Supplementary Information for:

A soft x-ray spectroscopic perspective of electron localization and transport in tungsten doped bismuth vanadate single crystals

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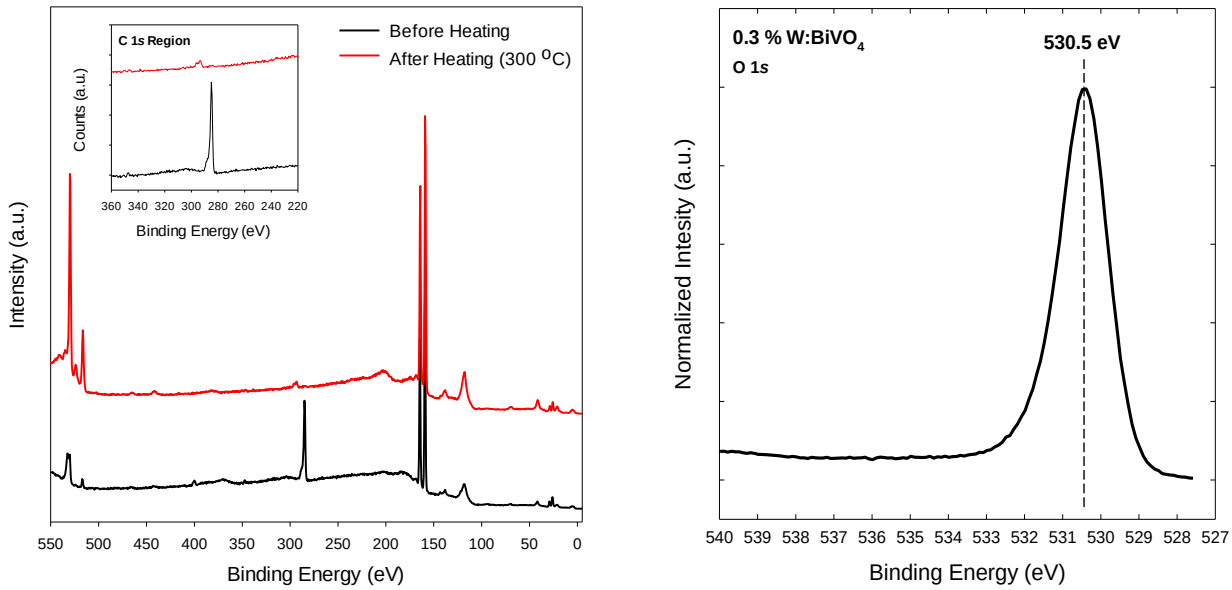
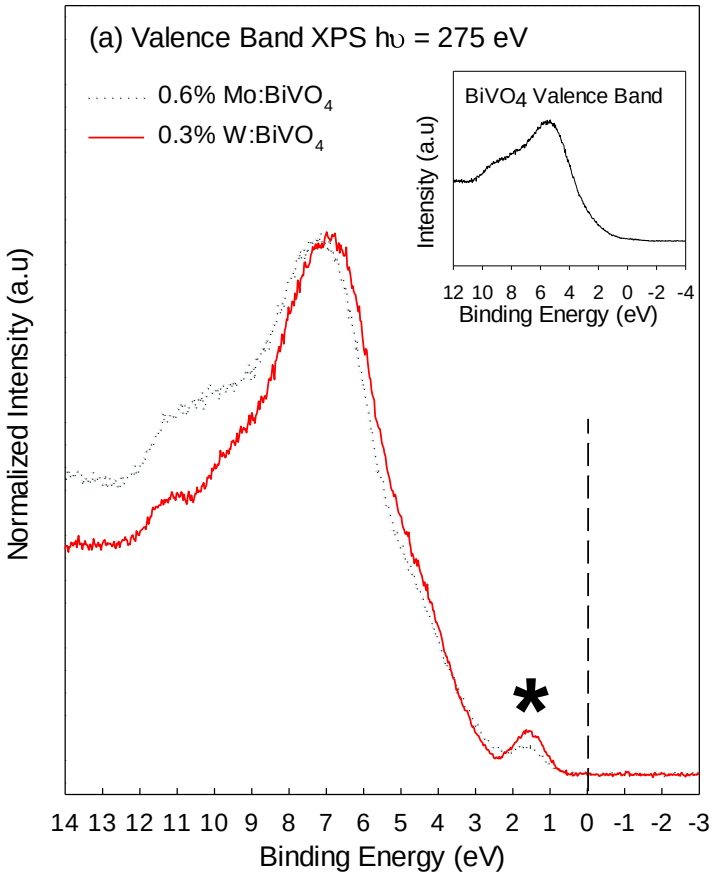
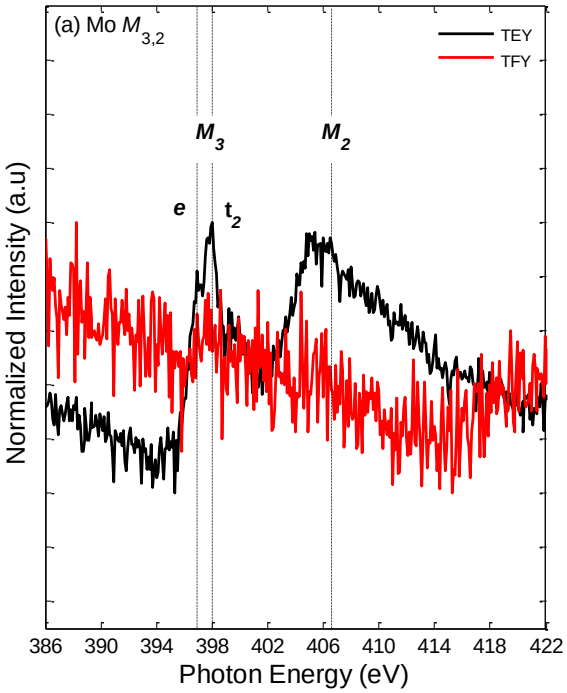


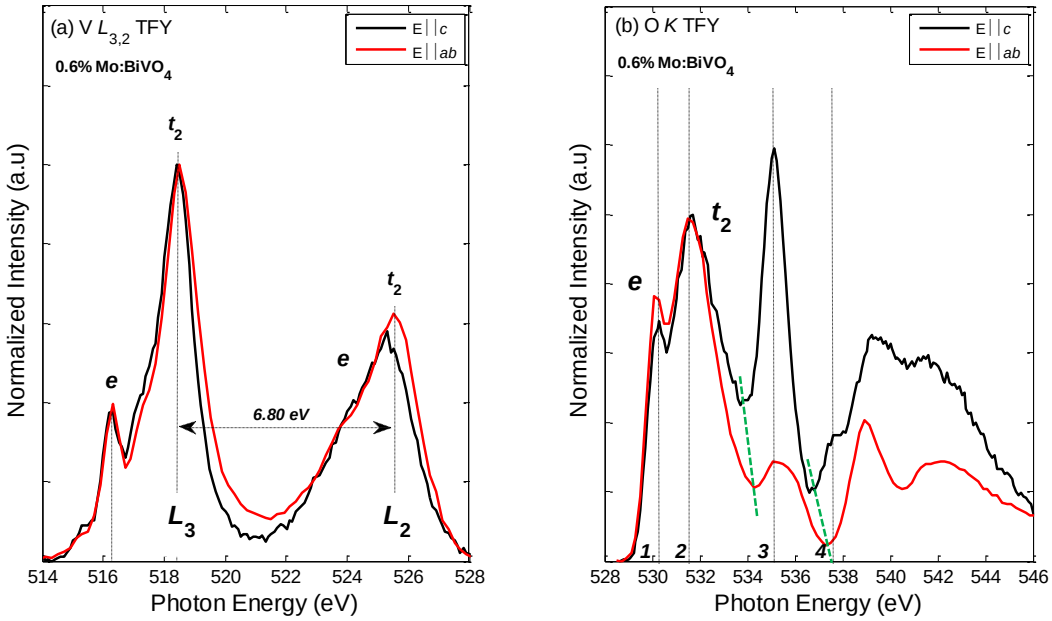
Supplementary Figure 1. (a) XPS survey spectra for the 0.3 % W:$BiVO_4$ single crystal before (black) and after (red) cleaning at 300 ^oC in a 1×10^{-6} Torr oxygen atmosphere. The inset shows an expanded view of the C 1s region before and after annealing. **(b)** The O1s XPS spectrum is dominated by an intense peak at 530.5 eV due to lattice oxygen in the $BiVO_4$ crystalline array. The absence of high binding energy hydroxyl shoulder features at ~532eV further demonstrates that a clean surface was obtained following annealing.



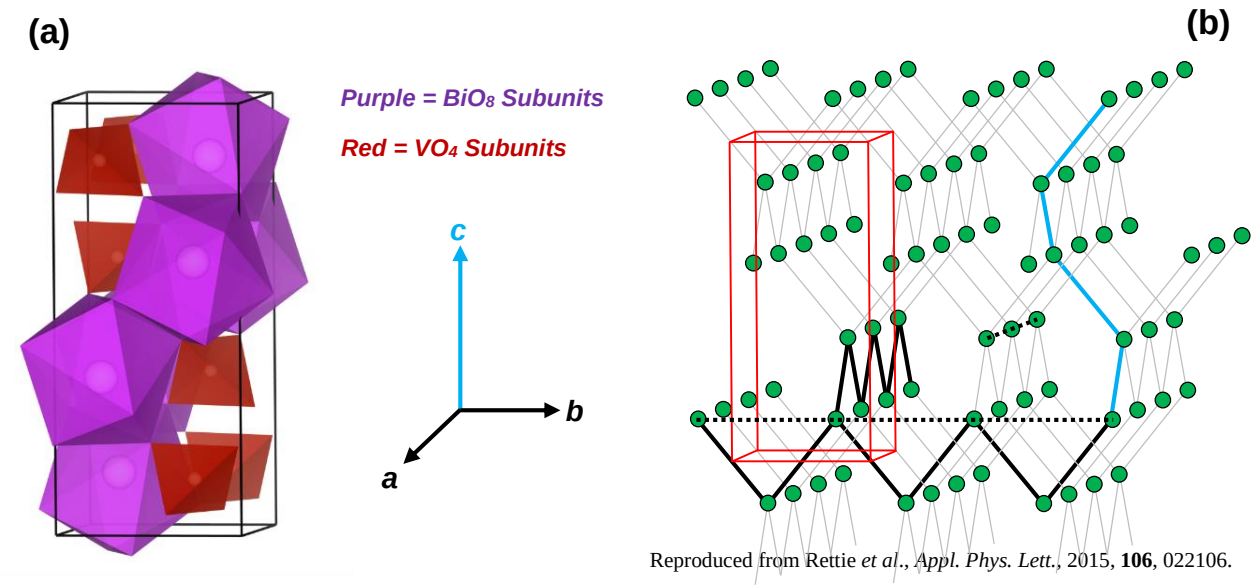
Supplementary Figure 2. Valence band PES for 0.3% W:$BiVO_4$ and 0.6% Mo:$BiVO_4$, collected using an incident photon energy (hν) of 275 eV.



Supplementary Figure 3. Mo $M_{3,2}$ XAS spectra for 0.6% Mo:$BiVO_4$ recorded in the TEY and TFY modes.

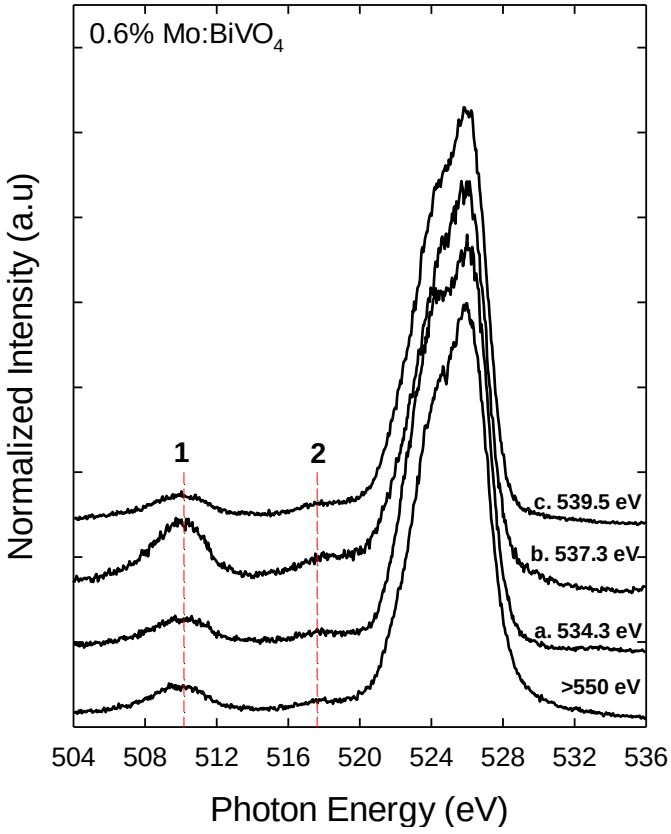


Supplementary Figure 4. (a) V $L_{3/2}$ XAS TFY spectra for 0.6% Mo:$BiVO_4$ recorded with incident photon polarizations parallel (blue) to the *c*-axis and parallel (red) to the *ab*-plane. (b) Corresponding O *K*-edge XAS TFY spectra for the 0.6% Mo:$BiVO_4$ single crystal recorded with incident photon polarizations parallel (blue) to the *c*-axis and parallel (red) to the *ab*-plane.



Reproduced from Rettie *et al*., *Appl. Phys. Lett.*, 2015, **106**, 022106.

Supplementary Figure 5. (a) Schematic diagram of the $BiVO_4$ crystal structure showing the BiO_8 (purple) and VO_4 (subunits). The arrangement of V sites in the $BiVO_4$ structure which results in shorter 'Next-Nearest-Neighbor' (NNN) hops in the *ab*-plane relative to NNN hops along the *c*-axis – as depicted in Ref 8 by Rettie *et al*.



Supplementary Figure 6. O *K*-edge resonant X-ray emission spectra for 0.6% Mo:$BiVO_4$. The spectra were recorded following irradiation with incident photon energies of 534.3 eV, 537.3 eV, 539.5 eV and >550 eV.