

Supporting information

Construction of type-II BiVO₄/BiOI heterojunction for efficient photoelectrocatalytic degradation of β-naphthol and coal gasification wastewater under visible-light irradiation

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2. Experimental

2.1 Materials and reagents

β -naphthol, Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), dimethyl sulfoxide (DMSO), vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$) and p-benzoquinone were bought from Shanghai Macklin Biochemical Co., Ltd. Sodium sulfate anhydrous (Na_2SO_4), sodium hydroxide (NaOH) and potassium iodide (KI) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. All these chemical reagents were of analytic grade and used without any further purification. Fluorine-doped tin oxide (FTO) conductive glass ($14 \Omega \text{ cm}^{-1}$, $50 \times 50 \times 2.2 \text{ nm}$) were obtained from Wuhan Jinge-solar Energy Technology Co., Ltd. Ultrapure water was employed throughout the experiment.

2.2 Synthesis of $\text{BiVO}_4/\text{BiOI}$ photoanode

The $\text{BiVO}_4/\text{BiOI}$ (BVOI) electrode was prepared by two-step electrodeposition approach. Firstly, the BiVO_4 was synthesized onto the FTO substrate by the electrodeposition-annealing approach reported in our previous report ^[1]. KI was dissolved in deionized water to prepare 100 mL of 0.4 M KI solution and the pH was adjusted to 1.7 by adding HNO_3 dropwise. Secondly, a certain amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was added into the above KI solution to obtain the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution with the concentration of 0.4 M. A 0.2 M p-benzoquinone solution of 40 mL was synthesized by dissolving p-benzoquinone in absolute ethanol, then the two solution was mixed and stirred for 5 min before electrodeposition. Afterwards, the electrodeposition was performed in a three-electrode system at -0.15 V for 5 min to obtain the BiOI nanosheet with BiVO_4 , Pt foil and SCE as the working electrode,

counter electrode and reference electrode, respectively. Finally, the electrode was washed by deionized water and dried in air, which was named as BVOI electrode. BiVO₄/BiOI electrodes with different amounts of BiOI deposition were prepared by controlling the electrodeposition time of the second step (150 s, 300 s and 450 s), which were named BVOI-150, BVOI-300 and BVOI-450 electrodes, respectively.

2.3 Characterization

The structure and morphology of BVO, BOI and BVOI electrodes were investigated using an ULTRA 55 scanning electron microscope (SEM, ZEISS, Germany) and energy dispersive spectrometer (EDS). The X-ray diffraction (XRD) patterns were performed by a D8 Advance X-ray diffractometer (Bruker, Germany) equipped a Cu K α radiation source ($\lambda=0.15418$ nm) at a scanning rate of 5° min⁻¹. UV-vis DRS of the as-synthesized composites were obtained using UV-vis spectrophotometer (SHIMADZU, UV-3600PLUS, Japan). The TOC content was measured by TOC analyzer (Elenmentar, 39191013, Germany), and the measurement range was 0-25 mg L⁻¹ to 0-250 mg L⁻¹, the reproducibility was within the range of $\pm 2\%$, and the measurement period was 4 min. The organic components of coal gasification wastewater were qualitatively analyzed by the 7890B-5975C gas chromatography-mass spectrometry (GC-MS) produced by Agilent Company USA, and the HP-5MS capillary column was used as the chromatographic column with a flow rate of 1.0 mL min⁻¹. The elemental analysis of samples was determined by X-ray photoelectron spectra (XPS) on a VG Escalab 250 spectrometer (Thermo Scientific, USA). The reactive species were determined by Electron paramagnetic resonance

(EPR) spectra with a BrukerA300 EPR spectrometer, during which 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was employed as a spin trap in the detection of radicals, and 10 mg of catalyst powder was dispersed in 5 mL methanol and ultrasound, then 100 μ L DMPO solution (100 mM) was added into the above 200 μ L mixed solution and put in the capillary of EPR spectra.

2.4 Photoelectrochemical performance of electrodes

The photoelectrochemical properties of as-synthesized electrodes were investigated by the electrochemical workstation (CHI760E, Shanghai Chenhua Co., Ltd) under visible light irradiation supplied by 300 W high uniformly integrated xenon light source (PLS-FX300HU, Beijing Perfetlight Co., Ltd) with a cutoff filter ($\lambda > 420$ nm) in three-electrode system equipped with an Ag/AgCl (saturated KCl) as the reference electrode, a Pt foil as the counter electrode and as-prepared BVOI samples as the working electrode. The transient photocurrent measurement was performed in a 0.1 M Na₂SO₄ solution as the electrolyte and recorded by I-T curves with a bias voltage of 0 and 2 V for 400 s. The linear sweep voltammetry (LSV) measurements were investigated by applying an increasing potential from 0 to 2.8 V at a sweep rate of 10 mV s⁻¹. Moreover, electrochemical impedance spectroscopy (EIS) tests were performed at open circuit potential over a frequency range from 0.01 to 100000 Hz, and the EIS Nyquist plot was fitted by the ZView analysis software. In addition, the Mott-Schottky measurement of the as-prepared electrodes was performed in a 0.1 mol·L⁻¹ Na₂SO₄ solution and recorded by a $1/C^2$ - V plot.

2.5 Photoelectrocatalytic degradation of β -naphthol

The photoelectrocatalytic (PEC) degradation of β -naphthol was also performed in the above three-electrode system with 0.1 M Na_2SO_4 solution as electrolyte. And the as-prepared BVOI electrode was employed as the working electrode with an active area of 4 cm^2 , the Pt foil and Ag/AgCl were used as the counter electrode and reference electrode, respectively. 300 mL of 10 mg L^{-1} of β -naphthol solution was employed as the pollutant in all degradation experiments, and the pH was adjusted by 0.1 M NaOH and 0.1 M H_2SO_4 . The concentration of β -naphthol at different time intervals was determined using UV-Vis spectrophotometry approach with 224 nm of the measuring wavelength. The degradation rate was calculated by the following equation:

$$\text{Degradation rate} = \frac{C_0 - C_t}{C_0} * 100\% \quad (1)$$

where C_0 and C_t (mg L^{-1}) are the concentration of β -naphthol at initial time and sampling time, respectively. All experiments were repeated twice to ensure the reproducibility.

2.6 Purification of coal gasification wastewater (CGW)

300 mL of coal gasification wastewater was selected as the target contaminant adding Na_2SO_4 as the electrolyte. And the as-synthesized BVOI-300 electrode was employed as the working electrode with an active area of 4 cm^2 , the Pt foil and Ag/AgCl were used as the counter electrode and reference electrode, respectively. The total organic carbon (TOC) content of 2 mL solution was measured by TOC analyzer every 1 h, and the organic components of CGW were detected by GC-MS analyzer. The removal rate of CGW was calculated by the following equation:

$$\text{Removal rate} = \frac{T_0 - T_t}{T_0} * 100\% \quad (2)$$

where T_0 and T_t (mg g^{-1}) are the TOC content of CGW at initial time and sampling time, respectively.

2.7 Radical capture experiments

The radical capture experiments were conducted for the β -naphthol degradation test over BVOI-300 photoanode. Before photoelectrocatalytic degradation, sacrificial agents, such as 10 mmol methanol (MeOH), 10 mmol isopropanol (IPA) and 1 mmol p-benzoquinone (BQ), were dispersed in the β -naphthol solution to probe the presence of holes (h^+), hydroxyl radicals (HO^\bullet) and superoxide radicals ($O_2^{\bullet-}$), respectively.

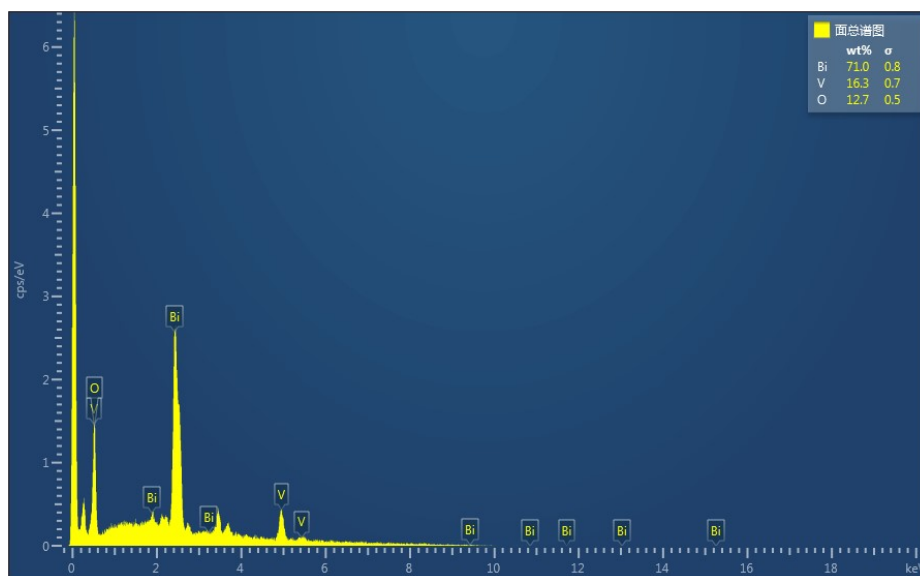
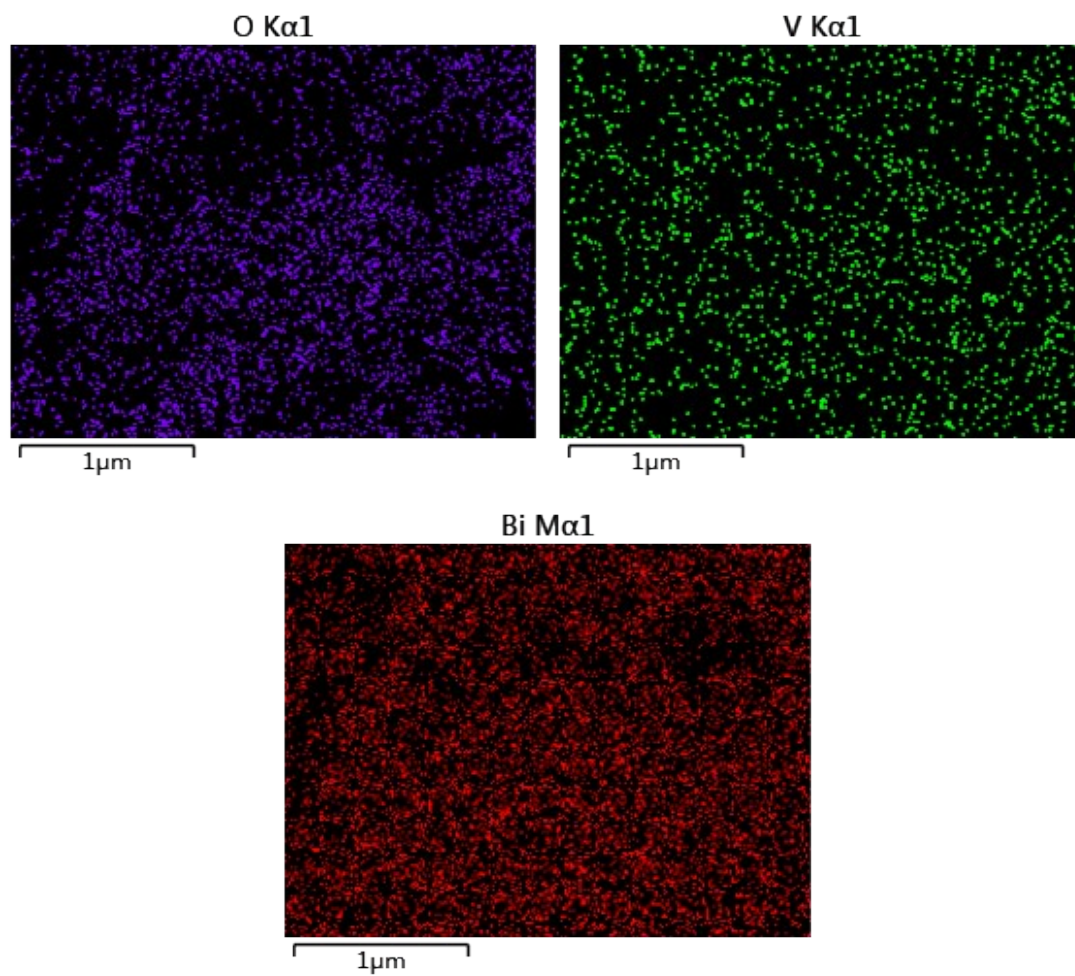


Figure S1. Elemental mappings and energy dispersive spectrum (EDS) of BiVO_4

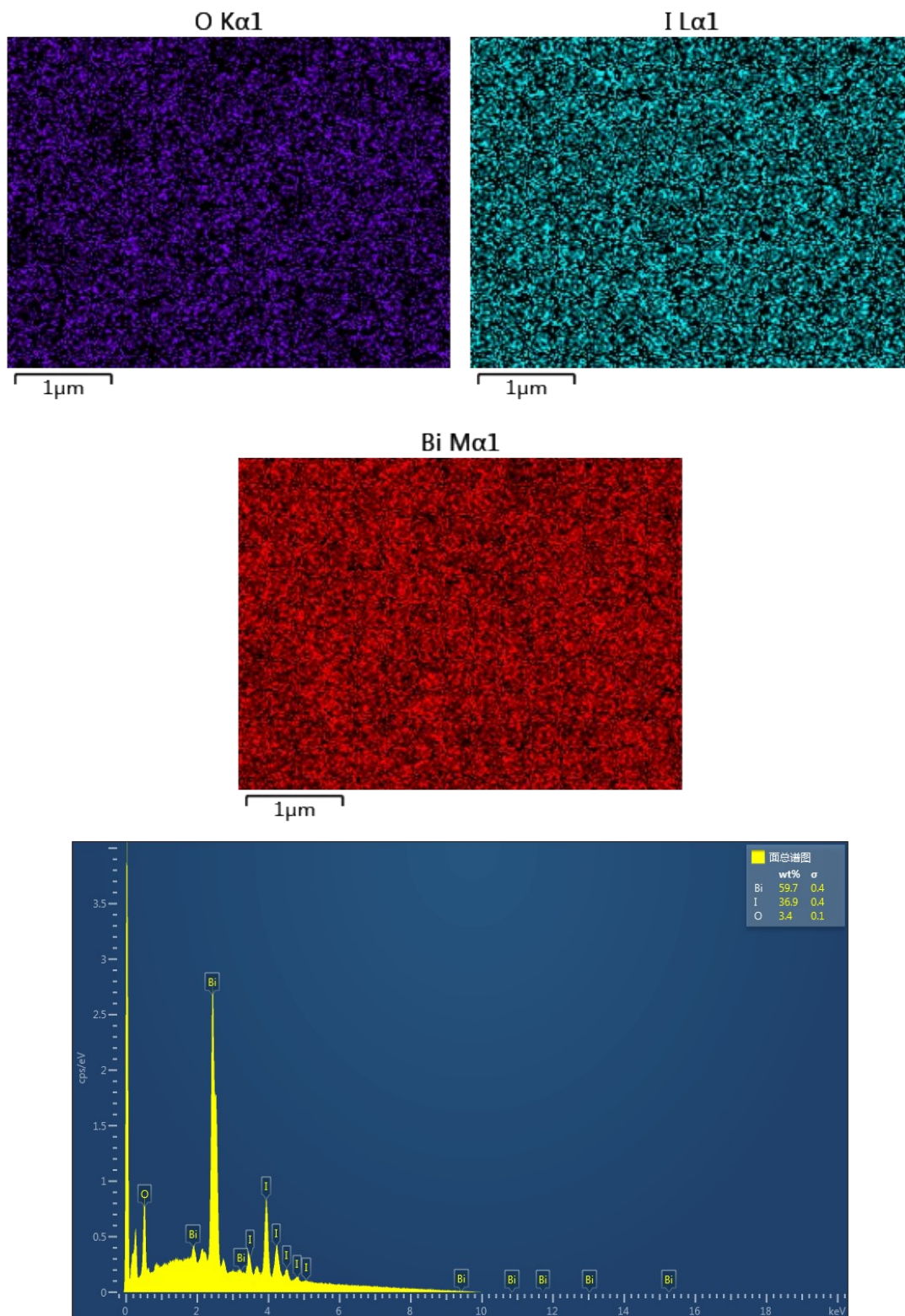


Figure S2. Elemental mappings and energy dispersive spectrum (EDS) of BiOI

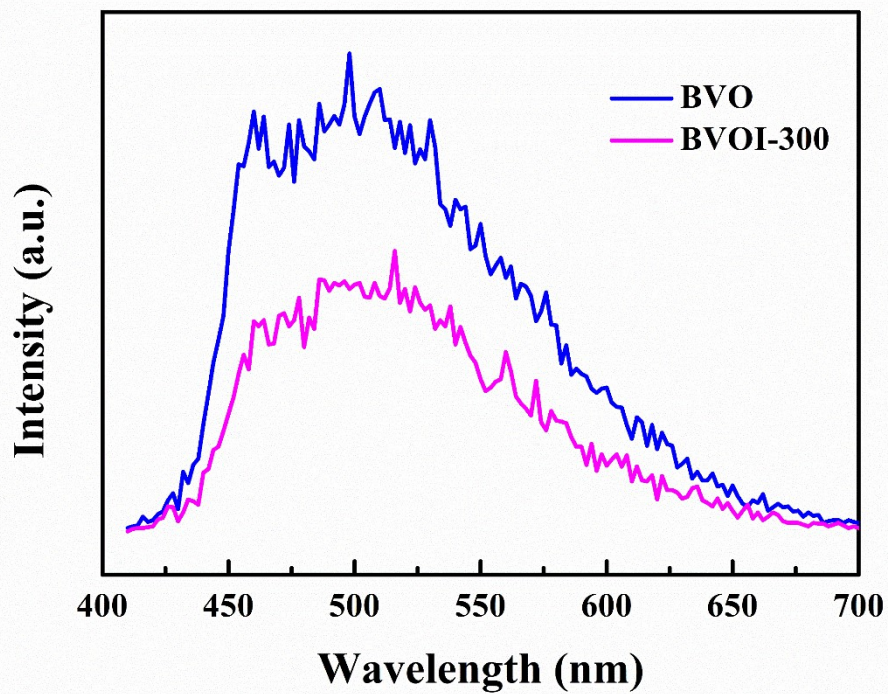


Figure S3. PL spectra of BVO and BVOI-300

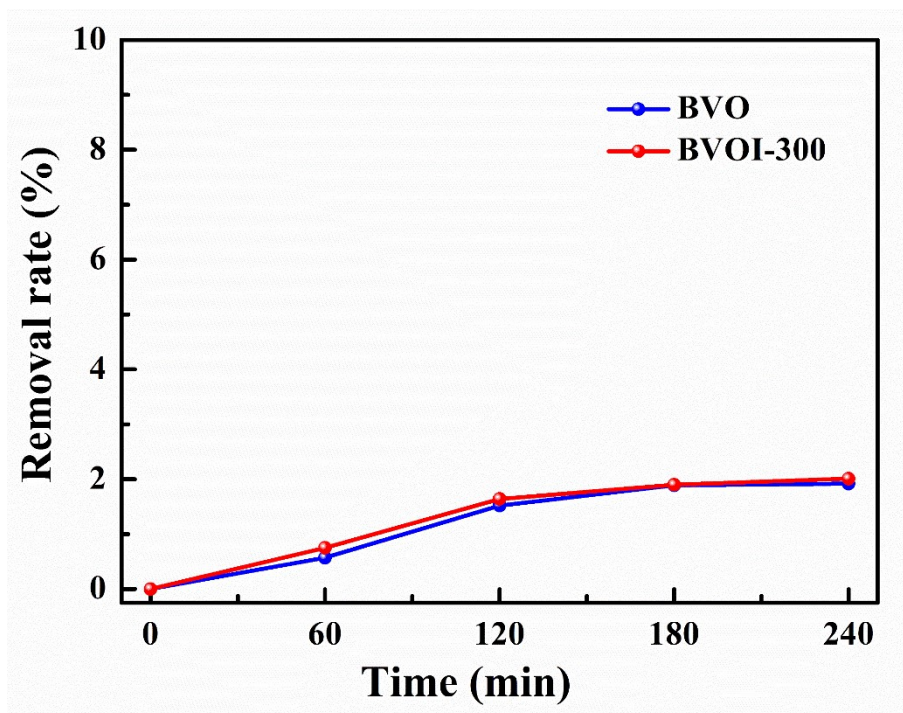


Figure S4. The adsorption properties of BVO and BVOI-300 for β -naphthol under dark condition

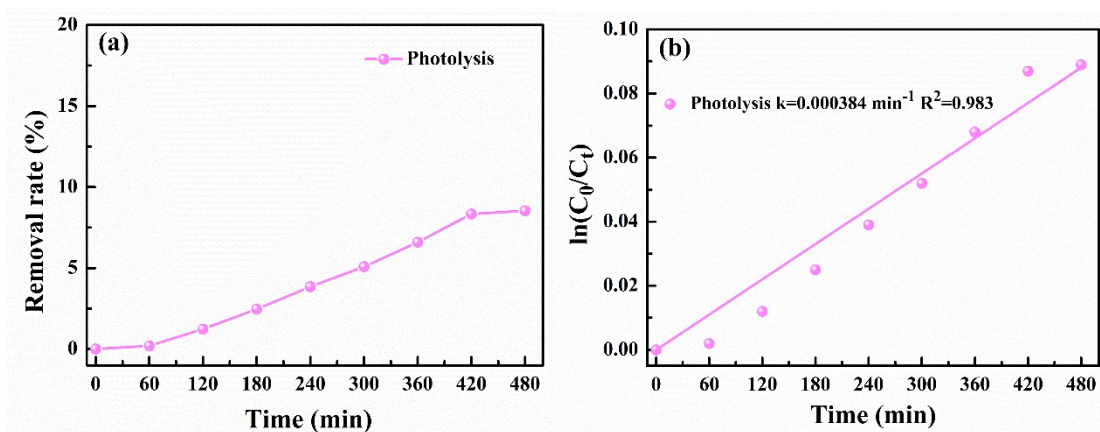


Figure S5. (a) the degradation of β -naphthol in photolysis system and (b) the relevant kinetic fitting curves

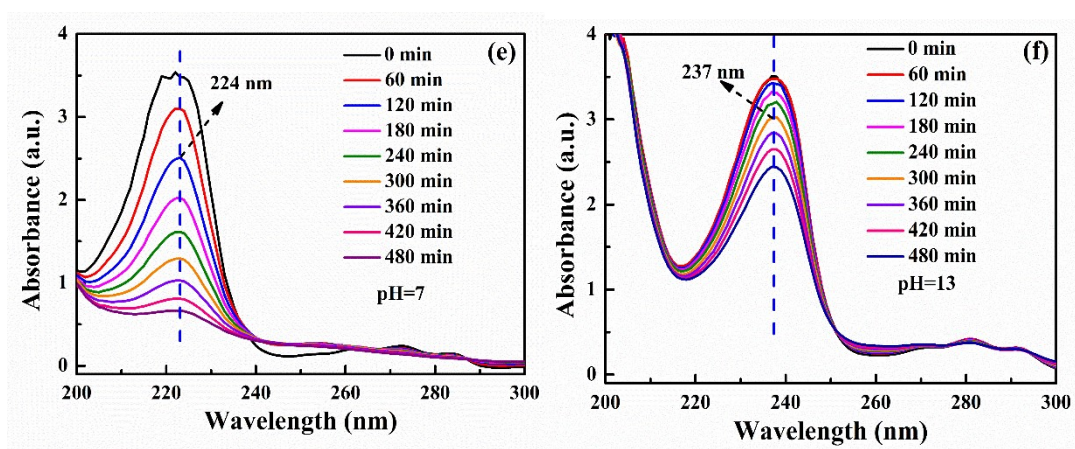


Figure S6. The UV-Vis adsorption spectra of β -naphthol during the PEC degradation process by BVOI-300 photoanode at (a) pH=7 and (b) pH=13

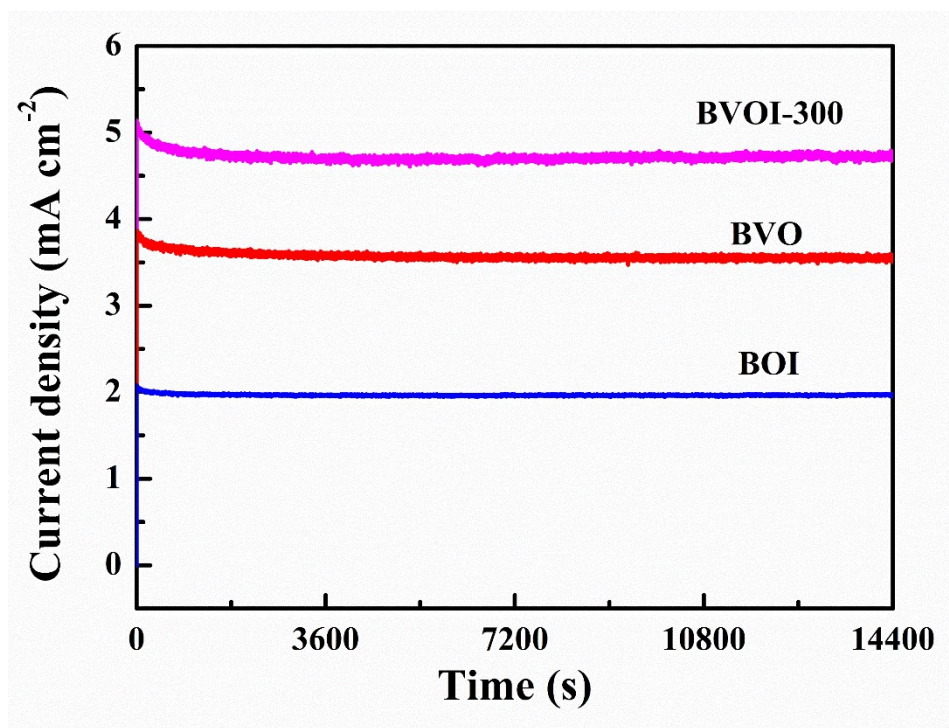


Figure S7. The I-T curves of BVO, BOI and BVOI-300 photoanodes during PEC β -naphthol process

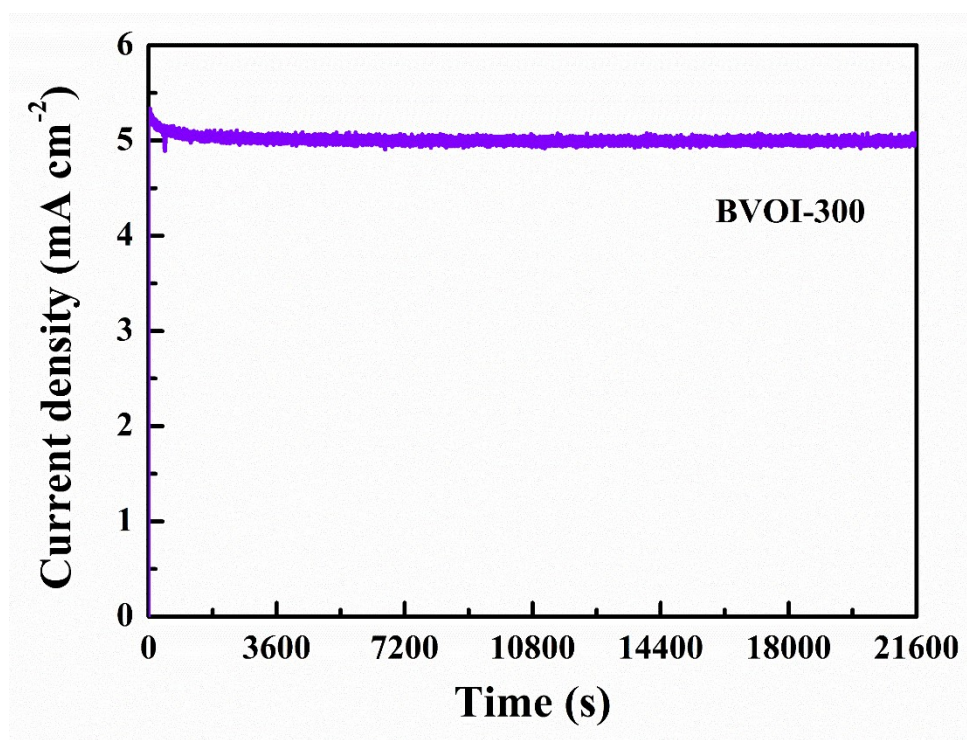


Figure S8. The I-T curves of BVOI-300 photoanodes during PEC coal gasification wastewater process

References

- [1] H. Fan, G. Yi, Z. Zhang, X. Zhang, P. Li, C. Zhang, L. Chen, Y. Zhang, Q. Sun, Fabrication of Ag particles deposited BiVO₄ photoanode for significantly efficient visible-light driven photoelectrocatalytic degradation of β -naphthol. *J. Environ. Chem. Eng.* 2022, **10**, 107221.