

Electronic Supplementary Information
for
“Unveiling Photocatalytic Functionalities of (Gd³⁺, Mo⁶⁺)
Co-doped BiVO₄ Nanoparticles: Experimental-DFT Approach”

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I. SUPERCELL STRUCTURE

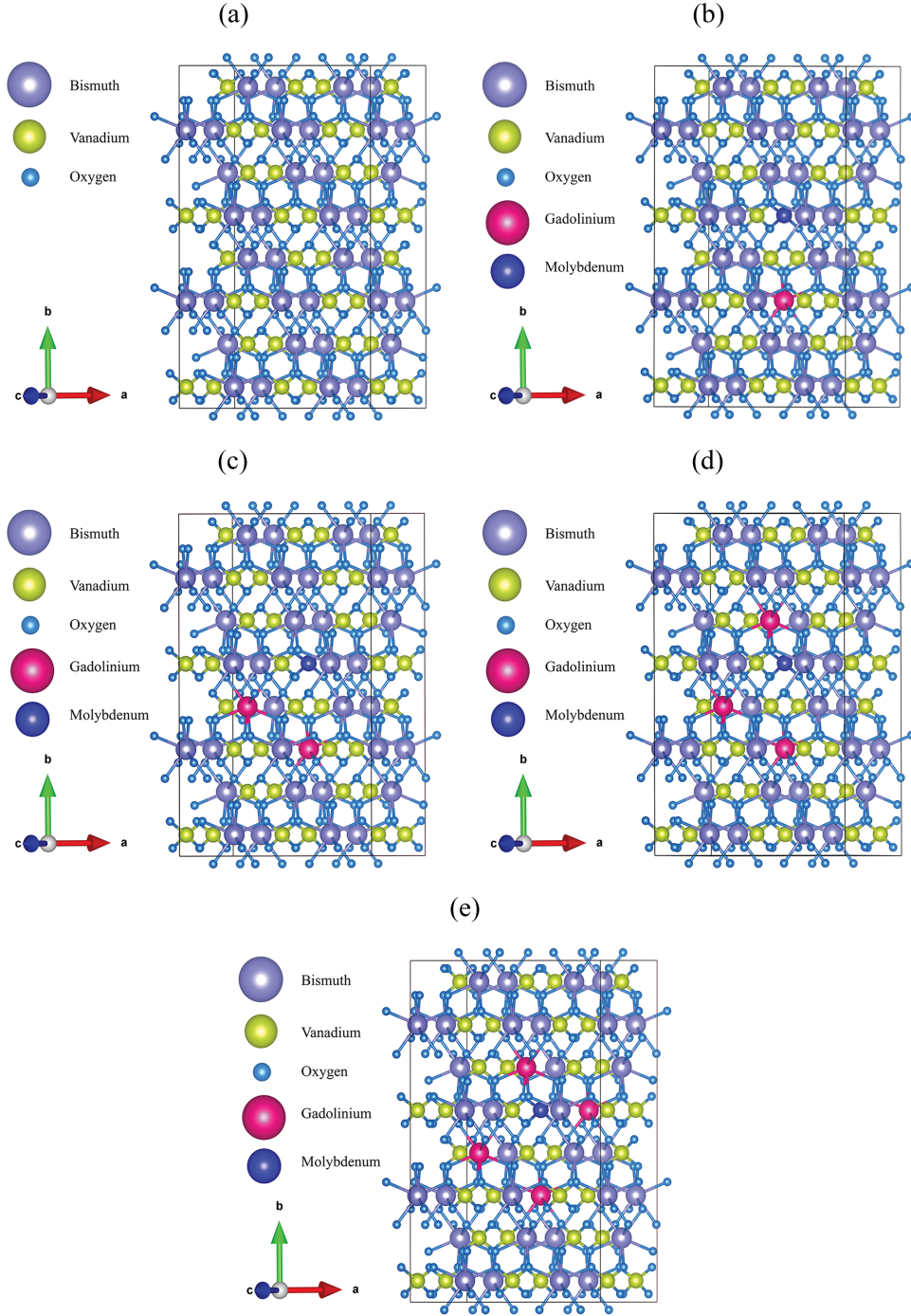


FIG. S1. $2 \times 2 \times 2$ supercell structure of (a) u-BVO, (b) 3.125% Gd and 3.125% Mo co-doped G3M3-BVO, (c) 6.25% Gd and 3.125% Mo co-doped G6M3-BVO, (d) 9.375% Gd and 3.125% Mo co-doped G9M3-BVO, and (e) 12.5% Gd and 3.125% Mo co-doped G12M3-BVO.

II. X-RAY DIFFRACTION ANALYSIS

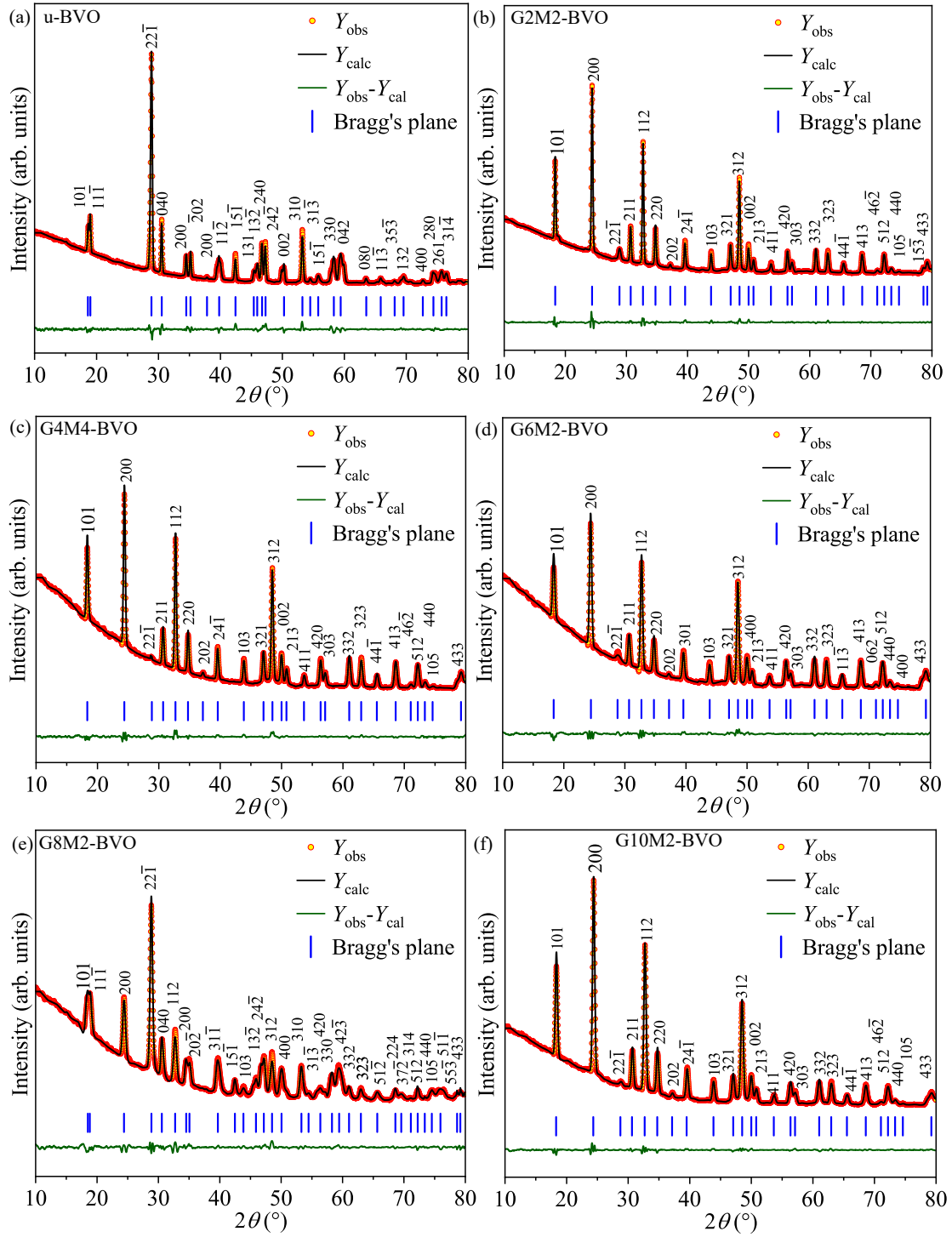


FIG. S2. Rietveld refinement of powder XRD of (a) u-BVO, (b) G2M2-BVO, (c) G4M2-BVO, (d) G6M2-BVO, (e) G8M2-BVO, and (f) G10M2-BVO.

TABLE S1. Experimental Crystallographic Parameters of , Bond Angles, and Bond Lengths measured for u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO samples.

Crystallographic Parameters, Bond Lengths and Bond Angles										
Sample/DFT	Sym.	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å ³)	$d_{\text{Bi-O}}$ (Å)	$d_{\text{V-O}}$ (Å)
BVO	$C2/c$	7.2616(2)	11.7142(1)	5.1012(2)	90	134.247	90	310.8442(1)	2.333(×2), 2.414(×2)	1.669(×2), 1.776(×2)
G2M2-BVO	$I41/amd$	7.2988(2)	7.2988(3)	6.4560(1)	90	90	90	343.9274(2)	2.411(×4), 2.5119(×4)	1.688(×4)
	$C2/c$	7.2791(2)	11.6743(1)	5.1062(2)	90	134.457	90	309.6951(2)	2.418(×2), 2.444(×2)	1.743(×2), 1.751(×2)
G4M2-BVO	$I41/amd$	7.2967(3)	7.2967(2)	6.4541(1)	90	90	90	343.6811(2)	2.377(×4), 2.514(×4)	1.721(×4)
	$C2/c$	7.2741(2)	11.7477(2)	5.1551(2)	90	134.626	90	313.5153(2)	2.414(×2), 2.462(×2)	1.749(×2), 1.758(×2)
G6M2-BVO	$I41/amd$	7.2978(3)	7.2978(2)	6.4531(1)	90	90	90	343.6727(2)	2.410(×4), 2.515(×4)	1.6878(×4)
	$C2/c$	7.2479(2)	11.6139(2)	5.1632(2)	90	134.588	90	309.5274(2)	2.402(×2), 2.447(×2)	1.744(×2), 1.749(×2)
G8M2-BVO	$C2/c$	7.2668(3)	11.6892(1)	5.1023(3)	90	134.312	90	310.1215(1)	2.415(×2), 2.445(×2)	1.746(×2), 1.749(×2)
	$I41/amd$	7.2899(2)	7.2898(2)	6.4483(1)	90	90	90	342.6769(2)	2.40(×4), 2.509(×4)	1.812(×4)
G10M2-BVO	$I41/amd$	7.2974(2)	7.2974(4)	6.4531(2)	90	90	90	343.6183(4)	2.409(×4), 2.510(×4)	1.686(×4)
	$C2/c$	7.3178(3)	11.6812(1)	5.03013(2)	90	134.267	90	307.865(1)	2.411(×2), 2.431(×2)	1.739(×2), 1.749(×2)
									2.436(×2), 2.533(×2)	

TABLE S2. Rietveld refined parameters and $ms-tz$ phase percentages ζ_{ms} and ζ_{tz} for u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO samples.

Rietveld Refined Parameters							
Sample	Symm.	ζ_{ms} (%)	ζ_{tz} (%)	R_p (%)	R_{wp} (%)	R_{exp} (%)	χ^2
u-BVO	$C2/c$	100	0	6.78	5.76	4.45	1.67
G2M2-BVO	$I41/amd$	10.44	89.56	5.89	5.13	3.74	1.88
	$C2/c$			6.56	5.78	5.60	1.95
G4M2-BVO	$I41/amd$	12.58	87.42	10.22	7.35	5.44	1.82
	$C2/c$			7.26	6.19	4.44	1.94
G6M2-BVO	$I41/amd$	16.7	83.3	10.91	6.44	4.84	1.77
	$C2/c$			10.35	6.19	4.27	2.11
G8M2-BVO	$C2/c$	64.21	35.79	8.91	8.31	5.20	2.55
	$I41/amd$			8.35	6.19	4.07	2.31
G10M2-BVO	$I41/amd$	11.1	88.9	11.6	10.2	6.49	2.45
	$C2/c$			12.1	10.3	6.64	2.38

TABLE S3. The Crystallite Size, Defect Density, and Strain measured from the 101, $22\bar{1}$ and 200 Bragg plane Full-width-half-maximum (FWHM) for u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO.

XRD Peak Analysis						
Sample	Bragg's		FWHM ($^{\circ}$)	Crystallite Size, D (nm)	Defect Density δ ($\times 10^{-3}\text{nm}^2$)	Strain ϵ ($\times 10^{-3}$)
	Plane	$2\theta(^{\circ})$				
u-BVO	(101)	18.741	0.229	35.016	0.816	6.079
G2M2-BVO	(101)	18.334	0.264	30.525	1.073	7.128
G4M2-BVO	(101)	18.364	0.286	28.165	1.261	7.713
G6M2-BVO	(101)	18.401	0.298	26.998	1.372	8.030
G8M2-BVO	(101)	18.546	0.562	14.312	4.882	15.030
G10M2-BVO	(101)	18.420	0.308	26.193	1.458	8.268
u-BVO	($22\bar{1}$)	28.941	0.319	25.715	1.512	5.395
G2M2-BVO	($22\bar{1}$)	28.883	0.442	18.552	2.905	7.492
G4M2-BVO	($22\bar{1}$)	28.811	0.219	37.480	0.712	3.717
G6M2-BVO	($22\bar{1}$)	28.928	0.267	30.723	1.059	4.517
G8M2-BVO	($22\bar{1}$)	28.937	0.413	19.866	2.534	6.984
G10M2-BVO	($22\bar{1}$)	28.874	0.283	28.997	1.189	4.795
G2M2-BVO	(200)	24.383	0.269	30.258	1.092	5.425
G4M2-BVO	(200)	24.411	0.289	28.058	1.270	5.844
G6M2-BVO	(200)	24.452	0.305	26.620	1.411	6.148
G8M2-BVO	(200)	24.485	0.366	22.236	2.022	7.351
G10M2-BVO	(200)	24.473	0.326	24.949	1.606	6.555

III. RAMAN PEAK ASSIGNMENT

The room temperature (RT) Raman peaks for u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO samples are identified with the symmetry of the underlying lattice in Table S4.

TABLE S4. RT experimental Raman peaks of u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO. ELM: External Lattice Mode. SBM: Symmetric Bending Vibrations, SST: Symmetric Stretching, AD: Asymmetric Deformation, SD: Symmetric Deformation, AST: Asymmetric Stretching.

Raman Peak Analysis							
u-BVO	G2M2	G4M2	G6M2	G8M2	G10M2		
-BVO	-BVO	-BVO	-BVO	-BVO	-BVO		
(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	Symm.	Peak Assignment
115(2)	113(2)	113(2)	116(2)	115(2)	113(2)	B_g	[VO ₄] ³⁻ ELM
189(2)	—	—	208(2)	182(2)	—	A_g	[VO ₄] ³⁻ ELM
—	247(2)	247(2)	247(2)	247(2)	247(2)	A_g	Bi-O SST
341(2)	341(2)	341(2)	341(2)	341(2)	341(2)	B_g	[VO ₄] ³⁻ AD
—	366(2)	366(2)	366(2)	360(2)	367(2)	A_g	[VO ₄] ³⁻ SD
—	731(2)	731(2)	732(2)	730(2)	730(2)	A_g	V-O SST
—	759(2)	760(2)	759(2)	760(2)	761(2)	B_g	V-O AST
811(2)	811(2)	811(2)	812(2)	815(2)	811(2)	B_g	V-O AST
—	854(2)	855(2)	853(2)	838(2)	855(2)	A_g	V-O SST

IV. FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

The FTIR absorption spectra of u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO were characterized according to the relevant chemical bond vibrations in Table S5.

TABLE S5. FTIR absorption of u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO. STV: Stretching Vibration, SBV: Symmetric Bending Vibrations, AST: Asymmetric Stretching, and BV: Bending Vibrations.

FTIR Peak Analysis						
u-BVO	G2M2	G4M2	G6M2	G8M2	G10M2	
-BVO	-BVO	-BVO	-BVO	-BVO	-BVO	
(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	Peak Assignment
366(4)	359(4)	368(4)	366(4)	374(4)	356(4)	Bi-O STV
404(4)	405(4)	406(4)	406(4)	404(4)	406(4)	Bi-O STV
476(4)	—	—	—	476(4)	—	[VO ₄] ³⁻ SBV
599(4)	—	—	—	608(4)	—	V-O AST
716(4)	680(4)	716(4)	702(4)	718(4)	710(4)	[VO ₄] ³⁻ AST
823(4)	786(4)	802(4)	804(4)	816(4)	818(4)	V-O STV
888(4)	—	—	—	—	—	V-O SST
1324(4)	1452(4)	1450(4)	1452(4)	1450(4)	1458(4)	C=O SST
	1620(4)	1624(4)	1628(4)	1620(4)	1628(4)	H ₂ O BV

V. EDX ANALYSIS

To perform chemical species identification, energy-dispersive X-ray spectroscopy (EDX) spectra for u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO are shown in Fig. S3. The characteristic energies of X-ray radiation of Bi ($L_\alpha = 10.79$ keV, $L_\beta = 13.00$ keV, $M_\alpha = 2.42$ keV and $M_\beta = 2.53$ keV), V ($K_\alpha = 4.95$ keV, $K_\beta = 5.42$ keV, $L_\alpha = 0.52$ keV and $L_\beta = 0.51$ keV), and O ($K_\alpha = 0.52$ keV) are present in the spectra. In the doped samples, the X-ray peaks at ($L_\alpha = 6.15$ keV, $L_\beta = 6.72$ keV) and ($M_\alpha = 2.39$ keV, $M_\beta = 2.57$ keV) bear the presence of Gd and Mo, respectively. These characteristic peaks are consistent with the results found in Ref. [1, 2]. The weight percent wt. (%) and atomic percent at. (%) of chemical species, Bi, V, O, Gd, and Mo, are displayed in Table S6.

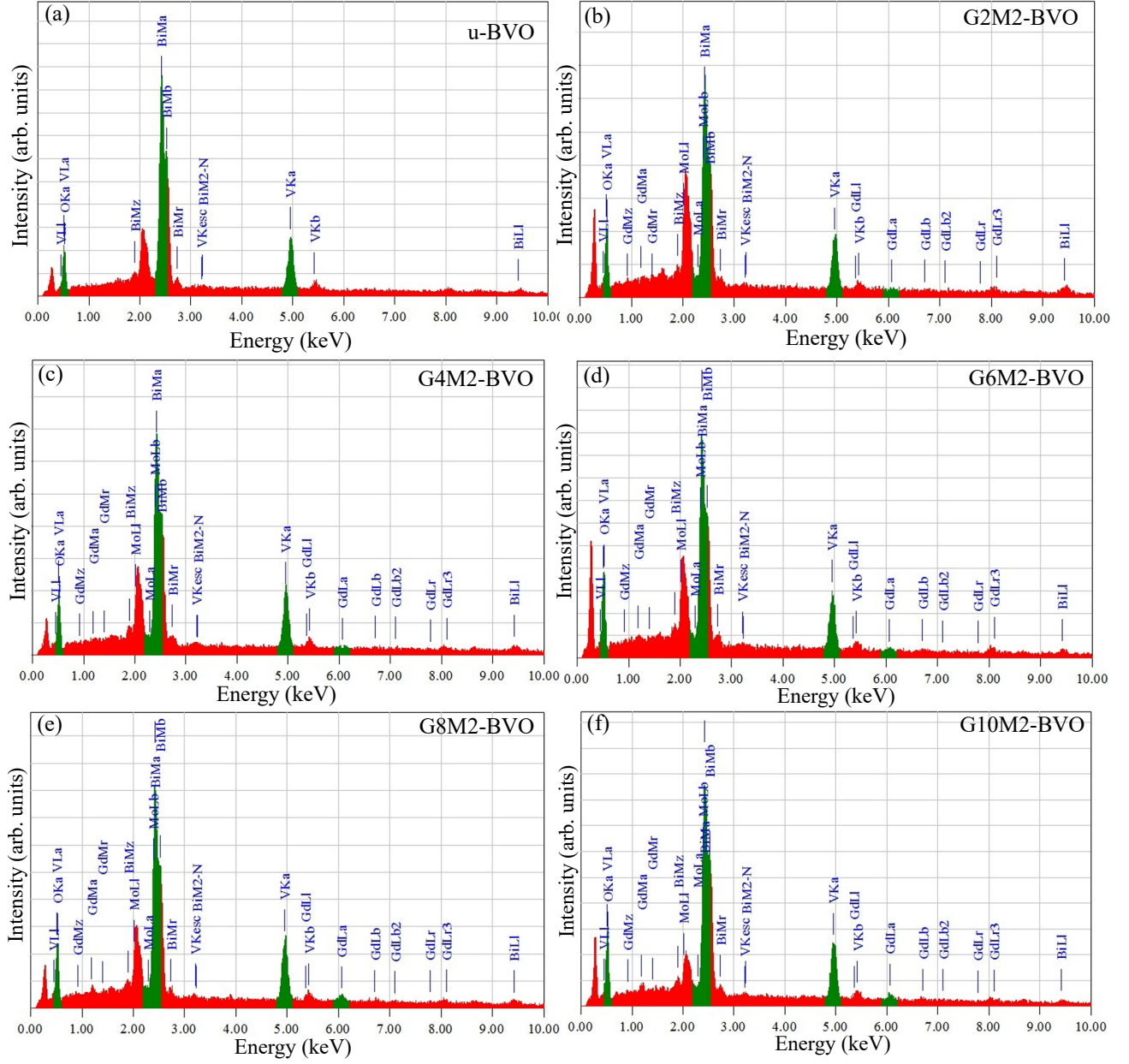


FIG. S3. EDX spectra of (a) u-BVO, (b) G2M2-BVO, (c) G4M2-BVO, (d) G6M2-BVO, (e) G8M2-BVO, and (f) G10M2-BVO.

TABLE S6. Chemical species identification and atomic parentage at. (%) and weight percentage wt. (%) concentration analysis using EDX (EDX Model: JED 2300) of u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO.

EDX Analysis					
Sample	Element	at. (%) (Theory)	at. (%) (Exp.)	wt. (%) (Theory)	wt. (%) (Exp.)
u-BVO	Bi	16.67	23.75	64.52	68.38
	V	16.67	30.76	15.73	21.59
	O	66.66	45.49	19.75	10.03
G2M2-BVO	Bi	16.33	19.80	63.25	64.58
	V	16.33	21.59	15.42	17.17
	O	66.68	56.14	19.76	14.02
	Gd	0.33	0.56	0.97	1.36
	Mo	0.33	1.92	0.60	2.87
G4M2-BVO	Bi	16	20.74	62.16	65.23
	V	16.33	22.78	15.46	17.46
	O	66.67	53.89	19.83	12.98
	Gd	0.67	0.63	1.95	1.49
	Mo	0.33	1.97	0.60	2.84
G6M2-BVO	Bi	15.67	18	61.06	61.86
	V	16.33	18.53	15.52	15.52
	O	66.67	60.12	19.89	15.82
	Gd	1.00	1.51	2.93	3.91
	Mo	0.33	1.84	0.60	2.90
G8M2-BVO	Bi	15.33	20.05	59.95	61.08
	V	16.33	23.65	15.57	17.56
	O	66.68	51.34	19.96	11.97
	Gd	1.33	2.75	3.92	6.29
	Mo	0.33	2.21	0.60	3.09
G10M2-BVO	Bi	15	19.97	58.84	62.58
	V	16.33	21.83	15.62	16.68
	O	66.67	54.32	20.02	13.03
	Gd	1.67	2.32	4.92	5.46
	Mo	0.33	1.57	0.60	2.25

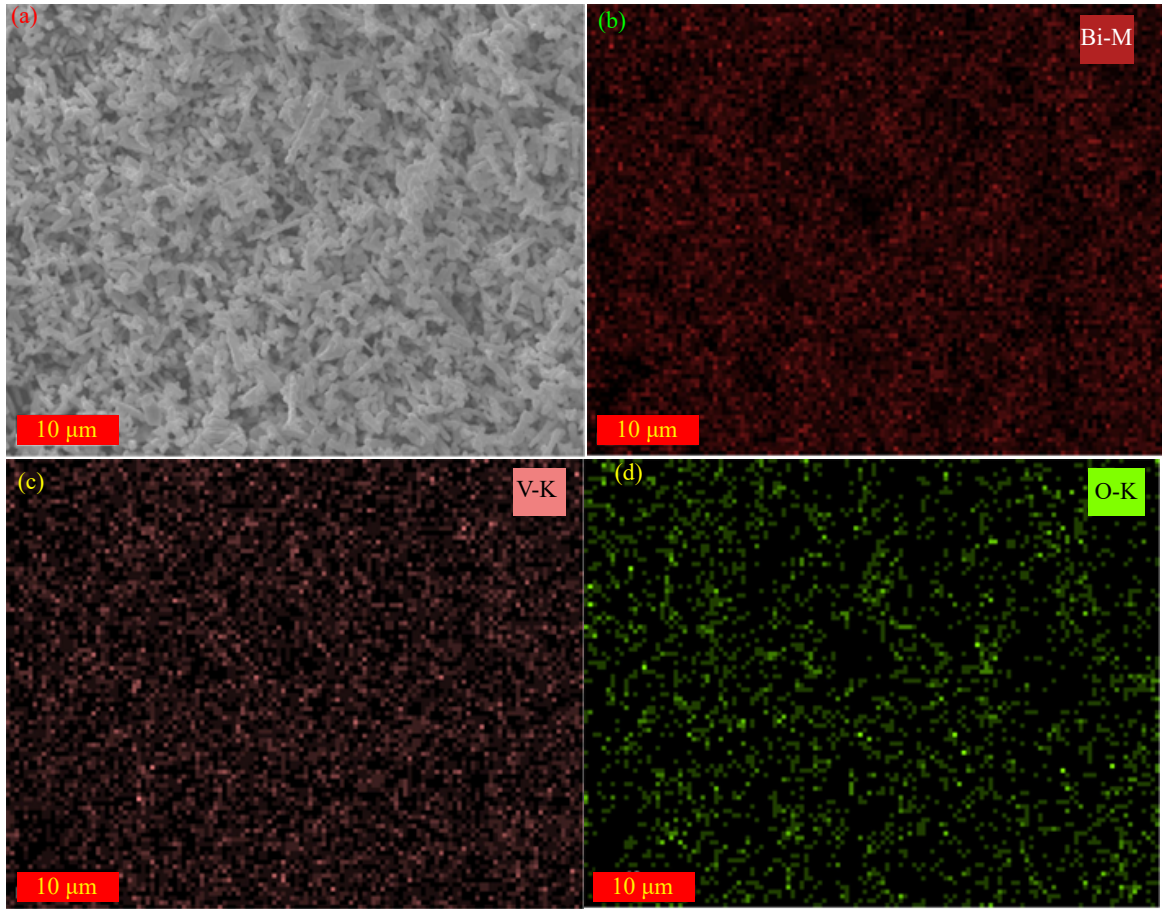


FIG. S4. (a) SEM micrograph of the EDX scan area of u-BVO, elemental spatial EDX mapping images of the constituent elements (b) Bi, (c) V, and (d) O.

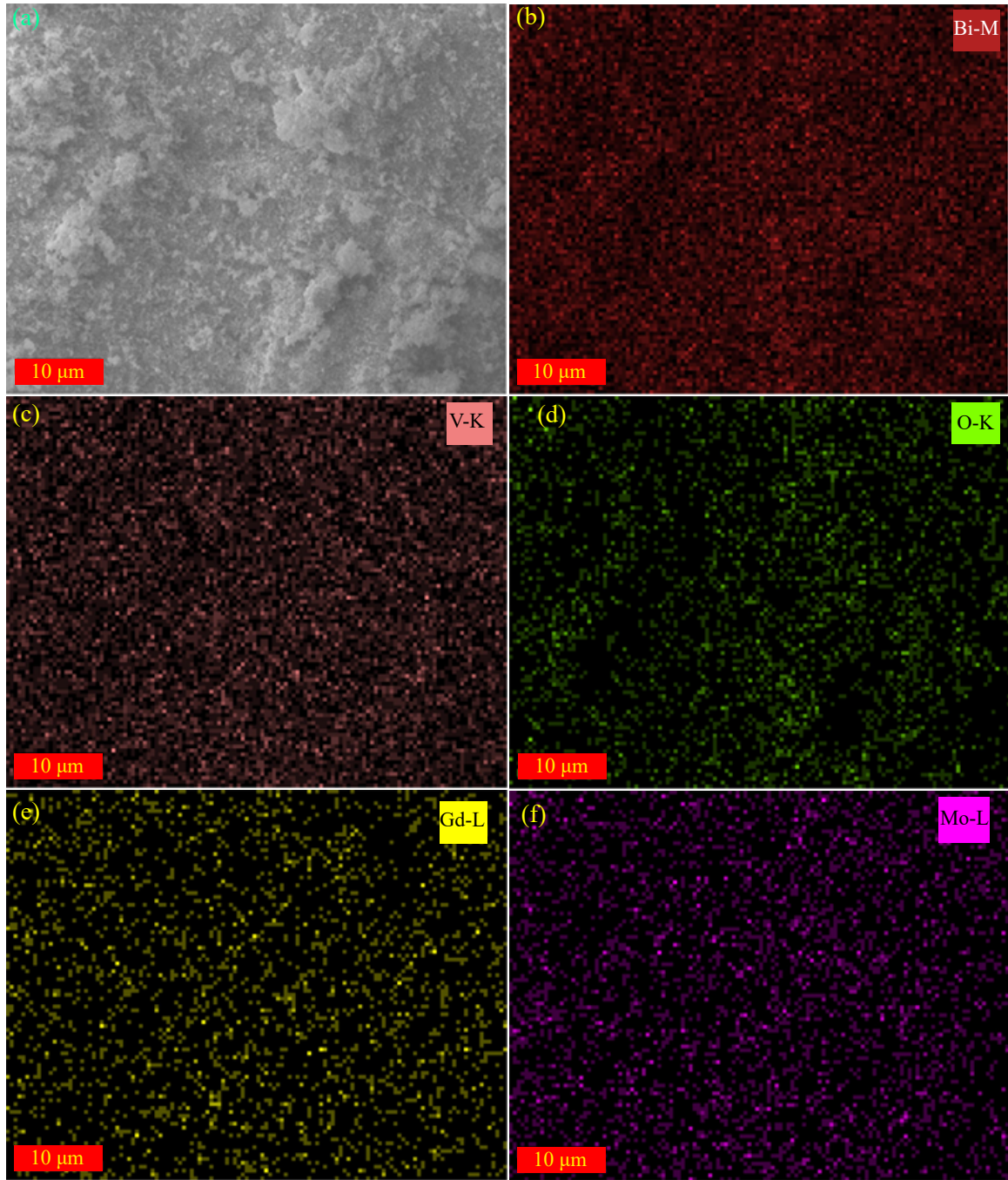


FIG. S5. (a) SEM micrograph of the EDX scan area of G6M2-BVO, elemental spatial EDX mapping images of the constituent elements (b) Bi, (c) V, (d) O, (e) Gd, and (f) Mo.

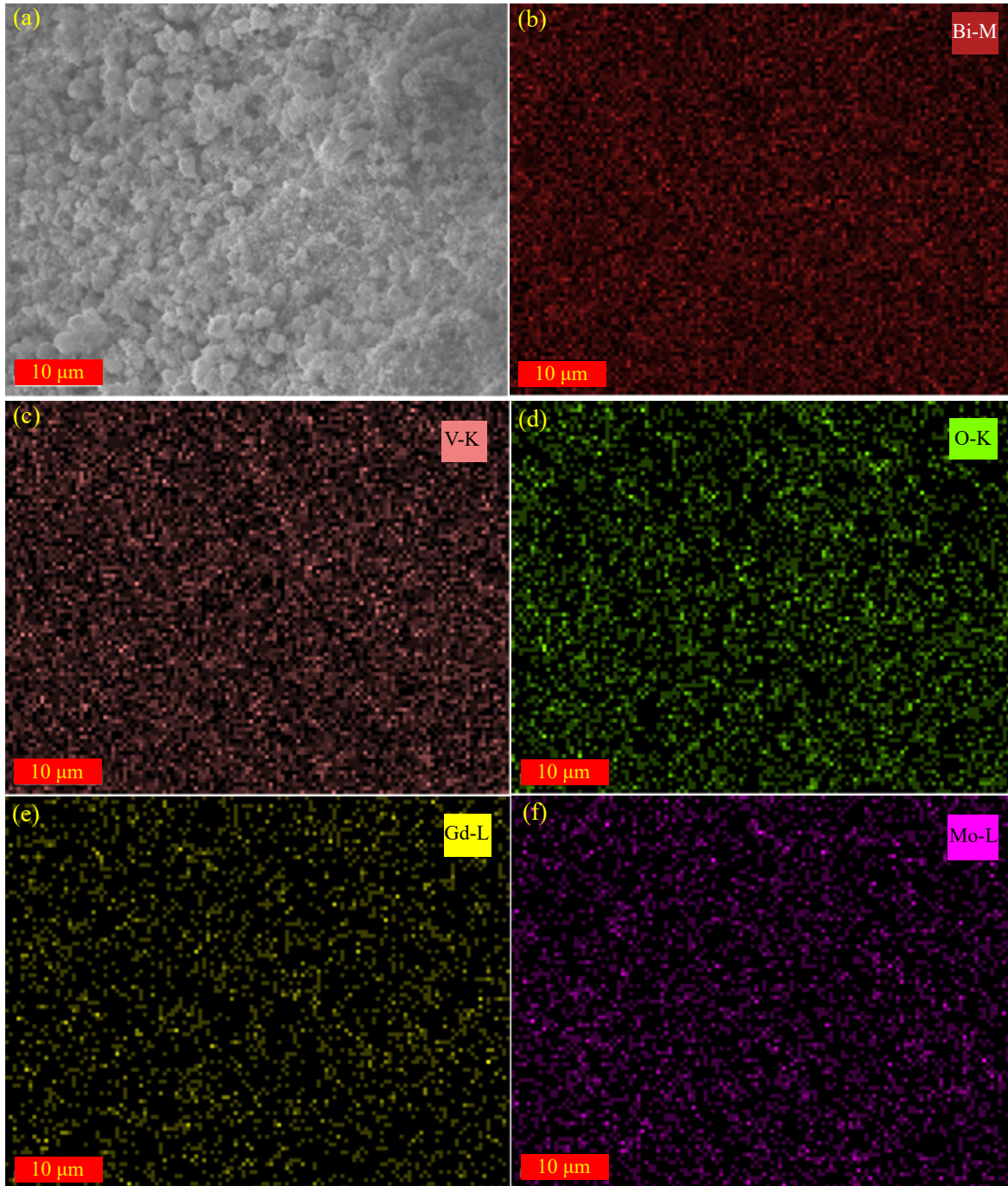


FIG. S6. (a) SEM micrograph of the EDX scan area of G8M2-BVO, elemental spatial EDX mapping images of the constituent elements (b) Bi, (c) V, (d) O, (e) Gd, and (f) Mo.

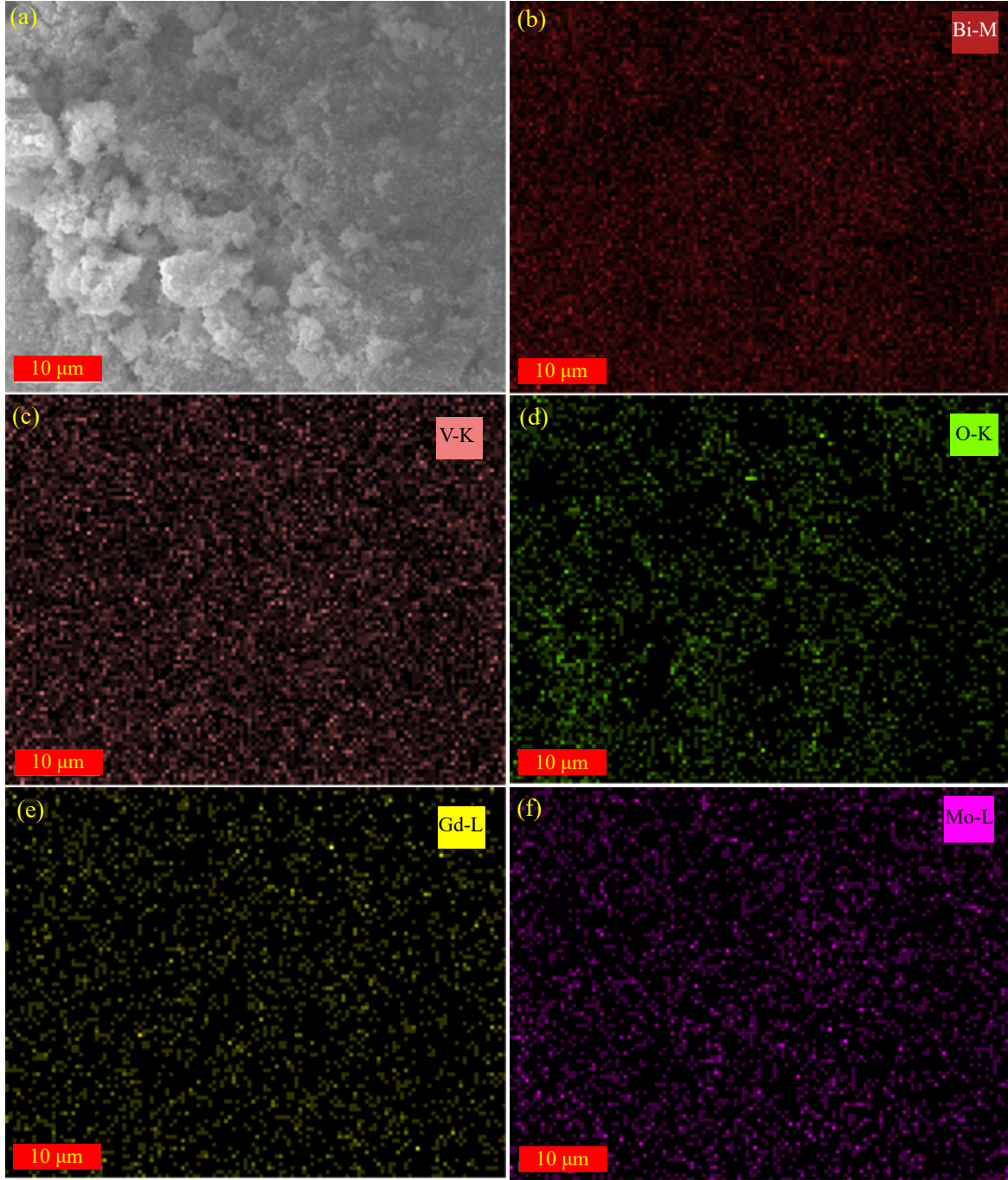


FIG. S7. (a) SEM micrograph of the EDX scan area of G10M2-BVO, elemental spatial EDX mapping images of the constituent elements (b) Bi, (c) V, (d) O, (e) Gd, and (f) Mo.

VI. ELECTRONIC BAND GAPS ESTIMATION

TABLE S7. Direct and indirect electronic band gap E_g for u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO samples.

Electronic Band Gap Analysis			
Sample	Direct Band Gap (eV)	Indirect Band Gap (eV)	Electronic Transition
u-BVO	2.53	2.41	V-3d $\rightarrow$ O-2p
G2M2-BVO	—	2.47	V-3d $\rightarrow$ O-2p
	2.99	2.84	Mo-4d $\rightarrow$ Gd-4f
G4M2-BVO	—	2.43	V-3d $\rightarrow$ O-2p
	3.01	2.86	Mo-4d $\rightarrow$ Gd-4f
G6M2-BVO	—	2.37	V-3d $\rightarrow$ O-2p
	3.05	2.93	Mo-4d $\rightarrow$ Gd-4f
G8M2-BVO	—	1.76	Mo-3d $\rightarrow$ O-2p
	2.59	2.45	V-3d $\rightarrow$ O-2p
	2.88	—	Mo-4d $\rightarrow$ Gd-4f

VII. PHOTOCATALYTIC MEASUREMENTS

TABLE S8. The summary of photocatalytic performances of u-BVO, G2M2-BVO, G4M2-BVO, G6M2-BVO, G8M2-BVO, and G10M2-BVO samples in degrading methylene blue (MB) in terms of Sample Concentration (S.C.), Dye Concentration (D.C.), Dye Degradation (D.D.), Reaction Time (R.T.), Reaction Rate (R.R.) and illumination source.

Photocatalytic Measurements Summary							
Sample/ Dye	S.C. (gm/L)	D.C. (ppm)	D.D. pH	R.T. (%)	R.T. (min)	R.R. (min ⁻¹)	Source
u-BVO/MB	1	50	10	81	180	0.00776	Hg-Xe
	1	100	10	19	180	0.00101	Hg-Xe
G2M2-BVO/MB	1	50	10	88	180	0.00983	Hg-Xe
	1	100	10	22	180	0.00109	Hg-Xe
G4M2-BVO/MB	1	50	10	91	180	0.01122	Hg-Xe
	1	100	10	33	180	0.00153	Hg-Xe
G6M2-BVO/MB	1	50	10	96	180	0.01524	Hg-Xe
	1	100	10	34	180	0.00180	Hg-Xe
G8M2-BVO/MB	1	50	10	88	180	0.00956	Hg-Xe
	1	100	10	35	180	0.00185	Hg-Xe
G10M2-BVO/MB	1	50	10	93	180	0.01251	Hg-Xe
	1	100	10	36	180	0.00189	Hg-Xe

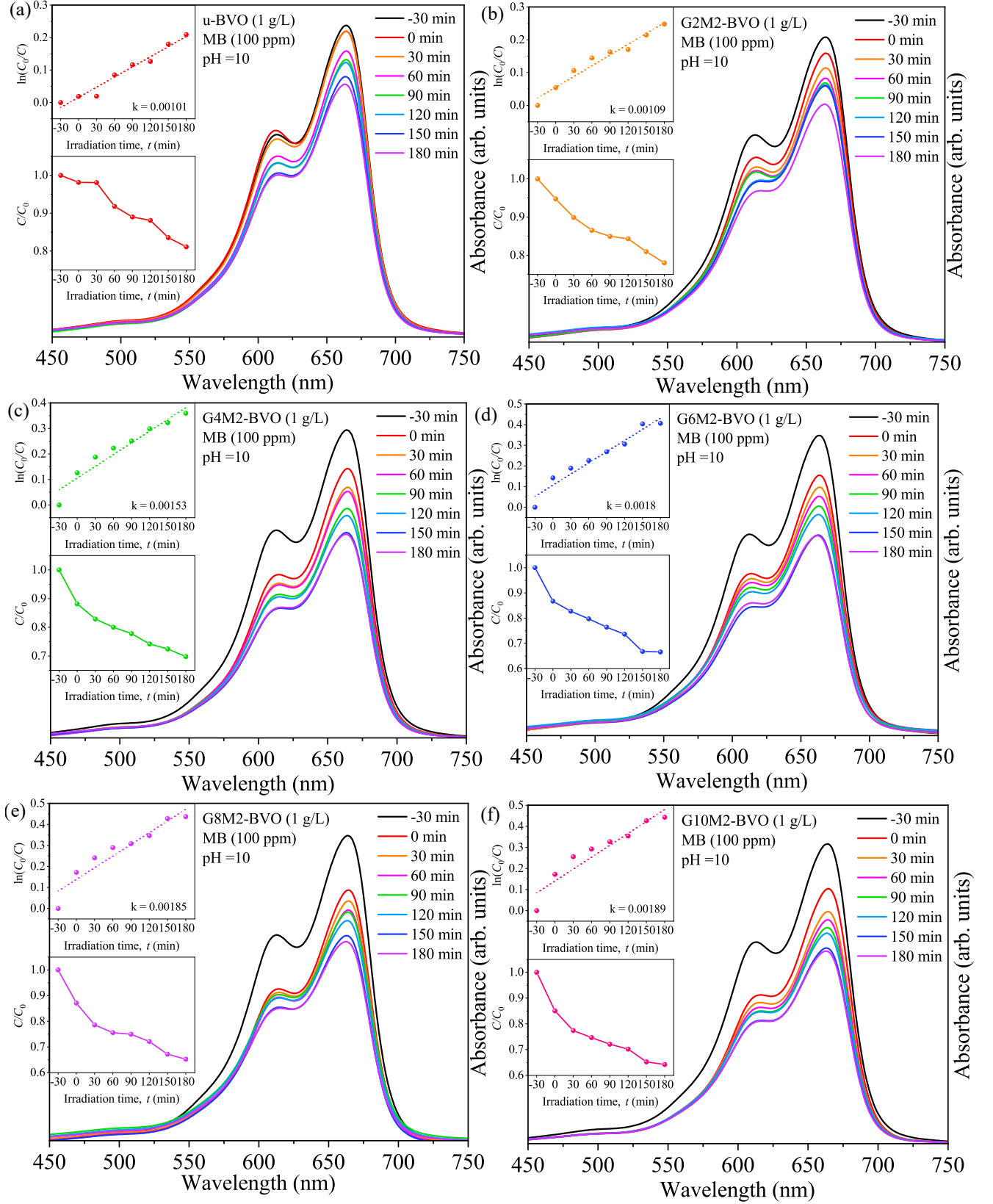


FIG. S8. The photocatalytic degradation measurements from UV-Vis absorption spectra of (a) u-BVO, (b) G2M2-BVO, (c) G4M2-BVO, (d) G6M2-BVO, (e) G8M2-BVO, and (f) G10M2-BVO. photocatalysts (1 g/L) with 100 ppm MB dye at pH = 10.

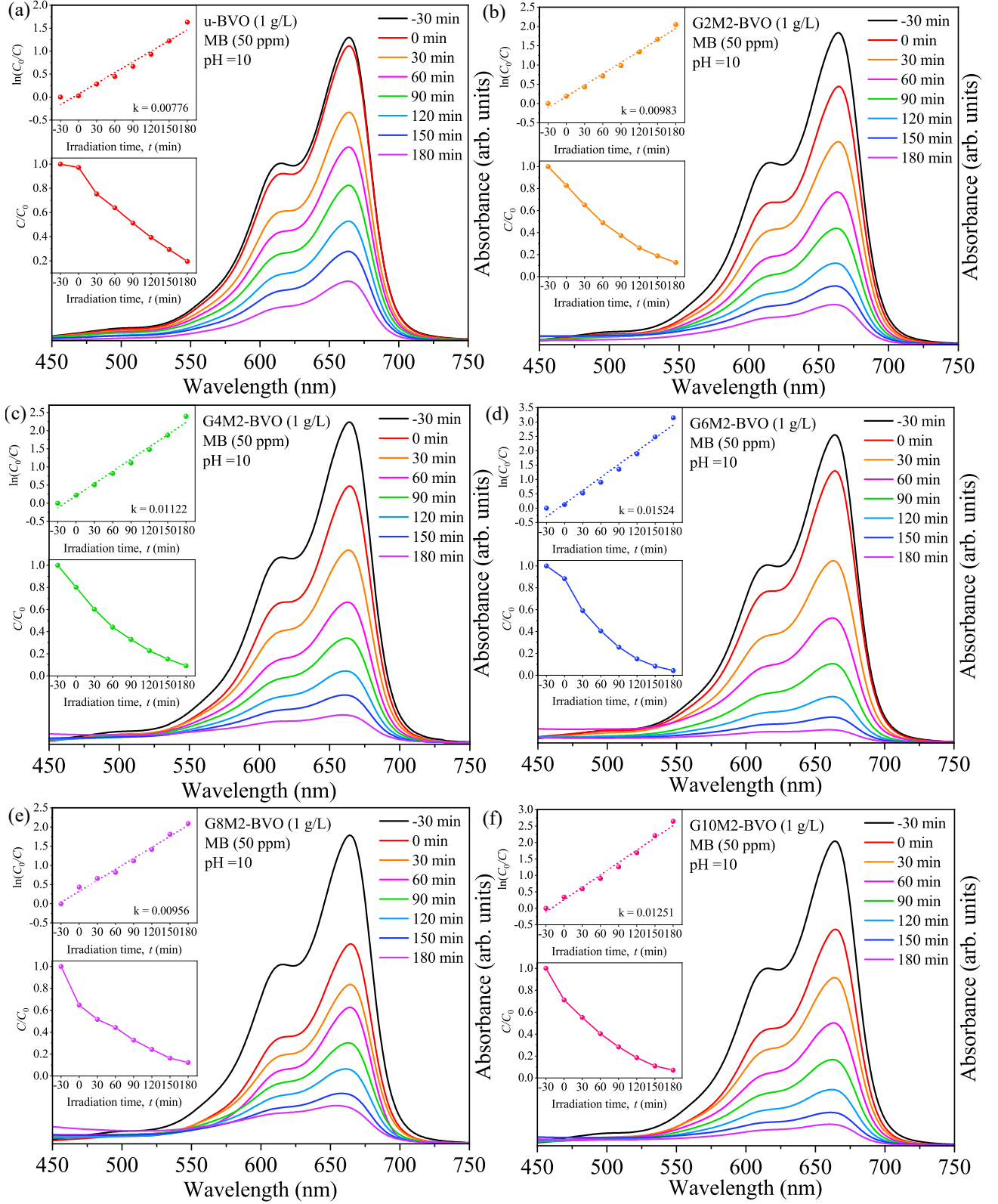


FIG. S9. The photocatalytic degradation measurements from UV-Vis absorption spectra of (a) u-BVO, (b) G2M2-BVO, (c) G4M2-BVO, (d) G6M2-BVO, (e) G8M2-BVO, and (f) G10M2-BVO photocatalysts (1 g/L) with 10 ppm RhB dye at pH= 2.

VIII. REDOX POTENTIAL ANALYSIS

TABLE S9. Redox potential (R.P.) V analysis concerning normal hydrogen electrode (NHE) for relevant photocatalytic reactions.

Redox Potential (R.P.) Analysis			
Reaction	R.P. (pH = 0)	R.P. (pH = 2)	R.P. (pH = 10)
$\text{O}_2 + \text{e}^- \rightarrow \cdot\text{O}_2^-$	-0.18	-0.29	-0.77
$2\text{H}^+ + \text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.695	0.577	0.105
$\text{H}_2\text{O}_2 + \text{H}^+ + \text{e}^- \rightarrow \cdot\text{OH}^- + \text{H}_2\text{O}$	0.8	0.68	0.21
$\text{OH}^- \rightarrow \cdot\text{OH} + \text{e}^-$	1.99	1.87	1.4
$\text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+ + \text{e}^-$	2.73	2.61	2.14

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- [2] Y. Shen, M. Huang, Y. Huang, J. Lin, and J. Wu, The synthesis of bismuth vanadate powders and their photocatalytic properties under visible light irradiation, *J. Alloys Compd.* **496**, 287 (2010).