Exploring $Bi_4V_2O_{11}$ as Photoanode for Water Splitting with a Wide Range of Solar Light Capture and Suitable Band Potential

DFT Calculation Method

The CASTEP module of the Materials Studio software (BIOVIA) was employed for the quantum chemistry calculations. Self-consistent periodic Density Functional Theory (DFT) was adopted to explore the electronic structure with Perdew-Burke-Ernzerhof (PBE) approximation and the Generalized Gradient Approximation (GGA) method. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme was selected as the minimization algorithm. And DFT-D correction was used for dispersion corrections. Hubbard U-corrections to the *d* electrons of V (LDA+U, effective U(V) = 2.5 eV) and spin-polarized were performed during the calculations. The energy cutoff is 340 eV and the SCF tolerance is 1.0×10^{-6} eV/atom. The optimization is completed when the energy, maximum force, maximum stress and maximum displacement are smaller than 1.0×10^{-5} eV/atom, 0.03 eV/ Å, 0.05 GPa and 0.001 Å, respectively. The Gamma point was set as $3 \times 3 \times 3$. Fermi level is simply defined as the valence band maximum (VBM) in the CASTEP code [1,2]. The calculated Density of States (DOS) and band structure of bulk $Bi_4V_2O_{11}$ are plotted along high symmetry directions in the brillouin zone.

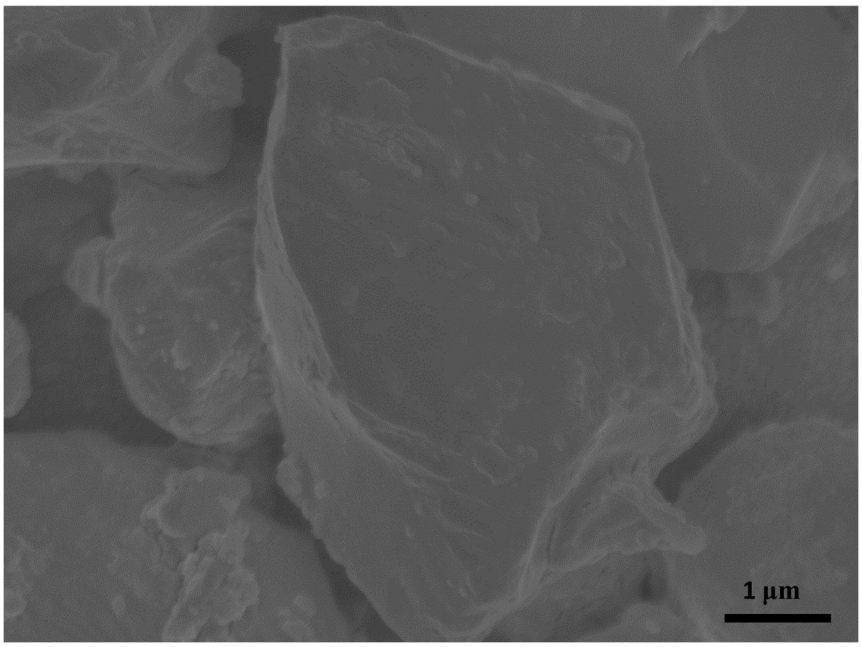

Figure S1. SEM images of as synthesized $Bi_4V_2O_{11}$ particles.

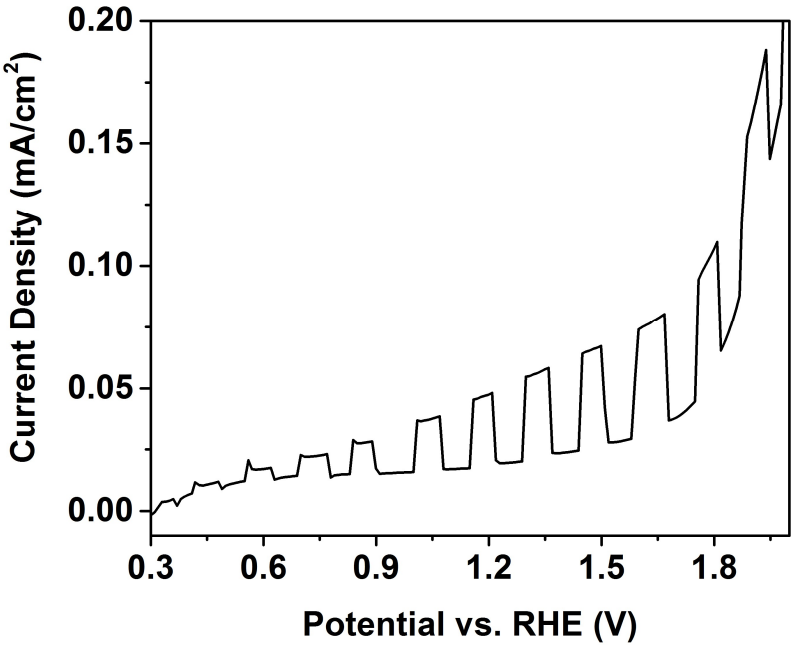

Figure S2. Photocurrent of pristine $Bi_4V_2O_{11}$ photoelectrode with W necking treatment.

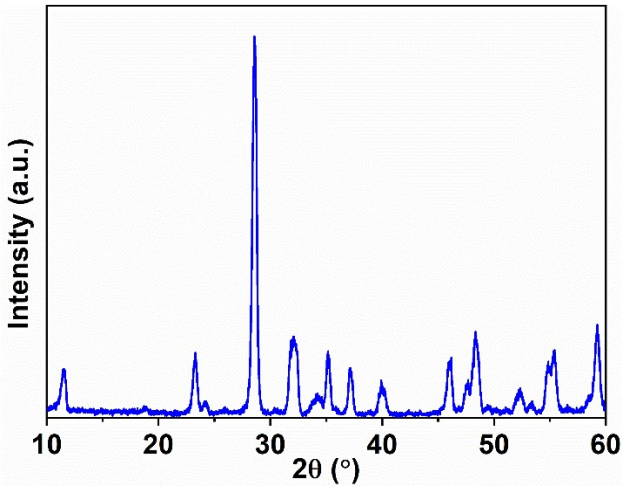

Figure S3. X-ray diffraction of Mo doped $Bi_4V_2O_{11}$ powder by solid state reaction.

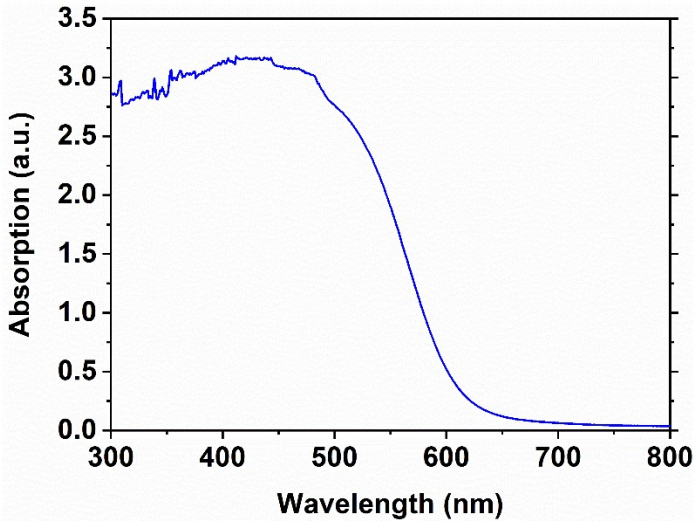

Figure S4. UV-vis light absorption spectrum of Mo doped $Bi_4V_2O_{11}$ powder.

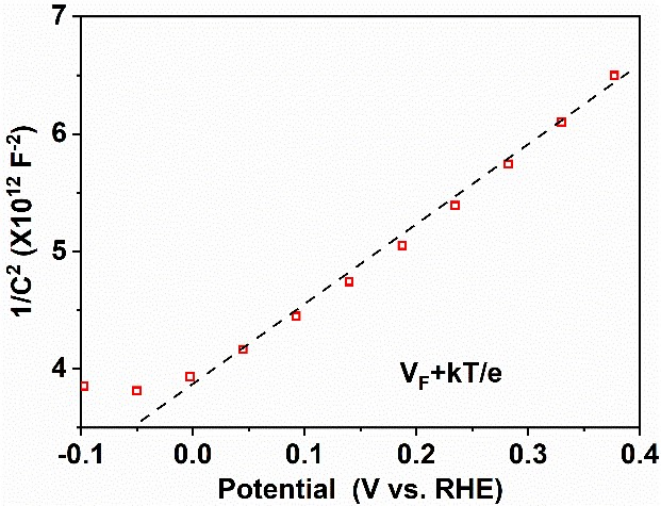

Figure S5. Mott Schottky plot of Mo doped $Bi_4V_2O_{11}$ film measured in 0.5 M Na_2SO_4 electrolyte under dark condition.

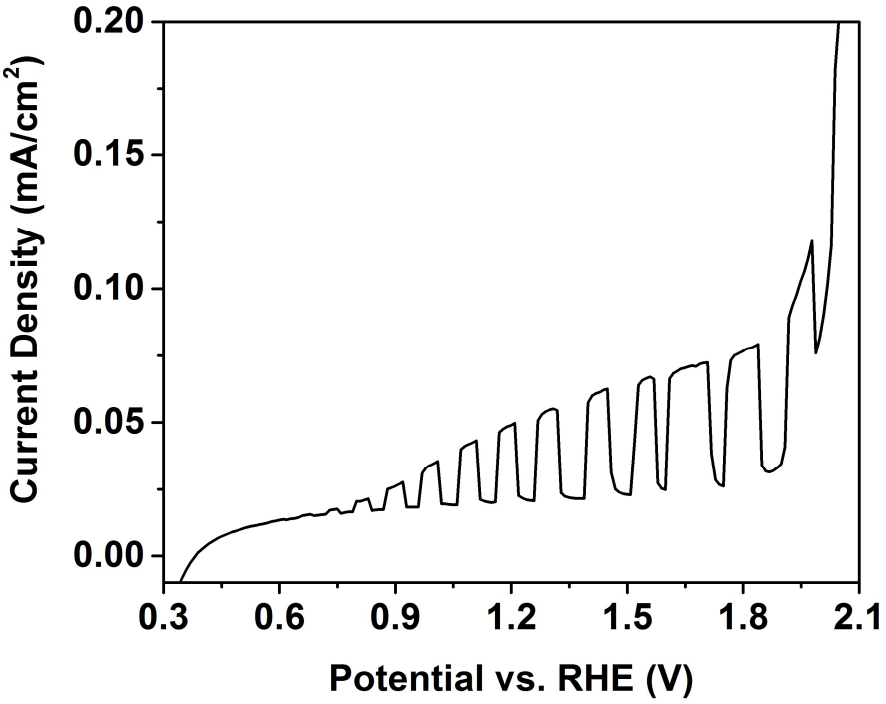

Figure S6. Photocurrent of WO_3 obtained by dropping the same amount as necking agent on FTO substrate and heated at 500 °C for 1h.

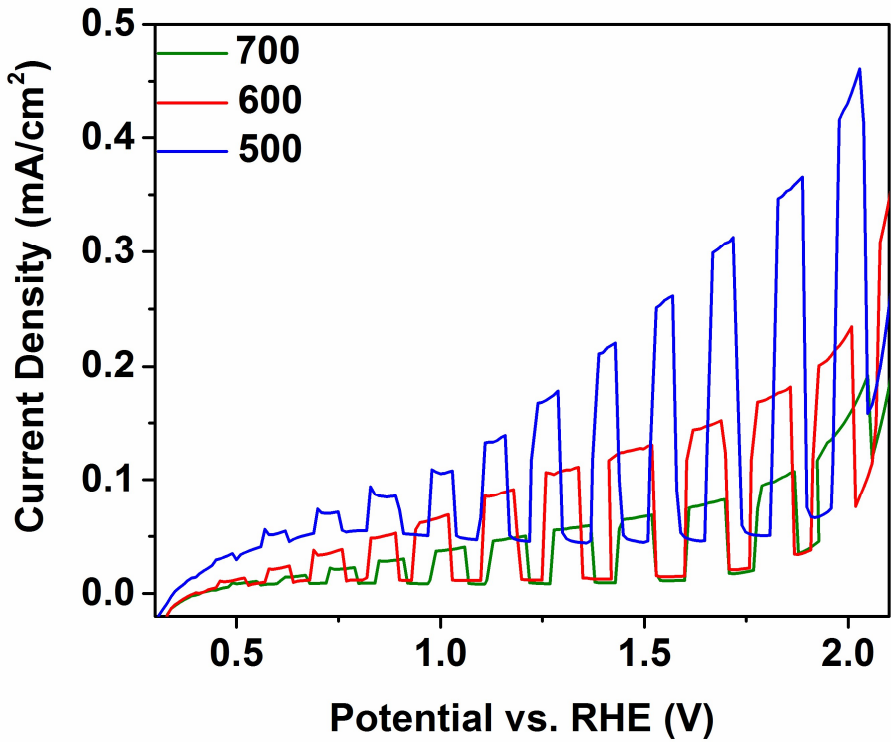

Figure S7. Photocurrent of W necking samples treated with different temperature.

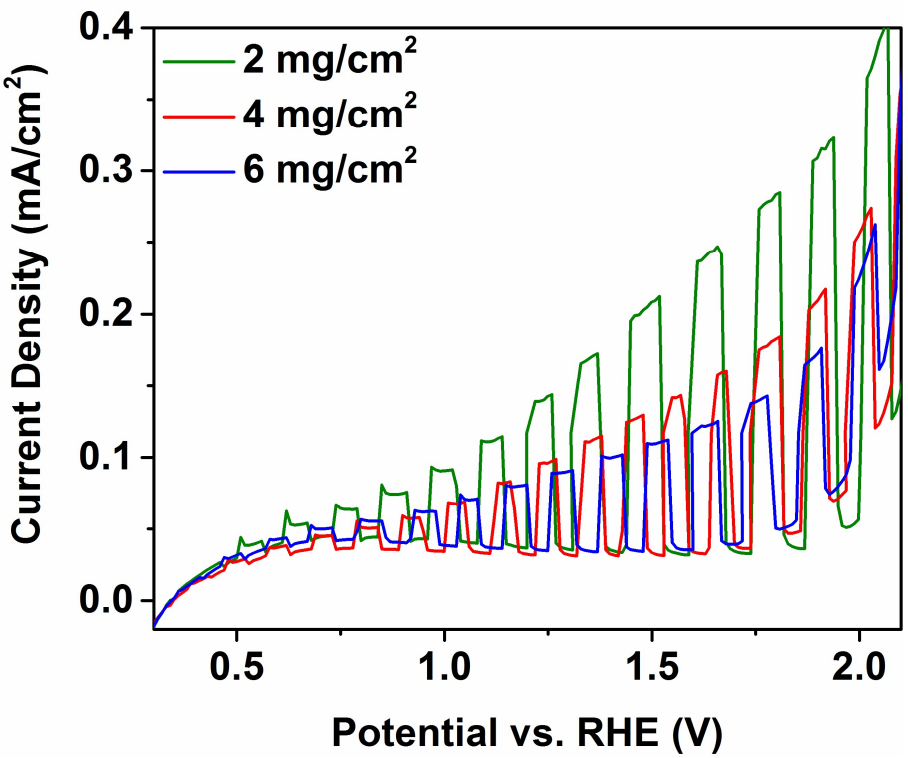

Figure S8. Photocurrent of samples with different amount of powder suspension dropped on the FTO substrates.

References

1. W. Liu, W. T. Zheng and Q. Jiang, Phys. Rev. B, First-principles study of the surface energy and work function of III-V semiconductor compounds. 2007, 75, 235322.
2. B. Engels, P. Richard, K. Schroeder, S. Blügel, P. Ebert and K. Urban, Phys. Rev. B, Comparison between ab initio theory and scanning tunneling microscopy for (110) surfaces of III-V semiconductors. 1998, 58, 7799-7815.