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Supplementary Information for

Unveiling the Role of a Tetragonal $BiVO_4$ as a Mediator for Dual Phase $BiVO_4$/g-C_3N_4 Composite Photocatalysts to Enable High Performance in Water Oxidation via Z-scheme Charge Transfer

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Experimental Section

Materials and sample preparation

$BiVO_4$ was synthesized by co-precipitation. Bismuth (Ⅲ) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$, 10.0 mmol, Sigma Aldrich, purity: 98 %) and ammonium metavanadate (NH_4VO_3, 10.0 mmol, Junsei Chemical, purity: 99.0 %) were dissolved in nitric acid (HNO_3, 2 M, 50 ml, Samchun) separately with magnetic stirring. Two solutions were mixed slowly. Then, a yellow homogeneous solution was obtained. The specific amount of urea ($(NH_2)_2CO$, Sigma Aldrich) was added in 30 ml of urea solution and stirred at room temperature for 24 h. The amount of urea was determined to give the crystal structures of bismuth vanadate and the increasing pH of solution was found to cause the crystallization of $BiVO_4$ in solution. Also, precipitates were washed with deionized water, centrifuged (10,000 rpm for 20 min), and freeze-dried. In addition, g-C_3N_4 was synthesized via the calcination of melamine at 823 K for 4 h in static air (temperature elevation rate: 5 K min^{-1}). It is notable that alumina crucible has to be covered by a lid for inhibiting sublimation during calcination. Moreover, composite photocatalysts using $BiVO_4$ and g-C_3N_4 were synthesized by the impregnated co-precipitation, where 0.2 g of g-C_3N_4 was impregnated in the 30 ml of $BiVO_4$ solution after urea was dissolved and the synthesis was proceeded in room temperature for 24 h.

Characterization

The morphologies of samples were determined through the scanning electron microscopy SEM (JSM-7600F, JEOL) analysis. Moreover, the energy dispersive spectrometer (EDS) and transmission electron microscopy (TEM) data were collected by the cs-corrected scanning transmission electron microscopy (JEM-ARM200F, JEOL). In addition, the powder x-ray diffraction (PXRD) patterns were obtained with a diffractometer (Smartlab, Rigaku) using a

Cu Kα radiation at the operating condition of 40 kV and 30 mA, where the diffraction patterns were scanned from 10° to 70° with a 0.02 step size. Also, the UV-Vis spectrum was acquired by the UV-visible spectrophotometer (Cary-300, VARIAN). Moreover, the lifetimes of charge carriers in the photocatalysts and photoluminescence were detected and calculated by the time-correlated single photon counting (TCSPC) (FL920, Edinburgh Instruments) method. Additionally, the x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) measurements were carried out in a 7D beam line at the Pohang Accelerating Laboratory (PAL, Republic of Korea), where a calibration of each K-edge spectrum was accomplished by employing the reference spectrum from the corresponding metal foil. Furthermore, the x-ray photoelectron spectroscopy (XPS) spectra were obtained through K-alpha, Thermo VG Scientific. In addition, the thermogravimetric analysis (TGA) of a sample was proceeded by TG209F3, NETZSCH. Also, the zeta potential of a sample in deionized water was measured by the particle size analyzer (LS-Z2, Otsukael). Also, the ultraviolet photoelectron spectroscopy (UPS) was measured by HIS 13 (FOCUS) with a source energy of 21.21 eV (gas type: He I).

Photocatalytic activity measurement

Photocatalytic water oxidation was detected in the flow reactor system. 5 ml min^{-1} of Ar gas flew continuously and carried gas from the customized gas-tight reactor that contains 10 ml of 0.05 M $AgNO_3$ aqueous solution with 10 mg of dispersed photocatalysts to a gas chromatography. For the activity test, $AgNO_3$ was used as sacrificial agent that can accept electrons from the photocatalyst. Photocatalytic activity was measured for 4 h with on-line gas injection in every 10 min. 300 W Hg (Xe) DC Arc lamp (66902, Newport) with AM 1.5G filter was used as a light source. In addition, an oxygen evolution rate was determined through a detection of oxygen in the standard gas using the on-line gas chromatography (Agilent 7890, thermal conductivity detector, Ar carrier, Molecular sieve 5A 60/80 column, 313 K for the oven temperature), where a known concentration of oxygen in the standard gas was used to measure the evolving oxygen concentration by photocatalytic water oxidation. The three-point-calibration analysis was also conducted by 10 % O_2, 0.51 % O_2 standard gas and Ar gas having no oxygen.

Isotope-labelling experiment

Isotopically-labelled $H_2{}^{18}O$ experiments were performed to trace the source of O_2 on photocatalytic water oxidation. The closed system for photocatalytic water oxidation was also achieved using 10mL Pyrex round flask, where 10 mg of photocatalysts were dispersed in 9 mL $H_2{}^{16}O$ and 1 mL $H_2{}^{18}O$ of 0.05 M $AgNO_3$ solution. In addition, the reactor was purged with Ar gas for 30 min to remove all remaining O_2 and to fill the reactor with only Ar gas. The photocatalytic reaction was also conducted with a 300W xenon lamp having the fitted IR blocking filter and AM1.5G filter. Moreover, the evolved ^{18}O containing gas in the dead volume of a reactor was injected in the GC-MS (Agilent, GC-7890A and MS-5975C) equipped with a capillary column (Supleco, 30 m × 0.32 mm) and MSD (Mass selective detector, inert triple-axis detector) for the identification of m/z 36.

Photoelectrochemical (PEC) electrode fabrication

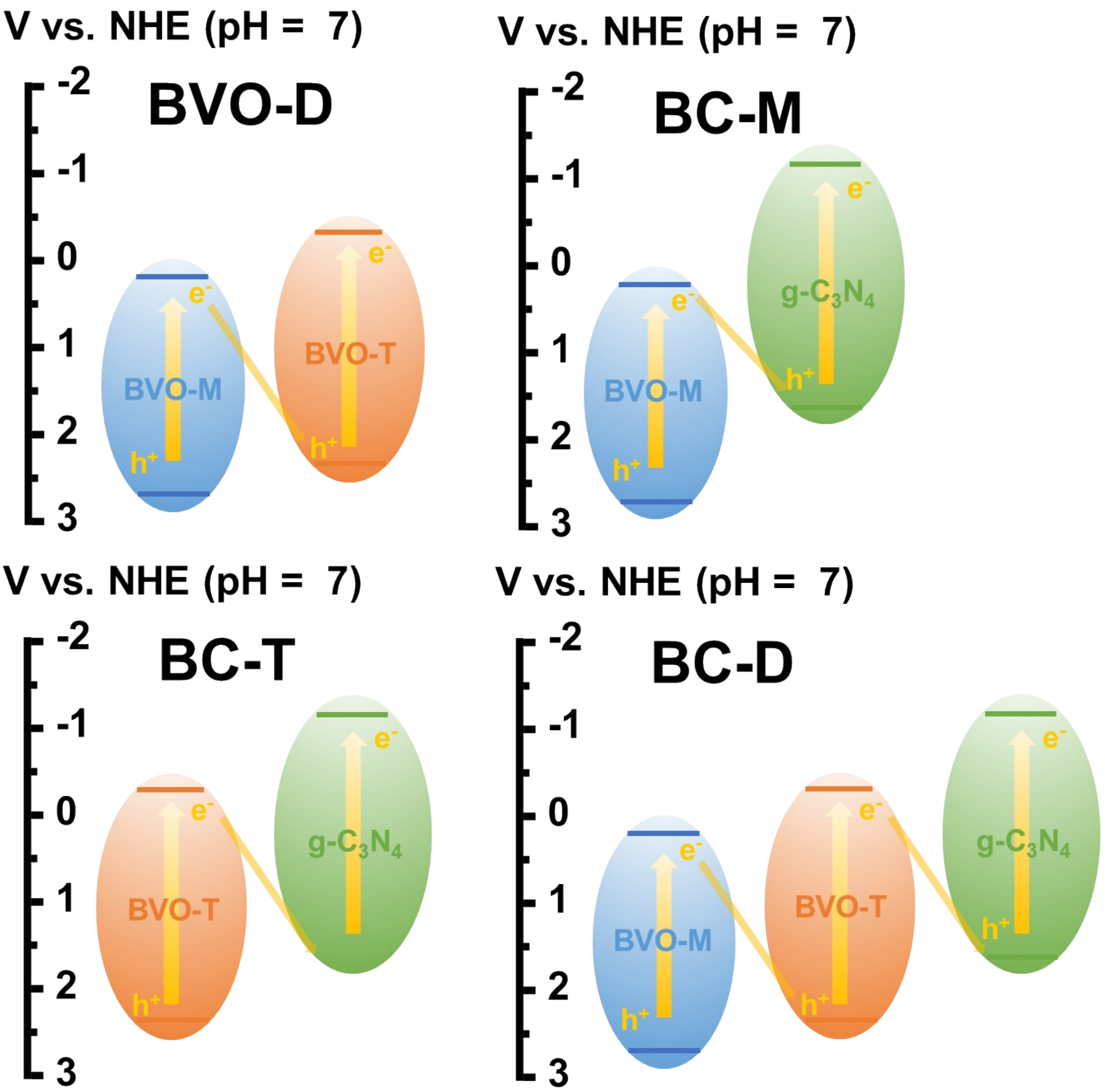
The PEC electrodes were fabricated by powder transfer method. First, 20 mg of the samples was suspended in 1 mL isopropanol. The suspension was dispersed by ultrasonication for 30 min. The dispersed suspension was deposited on a 3 × 3 glass substrate and dried for overnight under room temperature. Subsequently, Au layers having 300 nm thickness were deposited using vacuum evaporation. Finally, the Au film holding the particulate photocatalysts was touched each other with other carbon tape attached glass plate (about 3×3 cm) and then lifted off the primary glass plate. The separated PEC electrode was ultrasonicated for 30 min to remove excess powder.

Mott-Schottky experiment

The Mott-Schottky measurements were carried out by using PINE Instrument Quartz Photoelectrochemical Cell kit to the potentiostat (Biologic SP-240). The Hg/HgO reference electrode and Pt counter electrode were used to measure Mott-Schottky properties. An aqueous electrolyte of 1 M KOH (pH 14) was continuously purged with Ar gas (99.999%) during reaction. 300 W Xe arc lamp (ORIEL) equipped with NEWPORT liquid (infra-red light) filter, light shaping diffuser (homogenizer) were used for a light irradiation. Also, the intensity of light is one sun condition (100 mW/cm^2) under AM 1.5G illumination. The measured potentials (vs. the Hg/HgO) were converted into the reversible hydrogen electrode (V_{RHE}) scale by using the Nernst equation of

$$V_{RHE}=V_{Hg/HgO}+ 0.059 \times \mathrm{pH} + Vo_{Hg/HgO} \text{ vs. NHE}$$

where $V_{Hg/HgO}$ is the experimental potential value against the 1 M KOH Hg/HgO reference electrode, pH is 14 at a 1 M KOH aqueous solution and $Vo_{Hg/HgO}$ vs. NHE is 0.098 V at room temperature.



Scheme S1. The proposed charge transfer processes in photocatalysts. BVO-M and BVO-T stands for monoclinic $BiVO_4$ and tetragonal $BiVO_4$ structures, respectively, BVO-D is the dual phase $BiVO_4$ composed of two BVO-M and BVO-T phases, BC-M stands for the composite photocatalyst composed of BVO-M and g-C_3N_4, BC-T stands for the composite photocatalyst composed of BVO-T and g-C_3N_4, and BC-D stands for the composite photocatalyst composed of BVO-M, BVO-T, and g-C_3N_4.

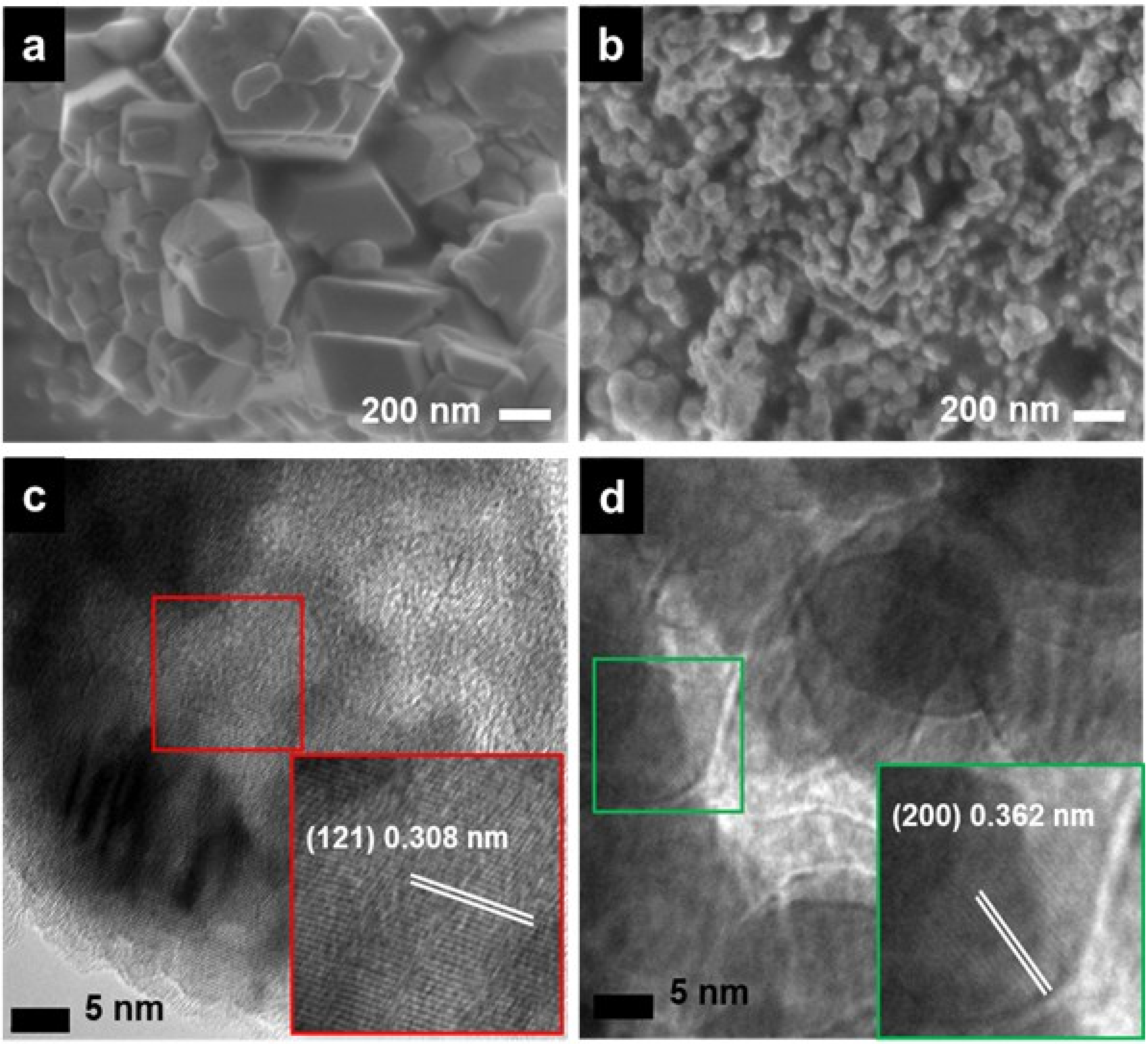


Figure S1. The SEM and TEM images for monoclinic scheelite and tetragonal zircon-type $BiViO_4$ structures. The SEM images of (a) BVO-M and (b) BVO-T. The TEM images of (c) BVO-M and (d) BVO-T.

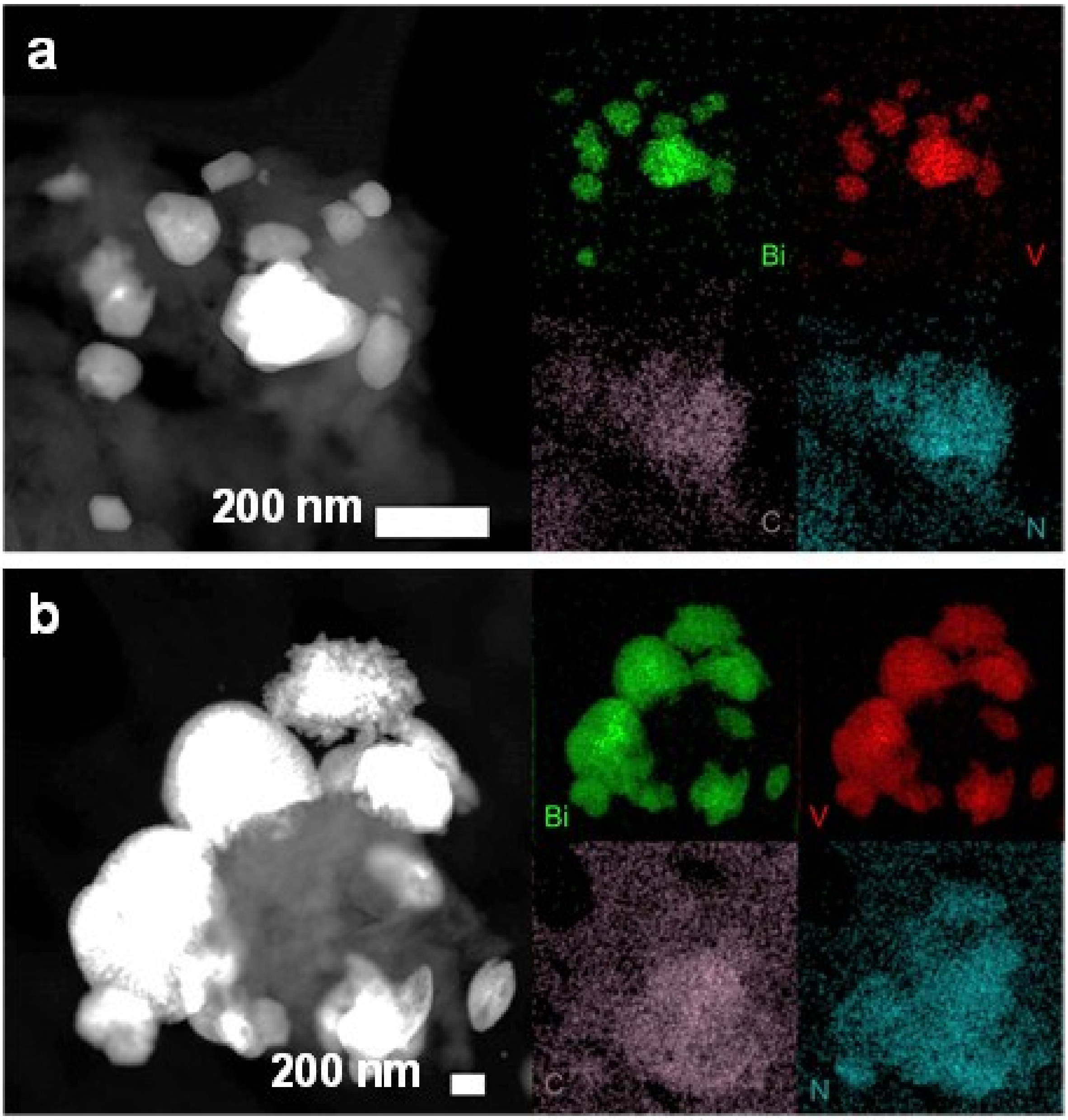


Figure S2. The EDS mapping images of the prepared composite catalysts. Those for (a) BC-M, (b) BC-T

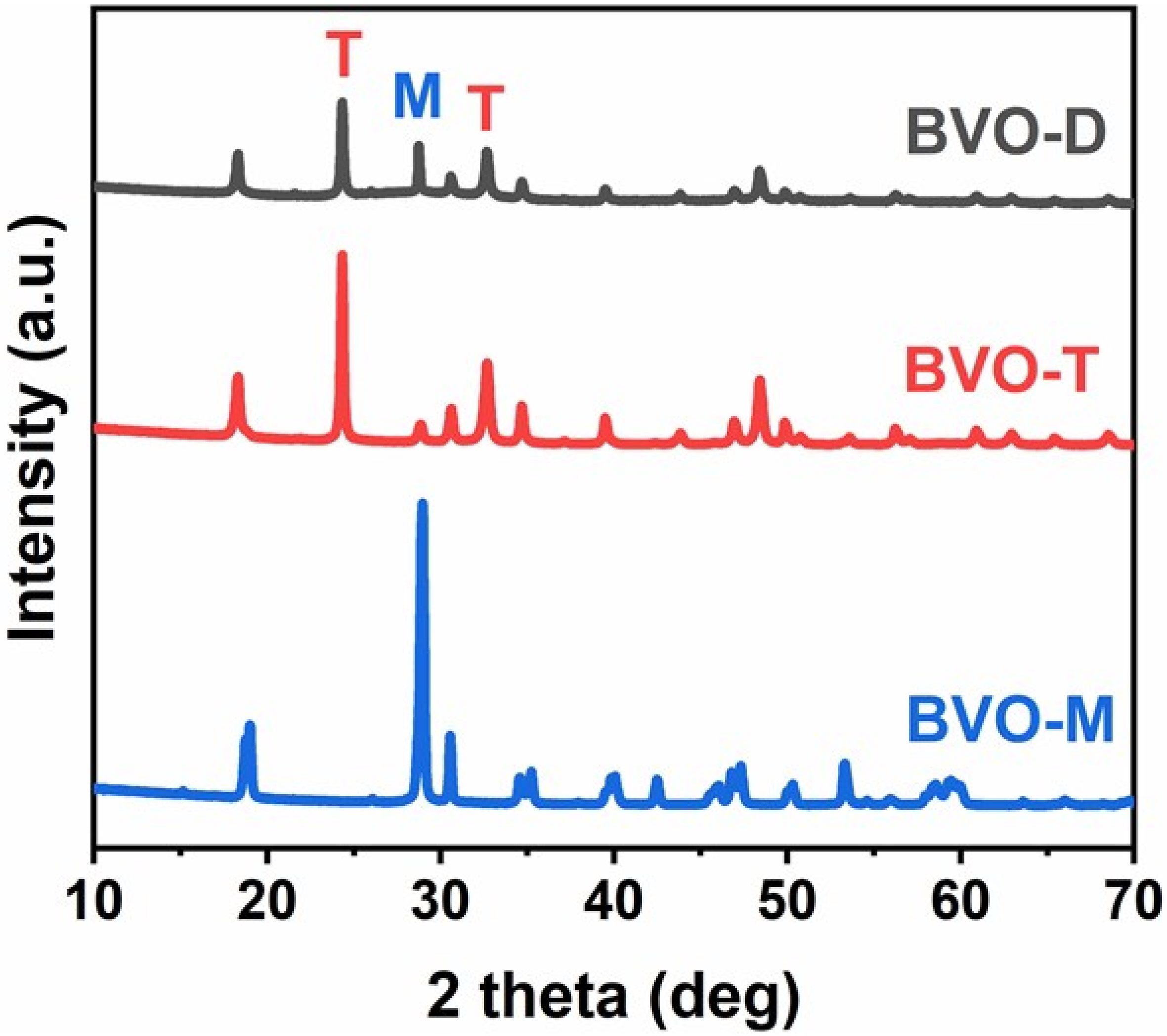


Figure S3. The XRD patterns of prepared BVO-D, BVO-T, and BVO-M structures.

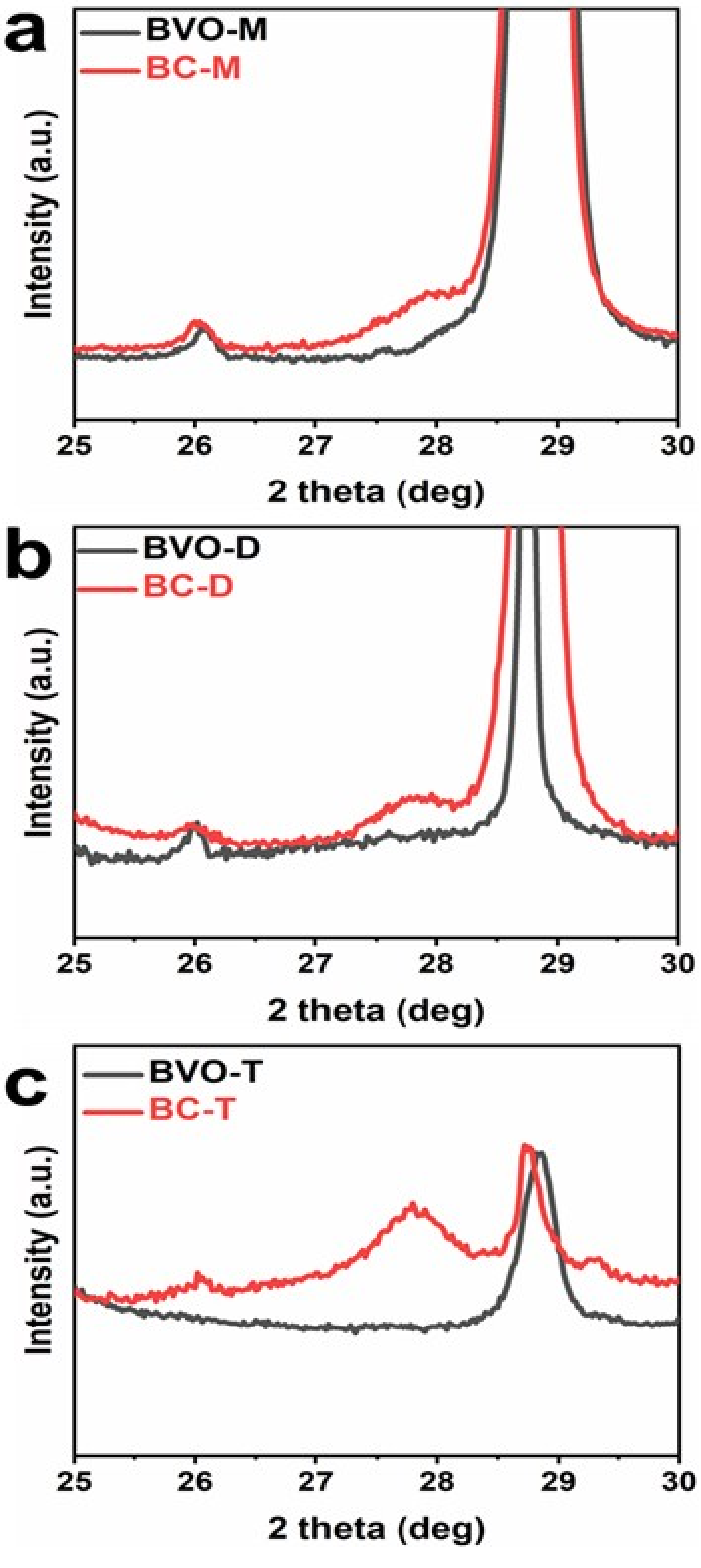


Figure S4. The XRD patterns verifying the existence of C_3N_4 in composite photocatalysts. Those for (a) BVO-M and BC-M, (b) BVO-D and BC-D, and (c) BVO-T and BC-T.

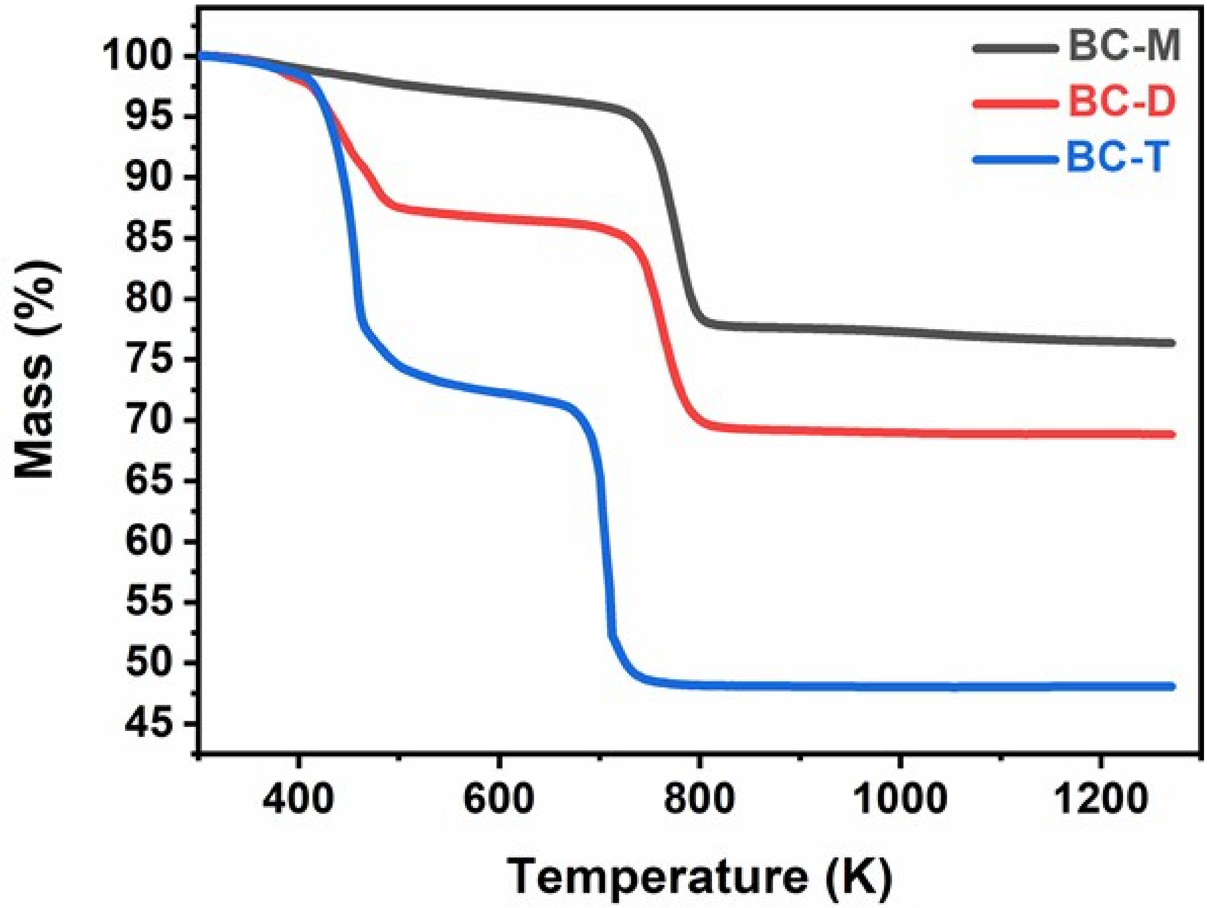


Figure S5. The TGA of the composite photocatalysts

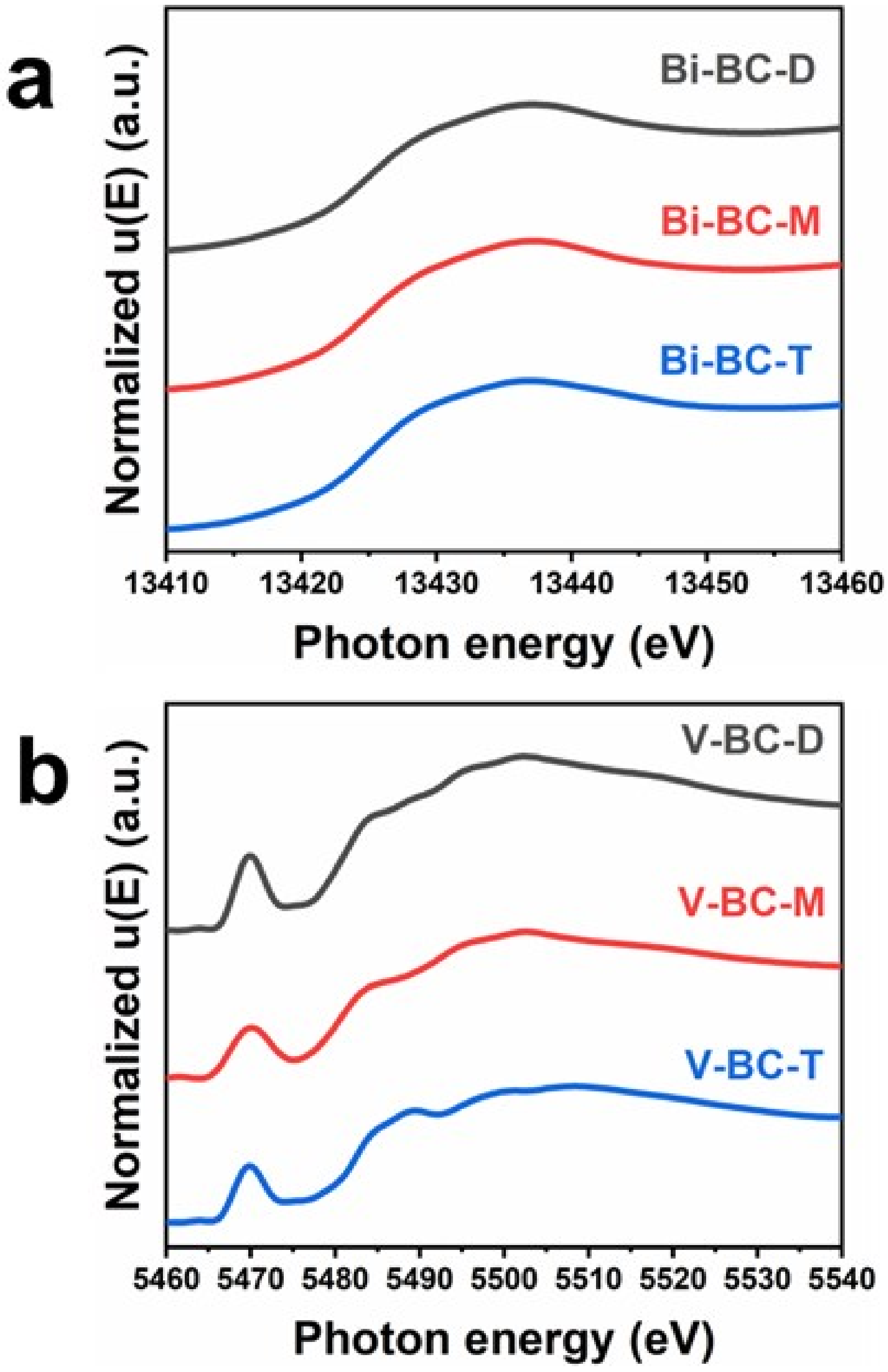


Figure S6. The XANES spectra. (a) The XANES spectra at the Bi L3-edge of the composite catalysts, where the sharp edge peaks at 13,430 eV are attributed to the dipole-allowed $2p^{3/2}$–6d transition. (b) The V K-edge XANES spectra showing the same trends as the Bi spectra, meaning that the V ions have the same oxidation state in the composites.

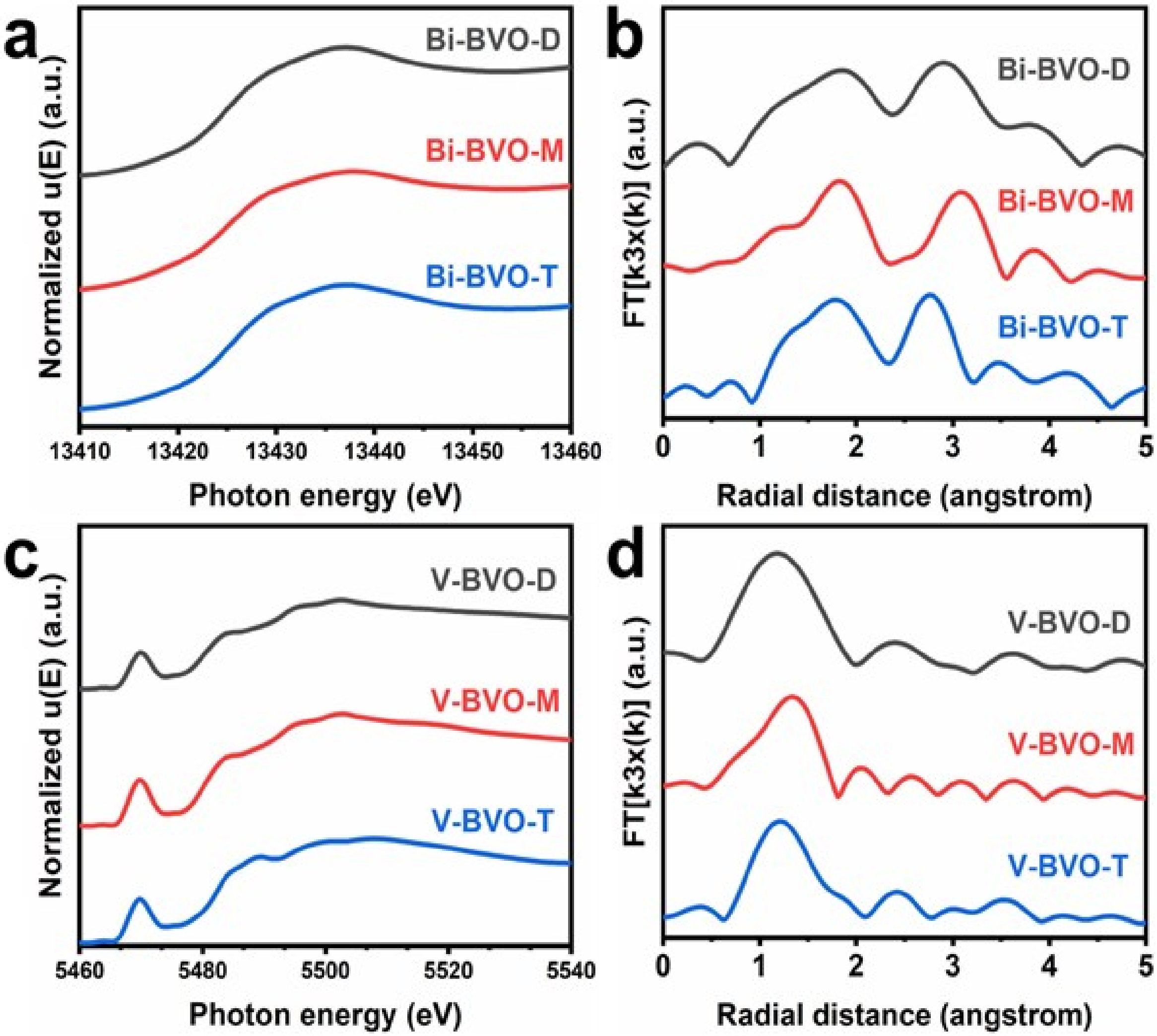


Figure S7. The XAS spectra obtained through XANES and EXAFS analyses. (a) The Bi XANES data, (b) the Bi EXAFS data, (c) the V XANES data, and (d) the V EXAFS data.

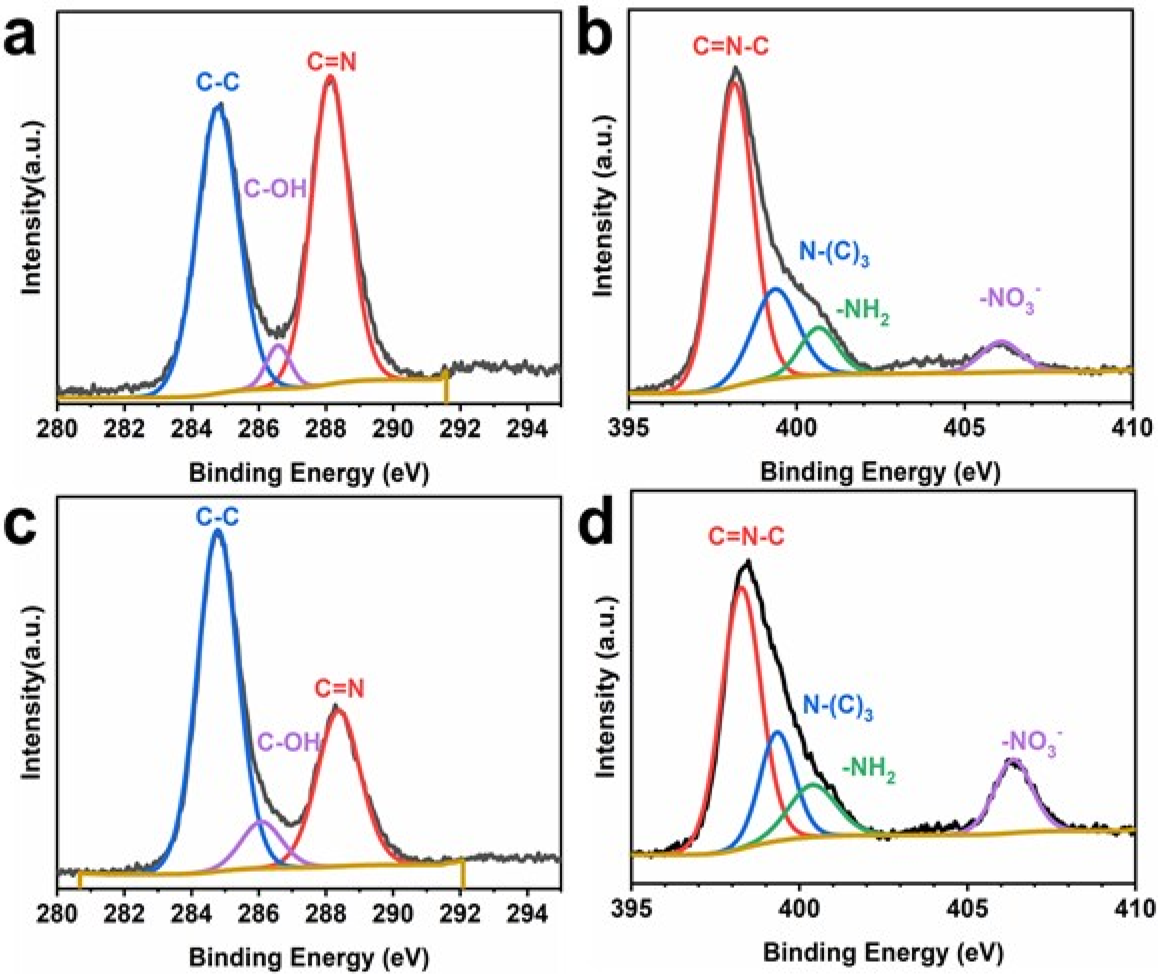


Figure S8. The XPS spectra of (a,b) BC-M and (c,d) BC-T structures.

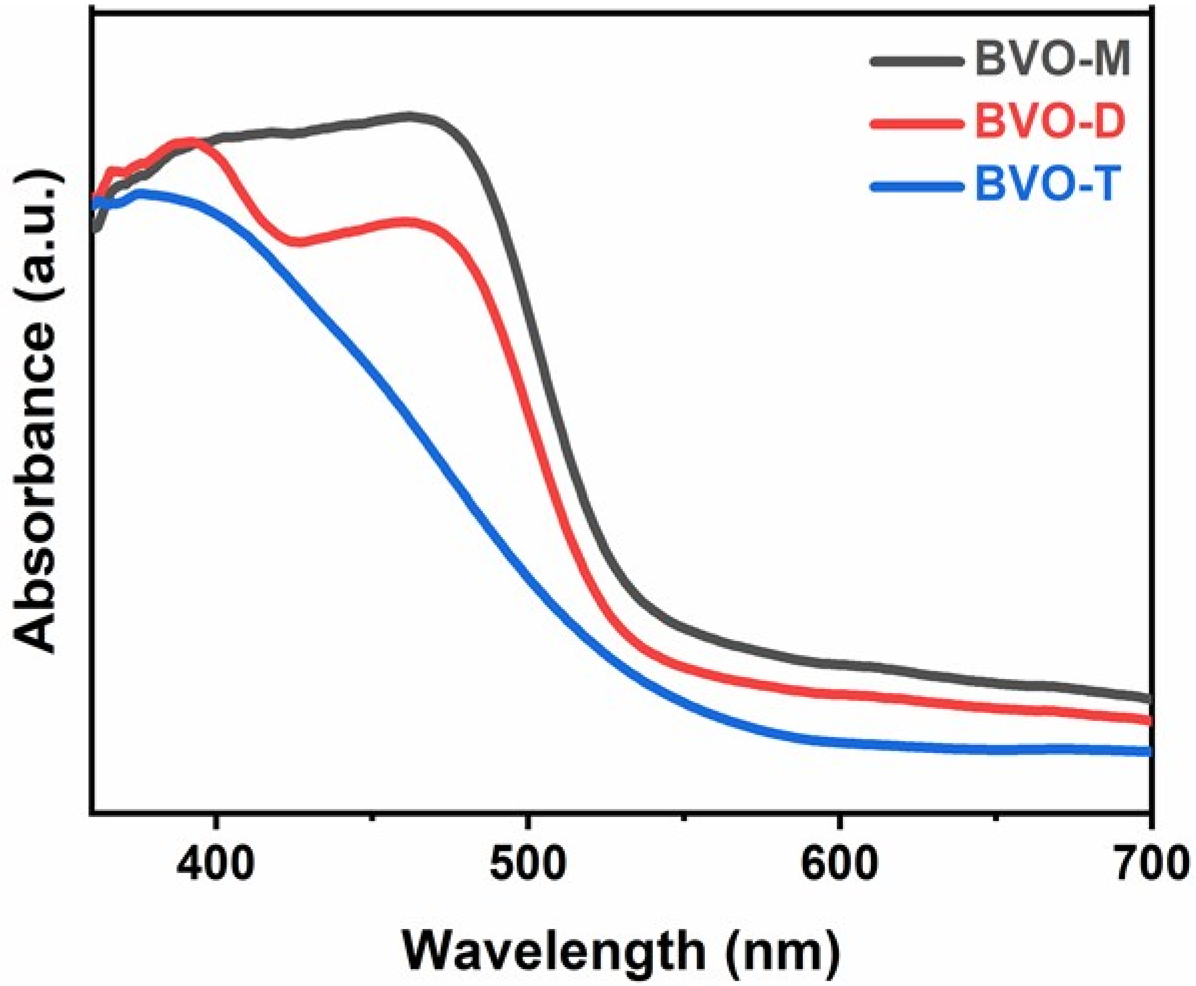


Figure S9. The UV-Vis spectra of BVO-M, BVO-D, and BVO-T samples.

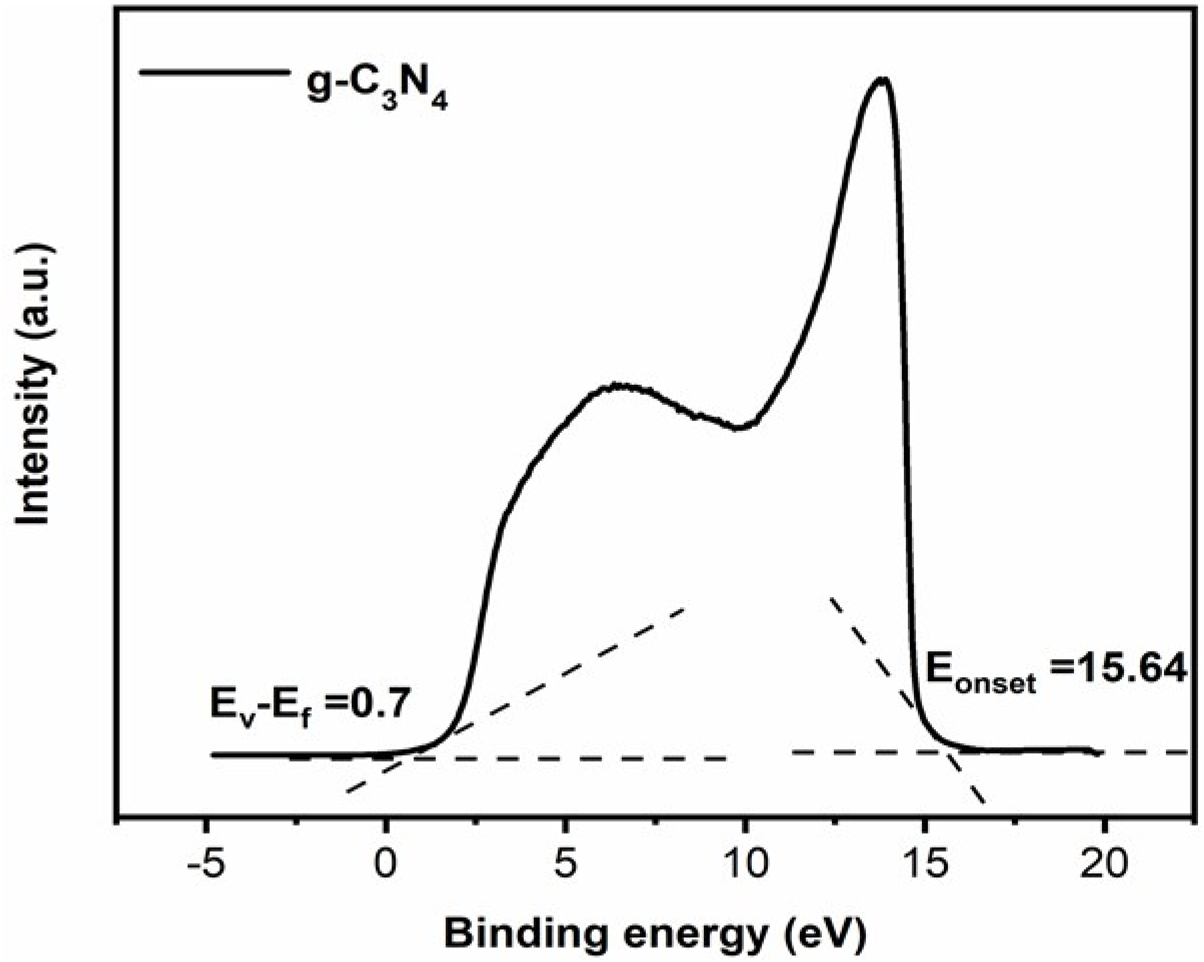


Figure S10. The ultraviolet photoelectron spectroscopy (UPS) spectrum of g-C_3N_4.

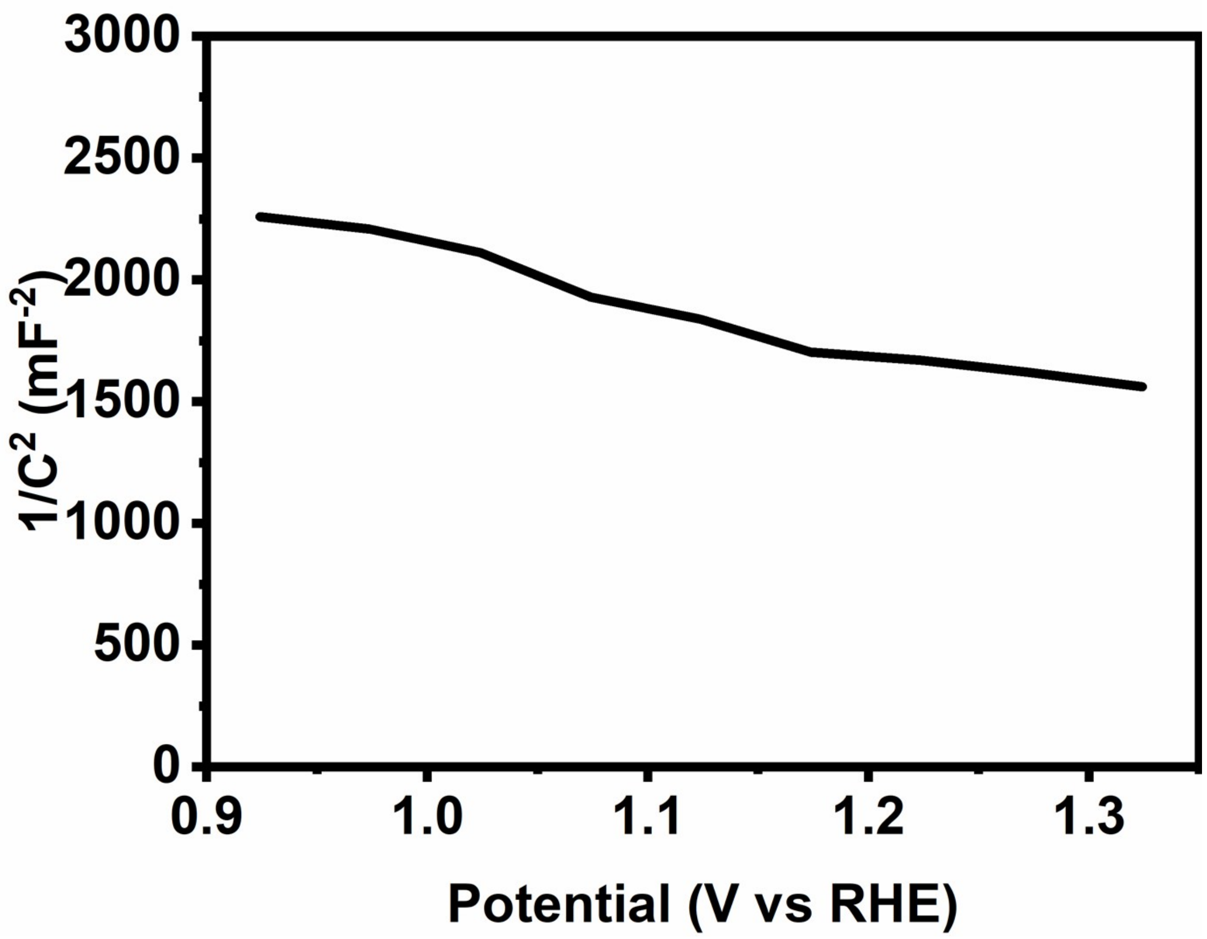


Figure S11. Mott-Schottky plot of BC-M.

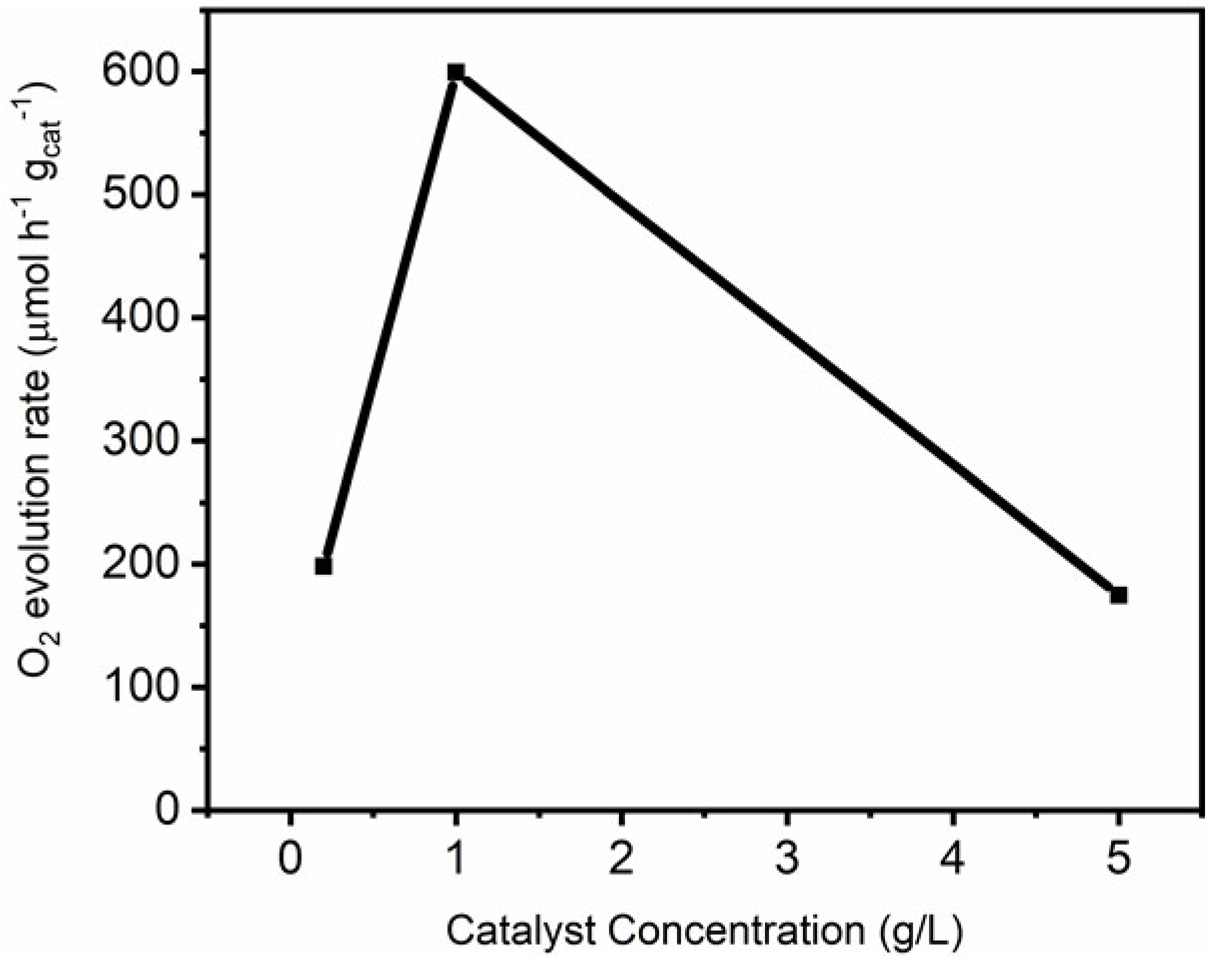


Figure S12. The optimal ratio for photocatalytic reaction.

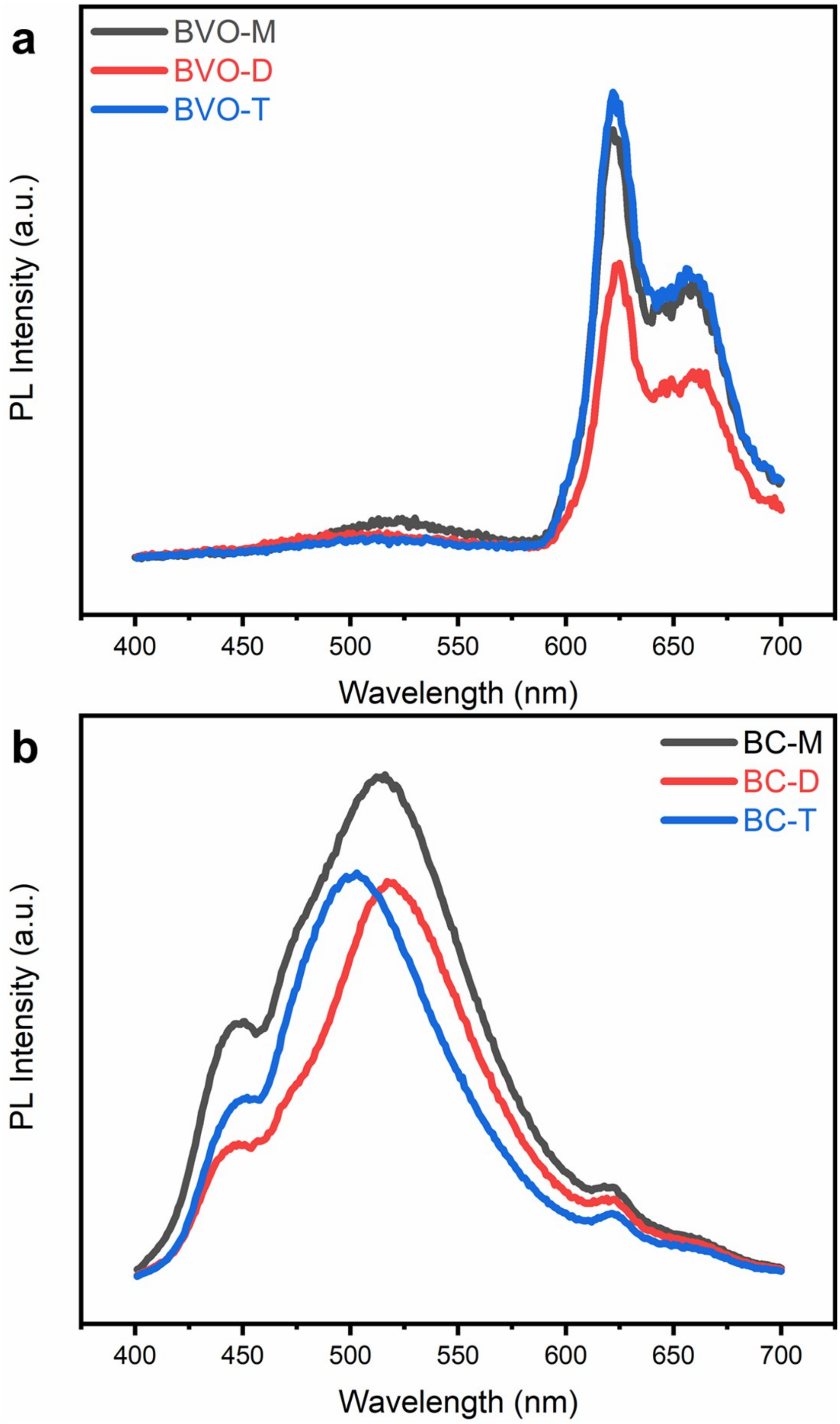


Figure S13. The PL intensities of prepared photocatalysts

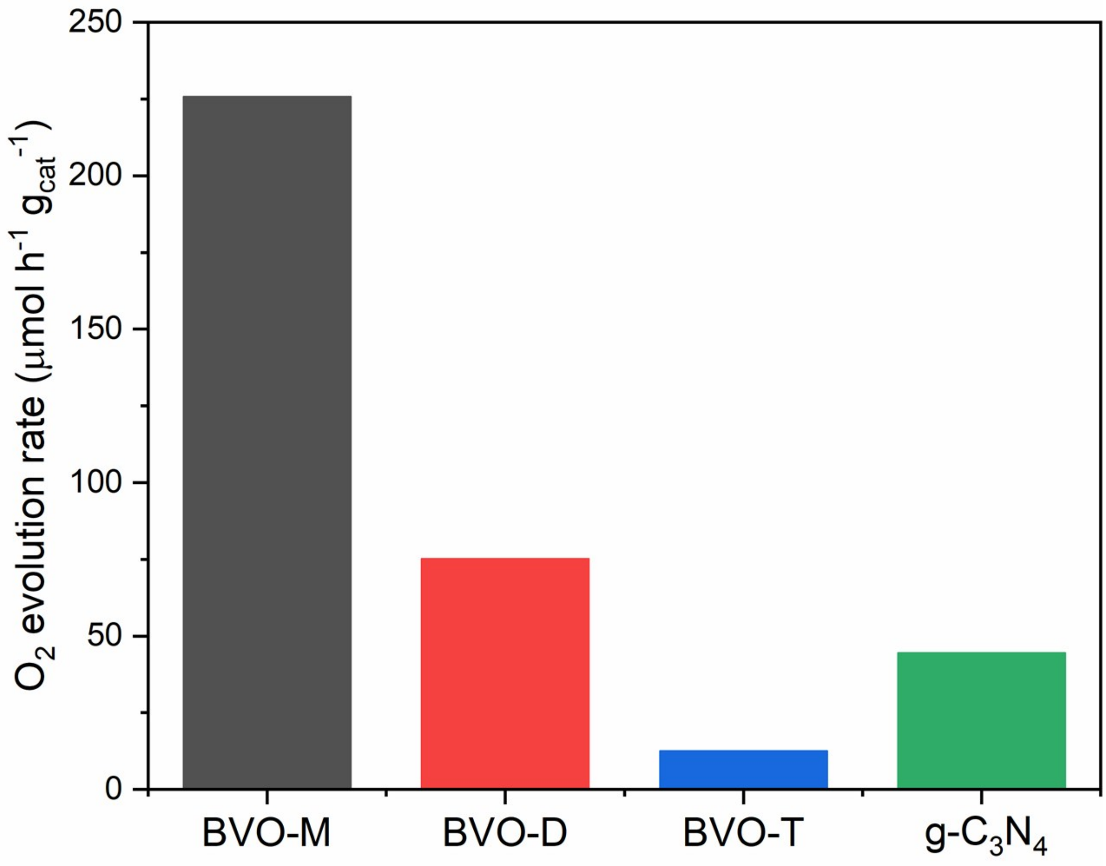
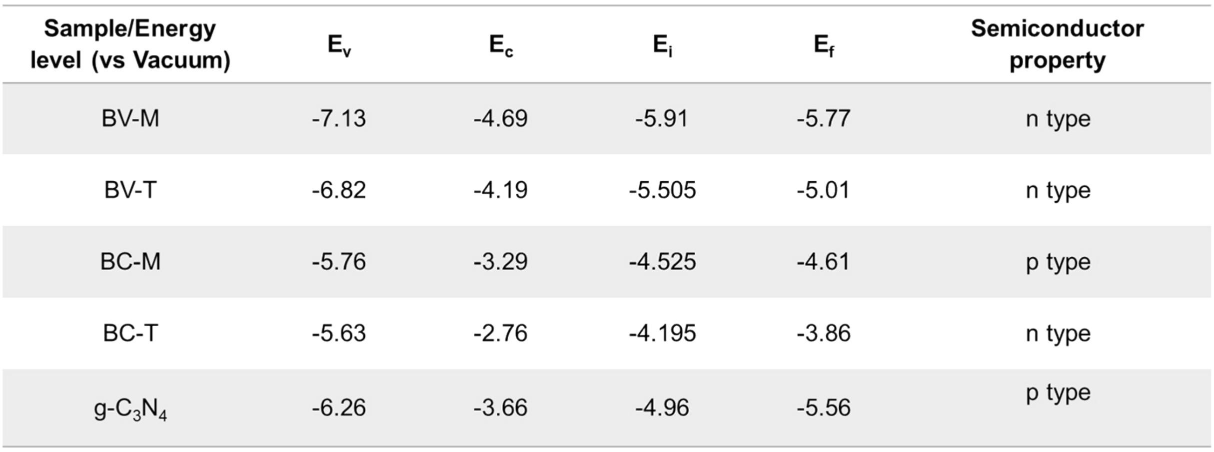
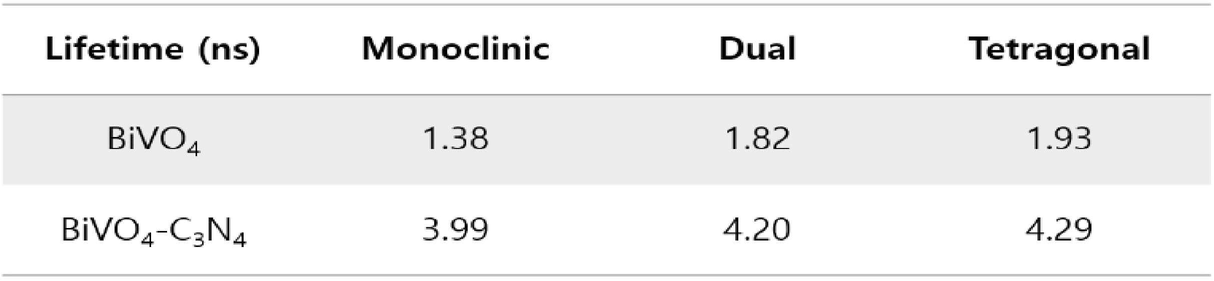


Figure S14. The oxygen evolution rates of $BiVO_4$ and g-C_3N_4 catalysts.



Sample/Energy level (vs Vacuum)	E_v	E_c	E_i	E_f	Semiconductor property
BV-M	-7.13	-4.69	-5.91	-5.77	n type
BV-T	-6.82	-4.19	-5.505	-5.01	n type
BC-M	-5.76	-3.29	-4.525	-4.61	p type
BC-T	-5.63	-2.76	-4.195	-3.86	n type
g-C_3N_4	-6.26	-3.66	-4.96	-5.56	p type

Table S1. The photocatalyst band energy levels calculated by the UPS analysis.



Lifetime (ns)	Monoclinic	Dual	Tetragonal
$BiVO_4$	1.38	1.82	1.93
$BiVO_4$-C_3N_4	3.99	4.20	4.29

Table S2. The lifetime data measured by the TCSPC measurements for charge carriers of prepared photocatalysts.