

Supporting Information

Tetragonal to Monoclinic Crystalline Phase Change of BiVO₄ via Microwave-Hydrothermal Reaction: In Correlation with Visible-Light-Driven Photocatalytic Performance

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Material Characterizations. A Rigaku Ultima IV X-ray diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 30 mA was used to scan the diffraction angles from 10° to 80° with step size of $0.02^\circ/\text{second}$ to carry out X-ray Diffraction Analysis (XRD) and compared with standard ICDD (International Centre for Diffraction Data). GSAS software and CIF files for both monoclinic scheelite and tetragonal zircon BiVO $_4$ phase were used for Rietveld analyses for all samples. The crystallite sizes of the samples were calculated using Scherrer equation. Raman spectroscopic analysis were performed using a room-temperature confocal Raman spectrometer (Renishaw in-Via) with laser excitation energy of 785 nm. The diffused reflection spectra (DRS) of the synthesized BiVO $_4$ samples were recorded using a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). The surface morphologies of the synthesized samples were imaged with a Field Emission-Scanning Electron Microscopy (FE-SEM). (Quanta-FEG450) equipped with an energy dispersive X-ray analyzer (Bruker). High Resolution Transmission Electron Microscopy images were carried out to obtain the images (HR-TEM) JOEL/JEM 2100USA. For HR-TEM analysis, the samples were initially dispersed in ethanol using an ultrasonicator and dropped on a copper grid. FLUOROLOG–FL3-11 (Jobin Yvon) were used to record the steady-state PL emission spectra with excitation wavelengths from 300 to 480 nm and spectral resolution of 3 nm. Time-resolved photoluminescence (TRPL) spectra were also measured using FLUOROLOG–FL3-11 with a 488 nm femtosecond laser.

Result and discussion

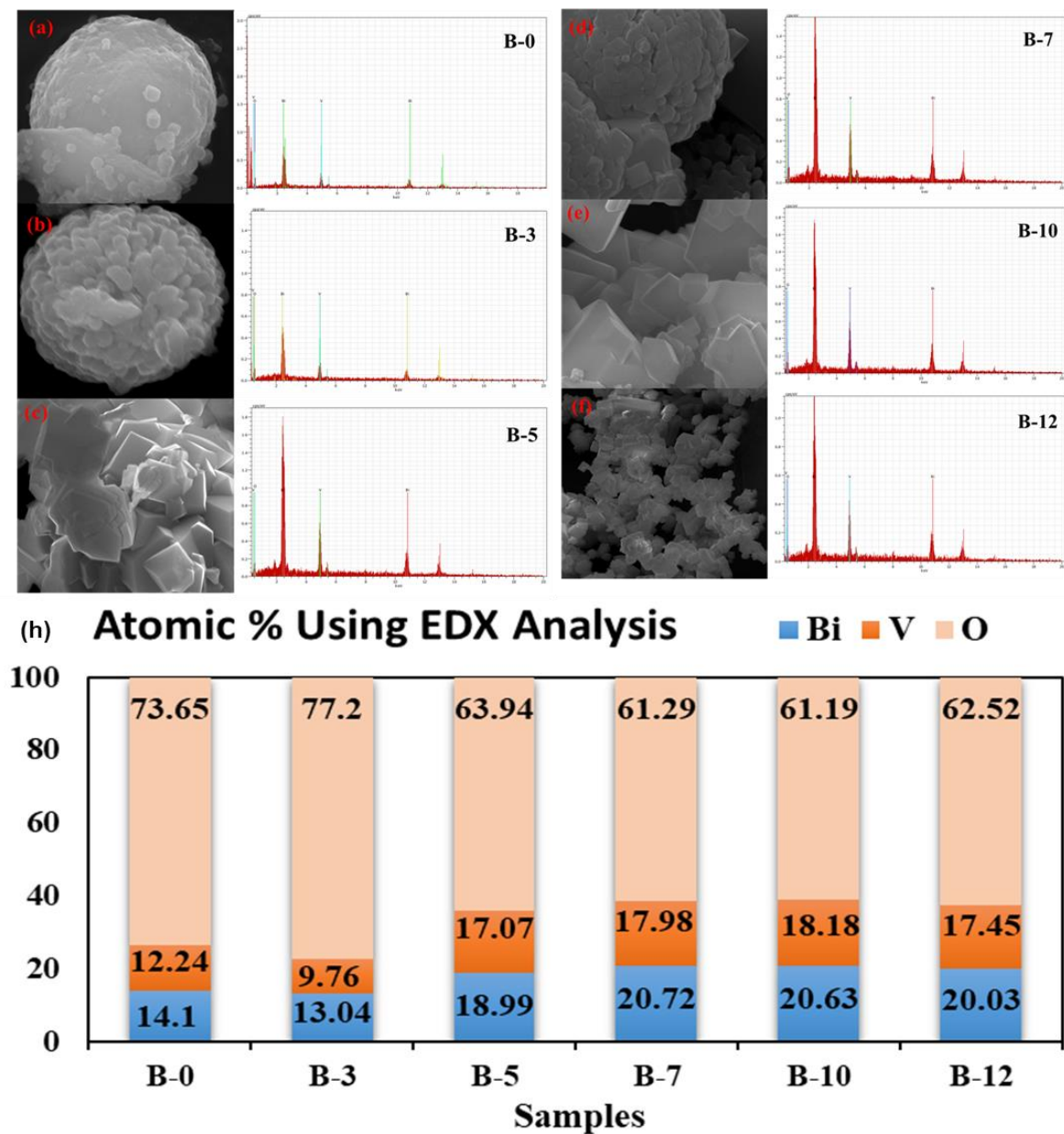


Figure S1. EDX spectra of BiVO₄ material synthesis at various hydrolysed time named as (b) B-0, (c) B-3, (d) B-5, (e) B-7, (f) B-10, and (g) B-12 samples and (h) Atomic weight % of elements of B-0 to B-12 samples.

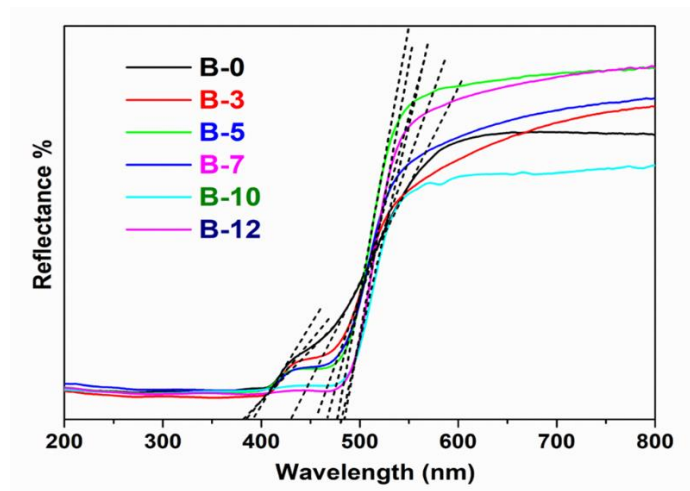


Figure S2. UV Reflectance spectra for B-0, B-3, B-5, B-7, B-10, and B-12 samples

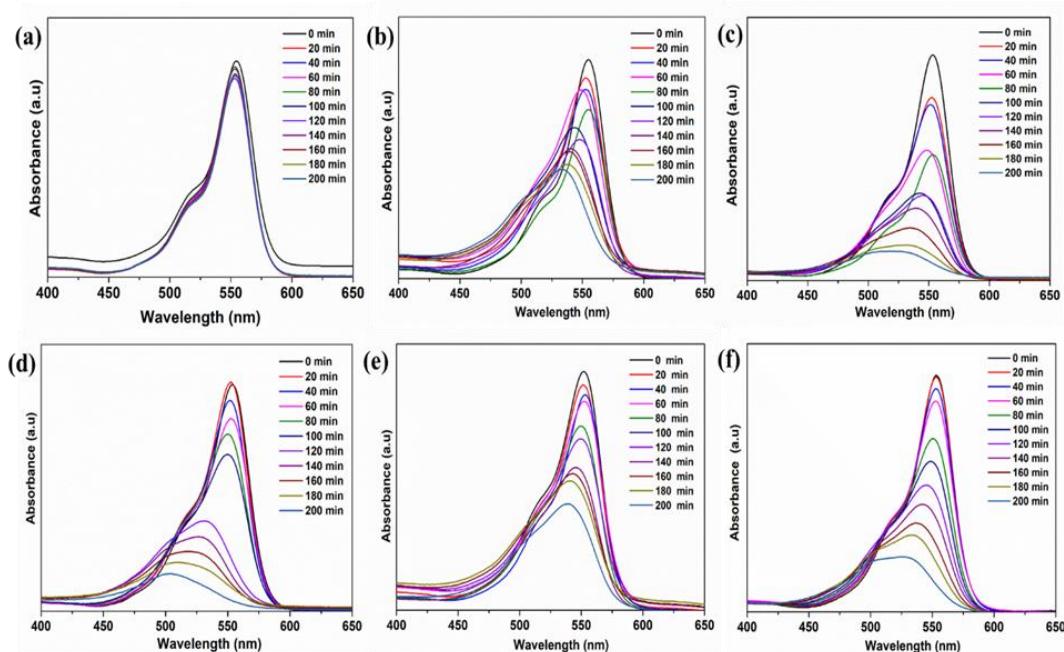


Figure S3. UV absorption of RhB aqueous solution (a) Blank Dye without photocatalyst, (b) B-0, (c) B-3, (d) B-5, (e) B-10, and (f) B-12 samples.

Photocatalyst test

The photocatalyst experiment was done near to the Advanced Functional Nanomaterials lab, Centre for Nanoscience and Technology, Pondicherry university campus (geographical location-12.0219° N, 79.8575° E), India. Solar intensity variation during the experiment was given in figure below.

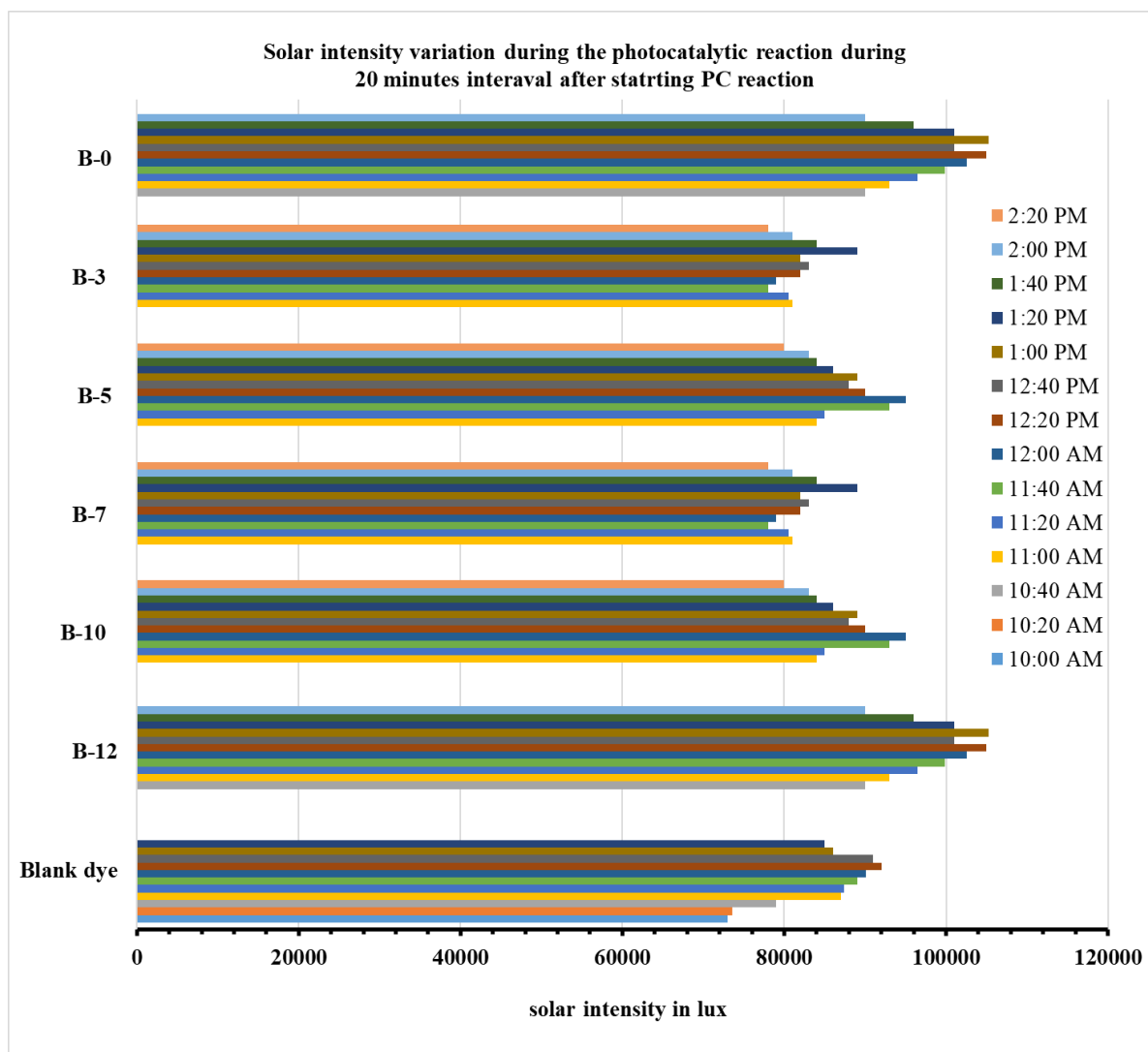


Figure S4 .Natural sun intensity variation during the Photocatalytic reactions (a) blank dye (b) B-0, (c) B-3, (d) B-5, (e) B-7, (f) B-10, and (g) B-12 samples. The intensity in lux.

Trapping experiment for detecting active species:

Description of trapping experiment for detecting active species during photocatalytic reaction in presence of B-7 material was done as previously reported.^{1,2} 2.5 mM IPA (isopropanol), 2.5 mM MeOH (methyl alcohol), and 2.5 mM EDTA-2Na (ethylenediamine tetraacetic acid disodium) were mixed with 250 ml aqueous solution Rhodamine B solution in presence of 0.250g B-7 material.

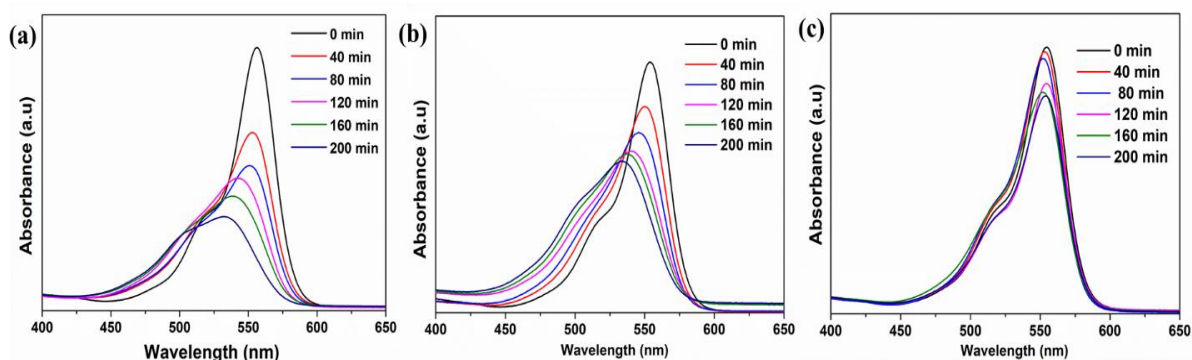


Figure S5. UV absorption spectra for trapping experiment for detecting active species of B-7, BiVO₄ photocatalytic material in presence of (a) IPA (b) MeOH (c) EDTA.

Recycle test:

In the recycle experiment, the recovered photocatalyst was centrifuge, washed with acetone for removing any impurities, and dried at 70°C for 10 h. Then, the photocatalyst was weighed again to add the lost portion and used for the next run.

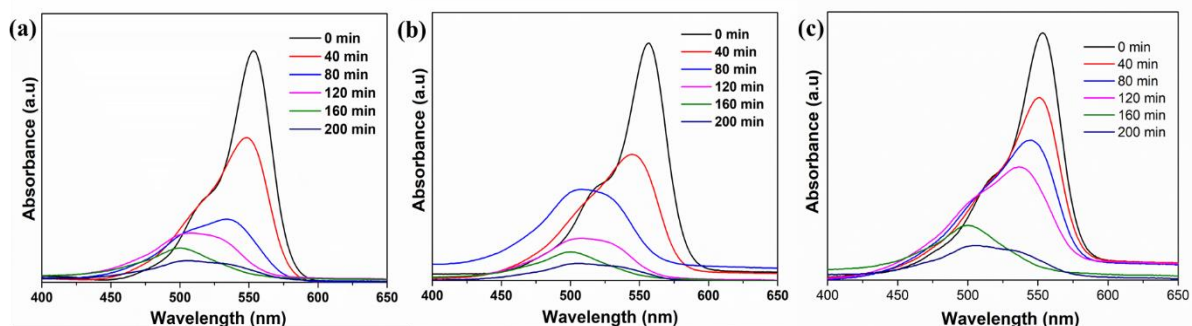


Figure S6. Recycle test absorption spectra for B-7, BiVO₄ photocatalytic material, (a) recycle test 1, (b) recycle test 2, (c) recycle test 3.

Table S1. XRD Rietveld Refinement Analysis structural features for BiVO₄ material.

S.No.	Rp	Rwp	χ^2	R _{Bragg}
B-0	18.91	24.97	1.419	13.06
B-3	17.68	23.27	1.429	11.34
B-5	12.83	25.06	1.883	12.83
B-7	17.99	24.59	1.509	11.47
B-10	21.63	28.71	1.832	15.73
B-12	19.88	27.38	1.534	12.55

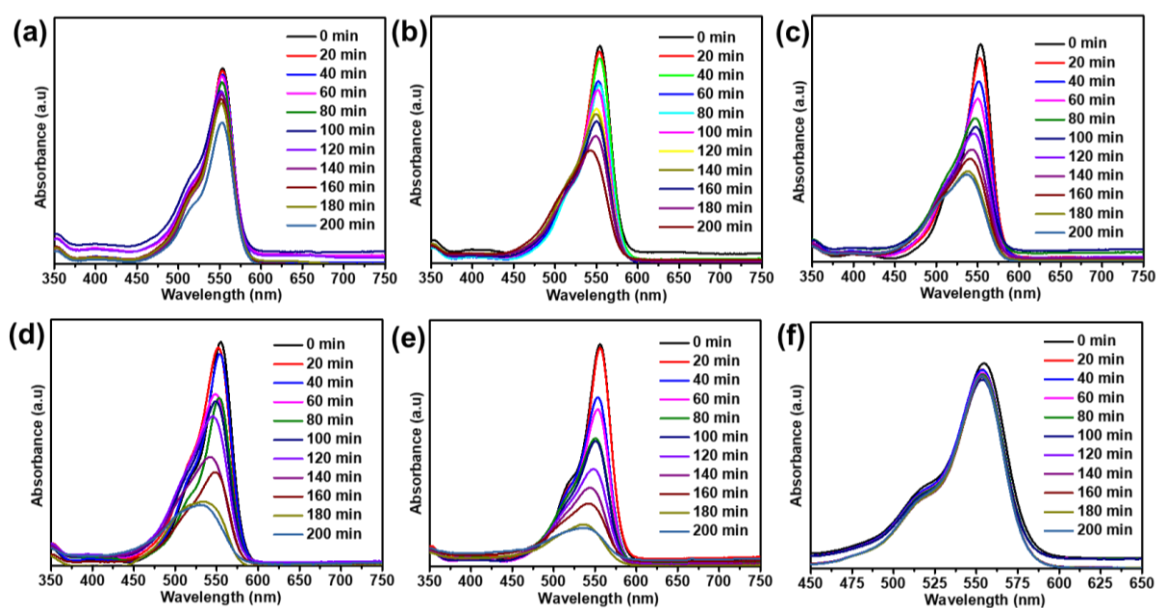


Figure S7. UV absorption curves of RhB aqueous solution under simulated sunlight in presence of (a) B-0, (b) B-3, (c) B-5, (d) B-7, (e) B-10 samples and (f) Blank Dye without photocatalyst.

References:

1. Dong, S.; Feng, J.; Li, Y.; Hu, L.; Liu, M.; Wang, Y.; Pi, Y.; Sun, J.; Sun, J. Shape-controlled synthesis of BiVO_4 hierarchical structures with unique natural-sunlight-driven photocatalytic activity, *Applied Catalysis B: Environmental*, **2014**, 152–153, 413–424.
2. Fan, T.; Chen, C.; Tang, Z. Hydrothermal synthesis of novel $\text{BiFeO}_3/\text{BiVO}_4$ heterojunctions with enhanced photocatalytic activities under visible light irradiation, *RSC Adv.*, **2016**, **6**, 9994-10000.
3. Liu, H.; Hou, H.; Gao, F.; Yao, X.; and Yang, W. Tailored Fabrication of Thoroughly Mesoporous BiVO_4 Nanofibers and Their Visible-Light Photocatalytic Activities, *ACS Appl. Mater. Interfaces*, **2016**, **8**, 1929–1936.