

## Photoelectrochemical Performance of Nanostructured BiVO<sub>4</sub>/NiOOH/FeOOH – Cu<sub>2</sub>O/CuO/TiO<sub>2</sub> Tandem Cell for Unassisted Solar Water Splitting

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### Supplementary Information

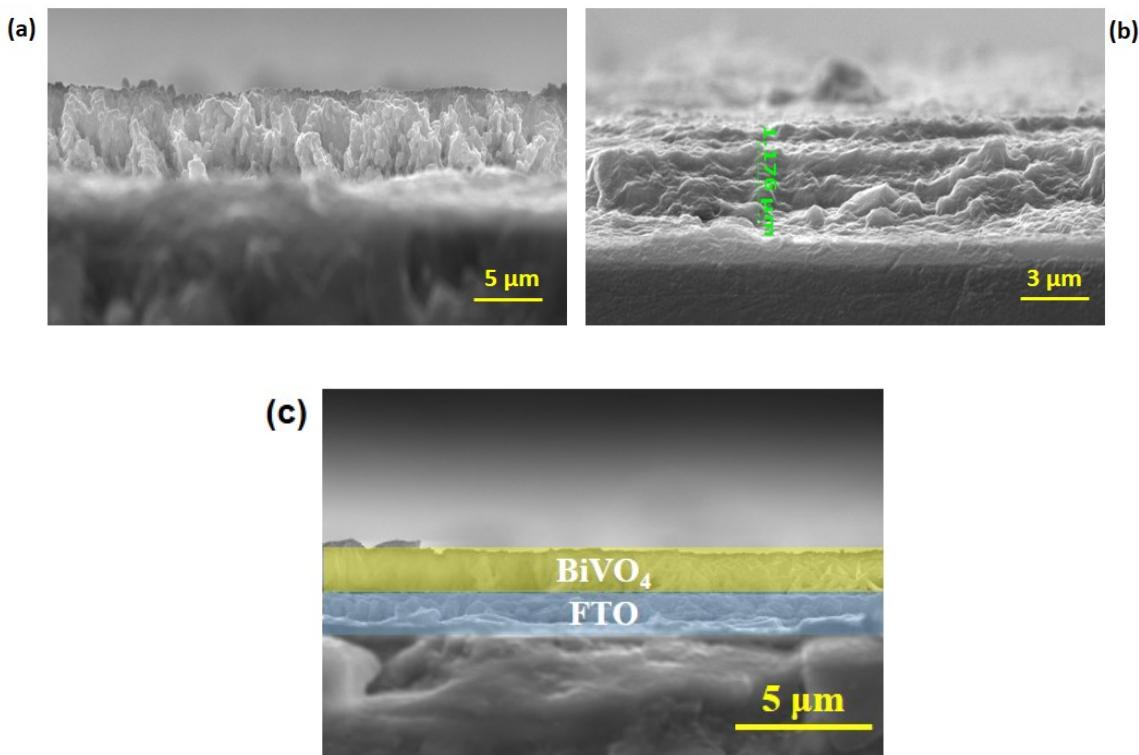


Figure S1, Cross sectional FESEM micrograph of (a) BiVO<sub>4</sub>/FeOOH/NiOOH photoanode and (b) Cu<sub>2</sub>O/CuO/TiO<sub>2</sub> photocathode, (c) Highlighted cross section for BiVO<sub>4</sub> nanostructures

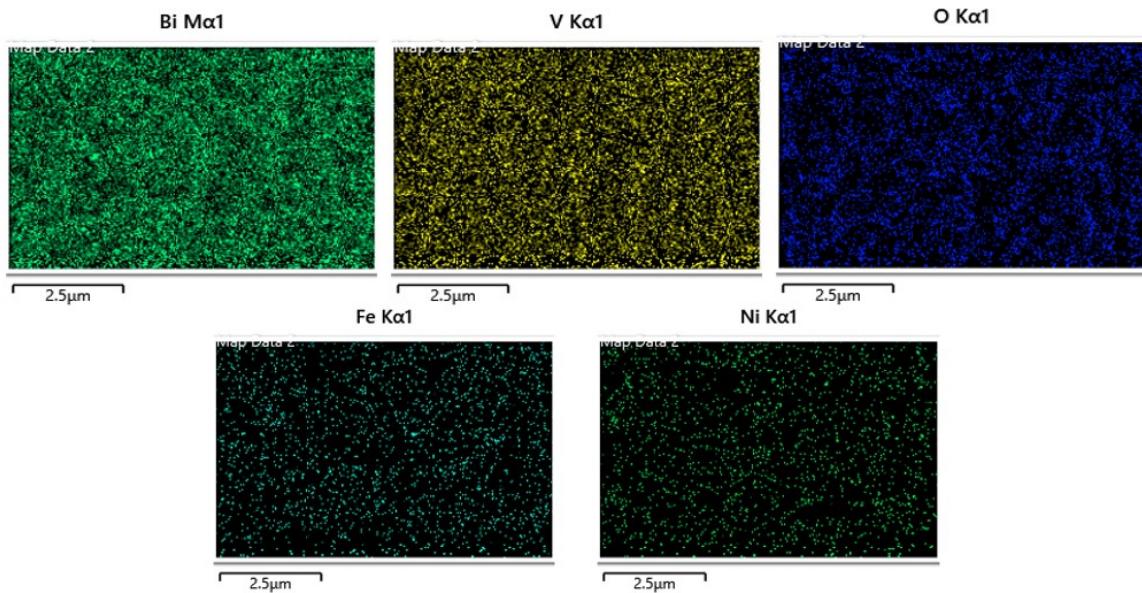


Figure S2, EDS color mapping of  $\text{BiVO}_4/\text{NiOOH}/\text{FeOOH}$  photoanodes

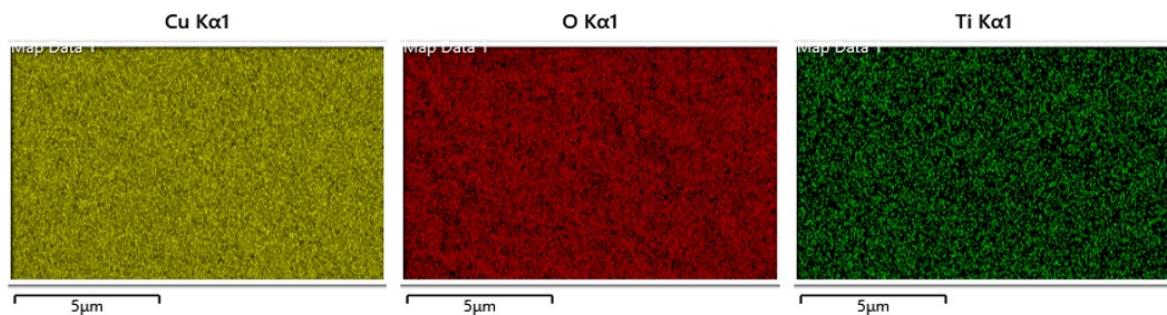


Figure S3, EDS color mapping of  $\text{Cu}_2\text{O}/\text{CuO}/\text{TiO}_2$  photocathode

<b>Raman Peak (<math>\text{cm}^{-1}</math>)</b>	<b>Peak significance</b>
<i>Photoanode</i>	
207.79	External mode of monoclinic $\text{BiVO}_4$
324.06 & 369.52	Symmetric and Asymmetric deformation of $\text{VO}_4^{3-}$
819.78	Symmetric stretch mode of V – O
<i>Photocathode</i>	
207.05	Second order Raman peak of cubic $\text{Cu}_2\text{O}$
614.56	Infrared allowed mode of $\text{Cu}_2\text{O}$
293.96	Characteristic peak of $\text{CuO}$

Table S1, Tabulation of significance of obtained Raman vibrational spectra of  $\text{BiVO}_4$  photoanodes and  $\text{Cu}_2\text{O}$  photocathodes

<i>Photoelectrodes</i>	<i>Bandgap (eV)</i>
<i>Photoanodes</i>	
$\text{BiVO}_4$	2.37 eV
$\text{BiVO}_4/\text{FeOOH}$	2.37 eV
$\text{BiVO}_4/\text{NiOOH}$	2.41 eV
$\text{BiVO}_4/\text{FeOOH/NiOOH}$	2.30 eV
$\text{BiVO}_4/\text{NiOOH/FeOOH}$	2.31 eV
<i>Photocathodes</i>	
$\text{Cu}_2\text{O}$	2 eV
$\text{Cu}_2\text{O}/\text{CuO}$	1.87 eV
$\text{Cu}_2\text{O}/\text{CuO/TiO}_2$	1.55 eV
$\text{CuO}$	1.54 eV

Table S2, Tabulation of absorption edge and bandgap of  $\text{BiVO}_4$  photoanodes and  $\text{Cu}_2\text{O}$  photocathodes

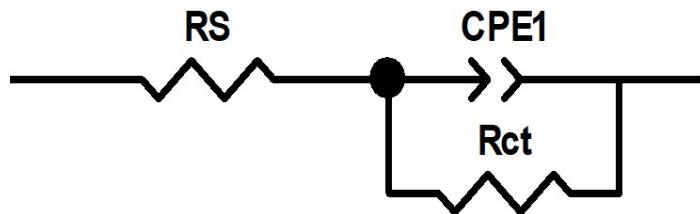


Figure S4, Equivalent circuit of  $\text{BiVO}_4$  and  $\text{Cu}_2\text{O}$  photocathodes obtained from Scribner's Z-View software under instant fit which is Randles-Ershel model

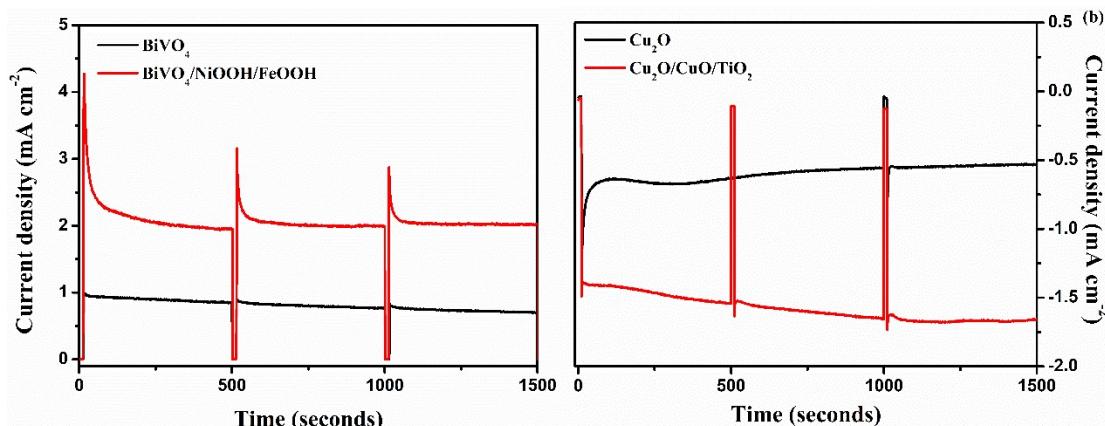


Figure S5, Photostability ( $j$  vs  $t$ ) curves of (a)  $\text{BiVO}_4$ ,  $\text{BiVO}_4/\text{FeOOH/NiOOH}$  photoanodes and (b)  $\text{Cu}_2\text{O}$ ,  $\text{Cu}_2\text{O}/\text{CuO/TiO}_2$  photocathodes tested in  $0.1 \text{ M Na}_2\text{SO}_4$  ( $\text{pH } 6$ ) in AM 1.5 G equipped illumination source with power intensity of  $100 \text{ mW cm}^{-2}$

Photoelectrodes	Operating current density (mA cm <sup>-2</sup> )	Operating voltage (V) vs RHE
<i>BiVO<sub>4</sub>/NiOOH/FeOOH vs Cu<sub>2</sub>O/CuO/TiO<sub>2</sub></i>	<i>0.344 mA cm<sup>-2</sup></i>	<i>0.51 V</i>
<i>BiVO<sub>4</sub>/NiOOH/FeOOH Vs Cu<sub>2</sub>O/CuO/TiO<sub>2</sub> (illumination to photocathode filtered by photoanode)</i>	<i>0.202 mA cm<sup>-2</sup></i>	<i>0.42 V</i>

Table S3, Tabulation of operating points of the proposed tandem PEC cell obtained by overlayed absolute LSV responses.

### Calculation of Solar-to-Hydrogen conversion efficiency

$$\eta_{\text{STH}} = \frac{J_{\text{op}} \times 1.23 \text{ V}}{P_{\text{in}}} \quad (1.1)$$

Where  $\eta_{\text{STH}}$  is the solar-to-hydrogen conversion efficiency,  $J_{\text{op}}$  is the current density at the operating point and  $P_{\text{in}}$  is the power density of the incident illumination.

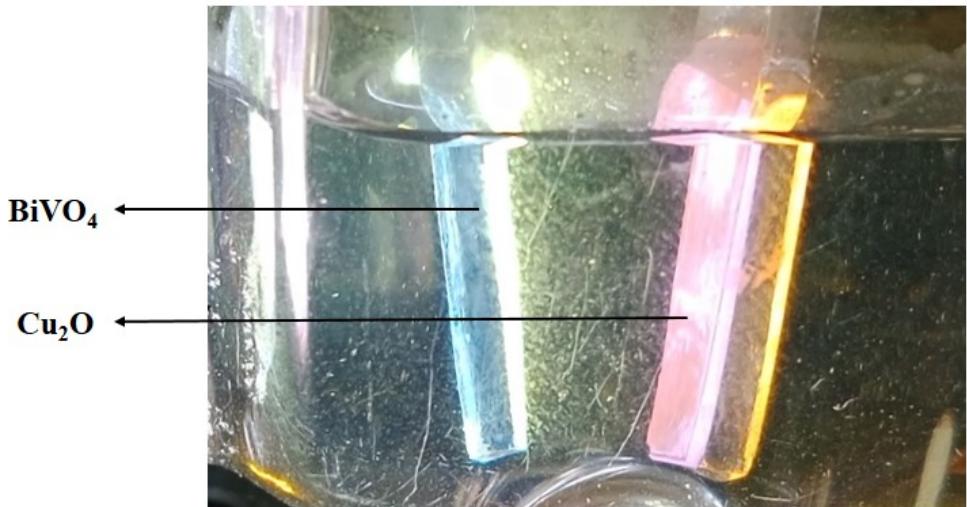


Figure S6, Photograph of constructed BiVO<sub>4</sub>-Cu<sub>2</sub>O tandem PEC cell