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Supporting Information

Template-engineered epitaxial BiVO₄ photoanodes for efficient solar water splitting

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Supporting figures



Figure S1. Out-of-plane θ - 2θ XRD patterns for (a) bare BiVO₄ with various thicknesses, (b) bare γ -WO₃ with various thicknesses, (c) epitaxial BiVO₄ on the γ -WO₃ template layer of various thicknesses grown on the SRO-buffered STO (001) substrate.

Supporting figures



Figure S2. AFM surface morphology image of (a) STO (001) substrate, (b) 50-nm-thick SRO on STO (001) substrate.

Supporting figures



Figure S3. Top-view SEM images of epitaxial $BiVO_4$ on the (a) 30-nm, (b) 100-nm, (c) 200-nm-thick γ -WO₃ template layer grown on the SRO-buffered STO (001) substrate.



Figure S4. Linear sweep voltammetry curves (LSVs) of (a) bare BiVO₄ with various thicknesses, (b) bare γ -WO₃ with various thicknesses under the illumination of a solar simulator (AM 1.5G, 100 mW cm⁻²) in 0.5 M Na₂SO₄ with 0.5 M Na₂SO₃ aqueous solution. Insets show the plot of photocurrent density at 1.23 V *vs.* RHE of bare BiVO₄ and bare γ -WO₃ with various thicknesses.



Figure S5. O_2 evolution (left *y*-axis) and faradaic efficiency (right *y*-axis) of 100-nm-thick BiVO₄ on the 30-nm-thick γ -WO₃ template on the SRO-buffered STO (001) substrate measured at 1.23 V *vs.* RHE in 0.1 M Na₂SO₄ electrolyte under simulated AM 1.5G illumination.

Table S1. Photocurrent densities of polycrystalline BiVO₄-based heterojunction photoelectrodes for PEC water splitting reported recently. (PADD: polymer-assisted direct deposition, GLAD: glancing angle deposition, ED: electrodeposition)

Year	Photoelectrode	Electrolyte	Performance	Method	Ref.
2015	Co-Ci/BiVO ₄ /WO ₃	0.1 M KHCO3	~3.50 mA cm ⁻² at 1.23 V <i>vs.</i> RHE	PADD	S1
2016	BiVO ₄ /WO ₃ /SnO ₂	0.5 M Na ₂ SO ₄ in a 0.1 M NaPi with 0.2 M H ₂ O ₂ as hole scavenger	~2.50 mA cm ⁻² at 1.23 V <i>vs.</i> RHE	PLD	S2
2016	Sb:SnO ₂ /BiVO ₄ core/shell	Phosphate buffer with 1 M Na ₂ SO ₃	~7.97 mA cm ⁻² at 1.23 V vs. RHE	hydrothermal reaction + drop- casting	\$3
2016	BiVO ₄ /WO ₃	0.5 M KPi + 1 M Na ₂ SO ₃	~4.55 mA cm ⁻² at 1.23 V <i>vs.</i> RHE	GLAD + Pulsed ED	S4

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