Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

W:$BiVO_4$ /$BiVO_4$ graded photoabsorbers on WO_3 mesoporous electrode for enhanced photoelectrocatalytic solar light driven water oxidation

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S1. Raman Spectra

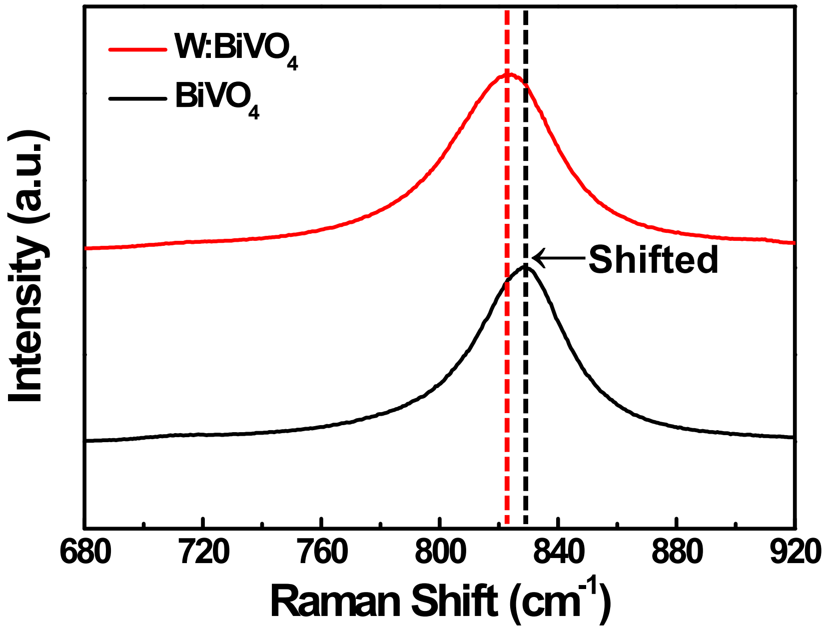


Figure S1. Raman spectra of $BiVO_4$ and $W:BiVO_4$.

S2. SEM with EDS mapping

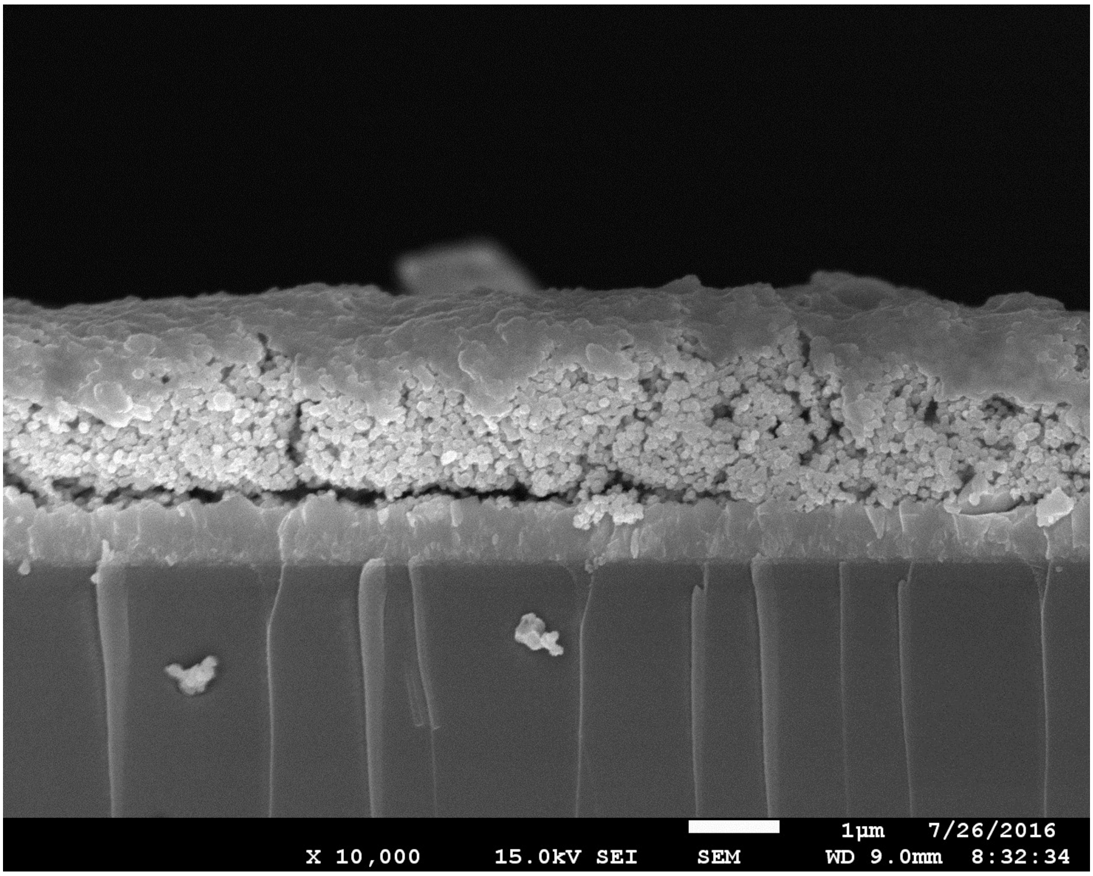


Figure S2. Cross sectional SEM images of WO_3/W:$BiVO_4$/$BiVO_4$ electrode.

S3. J-V measurements at dark condition

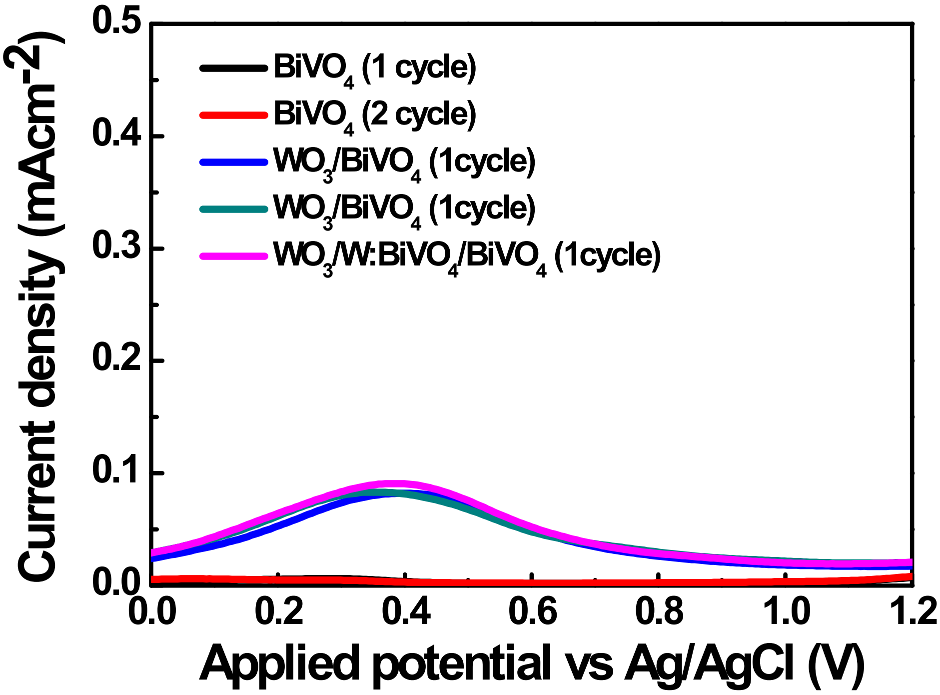
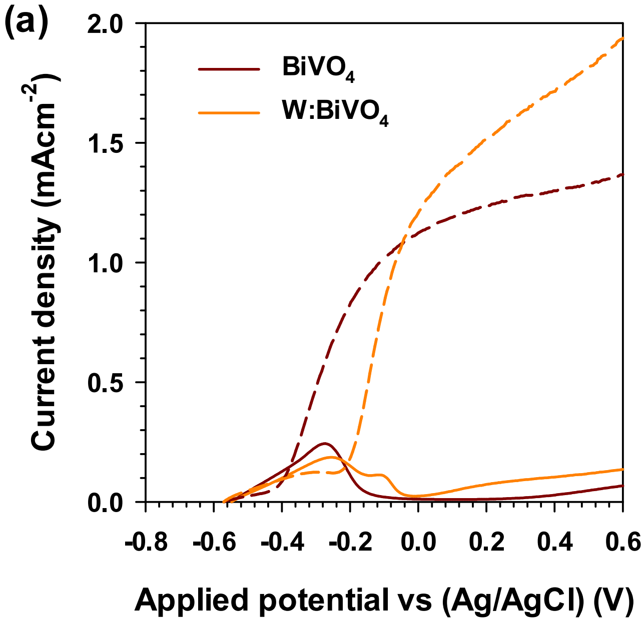


Figure S3. JV plots of different photoanodes assited PEC cells (measured at dark conditions).

S4. Photoelectrochemical experiments



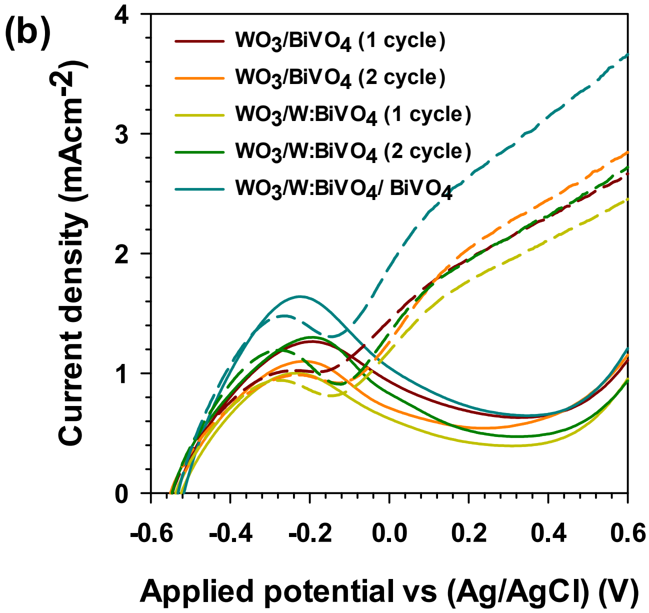


Figure S4. J-V plot of different photoanodes measured in the 0.5 M potassium phosphate electrolyte with presence (dotted line) and absence of Na_2SO_3 (solid line) hole scavenger (a) single photoabsorbers and (b) hetero and multinary $WO_3/BiVO_4$ photoabsorbers.

From Figure S4 (a) and (b), the photocurrent of the sulfide oxidation is higher than the water oxidation due to efficient hole scavenging from photoanode surface to the electrolyte.[1, 2] Interestingly, W doped $BiVO_4$ electrode shows higher sulfide oxidation due to enhanced charge separation from electrode surface to electrolyte species (**Figure S4a**). The $BiVO_4$ and

W:BiVO_4 photoabsorber layer coated onto WO_3 backbone layer result higher sulfite oxidation (**Figure S4b**) compared to directly coated onto conducting substrate.

Further comparing the sulfite oxidation performance in between the BiVO_4 and W:BiVO_4 photoabsorbers coated WO_3 photoanodes under identical coating conditions (i.e 1 and 2 coating cycles of secondary photoabsorbers) the photocurrent showed less difference between WO_3/BiVO_4 and WO_3/W:BiVO_4 (~2.4- 2.8 mAcm^{-2} at 0.6 V vs Ag/AgCl). This explain that there is no significant optical absorbance enhancement effect in W:BiVO_4 layer compare to pristine BiVO_4 towards sulfite oxidation. Interestingly, after inserting the W:BiVO_4 interfacial layer at WO_3/BiVO_4 photoanode, it results significantly higher photocurrent ~3.6 mAcm^{-2} at 0.6 V vs Ag/AgCl than the WO_3/BiVO_4 and WO_3/W:BiVO_4 photoanodes. Here the coating quantity of WO_3/BiVO_4 and WO_3/W:BiVO_4 electrodes are similar to WO_3/ W:BiVO_4 /W:BiVO_4 cascade layer. This ensures the charge separation process induced water oxidation process takes place at WO_3/ W:BiVO_4 /W:BiVO_4 cascade structure.

S5. Phototransient profile

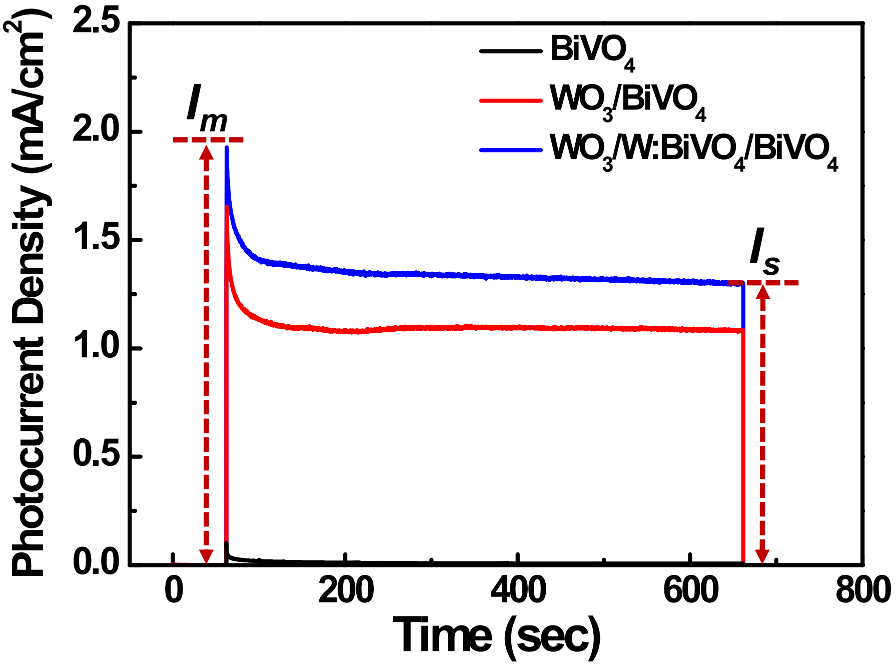


Figure S5. Phototransient plots of different photoanode based PEC cells (the measurements were recorded at 0.7 V vs Ag/AgCl applied potential, 0.5 M Na_2SO_4 electrolyte is used).

S6. Impedance analysis

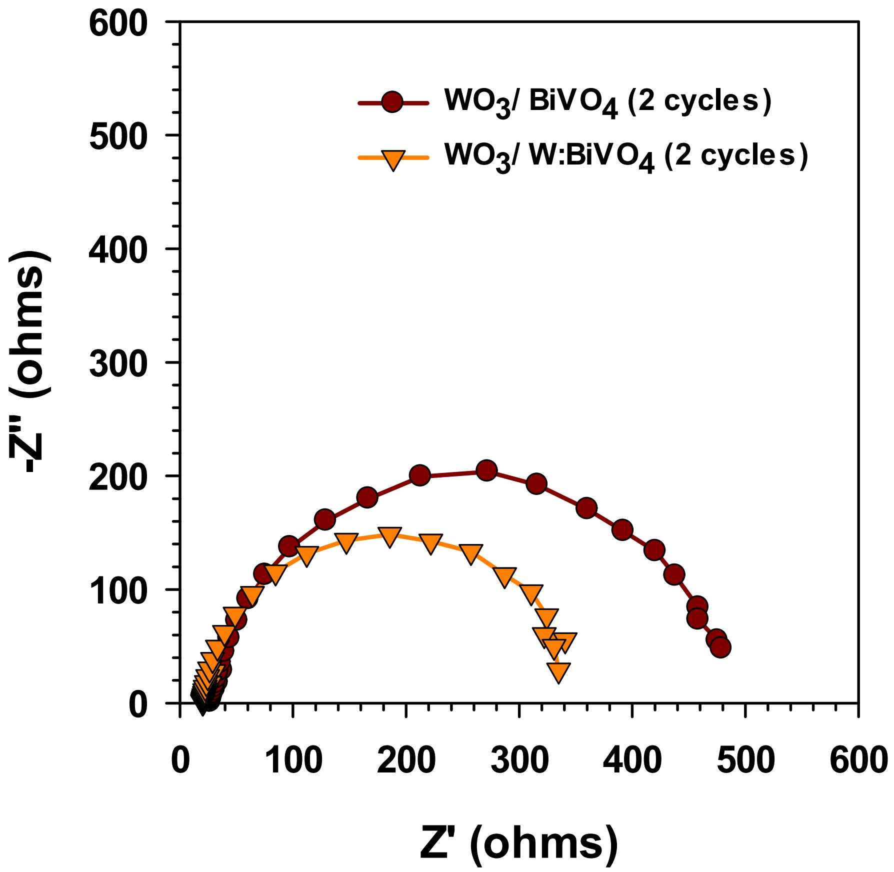


Figure S6. Nyquist spectra of $WO_3/BiVO_4$ and $WO_3/W:BiVO_4$ electrodes at 1 M Na_2SO_4 electrolyte. Note that the measurements were recorded under light irradiation 100 $mWcm^{-2}$.

The **Figure S6** depicts the Nyquist plots of $BiVO_4$ and W doped $BiVO_4$ photoabsorber layer identically coated onto WO_3 layers. Though the thickness of both photoabsorber layers are identical (2 coating cycles), the W doped $BiVO_4$ layer exhibit less charge transfer resistance. This is attributed to enhanced conductivity of BiVO4 by W doping carriers as is explained in the main text.

References:

1. **T. W. Kim and K.-S. Choi, *Science*, 2014, 343, 990-994.**
2. **T. W. Kim, Y. Ping, G. A. Galli and K.-S. Choi, *Nature Communications*, 2015, 6, 8769.**