

## Supporting Information

### Highly efficient photoelectrochemical hydrogen generation using $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}$ sensitized platelike $\text{WO}_3$ photoelectrodes

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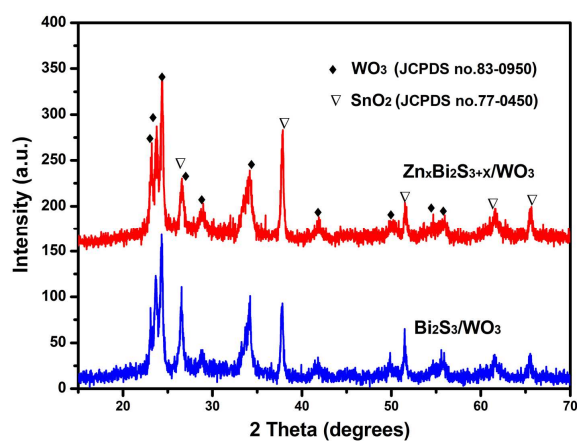
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### Supplementary methods

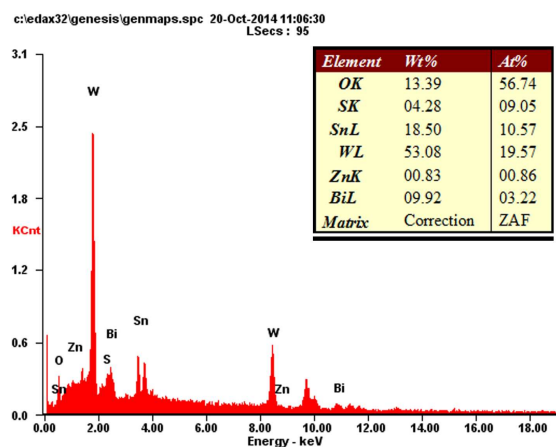
The crystalline phase of the electrodes was characterized by X-ray powder diffraction (XRD, D/Max2250, Rigaku Corporation, Japan). The local composition of  $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}/\text{WO}_3$  film was analyzed by an area scan of energy dispersive X-ray spectrometer (EDS) using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Raman spectra of the pure  $\text{Bi}_2\text{S}_3$  and  $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}$  films were recorded with a LabRAM HR800 Raman analyzer using an excitation laser source of 532 nm wavelength. The pure  $\text{Bi}_2\text{S}_3$  and  $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}$  films were prepared on

the FTO by a same SILAR method and the dipping procedure was repeated 30 times. Photocurrent-time plot of the photoelectrodes was obtained at -0.1 V vs. Ag/AgCl under continuous illumination. The Mott–Schottky plots of the photoelectrodes were measured by the electrochemical analyzer at the AC frequency of 1 kHz.

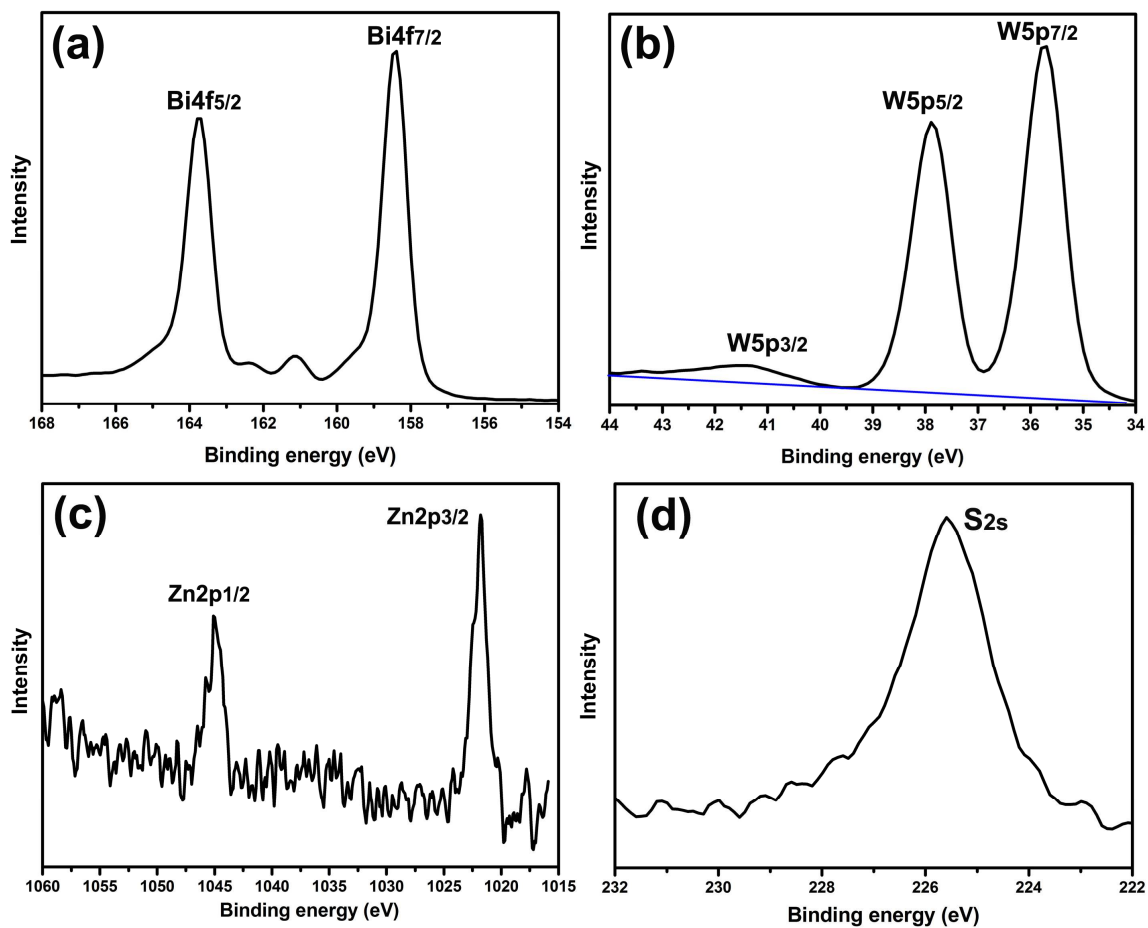
## Supplementary data



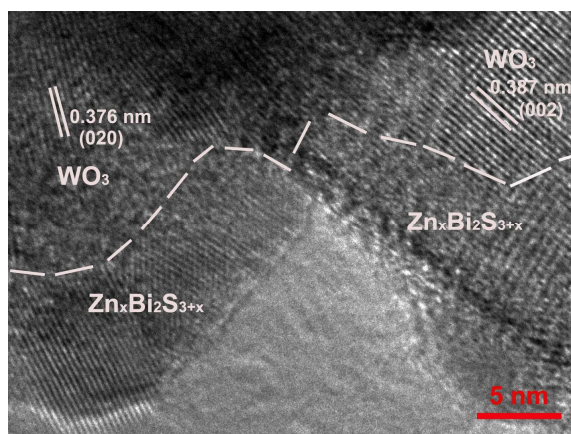
**Figure S1.** XRD patterns of  $\text{Bi}_2\text{S}_3/\text{WO}_3$  film and  $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}/\text{WO}_3$  film



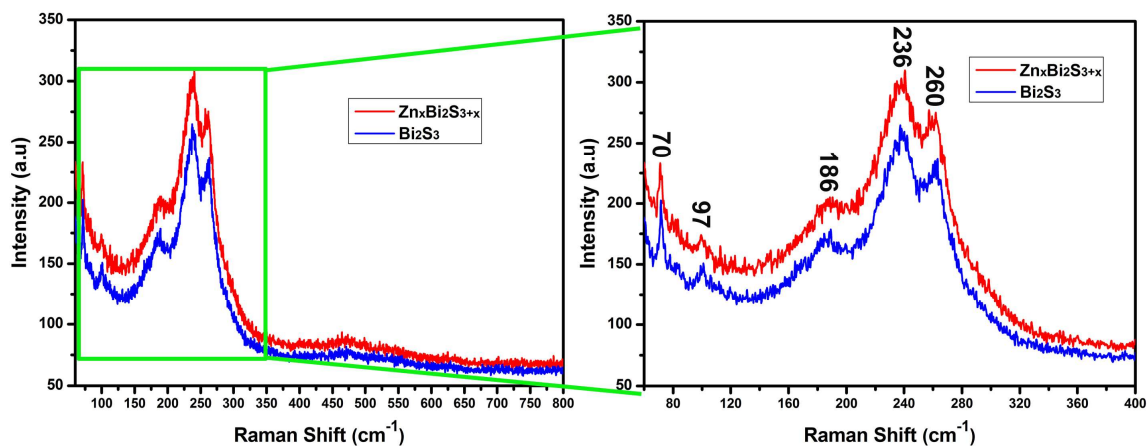
**Figure S2.** EDS spectra of  $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}/\text{WO}_3$  film.



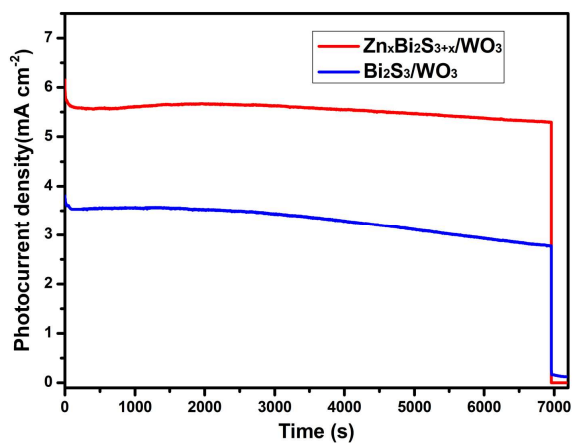
**Figure S3** XPS spectra for Bi (a), W (b), Zn (c), S (d) of the  $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}/\text{WO}_3$  film



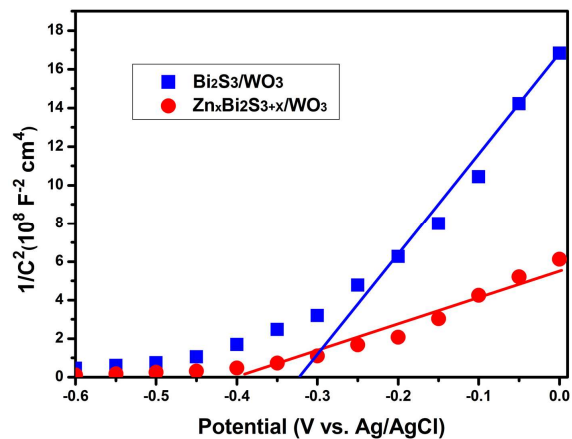
**Figure S4.** HRTEM images of  $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}/\text{WO}_3$  plate



**Figure S5.** Raman spectrum of pure  $\text{Bi}_2\text{S}_3$  and  $\text{Zn}_x\text{Bi}_2\text{S}_{3+x}$  film on the FTO substrates



**Figure S6.** Photocurrent-time plot of the photoelectrodes at -0.1 V vs Ag/AgCl.



**Figure S7.** Mott-Schottky plots of the photoelectrodes