Journal of Materials Chemistry A

ARTICLE

Photocharged $BiVO_4$ Photoanodes for Improved Solar Water Splitting

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Electronic Supplementary Information

Experimental

Preparation of $BiVO_4$ thin film photoanodes

Thin films of 200 nm thick $BiVO_4$ were prepared by spray pyrolysis on FTO coated glass substrates (fluorine-doped tin dioxide, 15 Ω/□, TEC-15, Hartford Glass Co.). FTO substrates were rinsed with a Triton solution, sulphuric acid, acetone and ethanol, and subsequently cleaned using an UV ozone cleaner (Novascan). The precursor solution was made by dissolving 4 mM $Bi(NO_3)_3{\cdot}5H_2O$ (98%, Alfa Aesar) in acetic acid (98%, Sigma-Aldrich) and adding an equimolar amount of vanadium in the form of $VO(AcAc)_2$ (99%, Alfa Aesar) dissolved in absolute ethanol (Sigma-Aldrich). The substrate temperature during spraying was maintained at 450 °C, as measured by a thermocouple pressed to the top of the substrate surface. The spray deposition was carried out using an automated spray setup with Quickmist air atomizing spray nozzle driven by an overpressure of 0.06 MPa of nitrogen gas. The nozzle–substrate distance was kept constant at 20 cm. The precursor solution was placed 20 cm below the nozzle and fed to the nozzle via the siphoning effect induced by the nitrogen gas flow. Each spray cycle consisted of 5 s of spray time and 55 s of delay time to allow solvent evaporation, and a total of 200 cycles were used to deposit the films.

Prior to deposition of the $BiVO_4$, a SnO_2 interfacial layer (~80 nm) was deposited onto the FTO substrate to prevent recombination at the FTO/$BiVO_4$ interface. 0.1 M $SnCl_4$ (99%, Acros Organics) solution in ethyl acetate (99.5%, J.T. Baker) was used as the precursor solution. The SnO_2 layer was deposited at 425 °C using five spray cycles (5 s on, 55 s off) in a gravity-assisted siphoning mode, where the precursor solution was placed 30 cm above the nozzle. After deposition, the SnO_2/$BiVO_4$ samples were subjected to an additional 2 h heat treatment in a tube furnace at 450 °C in air. Spray deposition was performed on FTO substrates of 50 x 50 mm in size which were eventually cut into 20 x 10 mm samples.

Material characterization

AFM surface scans were performed using an NT-MDT Ntegra apparatus coupled with an NT-MDT P8 XPM controller, with an NT-MDT NSG30 cantilever mounted. Scans were taken over an area of 2x2 and 1x1 µm, with a 1 Hz frequency and a resolution of 512x512 points.

The morphology of thin films was investigated with SEM microscopy (JEOL JSM-6010LA instrument equipped with a tungsten hairpin filament). Samples were investigated in the secondary electron imaging mode (SEI), using an Everhart-Thornley type of detector. SEM images were collected using the accelerating voltage of 20 kV, at a working distance of 10 mm.

Structural analysis was performed with a Bruker D8 Advance X-ray diffractometer (Co-Kα, λ = 0.178897 nm) equipped with a LynxEye detector in a Bragg-Brentano configuration.

Results

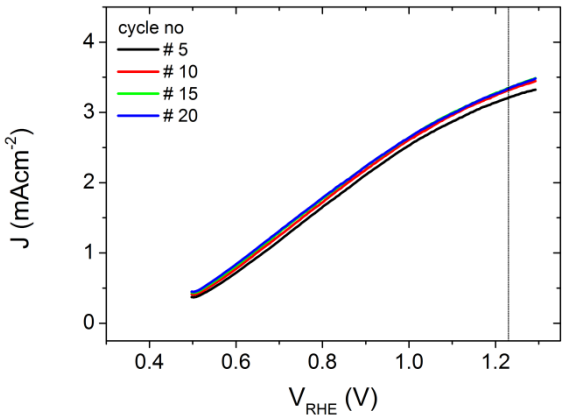

Fig. S1 The JV performance of the photocharged BiVO4 photoanodes for up to 20 cyclic voltammetric sweeps.

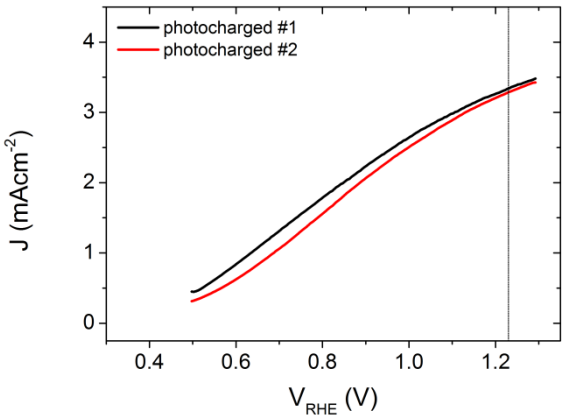

Fig. S2 The JV performance of a photocharged BiVO4 photoanode (black), which was subsequently left in the cell for 24 h to discharge under dark conditions and recharged back again (red).

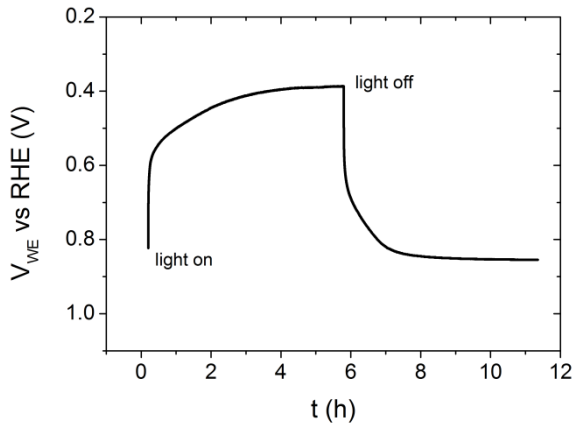

Fig. S3 Transients recorded for E_f equilibration in the OC configuration, $BiVO_4$ in 0.1 K-P_i

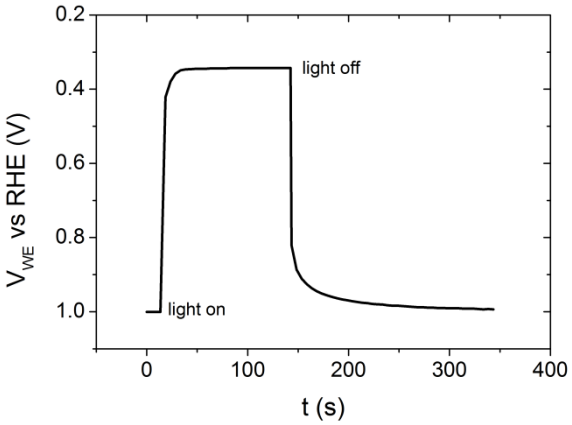

Fig. S4 Transients recorded for E_f equilibration in the OC configuration, $BiVO_4$ in presence of H_2O_2

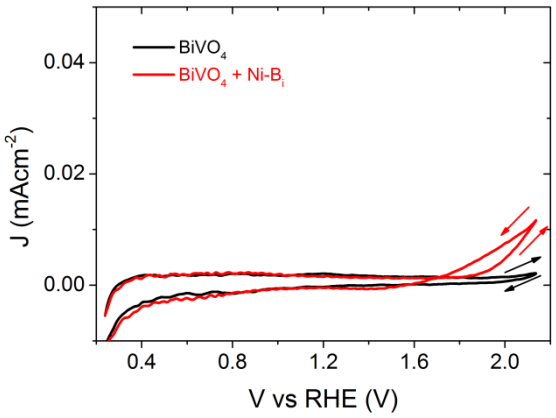

Fig. S5 J-V characteristics for $BiVO_4$ and $BiVO_4$ catalysed with Ni-B_i.

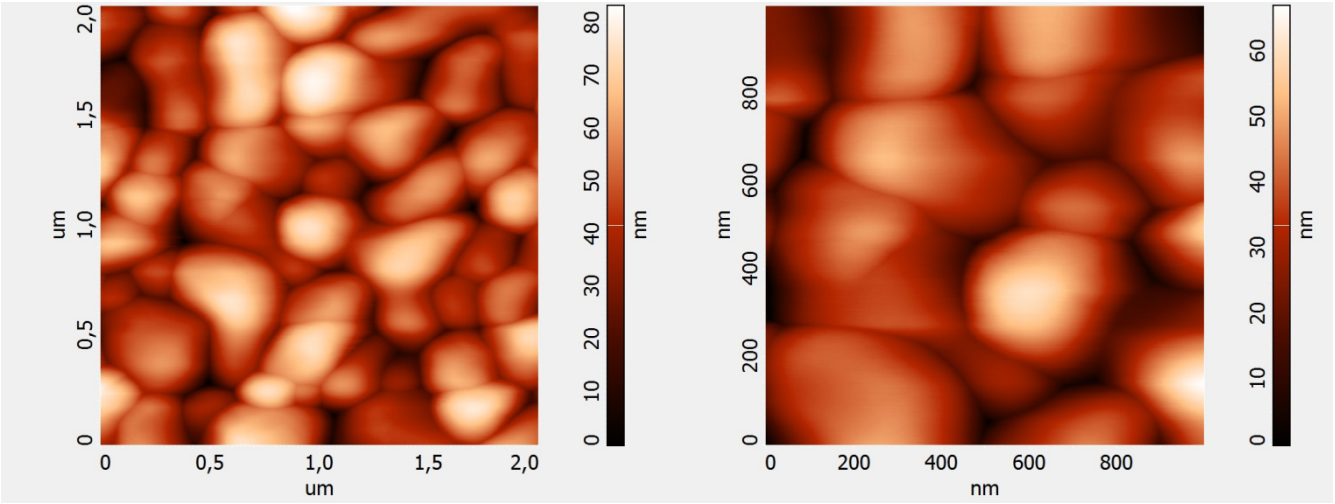

Fig. S6 AFM scans of untreated 200 nm $BiVO_4$ films: 2 x 2 µm and 1 x 1 µm.

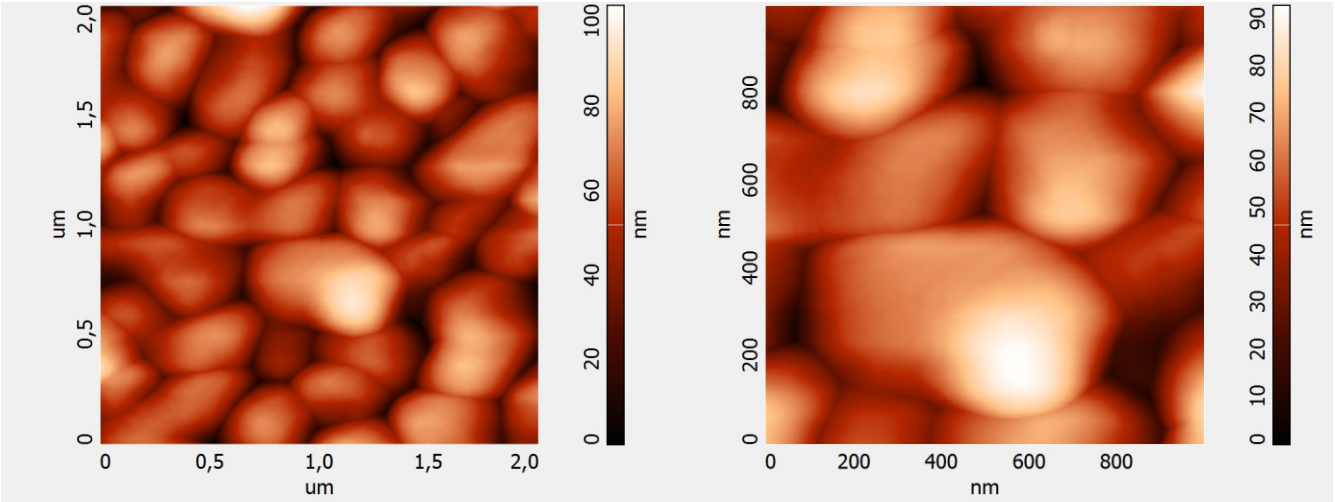

Fig. S7 AFM scans of photocharged 200 nm $BiVO_4$ films: 2 x 2 µm and 1 x 1 µm.

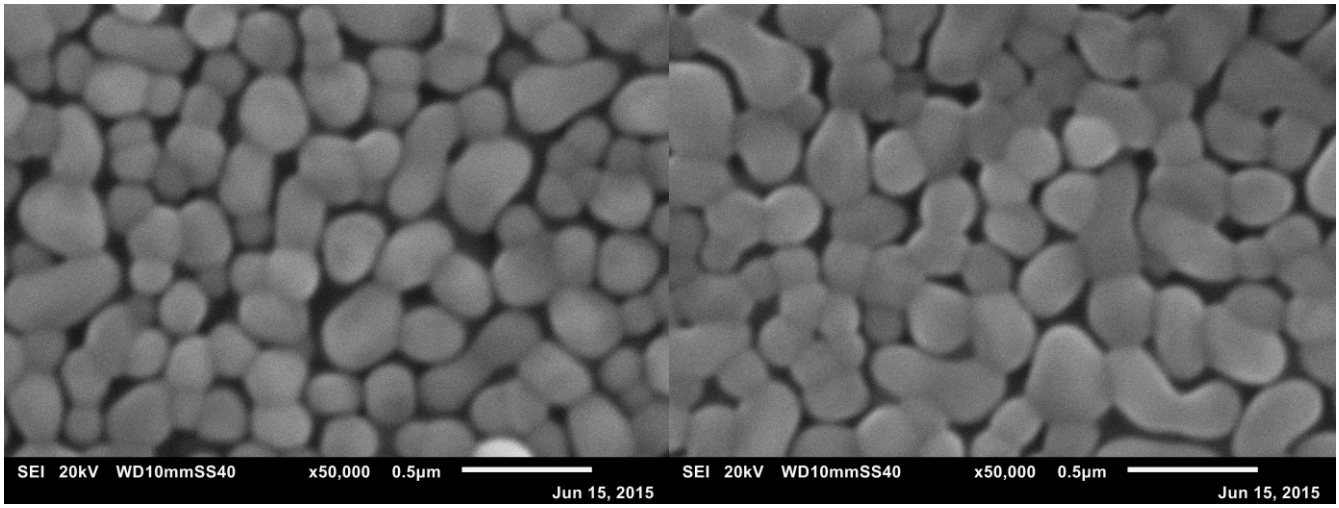

Fig. S8 SEM images of untreated 200 nm $BiVO_4$ films.

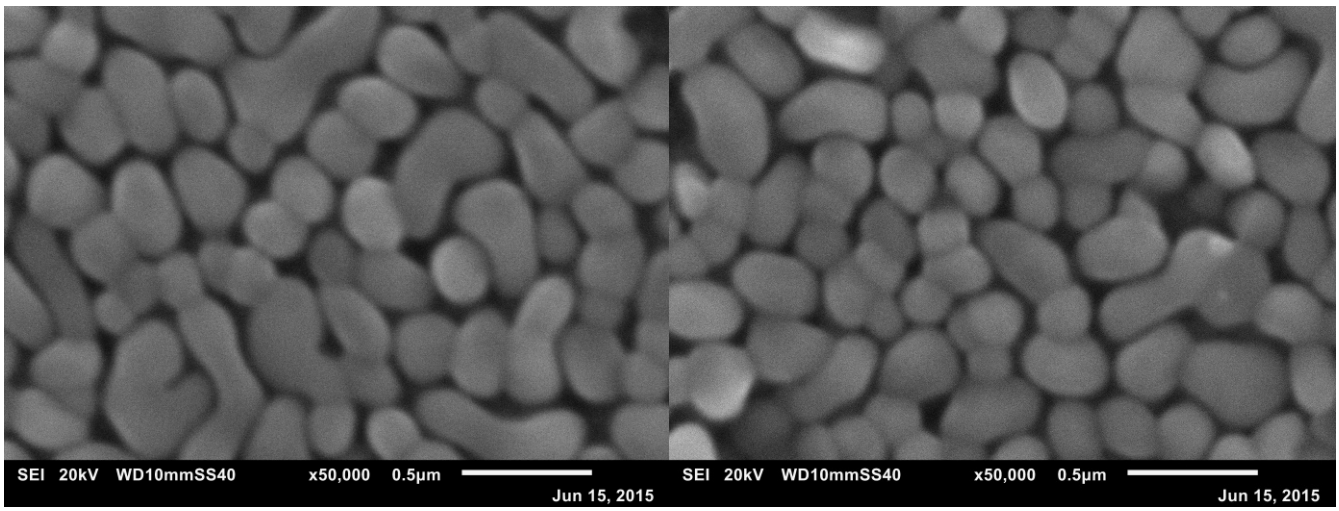

Fig. S9 SEM images of photocharged 200 nm $BiVO_4$ films

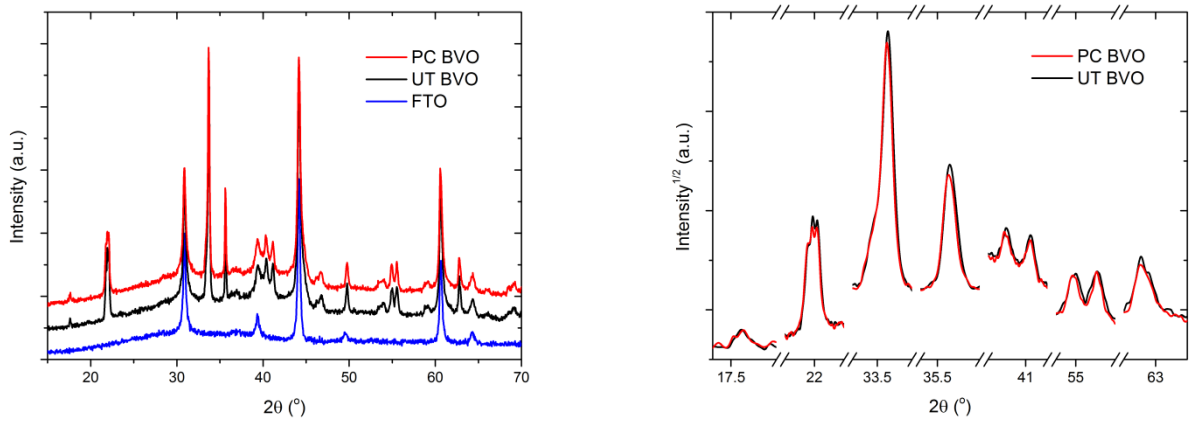

Fig. S10 XRD spectra of 200 nm $BiVO_4$ films before and after photocharging (a) full range (b) the most intense $BiVO_4$ peaks.

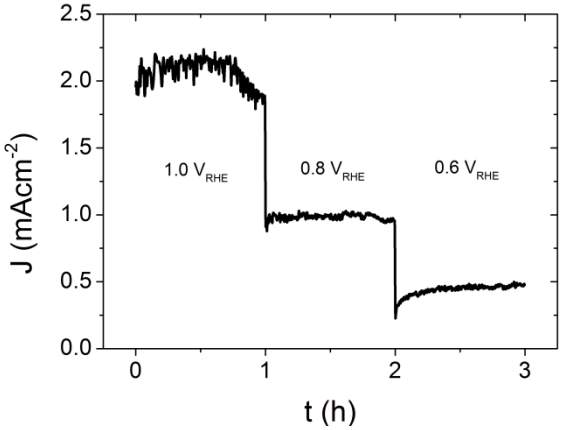

Fig. S11 Chronoamperometric measurements of photocharged $BiVO_4$ films held at 1.0, 0.8 and 0.6 V_{RHE} with a one hour duration per potential step.