Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Ultrafast fabrication of highly active $BiVO_4$ photoanodes by hybrid microwave annealing for unbiased solar water splitting

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Supplementary Calculation

Surface/bulk charge separation efficiencies (η_{surf})

For quantitative assessment of charge separation efficiency, photocurrent comparison between water oxidation/hole scavenger (SO_3^{2-}) was used.

Water oxidation: $2H_2O + 4h^+ \rightarrow 4H^+ + O_2$, E^o=1.23 V_{RHE}

Sulfite oxidation: $SO_3^{2-} + h^+ \rightarrow SO_3^-$, E^o=0.73 V_{RHE}

Light absorption by a photocatalyst generates absorbed photocurrent (J_{abs}) that undergoes two major losses of bulk and surface recombination. Hence the measured photocurrent during water oxidation (J^{H2O}) is expressed by;

$$J^{H2O} = J_{abs} \times \eta_{bulk} \times \eta_{surf}$$

where η denotes the charge separation yield in the bulk of semiconductor (η_{bulk}) or on the surface (η_{surf}). Since the surface charge separation yield of SO_3^{2-} is almost 100% ($\eta_{surf} = 1$), as discussed above, the photocurrent from its oxidation can be expressed as follows:

$$J^{SO3} = J_{abs} \times \eta_{bulk}$$

The J_{abs} value of $BiVO_4/WO_3$ was estimated to be ~5 mA/cm^2 from calculation from AM 1.5G radiation region and UV-vis absorbance spectrum shown below. η_{bulk} , η_{surf} can be derived in photocurrent comparison form.

$$\eta_{bulk} = J^{SO3} / J_{abs}$$

$$\eta_{surf} = J^{H2O} / J^{SO3}$$

For calculation, correlation between absorbance and radiation proposed by Choi's group [1] was used as below.

$$P_d = P_0 10^{-A}$$

$$P_{abs} = P_0(1\text{-}10^{-A})$$

P_0 (unit : mWcm^{-2}nm^{-1}) is provided power by solar simulator (in this case, AM 1.5G), P_{abs} is power of light actually absorbed by photoanode and P_d is power of light not absorbed to photoanode but dissipated (reflection and penetration). A is absorbance of photoanode and LHE (light harvesting efficiency) is defined as 1-10^{-A}. So light which is not absorbed at photoanode will be 10^{-A}. Integrated $P_{abs}(\lambda)$ (mWcm^{-2}nm^{-1}) along with wavelength λ gives total power (unit of mWcm^{-2}) which is power of light absorbed by photoanode (maximum power of photoanode). Below formula shows such relationship photon absorption (J_{abs}).

$$J_{abs}\left(\frac{mA}{cm^2}\right) = \int_{\lambda_1}^{\lambda_2} \frac{\lambda}{1240} P_{abs}(\lambda) d\lambda \quad \left(\frac{mW}{cm^2}\right)$$

Supplementary Table

Table S1 Surface elemental composition analyzed by XPS spectra.

Photoanode/annealing system (time)		C (%)	O (%)	Bi (%)	V (%)	Mo (%)	W (%)
$BiVO_4$	FA (300 min)	42.1	37.8	13.6	6.5		
	HMA (6 min)	45.8	33.6	15.1	5.5		
1% Mo:$BiVO_4$	FA (300 min)	34.0	46.4	12.9	6.3	0.4	
	HMA (6 min)	45.9	35.0	13.9	4.9	0.3	
$BiVO_4$/WO_3	FA(300 min)	43.0	35.0	11.9	5.8		0.3
	HMA (6 min)	42.1	37.0	13.4	5.6		1.9

Supplementary Figures

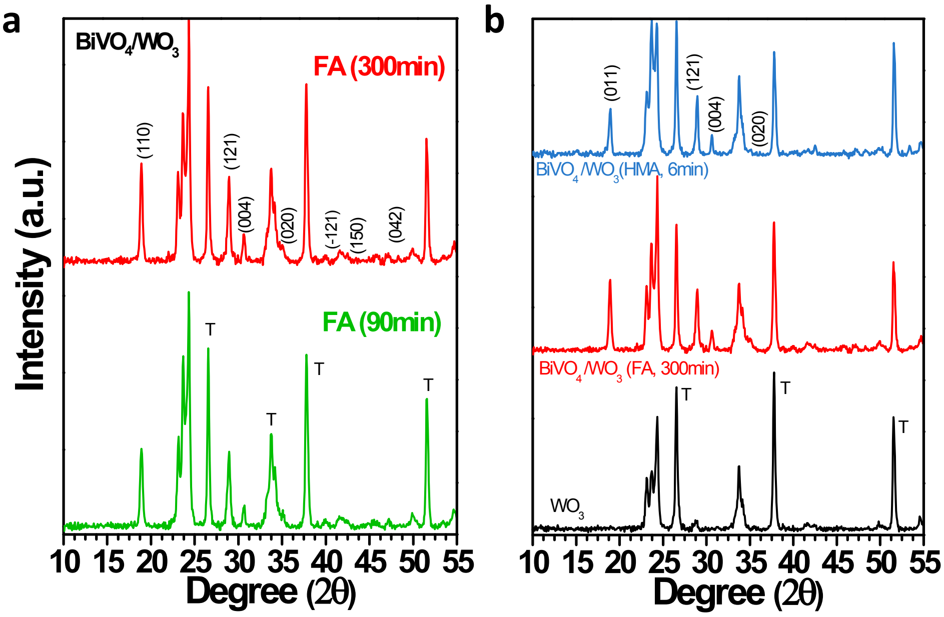

Figure S1. (a) XRD spectra of $BiVO_4/WO_3$ fabricated by FA with different lengths of annealing time. (b) Comparison of $BiVO_4/WO_3$ films made by FA (300 min) and HMA (6 min).

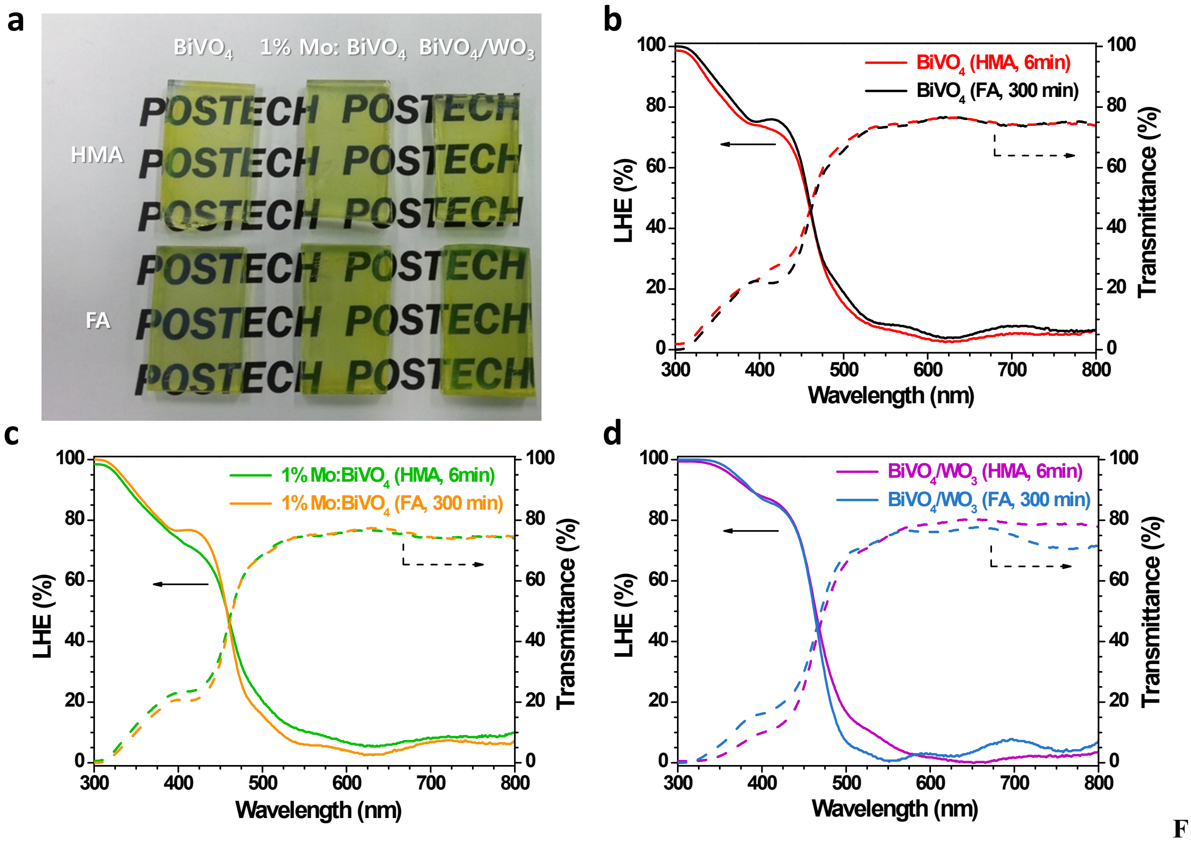

Figure S2. (a) Photographs of $BiVO_4$ films prepared with two annealing methods (FA and HMA). Optical properties (LHE=1-10$^{-absorbance}$, transmittance) of $BiVO_4$ (b), 1% Mo:$BiVO_4$ (c) and $BiVO_4/WO_3$ (d). Light harvesting efficiency (LHE) of samples corresponded to J_{abs} = ~3.6 mA/cm^2 ($BiVO_4$, 1% Mo:$BiVO_4$) and ~4.5 mA/cm^2 ($BiVO_4/WO_3$).

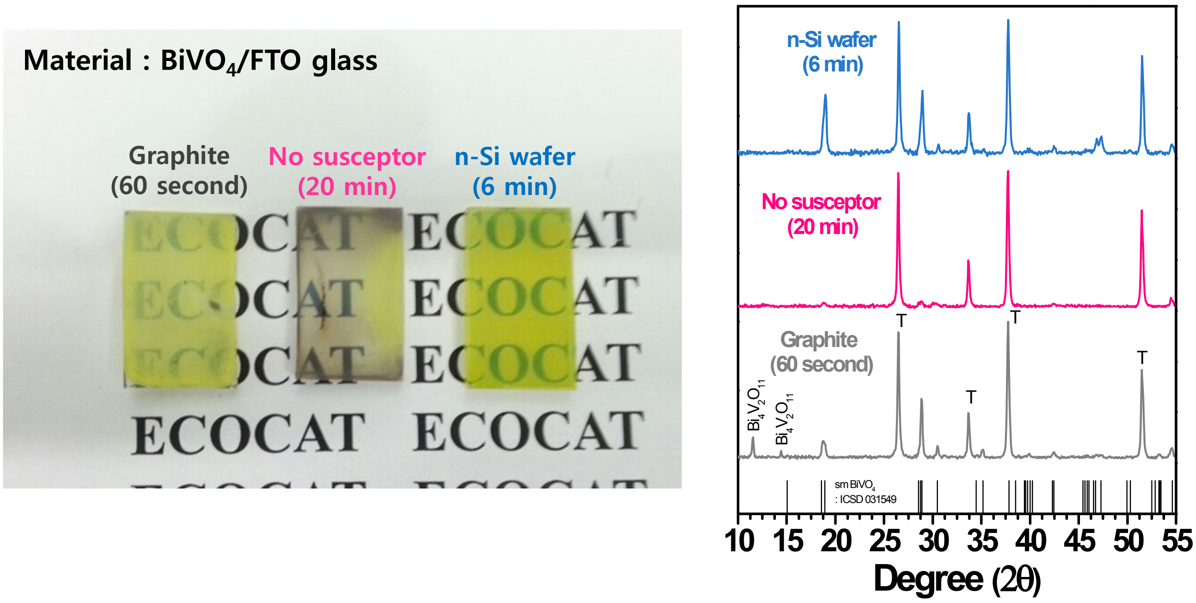

Figure S3. (a) Photographs of $BiVO_4$ films prepared by HMA with different susceptors (graphite, no susceptor and n-type Si wafer). (b) XRD patterns of the films. The letter 'T' stands for pattern of FTO (SnO_2). Reference pattern for scheelite monoclinic $BiVO_4$, ICSD 01-075-1866 is also shown.

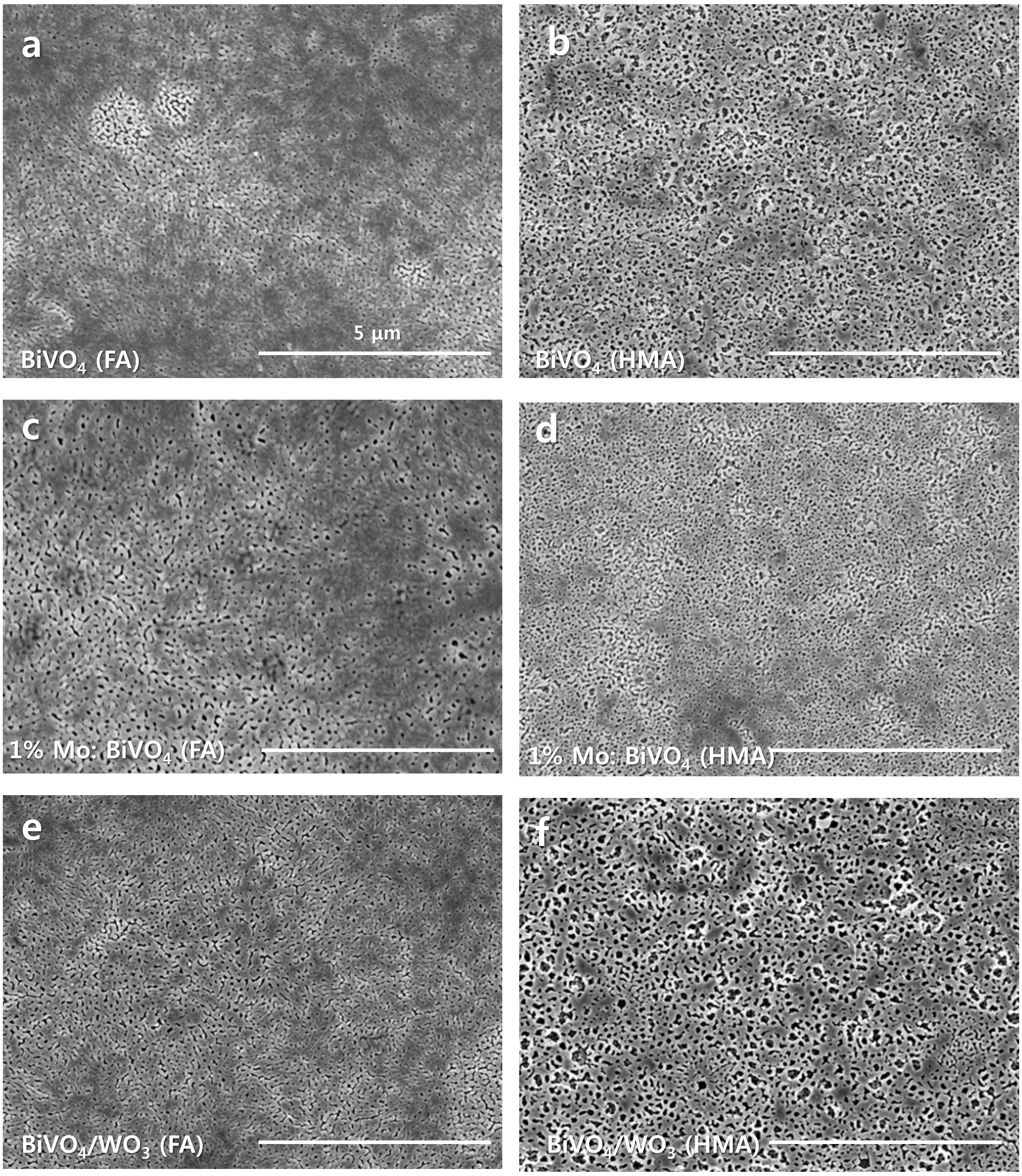

Figure S4. Scanning electron micrographs of (a, b) $BiVO_4$, (c, d) 1% Mo: $BiVO_4$ and (e, f) $BiVO_4/WO_3$ with different annealing methods. (a,c,e) FA, (b,d,f) HMA. Annealing times are set for 300 min (FA) and 6 min (HMA). Scale bar: 5.0 µm.

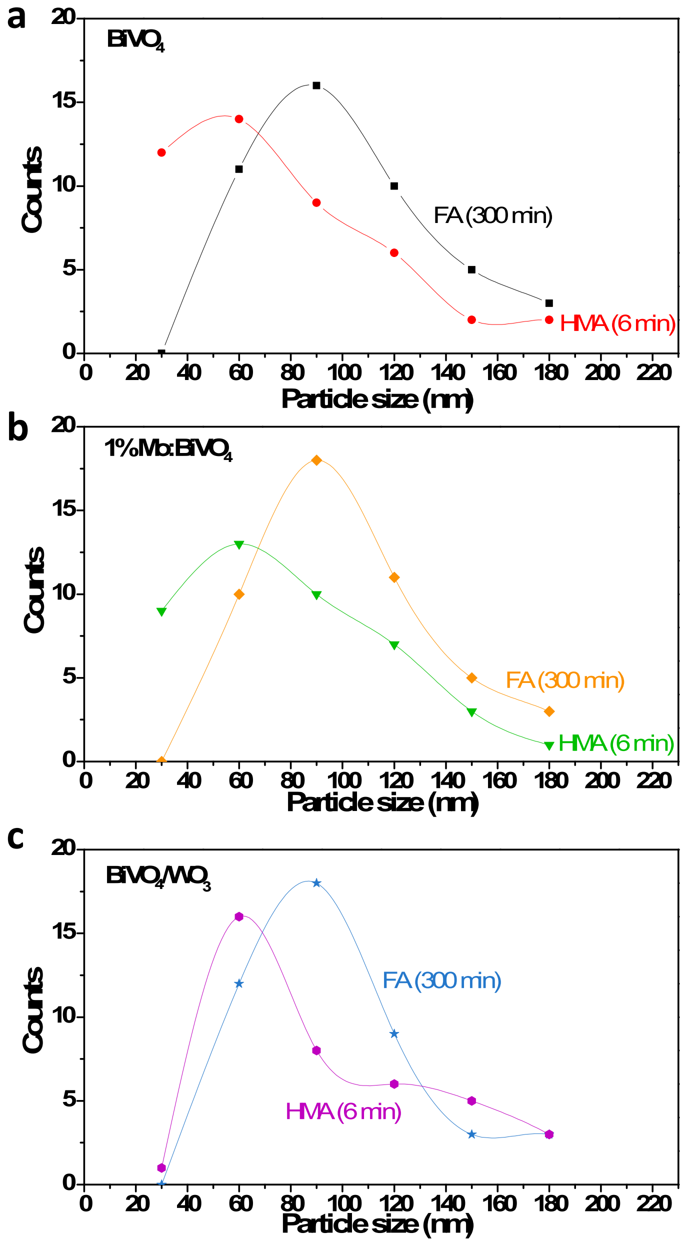

Figure S5. Particle size count from SEM image (count area: 500 nm X 1000 nm) for (a) $BiVO_4$, (b) 1% Mo:$BiVO_4$ and (c) $BiVO_4/WO_3$ annealed with FA and HMA. Overall count number of HMA samples (~35) is lower than furnace (~45) owing to larger portion of pores on HMA samples on same count area size. Average feature size was decided via using top count size (60~90 nm for furnace samples, 30~60 nm for HMA samples) with deviation of 2^{nd}, 3^{rd} highest count. Calculated result was marked at Table 1.

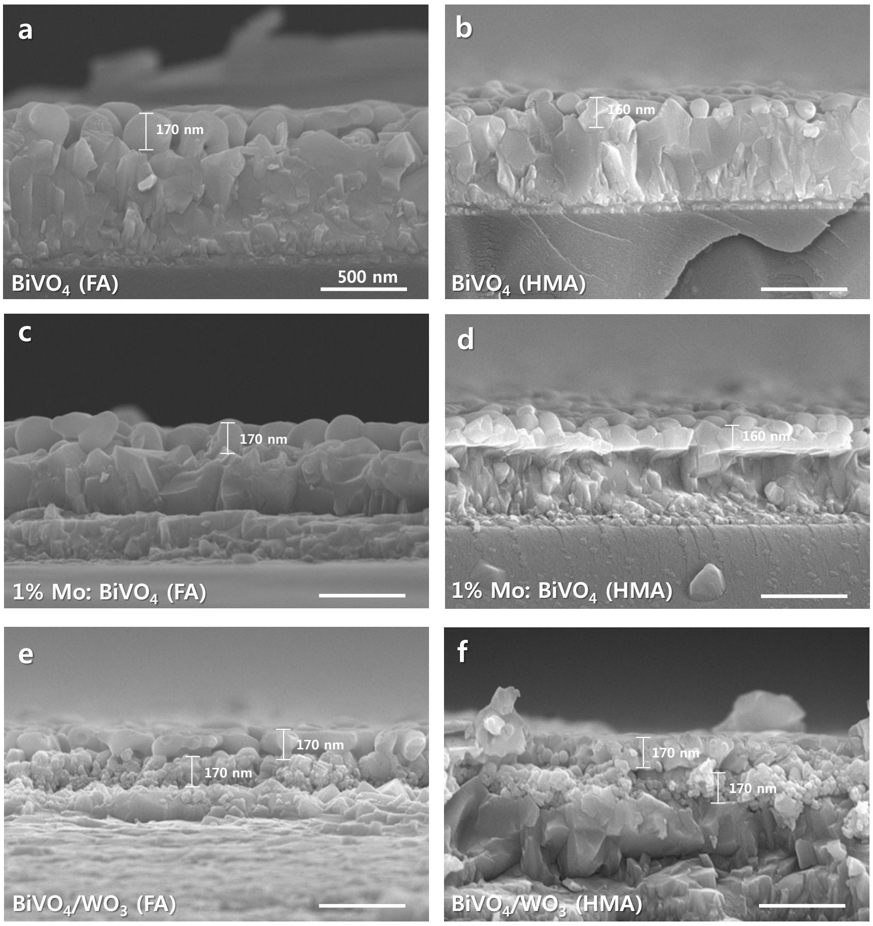

Figure S6. Cross section SEM image of (a, b) $BiVO_4$, (c, d) 1% Mo:$BiVO_4$ and (e, f) $BiVO_4/WO_3$ film with different annealing system (furnace and HMA).

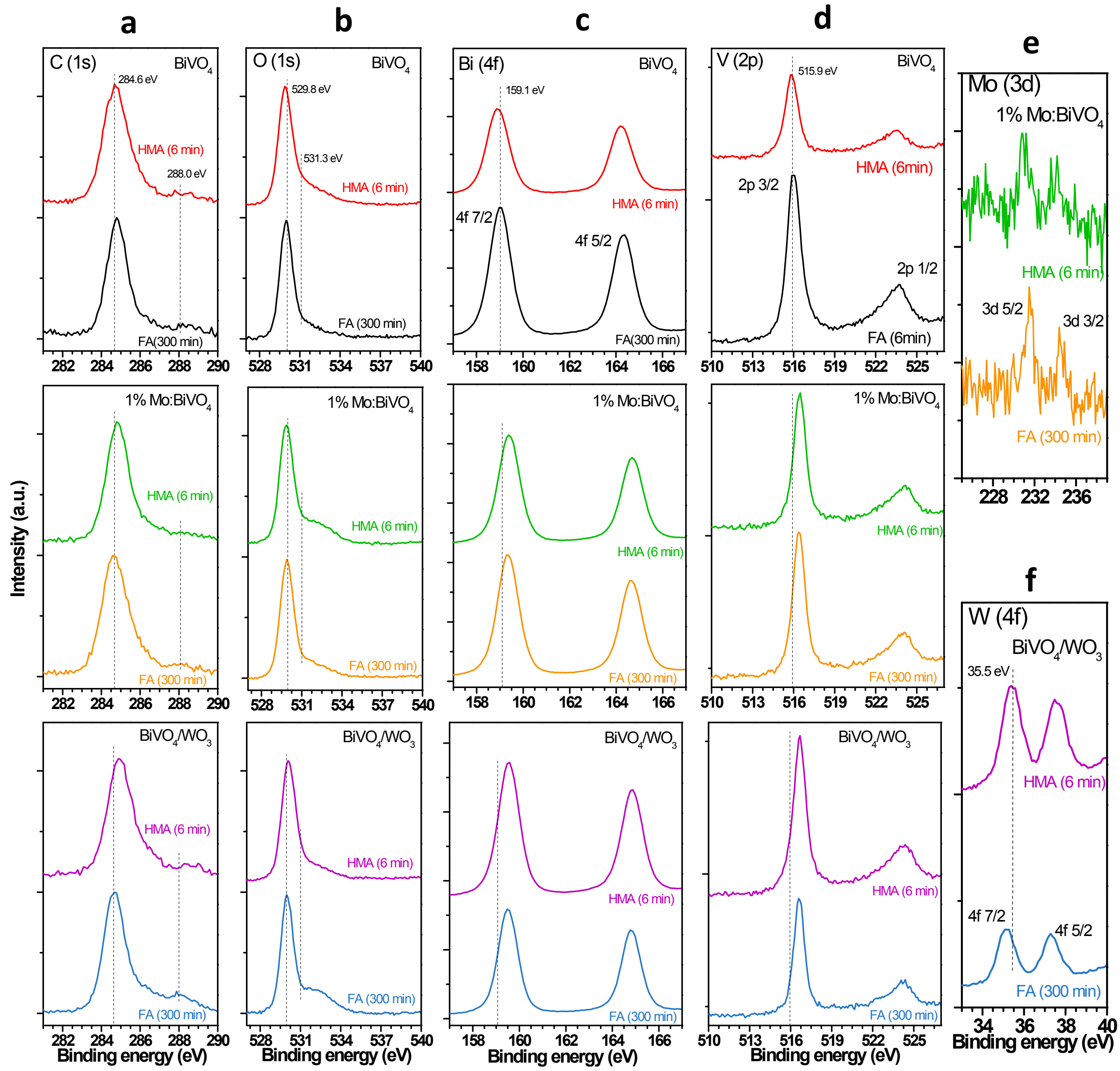

Figure S7. X-ray photoelectron spectra (XPS) of (a) C 1s (284.5 eV for C-C, 288.0 eV for carbonate or hydrocarbon), (b) O 1s (529.8 eV for metal oxide, 531.3 eV for –OH), (c) Bi 4f (159.1 eV for Bi^{3+} as metal oxide), (d) V 2p (515.9 eV for V^{5+} as metal oxide), (e) Mo 3d and (f) W 4f (35.5 eV for W^{6+} for WO_3). Samples used for analysis are $BiVO_4$, 1% Mo:$BiVO_4$ and $BiVO_4/WO_3$ made with FA (300 min) and HMA (6 min). Information of binding energy was referred from [2-5]

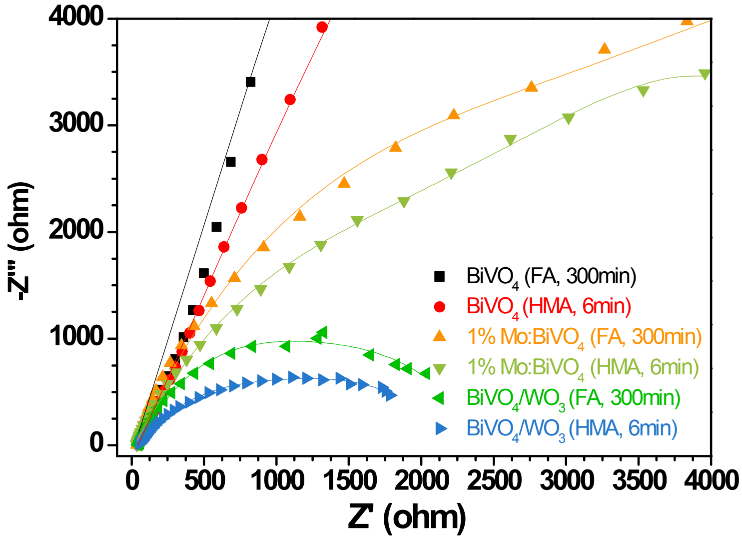

Figure S8. Nyquist plots in 0.5 M KPi buffer under illumination of 1 sun (100 mW/cm^2) with applied bias of 0.63 V *vs*. Ag/AgCl.

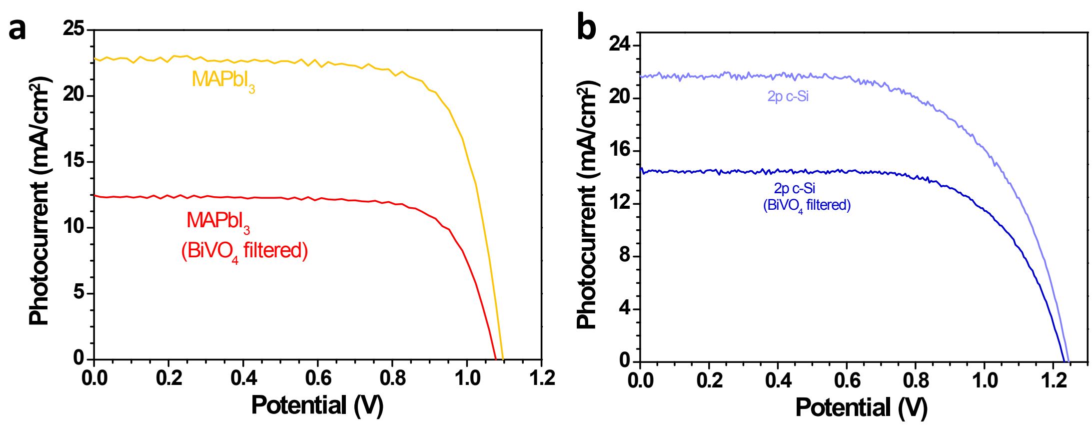

Figure S9. IV curves of (a) $MAPbI_3$ perovskite solar cell and (b) 2p (parallel alignment) c-Si solar cell with/without $BiVO_4/WO_3$ (HMA, 6min) filter.

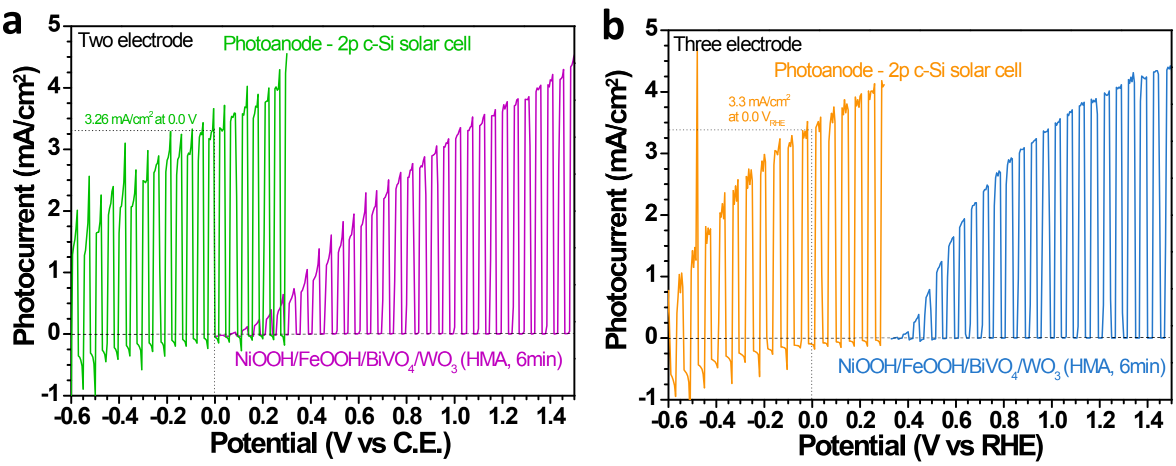

Figure S10. IV curves of $NiOOH/FeOOH/BiVO_4/WO_3$ (HMA, 6min) photoanode – 2p c-Si tandem cell measured in (a) two and (b) three electrode configurations. Measurements were conducted under AM 1.5G (100 mW/cm^2) illumination in 0.5 M KPi (pH 7.0), the scan rate of 20 mV/cm^2 (backward) and front side illumination. Active area was 0.42 cm^2. Electrolyte was purged with Ar gas.

SUPPLEMENTAY REFERENCES

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