Electronic Supplementary Information (ESI)

Cobalt-phosphate (Co-Pi) catalyst modified Mo-doped $BiVO_4$ photoelectrodes for solar water oxidation

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Experimental detail

The Photoelectrochemical setup for the action spectra consisted of a 100 W tungsten arc lamp housing with an LPS-220 lamp power supply (Photon Technology International), a model SID-101 monochromator (Photon Technology International), and an EG&G model 263A potentiostat/galvanostat (Princeton Applied Research). Light exiting the monochromator was chopped at 37 Hz, and an optical filter was used to block any second-order diffraction. The signal was detected using a Stanford Research Systems model SR830 DSP lock–in amplifier using the chopping frequency as a reference. The spectral output of the lamp and monochromator was measured using a thermopile detector in place of the electrochemical cell. The voltage output from the thermopile is proportional to the incident power and it was plotted vs photon energy. To obtain photon flux from this plot, the photocurrent signal at each wavelength was divided by the energy (eV) of that wavelength. The semiconductor photocurrent spectrum was divided by the photon flux spectra to get a normalized spectrum. In these tests the electrode was held at 0.7 V vs. Ag/AgCl (3M KCl) and the photocurrent at each monochromatic light was registered

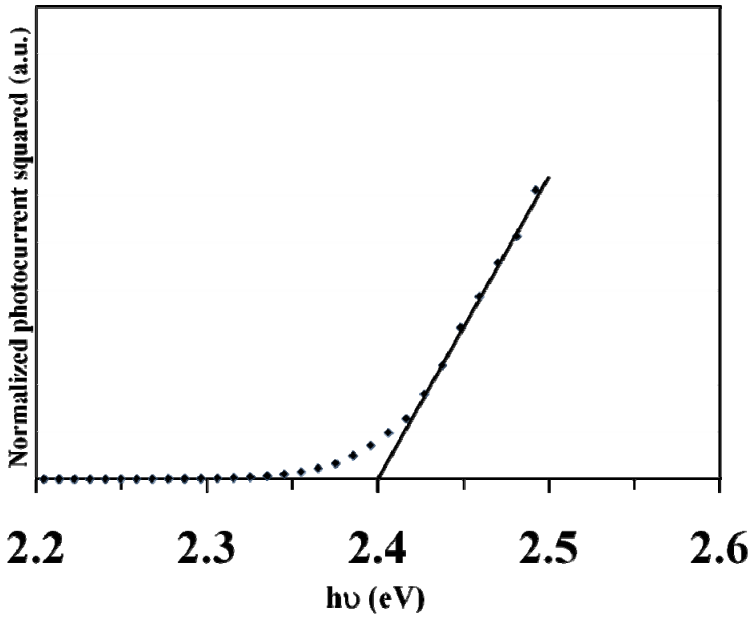

Fig. S1 Photocurrent action spectrum of $BiV_{0.98}Mo_{0.02}O_4$ electrode measured in 1 mM Na_2SO_3 aqueous solution (pH7 phosphate buffered), applied bias 0.7 V vs. Ag/AgCl.

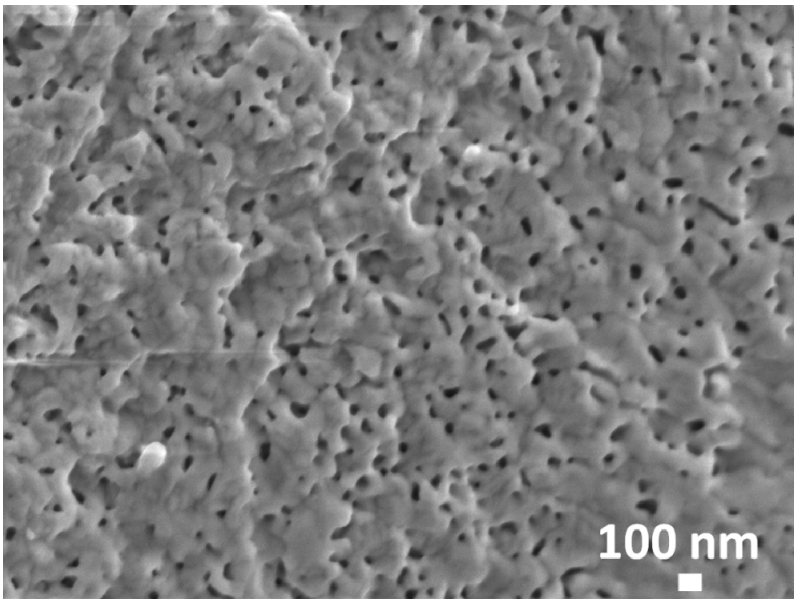

Fig. S2 SEM image of porous $BiV_{0.98}Mo_{0.02}O_4$ electrode at X30000 resolution.

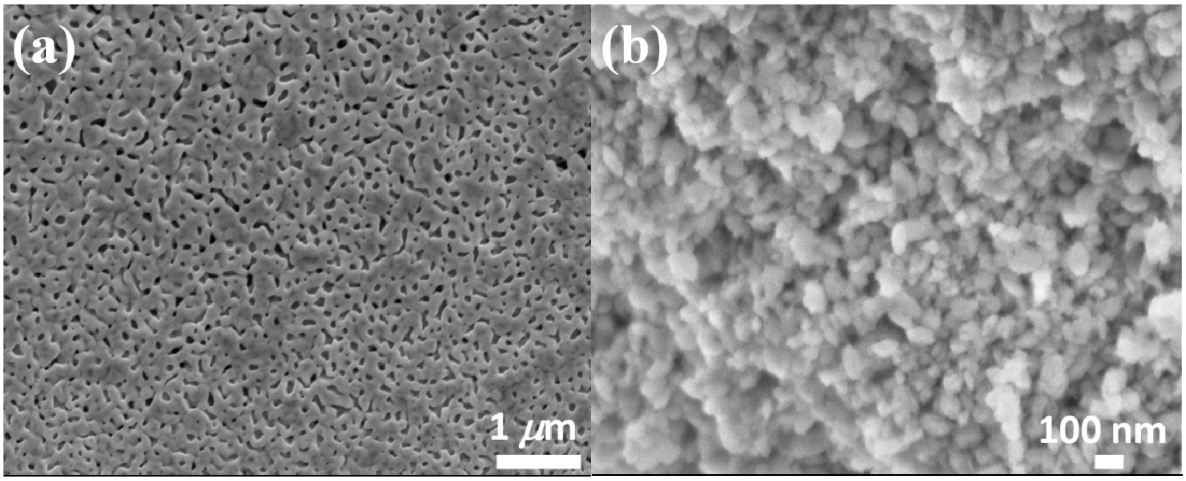

Fig. S3 SEM images of undoped $BiVO_4$ electrodes porous (a) and nonporous(b) prepared in the presence and absence of SDS.

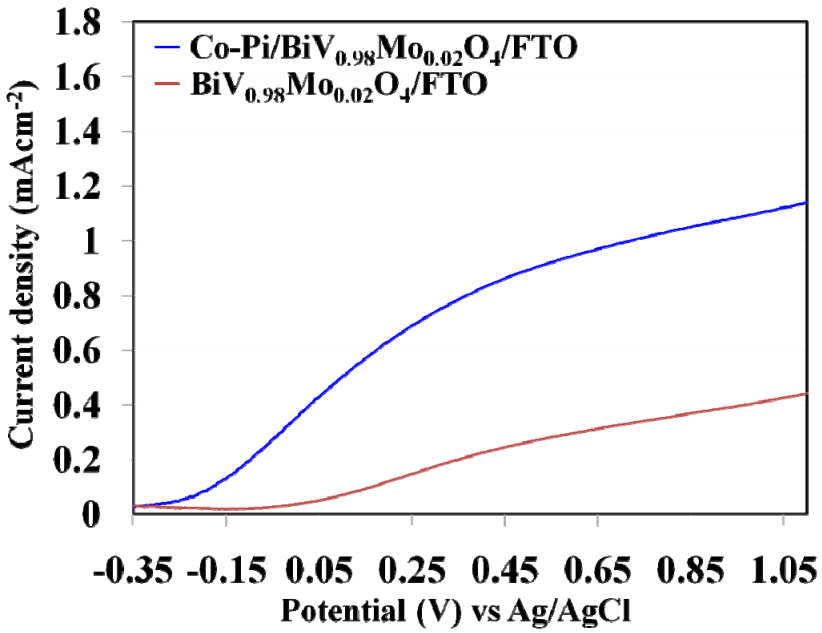

Fig. S4 Linear sweep voltammograms of $BiV_{0.98}Mo_{0.02}O_4$ (red) and Co-Pi/ $BiV_{0.98}Mo_{0.02}O_4$ (blue) electrodes measured (scan rate, 25 mV/s) with continuous light (100 mW/cm^2) in 0.5M Na_2SO_4 (pH7) solution.

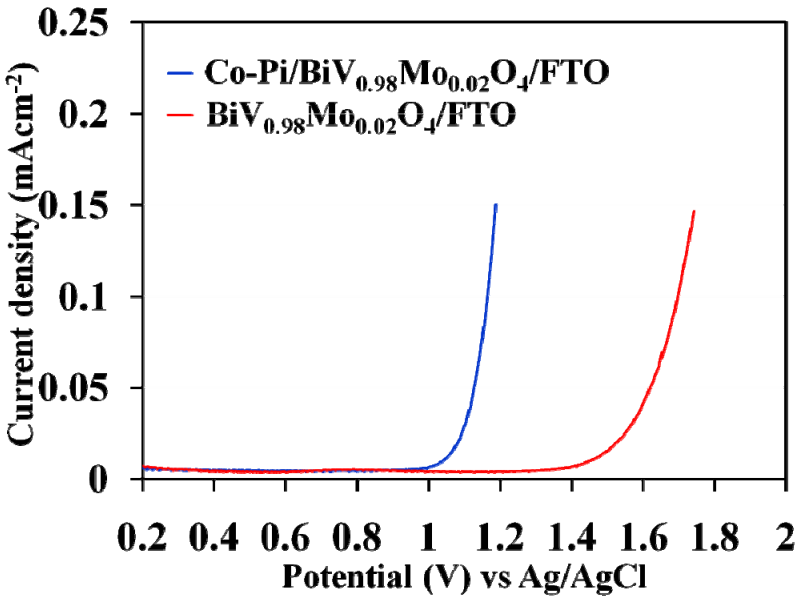

Fig. S5 Linear sweep voltammograms of $BiV_{0.98}Mo_{0.02}O_4$ (red) and Co-Pi/ $BiV_{0.98}Mo_{0.02}O_4$ (blue) electrodes measured (scan rate, 25 mV/s) under dark using 0.5M Na_2SO_4 aqueous solution in phosphate buffer (pH7) electrolyte.

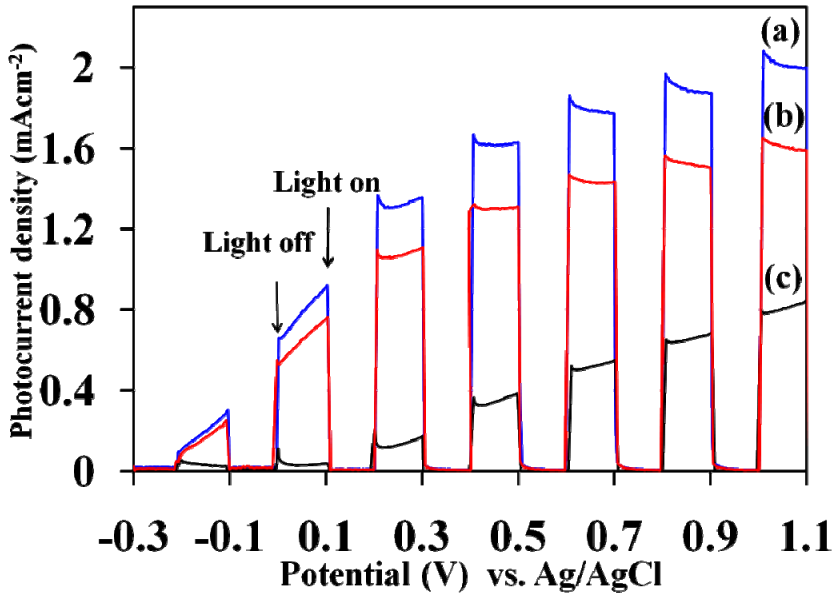

Fig. S6 Photocurrent-potential characteristics of $BiV_{0.98}Mo_{0.02}O_4$ electrodes modified with photo-assisted electrodeposited Co-Pi OEC (a); electrodeposited Co-Pi OEC (b) and unmodified $BiV_{0.98}Mo_{0.02}O_4$ electrode (c) measured in 0.5 M Na_2SO_4.

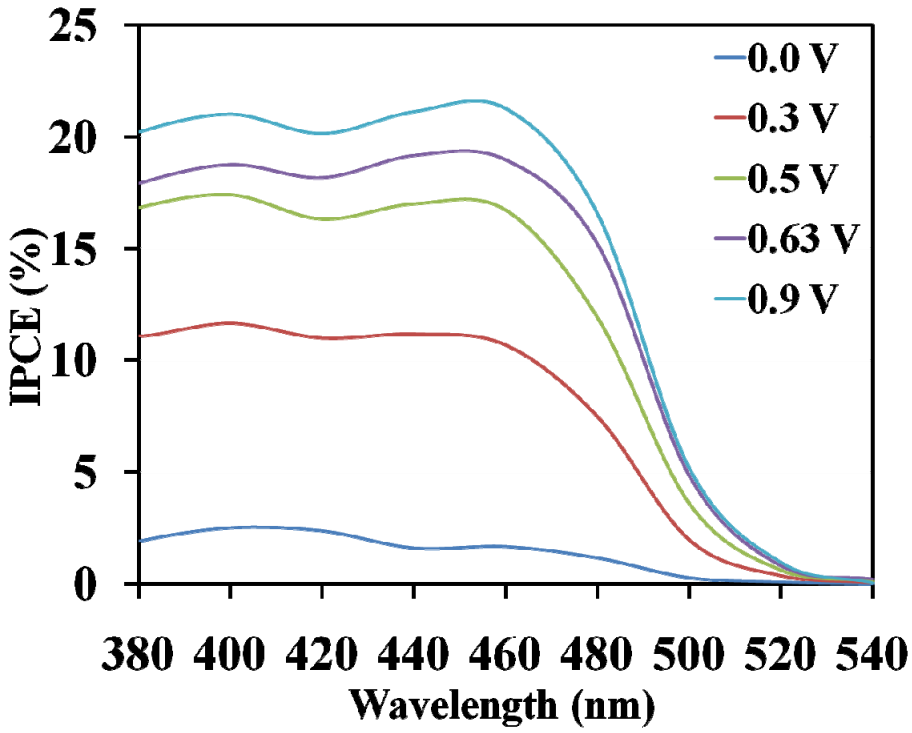

Fig S7 IPCE plot of $BiV_{0.98}Mo_{0.02}O_4$ electrode measured at 0.0, 0.3, 0.5, 0.63, 0.9 V *vs*. Ag/AgCl in 0.5 M Na2SO4 (pH 7 phosphate buffered).

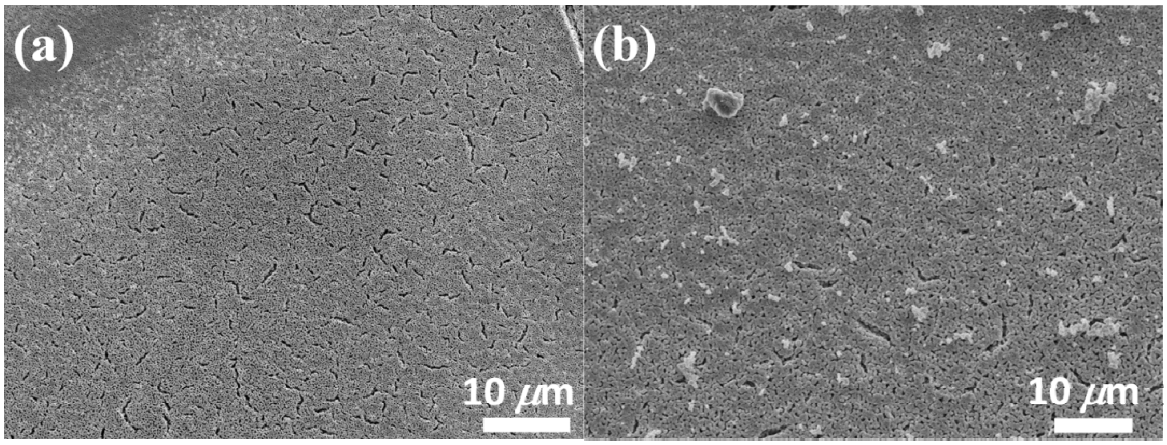

Fig S8 SEM images of $BiV_{0.98}Mo_{0.02}O_4$ (a) and Co-Pi/$BiV_{0.98}Mo_{0.02}O_4$ electrodes after 24 h of durability test.