

Supporting Information for

Polydopamine assisted transformation of ZnO from nanospheres to nanosheets grown in nanoporous BiVO₄ films for the improved photocatalytic performance

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1. Experimental section

1.1. Chemicals

ZnC₄H₆O₄·2H₂O (95%), Bi(NO₃)₃·5H₂O (98%), NH₄VO₃, KOH (98%), (3-Aminopropyl) trimethoxysilane (97%), polyethylene glycol 600 (PEG-600), ammonia solution (25%), dopamine hydrochloride, and ethylene glycol were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemicals used were of analytical grade. Deionized water was used to prepare all the solutions.

1.2. Synthesis of ZnO quantum dots (QDs)

ZnO QDs were obtained through a sol-gel approach. Zinc acetate dihydrate (ZnAc, 1.1 g) was added in ethanol (50 mL), and the solution was refluxed at 78 °C for 2 h. Another solution of potassium hydroxide (0.392 g) in ethanol (5 mL) was prepared by sonication. The two solutions were mixed slowly by cooling the mixture below 10 °C. Deionized water (0.5 mL) and (3-Aminopropyl) trimethoxysilane (80 μL) were added into the resultant mixture until the solution turned milky white. The ZnO QDs were washed thrice with ethanol and centrifuged at 6000 rpm for 3 min.

1.3. Fabrication of ZnO nanospheres

ZnO nanospheres were prepared using a two-step method. In the primary reaction, 0.1M ZnAc solution (0.03 mol ZnAc was dissolved in 0.3 L diethylene glycol) was refluxed at 160 °C, and the temperature was maintained for 1 h. After cooling to room temperature, the solution was centrifuged, and the supernatant was separated for the secondary reaction.

The secondary reaction was similar to the primary reaction, except those different amounts of supernatant prepared from the primary reaction were added to the solution before reaching the target temperature (160 °C). It was noted that the amount of supernatant added such as 15, 10, and 3 mL corresponds to 100, 200, and 300 nm size nanospheres, respectively. The solution was stirred at 160 °C for 1 h. Then, the product was cooled to room temperature and centrifuged to obtain the precipitate. After washing the sample with deionized water, the precipitate was stored and labeled as ZnO nanospheres. The same weight of obtained ZnO QDs and nanospheres (0.1 g) were dispersed in 10 mL ethanol solution.

1.4. Preparation of polydopamine (PDA) mesh

PDA mesh was obtained by the following three steps procedure: (i) absolute ethanol (20 mL) and ammonia solution (0.5 mL, 25%) were added to a beaker containing deionized water (45 mL) under stirring for 15 min at room temperature. (ii) dopamine hydrochloride (0.25 g) was dissolved in 5 mL deionized water and added to the above mixture. (iii) stainless steel mesh (5cm × 5cm) was placed in the beaker. The PDA got loaded on the mesh through self-polymerization after stirring the contents for 48 h at room temperature.

1.5. Fabrication of BVO/ZnO-QDs/100/200/300 heterostructures

The fabrication of BVO/ZnO-100/200/300 heterostructures using a simple SSDC method is shown in Scheme 1. The specific steps were as follows: (i) Two solutions of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 dissolved separately in ethylene glycol solution (75 mM) were prepared. Then, 0.68 g PEG-600 was dissolved in another 20 mL ethylene glycol

solution. (ii) The above three solutions were mixed in stoichiometric ratio slowly to prepare a precursor solution in the following proportions: 5 mL $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ solution, 5 mL NH_4VO_3 solution, and 2.5 mL PEG-600 solution. (iii) 3.6 mL precursor solution and 0.4 mL ZnO solution (0.1g of ZnO (QDs or different size nanospheres) dispersed in 10 mL ethanol solution) were mixed and PDA mesh was immersed in the mixture for one minute. Finally, the mesh slide covered with the mixture was first dried in an oven at 150 °C for 60 min and then annealed in a muffle furnace at 500 °C for 2.5 h. Finally, about 5 mg of catalyst was successfully loaded on the PDA mesh. The heterostructures of BVO/ZnO-100, BVO/ZnO-200, BVO/ZnO-300, and BVO/ZnO QDs were obtained by adding ZnO solution containing ZnO nanospheres of 100 nm, 200 nm, 300 nm, and ZnO QDs, respectively, to the precursor solution. The precursor solution without the addition of ZnO solution produced pristine BiVO_4 .

1.6. Characterization

X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima IV instrument (Tokyo, Japan) utilizing $\text{Cu K}\alpha$ radiation (40 kW) recorded from 10° to 90° with a scanning rate of 5 °/min. Scanning electron microscopy (SEM) measurements were carried out using a field-emission scanning electron microscope (JSM-7800F, JEOL, Tokyo, Japan) operated at an accelerating voltage of 5 kW. Transmission electron microscopy (TEM) measurements were carried out using a JEOL JEM-2100 Plus transmission electron microscope (Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5000 Versa Probe III (Chanhassen, MN, USA). Raman spectra were recorded on a Renishaw inVia Plus

Micro-Raman spectroscopy system (Wotton-under-Edge, UK). The light source was supplied by a 300 W Xe lamp (CEL-HXF300, AULTT, China), and air mass (AM) 1.5 was used to simulate sunlight, which was calibrated to 100 mW/cm² using a strong light optical power meter (CEL-NP2000, CEAULIGHT). UV-Vis Spectrophotometer was performed on an UV-2550 (Shimadzu) spectrometer.

1.7. Photocatalytic activity tests

The photocatalytic activities of the BiVO₄/ZnO mesh were evaluated by photodegradation of MB and CR under simulated solar light illumination at room temperature. The experimental details were as follows: BiVO₄/ZnO mesh which loading density was 0.2 mg/cm² was placed in a 40 mL MB or CR aqueous solution at a concentration of 5 mg/L in a 250 mL beaker. Irradiated from the top with a 300 W xenon arc lamp as a light source, equipped with a simulated solar light filter to trigger the photocatalytic reaction. The photocatalytic solution was taken out at regular intervals to examine the samples using a UV-Vis absorption spectrophotometer. In the degradation of CR, the photocatalysts were removed by centrifugation method at 8000 rpm for 3 min. While in the degradation of MB, the photocatalysts were filtered by a 0.22 μm PTEE syringe filter to remove the catalyst.

For the active species trapping experiment, radical scavengers (Ethylene diamine tetraetic acid (EDTA), benzo-quinone (BQ) and tertiary butanol (TBA)) (1 mM) was added into the photodegradation system of CR to scavenge holes (h⁺), ·O₂⁻ and ·OH, respectively. The solution was collected and centrifugated at 8000 rpm to remove the catalyst, and then analyzed at 285 nm by an UV-vis spectrophotometer.

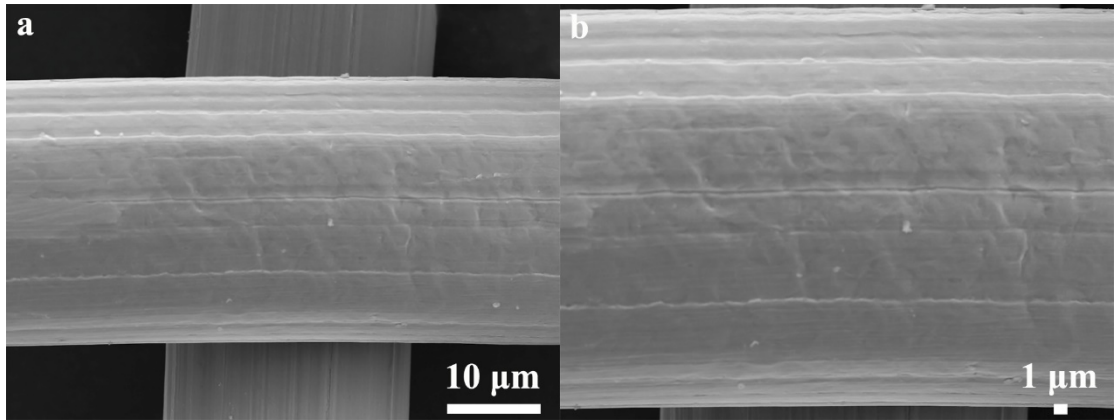


Fig. S1 SEM images of stainlessness steel mesh.

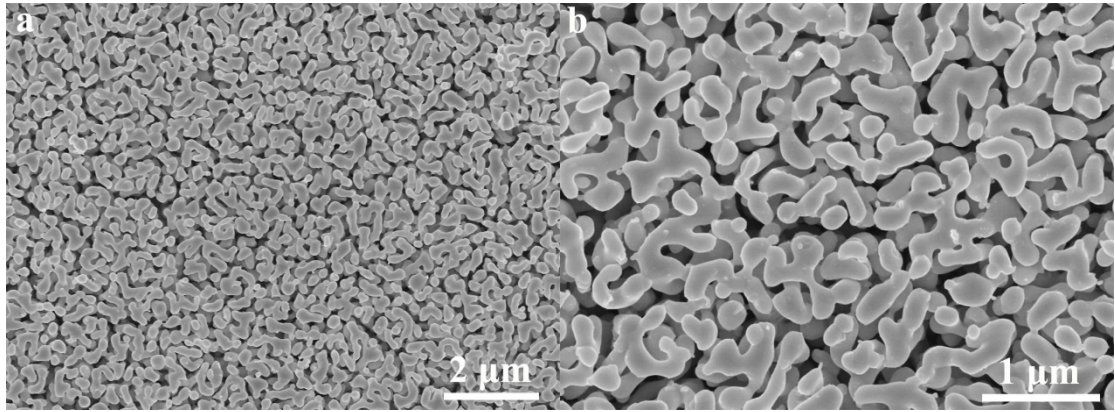


Fig. S2 SEM images of nanoporous BiVO₄ on FTO substrate.

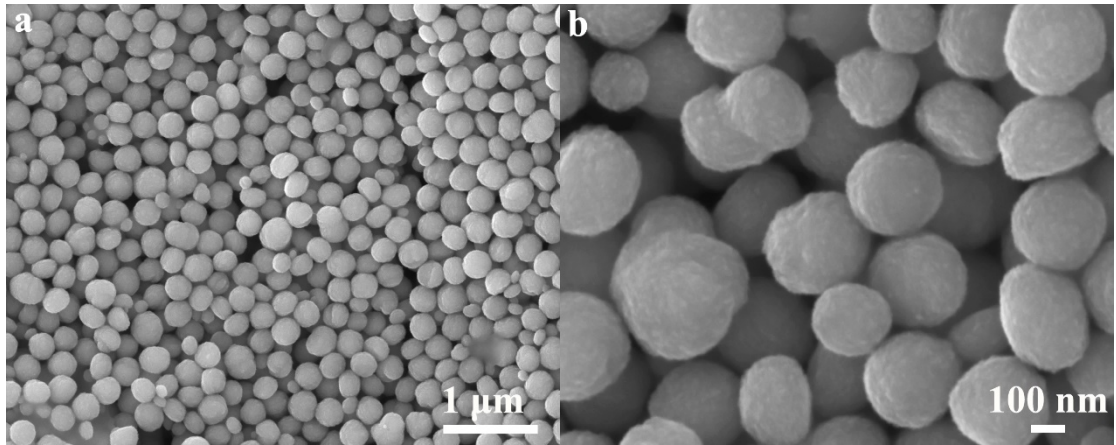


Fig. S3 SEM images of ZnO nanospheres with a dimension of 300 nm.

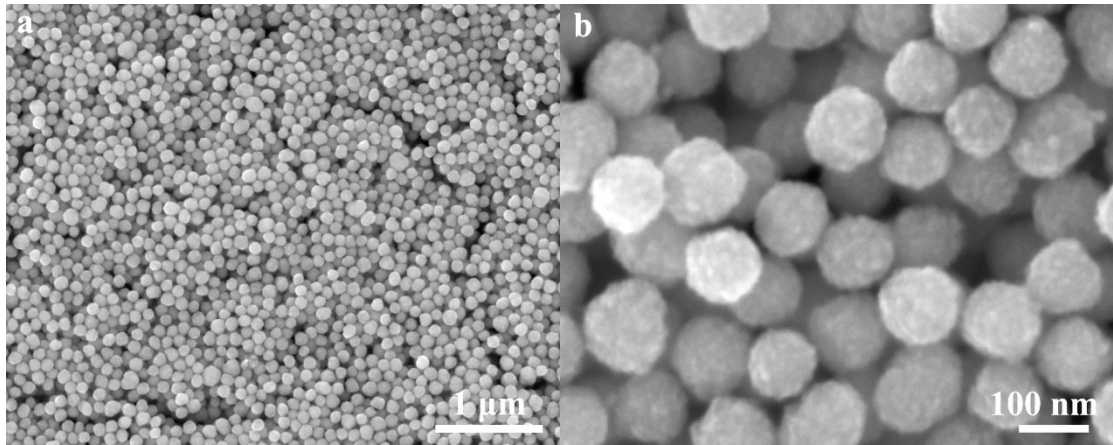


Fig. S4 SEM images of ZnO nanospheres with a diameter of 100 nm.

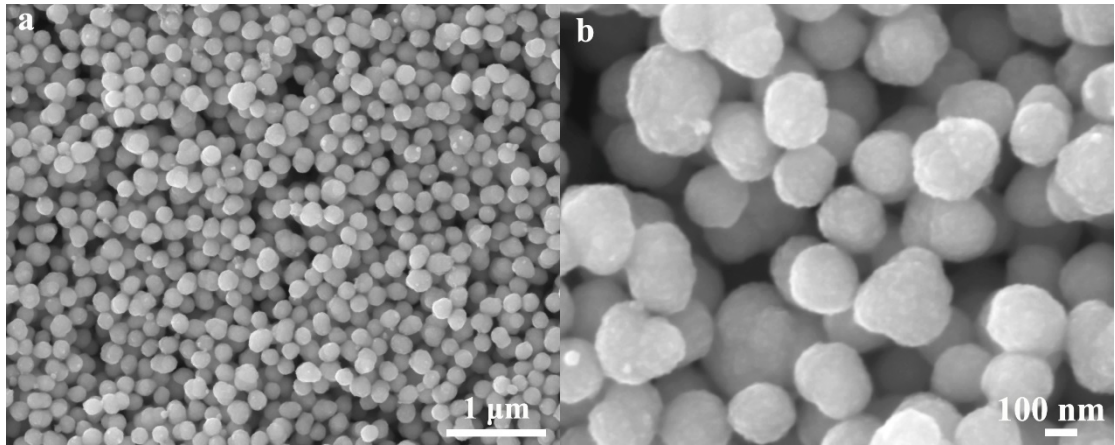


Fig. S5 SEM images of ZnO nanospheres with a dimension of 200 nm.

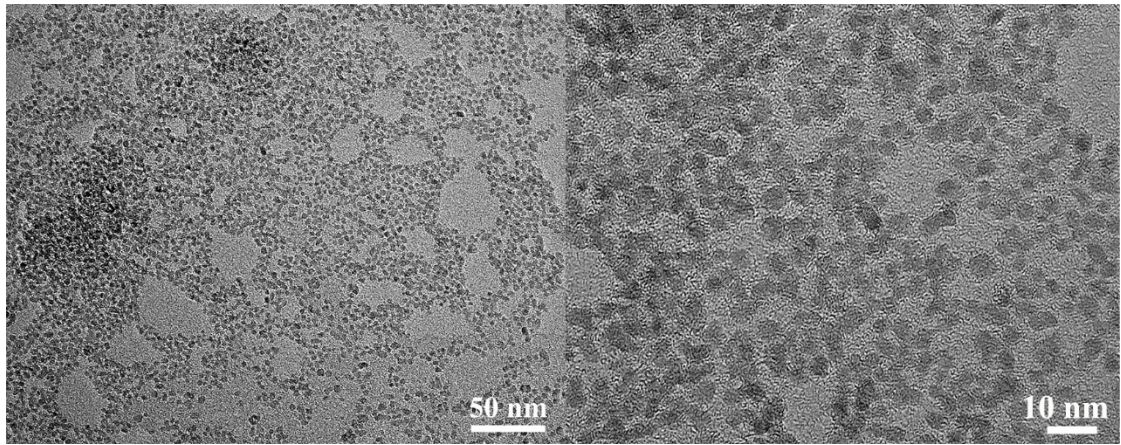


Fig. S6 TEM images of ZnO QDs.

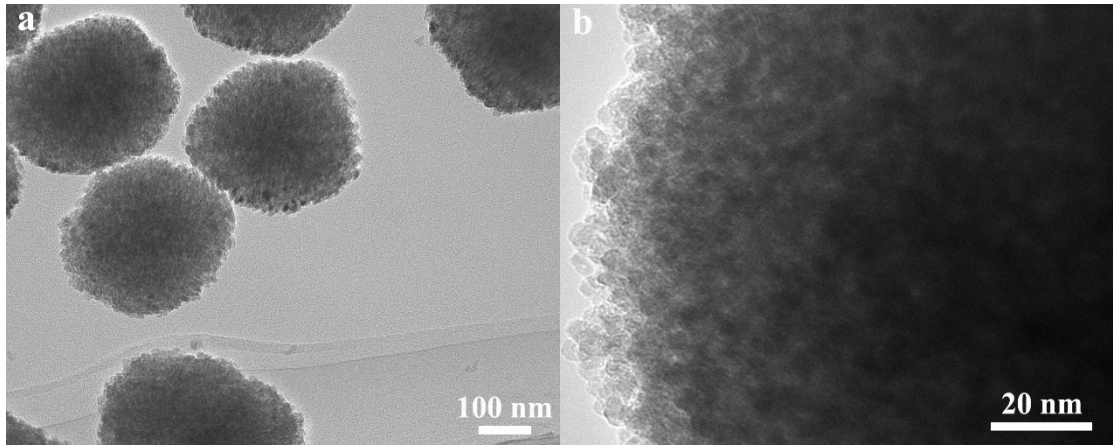


Fig. S7 TEM images of ZnO nanospheres with a dimension of 300 nm.

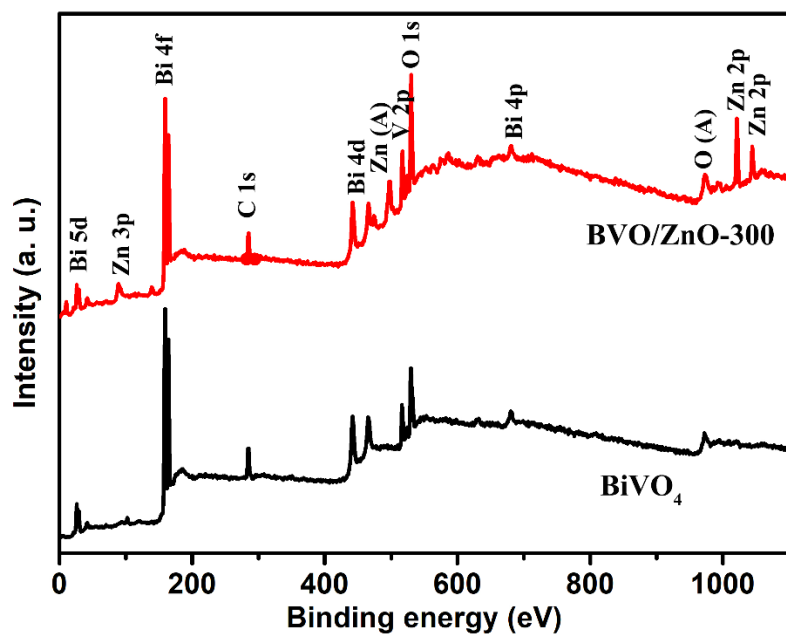


Fig. S8 X-ray photoelectron spectroscopy survey spectra of BiVO₄ and BVO/ZnO-300.

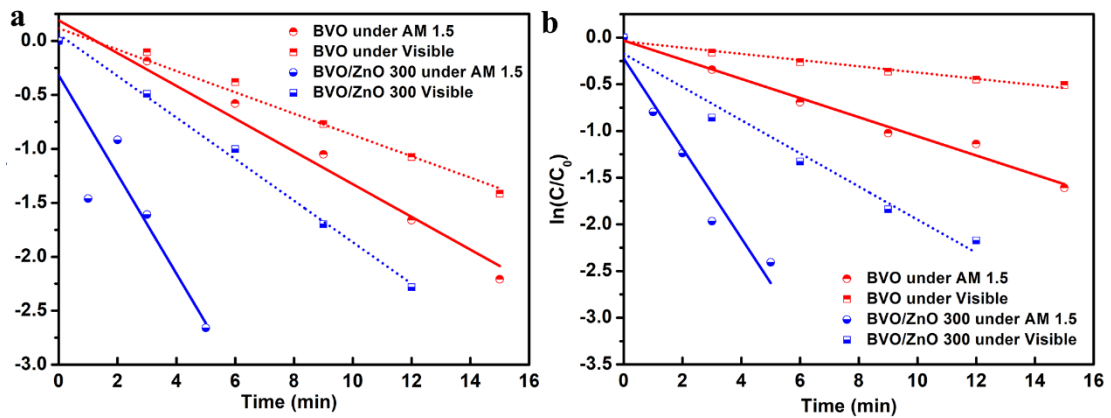


Fig. S9 The first order kinetic plots of $\ln(C/C_0)$ vs time for the photodegradation of (a) CR and (b) MB on BiVO₄ and BVO/ZnO-300 under AM 1.5 and visible light.

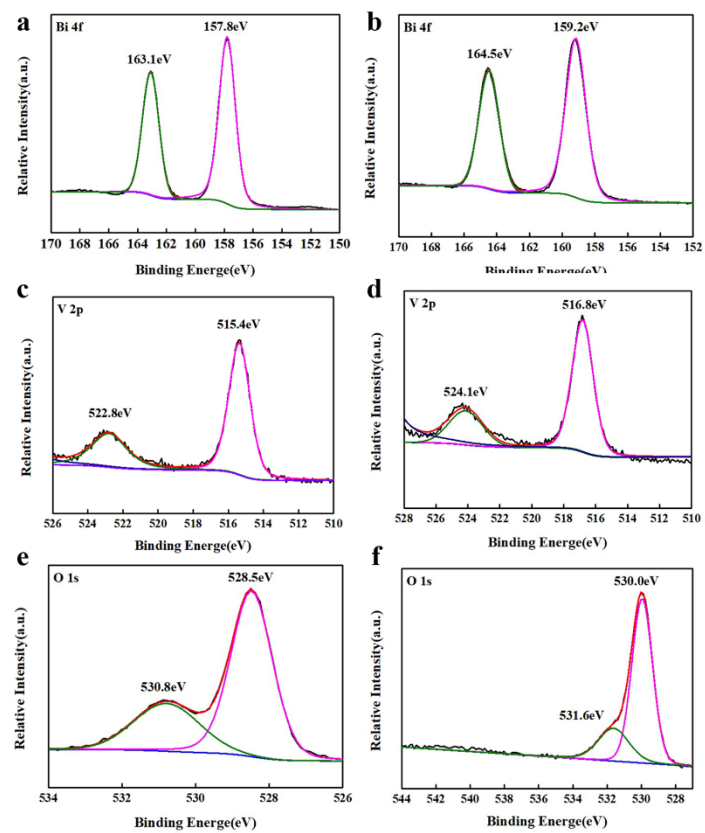


Fig. S10 XPS spectra of (a, c and e) BVO and (b, d and f) BVO/ZnO-300.

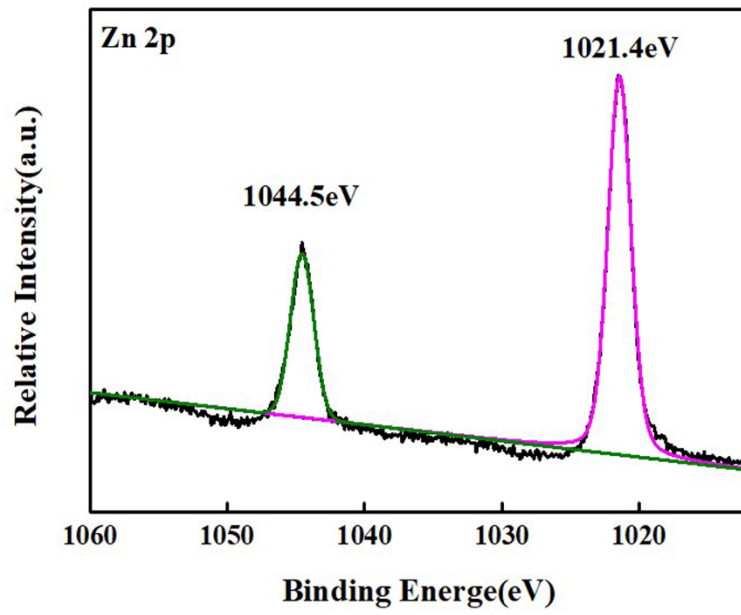


Fig. S11 XPS spectra of Zn 2p of BVO/ZnO-300.

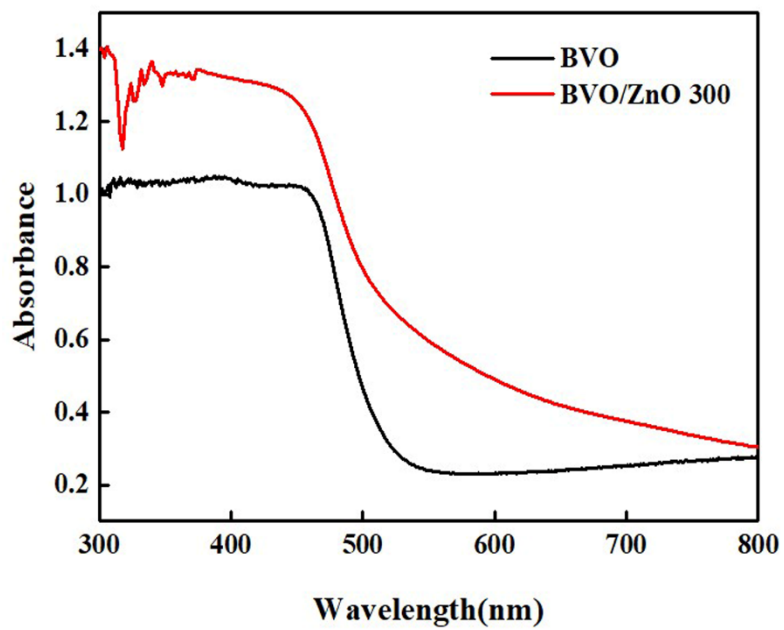


Fig.S12 The UV-Vis spectra of BiVO_4 and $\text{BiVO}_4/\text{ZnO-300}$ heterostructures.

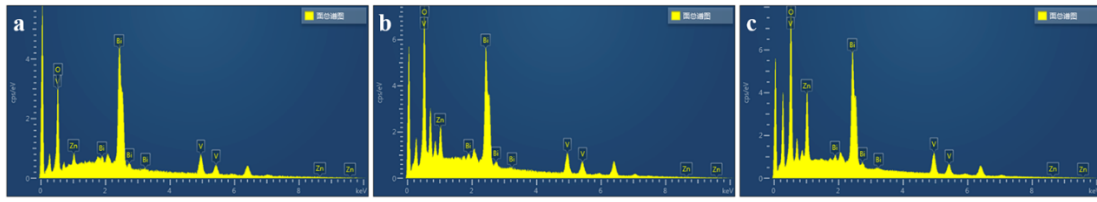


Fig. S13 EDS of (a) BVO/ZnO-100 (b) BVO/ZnO-200 and (c) BVO/ZnO-300

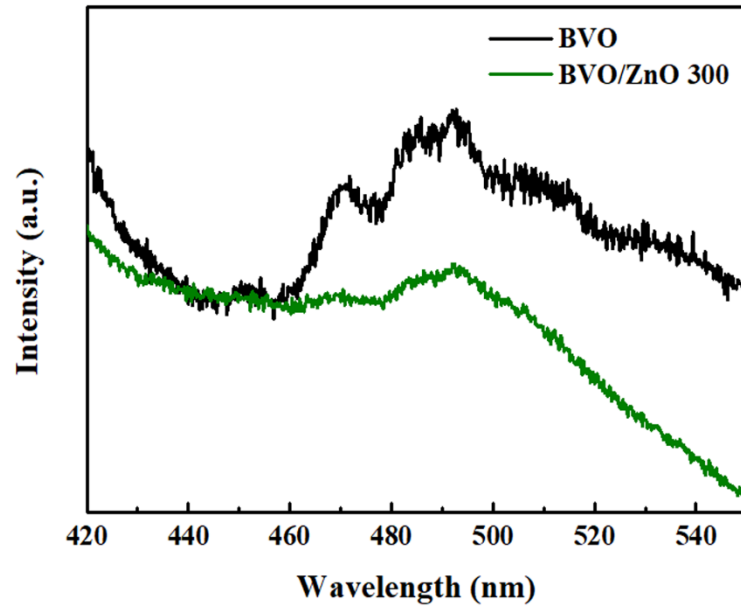


Fig. S14 The photoluminescence spectrum of BVO and BVO/ZnO-300.

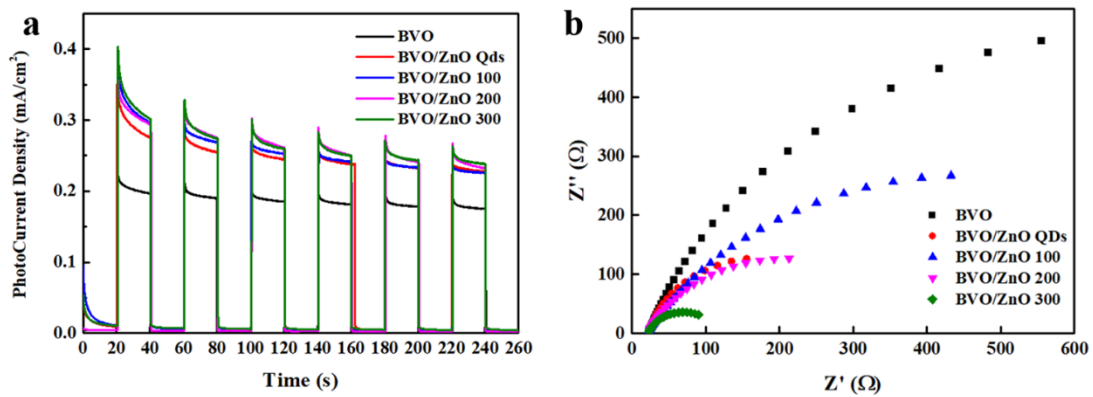


Fig. S15 The (a) photocurrent responses and (b) ESI of BVO-based samples.