Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Ultrathin Porous Bi_5O_7X (X=Cl, Br, I) Nanotubes for Effective Solar Desalination

Yang Liu, Zheng Jiang, Xinyi Zhang, Pei Kang Shen*

Collaborative Innovation Center of Renewable Energy Materials, Guangxi Key Laboratory of Electrochemical Energy Materials, College of Chemistry and Chemical Engineering, State Key Laboratory of Processing for Non-ferrous Metal and Featured Materials, Guangxi University, Nanning, 530004, P. R. China.

*E-mail: pkshen@gxu.edu.cn

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1. Experimental details

Materials

$Bi(NO_3)_3 \cdot 5H_2O$, ethylene glycol, ethanol, ammonium hydroxide are Analytial reagent, which purchased from Shanghai Macklin Biochemical Co., Ltd and used without further chemical treatment.

Synthesis of micro-rods

0.8g $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 200ml deionized water by ultrasonic wave, a clear and transparent solution was obtained. After 2 hours standing, the white precipitate would appear in the bottom of the solution. It was collected and washed by suction filtration, the micro-rods were fabricated by self-assembling in water.

Synthesis of hexagonal micro-disks

0.8g $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 200ml deionized water by ultrasonic wave, a clear and transparent solution was obtained. The homemade devices (Fig. S3) were used to fabricate the hexagonal micro-disks. The nitrogen, which carry the ammonia into the above clear and transparent solution, flew through the ammonia water. The bubbles were small and slow, the white precipitate was generated during the process. It was collected and washed by suction filtration, the hexagonal micro-disks were fabricated by self-assembling in water.

Synthesis of long micro-boxes

0.8g $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 200ml deionized water by ultrasonic wave, a clear and transparent solution was obtained. The homemade devices were used to fabricate the long micro-boxes. Two electrodes (copper sheet) were put into the above solution, and a 0.4 V voltage was applied in the electrodes. After 30 minutes, the cathode was washed with deionized water and ethyl alcohol. The long micro-boxes were obtained on the cathode.

Synthesis of mixed micro-rods and nano-flowers

0.2g $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 50ml deionized water by ultrasonic wave, a clear and transparent solution was obtained. Almost immediately the above solution was put in the freezing compartment (-20℃) of the fridge. After an hour, the solution

turned into ice, then took the ice out and it melted into solution. The white precipitate was washed with deionized water and ethyl alcohol. The mixed micro-rods and nano-flowers were obtained.

Synthesis of nano-flowers

0.1g $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 30ml ethylene glycol, then 10ml ethanol was added to the above solution. 20ml deionized water was put drop by drop into it and stirred the solution for 24 hours. The white precipitate was washed with deionized water and ethyl alcohol. The nano-flowers were obtained.

Synthesis of the 5nm Bi_5O_7I nanotubes

250mg $Bi(NO_3)_3 \cdot 5H_2O$ were dissolved in 20ml ethylene glycol, the mixed solution of 15ml oleylamine and 15ml ethanol were added in the above solution with stirring, 20mg KI were dissolved in the solution later, 20ml deionized water was put drop by drop into it and stirred the solution for 12 hours. The 5nm Bi_5O_7I nanotubes were separated by a centrifuge (12000 $r \cdot min^{-1}$), washed it with n-heptane and absolute ethanol for several times and finally dried it at 60 ℃ for 10 hours.

Based on the above synthetic procedures, the different quantity of raw material were implemented to study the effect to the morphology. The detail is shown in the table below:

Table S1. Synthesis with different quantity of raw material.

Parameter \ Number	BOI	BOI-2	BOI-3	BOI-4	BOI-5	BOI-6
$Bi(NO_3)_3 \cdot 5H_2O$/mg	250	250	250	250	250	250
ethylene glycol/ml	20	20	20	20	20	20
KBr/mg	28	10	28	28	28	28
Water/ml	20	20	5	20	20	20
Mixing time/h	12	12	12	3	12	12
Temperature/℃	40	40	40	40	20	40
Oleylamine/ml	15	15	15	15	15	5

Table S2. Synthesis of BOC, BOB and BOI with different quantity of raw material.

Parameter \ Number	BOC	BOB	BOI
$Bi(NO_3)_3 \cdot 5H_2O$/mg	250	250	250
ethylene glycol/ml	20	20	20
KCl/mg	13	0	0
KBr/mg	0	20	0
KI/mg	0	0	28
Water/ml	20	20	20
Mixing time/h	12	12	12
Temperature/℃	40	40	40
Oleylamine/ml	15	15	15

Materials Characterization

Powder X-ray diffraction (XRD) pattern was recorded on a Rigaku SMARTLAB 3kW diffractometer with Cu Kα radiation (λ=1.5418 Å). X-ray photoelectron spectroscopy (XPS) was implemented on Escalab 250Xi (Thermo Fisher Scientific) using Al as the excitation source. Scanning electron microscopy (SEM) images were recorded on a Hitachi SU8220 filed-emission SEM at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) measurements were performed on a Titan G2 ETEM system at an accelerating voltage of 300 kV. The electrical resistivity was recorded on a conductivity meter (DDSJ-308F, Rex, Shanghai). The absorption spectra were performed using diffuse reflection spectra (DRS, Shimadzu UV3600), Brunauer–Emmett–Teller (BET) surface areas were carried out using nitrogen adsorption apparatus (Micromeritics ASAP-2460). The chemisorbed N_2 were performed in N_2 temperature programmed desorption experimets using a TCD as tetector. Mott–Schottky plots were determined using electrochemical working station (AUTOLAB, AUT86327) at frequency of 1000 Hz and 2000 Hz in dark. The Zeta potential was tested by Zetasizer Nano ZS90.

Computational details

The density functional theory (DFT) calculations were performed by using the CASTEP software package. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was adopted to describe the exchange and correlation potential. Ultra-soft pseudo-potential was adopted to simulate the ion-electron interaction. Cutoff energy for plan-wave expansion is set to be 571.4 eV, and the k-points grid was 1×5×1.

Performance test of desalination

279.0mg BOC (0.234mmol), 289.4mg BOB (0.234mmol) and 300.4mg BOI (0.234mmol) nanotubes were dispersed in 30ml NaCl solution (0.06M) in a 40ml specially-made bottle, the mixed solution was stirred in a bottle for 30 minutes in the dark with high-purity N_2 bubbled at a flow rate of 50 $mL \cdot min^{-1}$. After that, the mixed solution was stirred under a xenon lamp (280nm-800nm). 3ml of the clear solution was collected by the specially-made filter rod which connected with a water pump (Scheme 1d and Fig. S39) every 10 minutes. The collected solution with different illumination time was analyzed by conductivity meter. The stability test was carryed out by 7 cycles (7×60 min), at the end of every cycle (60 min) the sample was rinsed and collected by centrifugal, and the new NaCl solution (0.06M) was add to the bottle again. After every cycle, the solution with illuminated was analyzed by conductivity meter.

2. Supplementary Notes

Formula derivation:

S is conductance, R is resistance, σ is electrical conductivity, F is area of the measuring electrodes, L is the distance of the measuring electrodes, a and b are the parameter. M is the concentration of the salt solution.

$$S = \frac{1}{R} \qquad \text{Equation S1}$$

$$S = \frac{1}{\rho} \bullet \frac{F}{L} \qquad \text{Equation S2}$$

$$\sigma = \frac{1}{\rho} \qquad \text{Equation S3}$$

$$R = \frac{\rho L}{F} = \frac{L}{F} \bullet \frac{1}{\sigma} \qquad \text{Equation S4}$$

$$\sigma = \frac{L}{F} \bullet \frac{1}{R} = \frac{L}{FR} \qquad \text{Equation S5}$$

$$\sigma = aM + b \qquad \text{Equation S6}$$

$$\sigma = aM + b = \frac{L}{FR} \qquad \text{Equation S7}$$

$$\begin{aligned} R &= \frac{L}{F(b + aM)} \\ &= \frac{1}{\frac{Fb}{L} + \frac{Fa}{L}M} \qquad (k_1 = \frac{Fb}{L},\ k_2 = \frac{Fa}{L}) \\ &= \frac{1}{k_1 + k_2 M} \end{aligned} \qquad \text{Equation S8}$$

3. Supplementary Figures

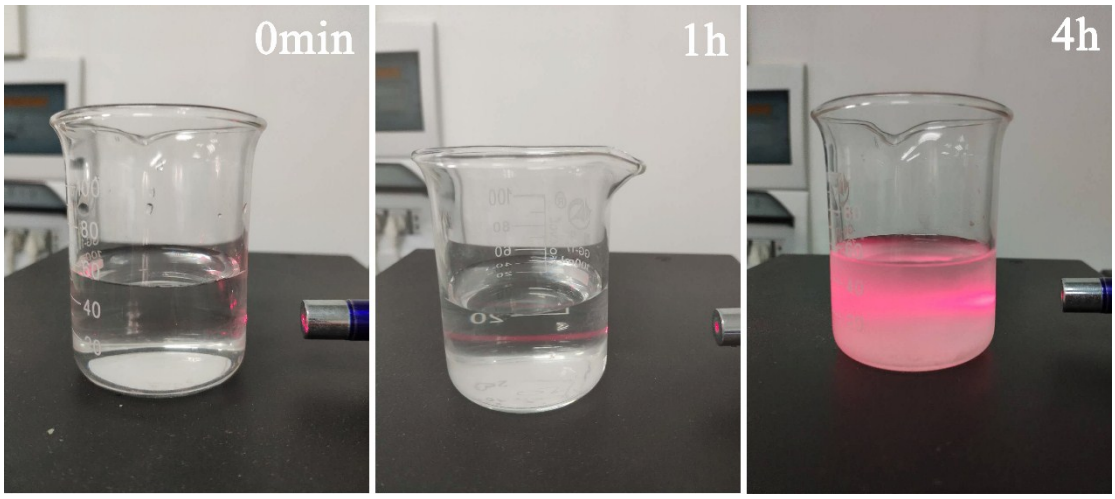

Fig. S1 The evolution of the self-assembly behavior from solution to micro-rods.

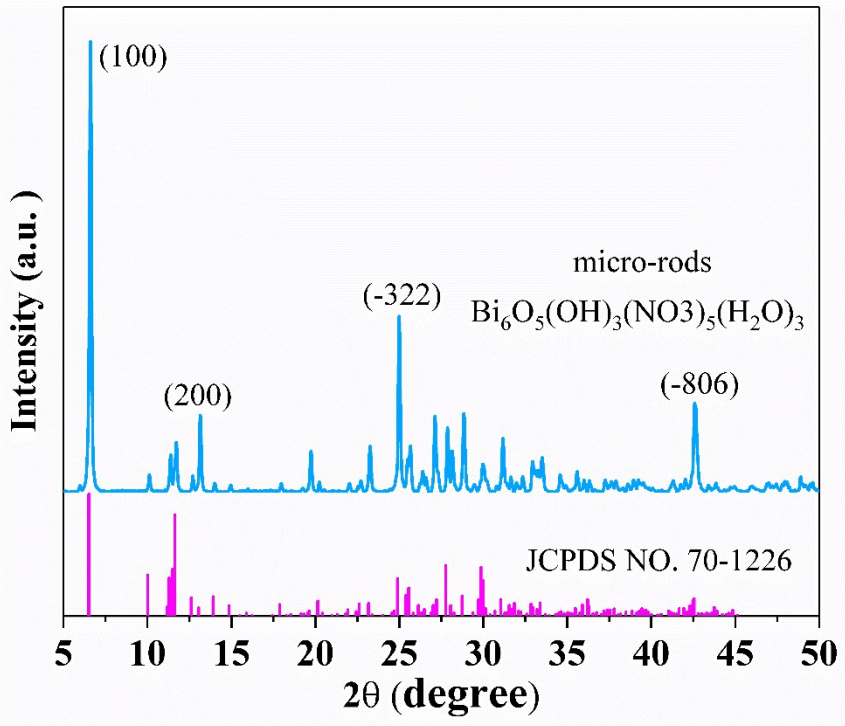

Fig. S2 The XRD pattern of the micro-rods.

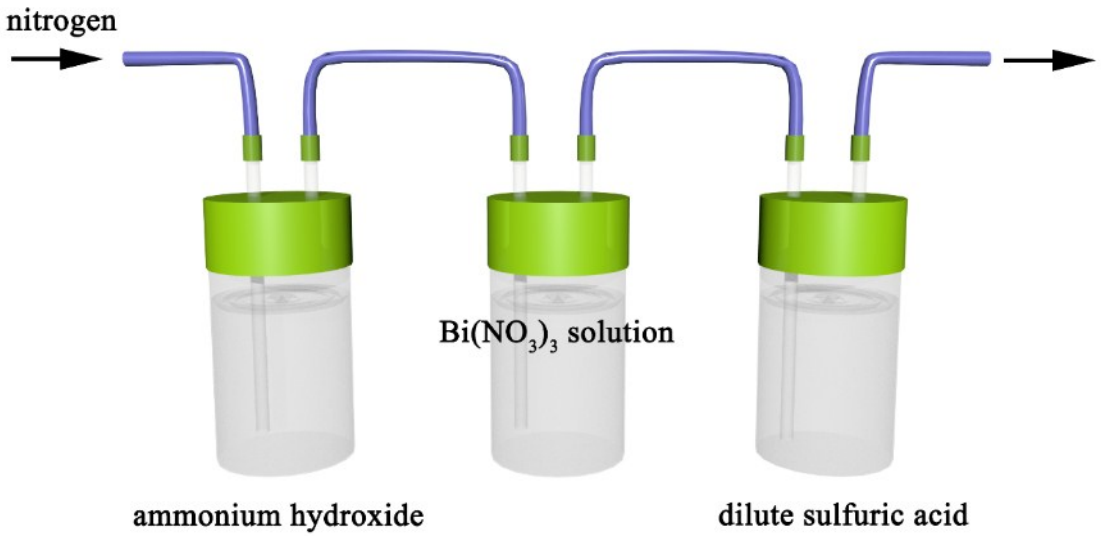

Fig. S3 The synthetic illustration of hexagonal micro-disks.

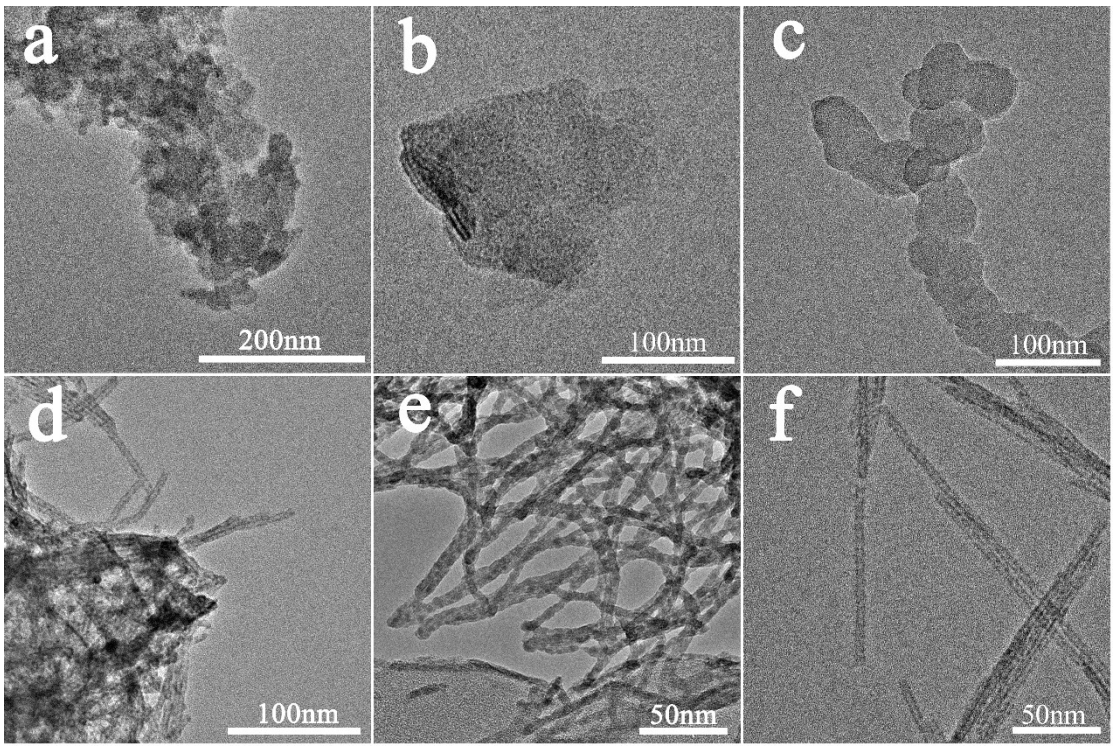

Fig. S4 The TEM images of (a) BOI-3, (b) BOI-4, (c) BOI-6, (d) BOI-4, (e) BOI-2, (f) BOI.

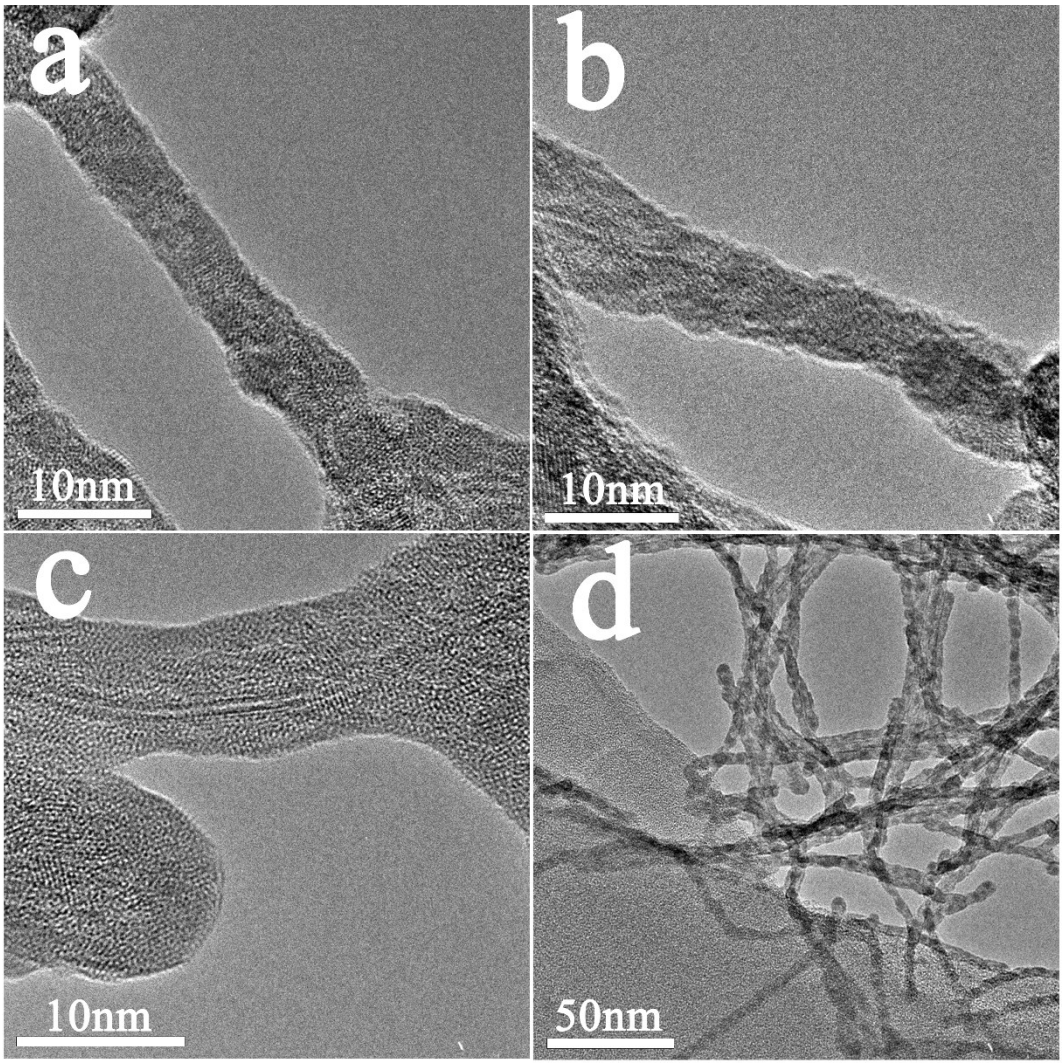

Fig. S5. Different fine structures of BOB2.

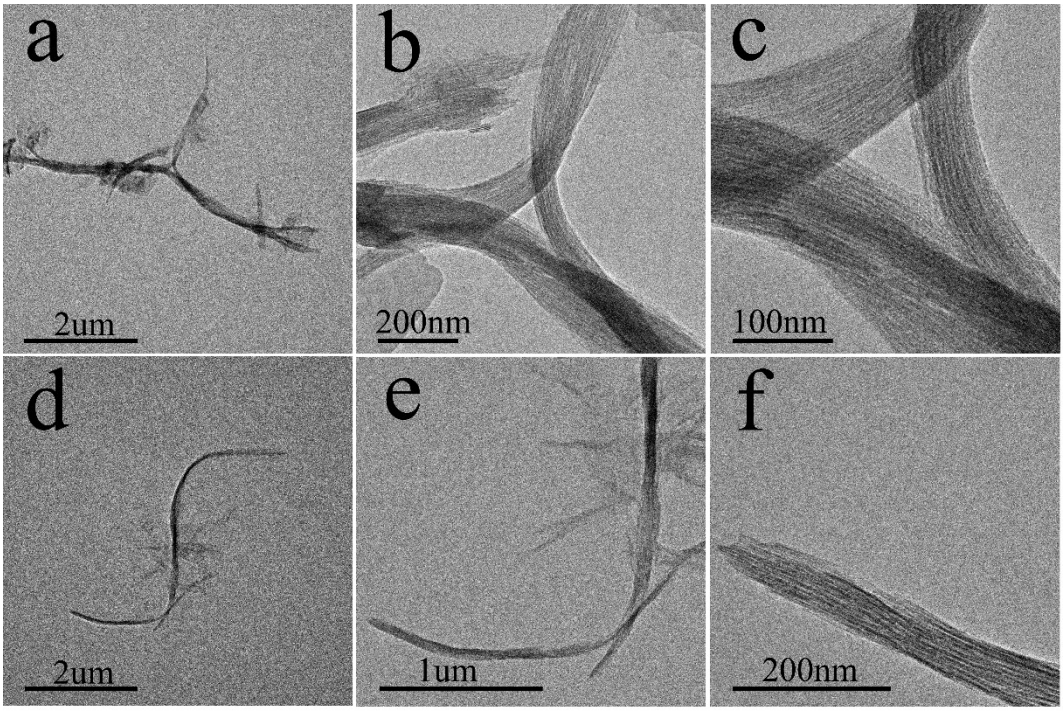

Fig. S6 Low-magnification SEM images of BOI.

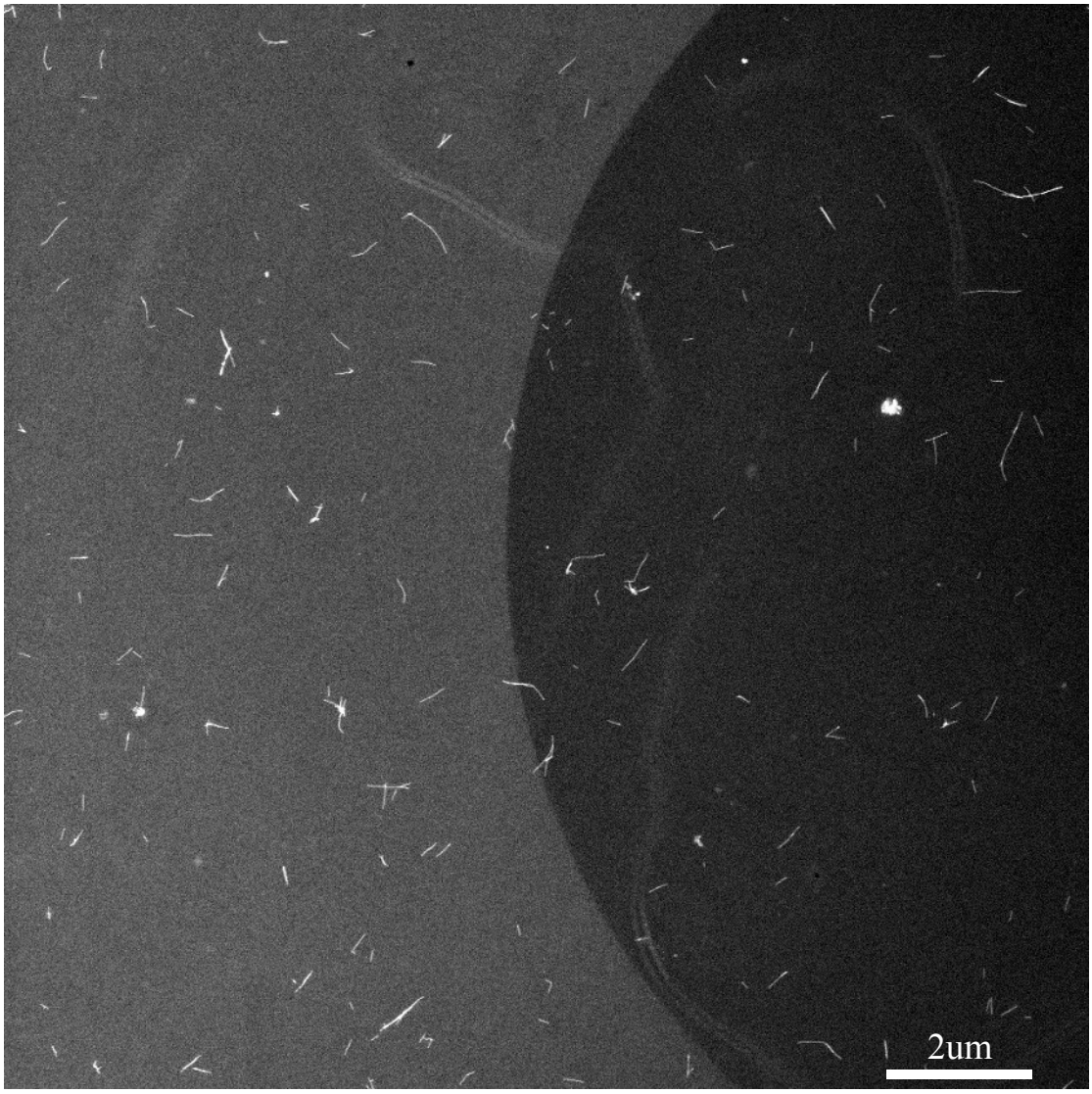

Fig. S7 The large-scale SEM image of BOI.

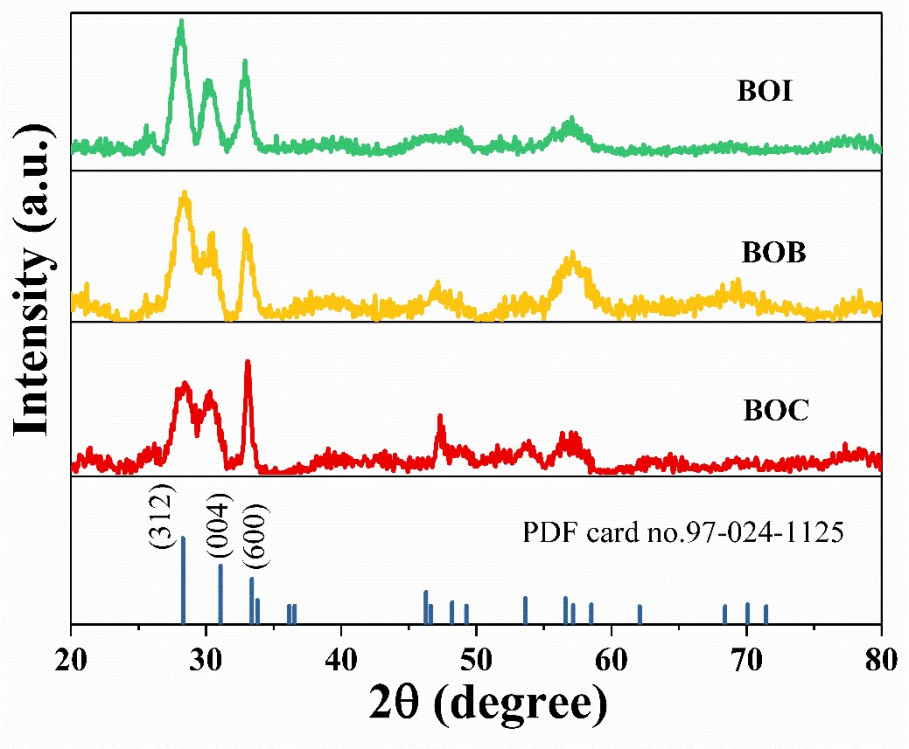

Fig. S8 The PXRD of BOC, BOB and BOI, the bottom is the PDF card no. 97-024-1125 (Bi_5O_7Br).

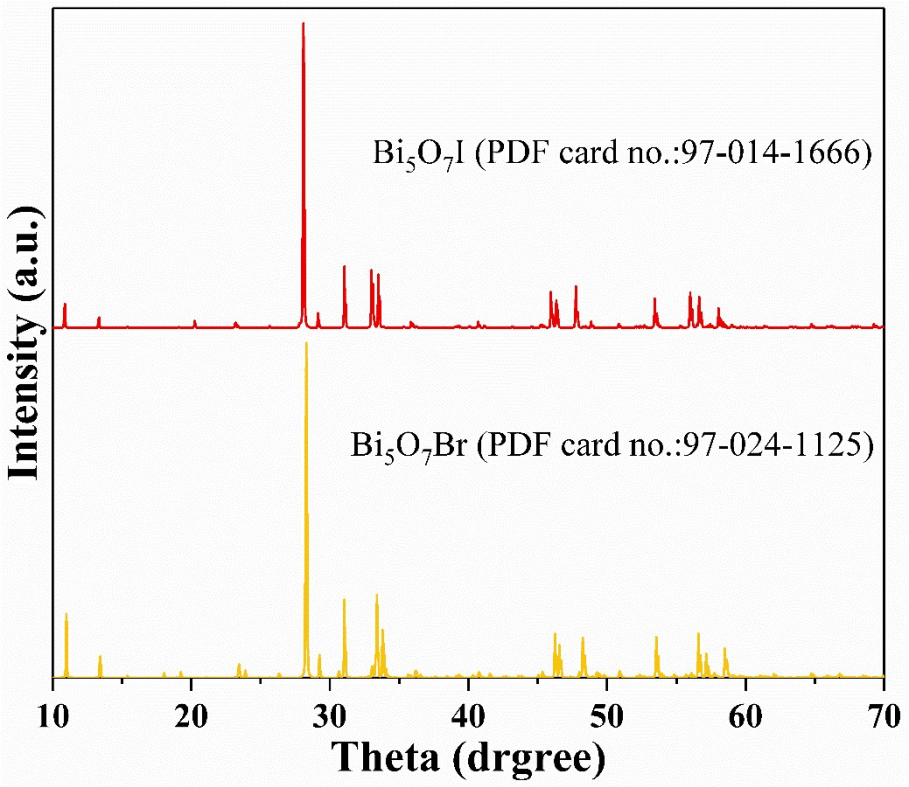

Fig. S9 The simulate powder diffraction of Bi_5O_7Br and Bi_5O_7I.

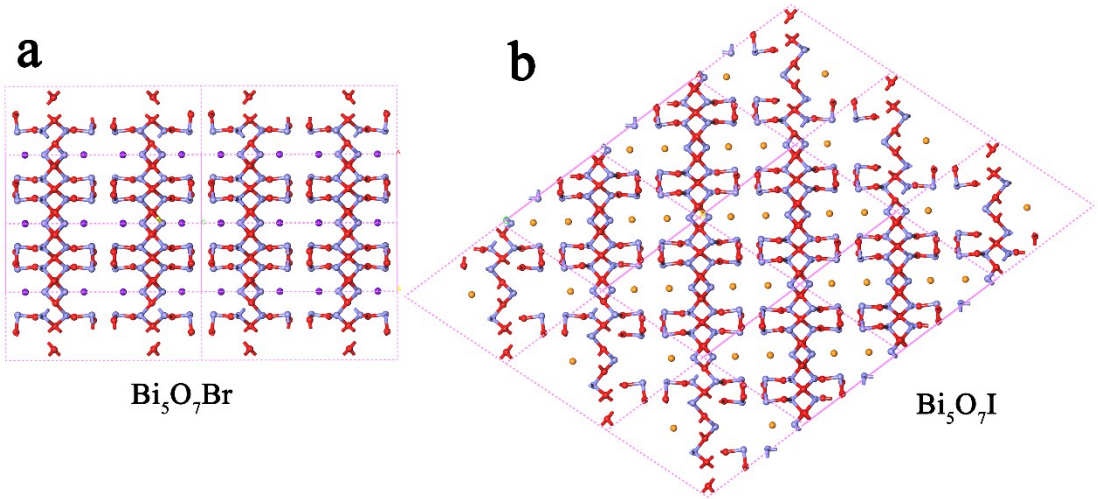

Fig. S10 The patulous primitive cell of BOB and BOI.

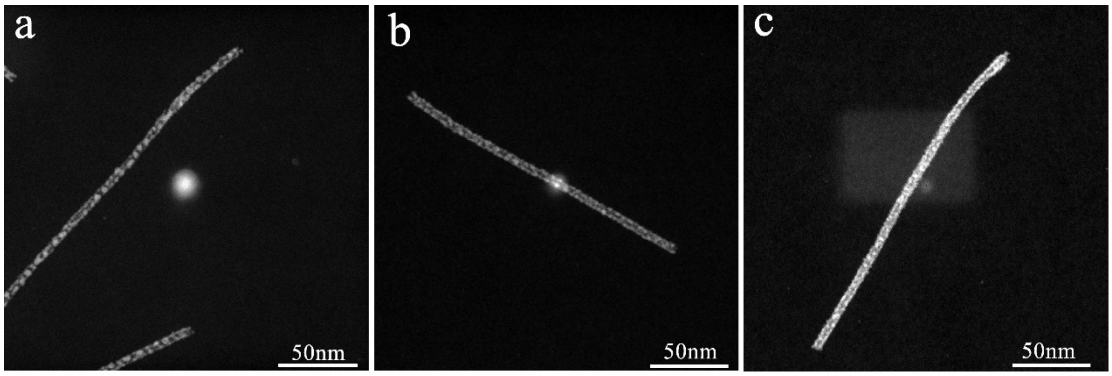

Fig. S11 The HAADF-SEM images of (a) BOC, (b) BOB and (c) BOI.

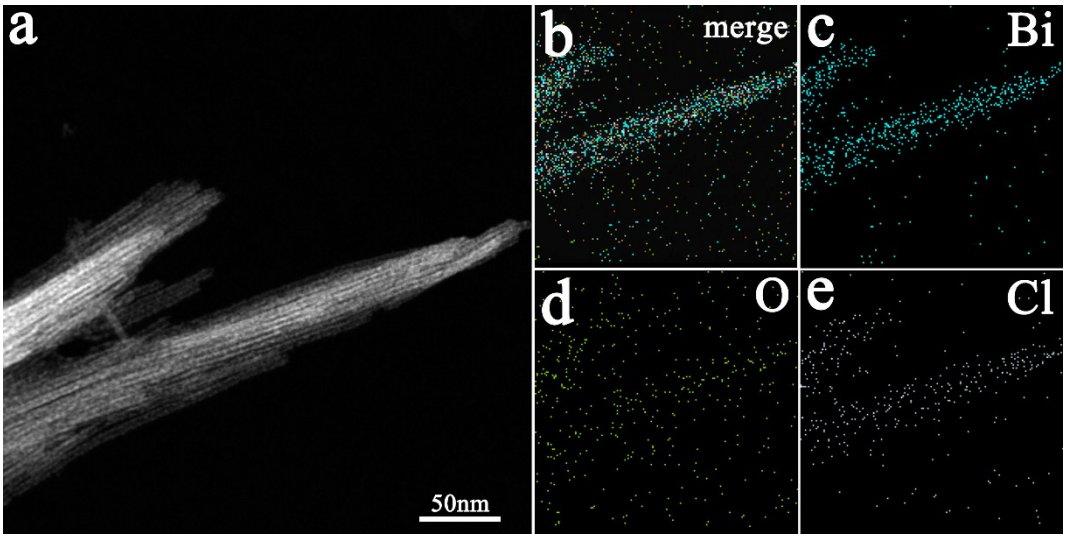

Fig. S12 The element mapping of BOC.

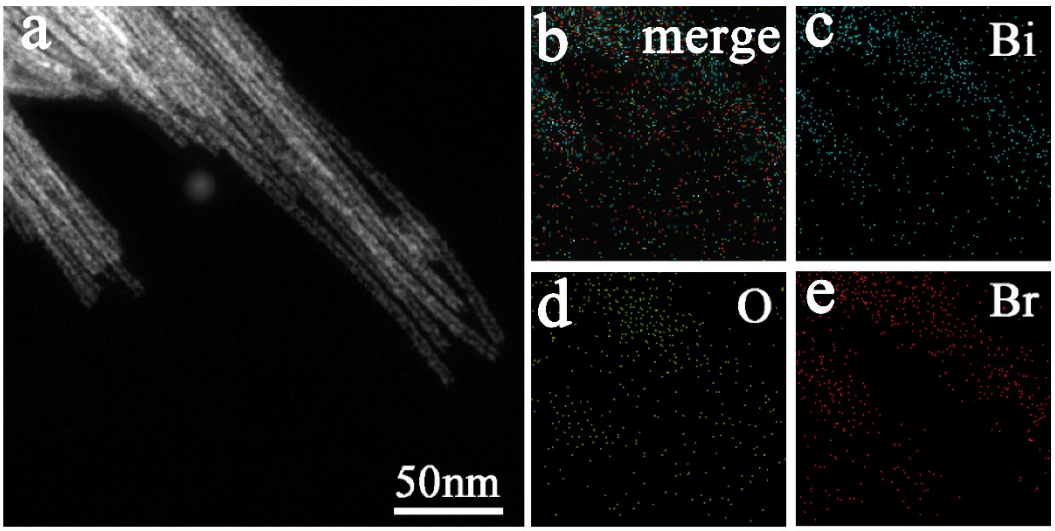

Fig. S13 The element mapping of BOB.

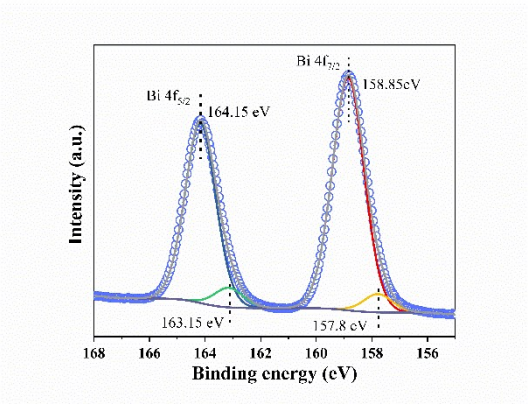

Fig. S14 Fitted XPS Bi 4f spectra of the BOC.

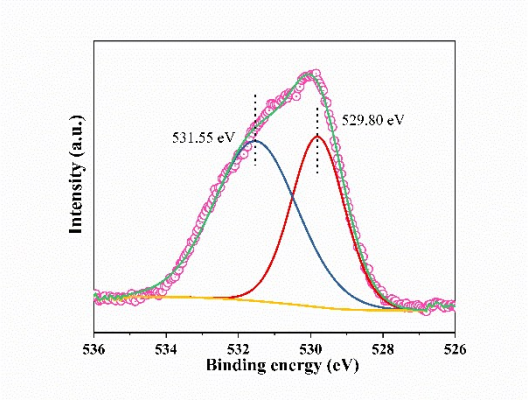

Fig. S15 Fitted XPS O 1s spectra of the BOC.

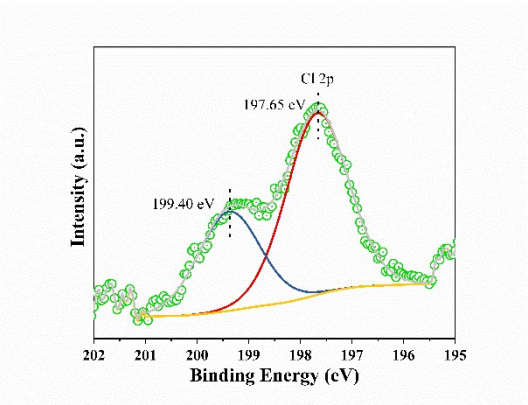

Fig. S16 Fitted XPS Cl 2p spectra of the BOC.

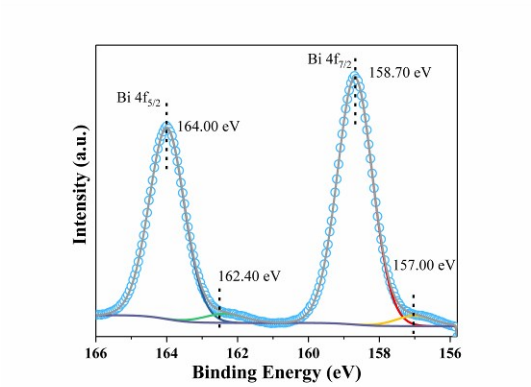

Fig. S17 Fitted XPS Bi 4f spectra of the BOB.

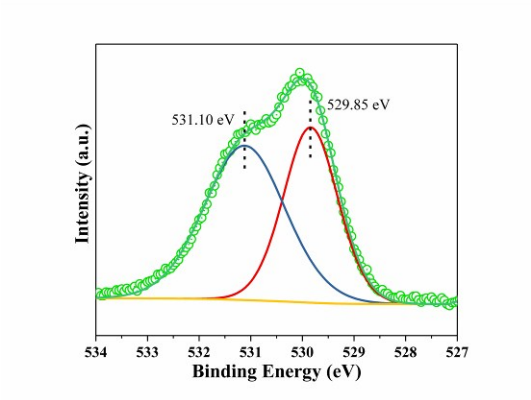

Fig. S18 Fitted XPS O 1s spectra of the BOB.

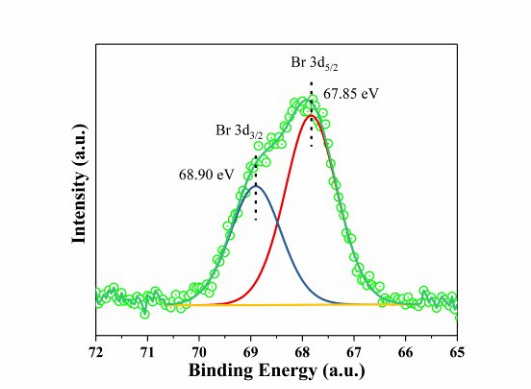

Fig S19 Fitted XPS Br 3d spectra of the BOB.

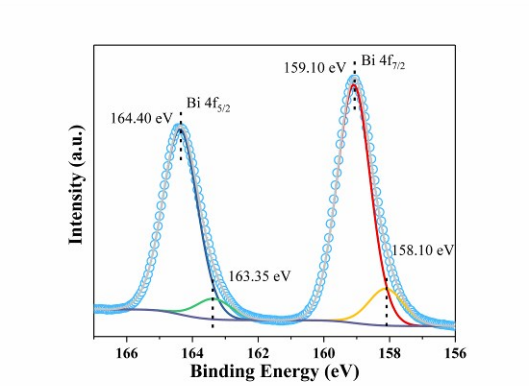

Fig. S20 Fitted XPS Bi 4f spectra of the BOI.

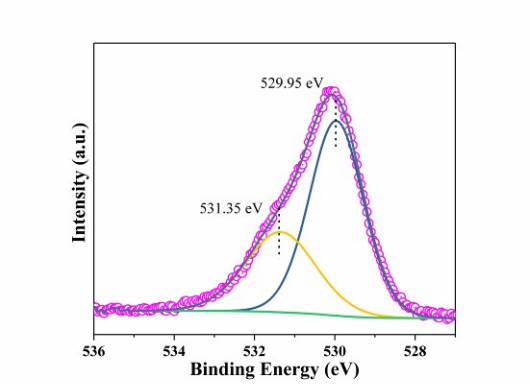

Fig. S21 Fitted XPS O 1s spectra of the BOI.

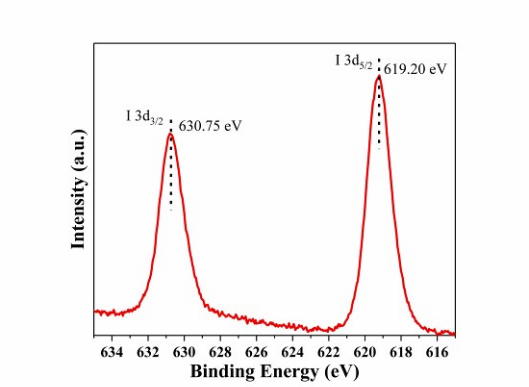

Fig. S22 high-resolution XPS I 3d spectra of the BOI.

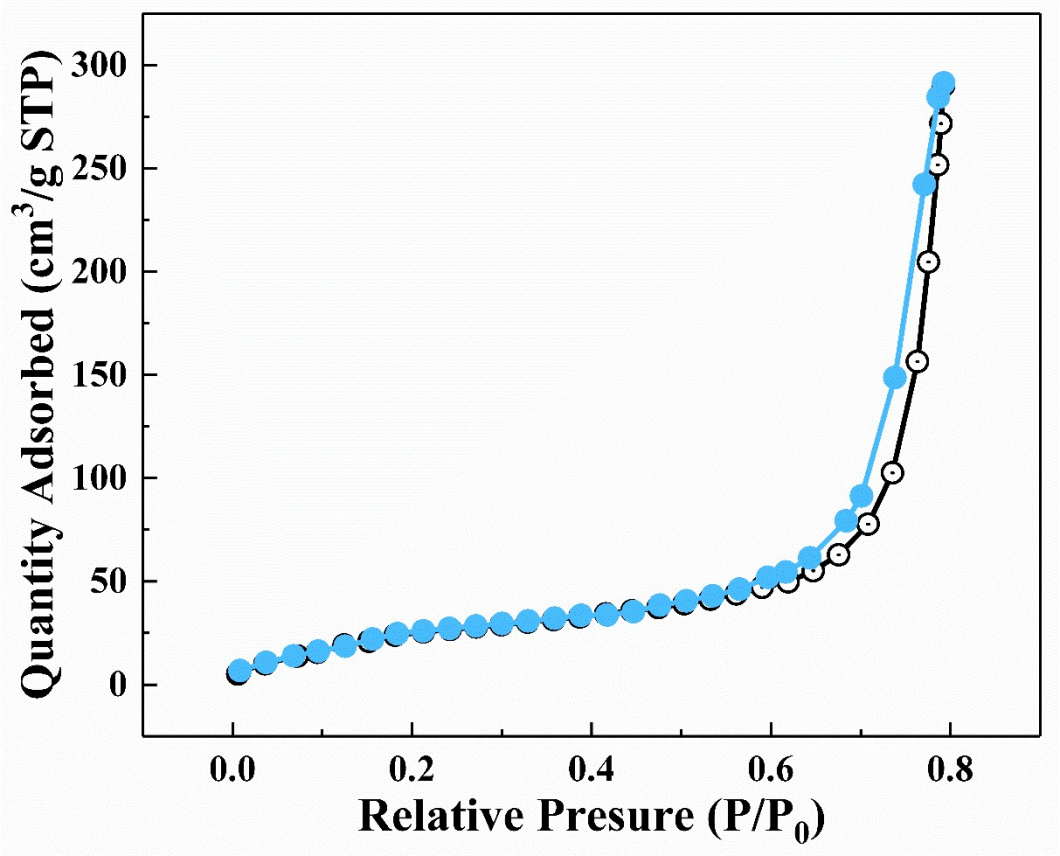

Figure S23. N_2 adsorption–desorption isotherm of BOC.

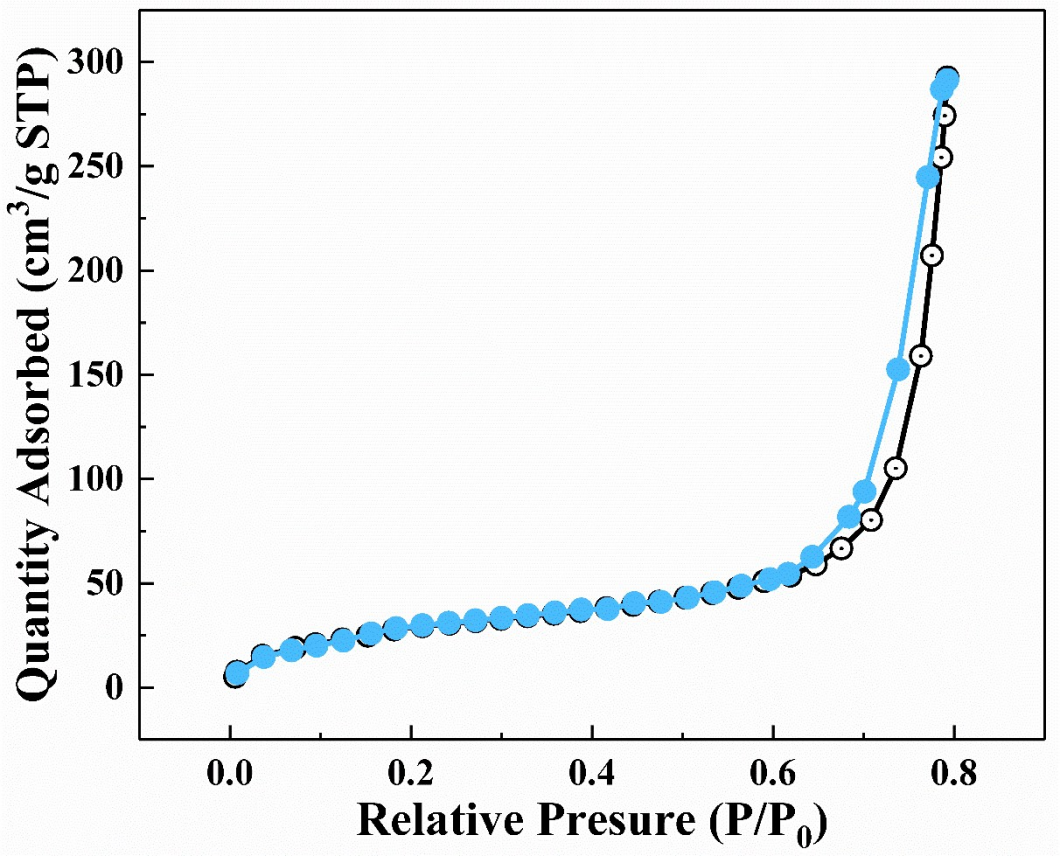

Figure S24. N_2 adsorption–desorption isotherm of BOB.

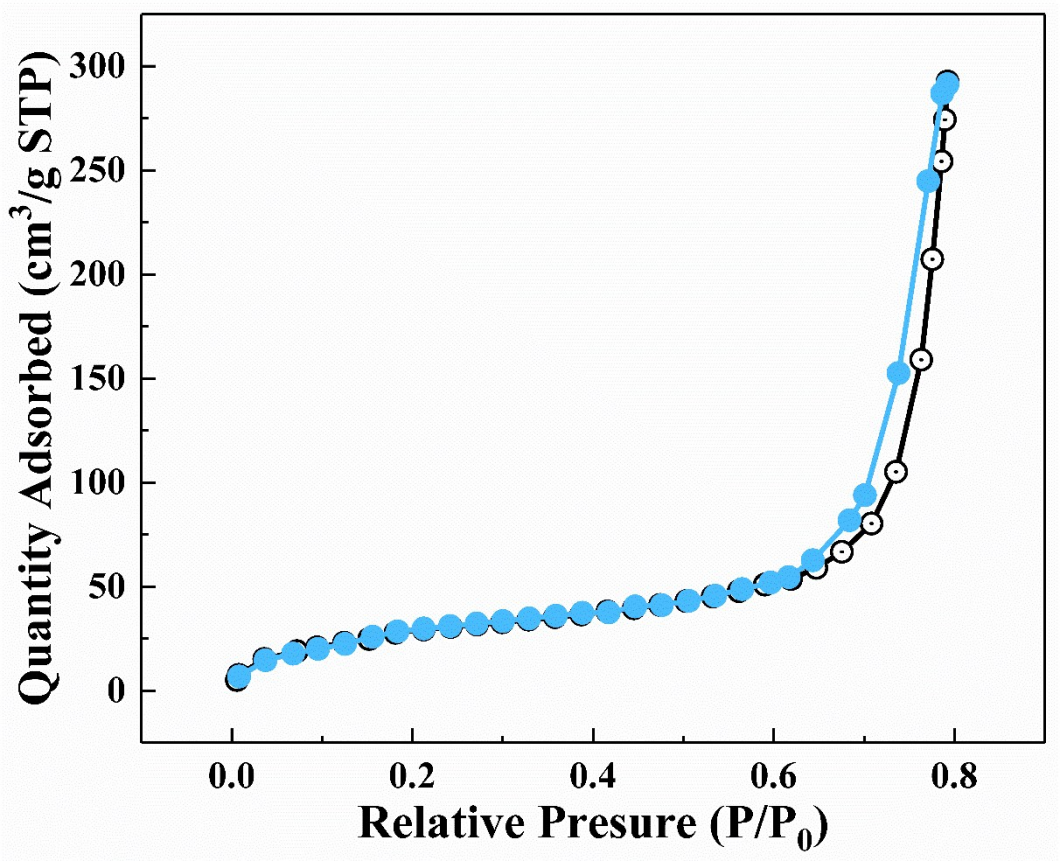

Figure S25. N_2 adsorption–desorption isotherm of BOI.

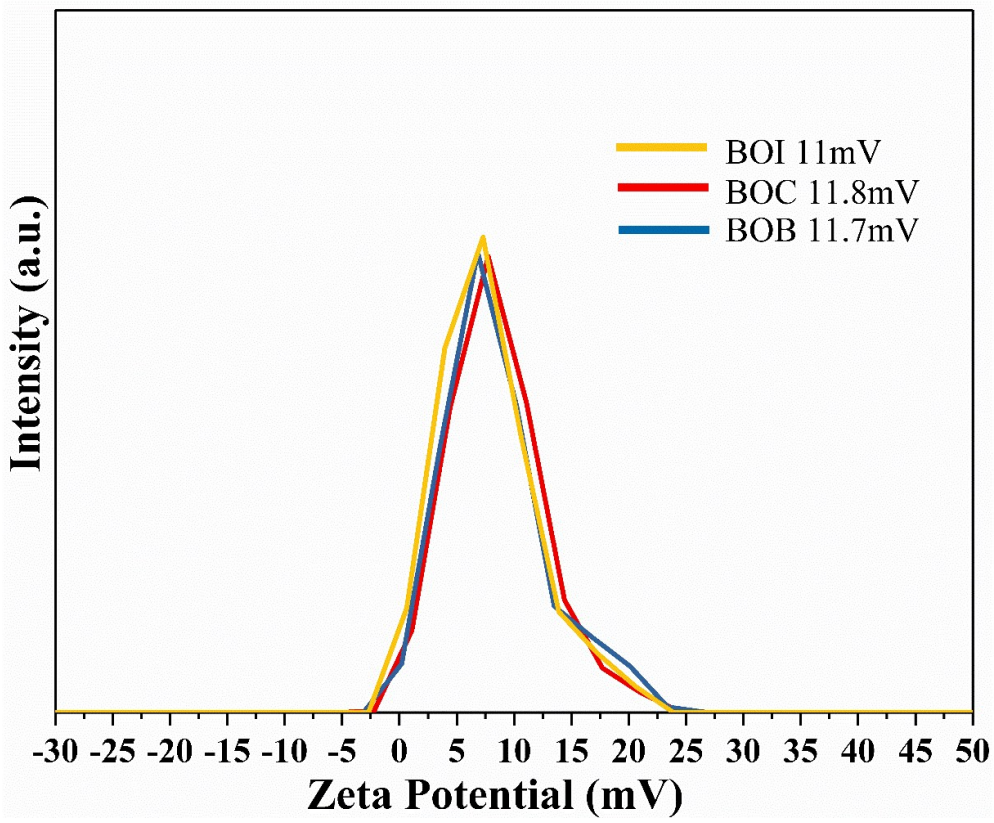

Fig. S26 The Zeta potential of BOC, BOB and BOI.

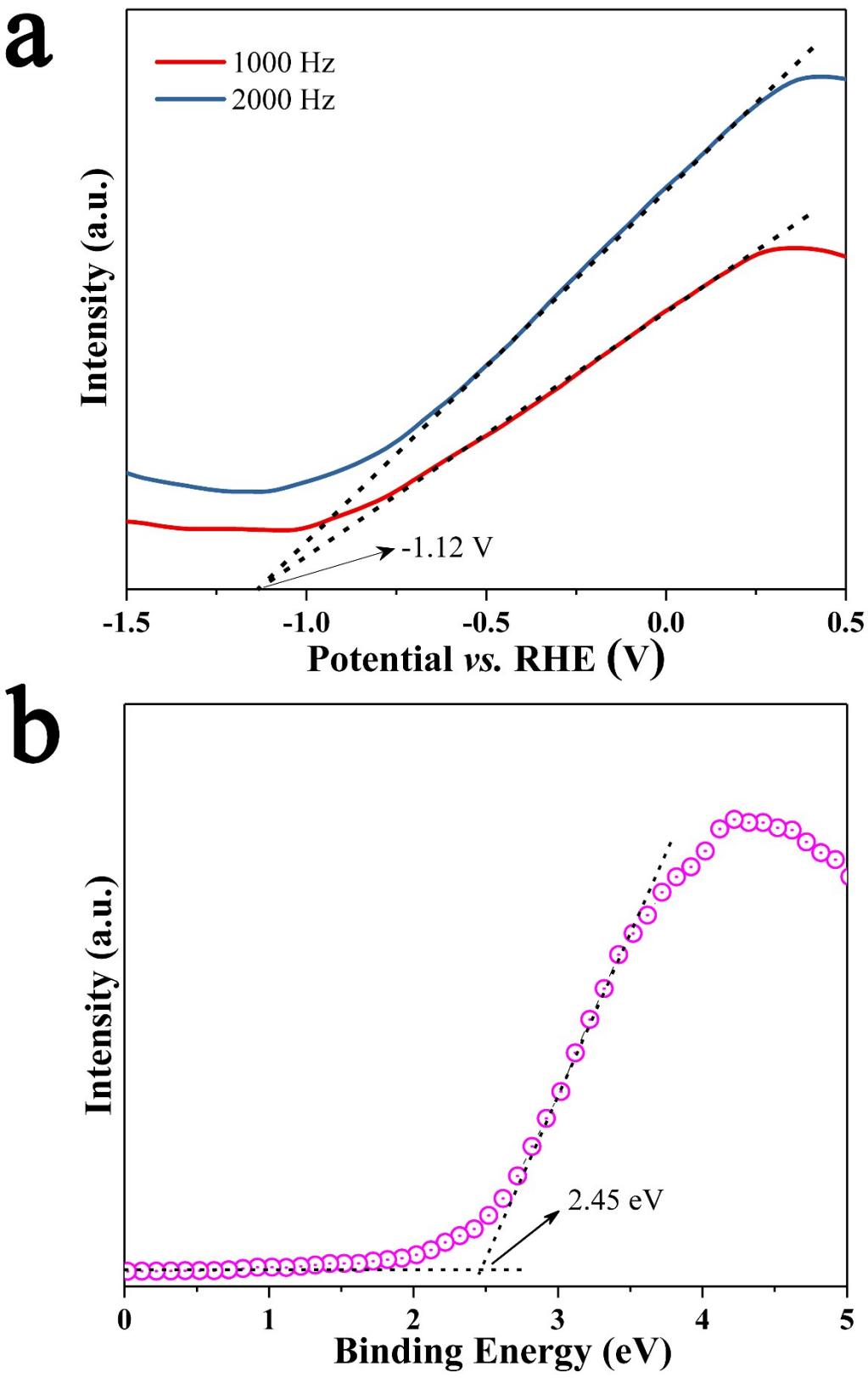

Fig. S27 The (a) Mott-Schottky plots in 0.5 M Na_2SO_4 aqueous solution and (b) Valence-band XPS spectrum of BOC.

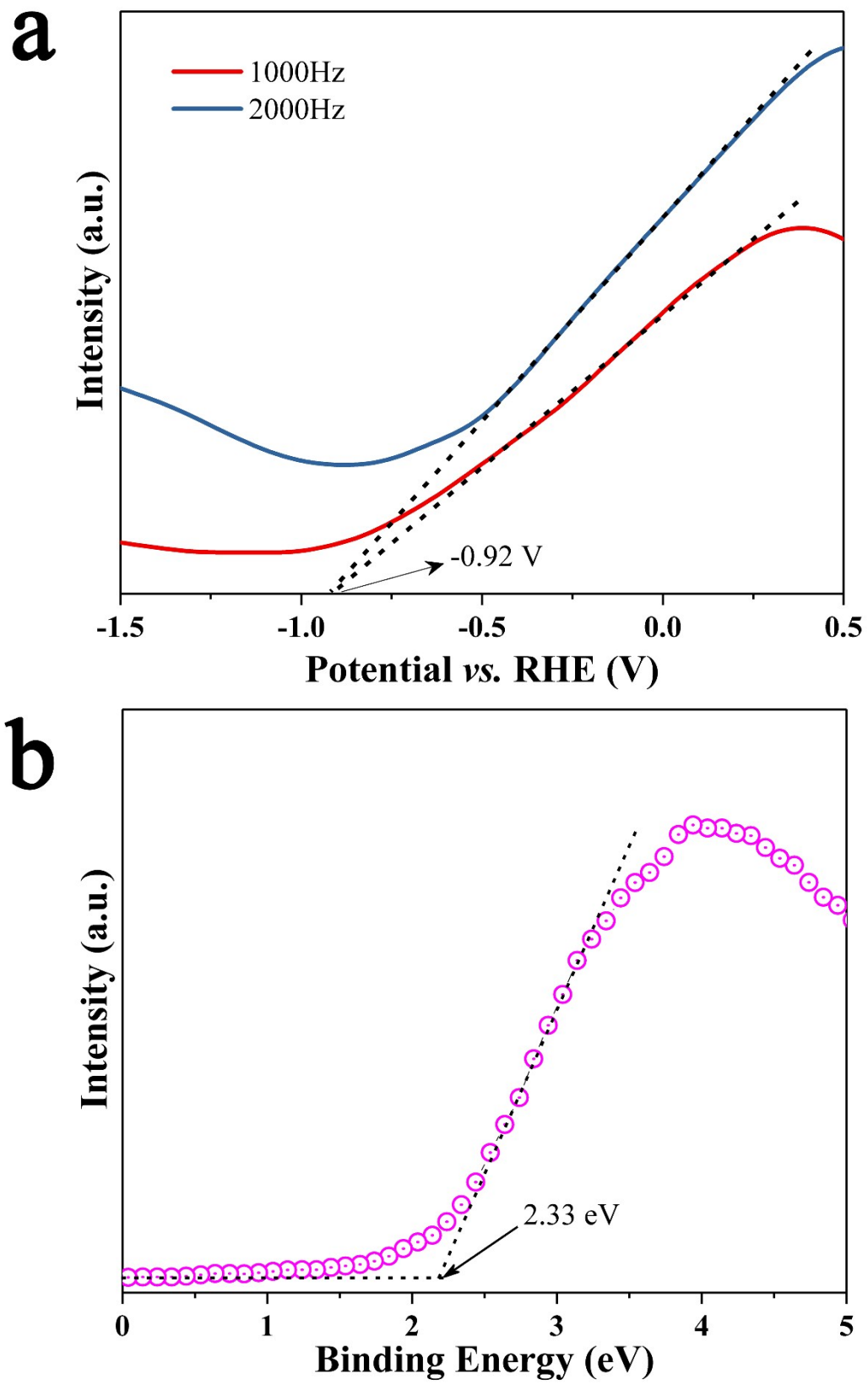

Fig. S28 The (a) Mott-Schottky plots in 0.5 M Na_2SO_4 aqueous solution and (b) Valence-band XPS spectrum of BOB.

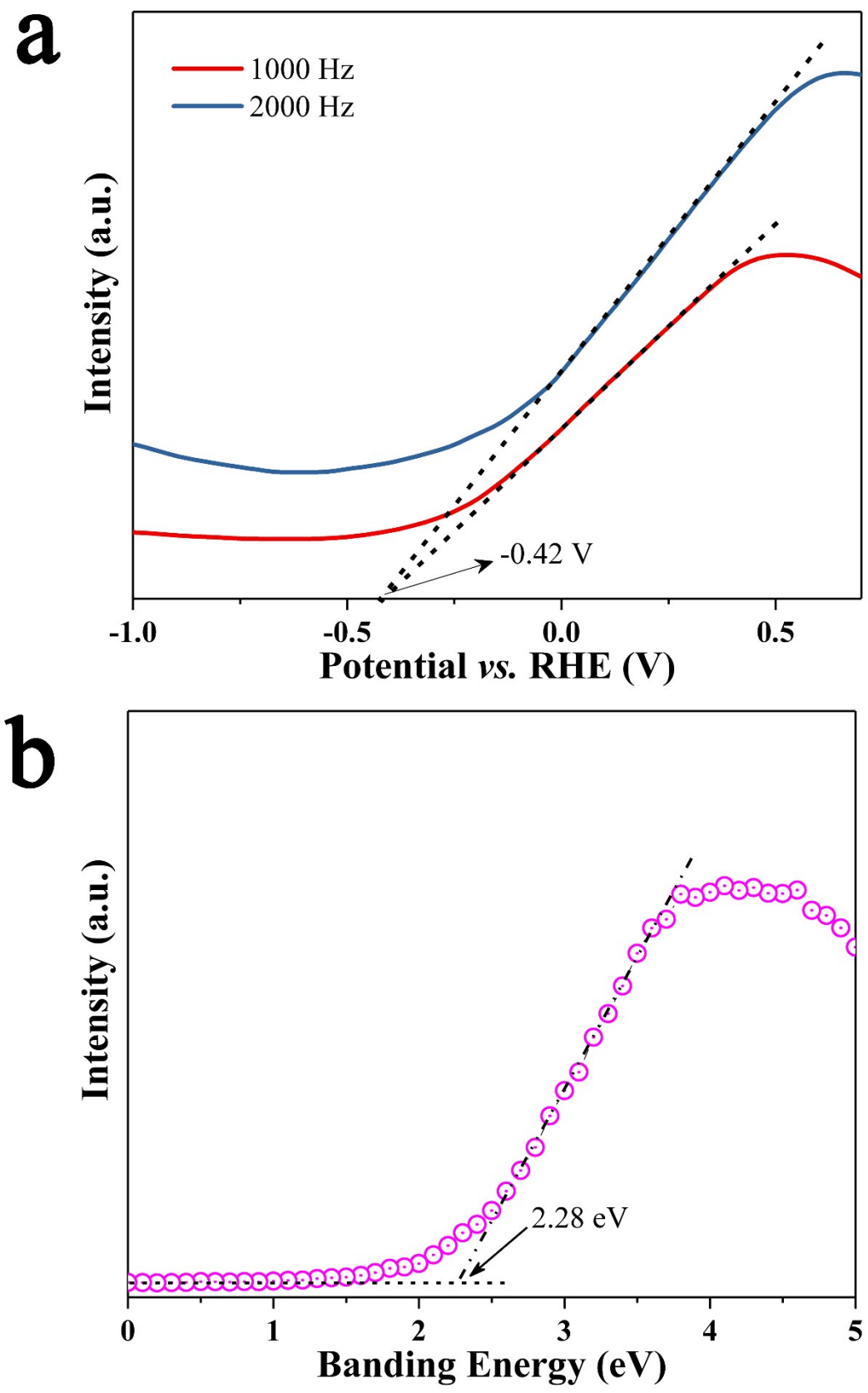

Fig. S29 The (a) Mott-Schottky plots in 0.5 M Na_2SO_4 aqueous solution and (b) Valence-band XPS spectrum of BOI.

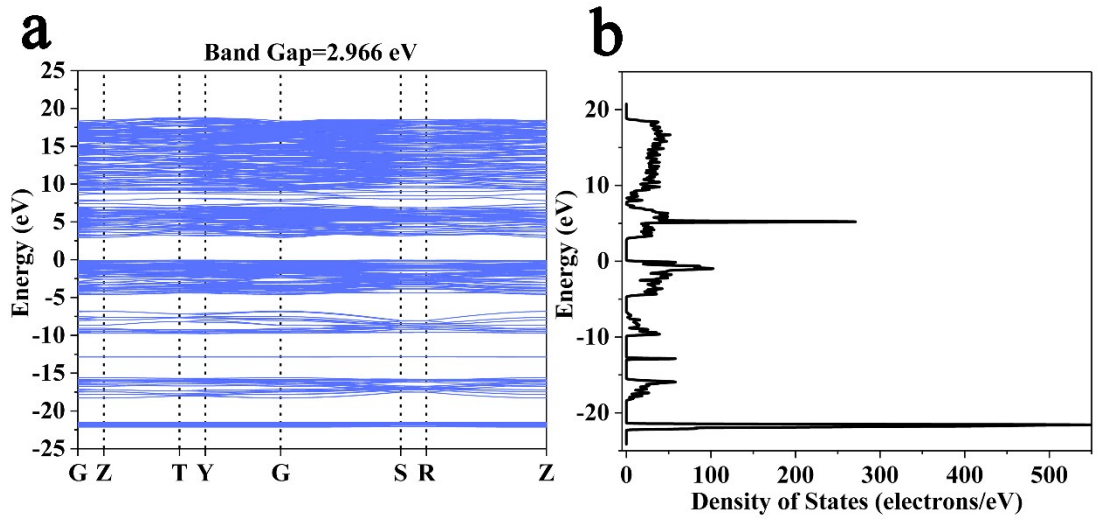

Figure S30. (a) The calculated energy band and (b) the total DOS of Bi_5O_7Cl.

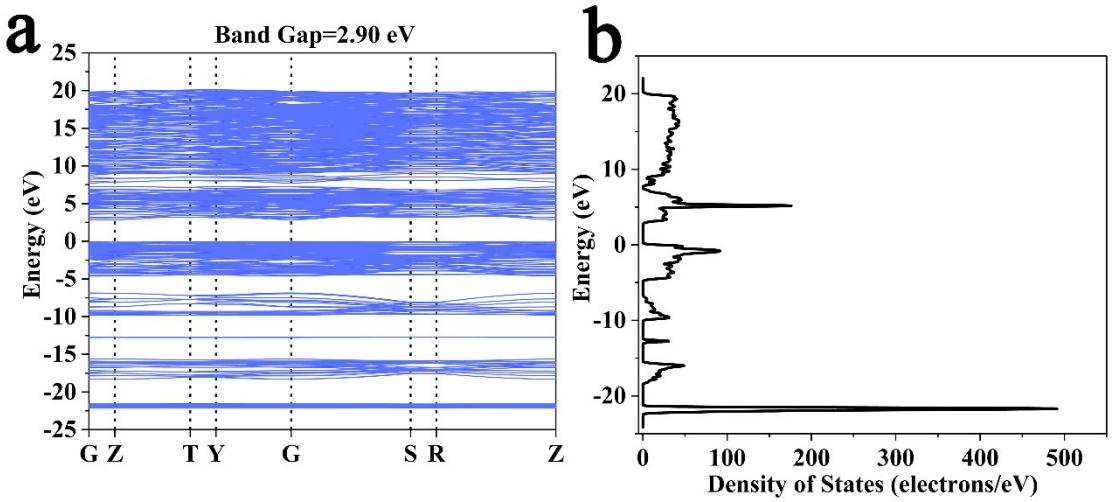

Fig. S31 (a) The calculated energy band and (b) the total DOS of Bi_5O_7Br.

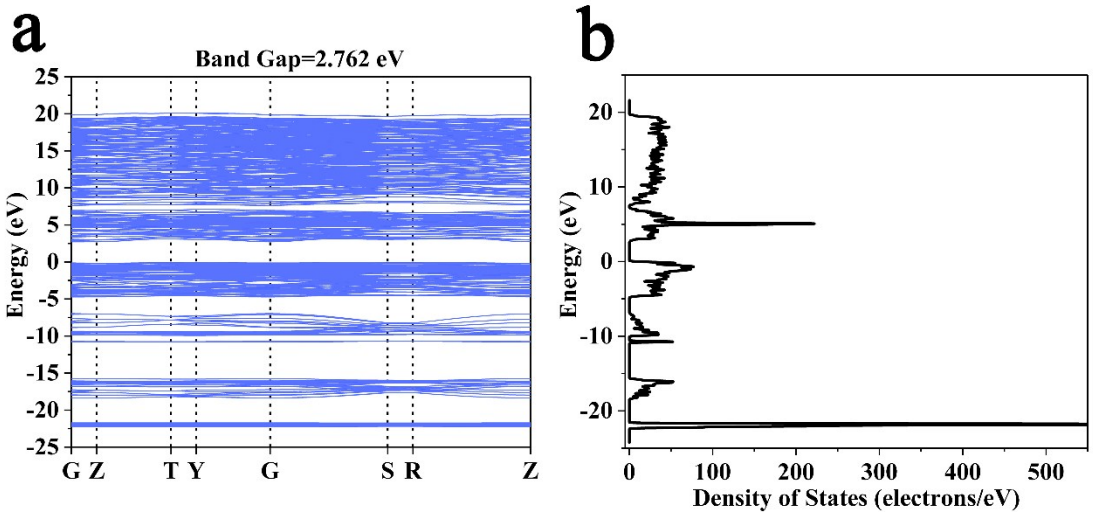

Fig S32 (a) The calculated energy band and (b) the total DOS of Bi_5O_7I.

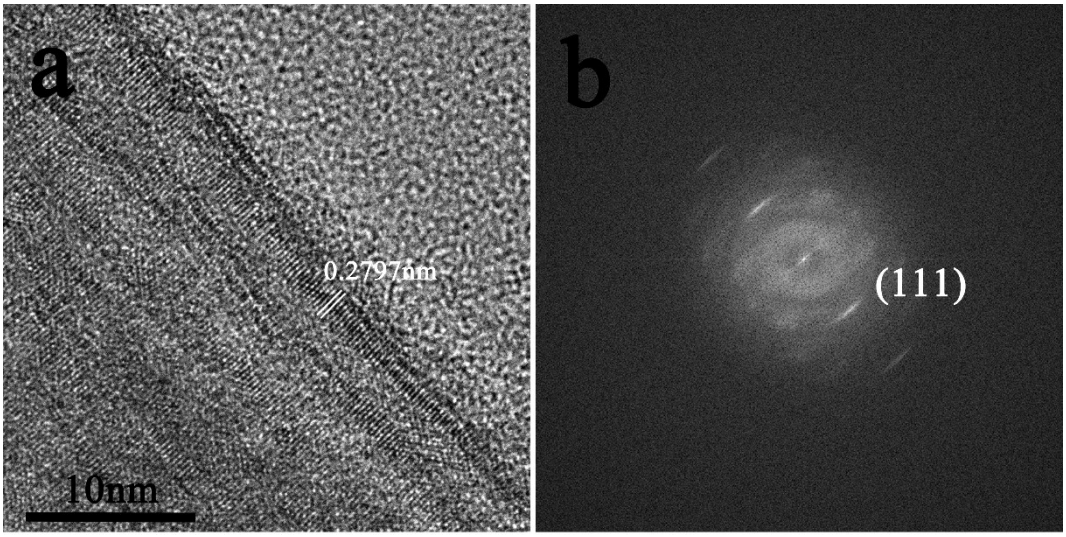

Figure S33 TEM (a) and FFT (b) images of BOI with photoreduction.

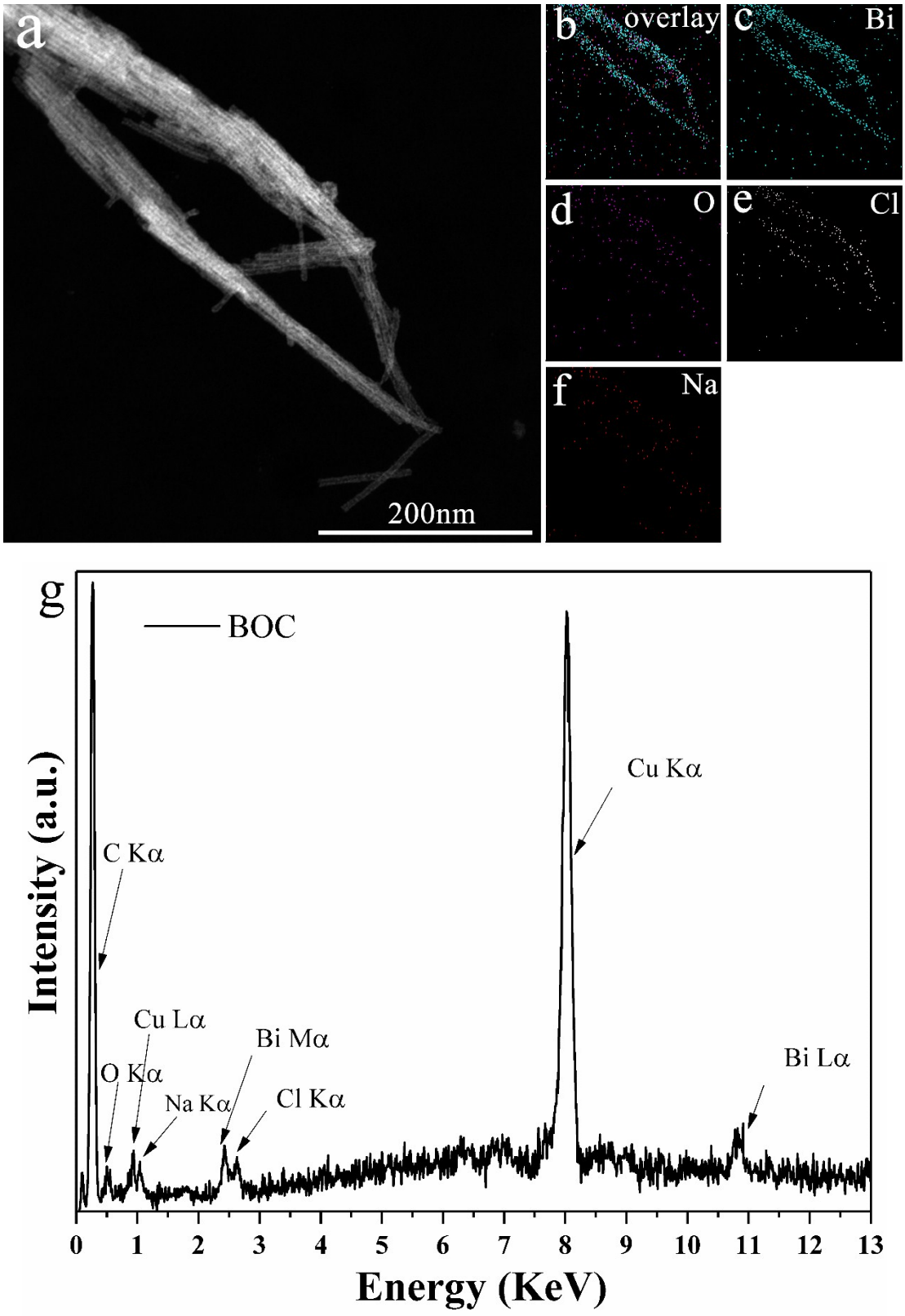

Fig. S34 The (a-f) element mapping and (g) EDX of BOC.

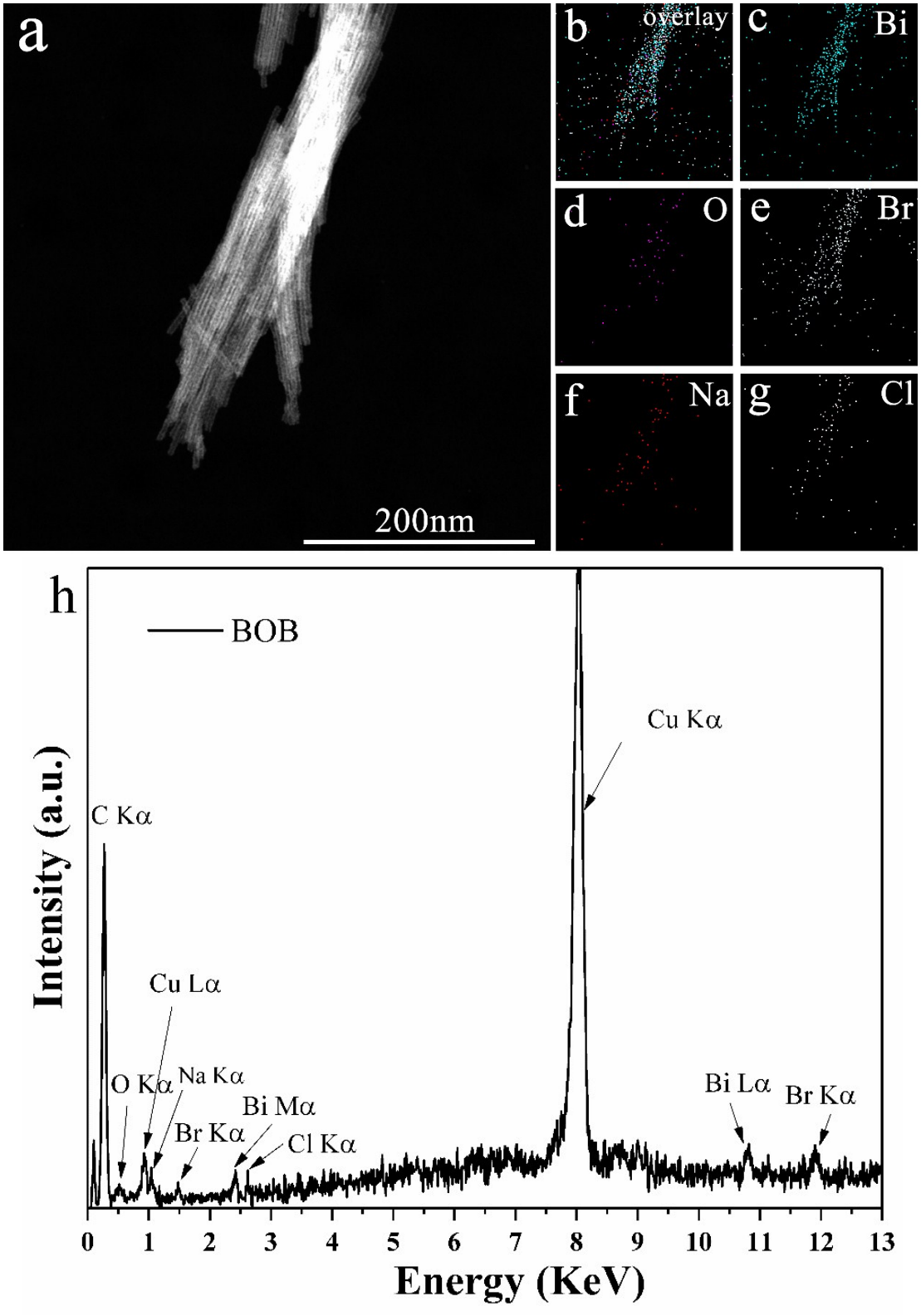

Fig. S35 The (a-f) element mapping and (g) EDX of BOB.

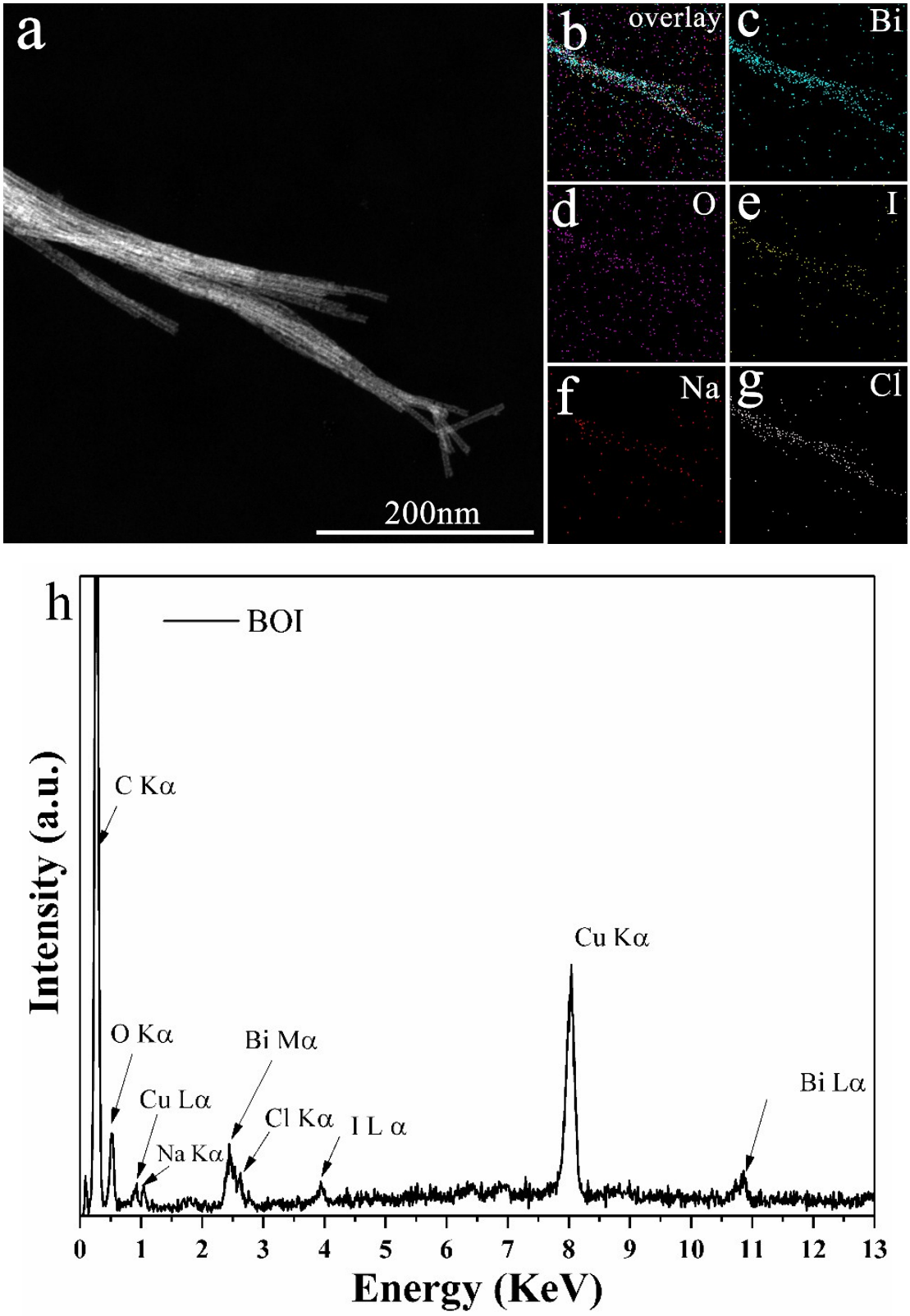

Fig. S36 The (a-f) element mapping and (g) EDX of BOI.

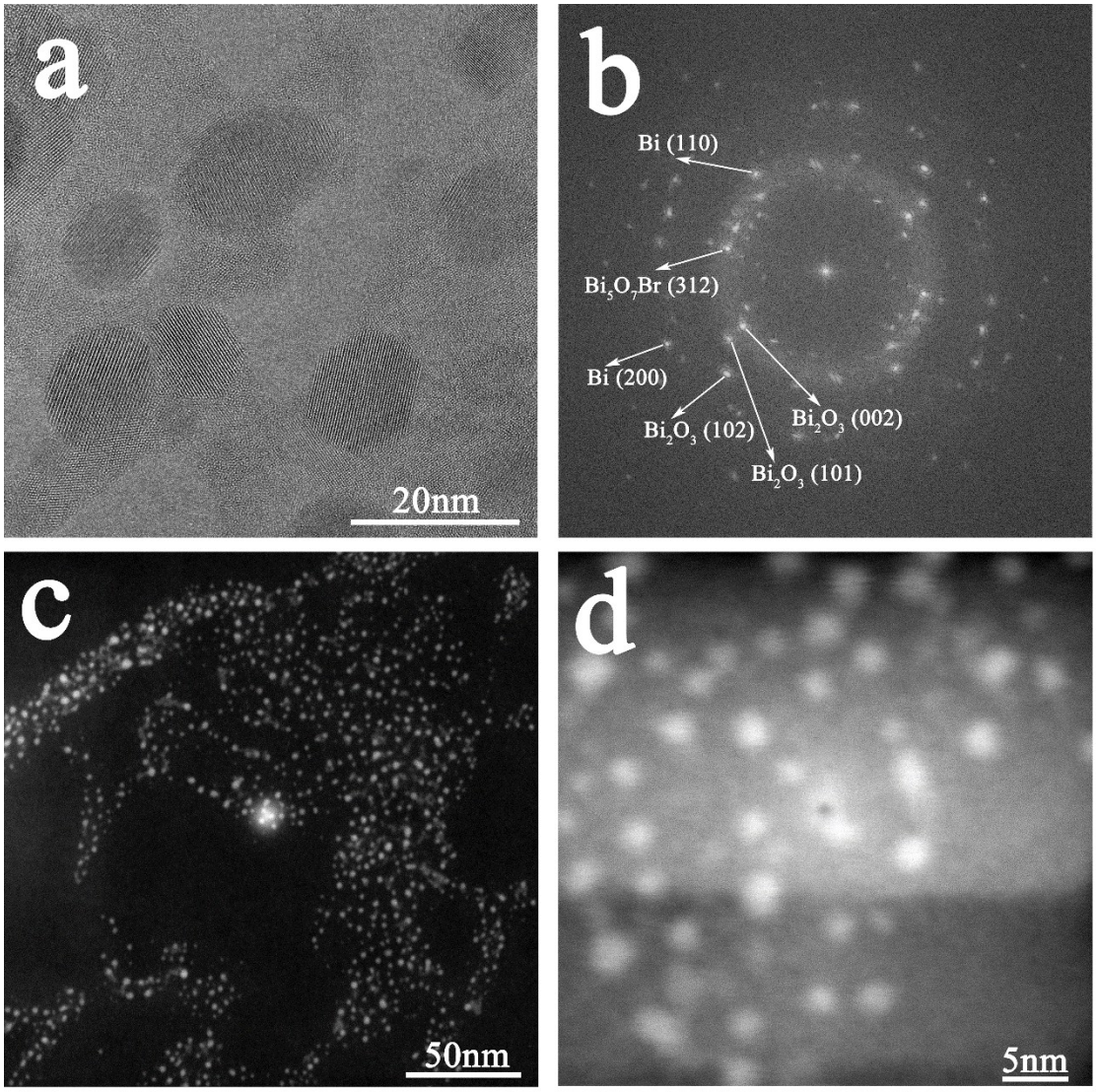

Fig. S37 (a) The high-resolution TEM, (b) Fast Fourier Transform (FFT) and (c,d) HAADF-TEM images of BOC after 7 cycles under light condition.

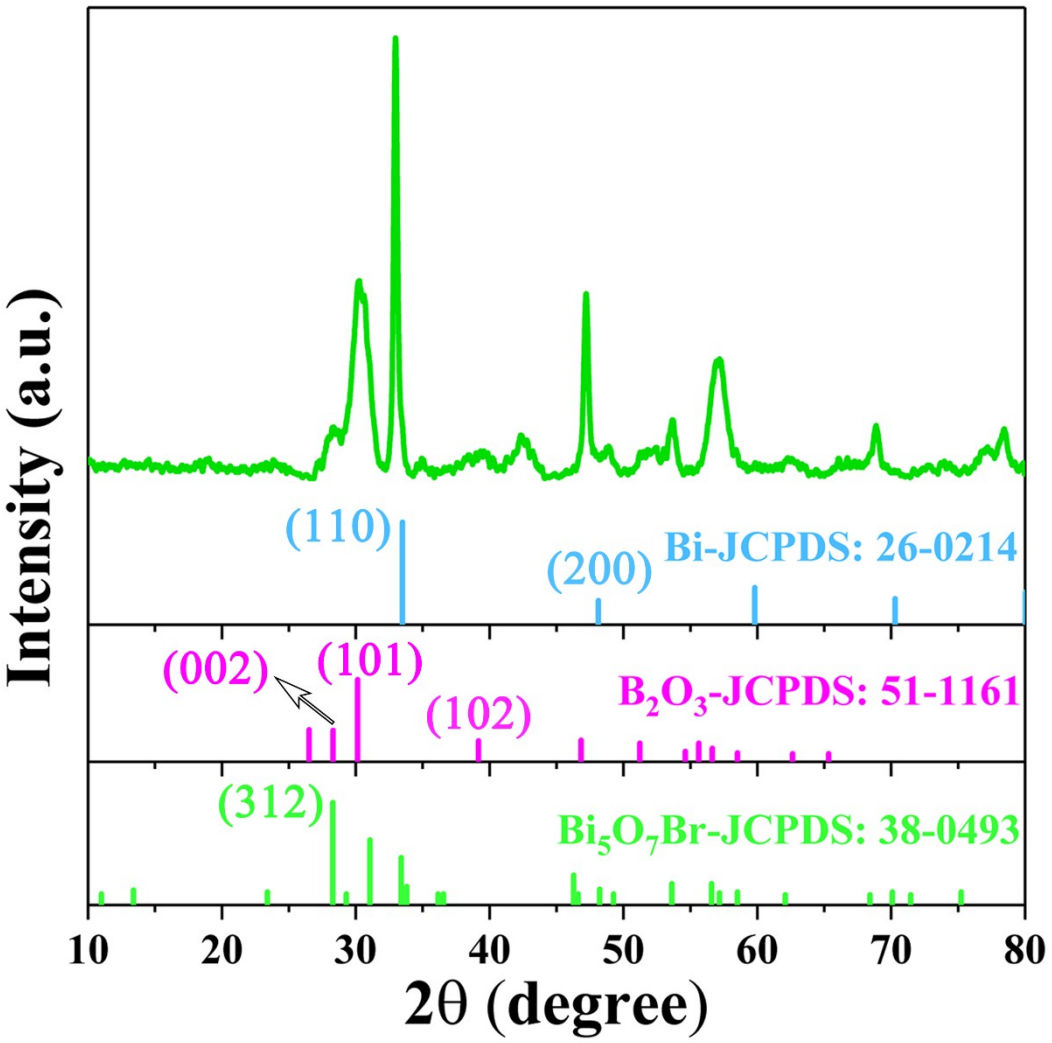

Fig. S38 The XRD pattern of BOC after 7 cycles under light condition.

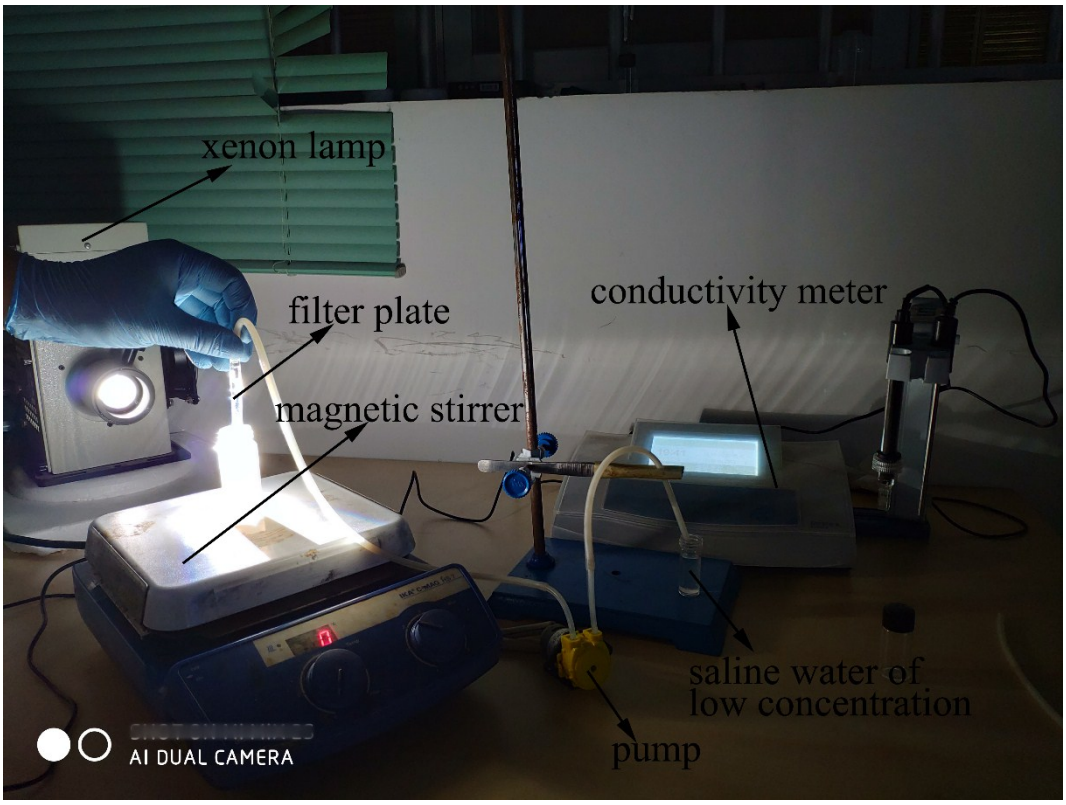

Fig. S39 The presentation images of the actual measurement.