Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Formation and suppression of defects during heat treatment of $BiVO_4$ photoanodes for solar water splitting

Marlene Lamers[a], Sebastian Fiechter[a], Dennis Friedrich[a], Fatwa F. Abdi*[a] and Roel van de Krol*[a]

[a]*Institute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH,*

Hahn-Meitner-Platz 1, Berlin 14109, Germany

[*]*Email: fatwa.abdi@helmholtz-berlin.de, roel.vandekrol@helmholtz-berlin.de*

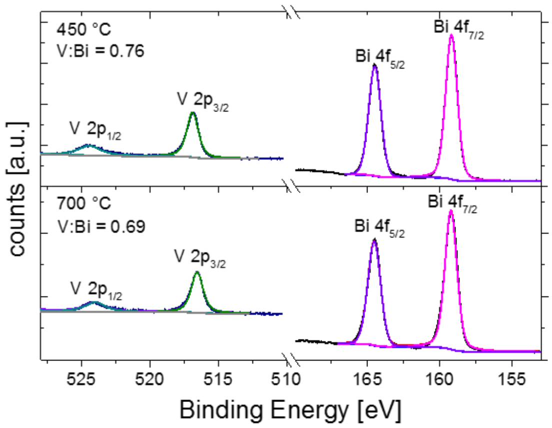


Fig. S1. V 2p and Bi 4f core level X-ray photoelectron spectra of $BiVO_4$ films annealed at 450 °C (top) and 700 °C (bottom) in air. The V:Bi ratios were determined from the relative areas of the XPS peaks.

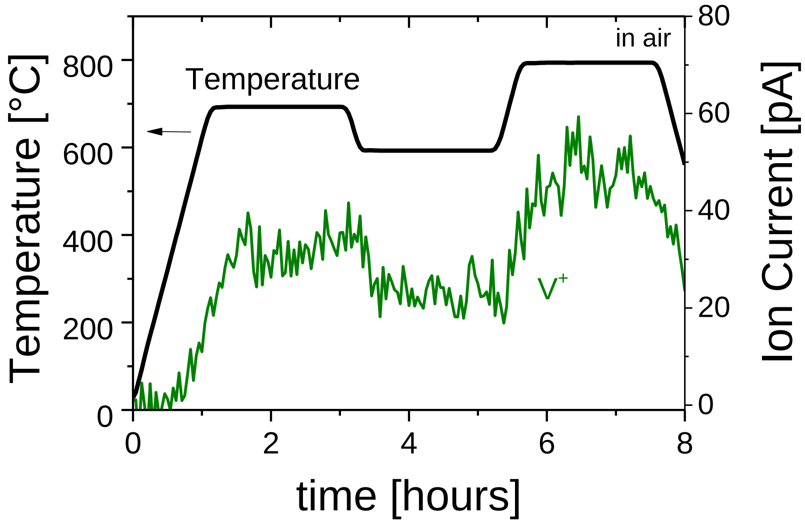


Fig. S2. Mass spectroscopy (MS) analysis of $BiVO_4$ powders in air. Temperature-time curve during the MS analysis (black) and ion currents for mass-to-charge ratios (m/q) of 51 correspond to V+ (green).

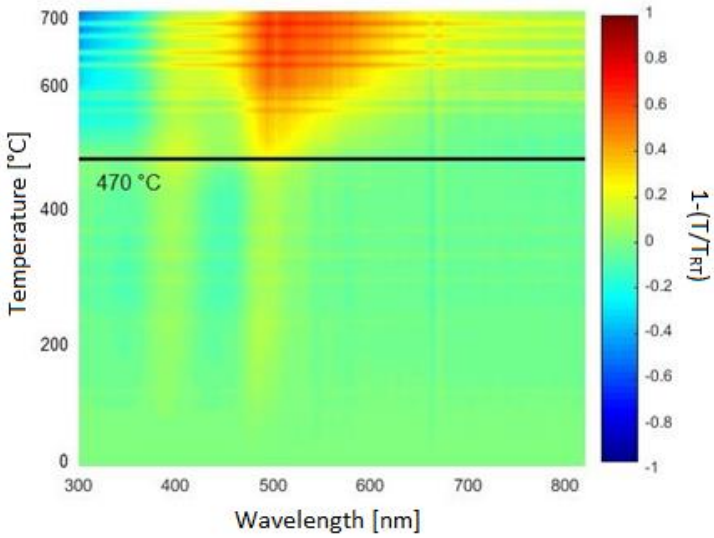


Fig. S3. In-situ optical monitoring of the $BiVO_4$ film annealed in air. The x-axis is the wavelength (nm) and the y-axis is the temperature (°C). The color indicates the change in optical absorption with respect to the transmission at room temperature (T_{RT}). An increase of absorption with a central wavelength of ~500 nm starts to occur at ~470 °C.

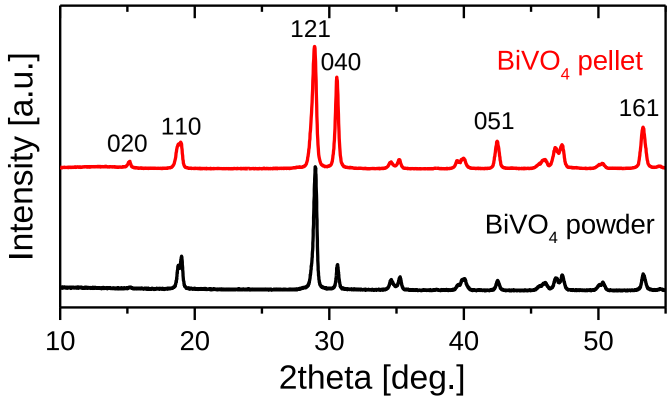


Fig. S4. X-ray diffractograms of $BiVO_4$ powder and pellet. A stronger (010) orientation is found in the $BiVO_4$ pellet.

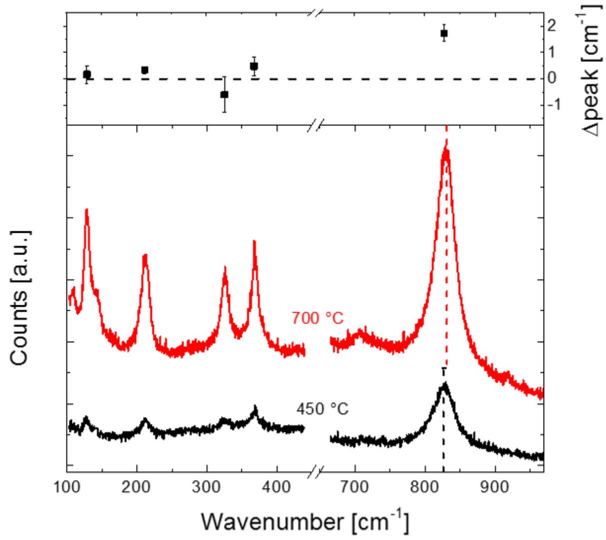


Fig. S5. Raman spectra of monoclinic $BiVO_4$ annealed in air at 450 °C and 700 °C for 2 h. The symmetric V-O stretching mode peak at ~826 cm^{-1} is shifted to a larger wavenumber upon annealing at 700 °C. The peaks at 368, 326, 212 and 127 cm^{-1} remain the same and are assigned to δ_s (VO_4), δ_{as} (VO_4) and the external modes, respectively.[37] The top plot shows the difference in the peak position (Δ_{peak}) for all the vibrations.

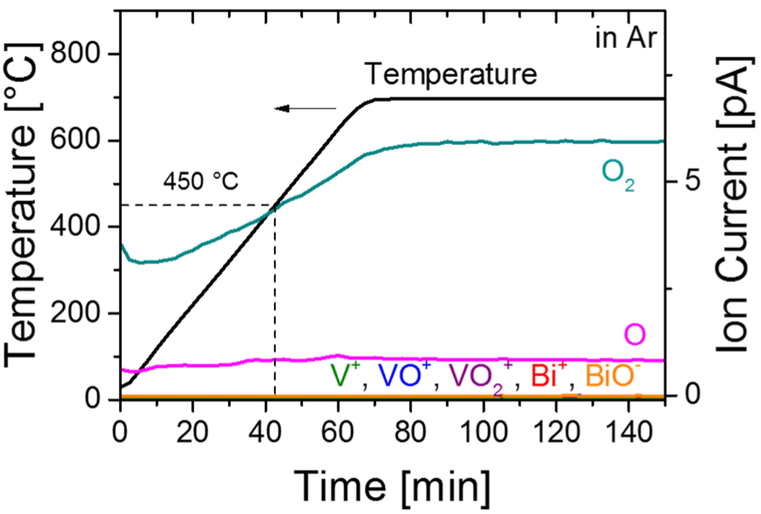


Fig. S6. Mass spectrometry (MS) analysis of $BiVO_4$ powder in Ar atmosphere. Temperature-time curve during the MS analysis (black) and mass-to-charge ratios (m/q) of 16, 32, 51, 67, 83, 209 and 225 corresponding to O (pink), O_2 (turquoise), V^+ (green), VO^+ (blue), VO_2^+ (purple), Bi^+ (red), and BiO^- (orange) are shown. The increase of the O_2 signal with temperature indicates the formation of oxygen vacancies ($V_O^{\bullet\bullet}$), based on the following defect formation reaction: $O_O^\times \rightleftharpoons \frac{1}{2} O_2(g) + V_O^{\bullet\bullet} + 2e'$.

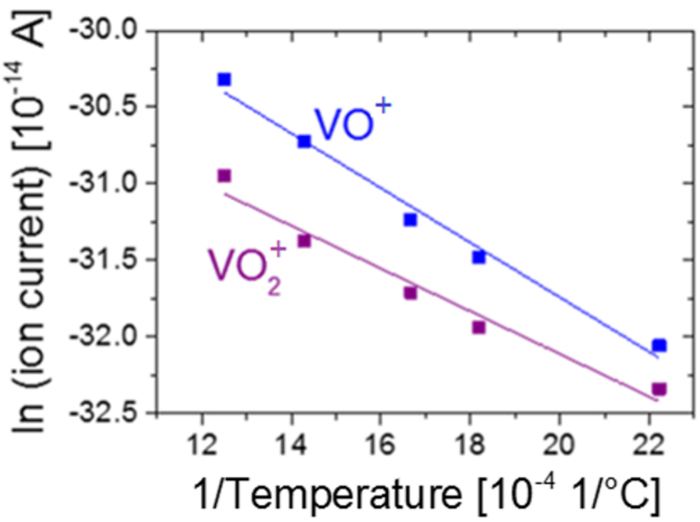


Fig. S7. Natural logarithm of ion current as a function of reciprocal temperature for the detected MS signals of VO^+, and VO_2^+. The activation energy can be obtained from the slope of the curve, since ion current (I) is correlated to the activation energy (E_A) and temperature (T) according to the Arrhenius relationship ($I = Ae^{\frac{-E_A}{kT}}$). Here, A is a constant and k is the Boltzmann constant.

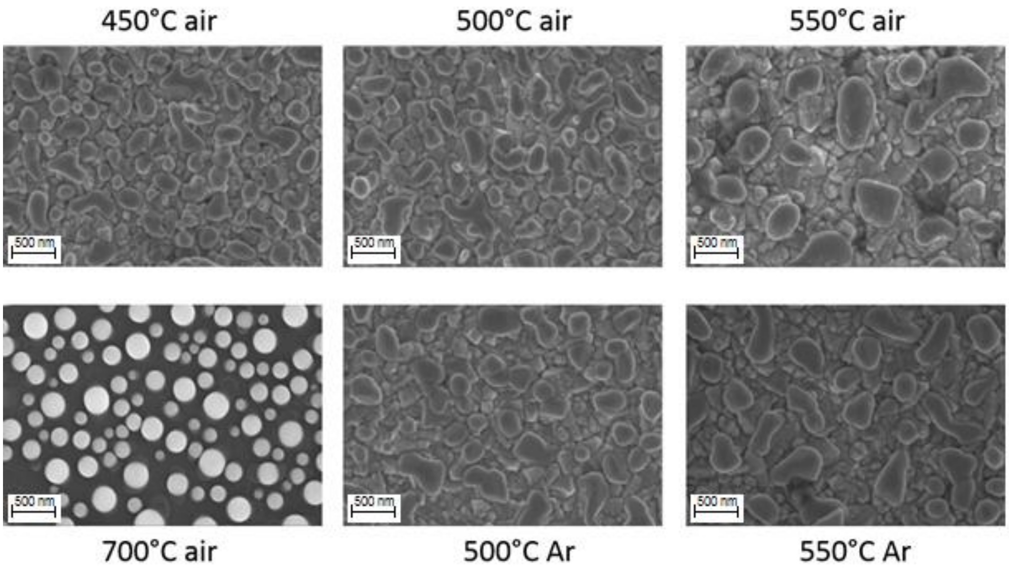


Fig. S8. SEM images of $BiVO_4$ films annealed in air and Ar at different temperatures in the range from 450 °C to 700 °C.

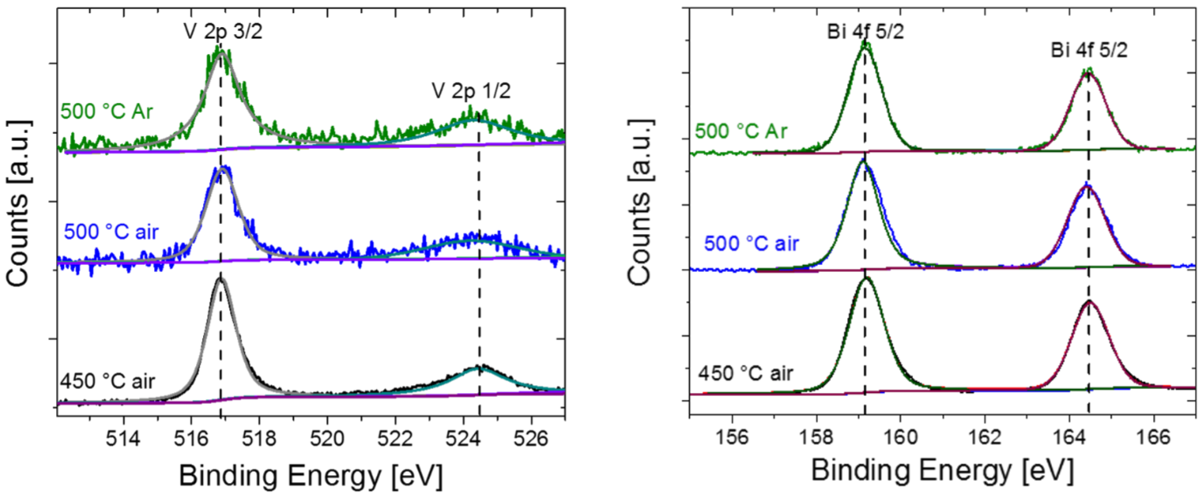


Fig. S9. V 2p (left) and Bi 4f (right) core levels X-ray photoelectron spectra of $BiVO_4$ films annealed at 450 °C and 500 °C in air and 500 °C in Ar. Comparison of the O 1s spectra was difficult since they also contain contributions from the exposed FTO substrate due to the roughness/porosity of the $BiVO_4$ films.

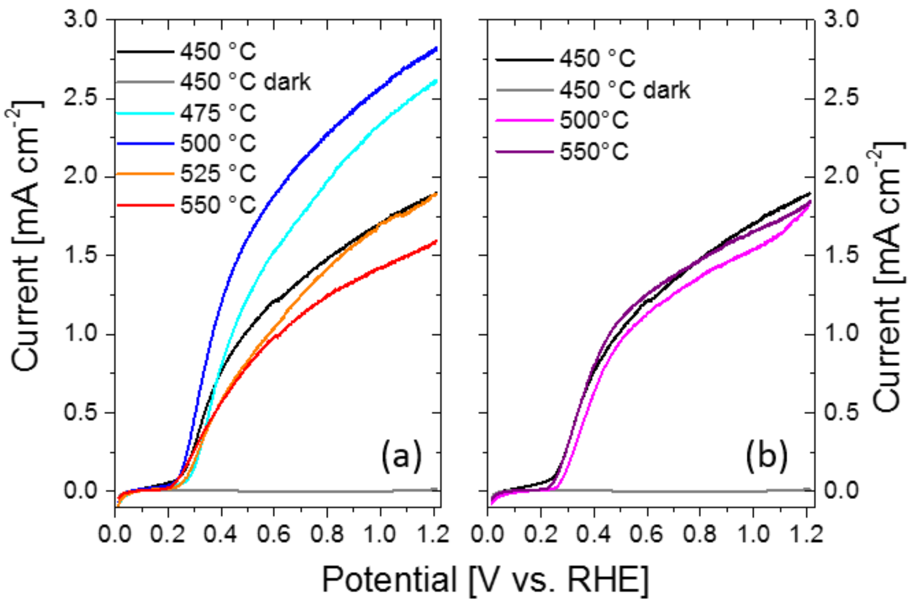


Fig. S10. AM1.5 photocurrent-voltage curve of $BiVO_4$ films annealed in **(a)** air and **(b)** Ar at temperatures ranging from 450 to 550°C. The electrolyte is 0.1 M phosphate buffer (pH 7) with added Na_2SO_3 as a hole scavenger.

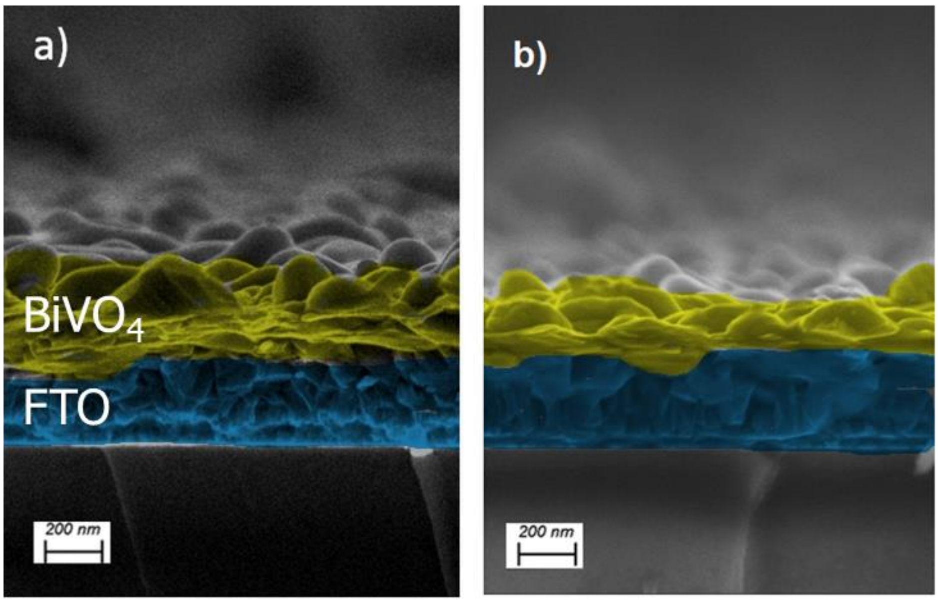


Fig. S11. Cross-sectional SEM images of $BiVO_4$ films annealed in air at 450 °C (a) and 500 °C (b). The thicknesses of both films are ~100 nm and ~110 nm, respectively.

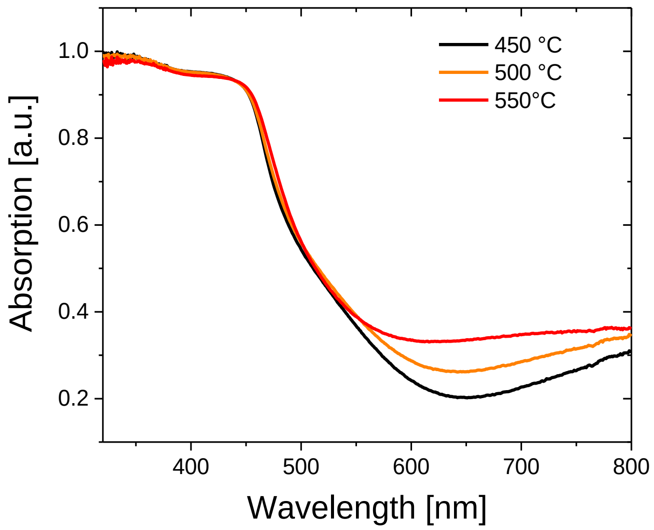


Fig. S12. UV-Vis spectra of $BiVO_4$ films annealed in air at 450 °C (black), 500 °C (orange) and 550 °C (red).

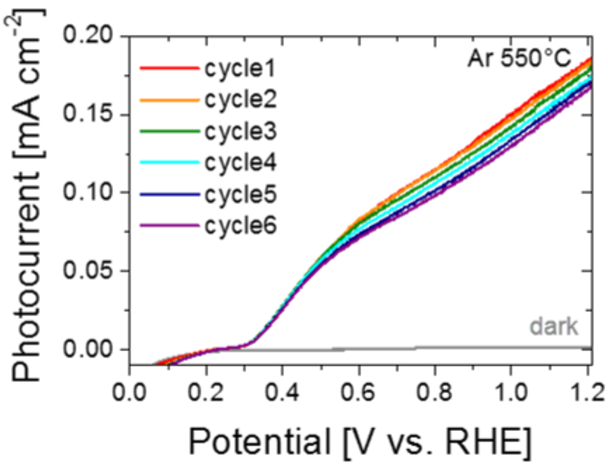


Fig. S13. AM1.5 photocurrent-voltage curves of $BiVO_4$ films annealed in Ar at 550°C for 2h. Positive excursion of bias potential is shown to not positively affect the photoelectrochemical performance since the photocurrent-voltage curve slightly decreases with increasing cycles. The electrolyte is 0.1 M phosphate buffer (pH ~7). The dark current is shown in grey.

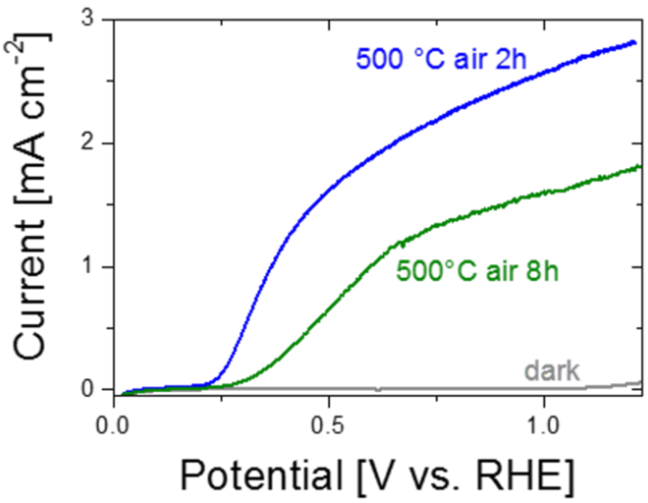
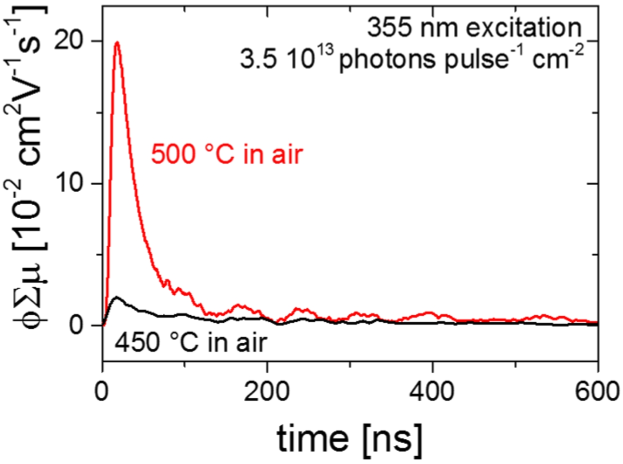


Fig. S14. AM1.5 photocurrent-voltage curve of $BiVO_4$ films annealed in air at 500 °C for 2h (blue) and 8h (green). The electrolyte is 0.1 M phosphate buffer (pH 7) with added Na_2SO_3 as a hole scavenger. The dark current is shown in grey.



Fig, S15. Time resolved microwave conductivity (TRMC) signals of 100 nm thick $BiVO_4$ films annealed at 450 °C and 500 °C in air measured using a 355 nm laser with an intensity of 3.5×10^{13} photons $pulse^{-1}$ cm^{-2}.

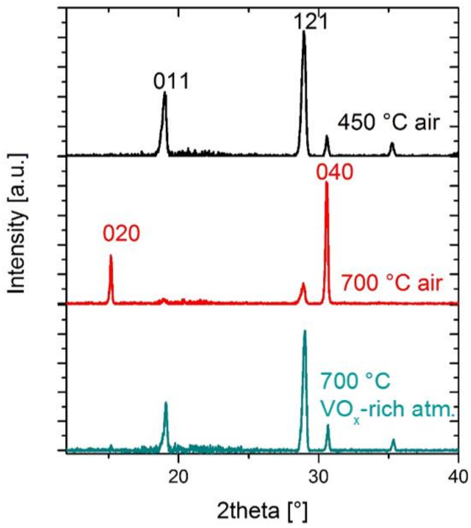


Fig. S16. X-ray diffractograms of $BiVO_4$ films annealed in air at 450 °C and 700 °C as well as in a VO_x-rich atmosphere (i.e., air + $BiVO_4$ powders) at 700 °C. The corresponding diffraction peaks of monoclinic $BiVO_4$ are labeled accordingly.

Table S1. Specific surface area of $BiVO_4$ films post-annealed in air between 450 and 550 °C obtained from AFM measurements on a projected area of 5 × 5 μm^2.

Temperature	Specific surface area in μm^2
450 °C in air	31
500 °C in air	33.5
550 °C in air	31.6
500 °C in Ar	31

1. S. Nikam, S. Joshi, *RSC Adv.*, **2016**, *6,* 107463.