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Supplementary Information

Facile 2D In₂Se₃ protection for enhanced BiVO₄ stability in highly alkaline photoelectrochemical water splitting

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Fig. S1: The photographic image of exfoliated In₂Se₃ nanosheets dispersed in N-Methyl-2pyrrolidone (NMP).



Fig. S2: (a) The powder XRD pattern of bulk (flake) In_2Se_3 and exfoliated (Exfo.) In_2Se_3 , (b) the demonstration of the full width at half maxima (FWHM) at the major In_2Se_3 (JCPDS#: 34-1279) peak at ~ 18.5 °. The significant diminishing of the most intense peak and peak broadening ascribes the exfoliation of In_2Se_3 .^[1,2]



Fig. S3: The TEM micrograph of exfoliated In_2Se_3 .



Fig. S4: The XRD pattern of $BiVO_4$ and $BiVO_4/In_2Se_3$. A peak due to In_2Se_3 appeared on the monoclinic $BiVO_4$ (83-1699), which is attributed to the presence of In_2Se_3 .



Fig. S5: The high-resolution XPS binding energy position comparison between $BiVO_4$ and $BiVO_4/In_2Se_3$ (a) Bi 4f, (b) V 2p, and (c) O 1s peaks.



Fig. S6: The XPS curve fitting of (a) In 3d and (b) Se 3d of BiVO₄/In₂Se₃.



Fig. S7: The electrocatalytic water oxidation behavior of $BiVO_4$ and $BiVO_4/In_2Se_3$ in potassium borate (pH 9). The absence of performance in electrocatalytic water oxidation shows that In_2Se_3 has no oxygen evolution reaction (OER) catalysis feature. Moreover, effective charge transfer is viable with light illumination.



Fig. S8: (a) The UV-vis absorption spectrum of In_2Se_3 , (b) the photocurrent comparison of BiVO₄ and BiVO₄/In₂Se₃ under 455 nm, and 520 nm light illumination during sulfite oxidation in potassium borate electrolyte (pH 9). Even though In_2Se_3 absorbs light in the longer wavelength region, it has no significant contribution to the photocurrent generation at longer wavelengths. This can be explained by the negligible difference in photocurrent under 520 nm, where BiVO₄ has a very small IPCE.



Fig. S9: The transient current-time curve of $BiVO_4$ and $BiVO_4/In_2Se_3$ at 0.4 V vs RHE for water oxidation, and (b) fast-transient response of $BiVO_4$ and $BiVO_4/In_2Se_3$ at a set-up potential ranging from 0 V – 1.23 V vs RHE during sulfite oxidation. All experiments were done in a potassium borate buffer (pH 9) under 455 nm blue light illumination.



Fig. S10: The Mott-Schottky (MS) plot of $BiVO_4$ and $BiVO_4/In_2Se_3$ recorded in the dark at 500 Hz frequency and 10 mV amplitude in 1 M potassium borate buffer (pH 9). The slope of the MS plot of $BiVO_4$ and $BiVO_4/In_2Se_3$ is almost similar, indicating that the coating of In_2Se_3 could not change the carrier density of $BiVO_4$.



Fig. S11. The IPCE and estimated integrated photocurrent density (I_{int} .) comparison between $BiVO_4$ and $BiVO_4/In_2Se_3$ in 1 M potassium borate (pH 9) under the illumination of various monochromatic LED lights at 1.23 V vs RHE.



Fig. S12: (a) the photocurrent and (b) stability comparison of $BiVO_4$ and $BiVO_4/In_2Se_3$ for water oxidation in phosphate buffer (pH 12.3) under the illumination of 455 nm blue light.



Fig. S13: Cyclic voltammogram of BiVO₄ and BiVO₄/In₂Se₃ recorded with 2000 mV/s in the dark after 2V vs Ag/AgCl oxidation for 3 min illumination (455 nm) in potassium borate (pH 9) buffer. The first cathodic scan (right to left) equivalent to the electrons in the conduction band recombined with holes becomes more intense for BiVO₄ than BiVO₄/In₂Se₃. The irreversible reduction peak at 1.25 V vs RHE is due to VO₂⁺ to VO²⁺ for BiVO₄, which is more intense than BiVO₄/In₂Se₃. This implies that most of the generated electron undergoes a reduction of vanadium species.^[3,4] Moreover, widening the reversible redox peak (V⁴⁺/V⁵⁺)

around 0.6 V vs. RHE shows that $BiVO_4$ is more likely exposed to oxidation than $BiVO_4/In_2Se_3$. The voltammogram also suggests that In_2Se_3 significantly suppresses the oxidation of $BiVO_4$. As shown, the $BiVO_4$ oxidation was observed at 1.3 V vs RHE before the real water oxidation potential. In the case of $BiVO_4/In_2Se_3$, it starts near 1.8 V vs RHE, which is reasonable the on-set for the oxidation of H_2O .



Fig. S14: The photocurrent comparison of $BiVO_4/In_2Se_3$ at different mole ratios (%) of Ni:Ce in a 1 M potassium borate buffer (pH 9) under 455 nm blue light illumination.



Fig. S15: Characterizations of $BiVO_4/In_2Se_3/NiCeO_x$. (a) The HRTEM image and (b-j) the TEM/EDS elemental mapping, and (k) the EDS spectrum of $BiVO_4/In_2Se_3/NiCeO_x$.



Fig. S16: Chracterization of $BiVO_4/In_2Se_3/NiCeO_x$. (a) SEM image and (b-h) the SEM/EDS elemental mapping and (i) the EDS spectrum of $BiVO_4/In_2Se_3/NiCeO_x$ electrode.



Fig. S17: (a-c) The representative SEM image of $BiVO_4/In_2Se_3/NiCeOx$, (d) the stability comparison at 1.23 V vs. RHE under chopping light illumination, and (e-g) the reproducible test for photocurrent comparison between $BiVO_4/NiCeOx$ and $BiVO_4/In_2Se_3/NiCeOx$. All experiments were done in a potassium borate buffer (pH 9) under 455 nm blue light illumination.



Fig. S18: The EIS plot of $BiVO_4$, and $BiVO_4/In_2Se_3/NiCeO_x$ recorded at 0.6 V vs RHE in potassium borate buffer (pH 9) under 455 nm light illumination.



Fig. S19: The open circuit potential-time curve of (a) $BiVO_4$ and (b) $BiVO_4/In_2Se_3$ in dark conditions, and (c – d) the photocurrent of $BiVO_4$ and $BiVO_4/In_2Se_3$ in 0.2 M sulfite oxidation before and after open circuit test in the dark. Potassium phosphate buffer was used at pH 6.8 (KH₂PO₄/K₂HPO₄) and pH 12.3 (K₂HPO₄/K₃PO₄).



Fig. S20: (a) The potential-pH diagram of BiVO₄ derived from the material project.^[5] The diagram was generated using a balanced stoichiometric mix of 50% Bi and 50% V, with each ion (Bi and V) precisely set at 1 x 10⁻⁵ mol/kg concentration. The BiVO₄ stranded between the upper dashed line Oxygen Evolution Reaction (OER) and a lower dashed line Hydrogen Evolution Reaction (HER). BiVO₄ seems stable in a long-range pH (2 -12), but less stable in the region near the OER and HER lines. The BiVO₄ and derived species are grouped into three main regions (ions, solids, and mixed). (b) The potential-pH diagram of In₂Se₃ with 40% In and 60% Se according to the stochiometric ratio. In and Se concentrations are set to 1 x 10⁻⁵ mol/kg.



Fig. S21: the open circuit voltage-time curve of (a) $BiVO_4$ and (b) $BiVO_4/In_2Se_3$ with 455 nm light illumination, (c – f) the photocurrent in 0.2 M sulfite oxidation before and after open circuit voltage test in pH 6.8 and pH 12.3 phosphate ion buffer.



Fig. S22. The phase diagram of the predicted reduced In_2Se_3 (In_4Se_3) and oxidized In_2Se_3 ($InSe_2$) in an aqueous environment. The diagram is adapted from the material project website.^[5]



Fig. S23: The current–time of (a) $BiVO_4$ and (b) $BiVO_4/In_2Se_3$ at 1.23 V vs RHE, and (c -f) the photocurrent in 0.2 M sulfite oxidation before and after current – time test in pH 6.8 and pH 12.3 phosphate buffer.



Fig. S22: XRD comparison of BiVO4 and BiVO₄/In₂Se₃ before and after i-t test. (a) BiVO₄ and (b) BiVO₄/In₂Se₃ XRD analysis before and after i-t test at 0.6 V vs RHE in sulfite (0.4 M) oxidation at pH 12.3. under 455 nm (39 mW/cm²) blue light illumination. The XRD patterns reveal that bare BiVO₄ exhibits a slight decrease in the intensity of selected planes ((101), (011), (103), and (112)) after the stability test, indicating partial dissolution. In contrast, BiVO₄/In₂Se₃ shows no change in intensity for the same planes, demonstrating that In₂Se₃ effectively protects BiVO₄ from dissolution.

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Table S1: The predicted fitting results of Nyquist plots

Electrode	R1 (Ω)	R2 (Ω)	R3 (Ω)	C1 (μ F cm ⁻²)	C2 (μ F cm ⁻²)
BiVO ₄	34.06	155.7	481.4	13.6	77.3
BiVO ₄ /In ₂ Se ₃	33.66	137.3	437.6	15.7	93.2

Table S2: Comparison of performance and stability of $BiVO_4/In_2Se_3$ with related representative works of literature.

Photoanodes	Electrolyte	Photocurrent	IPCE	Stability (h)	Ref.
	environment	(mA/cm ²)	(%)		
BiVO ₄ /BP	pH 7.1 , 0.5 M	2.2	-	BiVO ₄ /BP/NiOOH =	[6]
	KiP, AM			60	
	1.5 G,				
	100 mW cm^{-2}				
BiVO ₄ /Bi	pH 9 , 1 M	3	-	$BiVO_4/Bi/NiOOH = 2$	[7]
	KB, AM 1.5				
	G				
BiVO ₄ /Ti ₃ C ₂	pH 9 , 1 M	2.72	38	BiVO ₄ /Ti ₃ C ₂ /Co ₃ O ₄	[8]
	KB, AM			=50	
	1.5 G,				
	$100 \mathrm{mW} \mathrm{cm}^{-2}$				
BiVO ₄ /TiO ₂	pH 12 , 1 M	3.5	-	40 h	[9]

	sulfite, AM				
	1.5 G,				
	$100 \mathrm{mW} \mathrm{cm}^{-2}$				
BiVO ₄ /Co ₃ O ₄	рН 9.5, 1 М	BiVO ₄ /Co ₃ O ₄	60	BiVO ₄ /Co ₃ O ₄ /NiOOH	[10]
	borate, 1.5 G,	= 4.5		= 90	
	100 mW cm ⁻²				
BiVO ₄ /ZnFe ₂ O ₄	pH 13, 0.1 M	3.2	40	BiVO ₄ /ZnFe ₂ O ₄ in	[11]
	КОН, АМ			Co^{2+} solution = 1	
	1.5 G, 100				
	mW cm ⁻²				
BiVO ₄ /In ₂ Se ₃	рН 12.3,	12.38 (in	40	BiVO ₄ /In ₂ Se ₃ in	In this
	phosphate in	sulfite)		sulfite = 40 h	work
	sulfite, 455				
	nm light, 39				
	mW/cm ²				
	pH 13	11.5 (in	24	BiVO ₄ /In ₂ Se ₃ in	In this
		sulfite)		sulfite = 40 h	work
BiVO ₄ /In ₂ Se ₃ /NiCeO _x	pH 9, 1 M	> 10 (for		~ 100 h	In this
	KB, 455 nm,	water			work
	39 mW/cm^2	9 mW/cm ² oxidation)			

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