Supporting Information

Promoting holes transfer for photoelectrochemical water oxidation through bioinspired manganese cluster catalyst lessoned from natural photosystem II

Bin Gao,[a] Tao Wang,*[a] Yang Li,[a] Xiaoli Fan,[a] Hao Gong,[a] Cheng Jiang,[a] Peng Li,[a] Xianli Huang,[a] Jianping He,*[a]

[a] College of Materials Science and Technology, Jiangsu Key Laboratory of Electrochemical Energy Storage Technologies, Nanjing University of Aeronautics and Astronautics, 211106, Nanjing, P.R. China.

*Corresponding Author, E-mail: wangtao0729@nuaa.edu.cn; jianph@nuaa.edu.cn

Experimental Section

***Preparation of Mn_4O_4-cubane*:** The preparation method of Mn_4O_4-cubane is based on the previous reports and has two steps.

(1) Synthesize of $[(bipy)_2MnO]_2(ClO_4)_3 \cdot 2H_2O$: Firstly, water solution of manganese acetate (0.3 M, 60 ml) and acetone solution of 2,2'-bipyridyl (1.75 M, 30 ml) are mixed well. Secondly, sodium acetate buffer solution (1M, 80ml, pH=4.5) is added into the previous solution and the pH of mixed solution is adjusted to 4.5 by acetic acid. Next, water solution of potassium permanganate (0.15 M, 50 ml) is dropwise added into the previous solution in the ice-water bath. Then, lithium perchlorate (26.25 mmol) is added and the mixed solution is stirred in the ice-water bath for 15 min. Finally, the product is collected by suction filtration, washing, and drying;

(2) Synthesize of $Mn_4O_4(O_2P(Ph)_2)_6$: Firstly, methanol solution of ammonium hydroxide (1 M, 0.8 ml) is added into methanol solution of diphenylphosphinic acid (0.16 M, 5 ml) under stirring. Next, the solvent in the mixed solution is removed under vacuum. Then, the residuum is dissolved in mixed solvent of acetonitrile and acetone (10 ml, $V_{acetonitrile}$:$V_{acetone}$=2:1), and acetonitrile solution of $[(bipy)_2MnO]_2(ClO_4)_3 \cdot 2H_2O$ (0.02 M, 10 ml) is added into the mixed solution subsequently. After stirring overnight, the brownish-red sediment appears and is collected by suction filtration, washing, and drying.

Preparation of photoanode:

The $BiVO_4$ photoanode is prepared via the spin coating of the seed layer and hydrothermal. In the process of spin coating, the precursor solution of the seed layer is obtained by mixing ammonium metavanadate solution (0.05 M) and bismuth nitrate solution (0.05 M). Both of them have ethylene diamine tetraacetic acid (0.1 M) to stabilize metal ion and the pH is adjusted to 10 by ammonia. In the process of hydrothermal, ethylene diamine tetraacetic acid (0.3 mmol) and bismuth nitrate (0.3 mmol) are added into deionized water (30 ml) firstly. Then, NaOH solution (2 M, 0.75 ml) is dropped into the as-prepared solution to adjust the pH.

After the powder is dissolved completely, ammonium metavanadate (0.3 mmol) is added into the previous solution. Next, the yellow and transparent solution is transferred into a Teflon-lined autoclave, and the pretreated FTO conductive glass leans against the wall of autoclave with the seed layer facing down. Finally, the Teflon-lined autoclave is sealed and maintained at 180 ℃ for 3 h. After the hydrothermal process, the $BiVO_4$ photoanode is calcined at 500 ℃ for 4 h to increase its crystallinity.

The $BiVO_4/Mn_4O_4$ photoanode is prepared via method of drop-coating. The methylene dichloride and alcohol mixed solution ($V_{methylene\ dichloride}$:$V_{alcohol}$=1:9) of Mn_4O_4-cubane (0.05 mM) is used as the precursor. In the process of drop-coating, 0.1 ml precursor solution is dropped on the surface of $BiVO_4$ photoanode and the hybrid photoanode is natural drying in air.

Characterization: The fourier transform infrared spectroscopy test (FTIR) is implemented on the FT-IR spectrometer (Perkin-Elmer) with the specpure KBr. A field emission scanning electron microscope (Hitachi, Co. S4800) is used to obtain the scanning electron microscopy images (SEM). The high-resolution transmission electron microscopy images (HRTEM) and elemental distribution mapping images are collected on a transmission electron microscope (JEOL, 2100F). The X-ray diffraction spectra (XRD) are obtained on an X-ray diffractometer (Bruker, D8) with Cu Kα radiation. The diffuse reflectance ultraviolet-visible spectra (UV-Vis) are obtained on an UV-Vis spectrophotometry (Shimadzu, UV-3600). The X-ray photoelectron spectra (XPS) are collected on an X-ray photoelectron spectroscopy (ESCALab220i-XL). The surface photovoltage (SPV) is recorded on a surface photovoltage spectrometer (Perfectlight, PL-SPV/IPCE1000).

(Photo)electrochemical measurements: All the electrochemical and photoelectrochemical tests are performed on the typical three-electrode cell with a saturated calomel electrode as the reference electrode and a platinum gauze electrode as the counter electrode. The 0.2 M neutral phosphate buffer solution is used to be the electrolyte. A xenon lamp (Perfectlight, PLS-

SXE300C, China) with an AM 1.5 G light filter provides illumination and the light intensity reaching the reactor is 100 $mW \cdot cm^{-2}$. The performance of electrochemical and photoelectrochemical is recorded on an electrochemical workstation (Zahner, IM6).

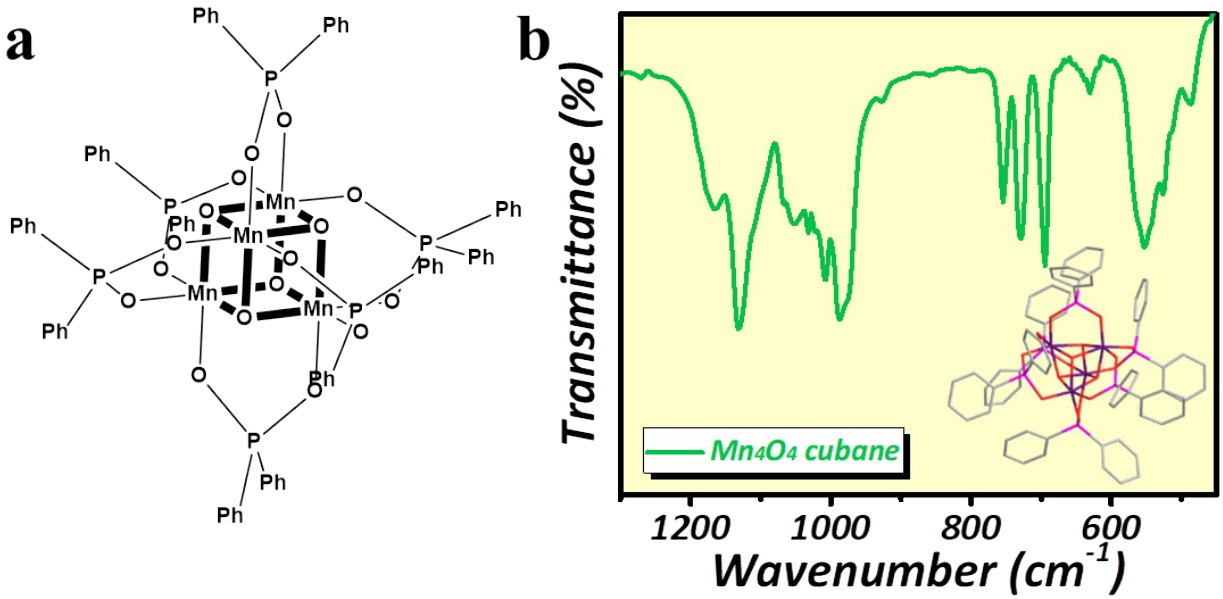

Figure S1. Molecular structure (a) and FTIR (b) of Mn_4O_4-cubane.

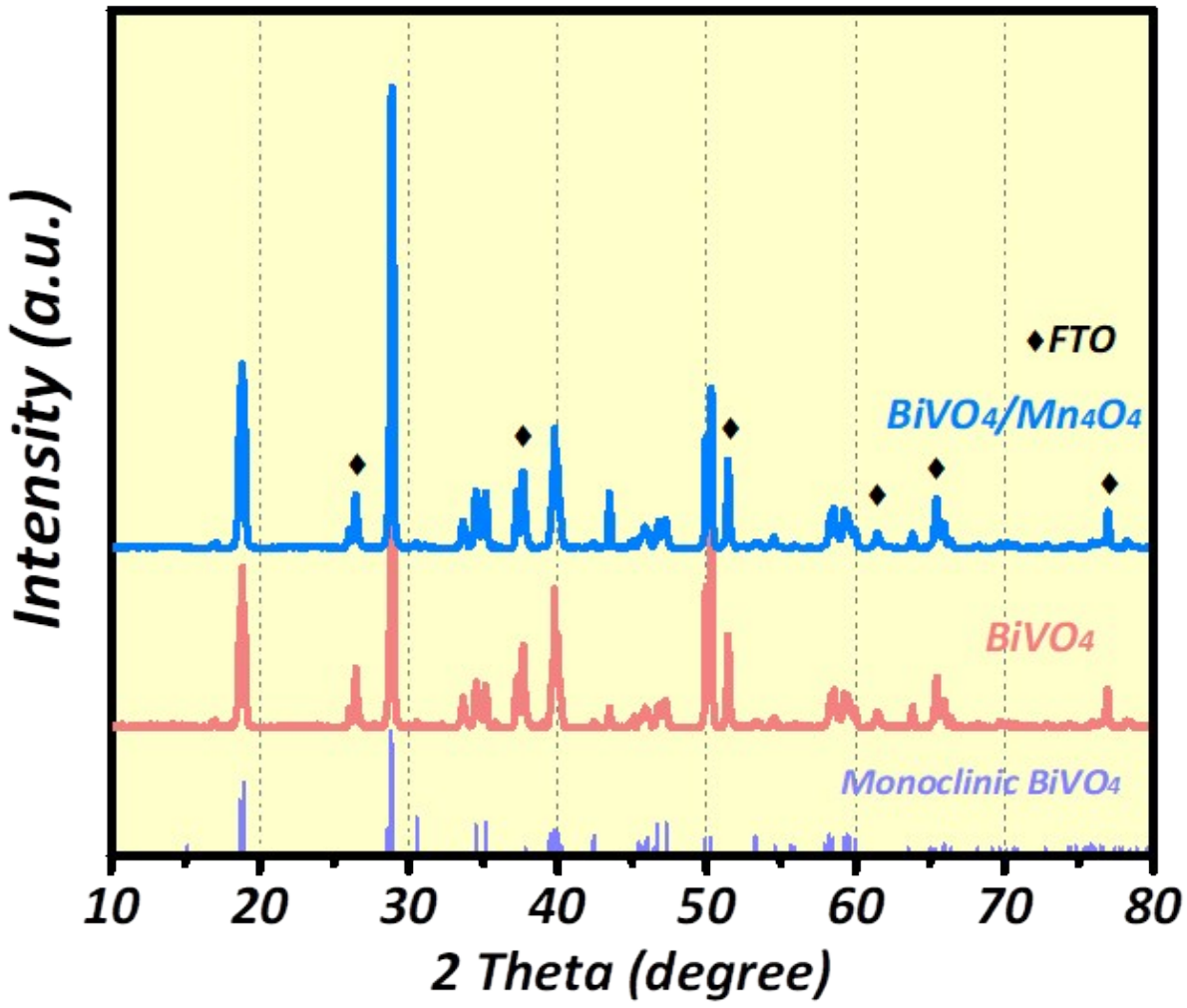

Figure S2. XRD spectra of $BiVO_4$ and $BiVO_4/Mn_4O_4$.

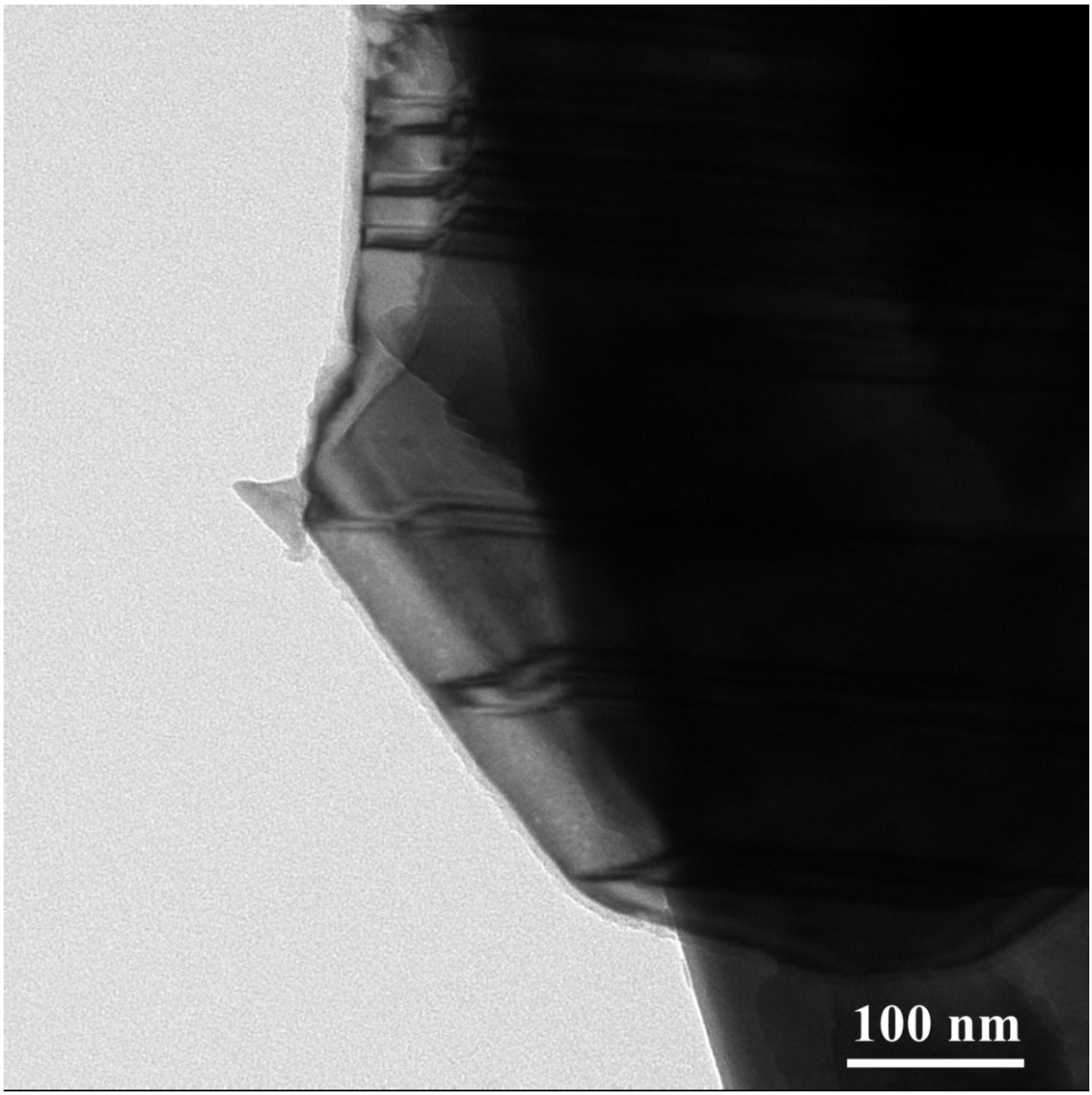

Figure S3. TEM image of $BiVO_4/Mn_4O_4$.

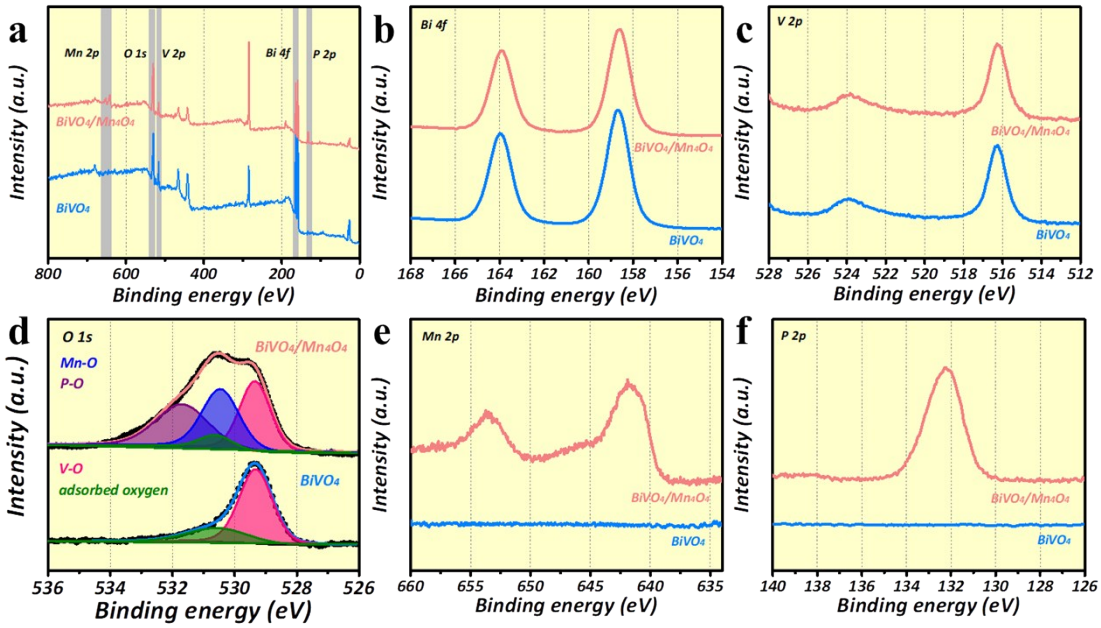

Figure S4. XPS survey spectra (a) and high-resolution of Bi 4f (b), V2p (c), O 1s (d), Mn 2p (e) and P 2p (f).

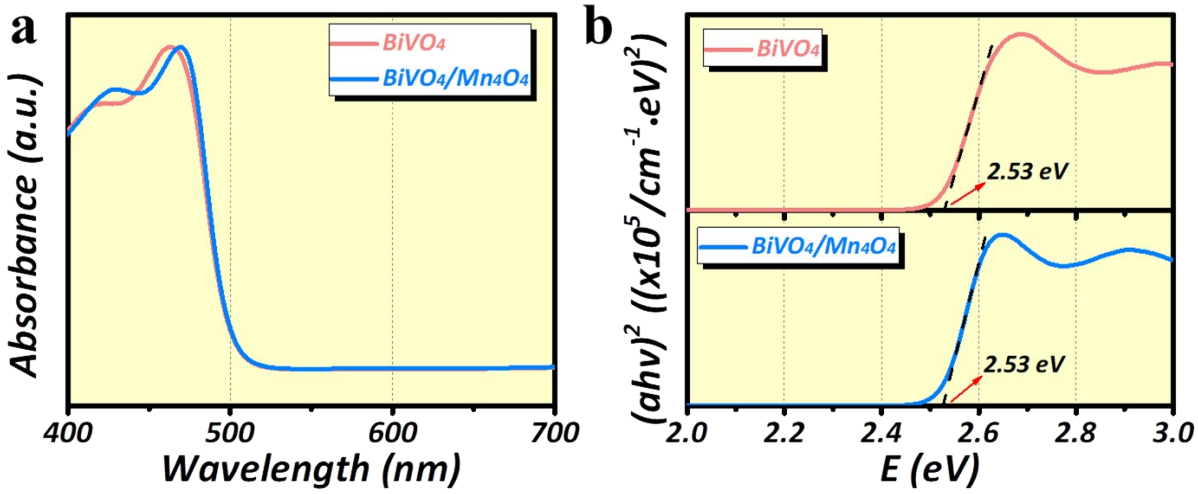

Figure S5. UV-Vis spectra (a) and Tauc-plots (b) of $BiVO_4$ and $BiVO_4/Mn_4O_4$.

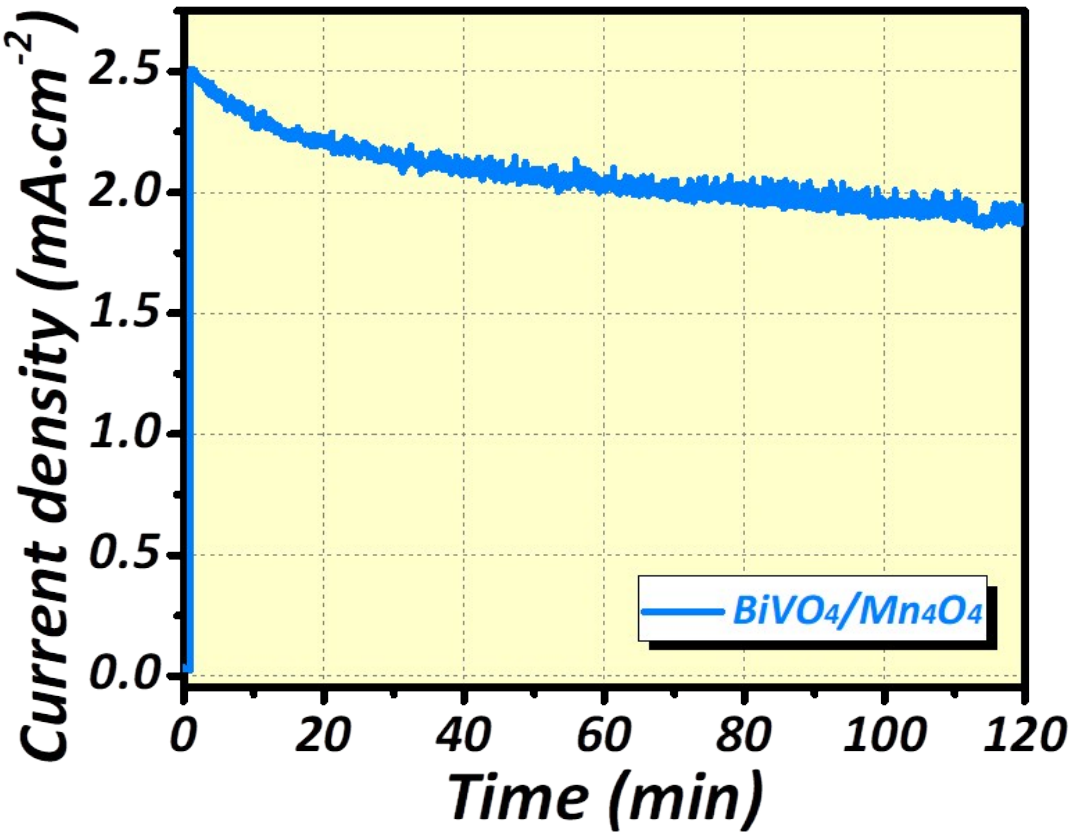

Figure S6. I-t curve of $BiVO_4/Mn_4O_4$.

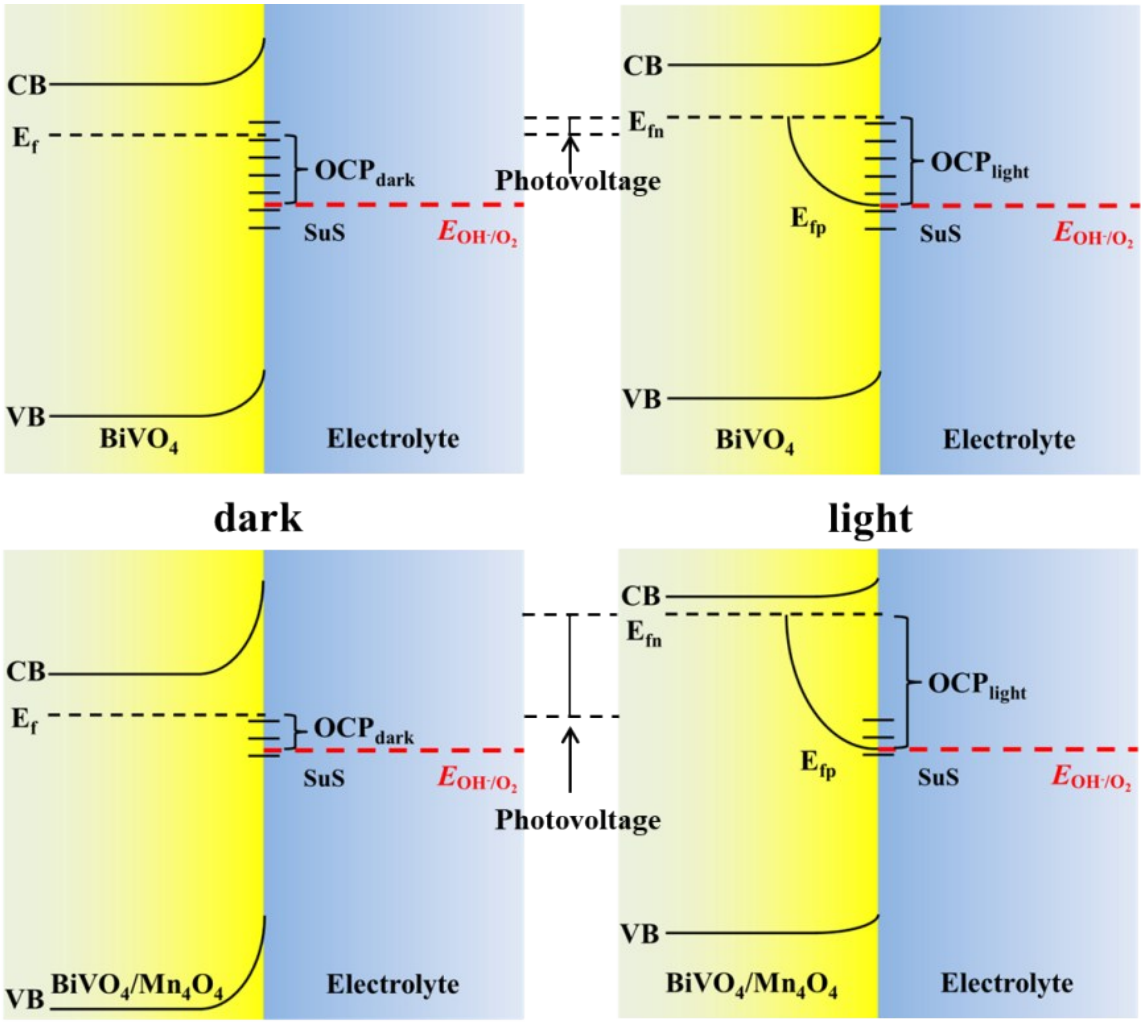

Figure S7. Band structure and band bending schematics of $BiVO_4$ and $BiVO_4/Mn_4O_4$.

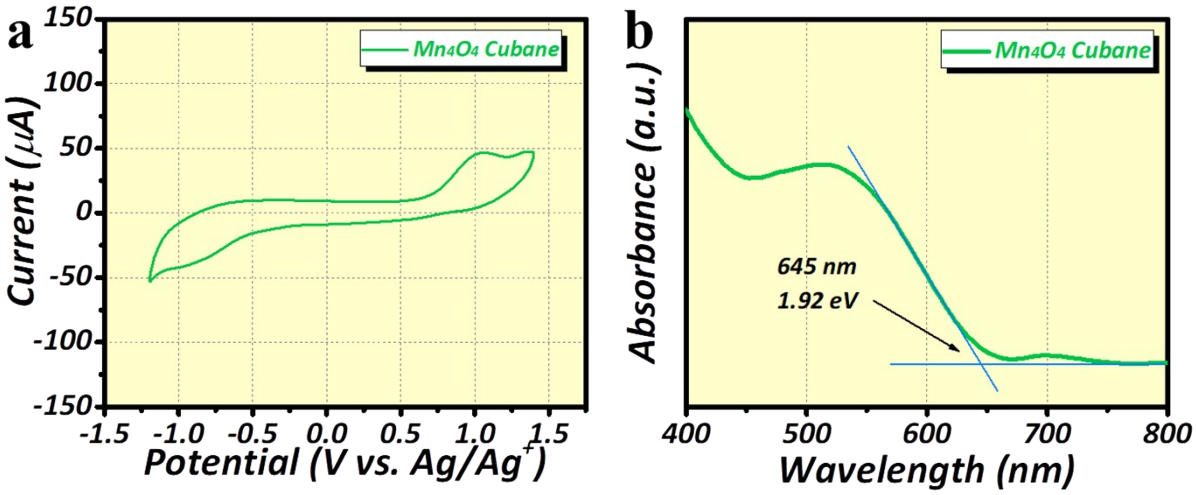

Figure S8. CV curves (a) and UV-Vis spectrum (b) of Mn_4O_4 Cubane.