

Electronic Supplementary Material (ESI)

3 D Hierarchical heterostructures of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ with enhanced oxygen evolution reaction from water under natural sunlight

Aniruddha K. Kulkarni, Rajendra P. Panmand, Yogesh A. Sethi, Sunil R. Kadam, Deepak. R. Patil, Anil V. Ghule * and Bharat B. Kale *

Figure S1

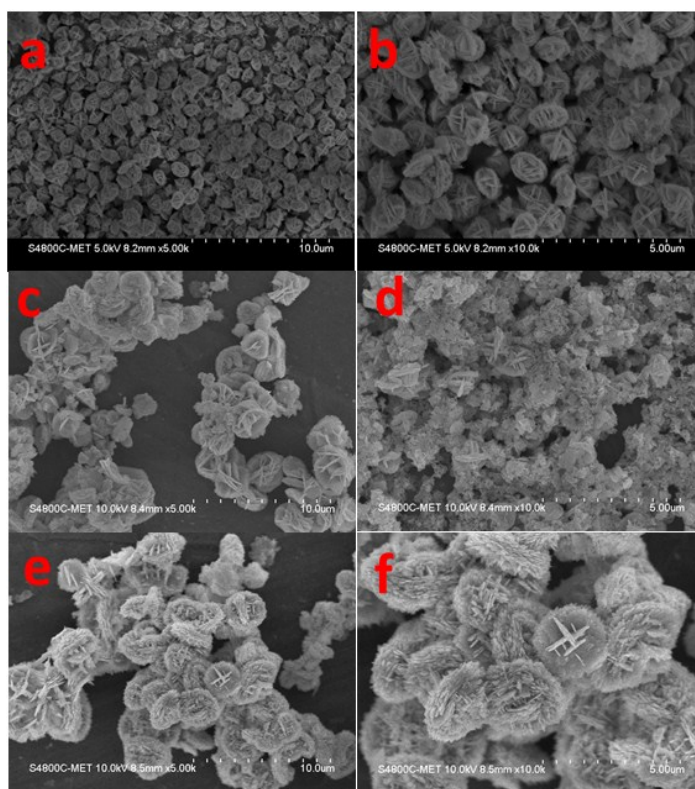
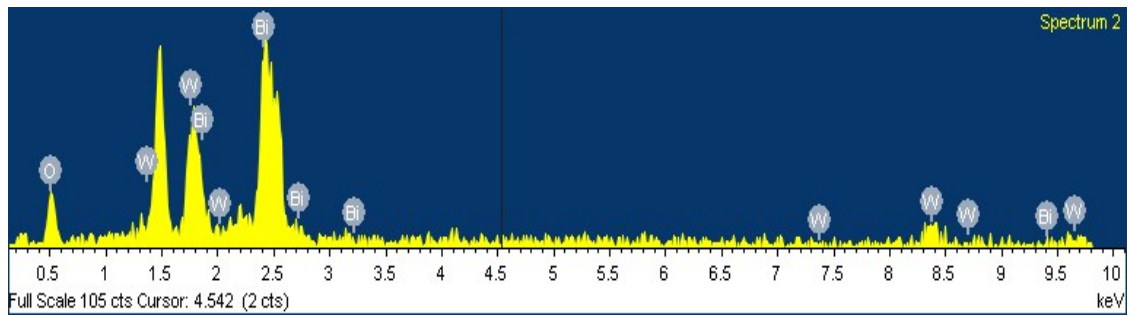


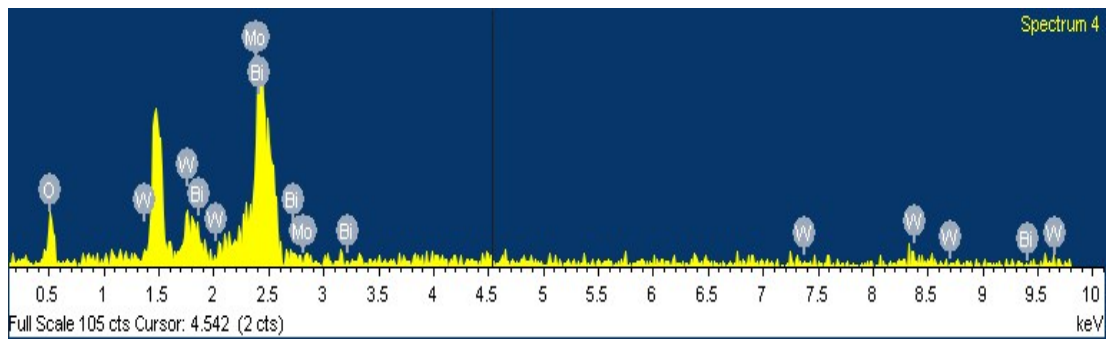
Figure S1: FE-SEM images (a, b) $\text{Bi}_2\text{W}_{0.8}\text{Mo}_{0.2}\text{O}_6$ (c, d) $\text{Bi}_2\text{W}_{0.4}\text{Mo}_{0.6}\text{O}_6$ and (e, f) $\text{Bi}_2\text{W}_{0.2}\text{Mo}_{0.8}\text{O}_6$

EDAX SPECTRA

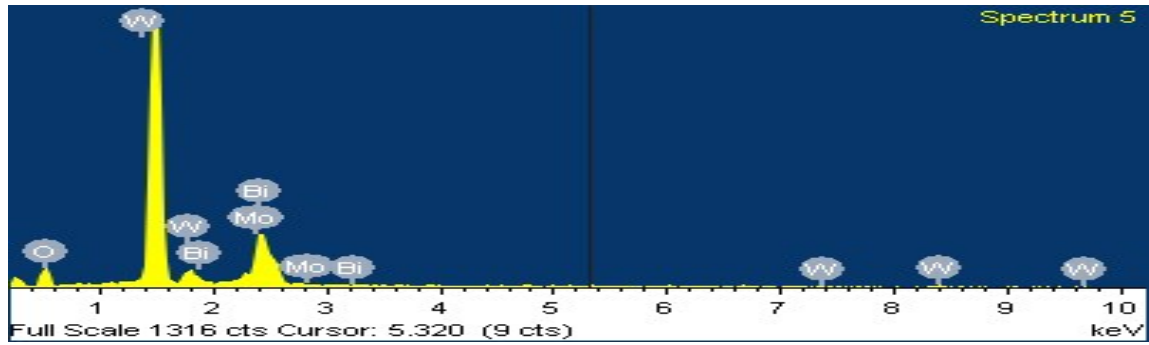
a) S1



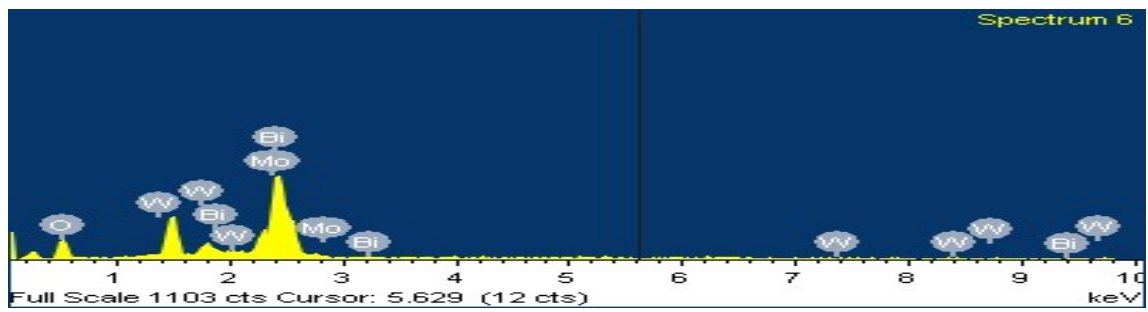
b) S3



c) S4



d) S5



e) S6

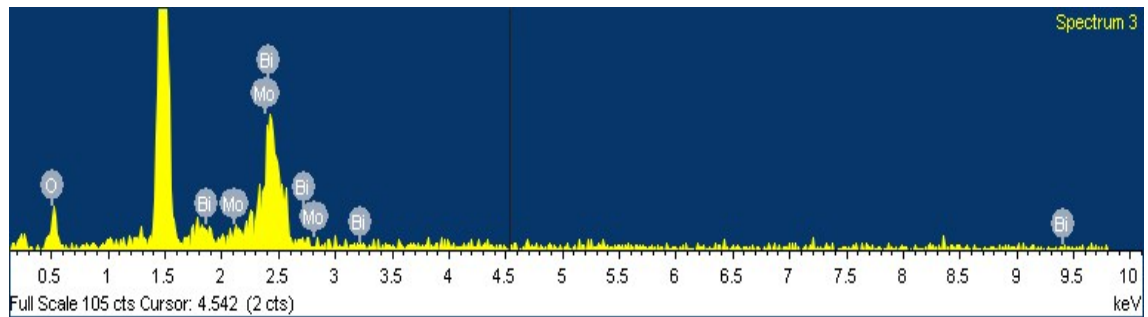


Table 1 Elemental Composition from EDAX**S1**

Element	Weight %	Atomic %
O K	19.91	75.78
W L	22.29	7.38
Bi M	57.80	16.84

S3

Element	Weight %	Atomic %
O K	23.83	78.04
W L	8.72	4.76
Mo L	8.15	2.32
Bi M	59.30	14.87

S4

Element	Weight %	Atomic %
O K	29.75	83.20
W L	5.40	2.52
Mo L	13.37	3.25
Bi M	51.47	11.02

S5

Element	Weight %	Atomic %
O K	25.96	79.46
W L	7.10	1.89
Mo L	10.75	5.49
Bi M	56.19	13.48

S6

Element	Weight %	Atomic %
O K	27.91	81.41
Mo L	9.48	4.61
Bi M	62.61	13.98

Figure S2

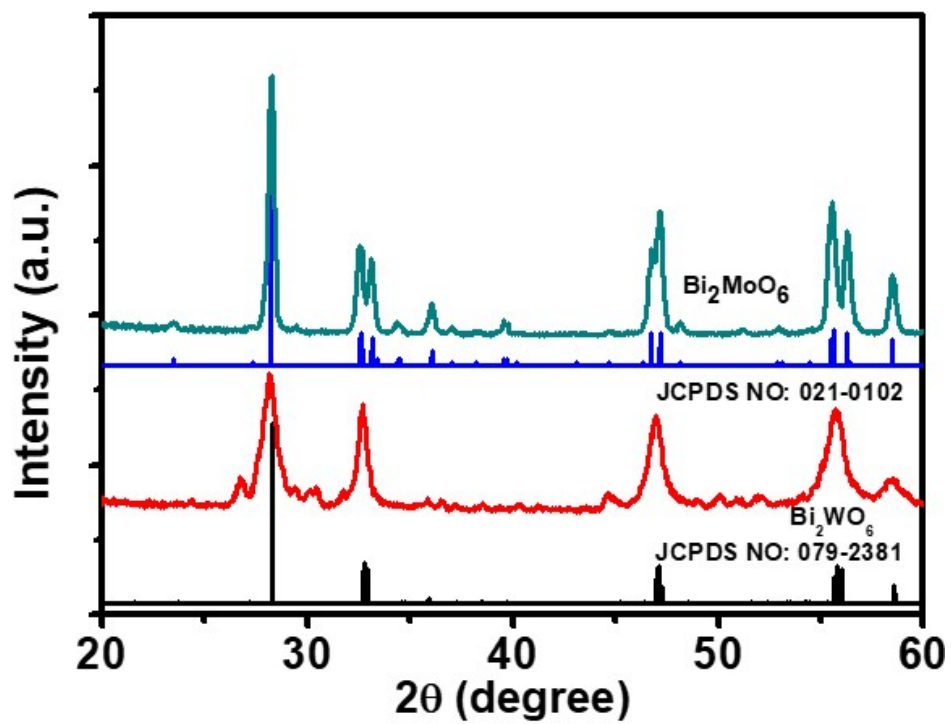


Figure S2: Comparative XRD patterns of Bi_2WO_6 and Bi_2MoO_6 with standard XRD pattern

Figure S3

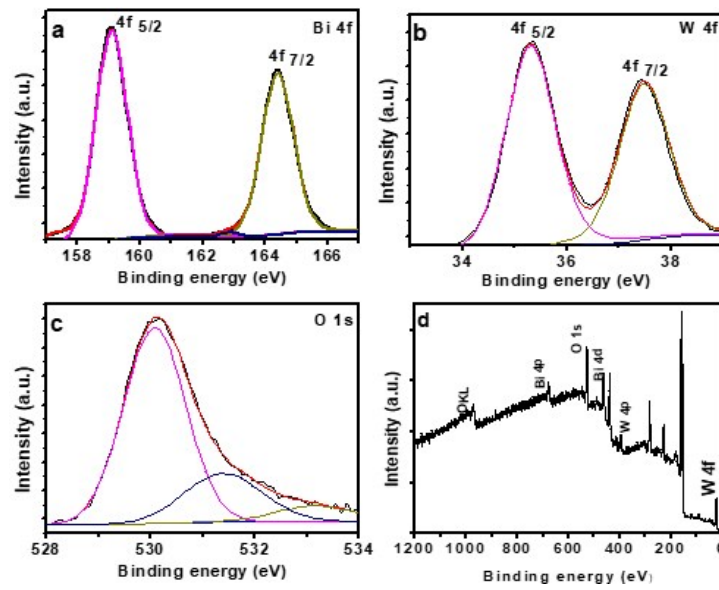


Figure S3: XPS spectra of Bi_2WO_6 (S1) a) Bi 4f b) W 4f c) O 1s d) survey spectrum

Figure S4

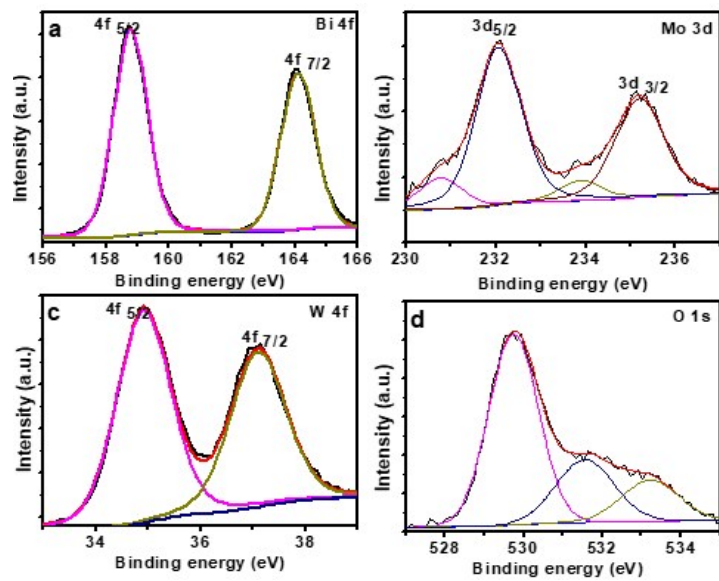


Figure S4: XPS spectra of $\text{Bi}_2\text{W}_{0.6}\text{Mo}_{0.4}\text{O}_6$ (S3) a) Bi 4f b) Mo 3d c) W 4f d) O 1s

Figure S5

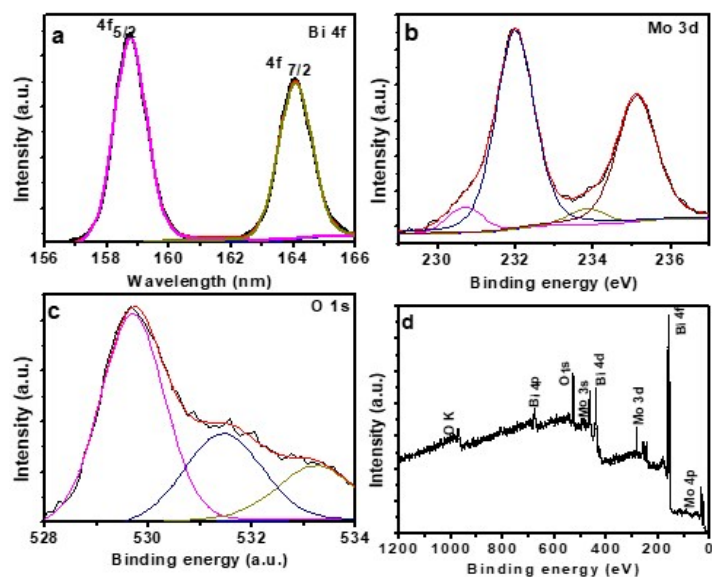


Figure S5: XPS spectra of Bi_2MoO_6 (S6) a) Bi 4f b) Mo 3d c) O 1s d) Survey spectrum

Table 2 Sample composition of Bi, Mo, W and O from $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$ from XPS

Compound	Bi	W	Mo	O
S1	22.18	10.30	-	67.51
S3	20.80	5.07	3.30	70.82
S6	19.58	-	7.72	72.70

Table 3 Composition of each precursor for synthesis of $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$

Sample code	$\text{Bi}(\text{NO}_3)_3$ in (mm)	Na_2WO_4 in (mm)	Na_2MoO_4 in (mm)	% of Bi:W:Mo (from ICP-AES)
S1	0.96	0.29	-	Bi 62.22%, W 23.41%
S2	0.96	0.23	0.048	
S3	0.96	0.17	0.096	Bi 63.15%, W 12.1 %, Mo 8.48%
S4	0.96	0.11	0.144	
S5	0.96	0.05	0.19	

S6	0.96	0.25	-	Bi 63.06%, Mo 17.11%
----	------	------	---	----------------------

Figure S6

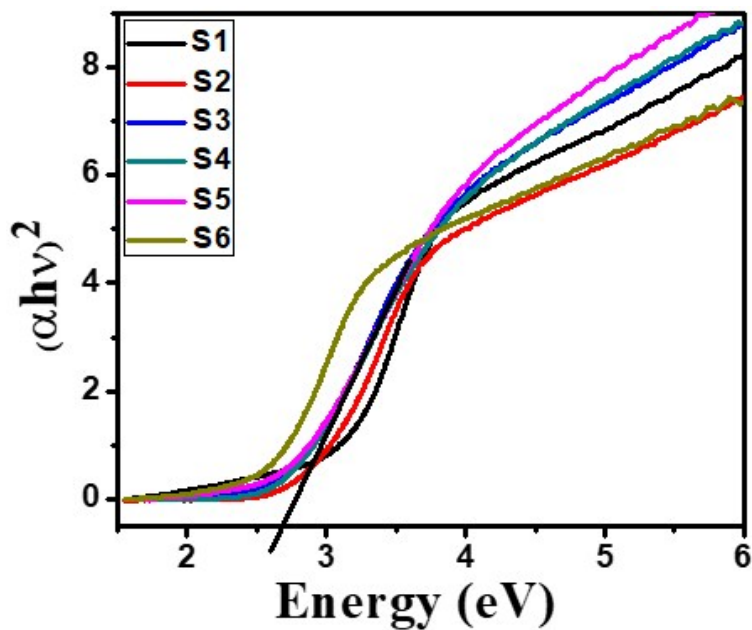


Figure S6: Tauc plot of samples S1) (Bi_2WO_6), S2) ($\text{Bi}_2\text{W}_{0.8}\text{Mo}_{0.2}\text{O}_6$), S3) ($\text{Bi}_2\text{W}_{0.6}\text{Mo}_{0.4}\text{O}_6$), S4) ($\text{Bi}_2\text{W}_{0.4}\text{Mo}_{0.6}\text{O}_6$), S5) ($\text{Bi}_2\text{W}_{0.2}\text{Mo}_{0.8}\text{O}_6$) and S6) (Bi_2MoO_6)

Figure S7

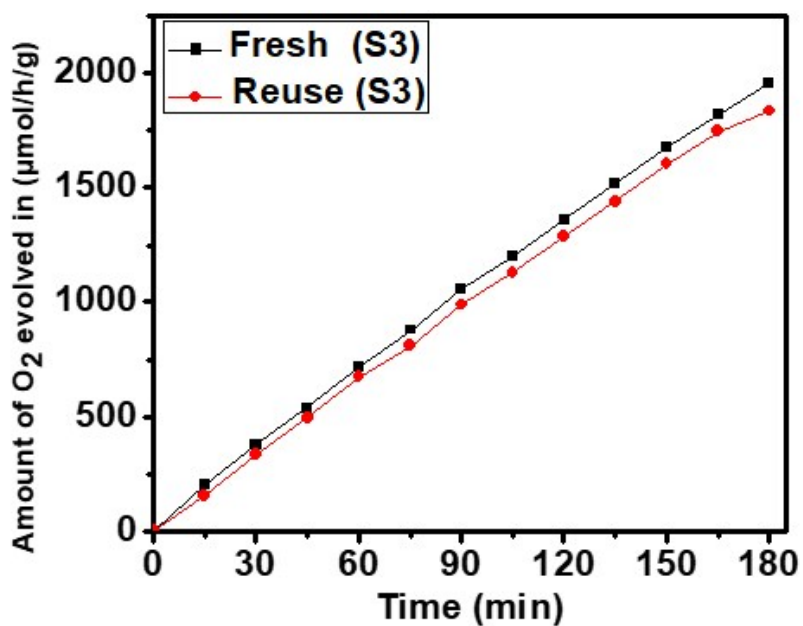


Figure S7: Recycle study of $\text{Bi}_2\text{W}_{0.6}\text{Mo}_{0.4}\text{O}_6$ (S3) for photocatalytic oxygen evolution reaction

Figure 8

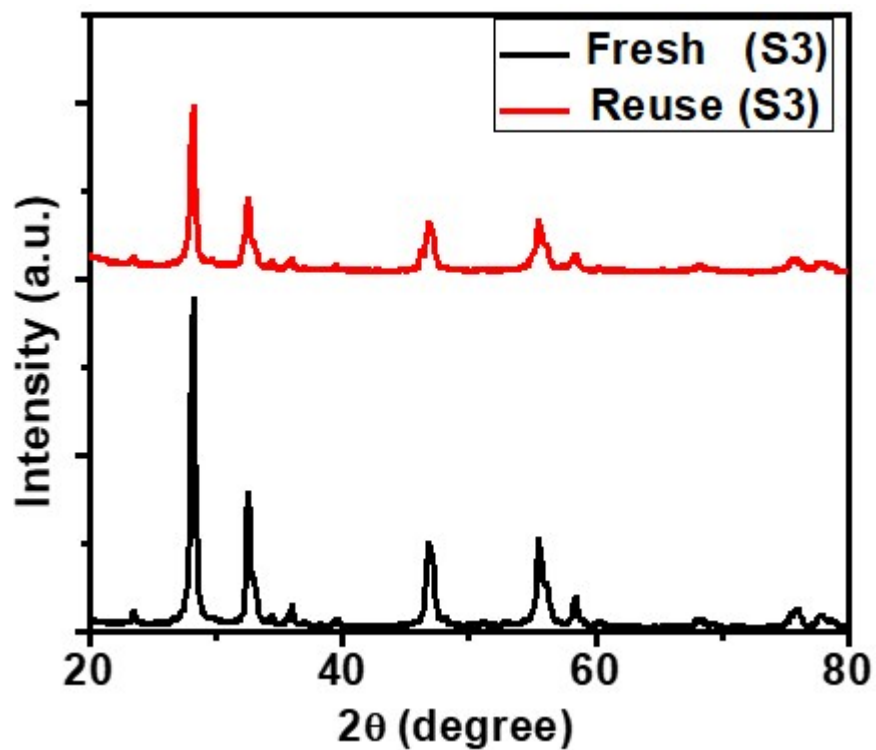


Figure 8: XRD pattern of sample (S3): after photocatalytic oxygen evolution reaction

Figure 9

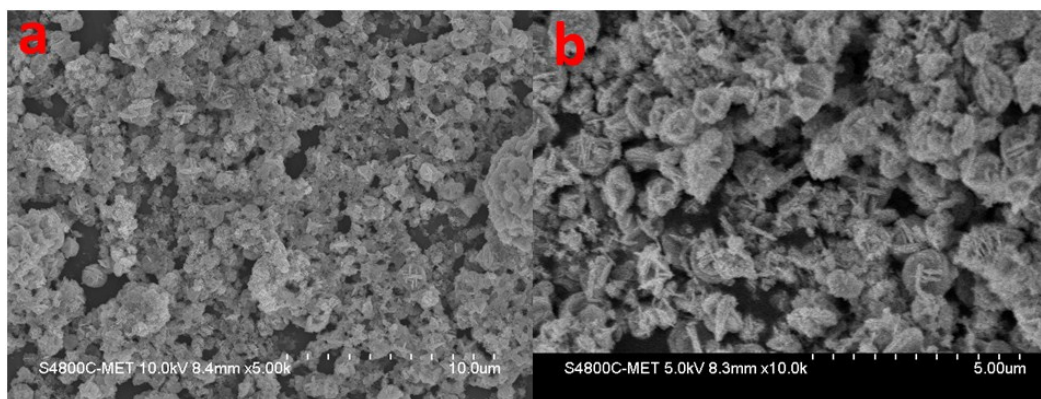


Figure 9: FESEM images of sample (S3) after photocatalytic reaction

Table 4 A comparison study of the photocatalysts in this work and previous reported BiVO₄ based photocatalysts for water oxidation reaction.

Photocatalyst	Light source	Wavelength(nm)	Sacrificial agent	Oxygen evolution rate (μmol/h/g)	References
Bi ₂ MoO ₆	300 W Xe	>300	Ag(NO) ₃	127	1
Bi ₂ WO ₆	450 W Xe	>420	Ag(NO) ₃	34	2
Mo-BiVO ₄	300 W Xe	> 420	Ag(NO) ₃	500	3
BiVO ₄	300 W Xe	>300	Ag(NO) ₃	82.8	4
Fe-BiVO ₄	300 W Xe	>300	Ag(NO) ₃	50	4
Fe/Mo BiVO ₄	300 W Xe	>300	NaOH/Na ₂ S ₂ O ₈	191.5	5
Bi ₂ WO ₆	Sunlight	>300	Ag(NO) ₃	116.5	Present work
Bi ₂ MoO ₆	Sunlight	>300	Ag(NO) ₃	81.2	Present work
MO-Bi ₂ WO ₆	Sunlight	>300	Ag(NO) ₃	652	Present work

References

- 1) Y. Shimodaira, H. Kato, H. Kobayashi, A. J. Kudo, Phys. Chem. B 2006, **110**, 17790–17797.
- 2) A. Kudo, S. Hijii, Chem. Lett. 1999, **10**, 1103–1104.
- 3) K. P. S. Parmar, H. J. Kang, A. Bist, P. Dua, J. S. Jang and J. S. Lee, ChemSusChem, 2012, **10**, 1926-1934.
- 4) S. M. Thalluri, C. M. Suarez, S. Hernandez, S. Bensaid, G. Saracco, N. Russo, Chem. Eng. J., 2014, **245**, 124-132.
- 5) R. Liu, J. Ren, D. Zhao, J. Ning, Z. Zhang, Y. Wang, Y. Zhong, C. Zheng, and Y. Hua, Inorg. Chem Front., 2017, **4**, 2045-2054.

