Supporting information

Reduced Monoclinic $BiVO_4$ for Improved Photoelectrochemical Oxidation of Water under Visible Light

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1. Experimental

The morphology and size of nanocrystals in the as-prepared films were characterized by using a field-emission scanning electron microscope (Zeiss ULTRA Plus) operated at an accelerating voltage of 5 kV. X-ray diffraction patterns (XRD) were recorded on a PANalytical X'Pert PRO instrument using Cu Kα radiation (40 kV, λ = 1.5406 Å) between 20° to 70° at a scanning rate of 0.067°/s. UV-visible diffusion reflectance spectra were measured on a UV-2550 (Shimadzu) spectrometer by using $BaSO_4$ as the reference. The elemental composition was determined by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD). Photoelectrochemical measurements were made using a three-electrode configuration with the $BiVO_4$ film as the working photoelectrode, saturated calomel electrode (SCE) as the reference electrode, and platinum foil as the counter electrode in 0.1 M Na_2SO_4. Sunlight was simulated with a 300 W xenon lamp and an AM1.5G filter (HSX-F300, Beijing NBeT Technology Co., Ltd), coupled with a 420 nm UV filter. The light intensity was set using a calibrated crystalline silicon solar cell. Photocurrent response and electrochemical impedance spectroscopy (EIS) were recorded using a CHI-660D potentiostat, with the data fit to an equivalent circuit model using ZView software. The superimposed alternating current (AC) signal was maintained at 5 mV, while the frequency was scanned between 100 kHz and 0.05 Hz at potentials between 0 and 0.8 V versus SCE in the dark and under illumination by visible light in an electrolyte of 0.1 M Na_2SO_4, with Pt as the counter electrode. The capacitance was extracted from the EIS spectra by use of an equivalent circuit Rs(CPE-Rp), where Rs is the ohmic contribution, CPE is the constant phase element that takes into account non-idealities in the capacitance of the Helmholtz layer, and Rp is the charge-transfer resistance. The curve of photocurrent response as a function of wavelength were measured using light from a 300 W xenon lamp that was focused by a parabolic reflector and passed through a monochromator, at 0.8 V bias versus SCE. Samples were measured using a $BiVO_4$ film as the working photoelectrode and platinum foil as the counter electrode in 0.1 M Na_2SO_4.

2. Electrochemical impedance spectra

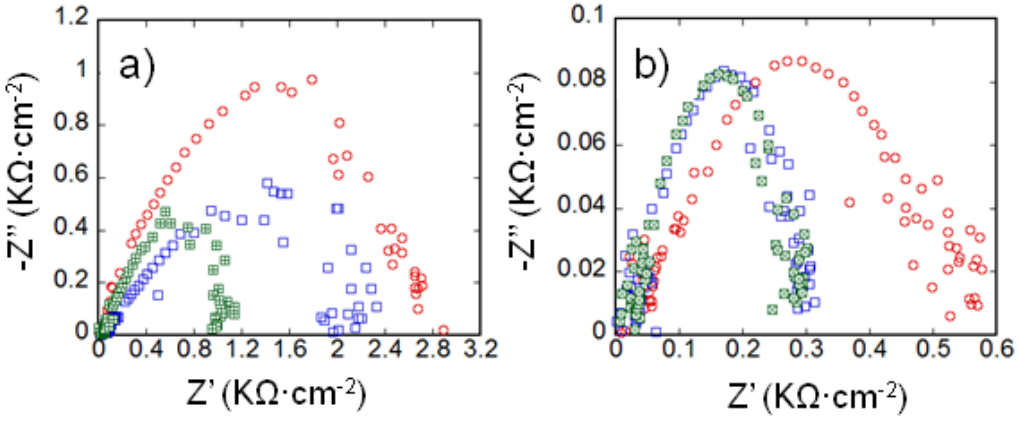

Fig. S1 Electrochemical impedance spectra of $BiVO_4$ film in 0.1 M Na_2SO_4, illuminated by visible light (λ＞420 nm). Red is the pristine $BiVO_4$, blue is the $BiVO_4$ film after electrochemical reduction at -1.0 V,

green is the $BiVO_4$ film after both electrochemical and $NaBH_4$ reduction. a) is illuminated from $BiVO_4$ side (front side), b) is illuminated from FTO side (back side).

3. XPS spectra

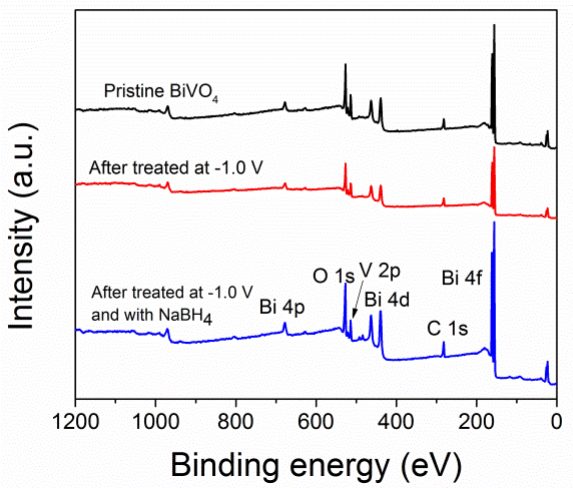

Fig. S2 XPS spectra of $BiVO_4$ film

4. Stability assay

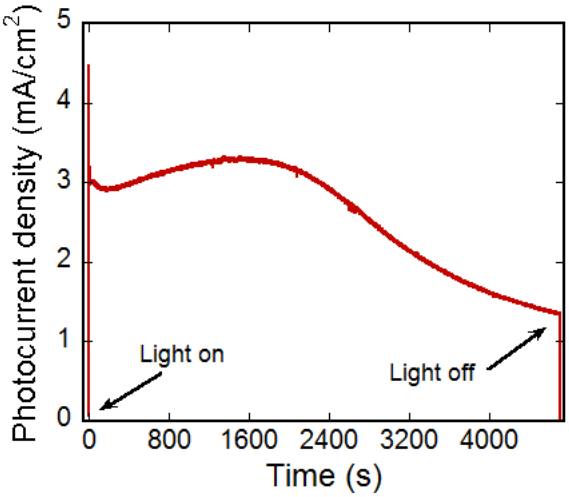

Fig. S3 *i-t* curve of the $BiVO_4$ after treated electrochemically at -1.0 V and followed with $NaBH_4$. Experiment was conducted at 1.0 V vs Ag/AgCl in 0.1 M Na_2SO_4 solution for 5000s.