Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The Effect of Mo doping on Charge Separation Dynamics and Photocurrent Performance of $BiVO_4$ Photoanodes

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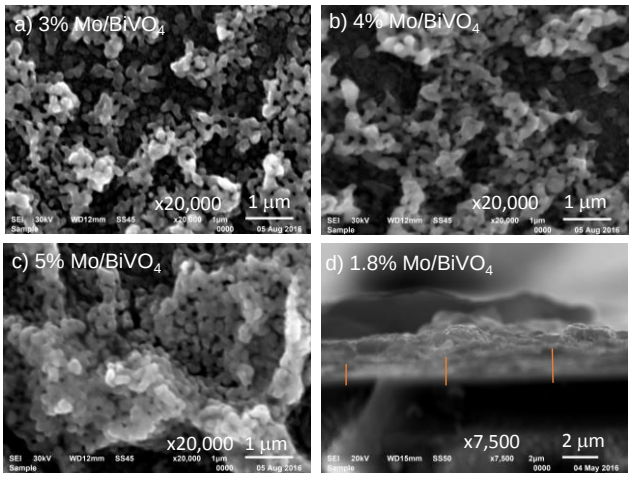


Figure S1: The SEM images of Mo-doped $BiVO_4$ films with 3% (a), 4% (b), and 5% (c) Mo concentration. (d) The SEM image of the cross-section of 1.8% Mo/$BiVO_4$/FTO/Glass.

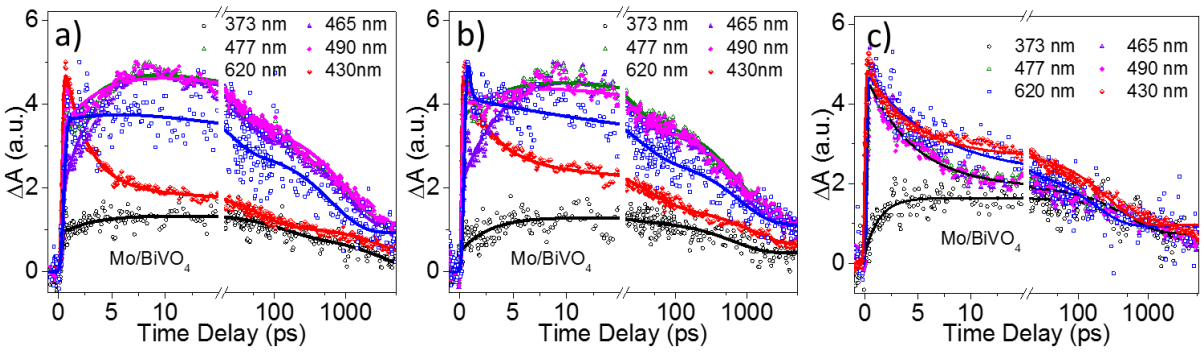


Figure S2: Probe-wavelength dependent kinetic traces of $Mo/BiVO_4$ films with 0.2% (a), 1.0% (b), and 1.8% (c) Mo concentration.

X-ray absorption spectroscopy (XAS) measurement. XAS was performed at Argonne National Laboratory at beamline 12-BM. A 13-element germanium detector was used to detect fluorescence from the sample at room temperature. A pre-sample ion chamber collected the reference signal and two additional ion chambers after the sample had a metal reference foil (Pt, V, and Mo) to collect metal spectrum for energy calibration.

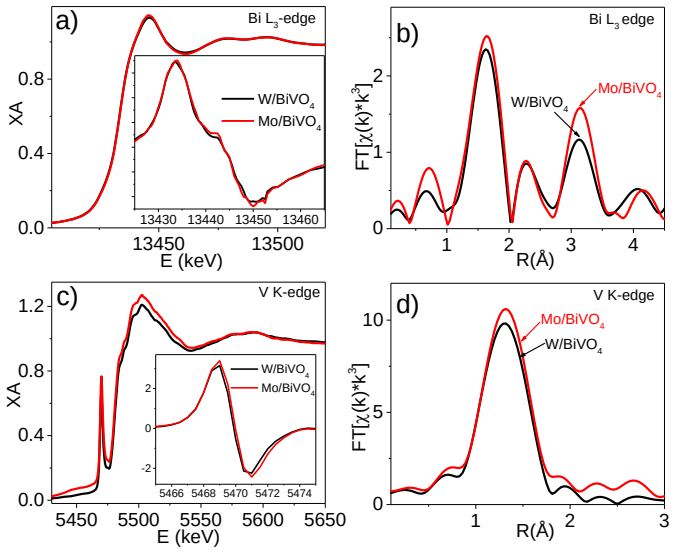


Figure S3: The comparison of XANES spectra of 1.8% W/$BiVO_4$ and 1.8% Mo/$BiVO_4$ at Bi L_3-edge (a) and V K-edge (c). The inset shows their corresponding first derivative spectra. Negligible energy shift was observed at both Bi and V center, suggesting insignificant oxidation state change at Bi and V sites between W and Mo doping. The comparison of Fourier-transform spectra at R-space for 1.8% W/$BiVO_4$ and 1.8% Mo/$BiVO_4$ at Bi L_3-edge (b) and V K-edge (d).

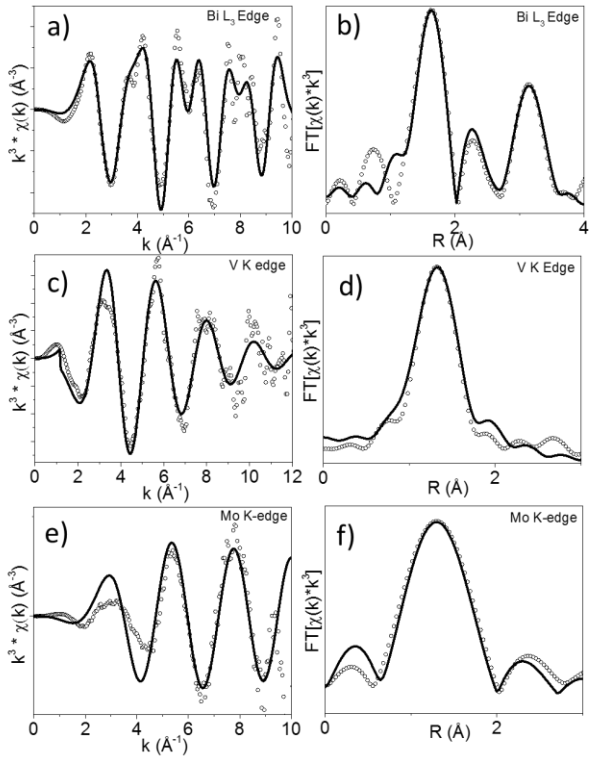
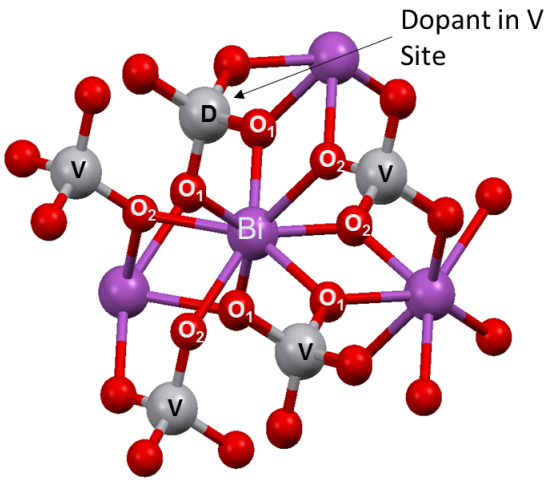


Figure S4. XAFS spectra (open dot) and the best fit (solid line) of 1.8% Mo/$BiVO_4$ film at Bi L_3-edge in k-space (a), Bi L_3-edge in R-space (b), V K-edge in k-space (c), V K-edge in R-space (d), Mo k-edge in k-space (e), and Mo k-edge in R-space (f).



Edge	Vector	N	Mo/$BiVO_4$		W/$BiVO_4$
			R (Å)	σ^2 (Å^2)	σ^2 (Å^2)
Bi L_3	Bi-O_1	4	2.27	.008	.008
	Bi-O_2	2	2.48	.009	.009
	Bi-O_2	2	2.59	.01	.01
	Bi-V_1	2	3.58	.008	.01
	Bi-V_2	2	3.72	.007	.01
	Bi-Bi	2	3.55	.022	.022
V k	V-O_1	2	1.69	.0090	.008
	V-O_2	2	1.76	.0075	.008
Mo K	D-O_1	2	1.77	.0005	-
	D-O_2	2	1.85	.0005	-

Figure S5: EXAFS Fitting results for Bi L_3-edge, V K-edge, and Mo K-edge. R is shown only once due to Mo/$BiVO_4$ and W/$BiVO_4$ fitting to the same parameters, in exception of the Debye-Waller factor.

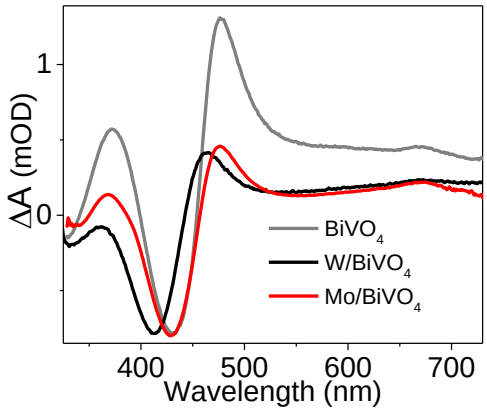


Figure S6: The comparison of femtosecond TA spectra at 0.5-1 ps time delay for un-doped, 1.8% W-doped, and 1.8% Mo-doped $BiVO_4$ films. The blue shift of the GS bleach of W/$BiVO_4$ compared to the un-doped and Mo-doped films is consistent with their steady state UV-visible absorption spectra.