

**Marked Enhancement in Electron-Hole Separation Achieved in the Low Bias
Region by Electrochemically Prepared Mo-Doped BiVO₄ Photoanodes**

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Electronic Supplementary Information (ESI)

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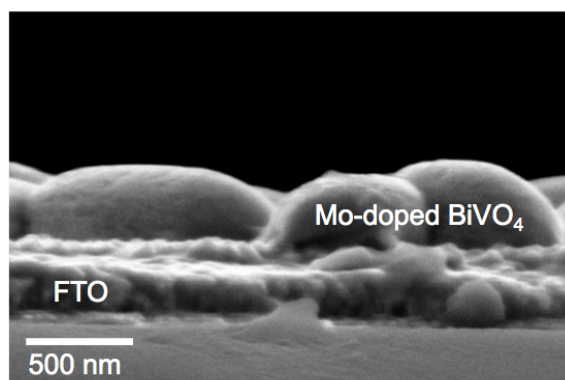


Figure S1. Representative side-view SEM of a Mo-doped BiVO₄ film. The average thickness is *ca.* 450 nm. The undoped BiVO₄ films used in this study were of similar thicknesses.

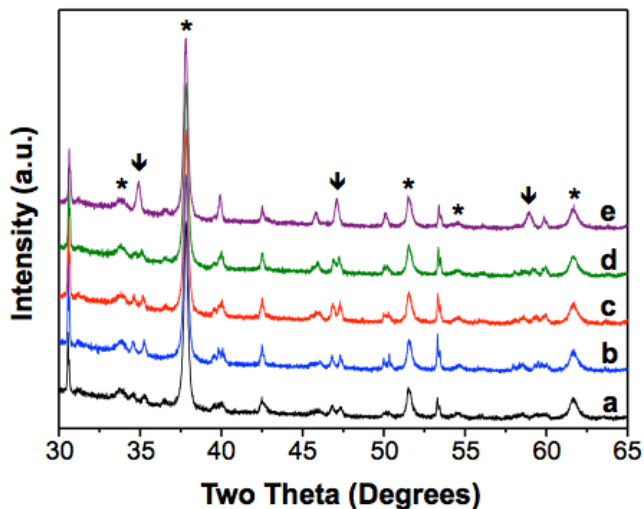


Figure S2. XRD patterns of (a) BiVO₄, (b) BiV_{0.99} Mo_{0.01}O₄, (c) BiV_{0.97} Mo_{0.03}O₄, (d) BiV_{0.94} Mo_{0.06}O₄ and (e) BiV_{0.91} Mo_{0.09}O₄. (a)-(c) show similar patterns but when the Mo content exceeds 6%, a transition from monoclinic to tetragonal crystal systems is observed. As 4-fold symmetry appears, *hkl* and *khl* peaks merge to one peak; the arrows indicate this effect. Asterisks indicate FTO substrate peaks.

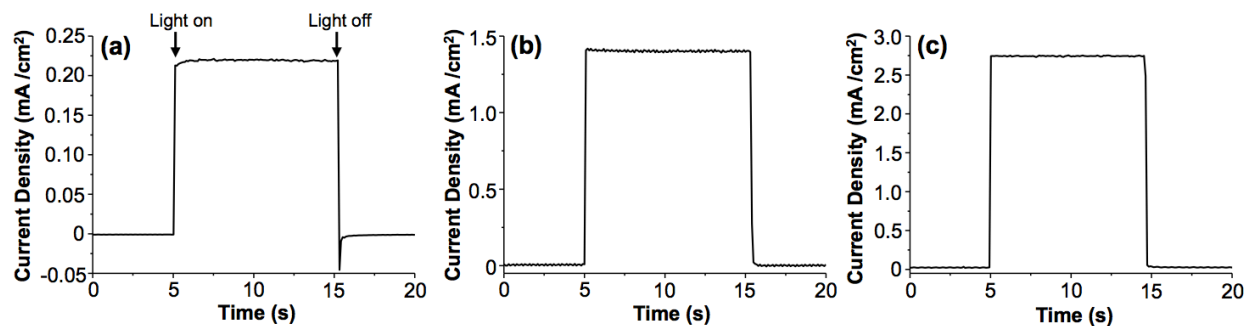


Figure S3. Photocurrent density vs. time (J - t) plots for a $\text{BiV}_{0.97}\text{Mo}_{0.03}\text{O}_4$ electrode measured for sulfite oxidation under AM 1.5G, $100 \text{ mW}/\text{cm}^2$ illumination in a phosphate buffer (pH 7) containing 1 M Na_2SO_3 at (a) 0.2 V vs. RHE, (b) 0.4 V vs. RHE, (c) 0.6 V vs. RHE. Even at 0.2 V vs. RHE, which is near the photocurrent onset potential for $\text{BiV}_{0.97}\text{Mo}_{0.03}\text{O}_4$ in this solution, the transient photocurrent observed is negligible, confirming the fast oxidation kinetics of sulfite.

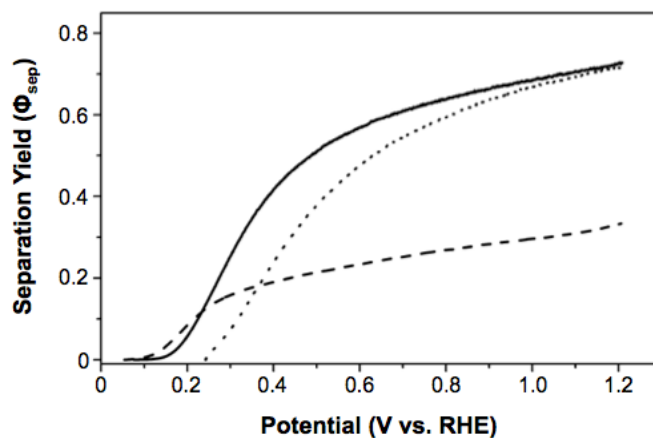


Figure S4. Φ_{sep} vs. V plots for BiVO_4 (dashed), $\text{BiV}_{0.97}\text{Mo}_{0.03}\text{O}_4$ (solid), and $\text{BiV}_{0.97}\text{Mo}_{0.03}\text{O}_4/\text{FeOOH}$ (dotted).

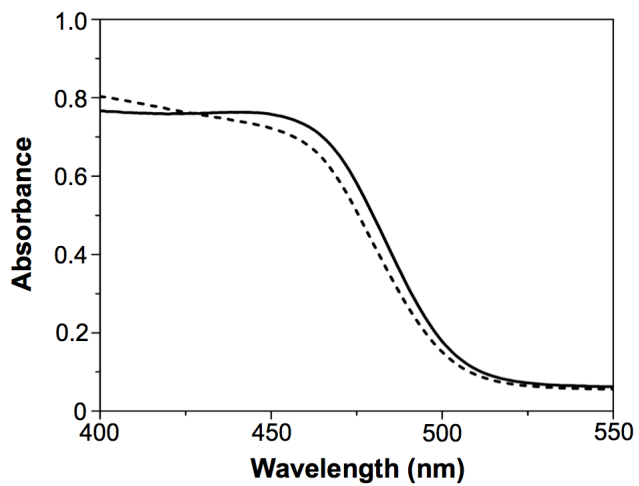


Figure S5. UV-vis absorption spectra of BiV_{0.97}Mo_{0.03}O₄ measured by front-side (dashed) and back-side (solid) illumination.

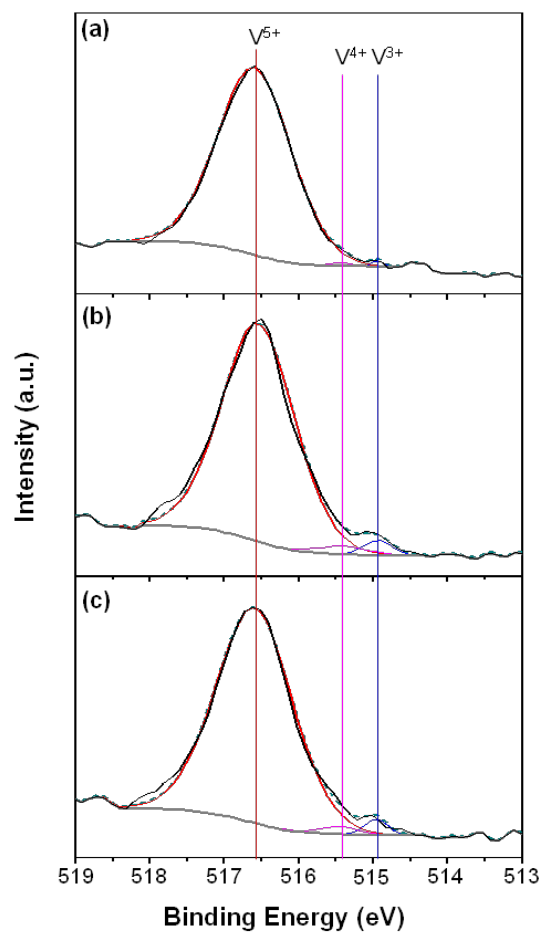


Figure S6. XPS spectra of V 2p_{3/2} for (a) BiVO₄, (b) BiV_{0.97}Mo_{0.03}O₄, and (c) BiV_{0.94}Mo_{0.06}O₄. (black solid: experimentally observed, green dotted: sum of the fitted curves, red: V⁵⁺, pink: V⁴⁺, blue: V³⁺, and gray: background)

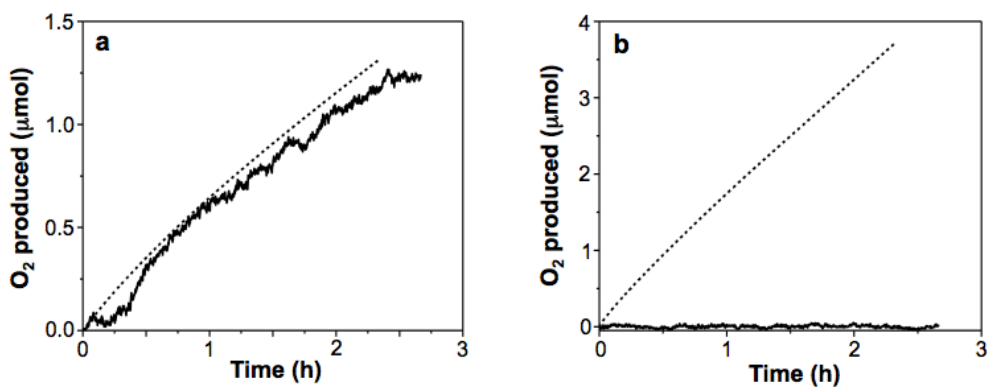


Figure S7. (a) O₂ detected by a fluorescence-based O₂ sensor (—), and O₂ calculated from photocurrent assuming 100% faradaic efficiency for O₂ evolution, (---) during AM 1.5G, 100 mW/cm² illumination of a BiV_{0.97}Mo_{0.03}O₄/FeOOH photoanode at 0.6 V vs. RHE in 0.1 M KH₂PO₄ buffer (pH 7). The photocurrent-to-O₂ conversion efficiency of BiV_{0.97}Mo_{0.03}O₄/FeOOH was calculated to be 95 ± 5%. (b) When the same measurement was performed in the presence of 1.0 M sodium sulfite, no O₂ was detected, indicating the kinetics of sulfite oxidation is much faster than the kinetics of water oxidation on the FeOOH surface.