

Supplementary information:

Interfacial defect engineering over fusiform bismuth vanadate photocatalyst enables to excellent solar-to-chemical energy coupling

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Experimental section:

The whole chemicals were analytical grade reagents and used as received without further purification.

Synthesis of materials

BiVO₄-OV Synthesis: Fusiform-shape morphology of BiVO₄-OV was prepared according to the special and simple hydrothermal method. In a typical synthesis procedure, 0.4 mmol Bi(NO₃)₃ · 5H₂O powder was dissolved in 16 ml glycerol under vigorous stirring for 1h. 0.4 mmol NaVO₃ · 2H₂O was dissolved in 16 ml deionized water accompanying with vigorous stirring for 0.5h until it became homogeneous and clarification under the room temperature environment. Then, the NaVO₃ · 2H₂O solution was drop wise added into the Bi(NO₃)₃ · 5H₂O solution under vigorous stirring for 0.5 h to form a yellowish suspension. Above solution was heated in a 50 mL Teflon-lined autoclave at 180 °C for 8 h for. Afterwards, the resultant precipitates were collected by centrifugation, and washed with distilled water and absolute ethanol repeatedly, and dried in air at 60 °C for 4 h. Finally, the prepared sample was recorded

for BiVO₄-OV.

BiVO₄-P synthesis: Since, the oxygen defects would vanish through redox reaction. The obtained BiVO₄-OV powder was calcined in a muffle furnace at 300 °C for 5h in the air. After the sample power was taken away from a muffle furnace at 20 °C temperature, immediately, was puted into hermetic bag to save. The prepared sample was recorded for BiVO₄-P.

photocatalytic activity:

The light source for photocatalytic reaction was a 300 W Xe lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd). And photocatalytic activities of as-prepared samples were determined by measuring the degradation rate of rhodamine B dye under different light irradiation. UV, Vis and NIR light was obtained by using a band-pass filter $\lambda=380$ nm, a cut off filter $\lambda>420$ nm and a cut off filter $\lambda>800$ nm, respectively. 20 mg the sample was dispersed in 50 mL RhB solution (10 mg/L) by sonication for 10 min. Then, solutions were stirred for 30 min in dark for adsorption-desorption equilibrium. Finally, the reaction solution was illuminated using different light sources for degradation of RhB at normal circumstances. At the given 20 min time intervals, 4 mL suspension was collected and catalyst was separated by centrifuge. Degradation of RhB was monitored by using a UV-visible spectrophotometer. The RhB concentration is marked C after light irradiation for a certain period of

time, and C_0 is the fundamental concentration of RhB at adsorption/desorption equilibrium in dark. ¹ The blank experiment of $\text{BiVO}_4\text{-OV}$ and $\text{BiVO}_4\text{-P}$ without illumination also was provided.

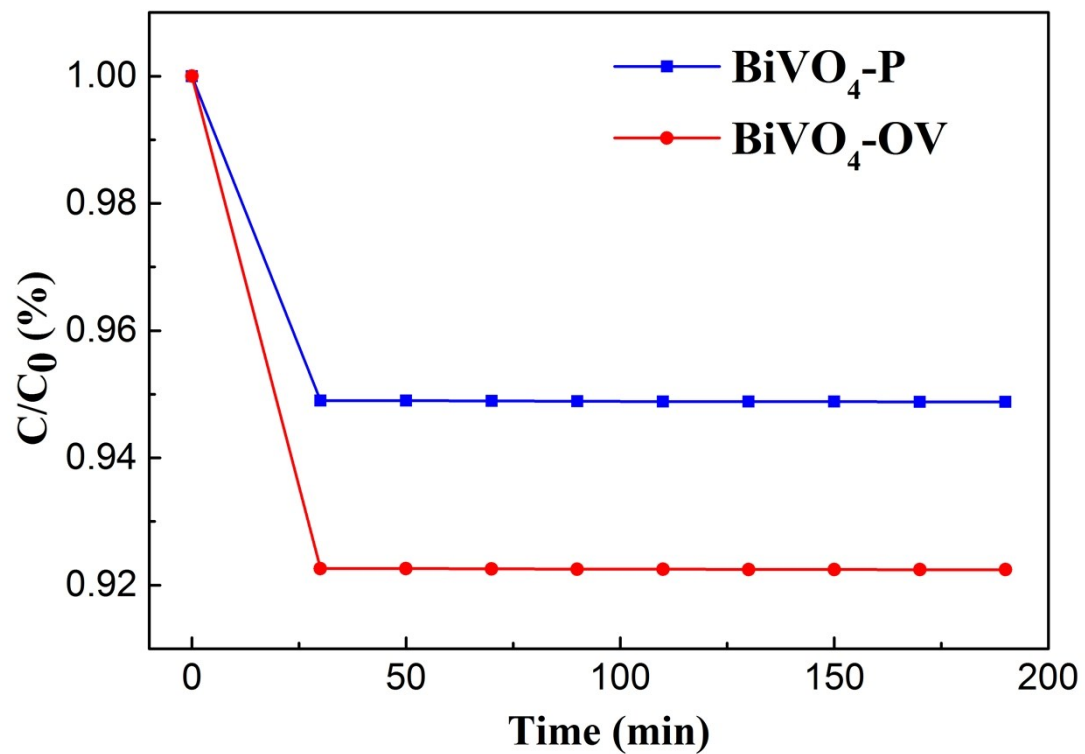


Fig. S1 RhB degradation without illumination

Active species (hydroxyl radicals) trapping experiments:

The experiments for detecting the active species were similar to photodegradation activity test, except 1.5 mM Isopropyl alcohol were added to quench hydroxyl radicals ($\bullet\text{OH}$). The RhB photodegradation activity test was conducted under the simulated solar light. The RhB photodegradation curve of (a) $\text{BiVO}_4\text{-OV}$ represents hydroxyl radicals trapping experiments, whereas, (b) $\text{BiVO}_4\text{-OV}$ represents the normal experiments.

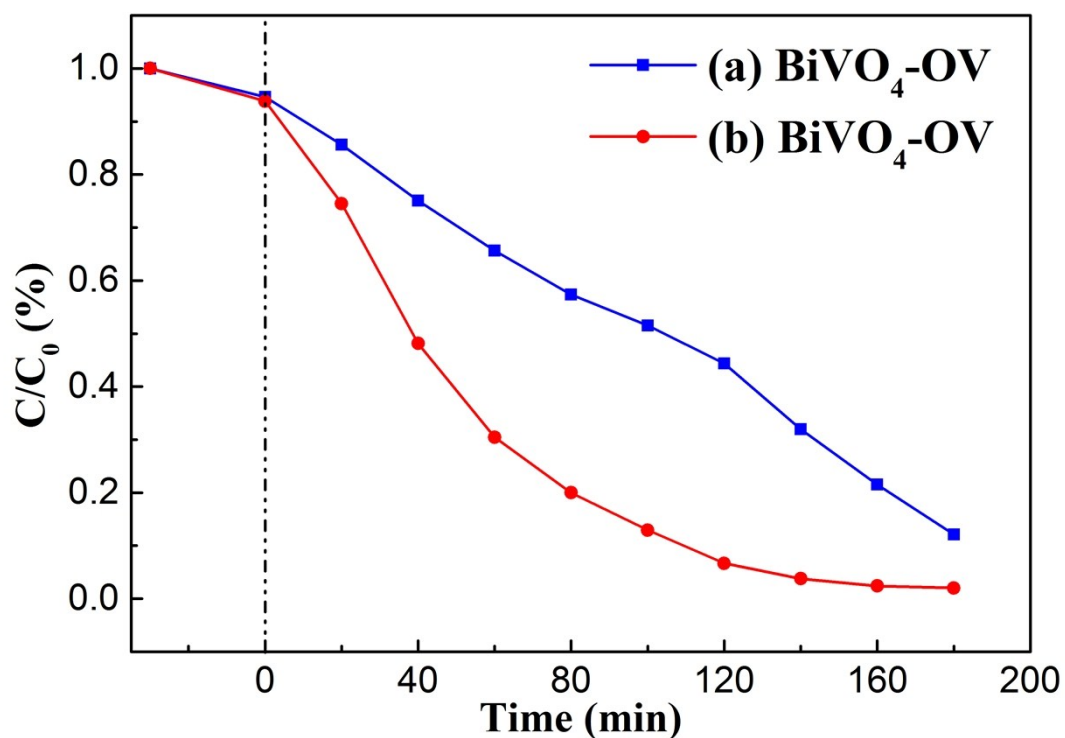


Fig. S2 hydroxyl radicals trapping experiment

It is established that $\text{BiVO}_4\text{-OV}$ can absorb solar light, which is attributed to the transition of the electrons from the valence band to the conduction band. Accordingly, under solar, irradiation, the direct

semiconductor excitation initiated photocatalytic reactions would take place over the BiVO_4 photocatalyst, which mainly involves the following three typical processes: (i) the electrons (e^-) in the VB can be excited to the CB with the generation of a same number of holes (h^+). (ii) The photogenerated electrons and holes are bulk diffusion and surface transfer. (iii) The surface oxidation reactions mediated by holes and/or its derivative active species. ² It should be noted that the holes photogenerated on the surface of BiVO_4 cannot react with $\text{OH}^-/\text{H}_2\text{O}$ to form $\bullet\text{OH}$, which is due to the fact that the oxidation ability of the holes in the VB level of Bi-containing oxide is inferior to the redox potential of forming $\bullet\text{OH}$ radicals [$\text{Bi}_2\text{O}_4/\text{BiO}^+$ (+1.31 eV) vs; $\bullet\text{OH}/\text{OH}$ (+1.99 eV) vs].³ Moreover, the observed $\bullet\text{OH}$ radical can produced via $\bullet\text{OH}/\text{H}_2\text{O}_2$. It is known that H_2O_2 can be generated through the superoxide radical anions ($\bullet\text{O}_2^-$) H_2O_2 . Herein, the superoxide radical anions ($\bullet\text{O}_2^-$) derived from the reaction of electrons with O_2 molecules. ⁴ The $\bullet\text{OH}$ radicals, the superoxide radical anions ($\bullet\text{O}_2^-$) and holes (h^+) should be responsible for the degradation of RhB during the photocatalytic process.

Material characterization

SEM: images were taken using a field-emission scanning electron microscope (JSM-7800F, JEOL).

TEM: The TEM analyses were performed by a JEOL JEM-2100F transmission electron microscope. Light absorption property was evaluated by UV-vis diffuse reflectance spectra (UV-vis DRS, CARY 100&300, VARIAN), BaSO₄ was used as a reflectance standard.

ESR: ESR spectra were recorded using ESR spectrometer A200 (Bruker, Karlsruhe, Germany) at room temperature.

XRD: The crystallinity and the purity of the as-prepared samples were characterized by powder X-ray diffraction (XRD) analysis on a Shimadzu XRD-6100 diffractometer at 40 kV and 40 mA with Cu-K α radiation.

Raman: Raman spectra were recorded using a LabRam-1B Raman spectroscope, with He-Ne laser excitation at 532, 633 and 785 nm.

XPS: Data were recorded at a scan rate of 0.07 s⁻¹ in the 2 θ range 10–70°. X-ray photoelectron spectroscopy (XPS) measurements were taken with a Thermo VG ESCALAB-250 system with Al-K α and Mg-K α source operated at 15 kV.

UV-vis DRS: Light absorption properties were evaluated using UV-vis diffuse reflectance spectra (UV-vis DRS, CARY 100&300, VARIAN), and BaSO₄ was used as a reflectance standard.

PL: The PL spectra of the photocatalysts were analysed using a Hitachi F-7000 fluorescence spectrophotometer.

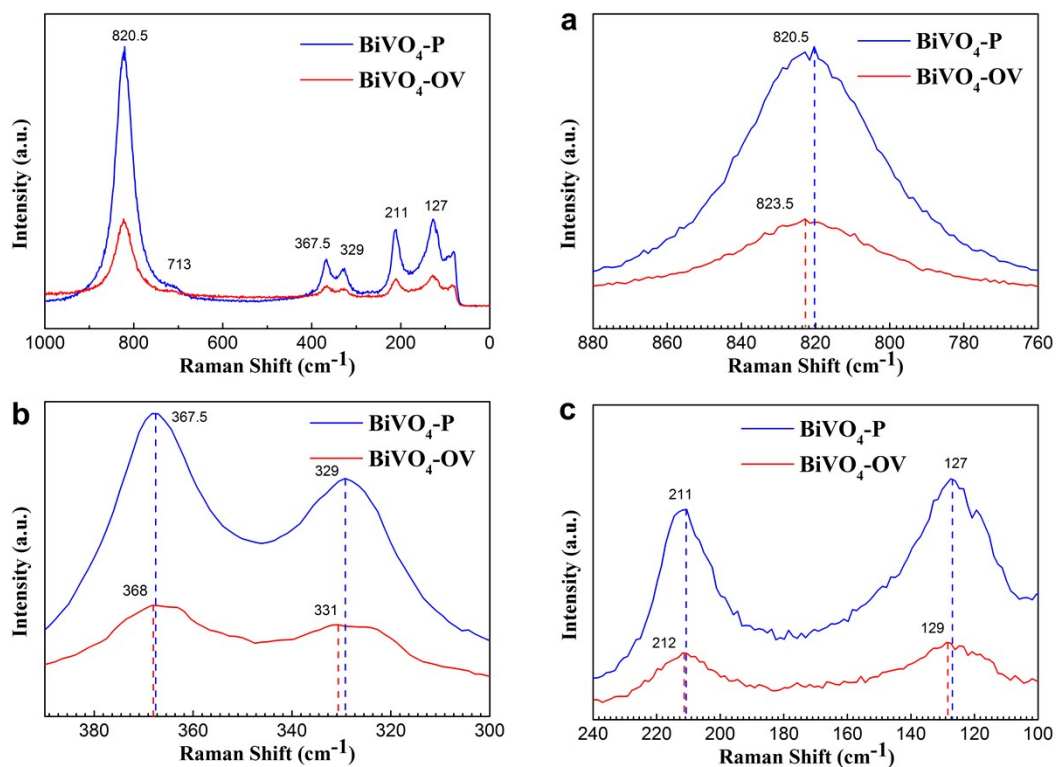


Fig. S3 Raman spectra (a laser line 532 nm)

The Raman spectra of BiVO₄-OV and BiVO₄-P (Fig. 2c, S3, S4) were performed by Raman spectroscopy used the Raman laser lines (633 nm, 532 nm and 785 nm, respectively). To clearly provide the structural information of the sample, a local comparison spectra about the lattice region of the Raman data is given in Fig. S3. The stretching modes of the vibrational modes of the V–O bonds, the asymmetric and symmetric formations of the VO₄ tetrahedron and the external mode (rotation/translation) are the Raman peaks of BiVO₄-OV, which slightly

shifted to low frequency compared to $\text{BiVO}_4\text{-P}$ (Fig. S3a-c). The red shift was likely due to the low charged and coordinated Bi atom produced by oxygen vacancies.⁶ The displacement of oxygen atoms due to oxygen vacancies, resulting in the lattice distortion and compressive stress state, was responsible for not only the red-shift but also the intensive broadening of the band.⁷

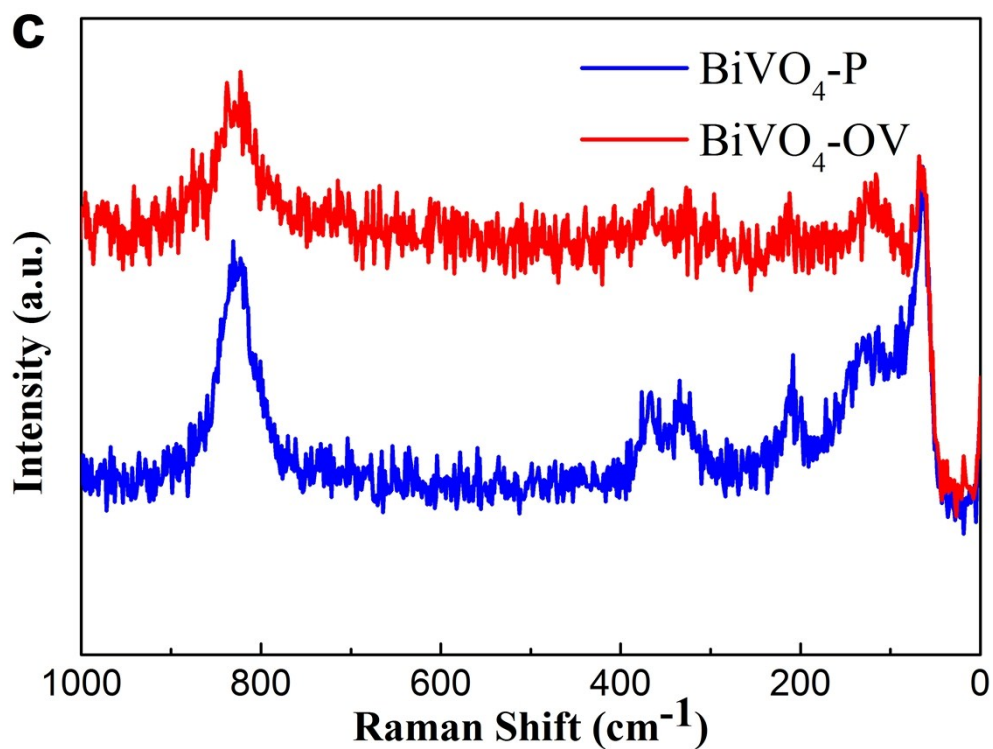


Fig. S4 Raman spectra (a laser line 785 nm)

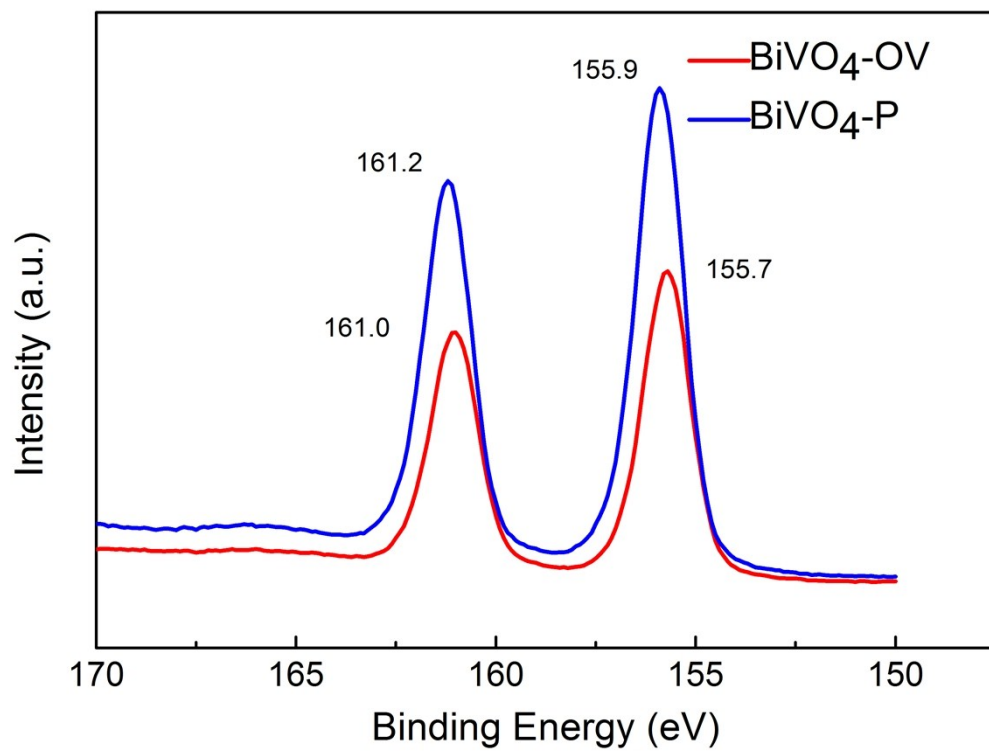


Fig. S5 the high resolution Bi 4f spectra of BiVO₄-OV and BiVO₄-P

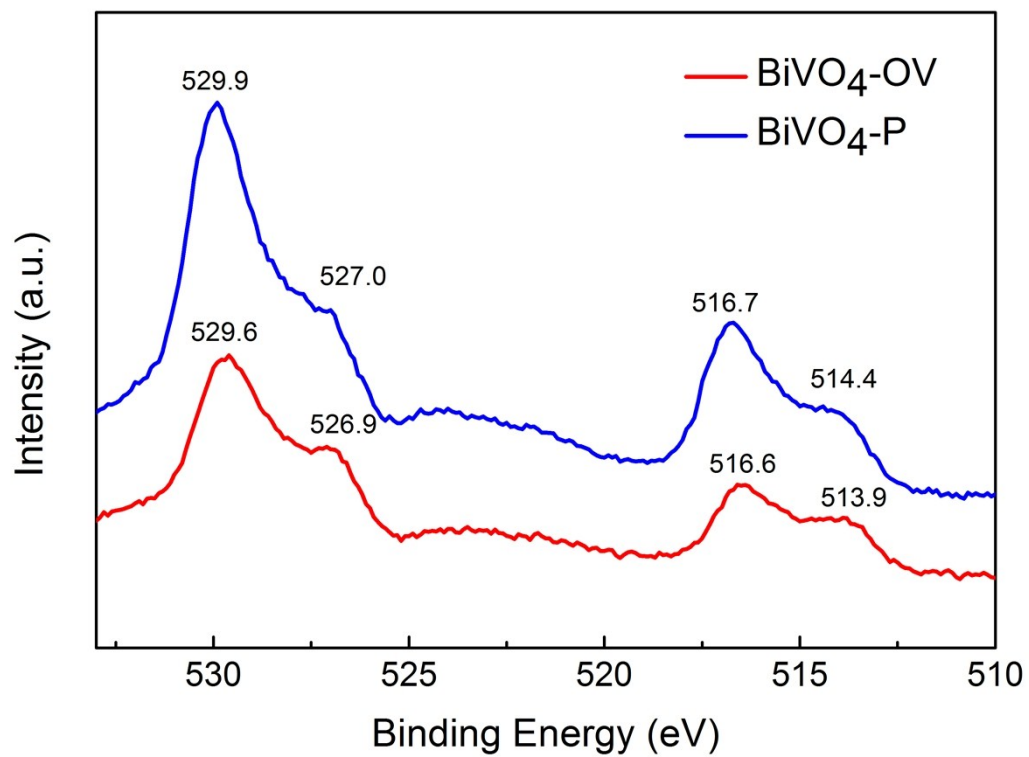


Fig. S6 the high resolution V 2p spectra of BiVO₄-OV and BiVO₄-P

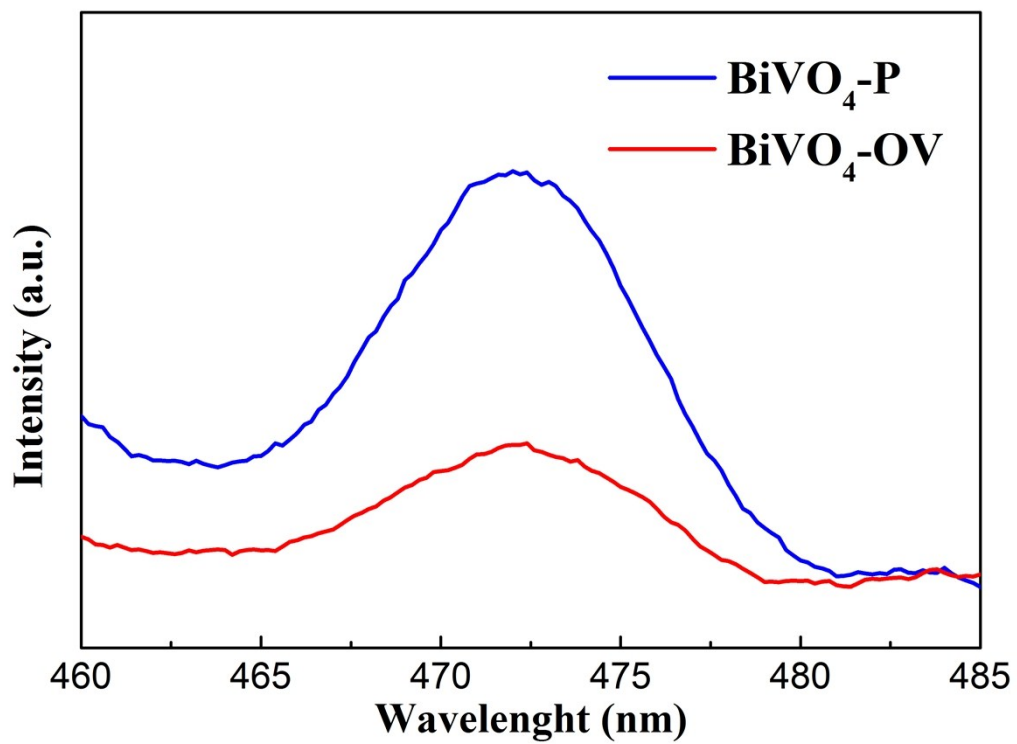


Fig. S7 PL spectra of the as-synthesized sample

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