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 peroxo-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.

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \, \text{pH} + E_{\text{Ag/AgCl}}^{0} (E_{\text{Ag/AgCl}}^{0} = +0.199 \, \text{V}) \]  

(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 WO₃, (b) bare BiVO₄, (c) BiVO₄/WO₃ and (d) BiVO₄/SnO₂/WO₃.

**Fig. S4** IPCE spectra of multi composite film, bare BiVO₄ and bare WO₃ photoelectrodes. The IPCE was measured at 1.2 V vs. RHE in a 0.1M KHCO₃ with CO₂ bubbling. The light was irradiated from semiconductor film side.
### Table S1: Photoelectrochemical properties of multi composite thin film photoelectrodes in two-electrode system.

<table>
<thead>
<tr>
<th>Run</th>
<th>Photoelectrode</th>
<th>Electrolyte</th>
<th>$J^*/$ mA cm$^{-2}$</th>
<th>$J_{op}^*/$ mA cm$^{-2}$</th>
<th>1.23-$E_{op}$/ V vs. RHE</th>
<th>$\eta_{sun}^{ex2}$/%</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>BiVO$_4$/WO$_3$ $^a$</td>
<td></td>
<td>1.90</td>
<td>1.30</td>
<td>0.340</td>
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<td>BiVO$_4$/SnO$_2$/WO$_3$ $^a$</td>
<td>0.1 M KHCO$_3$ $^c$</td>
<td>2.45</td>
<td>1.53</td>
<td>0.330</td>
<td>0.51</td>
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<td>BiVO$_4$/SnO$_2$/WO$_3$ $^b$</td>
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<td>3.41</td>
<td>1.83</td>
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<td>0.70</td>
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<tr>
<td>4</td>
<td>BiVO$_4$/WO$_3$ $^a$</td>
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<td>2.82</td>
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<td>0.420</td>
<td>0.85</td>
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<td>5</td>
<td>BiVO$_4$/SnO$_2$/WO$_3$ $^a$</td>
<td>2.5 M KHCO$_3$ $^d$</td>
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<td>1.83</td>
<td>0.468</td>
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<tr>
<td>6</td>
<td>BiVO$_4$/SnO$_2$/WO$_3$ $^b$</td>
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<td>4.38</td>
<td>2.87</td>
<td>0.469</td>
<td>1.35</td>
</tr>
</tbody>
</table>

$^a$ Single-stacked, $^b$ Double-stacked, $^c$ pH 6.88 with CO$_2$ bubbling, $^d$ pH 8.11 with CO$_2$ bubbling. Corrected photocurrent value ($J \times$ 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