BPM

A three-step process was used to prepare I-BiOCl/BPM (Figure S1). A mixture of 300 mL CMC aqueous solution (3.0 wt%) and 200 mL PVA aqueous solution (3.0 wt%) was stirred for 2 h to obtain PVA-CMC aqueous solution. The gelatinous PVA-CMC aqueous solution was poured on to a clean glass plate and dried at room temperature to form a membrane. Subsequently, the membrane was cross-linked with $FeCl_3$ aqueous solution (8.0 wt%) for 20 min and dried to obtain

cation-exchange membrane (area 50 cm^2).

The prepared I-BiOCl photocatalyst was added to 100 mL absolute ethanol, with ultrasonication to prevent aggregation of the nanoparticles, then poured on to the surface of cation-exchange membrane and dried to obtain I-BiOCl catalyst layer.

A mixture of 300 mL aqueous CS solution (3.0 wt%), 200 mL aqueous PVA solution(3.0 wt%), and 10 mL glutaraldehyde (0.25 %, cross-linking agent) was stirred for 2.5 h. Then casted on to the surface of the I-BiOCl catalyst layer and dried naturally in air to obtain I-BiOCl/BPM.

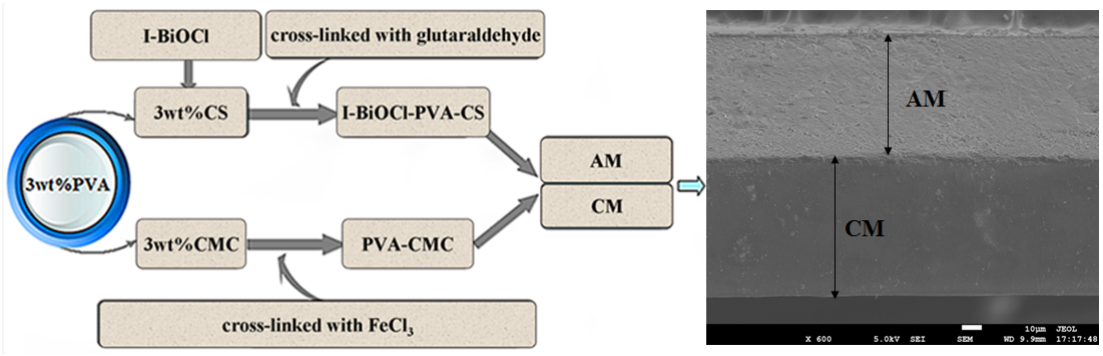


Figure S1. Schematic diagram of process for preparation of I-BiOCl BPM

4. Preparation of I-BiOCl photocatalyst

Typically, 3.16 g $NaBiO_3$•$2H_2O$ (10 mmol) was put into 100 mL bunsen beaker which contained 40 mL absolute ethyl alcohol to form $NaBiO_3$•$2H_2O$-EtOH suspension first. Then, 7.968 g KI was dissolved into 40mL of 1.2 mol L^{-1} hydrochloric acid to form the mixture solution. Subsequently, the mixture solution was added drop-wise into the $NaBiO_3$•$2H_2O$-EtOH suspension at the rate of one-drop per 10 seconds, resulting in the formation of a uniform yellow suspension. Half an hour later, the precipitate was filtrated and washed with de-ionized water for 3 times.

Finally, the I-BiOCl photocatalyst was obtained by drying the precipitate at room temperature. For the purpose of comparison, BiOCl sample was also prepared by a similar method except that KI was not added during the preparation process. The preparation procedure was depicted in figure S2.

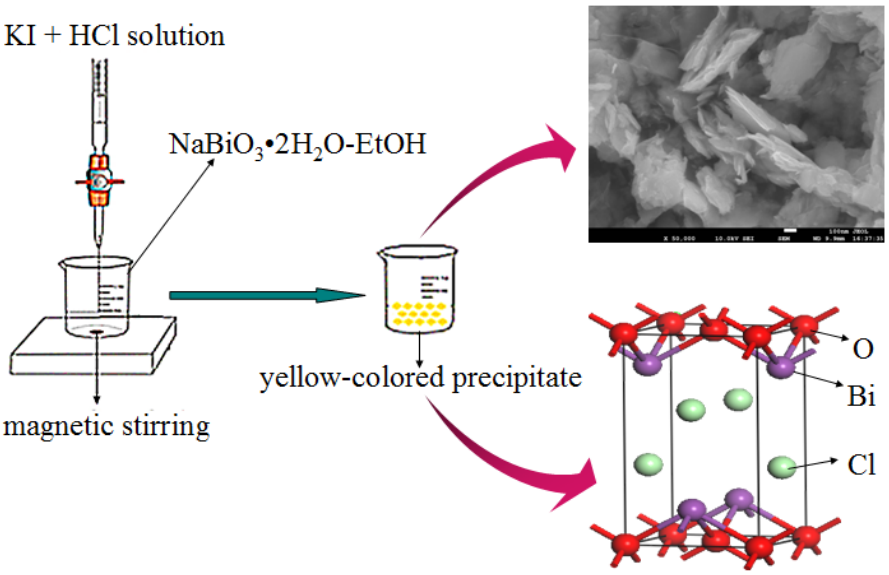


Figure S2. The preparation procedure of I-BiOCl photocatalyst

5. Measurement of the current-voltage curve (I-V curve) of the BPM-equipped cell

The I-V curve of the BPM-equipped cell was measured by use of a direct current source. The BPM was fixed between the cathode and anode chambers, as a separator. The catholyte and anolyte were both 200 mL 1.0 mol/L Na_2SO_4 solution. The anode and cathode were both graphite electrodes (area 2 cm^2). The I-V curve was measured both with and without sunlight irradiation. The average light intensity of solar-light was 1.17×10^5 lx during the experiments.

6. AC impedance spectroscopy of the BPM

The BPM was fixed between the cathode and anode chambers, as a separator. The working electrode was a graphite electrode, the counter electrode was a Pt wire, and the reference electrode was an Ag/AgCl electrode. The electrolyte was 200 mL 1.0 mol/L KCl solution. An electrochemical workstation (CHI660C; Shanghai Chenhua Instrument Company, China) was

used to perform AC impedance spectroscopy of the BPM. The average light intensity of solar-light was 1.16×10^5 lx during the experiments.

7. The current efficiency and energy consumption of H_2 generation

The water system used the I-BiOCl/bipolar membrane sandwich structure as a diaphragm to perform H_2 production from water splitting. The collection of gas bubbles is used by a draining water gathering gas method. The average light intensity of solar-light was 1.16×10^5 lx during the experiments. The equation of the efficiency of hydrogen gas production was illustrated below:

$$\text{Efficiency (\%)} = \frac{V_{real}}{V_{ideal}} \qquad \textbf{(1)}$$

where V_{real} (m^3) is the volume of the hydrogen production by a draining water gathering gas method, and V_{ideal} (m^3) is the volume by calculating from ideal gas equation at 303 K and 1 atm. The energy consumption can be defined by the following equation.

$$E = \int \frac{UIdt}{V} \qquad \textbf{(2)}$$

Here, U (V) and I (A) are the potential across the cell stack and current, respectively. V (m^3) stands for the volume of the hydrogen production by a draining water gathering gas method.

8. XRD patterns of BiOCl and I- BiOCl

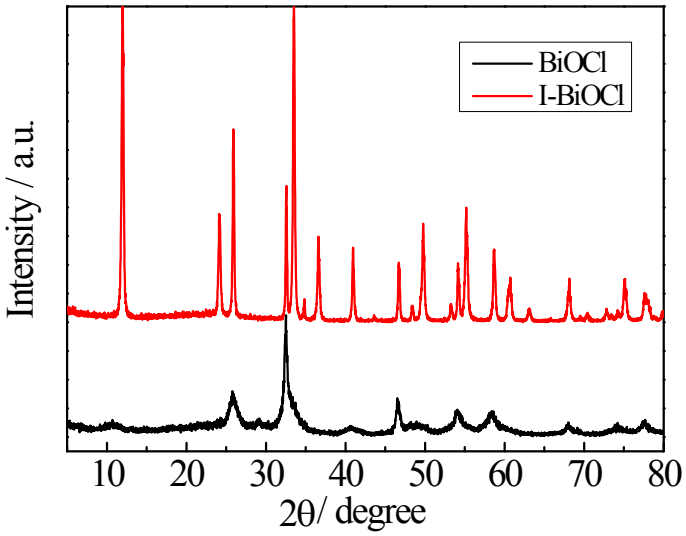


Figure S3. XRD patterns of BiOCl and I- BiOCl

9. UV-Vis patterns of BiOCl and I- BiOCl

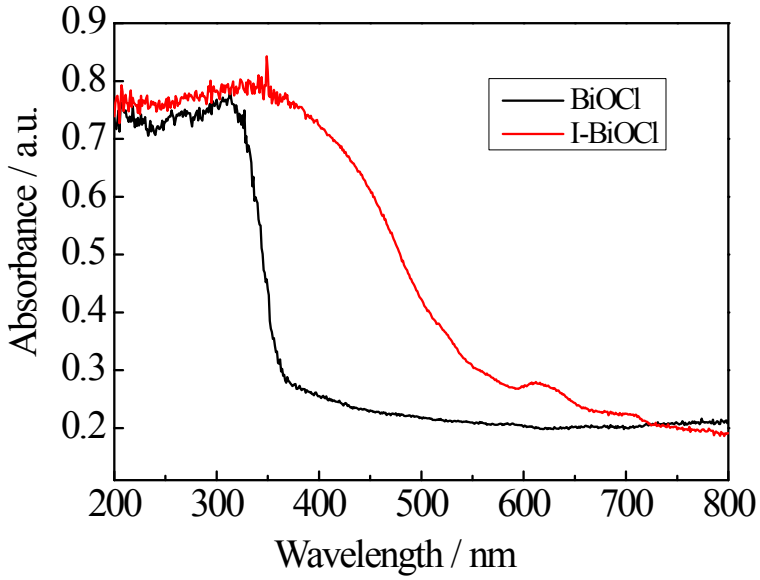
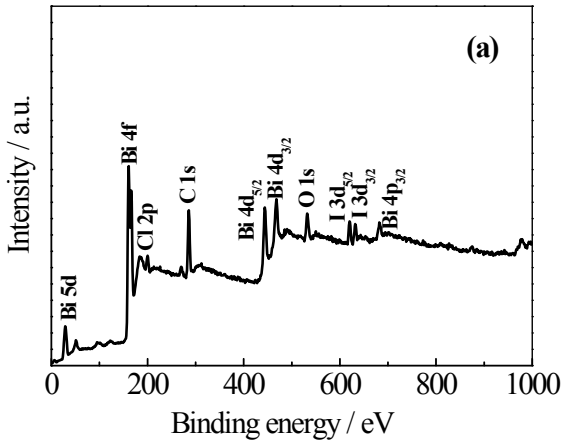


Figure S4. UV-Vis patterns of BiOCl and I- BiOCl

10. XPS survey spectrum of I-BiOCl (a) and XPS spectra of Bi 4f (b), Cl 2p (c), O 1s (d) and I 3d (e).



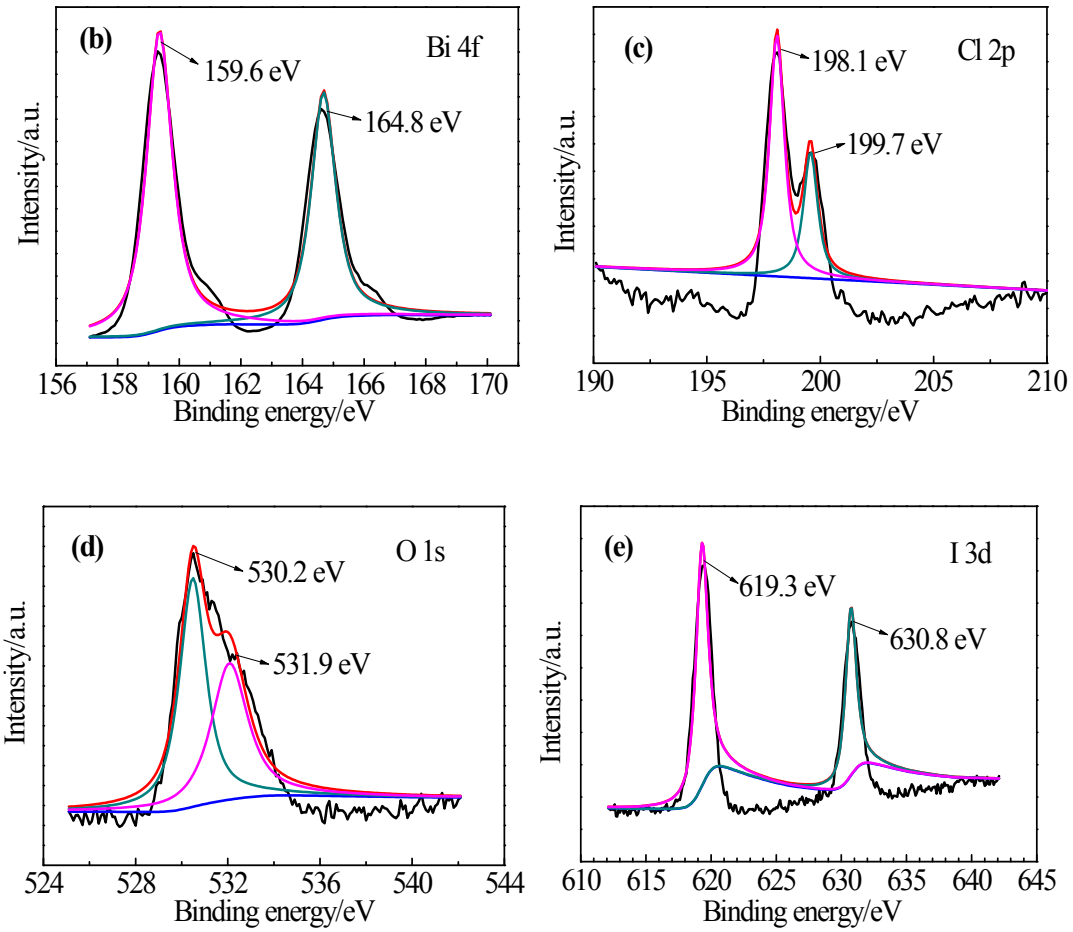


Figure S5. XPS survey spectrum of I- BiOCl (a) and XPS spectra of Bi 4f (b), Cl 2p (c), O 1s (d) and I 3d (e).

11. Contact angles of the BPM and I-BiOCl BPM.

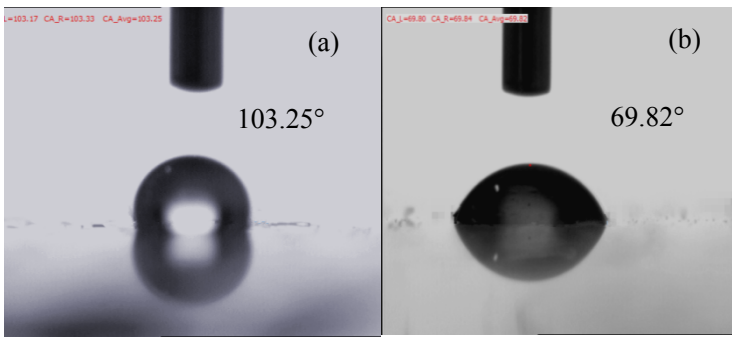


Fig.S6 Contact angles of the BPM (a) and I-BiOCl BPM (b)

12. pH-plot under illumination/dark in the anolyte and catholyte.

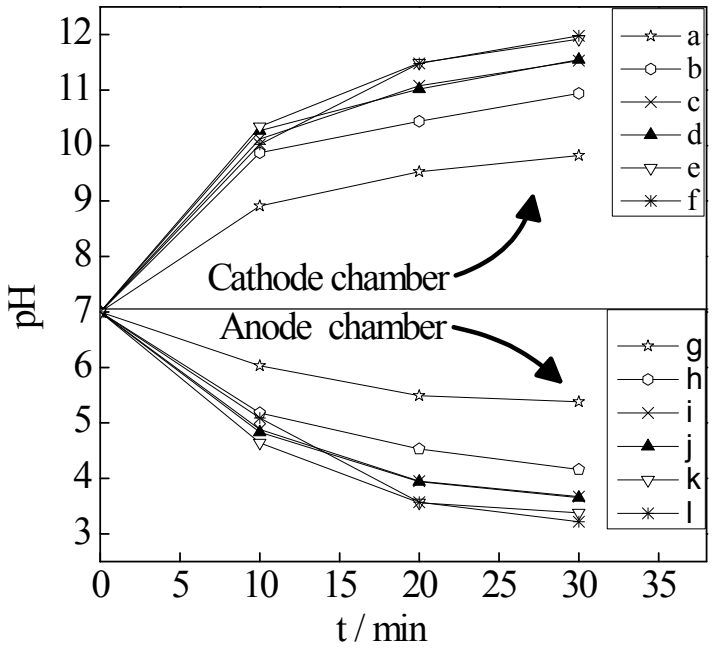


Figure S7 pH-plot under illumination/dark in the anolyte and catholyte

Cathode chamber: a I-BiOCl BPM (irradiation); b. BiOCl BPM (irradiation); c. I-BiOCl BPM (no irradiation); d. BiOCl BPM (no irradiation); e. BPM (irradiation); f. BPM (no irradiation)

Anode chamber: g. I-BiOCl BPM (irradiation); h. BiOCl BPM (irradiation); i. I-BiOCl BPM (no irradiation); j. BiOCl BPM (no irradiation); k. BPM (irradiation); l. BPM (no irradiation)

13. Experiment parameters under different condition

Table 1 I-BiOCl BPM (irradiation)

Current density/mA cm^{-2}	Voltage / V	Operation time/ h	V_{real} / mL	V_{ideal} / mL
20	2.3	0.5	74.6	165.7
30	2.5	0.5	137.8	196.8
40	2.6	0.5	260.0	333.3
50	2.7	0.5	312.5	372.0
100	3.0	0.5	595.2	692.1
150	3.3	0.5	883.9	982.1
200	3.5	0.5	1067.1	1159.9

Table 2 I-BiOCl BPM (no irradiation)

Current density/mA cm^{-2}	Voltage / V	Operation time/ h	V_{real} / mL	V_{ideal} / mL
20	2.9	0.5	86.3	196.1
30	3.1	0.5	166.1	276.7
40	3.4	0.5	261.5	402.3
50	3.7	0.5	385.4	550.5
100	4.3	0.5	716.6	930.7
150	4.9	0.5	1039.7	1350.3
200	5.1	0.5	1301.0	1548.8

Table 3 BiOCl BPM (irradiation)

Current density/mA cm^{-2}	Voltage / V	Operation time/ h	V_{real} / mL	V_{ideal} / mL
20	2.4	0.5	76.9	178.9
30	2.6	0.5	143.3	207.8
40	2.7	0.5	245.5	340.9
50	2.9	0.5	307.2	404.2
100	3.2	0.5	579.7	715.7
150	3.5	0.5	841.3	1001.6
200	3.9	0.5	1037.2	1206.1

Table 4 BiOCl BPM (no irradiation)

Current density/mA cm^{-2}	Voltage / V	Operation time/ h	V_{real} / mL	V_{ideal} / mL
20	3.3	0.5	82.5	202.2
30	3.5	0.5	170.5	282.1
40	3.6	0.5	285.7	446.4
50	3.9	0.5	393.1	579.2
100	4.4	0.5	723.6	992.3
150	5.1	0.5	1087.6	1401.0
200	5.3	0.5	1325.0	1597.8

Table 5 BPM (irradiation)

Current density/mA cm^{-2}	Voltage / V	Operation time/ h	V_{real} / mL	V_{ideal} / mL
20	3.4	0.5	102.4	222.6
30	3.6	0.5	179.9	310.3
40	3.7	0.5	308.3	467.2
50	4.2	0.5	403.8	588.4
100	4.5	0.5	740.2	1000.3
150	5.3	0.5	1104.2	1433.9
200	5.4	0.5	1298.1	1622.6

Table 6 BPM (no irradiation)

Current density/mA cm^{-2}	Voltage / V	Operation time/ h	V_{real} / mL	V_{ideal} / mL
20	3.6	0.5	102.1	227.3
30	3.9	0.5	175.1	318.4
40	4.5	0.5	306.4	494.2
50	4.7	0.5	424.0	624.1
100	4.9	0.5	729.2	1027.2
150	5.5	0.5	1086.1	1449.2
200	5.8	0.5	1316.3	1684.4