

SUPPORTING INFORMATION

The Synergistic Effect of Bi₂WO₆ Nanoplates and Co₃O₄ Cocatalyst for Enhanced Photoelectrochemical Properties

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Materials and Instruments

Potassium iodide (KI, $\geq 99.0\%$), Bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\geq 99.0\%$), Nitric acid (HNO_3 , 65.0-68.0%), Ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.7\%$), Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99.5\%$) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1,4-Benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$, $\geq 99.0\%$) was obtained from TianJin Guangfu Fine Chemical Research Institute. Ammonia solution (NH_3 , 25-28%) was obtained from Shanghai Zhongqin Chemical Reagent Co., Ltd. Cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\geq 99.5\%$) was purchased from Tianjin Kaixin Chemical Industry Co., Ltd. All the reagents were analytical grade and used without further purification. F-doped Tin Oxide (FTO) were purchased from Kunshan SunLaiTe New Energy Co., Ltd. FTO glass was ultrasonically cleaned for 20 min each in acetone, isopropanol, ethanol and deionized water, and then soaked in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (3:1, volum ratio) solution for 5h to make the surface uniformly hydrophilic.

The X-ray diffraction spectra (XRD) were characterized by Rigaku RINT-2000 instrument using $\text{Cu K}\alpha$ radiation (40 KV). The XRD patterns were recorded from 20° to 80° with a scanning speed of $0.1393^\circ/\text{s}$. Scanning electron microscopy (SEM) images were taken using a field-emission scanning electron microscope (JEOL-JSM6701F, Japan) with an accelerating voltage of 5 kV. Transmission electron microscope (TEM) measurements were performed on an FEI Tecnai TF20 microscope operated at 200 kV. The UV-vis diffuse reflectance spectra were carried out with a UV-2550 (Shimadzu) spectrometer. Raman spectra were detected by Raman Microscopes (LabRAM HR Evolution). X-ray photoelectron spectroscopy (XPS) was performed by an ESCALAB 250Xi photoelectron spectrometer utilizing X-ray monocheomatisation as the excitation source.

Preparation of BiOI nanoplates on FTO

BiOI nanosheets on FTO was prepared by cathodic deposition method reported in the literature.¹ In brief, a Bi-based solution was prepared by dissolving 0.98g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 50 mL of a 0.4 M KI solution after its pH was adjusted to 1.7 by adding HNO_3 . This solution was added into 20 mL of ethanol containing 0.23M 1,4-Benzoquinone, and was stirred for 30 min. The electrodeposition process was carried out in a typical three-electrode cell. A FTO ($1 \times 3 \text{ cm}^2$) working electrode, a Pt foil ($2 \times 2 \text{ cm}^2$) counter electrode, and a saturated Ag/AgCl (4M KCl) reference electrode were used. Cathodic deposition was performed potentiostatically at -0.1V vs. Ag/AgCl for a few minutes, which was equivalent to passing a total charge of 0.8 C.

Preparation of Bi_2WO_6 nanoplates photoanodes

The Bi_2WO_6 nanoplates photoanode were prepared by hydrothermal reaction. 30 mL W-based solution (120 mM $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) was added to a 50 mL Teflon-lined hydrothermal reactor. Whereafter, the as-prepared BiOI film was placed in the hydrothermal reactor and the reaction conducts for 3 h at 125°C . The reactor was cooled to the room temperature by ice-water bath, and then the resulting film (precursor Bi_2WO_6 nanoplates film, which was named pre-BWO) was collected and

washed with deionized water and dried with nitrogen. Subsequently, the Bi₂WO₆ film was calcined at 500, 550, 600, and 650 °C in the muffle furnace. The samples were named BWO-500, BWO-550, BWO-600, and BWO-650, respectively. The electrodes of BWO-600 were used for oxygen evolution co-catalysts modification.

Preparation of Co₃O₄/Bi₂WO₆ photoanodes

The Co₃O₄ nanoparticles were modified on Bi₂WO₆-600 electrodes by hydrothermal deposition method.² In brief, 5mM of Co(CH₃COO)₂·4H₂O was dissolved in 30 mL C₂H₅OH, followed by addition of 0.45~0.5 mL NH₃·H₂O (25%) under vigorous stirring. The as-prepared BWO-600 photoanodes was placed in a 50 mL autoclave, and then the Co-based solution was added into the autoclave. The hydrothermal reaction was conducted at 120 °C for 0.5h, 1h and 2h. After the reactor was cooled to the room temperature by ice-water bath, the electrodes were washed with deionized water and dried with N₂. The samples were named Co₃O₄/BWO-0.5h, Co₃O₄/BWO-600, and Co₃O₄/BWO-2h, respectively.

Preparation of Bi₂WO₆ particles photoanodes

The Bi₂WO₆ particles (BWO-particles) were prepared according to a method previously reported in the literature.³ Diethylenetriaminepentaacetic acid (10 mM) and NH₃·H₂O (3.75 mL) were added into 100mL hot DI water. After dissolution, the 5 mM Bi(NO₃)₃·5H₂O and 0.21 mM (NH₄)₁₀H₂(W₂O₇)₆ were added. The solution was stirred and heated at 90 °C until the solution became transparent. Then, the precursor solution (0.2 mL) was dripped onto the FTO and annealed at 500 °C for 2h.

Photoelectrochemical measurements

The photoelectrochemical properties were performed in an standard three-electrode system with a Pt foil (1.5cm×1.5cm) as the counter electrode, a saturated calomel electrode (SCE) as a reference electrode, and as-prepared samples were served as working electrodes with a surface area of 1cm², respectively. A 0.1M potassium phosphate buffer (pH=7.0) was used as the electrolyte. The optical-fibre light source (FX300, Beijing Perfect Light Technology Co., Ltd) was employed as illumination source to simulate sunlight, and the spectral range is between 350 nm to 800 nm. The light intensity was calibrated to 100 mW/cm² by Dual Channel Bench Power and Energy Meters Console (PM320E, THORLABS) equipped with Standard thermal power probe (S310C, THORLABS). The conversion between potentials versus SCE and versus Reversible Hydrogen Electrode (RHE) is performed using the equation below:

$$E_{\text{RHE}} = E_{\text{SCE (reference)}} + E_{\text{SCE}} + 0.0591 \times \text{pH}$$

$$E_{\text{SCE (reference)}} = 0.024\text{V vs. NHE at } 25\text{ }^{\circ}\text{C}$$

Where pH is a pH value of the electrolyte.

Linear sweep voltammograms (LSV) were measured with a scan rate of 10 mV/s. Amperometric i-t curves were tested at a bias voltage of 1.23 V (vs. RHE). The electrochemical impedance spectroscopy (EIS) measurements were characterized by

the CHI-660D workstation. EIS measurement were performed by applying 1.23 V (vs. RHE) at a frequency range from 0.01 Hz to 100 kHz with an amplitude of 5 mV under the light, and the measured spectra were fitted with ZSimpWin.

The incident photo to current efficiency (IPCE) was detected by a full solar simulator (Newport, Model 9600, 300W Xe arc lamp) equipped with a motorized monochromator (Oriel Cornerstone 130 1/8 m). IPCE values were measured at 1.23 V vs. RHE in 0.1 M potassium phosphate buffer using the same three-electrode system mentioned above for photocurrent density tests. IPCE was calculated by the following equation:

$$\text{IPCE (\%)} = (1240 \times I \text{ (mA/cm}^2\text{)}) / (P_{\text{light}} \text{ (mW/cm}^2\text{)} \times \lambda \text{ (nm)}) \times 100$$

Where I is the measured photocurrent density at a specific wavelength, λ is the wavelength of incident light and P_{light} is the measured light power density at that wavelength.

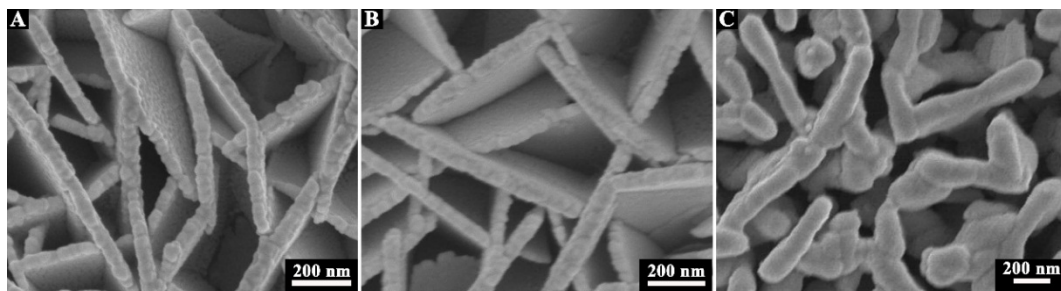


Figure S1: (A, B, and C) the high-magnification SEM images of BiOI, pre-BWO, and BWO-600.

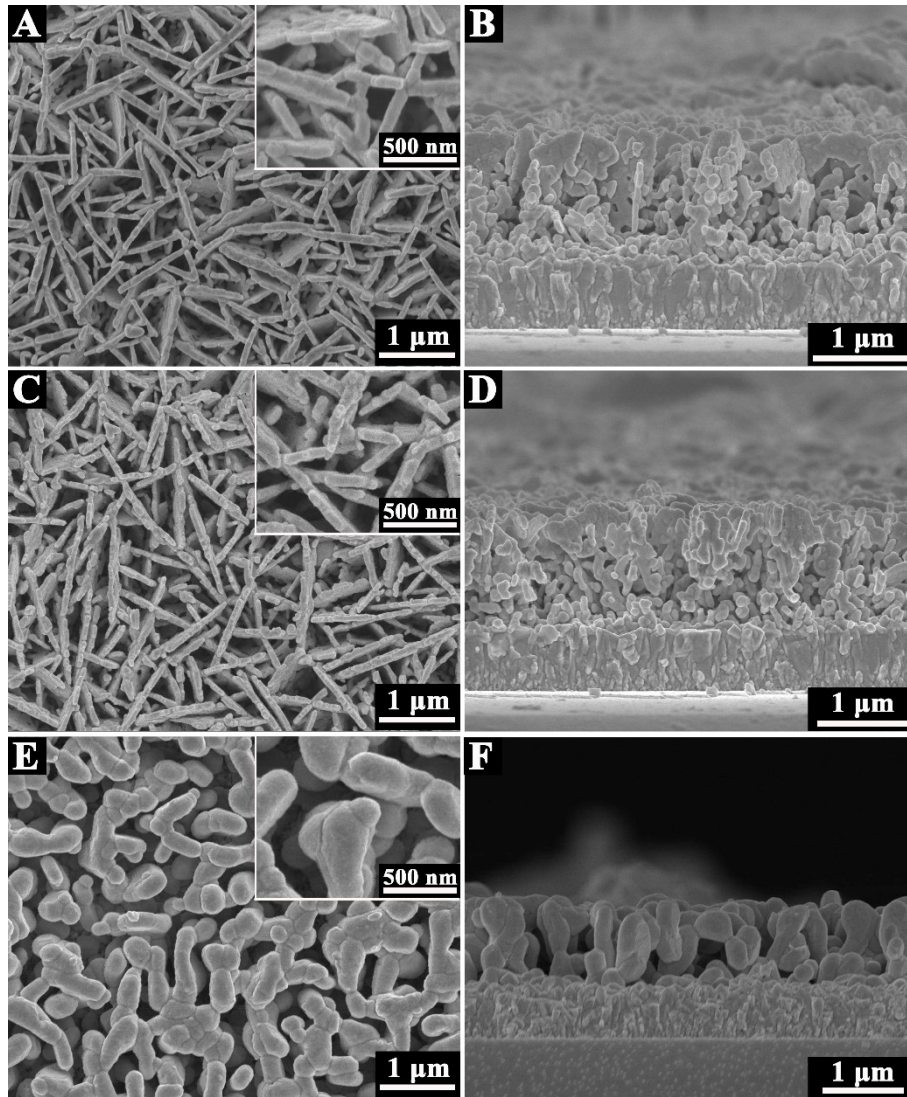


Figure S2: Top and the cross-section SEM images of BWO-500 (A and B), BWO-550 (C and D), BWO-650 (E and F). The inset of A, C, and E is the high-resolution SEM images for corresponding samples, respectively.

Results and discussions:

The typical scanning electron microscopy (SEM) images (Figure S2A-F) display the morphological characteristics of Bi_2WO_6 film at 500 °C, 550 °C, and 650 °C. The magnified SEM images were shown in the inset of Figure S2A, C, and E, respectively. It is clear that the film still has nanoplate structure from the top view under 500 °C (Figure 1A) and 550 °C (Figure 1C). However, further increasing the annealing temperature to 650 °C, the film becomes a single large particle shape from the point of Figure S2E. From the point of cross-section SEM images, it is obviously that the thickness of the film gradually decrease with the increase of the annealing temperature, which is may be due to the collapse of the structure.

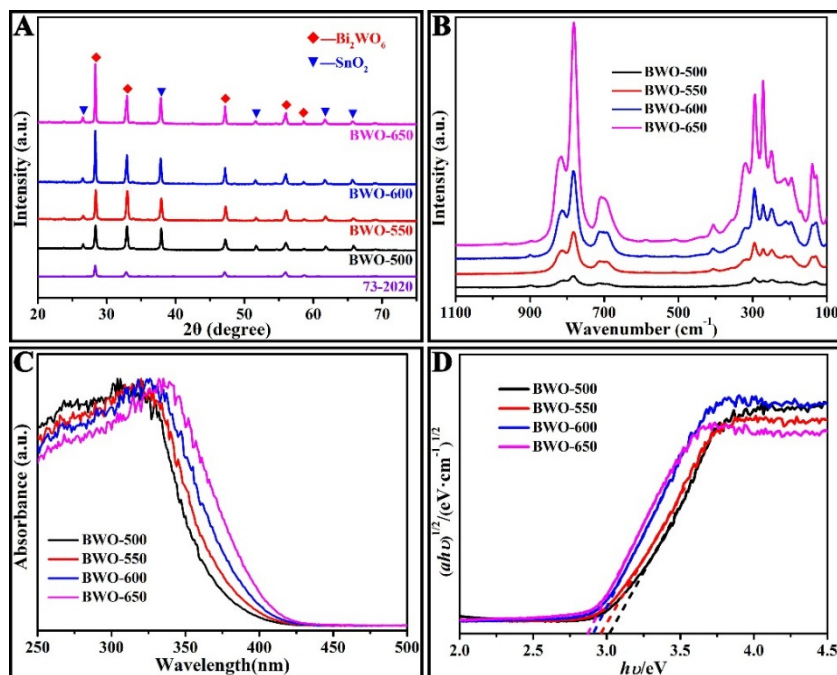


Figure S3: (A) XRD patterns, (B) Raman Spectrum and (C) UV-vis absorption spectrum of the Bi₂WO₆ under different annealing temperature; (D) Calculation of the band gaps of Bi₂WO₆ photoanodes with different annealing temperature by Tauc plots (from reflectance data).

Results and discussions

The X-ray diffraction indicated the phase of as-prepared samples and shown in Figure S3A, it obviously that all diffraction peaks correspond to the standard cards 73-2020. Interestingly, the lattice plane of (131) became narrower and higher from 500 °C to 650 °C, illustrating that the degree of crystallization of Bi₂WO₆ has been enhanced with the increase of annealing temperature. Besides, The Raman spectrum was used to further confirm the change of degree of crystallization. As shown in Figure S3B, the peak at 820 cm⁻¹ and 790 cm⁻¹ are associated with symmetric and antisymmetric stretching modes of O-W-O. The peaks at 700 cm⁻¹ is an antisymmetric bridging mode associated with the tungstate chain. The peaks in the range 180-600 cm⁻¹ are originate from the bending modes of WO₆ octahedra coupled with stretching and bending modes of Bi-O polyhedral. The peaks below 150 cm⁻¹ could be assigned to translations of the W and Bi ions.^{4,5} The full width at half maximum (FWHM) of characteristic peak became narrower as the annealing temperature increases, demonstrating again that the degree of crystallization has been enhanced with increasing temperature. As we all know, the higher the degree of crystallization, the more conducive to the transmission of electrons in the bulk of materials. Besides, Amano et al. has demonstration that crystallization of Bi₂WO₆ provided a red shift of the photo absorption edge.⁶ Therefore, the optical properties of the samples were investigated by UV-Vis absorption spectroscopy (Figure S3C), the absorption edge has exhibited a significant red-shift as the temperature from 500 °C to 650 °C, indicating that the photons absorption capability was enhanced with the increase of annealing temperature. The band gap is derived from the absorption spectrum by the Kubelka-Munk equation extrapolation, and shown in inset of Figure S3D.

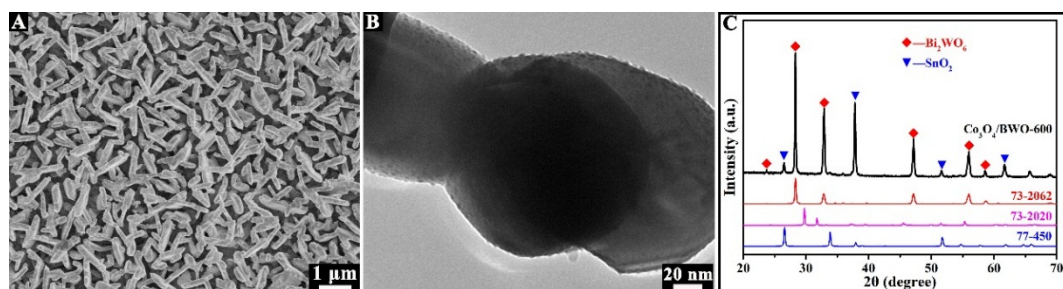


Figure S4: (A) SEM images, (B) Low-magnification TEM images, and (C) XRD patterns of $\text{Co}_3\text{O}_4/\text{BWO-600}$.

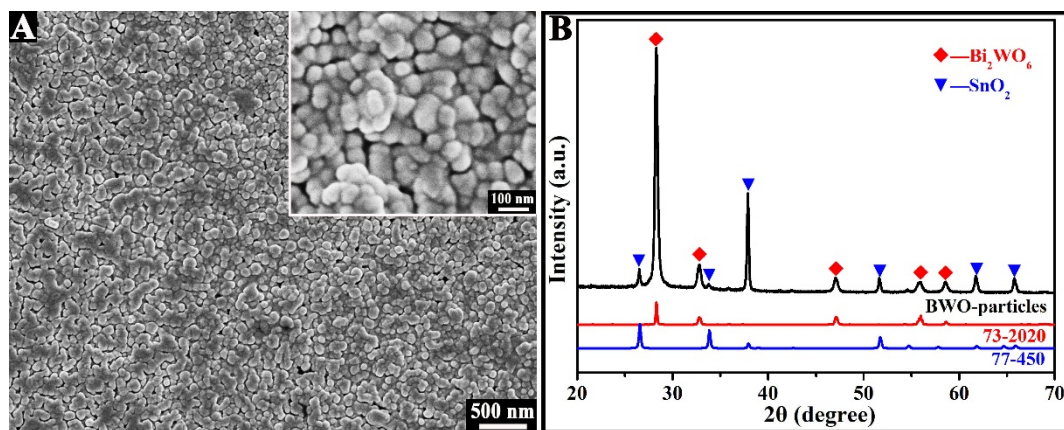


Figure S5: (A) SEM images and (B) XRD patterns of BWO-particles.

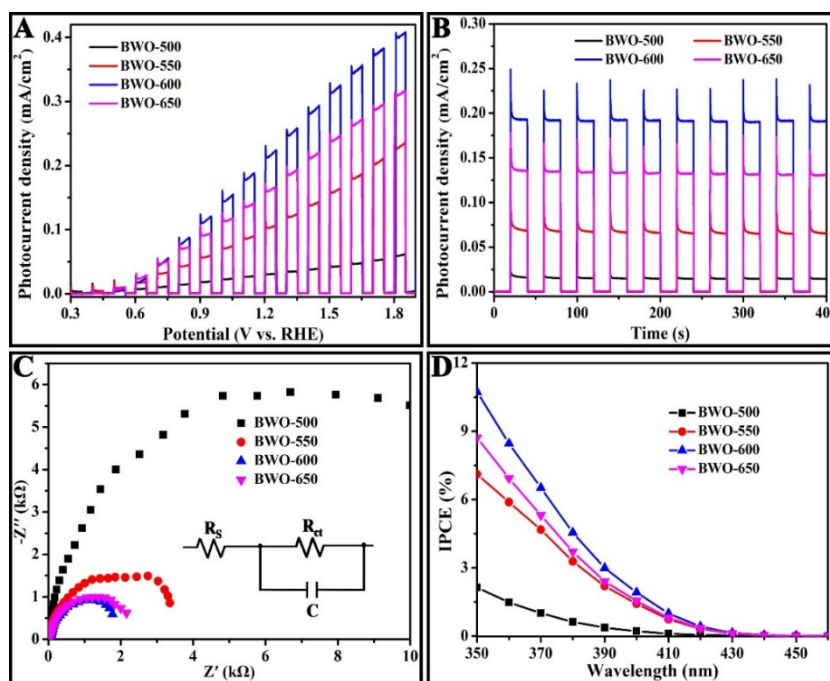


Figure S6: (A) Linear-sweep voltammograms curves, (B) amperometric i-t curves, (C) EIS and (D) IPCEs of BWO-500 (black), BWO-550 (red), BWO-600 (blue), BWO-650 (pink).

Results and discussions

Linear Sweep Voltammetry (LSV) curves of Bi₂WO₆ with different annealing temperature were shown in Figure S6A, and the test were carried out in 0.1 M potassium phosphate buffer (pH value is 7), and the light source is simulating solar light AM 1.5G (100 mW/cm²). The results indicated that the obtained photocurrent density of BWO-500 only about 0.04 mA/cm² at 1.23V vs. RHE. It is obviously that the photocurrent density enhanced to 0.23 mA/cm² under 600 °C, while the photocurrent density reduced with further increasing the temperature to 650 °C. In addition, the electrochemical impedance spectroscopy (EIS) and the incident photo-to-current conversion (IPCEs) of as-prepared samples were tested and shown in Figure S6C and D. More specifically, BWO-500 only reach an IPCE of 2.1% at 350 nm, while the BWO-600 could obtain an IPCE of 10.8% at the same wavelength. From the point of EIS, the BWO-600 exhibited a smaller radius of the arc than others, illustrating that the smaller interface resistance is one of the reasons for its better photocurrent density. Based on the SEM, XRD and Raman analysis, the synergistic effect of crystallization and 2D plate-like structure results in higher photocurrent density of BWO-600 than that of other samples. More specifically, with increasing the annealing temperature from 500 to 600 °C, the crystallization of Bi₂WO₆ photoanodes has been gradually improved, which could facilitate to the charge separation and transfer within 2D plate-like structure. However, further increasing the temperature up to 650 °C, the 2D nanoplate structure has been completely collapsed owing to higher annealing temperature, which would inevitably block the charge separation and transfer despite of the high crystallization. Therefore, the BWO-600 exhibits higher photocurrent density than other samples.

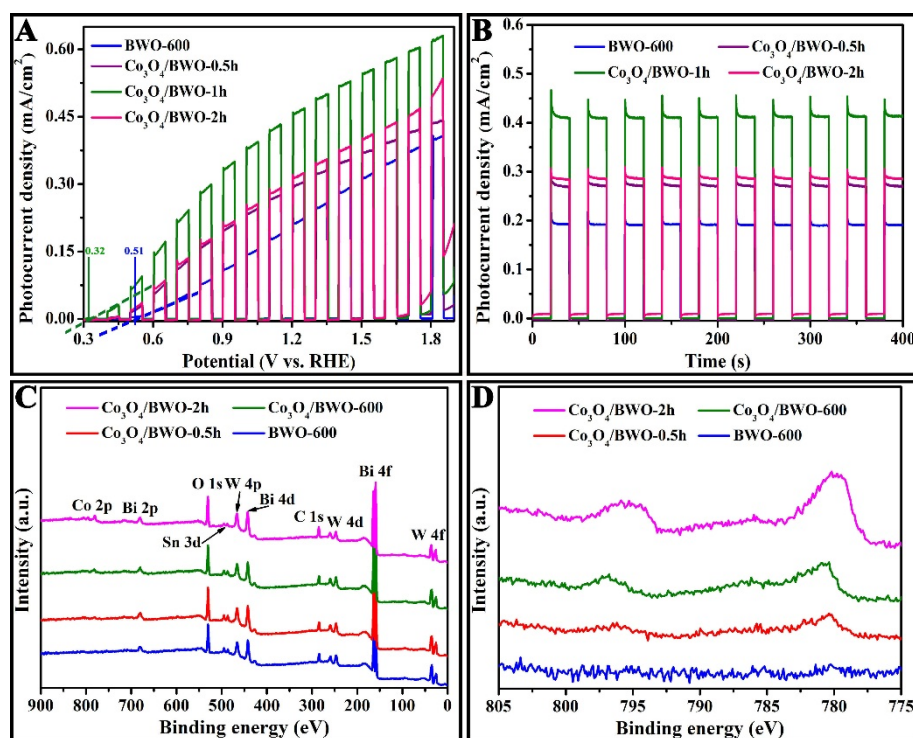


Figure S7: (A) Linear Sweep Voltammetry curves, (B) amperometric i-t curves, (C) the survey and (D) the Co 2p fine spectroscopy of BWO-600 (blue line), Co₃O₄/BWO-0.5h (red line), Co₃O₄/BWO-600 (green line), and Co₃O₄/BWO-2h (pink line), respectively.

Results and Discussions

As shown in Figure S7A, the photocurrent density was improved by the decoration of oxygen evolution co-catalyst Co₃O₄ nanoparticles, and the photocurrent density of 0.31 mA/cm², 0.45 mA/cm², and 0.33 mA/cm² (at 1.23 V vs. RHE) were obtained with the hydrothermal deposition time of Co₃O₄ was set to 0.5h, 1h, and 2h, respectively. The onset potential is determined as the intersection point of the tangent of the inflection point of the photocurrent rise with the dark current. It is clearly that the onset potential exhibited a significant cathodic shift, and the maximum movement is nearly ~200 mV. That illustrating a lower over-potential for water oxidation after the decoration of nanoparticles. The stability of Co₃O₄/BWO-(0.5h, 1h, and 2h) was tested by amperometric i-t curves at 1.23 V vs. RHE (Figure S7B), and all samples exhibit excellent stability. From the results of XPS (Figure S7C and D), it is obviously that the amount of Co₃O₄ nanoparticles on Bi₂WO₆ photoanodes are increased with the reaction time. In addition, the weight percentage of Co₃O₄ on the Bi₂WO₆ photoanodes was measured by the EDS technique, and the atomic percentage and corresponding weight percentage of different Co₃O₄/BWO samples have been listed in Table R1. Combined with the PEC behaviors, it can be concluded that the optimal loading weight percentage of Co₃O₄ is about 0.24 wt%.

	$\text{Co}_3\text{O}_4/\text{BWO}-0.5\text{h}$	$\text{Co}_3\text{O}_4/\text{BWO}-600$	$\text{Co}_3\text{O}_4/\text{BWO}-2\text{h}$
Atomic percentage (Co:Bi)	0.09%:16.21%	0.15%:14.61%	0.26%:15.17%
Weight percentage (Co_3O_4 : Bi_2WO_6)	0.13%	0.24%	0.39%

Table S1. The atomic percentage and weight percentage of $\text{Co}_3\text{O}_4/\text{BWO}-0.5\text{h}$, $\text{Co}_3\text{O}_4/\text{BWO}-600$, and $\text{Co}_3\text{O}_4/\text{BWO}-2\text{h}$.

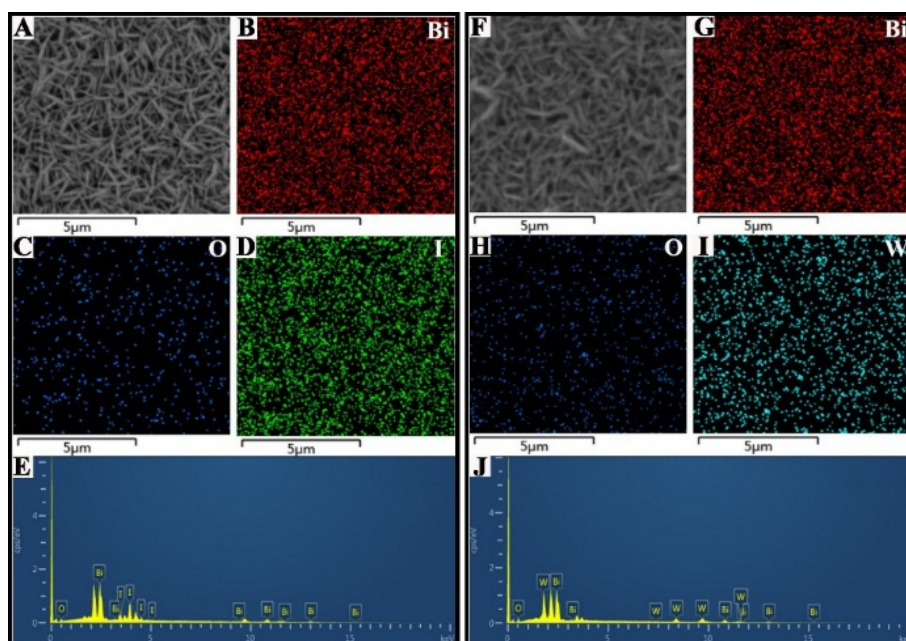


Figure S8. The elemental mappings of BiOI (A-D) and pre-BWO (F-I); the EDS spectrum images of BiOI (E) and pre-BWO (J).

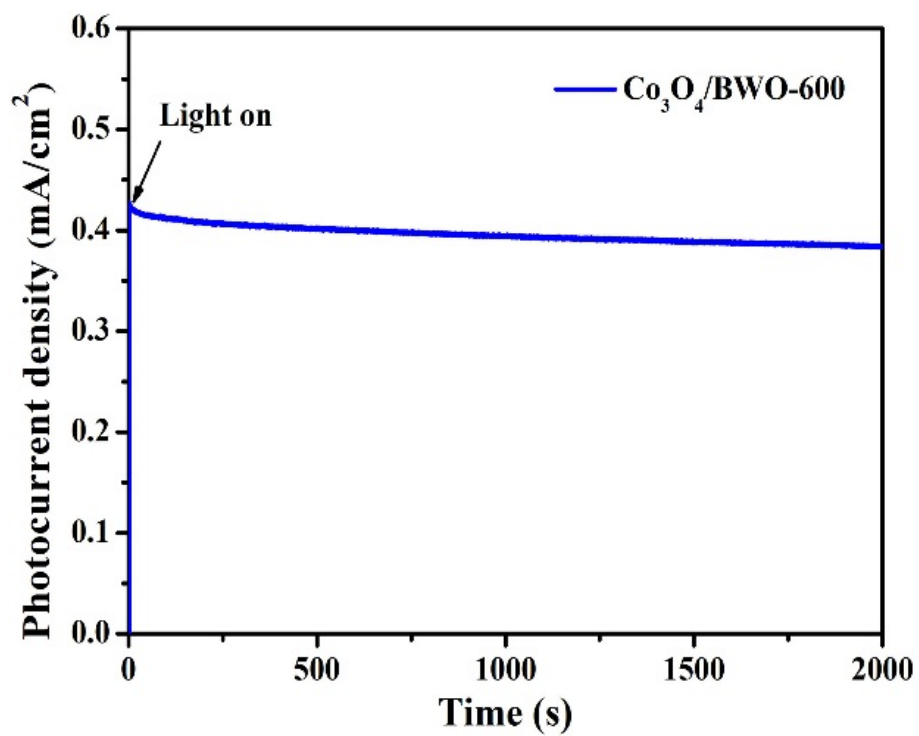


Figure S9. The stability of $\text{Co}_3\text{O}_4/\text{BWO-600}$.

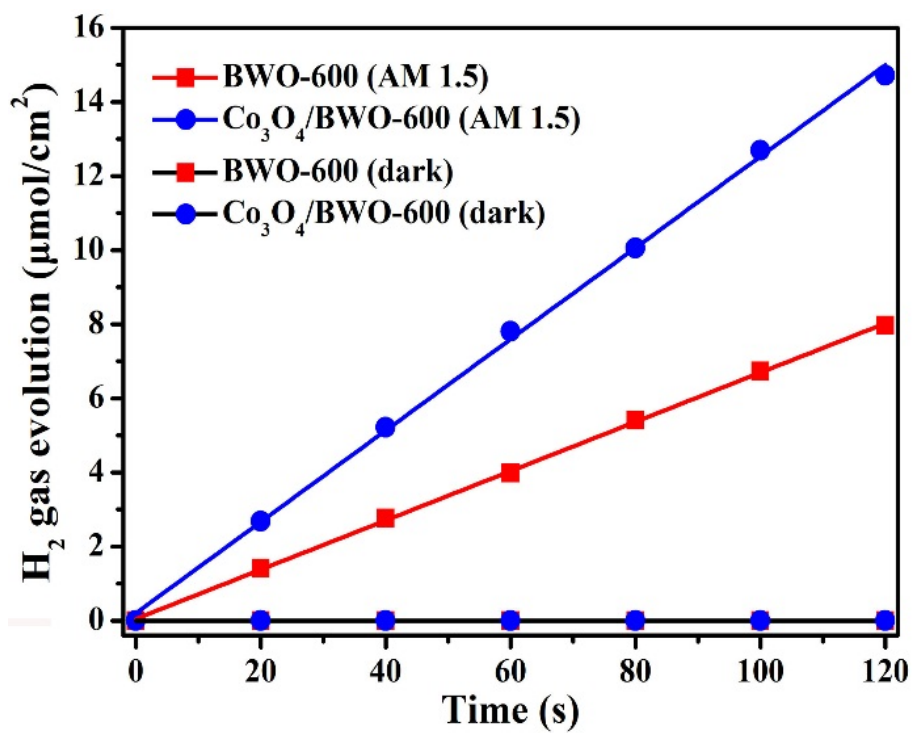


Figure S10. The yield of H_2 from BWO-600 and $\text{Co}_3\text{O}_4/\text{BWO-600}$.

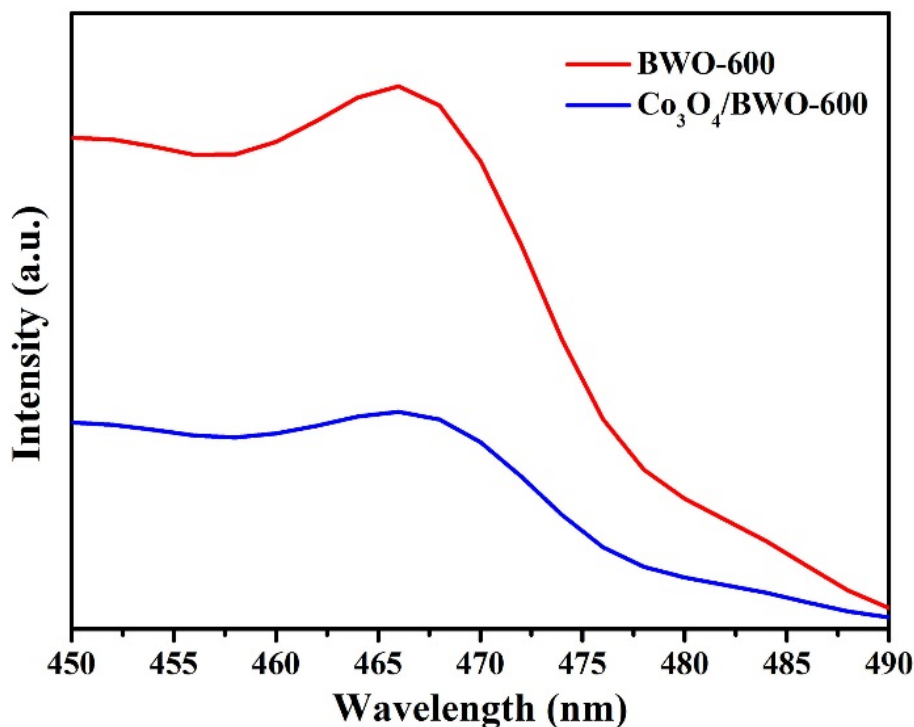


Figure S11. The PL spectrum of BWO-600 and Co₃O₄/BWO-600.

Results and Discussions

The photoluminescence (PL) spectra have been extensively utilized for exploring the charge separation ability in the semiconductor photoelectrodes. Thereby, the PL spectra of Co₃O₄/BWO as well as BWO have been tested and shown in Figure S11. It can be clearly seen that the PL peak intensity of Co₃O₄/BWO is much lower than that of pure BWO sample, demonstrating more efficient charge separation in Co₃O₄/BWO system than that of pure BWO sample. Moreover, it has been extensively reported that the Co₃O₄ co-catalyst could efficiently captures the photogenerated holes from semiconductor photoelectrode and facilitates the water oxidation reaction⁷⁻⁹. Thereby, it can be concluded from the PL results that the photogenerated holes could be efficiently transferred from Bi₂WO₆ to Co₃O₄ co-catalyst, and more efficient charge separation in the Co₃O₄/BWO photoelectrode has been achieved.

Notes and references

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