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Supporting Information

Unraveling compositional effects on the light induced oxygen evolution in Bi(V-Mo-X)O₄ material libraries

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X (X =W, Nb, Ta) material library Pulse DC (5 kHz, 1.2 µs) Bi_2O_3 ٧ Mo **RF** Watt DC Watt DC Watt Watt Bi(V-Mo-W)O₄ 180 370 40 55 Bi(V-Mo-Nb)O₄ 180 370 50 60 Bi(V-Mo-Ta)O₄ 180 370 50 60 BiVO₄ 180 370 -----

Table S1: Sputter power used to deposit the materials libraries.



Figure S1 Photograph of the pristine BiVO₄ ML after annealing (a). Arrows indicate the position of the targets and the dotted line the complete measurement area of the ML. Color-coded composition map of the V:Bi atomic ratio (b). Black dots indicate the measurement areas.



Figure S2 Photograph of the Bi(V-Mo-Ta)O₄ ML after annealing (a). Arrows indicate the position of the targets and the dotted line the complete measurement area of the ML. Color-coded composition map of the V:Bi atomic ratio (b), Mo concentration in at. % (c) and concentration of Ta in at. % (d) of the ML with respect to the coordinate system. Black dots represent the measurement areas.



Figure S3 Photograph of the Bi(V-Mo-Nb)O₄ ML after annealing (a). Arrows indicate the position of the targets and the dotted line the complete measurement area of the ML. Color-coded composition map of the V:Bi atomic ratio (b), Mo concentration in at. % (c) and concentration of Nb in at. % (d) of the ML with respect to the coordinate system. Black dots represent the measurement areas.



Figure S4 XRD patterns from all four corners of the Bi(V-Mo-X)O₄ MLs with X = Ta, W, Nb and the reference BiVO₄ ML. The expected peaks were obtained indicating monoclinic scheelite type BiVO₄ and a characteristic peak with highest intensity at 28.87° diffraction angle. No change of the diffraction pattern is observed for corners with high V-concentration (a) and V:Bi atomic ratio close to 50:50 with high (b) and low (c) transition metal concentration. The Bi-rich region (d) in the bottom corner of the coordinate system contained characteristic peaks indicating Bi₂VO₅ (orange color).



Figure S5 Color-coded map of the relative intensity of the characteristic monoclinic BiVO₄ peak at a diffraction angle of $2\theta = 28.87^{\circ}$ for the BiVO₄ ML, Bi(V-Mo-Ta)O₄ ML and the Bi(V-Mo-Nb)O₄ ML.



Figure S6. SEM images of selected measurement areas of the pristine $BiVO_4$ ML (a) and of the $Bi(V-Mo-X)O_4$ MLs with X = Ta (b), W (c) and Nb (d) along the diagonal over the ML starting from the bottom left corner to the upper right corner. In each SEM image the V:Bi ratio is labeled at top right, Mo at bottom left and X at top left for the presented measurement region. Regions with 0 at. % Mo kave a concentration of Mo below the detection limit of the EDX (1 %).



Figure S7 Raman spectra from the measurement areas at the four corners of all MLs. V-rich regions (a) exhibit no shift of the V-O symmetric stretching mode (v_s) at 829 cm⁻¹ in presence of transition metals except on the Bi(V-Mo-W)O₄ ML. In regions with near-equiatomic V:Bi ratio, the peak at 829 cm⁻¹ is shifted to lower wave numbers. Additionally a merging of the peaks at 328 cm⁻¹ and 369 cm⁻¹ is observed for high (b) and low (c) transition metal concentrations. These peaks are characteristic for the deformation mode of the VO₄-tetrahedron (δ_{as} and δ_s). For the BiVO₄ ML a peak at 850 cm⁻¹ is observed in Bi-rich regions characteristic for Bi₂VO₅. Additionally in some spectra the Mo-O-Mo stretching mode is observed at 870 cm⁻¹. In some spectra a peak at around 1000 cm⁻¹ is observed indicating the presence of VO₂. Peaks associated with the FTO substrate are marked with (*).



Figure S8 Photocurrent obtained by LSV using chopped light measured with the OSDC at the four corners of the coordinate system of all material libraries. The noise observed especially at potentials > 1.0 V vs. RHE is attributed to intensive gas evolution since gas bubbles may block the 1 mm cell opening of the Teflon tip. V-rich regions exhibited the highest photocurrent of up to 1 mA/cm² (high Nb concentration) (a). Photocurrents close to zero on the reference BiVO₄ ML are observed in V-rich (a) or Bi-rich regions (b). High concentrations of W or Nb decreased the photocurrent (b) compared to lower concentrations of dopants at the diagonal of near-equiatomic V:Bi ratio (c). The lowest PEC performance of all MLs was observed for Bi-rich regions (d). All MLs showed a substantial enhancement of the photocurrent on the bottom right corner of the coordinate system (c), where a V/Bi ratio close to one and low additional metal concentrations are present.



Figure S9 Dark current obtained from LSVs across the V (a) and W (c) gradient of the Bi(V-Mo-W)O₄ ML starting from the V-rich corner (red color) with high W concentration (35 at. %) to the corner with a V:Bi atomic ratio close to one with a W concentration of 21 at. %. For comparison the dark current of the pristine BiVO₄ ML across this line from V-rich to V:Bi atomic ratio of 0.52:0.48 is presented (b and d).

Incident photon-to-current-efficiency. For all ML the IPCE at 1.23 V vs. RHE in 0.1 M borate buffer (pH = 9) was calculated from wavelength dependent photocurrent spectroscopy during front-side illumination.^[1] The wavelengths were changed in 10 nm steps by opening and closing the shutter for 5 s and the photocurrent resulted by the substraction of the detected current in dark from the current measured under illumination. According to equation 1, the IPCE was calculated from the detected photocurrent (*i*) divided by the photonflux (\mathcal{O}) multiplied by the electric charge e.^[2] IPCE values were determined on all ML in regions with the highest PEC performance obtained from the high-throughput screening (Fig 4.) with Bi:V at. ratio close to 50:50 and low Mo content (< 2 at. %).



$$IPCE(\%) = \frac{i(\lambda)}{e\Phi(\lambda)} \cdot 100$$
(1)

Figure S10 Calculated IPCE depending on different wavelength at 1.23 V vs. RHE in 0.1 M borate buffer (pH = 9) for different ML. The IPCE is an average (illuminated area 0.196 cm²) of the material composition find at the point with the highest PEC activity during the high-throughput scan with Bi:V at. ratio close to 50:50 and < 2 at. % Mo.



Figure S11 Estimation of the band gap of selected points of highest PEC activity assuming an indirect band-to-band transition^[1,3] based on the IPCE measurements of Figure S10.

Electrochemical Impedance Spectroscopy (EIS). EIS measurements were performed with a PGSTAT204 (Methrom Autolab). To obtain comprehensive results from EIS at different applied bias potentials in the dark, first the potential range where no redox-reactions occur has to be identified. Figure S9 indicates in regions with higher V concentration oxidation reactions from V⁴⁺ to V⁵⁺ at 0.74 V vs. RHE (resulted from the formation of VO₂ in V-rich regions), while no oxidation peak was observed at near equiatomic ratio of Bi:V. Neverthless, cyclic voltammetry was performed with 5 mV/s starting at 0.74 V (vs. RHE) increasing the potential up to 1.74 V (vs. RHE) and decreasing to -0.26 V (vs. RHE) in 0.1 M borate buffer (pH = 9). An oxidation peak is observed at 0.45 V (vs. RHE) and a reduction peak at 0 V (Figure S12a) for the pristine BiVO₄ ML. For Bi(V-Mo-Nb)O₄, the reduction peak shifted to more cathodic potentials. Furthermore, the oxidation peak for near equiatomic Bi:V ratio was only observed after cathodic potentials (< 0.54 V) where applied (Fig. S9). Obvisouly, on the ML with near equiatomic ratio of Bi:V, V⁵⁺ is reduced to V⁴⁺ at 0 V or -0.14 V and then oxidized back to V⁵⁺ at 0.45 V. EIS was accomplished for different frequencies (100 kHz to 1 Hz, 10 mV amplitude) in regions on each ML starting at 0.74 V to 0.14 V (vs. RHE) in 0.1 M borate buffer (pH = 9) where the highest photocurrents and according to SEM images (Fig. S6) similar morphology were observed. Figure S12b shows a more ideal capacitor behavior in the dark on the pristine ML with near equiatomic Bi:V ratio, where no diffusion limited processes occur. In presence of two transition metals on the other MLs, a Warburg behavior (see modified equivalent ciruit) was observed at low frequencies, indicating diffusion-limited processes at 0.54 V (vs. RHE) in the dark. Taking the discussed results from Fig. S9 and Fig. 12a into account, the oxidation of V^{4+} to V^{5+} can be a reason which is supposed by the formation of V^{4+} centers due to the insertion of the transition metals into the BiVO₄ lattice.



Figure S12 a) CV in 0.1 M borate buffer (pH = 9). At 0 V a reduction peak occurs resulting from the V⁴⁺ formation on the BiVO₄ ML. The back scan shows an oxidation peak at 0.45 V indicating the back reaction. B) Impedance spectra at 0.54 V vs. RHE in 0.1 M borate buffer (pH = 9) in the dark on all different MLs with near equiatomic ratio of V:Bi, low transition metal concentration and highest PEC performance. As an insert the equivalent ciruit is added. At lower frequencies especially in presence of transition metals, the impedance behavior is determined by R_{CT} (and Warburg impedance Z_w for added transition metals) and the CPE of the equivalent circuit.

- [1] R. Gutkowski, D. Peeters, W. Schuhmann, J. Mater. Chem. 2016, 4, 7875–7882.
- [2] A. J. Bard, L. R. Faulkner, Electrochemical methods. Fundamentals and applications, 2nd ed., Wiley, New York, 2001.
- [3] a) Y. Liang, T. Tsubota, L. P. A. Mooij, R. van de Krol, J. Phys. Chem. C 2011, 115, 17594–17598; b) C. Jiang, R. Wang, B. A. Parkinson, ACS Comb. Sci. 2013, 15, 639–645;