

Highly efficient photoelectrochemical water splitting using a thin film photoanode of BiVO₄/SnO₂/WO₃ multi composite in carbonate electrolyte

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Supporting information

Experimental

Electrode preparation

BiVO₄/SnO₂/WO₃ photoelectrodes were prepared as follows. Precursor solutions of each oxide semiconductor were coated on F-doped SnO₂ conductive glass substrate (FTO, 10 Ωsq⁻¹, Nippon Sheet Glass Co.) using a spin-coater (1000 rpm, 15 s) and then calcinated at 500°C for 30 min for each coating. A WO₃ under layer was coated on the FTO substrate, followed by subsequent multi coatings for the SnO₂ middle layer and the BiVO₄ layer. The film thickness was controlled by the number of coatings applied and solution concentration. The precursor solution of SnO₂ and BiVO₄ were Sn⁴⁺, Bi³⁺ and V⁵⁺ in organic solvent (Symetrix Co., USA), respectively. The standard concentration of WO₃, SnO₂ and BiVO₄ precursor solutions were 1.4 M peroxy-tungstic acid, as reported in a previous paper;¹ 5 mM Sn⁴⁺ diluted with xylene; and a mixed solution in a 1:1 volume ratio of 0.2 M Bi³⁺ and 0.2 M V⁵⁺ diluted with butyl acetate, respectively.

Results

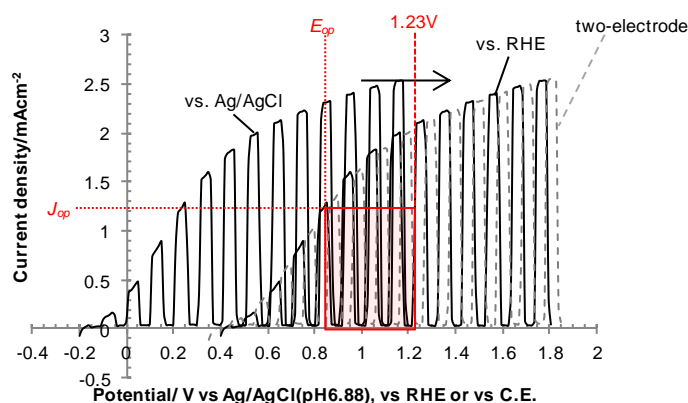


Fig. S1 Typical I-V curves of a BiVO₄/WO₃ photoanode with Pt counter electrode in a 0.1 M KHCO₃ aqueous solution with CO₂ bubbling (pH 6.88) at a light intensity 100mWcm⁻² (A.M. 1.5, 1 SUN). Scan rate; 50 mVs⁻¹. --- two electrodes system (V vs. C. E.), — three electrodes system. In three electrodes system, reference electrode was Ag/AgCl. Red rectangular area should be maximized.

For conversion the obtained potential (vs. Ag/AgCl) to RHE (NHE at pH = 0), the equation (1) was used.

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E_{\text{Ag/AgCl}}^0 \quad (E_{\text{Ag/AgCl}}^0 = +0.199\text{V}) \quad (1).$$

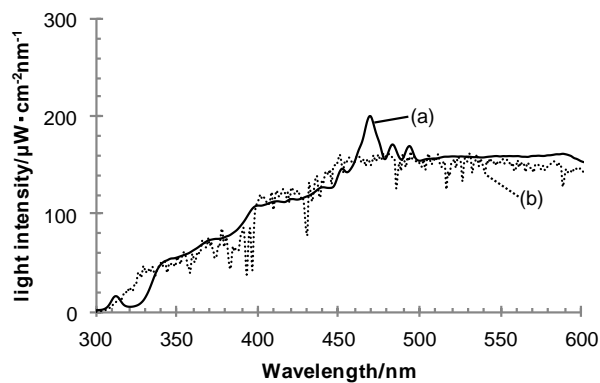


Fig. S2 Light intensity spectra of (a) solar simulator and (b) AM-1.5 1 SUN.

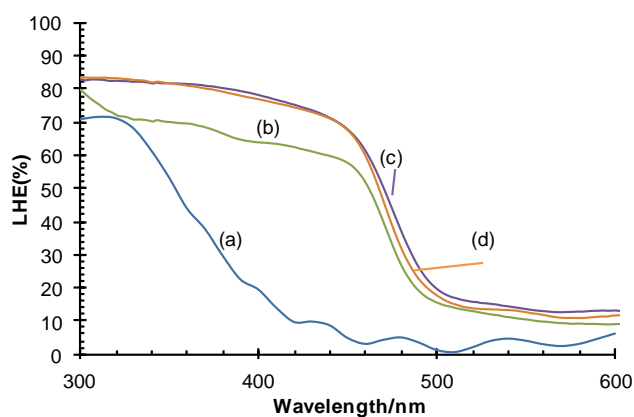


Fig.S3 LHE (=1-T-R) spectra of (a) bare WO_3 , (b) bare BiVO_4 , (c) $\text{BiVO}_4/\text{WO}_3$ and (d) $\text{BiVO}_4/\text{SnO}_2/\text{WO}_3$.

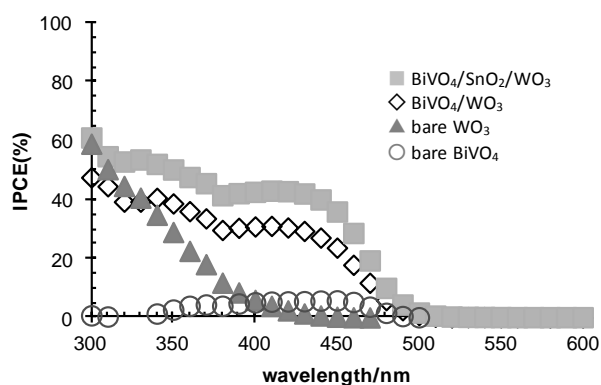


Fig.S4 IPCE spectra of multi composite film, bare BiVO_4 and bare WO_3 photoelectrodes. The IPCE was measured at 1.2 V vs. RHE in a 0.1M KHCO_3 with CO_2 bubbling. The light was irradiated from semiconductor film side.

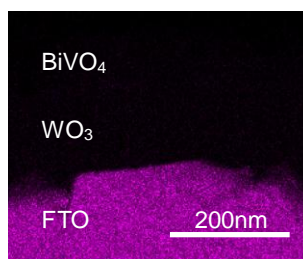


Fig.S5 Sn image (purple color) of TEM-EDX data for the cross-section of a BiVO₄/SnO₂/WO₃ photoelectrode.

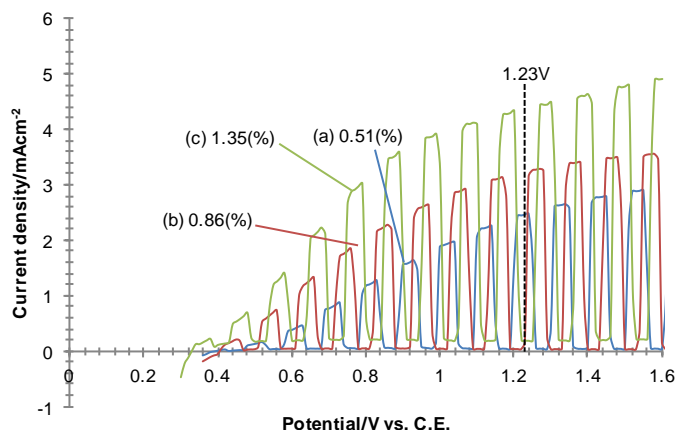


Fig.S6 I-V curves of multi composite thin film photoanodes to evaluate the $\eta_{\text{sun}}^{\text{ex2}}$ in a KHCO₃ aqueous solution with CO₂ bubbling. Light source: solar simulator (AM-1.5, 1 SUN). C.E.: Pt coil. Scan rate: 50 mVs⁻¹. (a) BiVO₄/SnO₂/WO₃ in 0.1 M electrolyte, (b) BiVO₄/SnO₂/WO₃ in 2.5 M electrolyte and (c) double-stacked of BiVO₄/SnO₂/WO₃ in 2.5 M electrolyte.

Table.S1 Photoelectrochemical properties of multi composite thin film photoelectrodes in two-electrode system.^g

Run	Photoelectrode	Electrolyte	J^e / mAcm ⁻²	J_{op}^f / mAcm ⁻²	1.23- E_{op} / V vs. RHE	$\eta_{\text{sun}}^{\text{ex2}}$ /%
1	BiVO ₄ /WO ₃ ^a		1.90	1.30	0.340	0.44
2	BiVO ₄ /SnO ₂ /WO ₃ ^a	0.1 M KHCO ₃ ^c	2.45	1.53	0.330	0.51
3	BiVO ₄ /SnO ₂ /WO ₃ ^b		3.41	1.83	0.380	0.70
4	BiVO ₄ /WO ₃ ^a		2.82	2.02	0.420	0.85
5	BiVO ₄ /SnO ₂ /WO ₃ ^a	2.5 M KHCO ₃ ^d	3.03	1.83	0.468	0.86
6	BiVO ₄ /SnO ₂ /WO ₃ ^b		4.38	2.87	0.469	1.35

^a Single-stacked. ^b Double-stacked. ^c pH 6.88 with CO₂ bubbling. ^d pH 8.11 with CO₂ bubbling. Corrected photocurrent value ($J \times \text{mismatch factor}$) ^e at 1.23 V vs. RHE and ^f at E_{op} V vs. RHE. ^g A white plate was put behind FTO glass to optical confinement.

References

1. K. Sayama, H. Hayashi, T. Arai, M. Yanagida, T. Gunji and H. Sugihara, *Appl. Catal. B: Environ.*, 2010, **94**, 150.