

SUPPLEMENTARY MATERIAL

Enhancing the Photocatalytic Performance of BiVO₄ for Micropollutant Degradation by Fe and Ag Photomodification

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Table S1. Full factorial design with coded variables (X) corresponding to experimental variables, i.e., pH and wt% of Fe^{2+} using during photomodification (Fe@BVO), and Ag^+ wt% for Ag-modified BiVO_4 (Ag@BVO) investigated for the photocatalytic degradation of CIP:

X_1	X_2	pH	wt% Fe	wt % Ag
-1	-1	4	5	1
0	-1	6	5	1
1	-1	8	5	1
-1	0	4	27.5	8
0	0	6	27.5	8
0	0	6	27.5	8
0	0	6	27.5	8
1	0	8	27.5	8
-1	1	4	50	15
0	1	6	50	15
1	1	8	50	15

Table S2. Analysis of variance for the model for CIP removal using Fe@BVO under simulated solar irradiation:

Source	F value	p value
Model	57.88	<0.0001
X_1	262.94	<0.0001
X_2	1.04	0.3471
X_1X_2	0.67	0.4436
X_1^2	21.32	0.0036
X_2^2	10.77	0.01682,

Table S3. Analysis of variance for the model for CIP removal using Ag@BVO under simulated 7 solar irradiation:

Source	F value	p value
Model	102.58	<0.0001
X_1	487.53	<0.0001
X_2	24.73	0.0025
X_1X_2	0.009	0.9258
X_1^2	0.51	0.5012
X_2^2	0.003	0.9549

Table S4. Analysis of variance (ANOVA) of the model for the removal of CIP with Ag@BVO:

X ₁	X ₂	X ₃	pH	wt % Ag	wt% Fe
-1	-1	-1	4	1	5
0	-1	-1	6	1	5
1	-1	-1	8	1	5
-1	0	0	4	8	27.5
0	0	0	6	8	27.5
0	0	0	6	8	27.5
0	0	0	6	8	27.5
1	0	0	8	8	27.5
-1	1	1	4	15	50
0	1	1	6	15	50
1	1	1	8	15	50

Table S5. Charge transfer resistance (R_{ct}) obtained by fitting the measured EIS data to a model equivalent electrical circuit shown on Figure S8; D depicts measurements in the dark and L depicts measurements performed under illumination:

Photoelectrode	$R_{ct} \times 10^4 (\Omega \text{ cm}^{-2})$	$\chi^2 \times 10^{-3}$
D-BVO	40.80	0.57
L-BVO	8.40	2.22
D-1% Ag@BVO	75.12	0.77
L-1% Ag@BVO	1.56	1.68
D-8% Ag@BVO	28.10	0.88
L-8% Ag@BVO	1.61	1.78
D-15% Ag@BVO	39.50	0.9
L-15% Ag@BVO	1.02	3.19
D-5% Fe@BVO	15.25	1.12
L-5% Fe@BVO	3.73	2.97
D-27.5% Fe@BVO	31.85	0.81
L-27.5% Fe@BVO	2.60	2.32
D-50% Fe@BVO	7.66	1.55
L-50% Fe@BVO	2.30	2.55

Figures

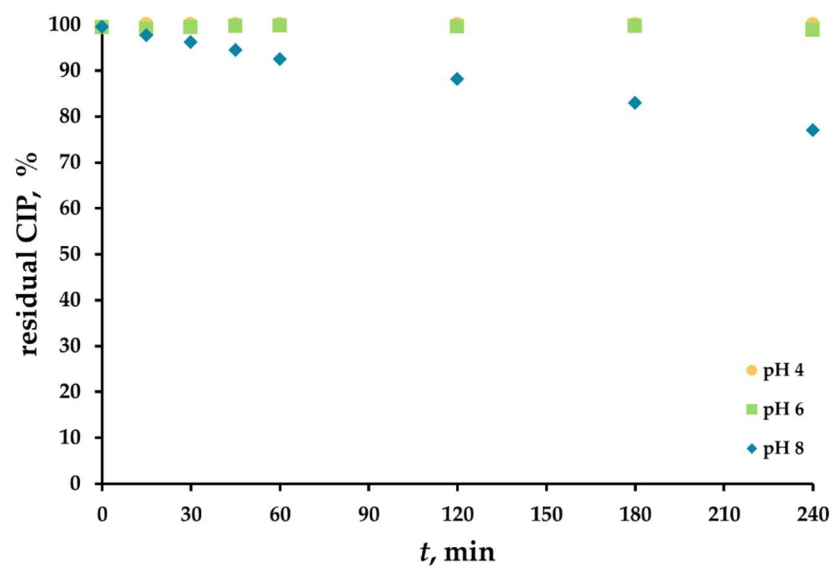


Figure S1. Extent of CIP photolysis under simulated solar irradiation at pH 4, pH 6 and pH 8.

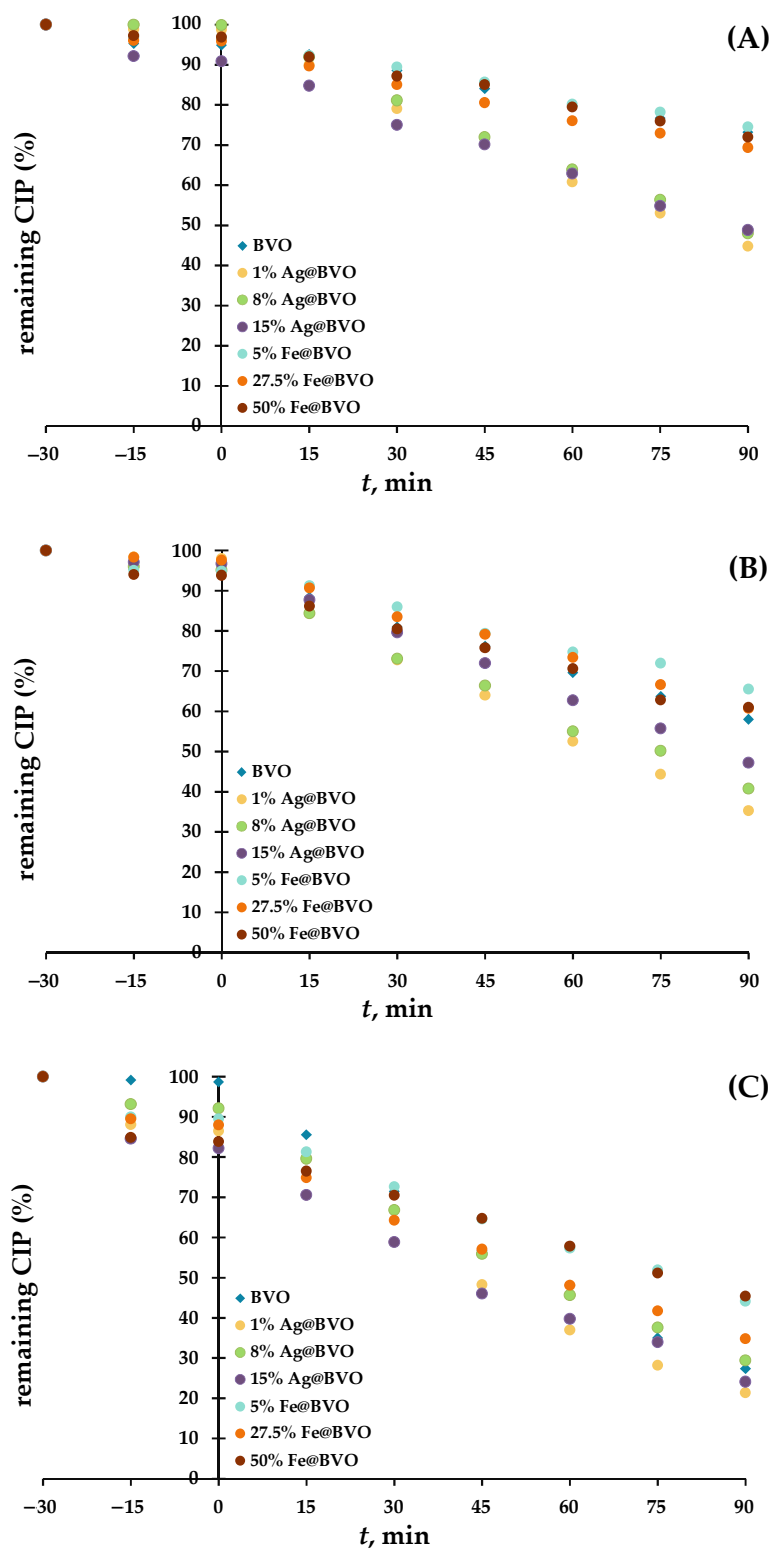


Figure S2. CIP remaining in solution during photocatalytic degradation (0 to 90 min) with BVO, Fe@BVO (5%, 27.5% and 50% wt. Fe) and Ag@BVO (1%, 8%, 15% wt. Ag), including the initial removal in the dark (from -30 to 0 min) at (A) pH 4, (B) pH 6 and (C) pH 8.

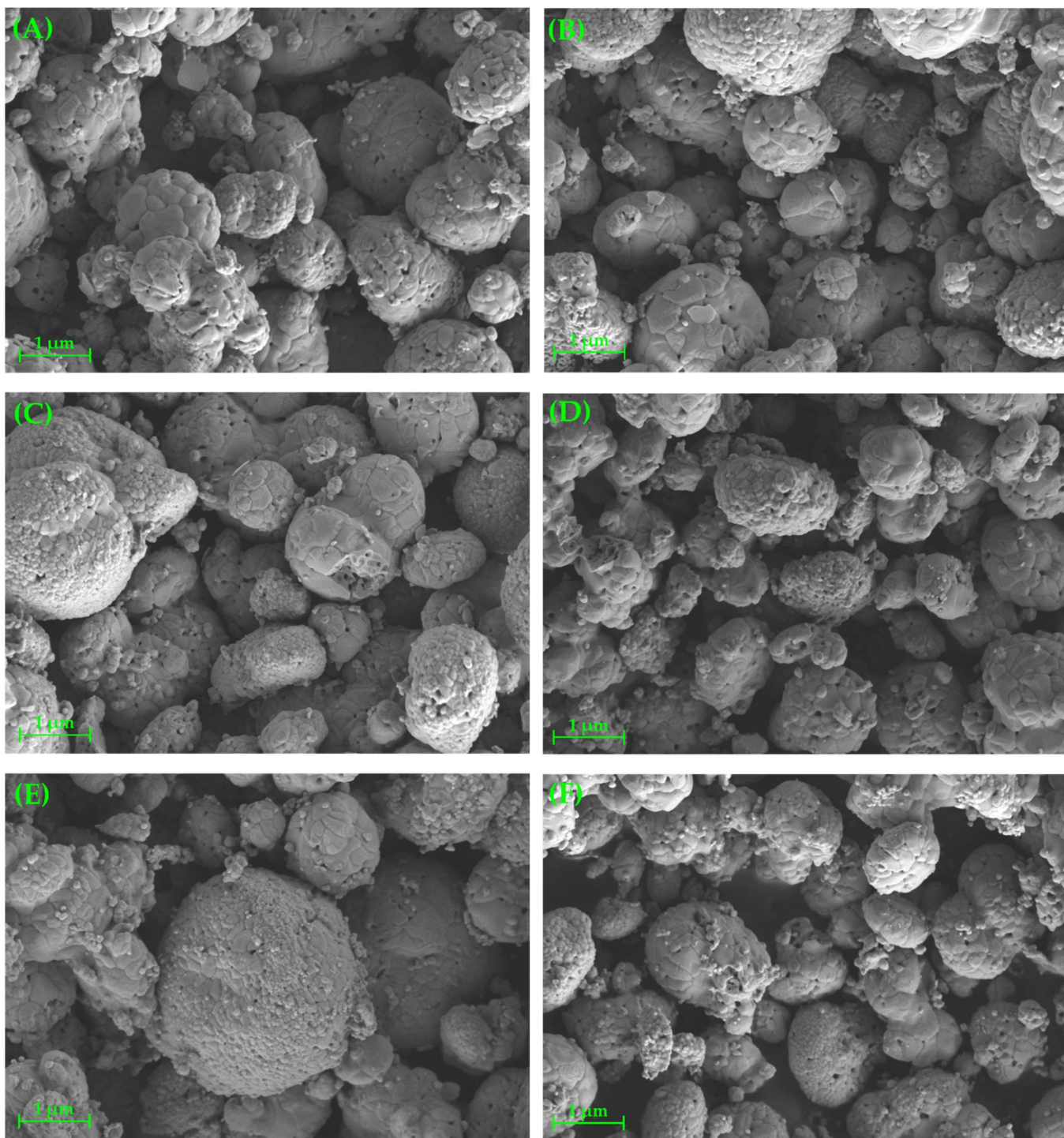


Figure S3. FE-SEM micrographs of Fe@BVO: (A) 5% wt. Ag, (B) 27.5% wt. Fe, (C) 50% wt. Fe; and Ag@BVO: (D) 1% wt. Ag, (E) 8% wt. Ag, (F) 15% wt. Ag.

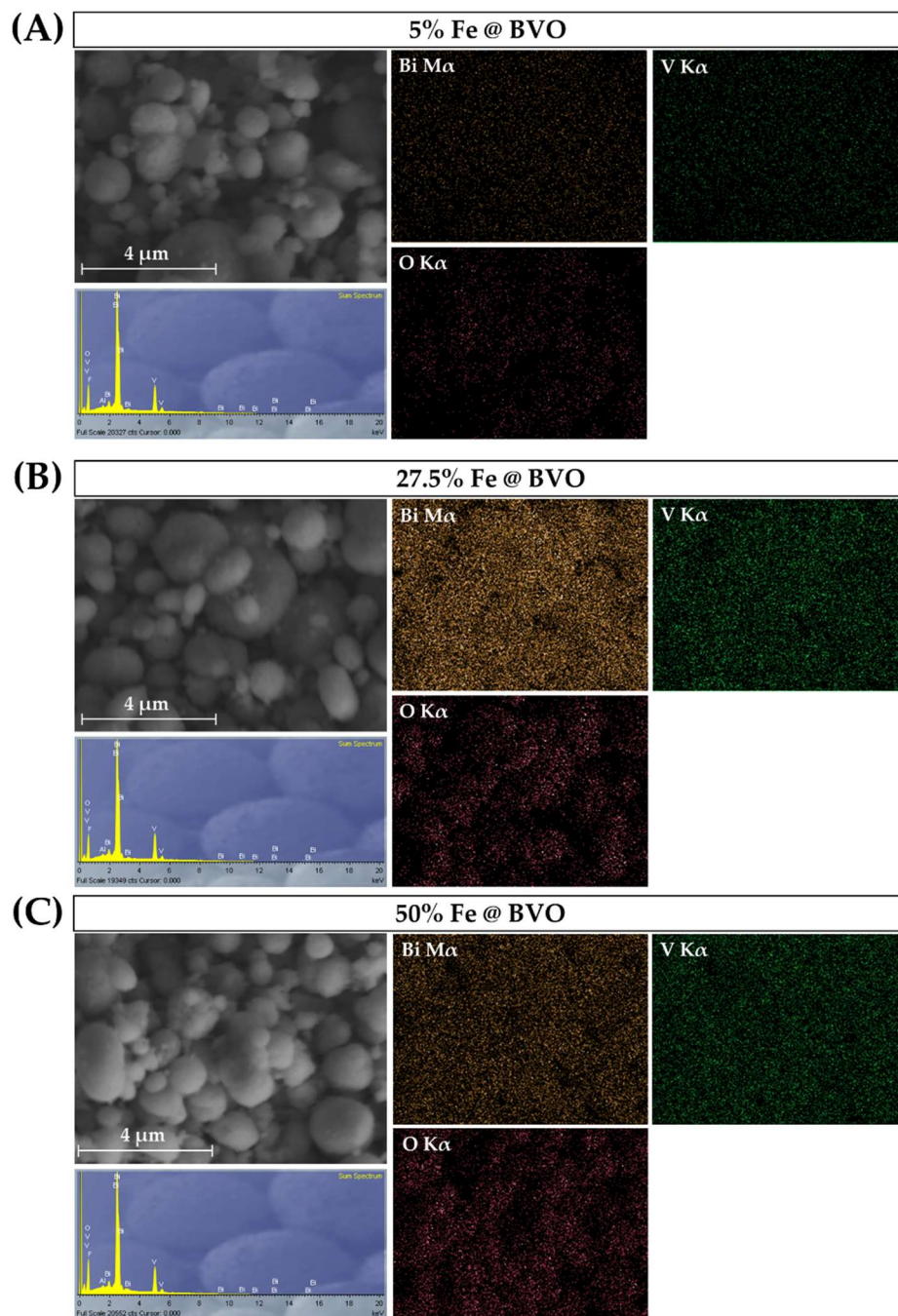


Figure S4. Energy dispersive X-ray (EDS) spectra of Fe@BVO samples, namely: (A) 5% wt. Fe, (B) 27.5% wt. Fe, (C) 50% wt. Fe content during photodeposition.

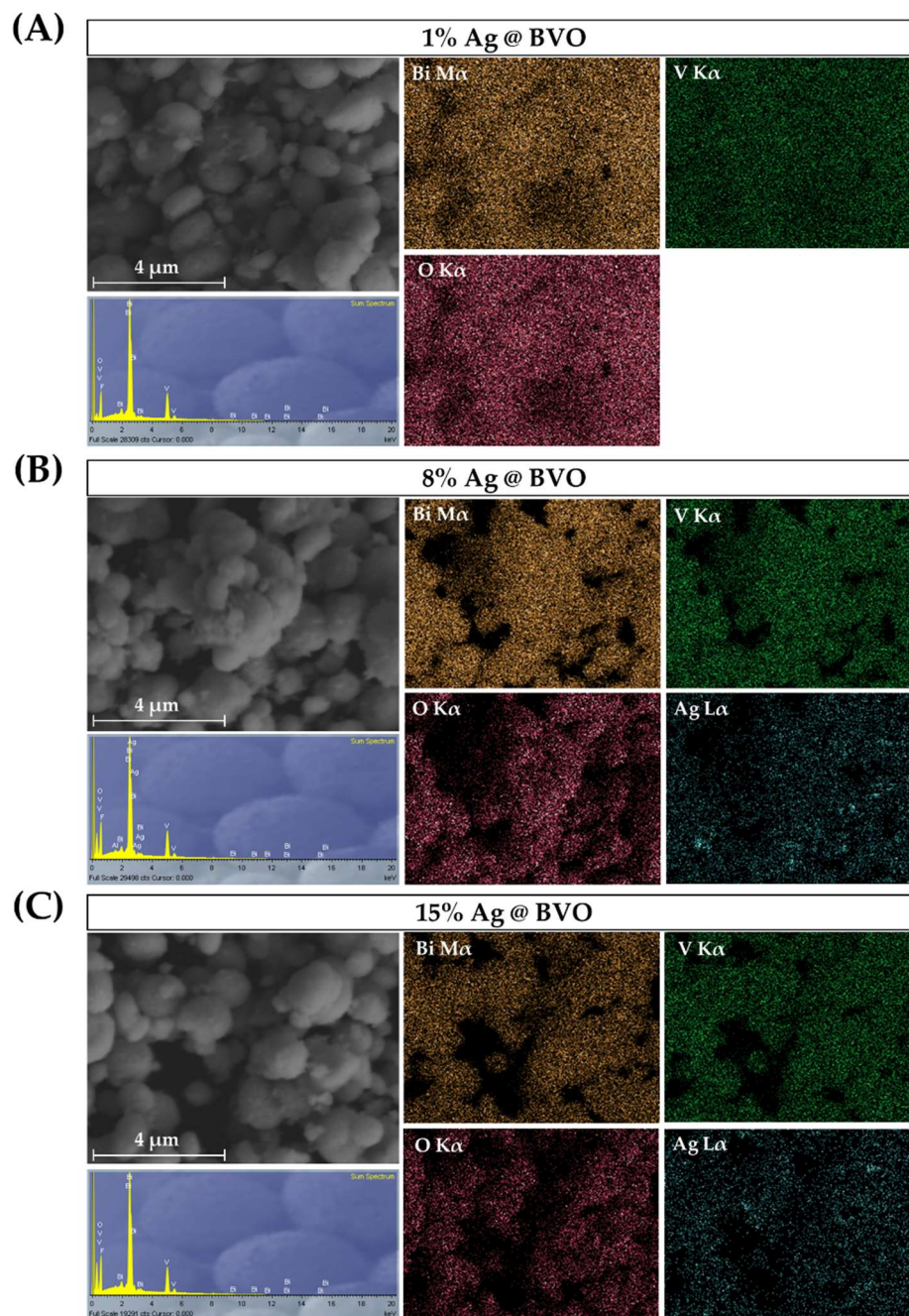


Figure S5. Energy dispersive X-ray spectra (EDS) of Ag@BVO samples including sum spectra for: (A) 1% wt. Ag, (B) 8% wt. Ag, (C) 15% wt. Ag loading on BiVO₄.

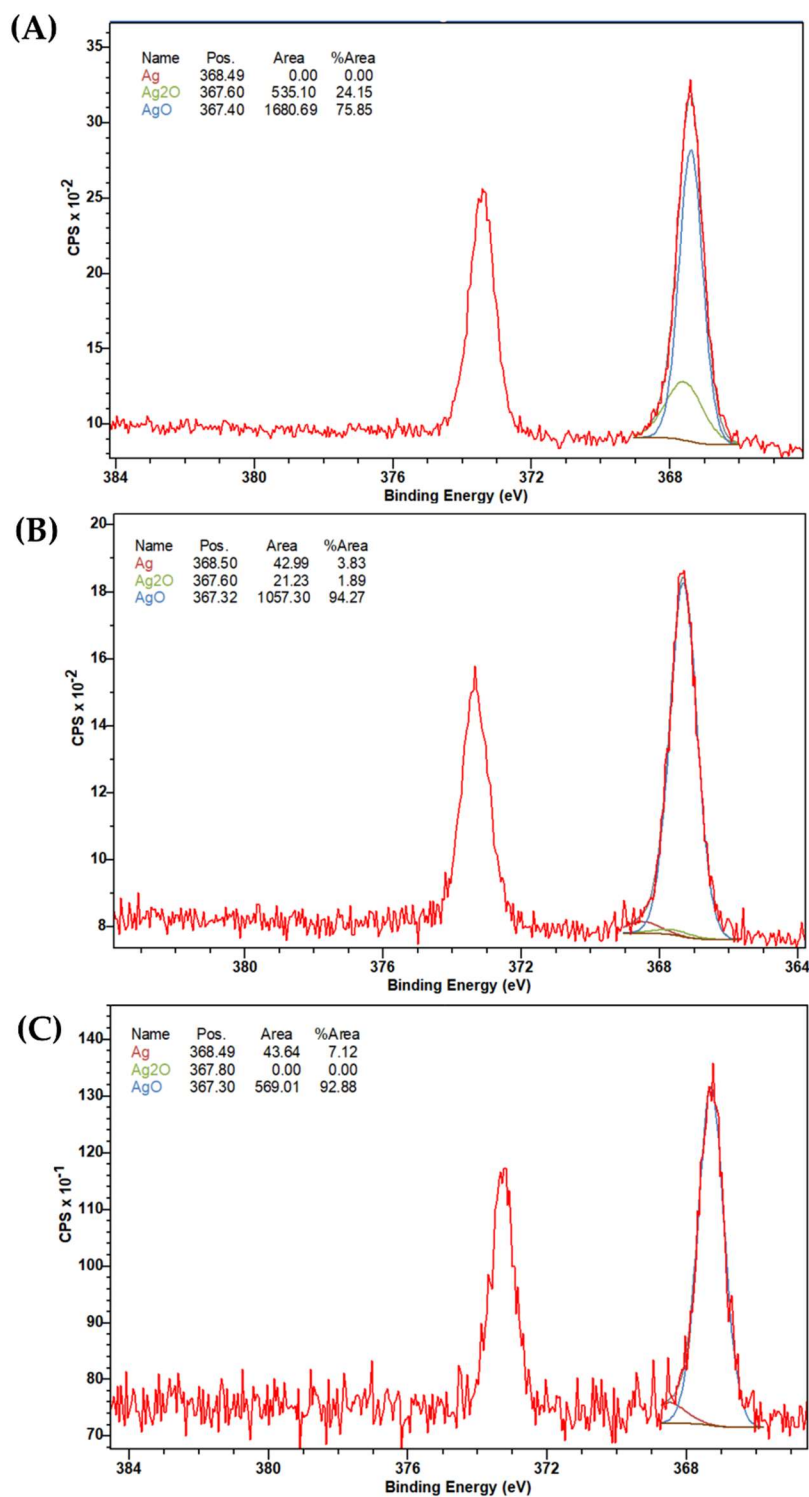


Figure S6. Deconvoluted X-ray photoelectron spectra (XPS) of Ag@BVO samples: (A) 1% Ag@BVO, (B) 8% Ag@BVO, (C) 15% Ag@BVO

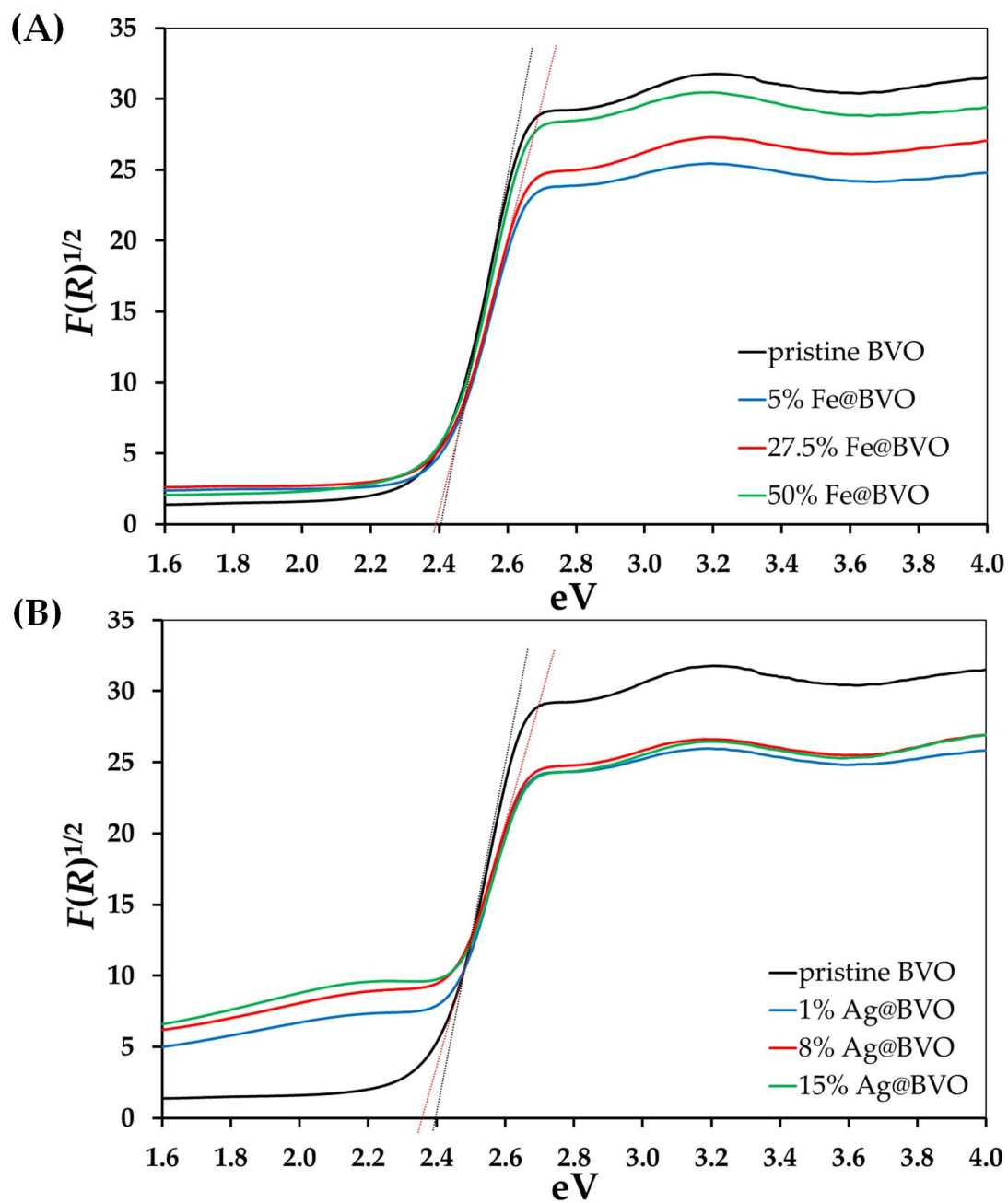


Figure S7. Diffuse reflectance spectra of (A) Fe@BVO and (B) Ag@BVO samples.

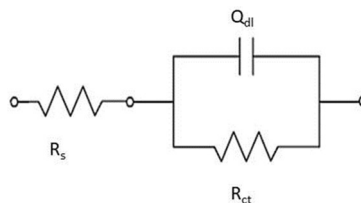


Figure S8. Model equivalent circuit used to fit EIS data. R_s represents the solution resistance, R_{ct} charge transfer resistance and Q_{dl} is a constant phase element related to the double layer capacitance.

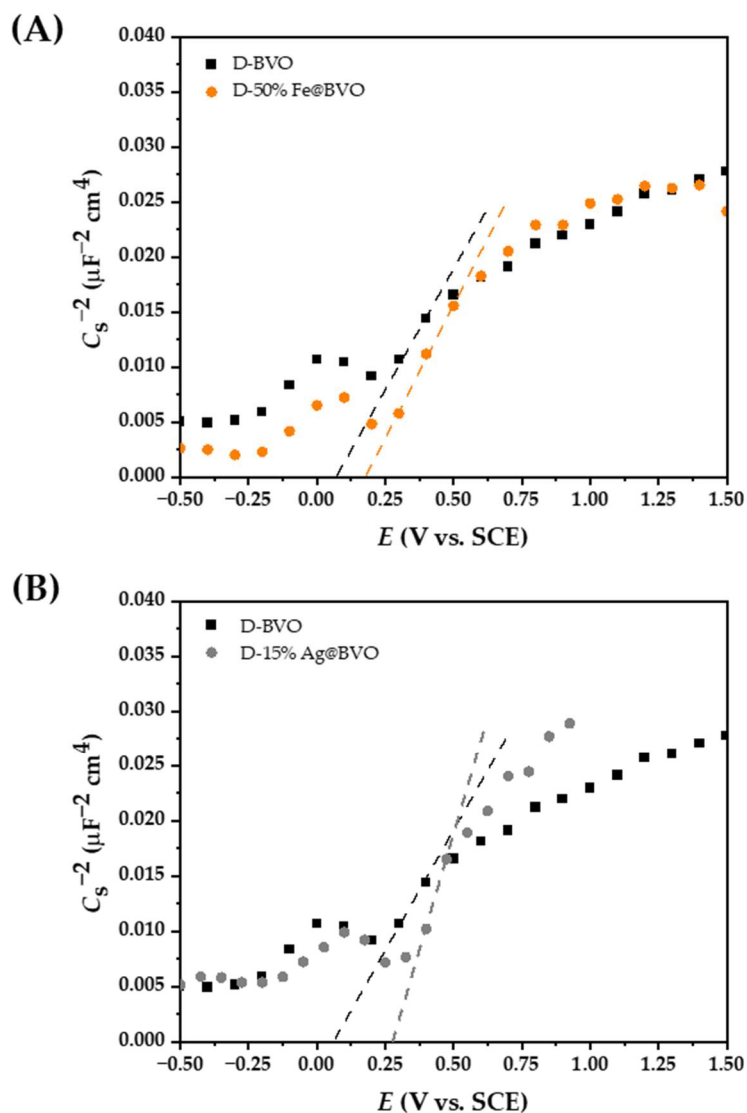


Figure S9. Mott-Schottky analysis of (A) 50% Fe@BVO and (B) 15% Ag@BVO.

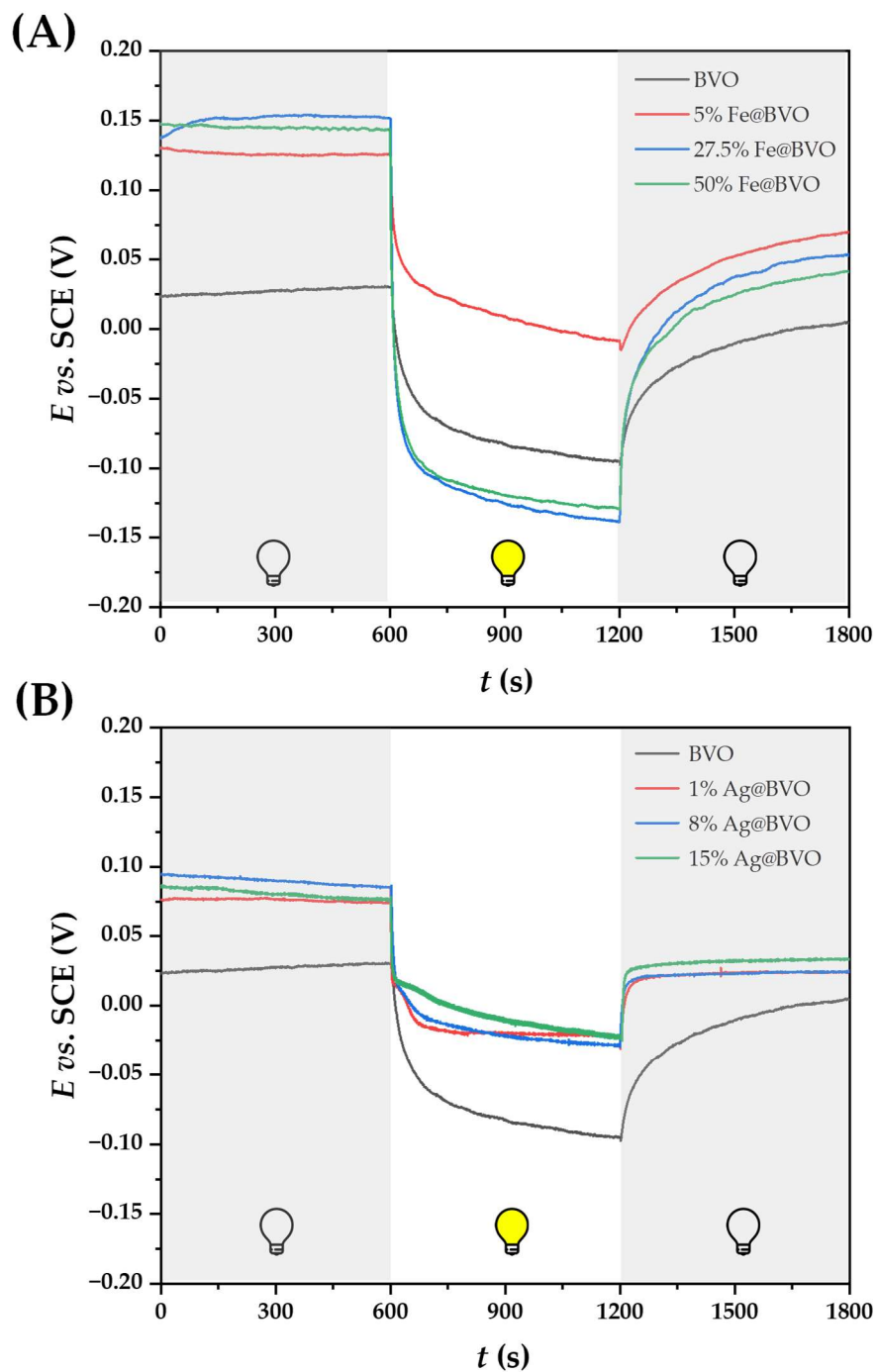


Figure S10. Open circuit potential (OCP) of (A) BVO and Fe@BVO photoelectrodes, (B) BVO and Ag@BVO photoelectrodes measured in the dark and under illumination.