Scheelite-related $M^{II}_xBi_{1-x}V_{1-x}Mo_xO_4$ (M^{II} – Ca, Sr) Solid Solutions Based Photoanodes for Enhanced Photoelectrochemical Water Oxidation

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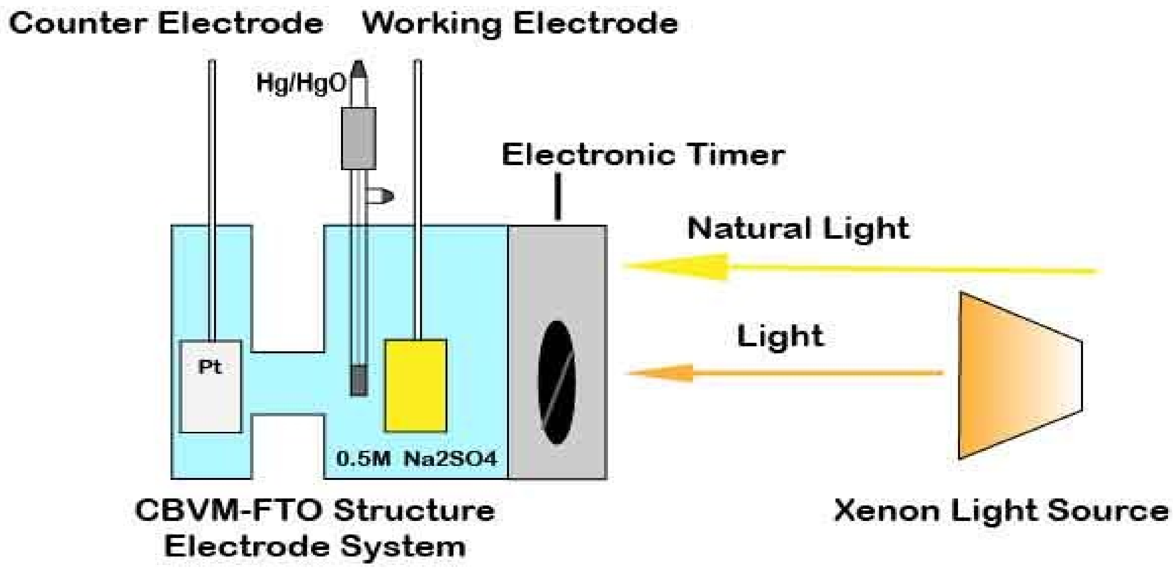


Fig. S1 Experiment Apparatus

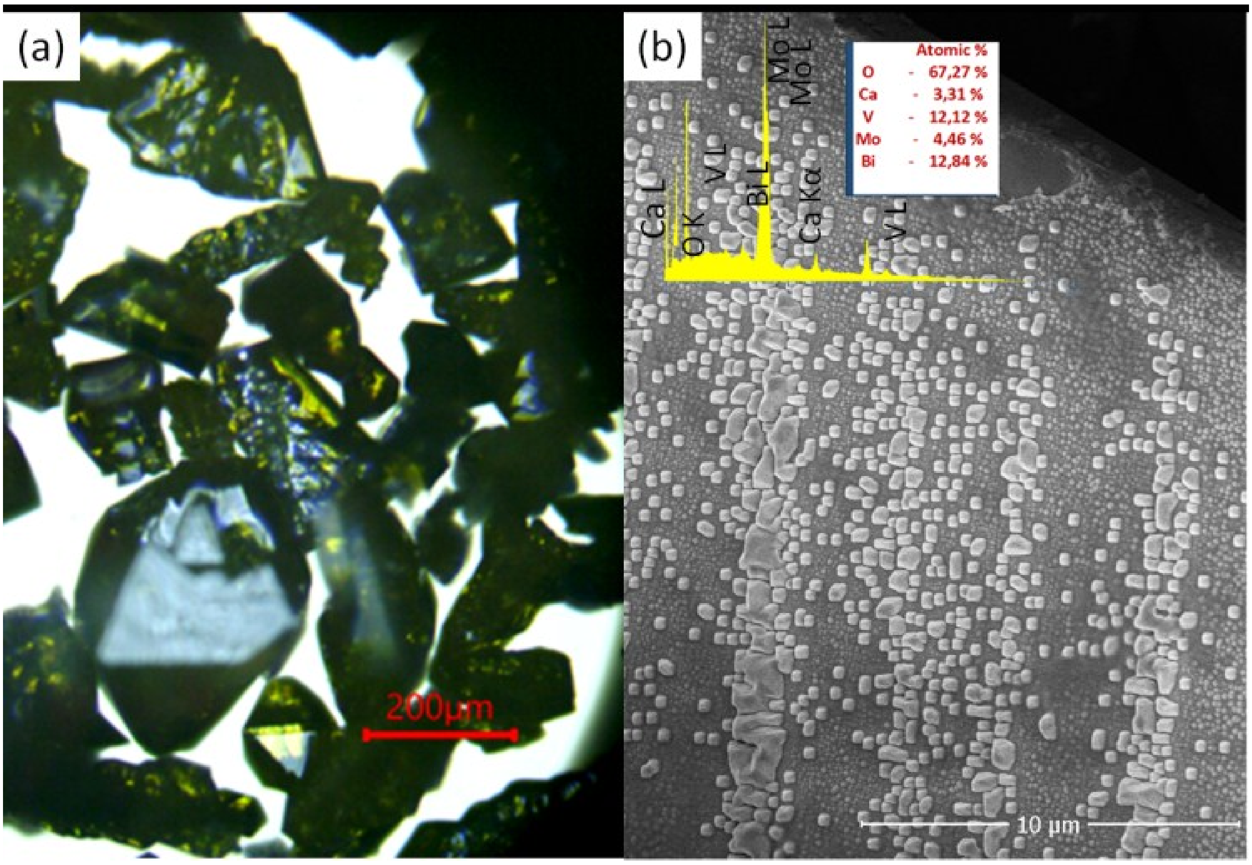


Fig. S2 Single crystals of $Ca_{0.126}Bi_{0.874}V_{0.874}Mo_{0.126}O_4$ photo (a) and SEM image of surfaces (insert is the associated EDS).

Table S1 Structural details for single-crystal $Bi_{0.874}Ca_{0.126}V_{0.874}Mo_{0.126}O_4$ and powdered $Bi_{0.5}Sr_{0.5}V_{0.5}Mo_{0.5}O_4$

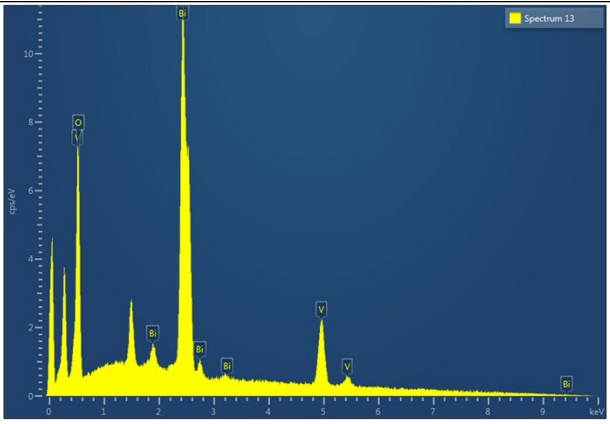
Crystal data		
Formula	$Bi_{0.874}Ca_{0.126}V_{0.874}Mo_{0.126}O_4$	$Bi_{0.5}Sr_{0.5}V_{0.5}Mo_{0.5}O_4$
Formula weight	308.3	285.74
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1$ (N80)	$I4_1/a$ (N88)
a, Å	5.1519(4)	5.26909(8)
c, Å	11.6330(8)	11.89254(19)
V, Å^3	308.76(4)	330.177(9)
Formula units, Z	4	4
Radiation type	Mo $K\alpha$ (λ = 0.71073 Å)	Cu $K\alpha$ (λ = 1.540598 Å)
Dx (Mg m−3)	6.632	
F(000)	530	
μ (mm^{-1})	52.95	
Temperature (K)	293	293
Data collection		
Diffractometer	Oxford Xcalibur-3 CCD area-detector	Shimadzu LabX XRD-6000
Scan	φ and ω	$2\theta_{step}$ = 0.02°
Absorption correction:	multi-scan (Blessing, 1995)	
Tmin, Tmax = 1	0.289, 1	
Measured reflections	2400	
Independent reflections	579	
Reflections with $I > 2\sigma(I)$	489	
R_{int}	0.070	
θ_{min}	36.2°	$2\theta_{min}$ = 10.041°
θ_{max}	4.3°	$2\theta_{max}$ = 105.061°
h, k, l	−8→7, −7→8, −11→19	
Refinement		
Refinement on F^2 $R[F^2 > 2\sigma(F^2)]$	0.054	
$wR(F^2)$	0.123	
S	1.90	
Reflections	579	
Parameters	30	34
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e·Å^{-3})	2.69, -5.44	
Friedel pairs	197	
R_p		9.660
R_{wp}		12.993
R_{exp}		4.474

Table S2. Atomic coordinates for $Bi_{0.874}Ca_{0.126}V_{0.874}Mo_{0.126}O_4$ and $Bi_{0.5}Sr_{0.5}V_{0.5}Mo_{0.5}O_4$

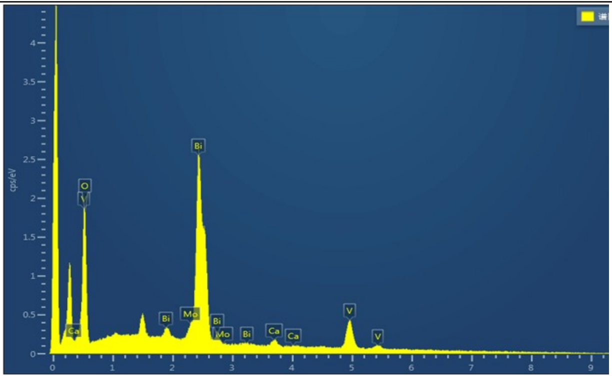
Atom	*Site*	*Occ.*	*x*	*y*	*z*
$Bi_{0.874}Ca_{0.126}V_{0.874}Mo_{0.126}O_4$					
Bi1	*4a*	*0.874(7)*	0.5	0.5	0.1248(3)
Ca1	*4a*	*0.126(7)*	0.5	0.5	0.1248(3)
V1	*4a*	*0.874(7)*	1	0	0.1267(9)
Mo1	*4a*	*0.126(7)*	1	0	0.1267(9)
O1	*8b*	*1*	0.8504(19)	0.250(3)	0.0438(18)
O2	*8b*	*1*	0.245(3)	0.131(2)	0.2027(19)
$Bi_{0.5}Sr_{0.5}V_{0.5}Mo_{0.5}O_4$					
Bi1	*4a*	*0.5*	0	0.25	0.625
Ca1	*4a*	*0.5*	0	0.25	0.625
V1	*4a*	*0.5*	-0.5	-0.25	0.625
Mo1	*4a*	*0.5*	-0.5	-0.25	0.625
O1	*16f*	*1*	-0.7479(13)	-0.3743(14)	0.5418(6)

Table S3 The EDS data for $M^{II}_{1-x}Bi_xV_xMo_{1-x}O_4$ (x =0-1) Solid Solutions

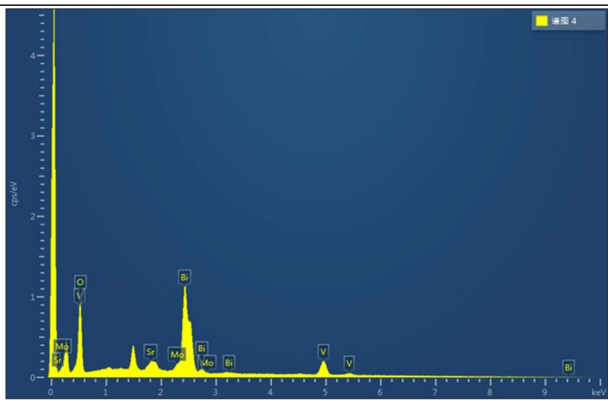
$BiVO_4$				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	65.50	17.7	64.51	16.67
V	16.34	18.1	15.73	16.67
O	18.17	64.2	19.76	66.66



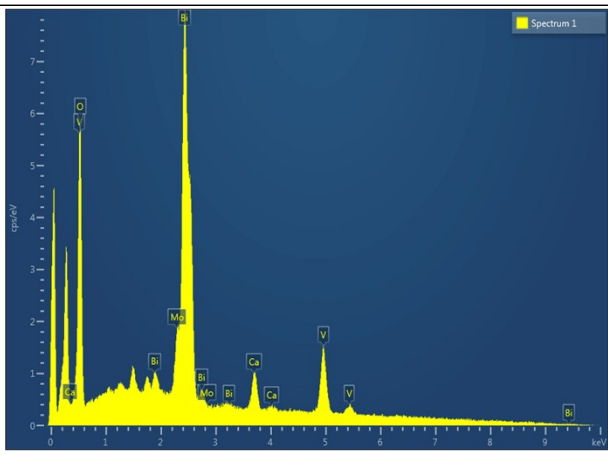
CBVM1				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	61.20	15.9	60.37	15.0
Mo	3.73	2.1	3.08	1.67
V	15.21	16.2	14.72	15.0
Ca	0.81	1.1	1.29	1.67
O	19.05	64.7	20.54	66.66



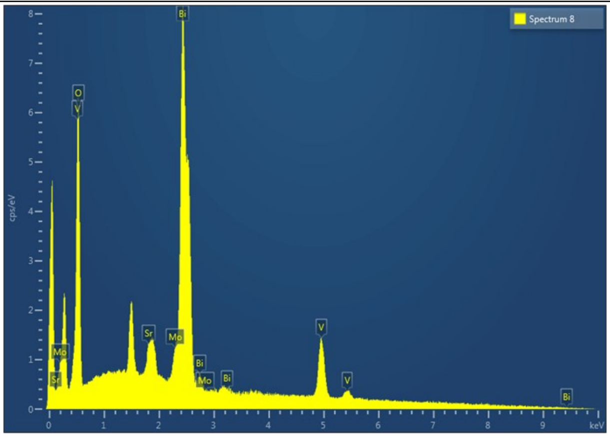
SBVM1				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	60.55	16.1	59.47	15.0
Mo	3.97	2.3	3.03	1.67
V	14.97	16.3	15.0	15.0
Sr	2.08	1.3	2.77	1.67
O	18.43	64.0	20.23	66.66



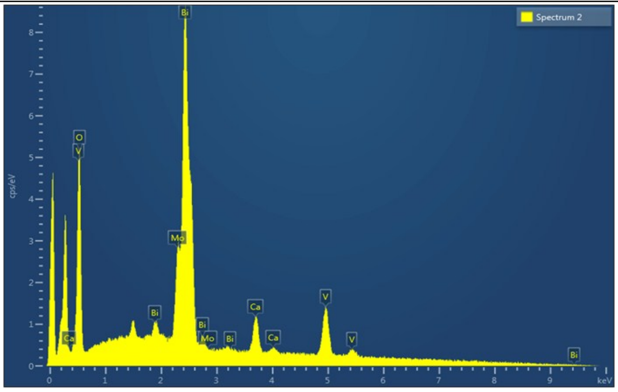
CBVM2				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	59.65	15.7	55.89	13.33
Mo	5.99	3.4	6.42	3.34
V	14.74	15.9	13.62	13.33
Ca	1.18	1.6	2.68	3.34
O	18.44	63.4	21.39	66.66



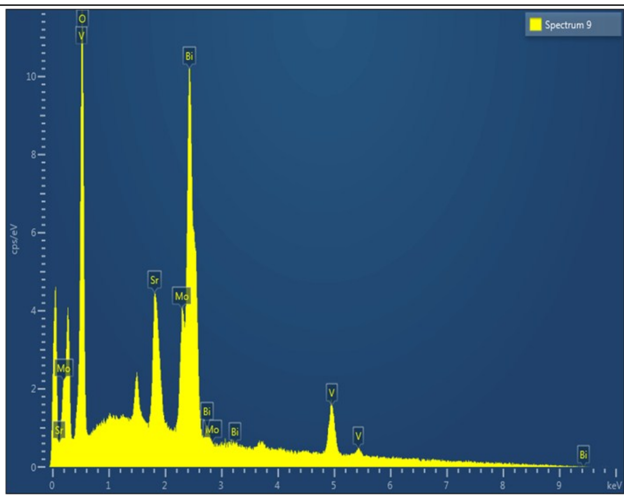
SBVM2				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	57.70	15.3	54.17	13.33
Mo	5.05	2.9	6.22	3.34
V	14.43	15.7	13.20	13.33
Sr	4.58	2.9	5.68	3.34
O	18.24	63.2	20.73	66.66



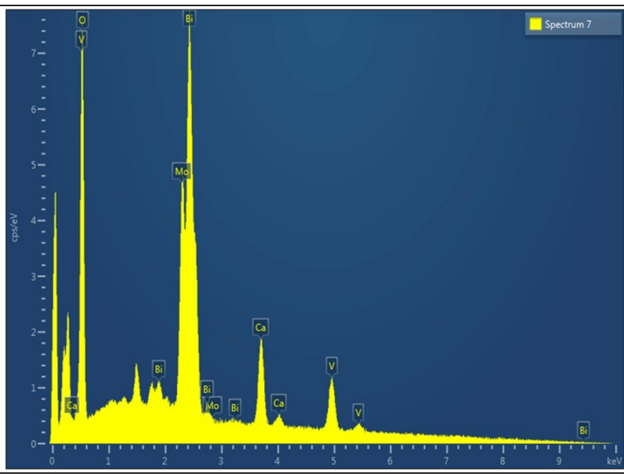
CBVM3				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	57.76	14.9	51.01	11.67
Mo	8.42	4.7	10.04	5.0
V	11.00	12.7	12.44	11.67
Ca	2.93	3.9	4.19	5.0
O	18.89	63.8	22.32	66.66



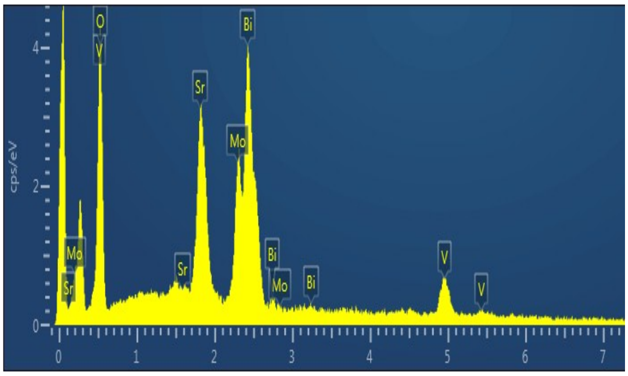
SBVM3				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	54.11	14.3	48.6	13.33
Mo	9.06	5.2	9.56	3.34
V	11.96	13.0	11.85	13.33
Sr	6.55	4.1	8.73	3.34
O	18.32	63.4	21.26	66.66



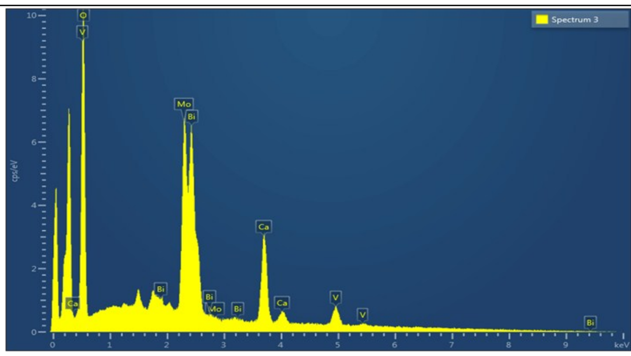
CBVM5				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	42.59	9.8	39.89	8.34
Mo	20.61	10.3	18.31	8.33
V	9.44	8.9	9.72	8.34
Ca	6.20	7.4	7.65	8.33
O	21.16	63.6	24.43	66.66



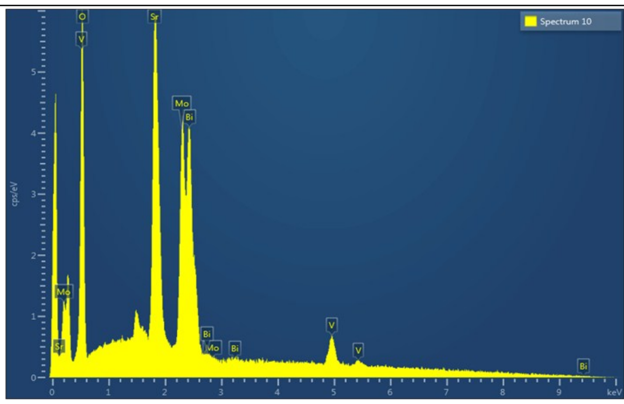
SBVM5				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	38.45	9.5	36.57	8.34
Mo	18.38	9.9	16.79	8.33
V	9.68	9.8	8.91	8.34
Sr	14.13	8.3	15.33	8.33
O	19.36	62.6	22.4	66.66



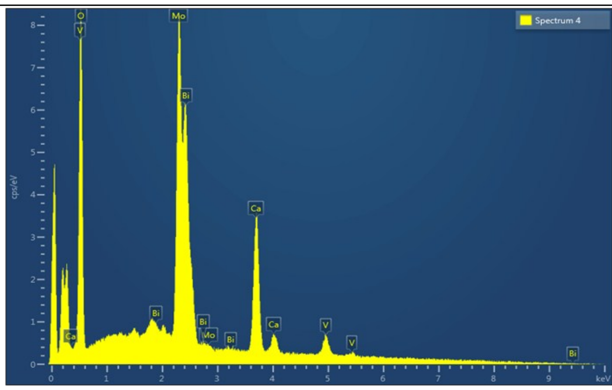
CBVM7				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	33.86	7.3	26.43	5.0
Mo	27.75	13.0	28.32	11.67
V	5.77	5.1	6.44	5.0
Ca	10.18	11.4	11.83	11.67
	22.44	63.2	26.98	66.66



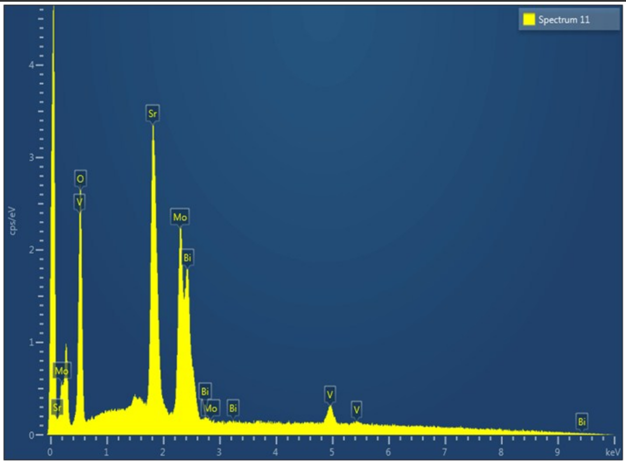
SBVM7				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	27.35	6.4	23.18	5.0
Mo	23.79	12.1	24.83	11.67
V	6.19	5.9	5.65	5.0
Sr	21.92	12.2	22.68	11.67
O	20.75	63.4	23.66	66.66



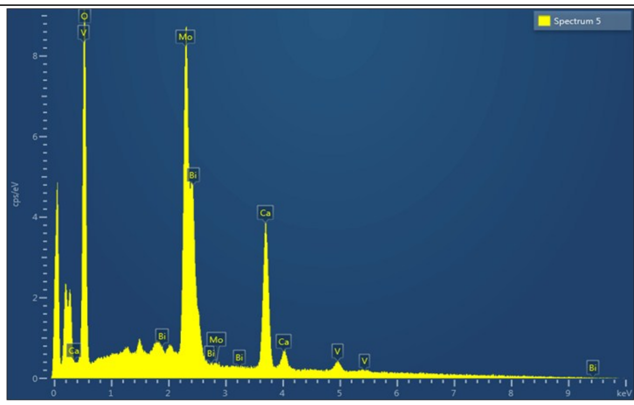
CBVM8				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	20.40	3.8	18.59	3.34
Mo	34.28	13.9	34.15	13.33
V	3.82	2.9	4.53	3.34
Ca	14.89	14.5	14.26	13.33
O	26.61	64.9	28.47	66.66



SBVM8				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	12.53	2.7	15.90	3.34
Mo	33.0	15.5	29.21	13.33
V	3.43	3.0	3.87	3.34
Sr	28.31	14.6	26.67	13.33
O	22.73	64.2	24.35	66.66



CBVM9				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	11.98	2.2	9.84	1.67
Mo	42.10	16.8	40.65	15.0
V	2.01	1.5	2.4	1.67
Ca	17.90	17.1	16.98	15.0
O	26.01	62.4	30.13	66.66



SBVM9				
	Found		*Calculated*	
	Wt. %	*At. %*	*Wt. %*	*At. %*
Bi	6.06	1.3	8.19	1.67
Mo	35.64	16.6	33.84	15.0
V	1.18	1.0	2.0	1.67
Sr	34.42	17.6	30.9	15.0
O	22.69	63.5	25.07	66.66

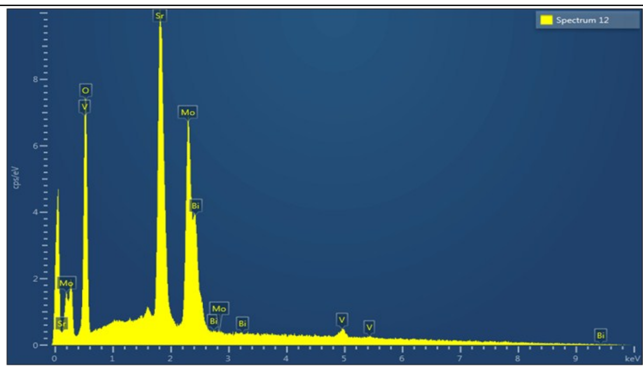


Table S4 Lattice Parameters (Å or Å^3) and calculated Eg values of $M^{II}_{1-x}Bi_xV_xMo_{1-x}O_4$ (x =0-1) Solid Solutions

Formula	**Abr.**	**a**	**c**	**V**	**Eg**
$BiVO_4$*	-	*a*= 5.197	*c* =11.702	309.9	2.34
		b= 5.096	*β*= 90.4		
$Ca_{0.1}Bi_{0.9}V_{0.9}Mo_{0.1}O_4$	CBVM1	5.1433(2)	11.6733(1)	308.81(3)	2.47
$Ca_{0.2}Bi_{0.8}V_{0.8}Mo_{0.2}O_4$	CBVM2	5.1553(1)	11.6512(2)	309.84(1)	2.50
$Ca_{0.3}Bi_{0.7}V_{0.7}Mo_{0.3}O_4$	CBVM2	5.1603(3)	11.1651(1)	310.43(3)	2.51
$Ca_{0.5}Bi_{0.5}V_{0.5}Mo_{0.5}O_4$	CBVM5	5.2065(1)	11.1451(1)	310.96(2)	2.72
$Ca_{0.7}Bi_{0.3}V_{0.3}Mo_{0.7}O_4$	CBVM7	5.2231(1)	11.4237(2)	311.61(1)	3.08
$CaMoO_4$[19]	-	5.3255	11.4298	331.8	3.64
$Sr_{0.1}Bi_{0.9}V_{0.9}Mo_{0.1}O_4$	SBVM1	5.16087(4)	11.7229(1)	313.18(3)	2.35
$Sr_{0.2}Bi_{0.8}V_{0.8}Mo_{0.2}O_4$	SBVM1	5.1882(1)	11.7713(3)	316.85(2)	2.58
$Sr_{0.3}Bi_{0.7}V_{0.7}Mo_{0.3}O_4$	SBVM1	5.2154(2)	11.8172(1)	321.44(2)	2.61
$Sr_{0.5}Bi_{0.5}V_{0.5}Mo_{0.5}O_4$	SBVM1	5.2691(3)	11.8926(2)	330.182(1)	2.81
$Sr_{0.7}Bi_{0.3}V_{0.3}Mo_{0.7}O_4$	SBVM1	5.3204(1)	11.9557(1)	338.43(2)	2.95
$Sr_{0.8}Bi_{0.2}V_{0.2}Mo_{0.8}O_4$	SBVM1	5.3473(4)	11.98(2)	342.67(2)	3.12
$Sr_{0.9}Bi_{0.1}V_{0.1}Mo_{0.9}O_4$	SBVM1	5.3696(1)	11.99(1)	345.82(4)	3.28
$SrMoO_4$ [30]	-	5.222(1)	11.425(3)	332.1	4.06

*$BiVO_4$ is indexed in monoclinic crystal system[19]

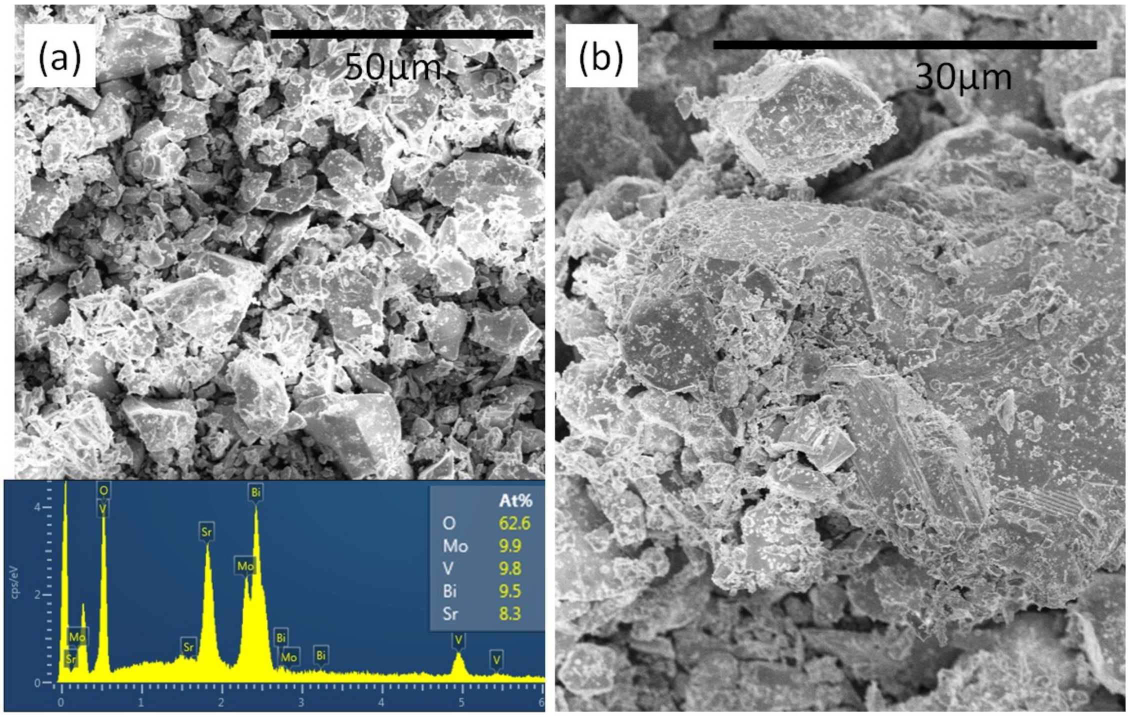


Fig. S3 SEM images of (a) SBVM5 powder (the insert is the associated EDS) and $BiVO_4$ prepared under the same conditions (b).

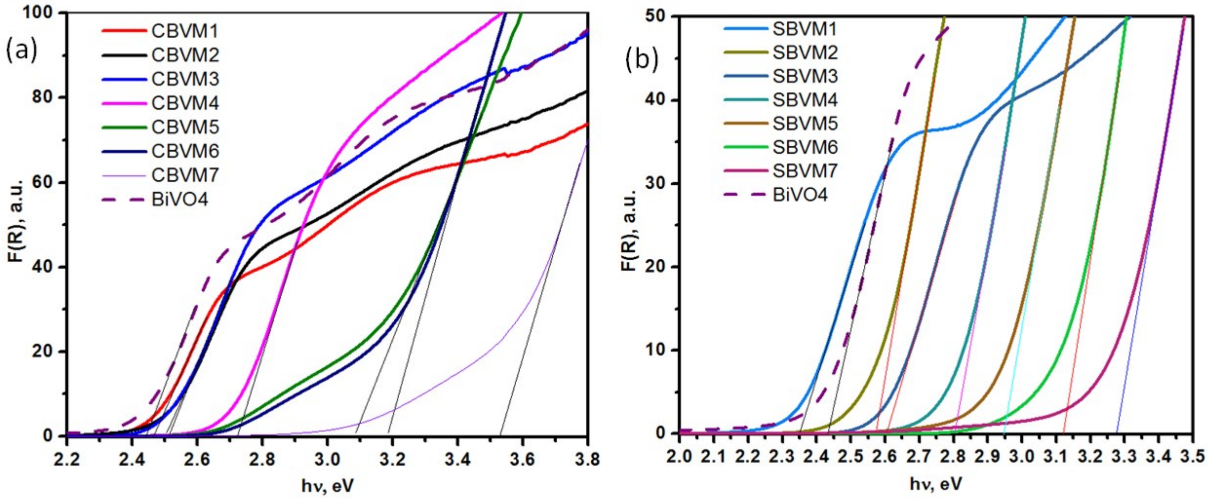


Fig. S4 Determination of bandgap values for pure $BiVO_4$ and $M^{II}_{1-x}Bi_xV_xMo_{1-x}O_4$ (x =0-1) solid solutions calculated using Kubelka –Munk function.

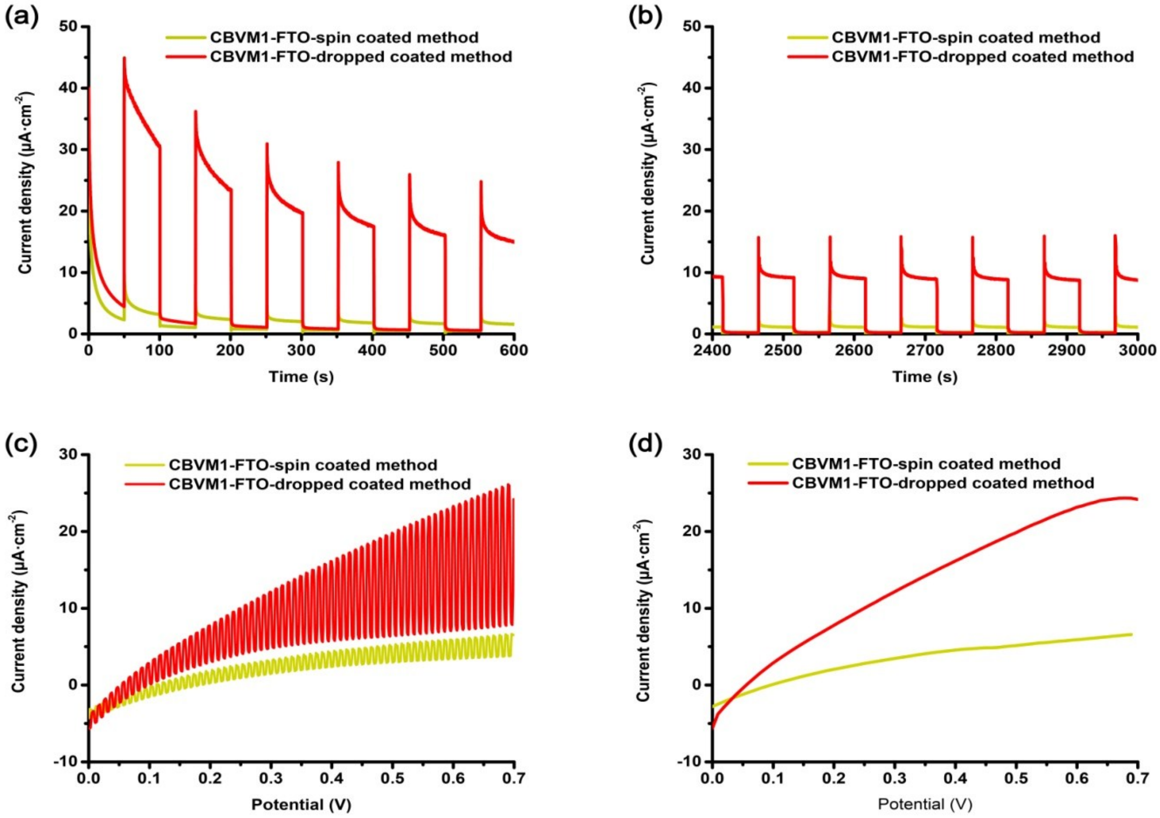


Fig. S5 Comparative testing of CBVM1-FTO performance prepared by different methods.

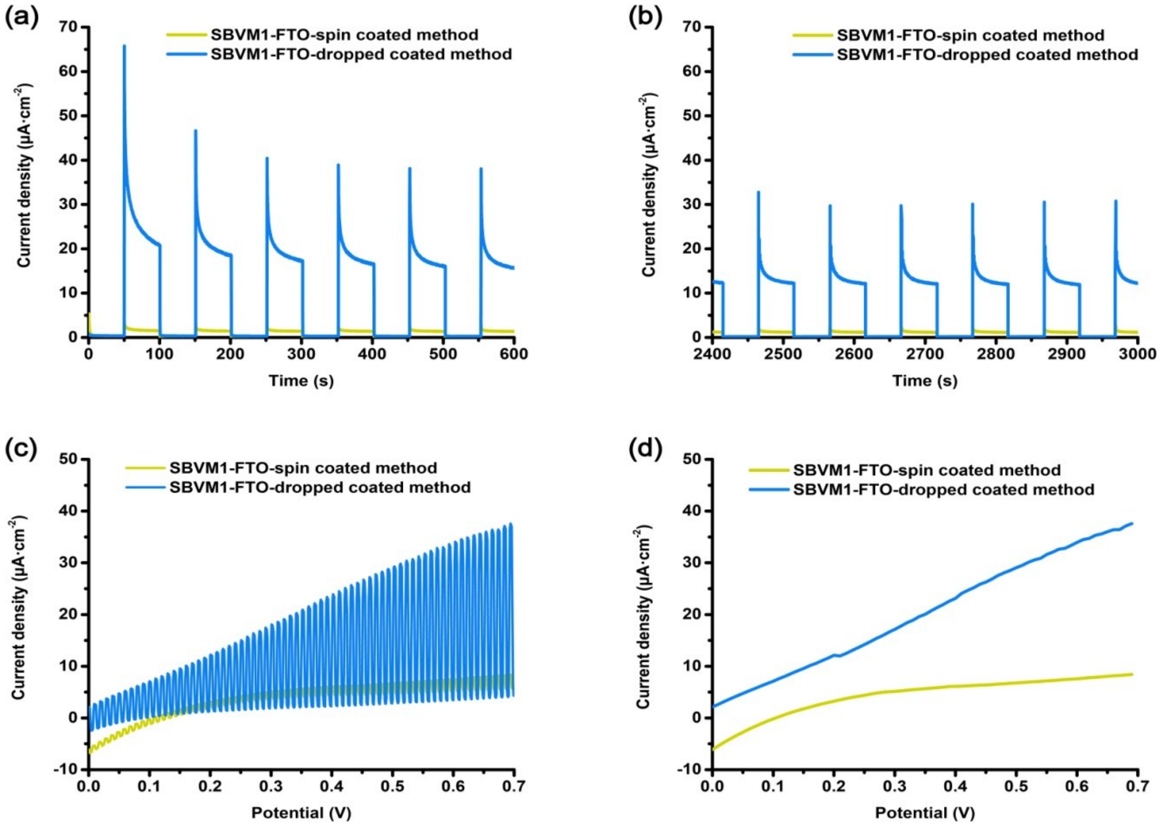


Fig. S6 Comparative testing of SBVM1-FTO performance prepared by different methods.

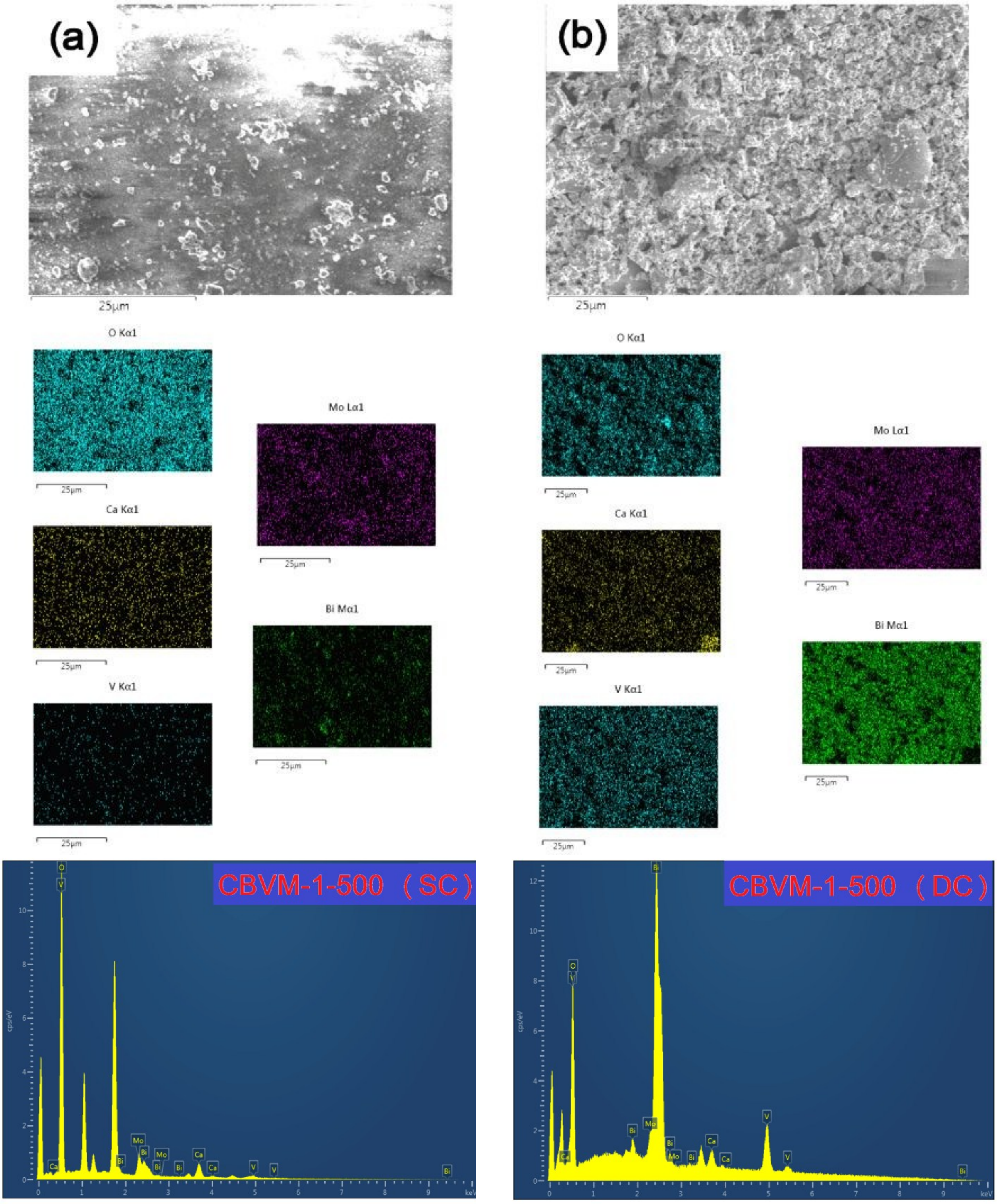


Fig. S7 SEM image and EDX mapping for CBVM-1 sample on the FTO surface prepared by spin-coating (a) and dropped –coating (b) methods after annealing at 500°C.

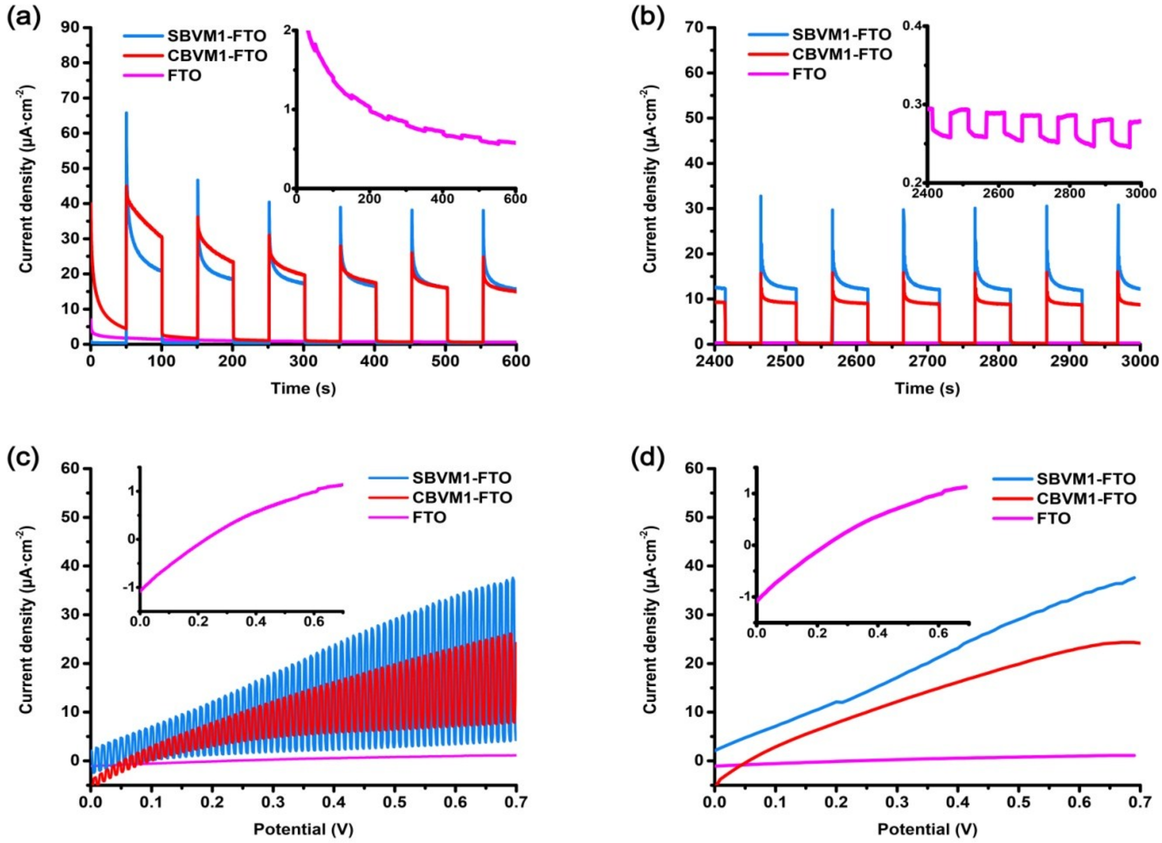


Fig. S8 The results of I-t tests and photocurrent – potential curves for FTO.

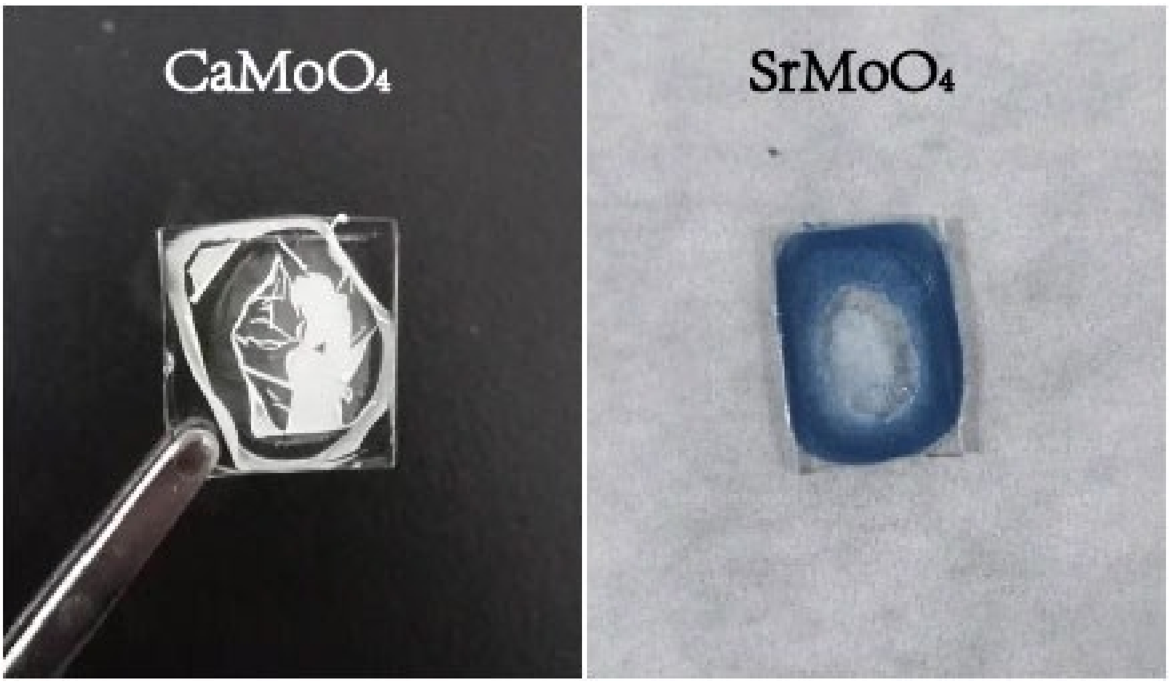


Fig. S9 Exfoliation of $CaMoO_4$-Nafion film from FTO surface and the view of the $SrMoO_4$-FTO electrode dried at 60°C.

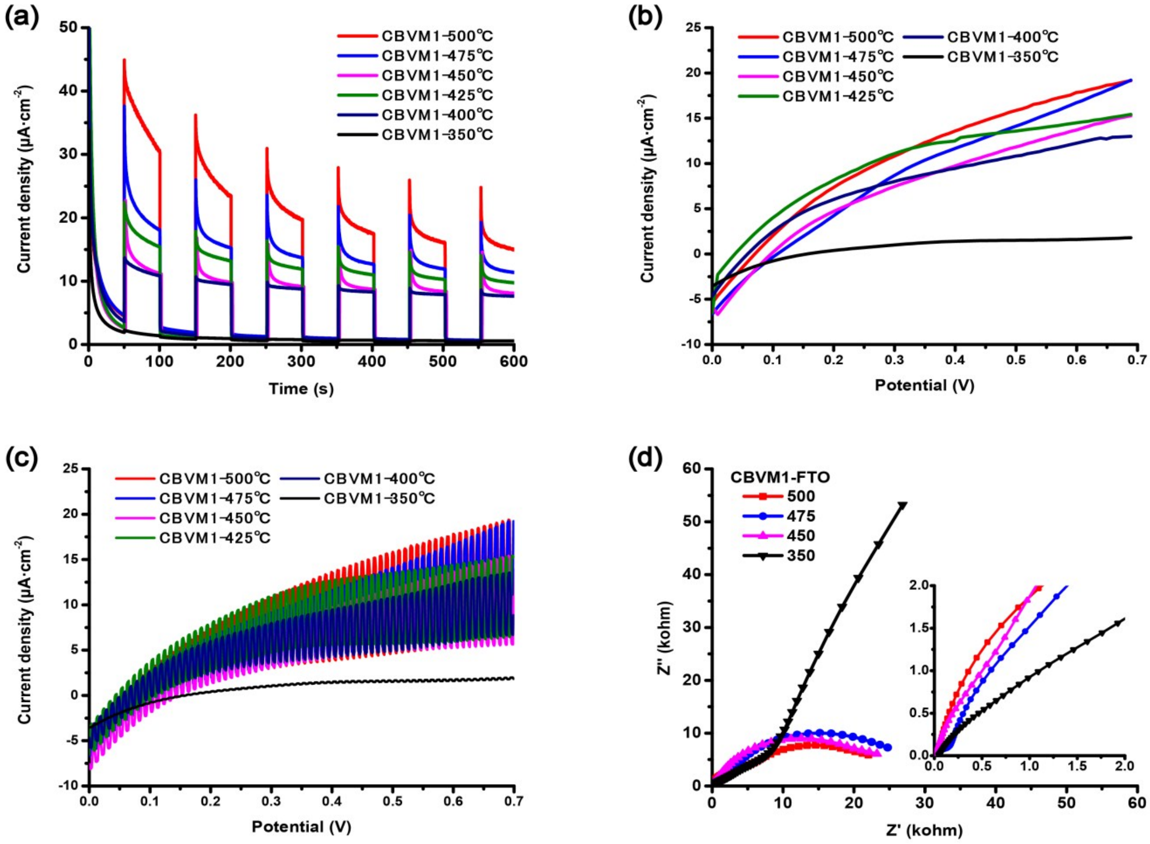


Fig. S10 Comparative testing of CBVM1-FTO performance after final annealing at different temperatures (a) photocurrent –time curves; (b) photocurrent–potential curves; (c) dependencies photocurrent–potential, that show the change in LSV values (d) the results of EIS spectroscopy (the insert – a high-frequency region of the spectra). All measurements have been taken in 0.5 M Na_2SO_4 solution. The chopped light with power of 100 mW·cm^{-2}.

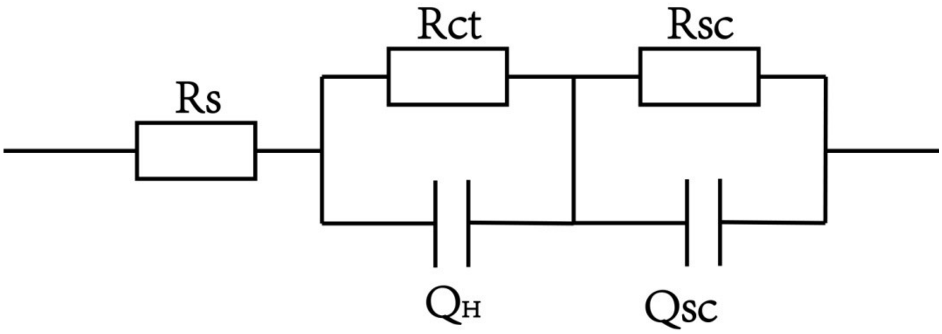


Fig. S11 The equivalent scheme for EIS measurement: R_s – solution resistance, R_{ct} – the resistance of electron transfer on a photoanode; Q_H – constant phase element (CPE),represents Helmholtz layer capacitance; Q_{SC} – constant phase element (CPE), represents space charge layer capacitance; R_{SC} is the space charge separation resistance Q is the constant phase element (CPE). Since the charge transport and transfer process is considered to be normally much faster in the bulk than that in the semiconductor-electrolyte interface, the low frequency response has been assigned to the semiconductor-electrolyte charge transfer behavior (R_{ct} and Q_H) while the high frequency response has been designated to the behavior in the semiconductor bulk ($_{RSC}$ and Q_{SC}) correspondingly.

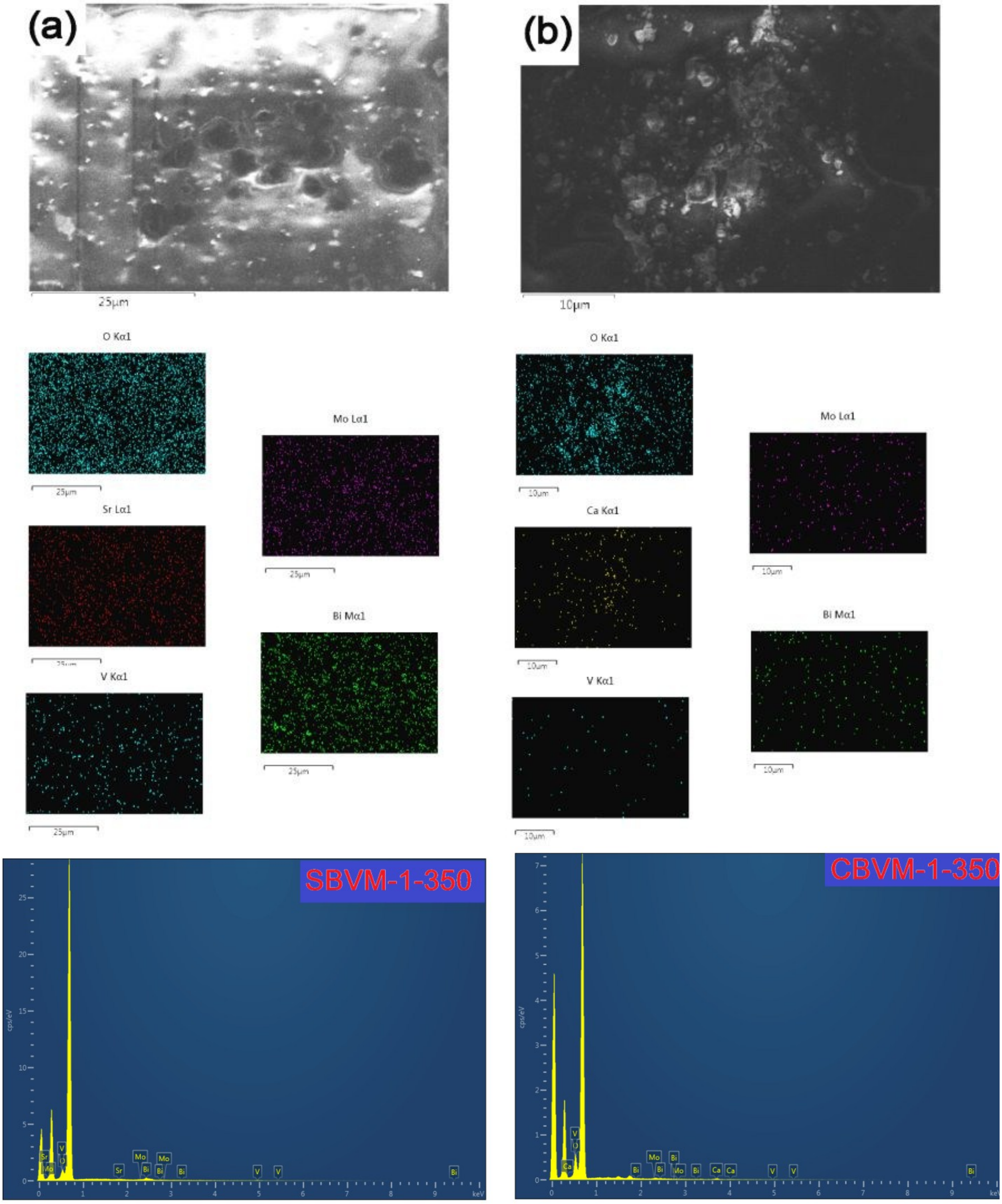


Fig. S12 SEM images and EDX mapping for samples SBVM-1 (a) and CBVM-1 (b) on the FTO surface after annealing at 350°C.

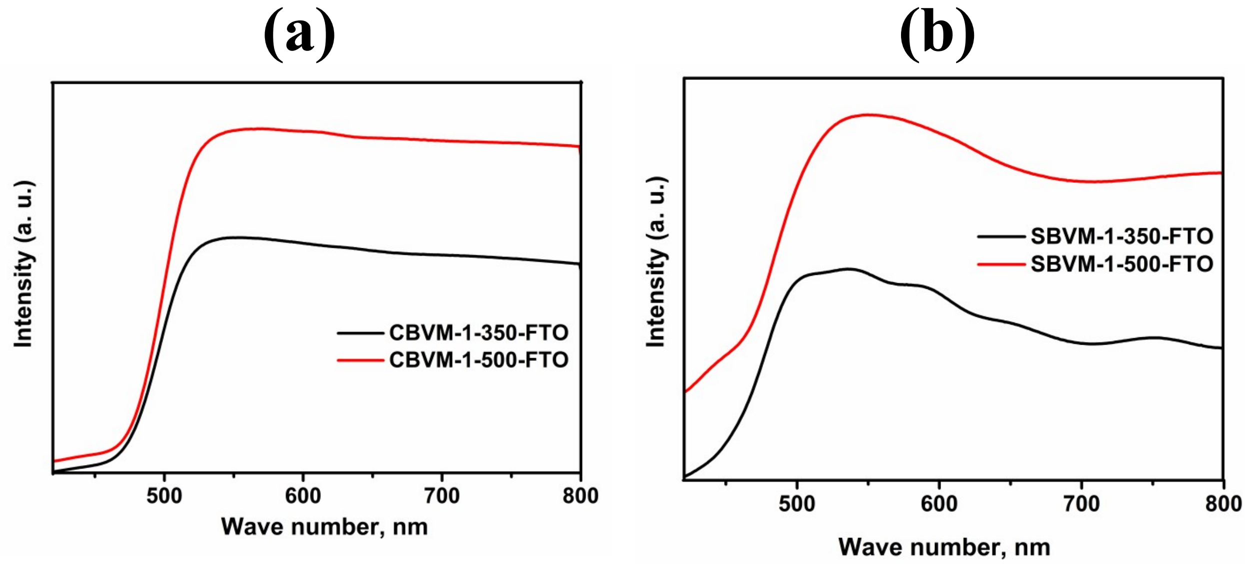


Fig. S13 UV-Vis diffuse reflectance spectra for electrodes after annealing at 350 and 500 ˚C: (a) CBMV-1-350-FTO and CBMV-1-500-FTO; (b) SBMV-1-350-FTO and SBMV-1-500-FTO.

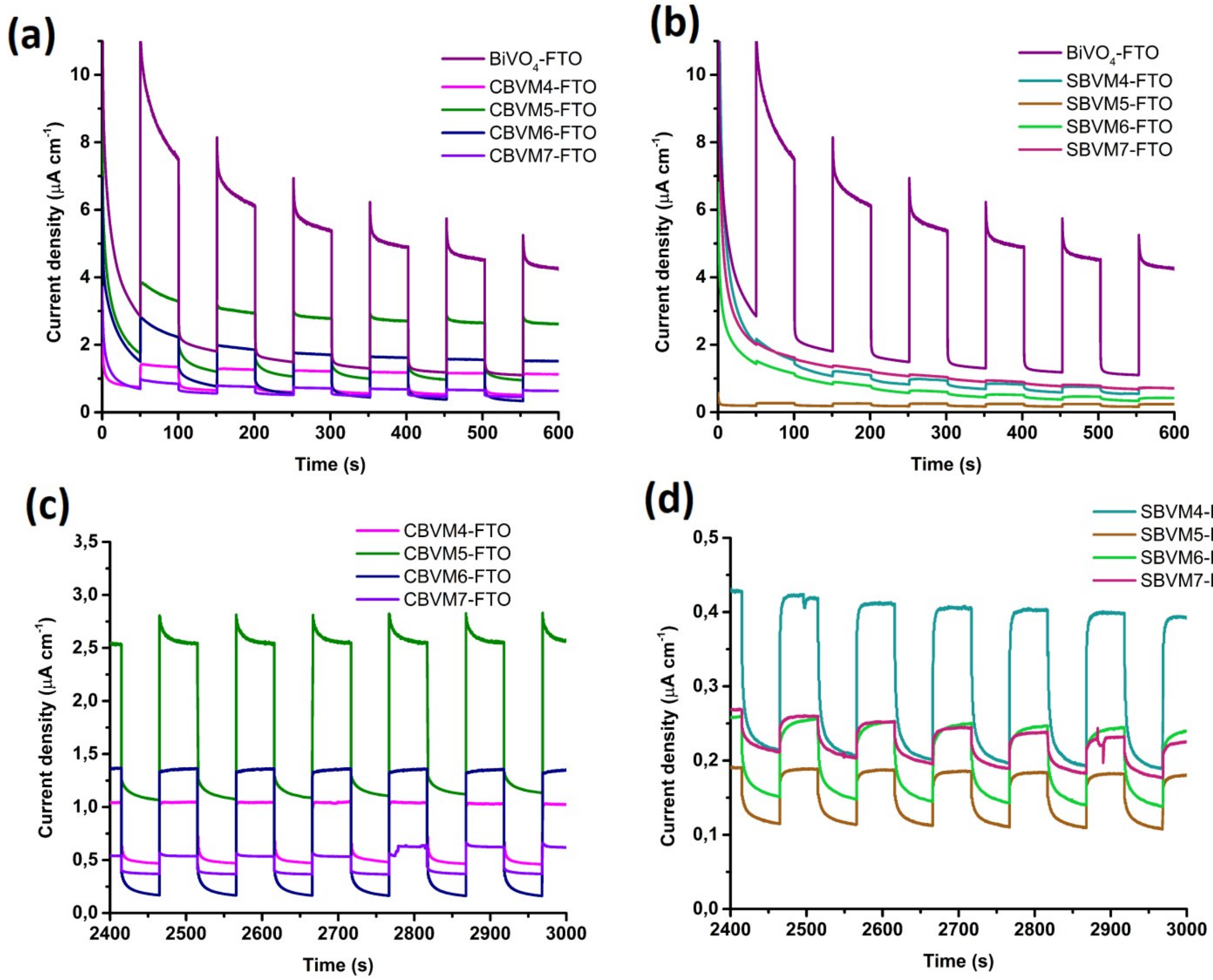


Fig. S14 The results of I-t tests for electrodes based on solid solution $M^{II}_xBi_{1-x}V_{1-x}Mo_xO_4$ (where M^{II} – Ca, Sr) within the values x = 0.5, 0.7, 0.8 i 0.9: (a, b) after 10 min of testing and (c,d) after photocurrent stabilization CBMV(4-7)-FTO, SBVM(4-7)-FTO, $BiVO_4$-FTO.

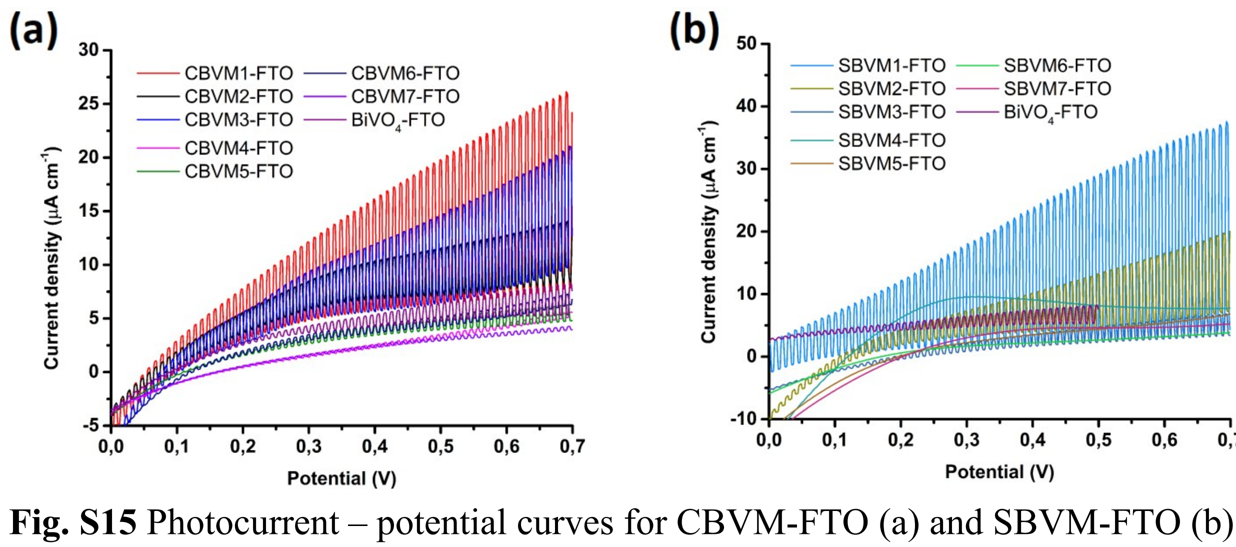


Fig. S15 Photocurrent – potential curves for CBVM-FTO (a) and SBVM-FTO (b) photoanodes.