Electronic Supplementary Information

A BiOCl/bipolar membrane as separator for regenerating NaOH in water-

splitting cells

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Fig. S1 The preparation procedure of BiOCl.



Fig. S2 XRD patterns of BiOCl and BiOCl-1.



Fig. S3 UV-Vis patterns of BiOCl and BiOCl-1.



Fig. S4 XPS survey spectrum of BiOCl.

Preparation of BiOCI/BPM sandwich structure

A three-step process was used to prepare BiOCl/BPM by a paste method.

Firstly, carboxymethyl cellulose (CMC, with 6.5-8.5% Na-content, Guoyao Chemicals Co. Ltd.) aqueous solution (3.0 wt.%) together with polyvinyl alcohol (PVA, molecular weight of 105000 g mol⁻¹) aqueous solution (3.0 wt%) was stirred for 2h and poured on a clean glass plate to form a membrane. Then, the membrane was cross-linked with FeCl₃ (8.0 wt.%, 10 min) and dried to obtain CM.

Secondly, The prepared BiOCl photocatalyst was added to 100 mL deionized water with ultrasonication to prevent aggregation, then poured on to the surface of CM and dried to obtain BiOCl interlayer.

Thirdly, Chitosan (CS, with 90 % N-deacetylation) aqueous solution (3.0 wt.%) together with PVA aqueous solution (3.0 wt%) was stirred for 2h. Then, 2 mL glutaraldehyde (25 % by volume in water) was added and stirred for another 2 h. Next, the mixture was poured on to the surface of BiOCl interlayer to form AM. Finally, the BiOCl /BPM sandwich structure composite was allowed to be totally dried at room temperature.

Measurement of the current density-voltage curve of the BiOCI/BPM

The I-V curve of the BPM-equipped cell was measured by use of a direct current source. The BiOCl/BPM was fixed between the cathode and anode chambers, as a separator. The catholyte and anolyte were both 50 mL 0.5 mol L^{-1} Na₂SO₄ solution. The anode and cathode were both graphite electrodes (area 2 cm²). The I-V curve was measured both with and without sunlight irradiation.

AC impedance spectroscopy of the BiOCl/BPM

Firstly, a clean graphite electrode was plunged into the thick CMC aqueous solution and then taken out of the solution and dried to form the CM. The CM was cross-linked with FeCl₃ solution for 20 min and dried. Next, the prepared BiOCl photocatalyst was coated on the surface of the CM. Finally, the coated electrode was plunged into the thick CS solution modified by glutaraldehyde, and then taken out of the solution and dried.

The working electrode was the coated graphite electrode, the counter electrode was a Pt wire, and the reference electrode was an Ag/AgCl electrode. The electrolyte was 100 mL 0.5 mol L^{-1} KCl solution. An electrochemical workstation (CHI660C; Shanghai Chenhua Instrument Company, China) was used to perform AC impedance spectroscopy.

The current efficiency and energy consumption of regenerating NaOH

In the process of experiment, a simulated caustic solution was also prepared according to the literature ^[10] and main compositions in Table S1.

Component	Concentration / mol L ⁻¹
NaOH	0.440
Na ₂ CO ₃	0.290
Na_2SO_4	0.048
Oil	Seldom

 Table S1
 The main components of spent caustic

In the experiment, the anode chamber was fed with the spent caustic (200 mL), the cathode chamber was fed with 0.3 mol L^{-1} Na₂SO₄ (200 mL) as the supporting electrolyte solution, and the central chamber was fed with 0.1 mol L^{-1} NaOH solution (200 mL). The CM and BiOCl/BPM were used as septum. The concentration of sodium hydroxide is measured with titration method, with the phenolphthalein as indicator. Current efficiency calculated using formula (1):

$$\eta = \frac{(C_t - C_o)VF}{It} \tag{1}$$

Where C_t and C_0 (mol L⁻¹) are the concentrations of NaOH at time t and 0, respectively; V(L) is the volume of solution in central chamber, Since the volume change of solutions can be ignored, the initial volume (V = 0.2 L) is acted as the volume of the whole process; F is the Faraday constant, equal to 96500 C mol⁻¹; and I (A) is the current. The energy consumption E (kWh kg⁻¹) was calculated by formula (2). U(V) is the cell voltage, I(A) is the current, and M is the molar mass of sodium hydroxide (40 g mol⁻¹).

$$E = \int \frac{UIdt}{(C_t - C_o)VM}$$
(2)

Na ₂ SO ₄ concentration /mol L ⁻¹	0.10	0.20	0.30	0.40	0.50
NaOH yield / mol L ⁻¹	0.0580	0.0535	0.0550	0.0504	0.0550
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Table S2 The yield of NaOH for different concentration of Na_2SO_4 .



Fig. S5 The current efficiency at different concentration of Na_2SO_4 .

NaOH initial concentration / mol L ⁻¹	0.10	0.20	0.30	0.40	0.50
NaOH yield / mol L ⁻¹	0.1103	0.1088	0.1077	0.1065	0.1008

Table S3 The yield of NaOH for different initial concentration of NaOH



Fig. S6 The influence of different initial concentration of NaOH on current efficiency