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) BiV₀.₉₉Mo₀.₀₁O₄, (c) BiV₀.₉₇Mo₀.₀₃O₄, (d) BiV₀.₉₄Mo₀.₀₆O₄ and (e) BiV₀.₉₁Mo₀.₀₉O₄. (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 BiV$_{0.97}$Mo$_{0.03}$O$_4$ electrode measured for sulfite oxidation under AM 1.5G, 100 mW/cm$^2$ illumination in a phosphate buffer (pH 7) containing 1 M Na$_2$SO$_3$ 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 BiV$_{0.97}$Mo$_{0.03}$O$_4$ in this solution, the transient photocurrent observed is negligible, confirming the fast oxidation kinetics of sulfite.

**Figure S4.** $\Phi_{sep}$ vs. V plots for BiVO$_4$ (dashed), BiV$_{0.97}$Mo$_{0.03}$O$_4$ (solid), and BiV$_{0.97}$Mo$_{0.03}$O$_4$/FeOOH (dotted).
Figure S5. UV-vis absorption spectra of Bi\text{V}_{0.97}\text{Mo}_{0.03}\text{O}_{4} measured by front-side (dashed) and back-side (solid) illumination.
Figure S6. XPS spectra of V 2p\textsubscript{3/2} for (a) BiVO\textsubscript{4}, (b) BiV\textsubscript{0.97}Mo\textsubscript{0.03}O\textsubscript{4}, and (c) BiV\textsubscript{0.94}Mo\textsubscript{0.06}O\textsubscript{4}. (black solid: experimentally observed, green dotted: sum of the fitted curves, red: V\textsuperscript{5+}, pink: V\textsuperscript{4+}, blue: V\textsuperscript{3+}, and gray: background)
Figure S7. (a) O$_2$ detected by a fluorescence-based O$_2$ sensor (---), and O$_2$ calculated from photocurrent assuming 100% faradaic efficiency for O$_2$ evolution, (---) during AM 1.5G, 100 mW/cm$^2$ illumination of a BiV$_{0.97}$Mo$_{0.03}$O$_4$/FeOOH photoanode at 0.6 V vs. RHE in 0.1 M KH$_2$PO$_4$ buffer (pH 7). The photocurrent-to-O$_2$ conversion efficiency of BiV$_{0.97}$Mo$_{0.03}$O$_4$/FeOOH was calculated to be 95 ± 5%. (b) When the same measurement was performed in the presence of 1.0 M sodium sulfite, no O$_2$ was detected, indicating the kinetics of sulfite oxidation is much faster than the kinetics of water oxidation on the FeOOH surface.