Supplementary Information

Photothermal Effect-Enhanced Photoelectrochemical Water Splitting of $BiVO_4$ Photoanode Modified with Dual-Functional Polyaniline

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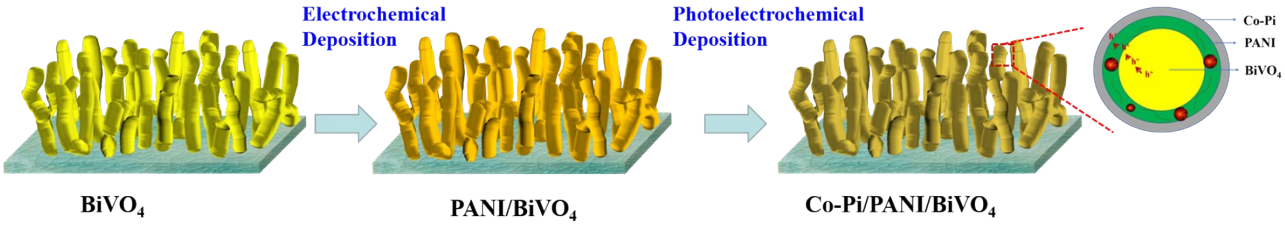
I. Preparation scheme of CPB photoanode.



Scheme S1 Schematic illustration of the fabrication of Co-Pi/PANI/$BiVO_4$ (CPB) composite photoanodes.

II. Analysis of photothermal effect of PANI

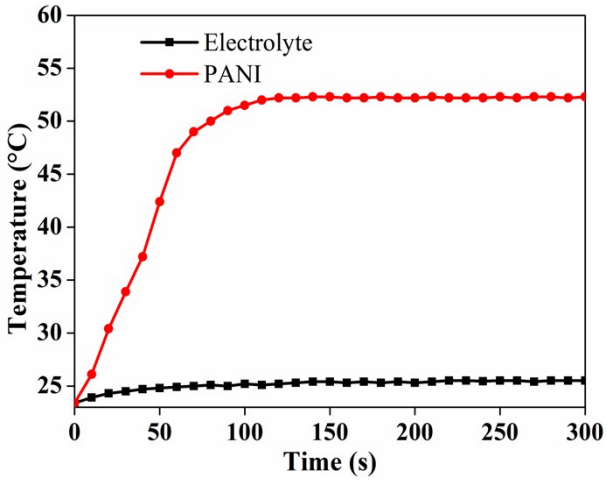


Fig. S1 Temperature-time plots of PANI and electrolyte solution.

III. Analysis of the effect of PANI loading amount

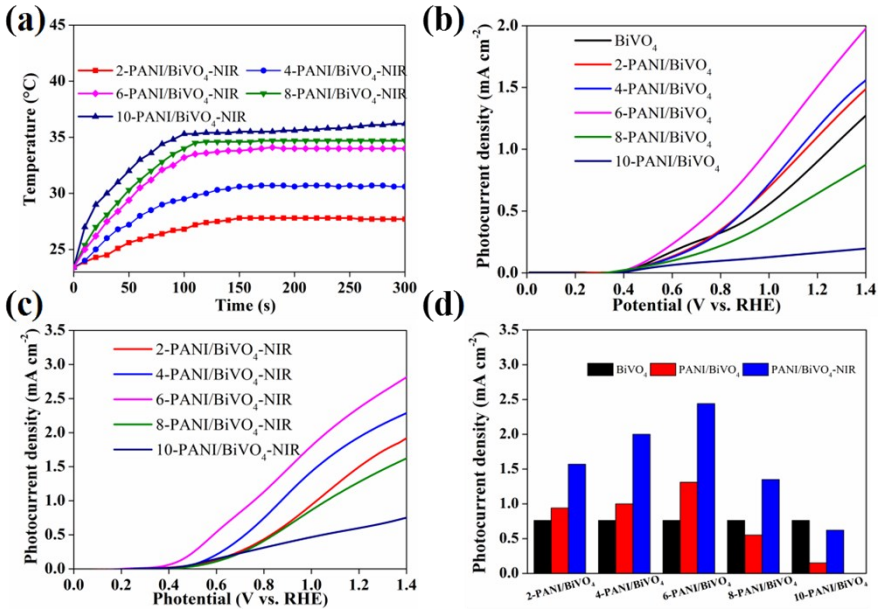


Fig. S2 (a) Temperature-time plots under different concentrations of PANI/$BiVO_4$ photoanode with NIR. (b) LSV curves of PANI loaded with different concentrations. (c) LSV curves of NIR irradiated by PANI with different concentration. (d) Histogram of PANI loaded with different concentrations under AM 1.5G illumination with or without NIR laser.

IV. XPS spectra of the CPB photoanode

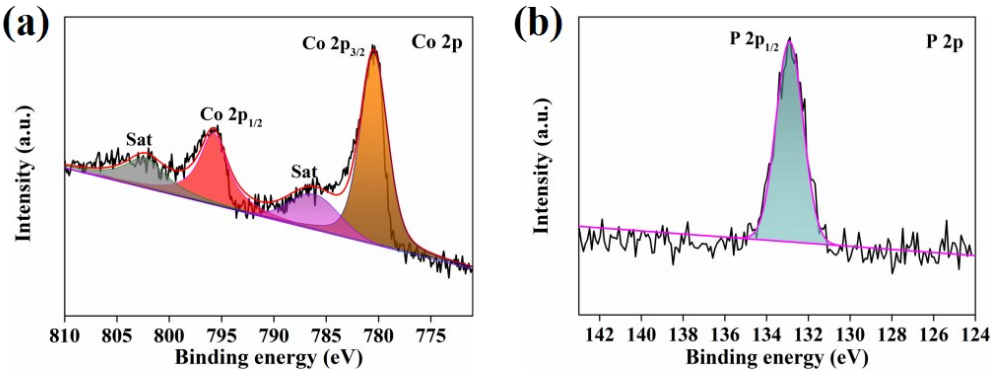


Fig. S3 High resolution XPS spectra of (a) Co 2p, (b) P 2p from CPB.

V. Temperature-time plots of different photoanodes

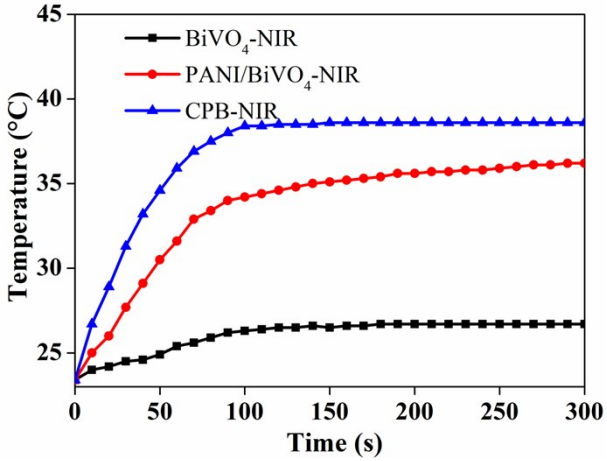


Fig. S4 Temperature-time plots of $BiVO_4$, PANI/$BiVO_4$ and CPB under AM 1.5G illumination with NIR light.

VI. Stability of CPB-NIR photoanode

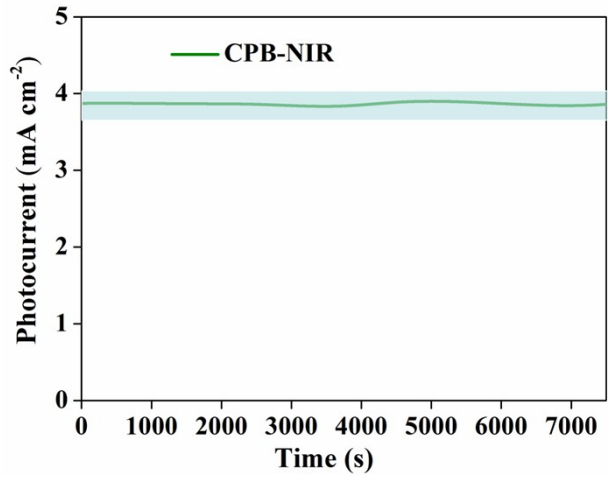


Fig. S5 Stability of CPB-NIR at 1.23 V_{RHE} under illumination for 7500 s in 0.5 M borate buffer (pH 7).

VII. Mott-Schottky plots of PANI

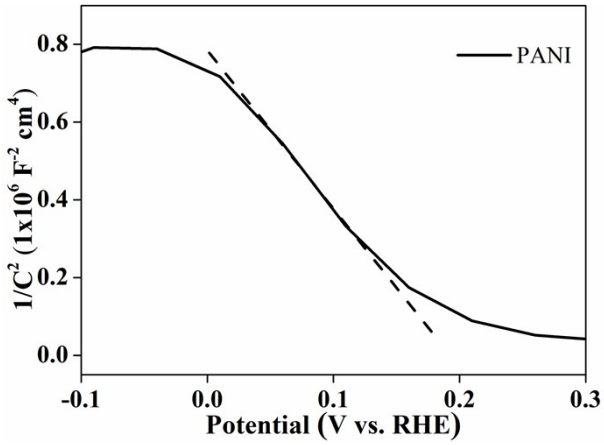


Fig. S6 Mott-Schottky plots of PANI at a frequency of 1000 Hz and an amplitude of 10 mV.

VIII. Photoluminescent spectra of different photoanodes

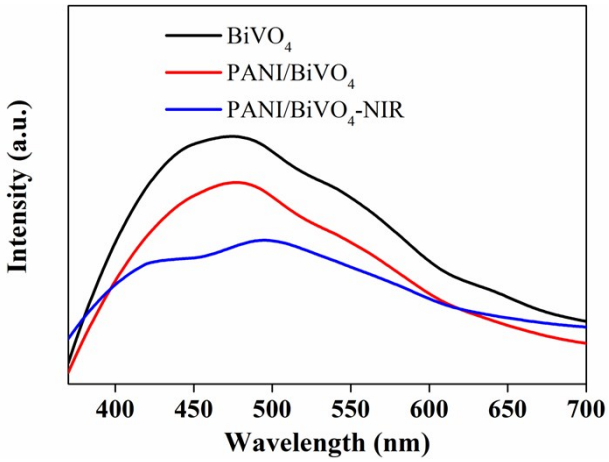


Fig. S7 Photoluminescent spectra of $BiVO_4$, PANI/$BiVO_4$, PANI/$BiVO_4$-NIR photoanodes at the excitation wavelength of 325 nm.

IX. Band structure of PANI/$BiVO_4$ heterojunction

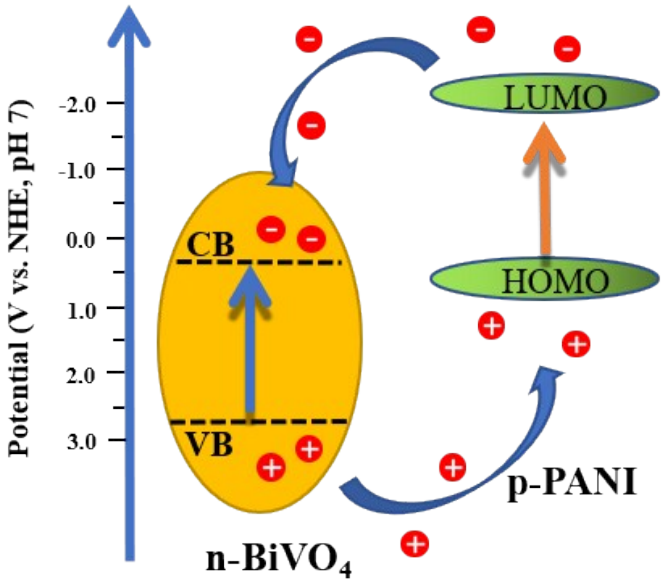


Fig. S8 Proposed band diagram and mechanism of charge separation for PANI/$BiVO_4$ heterojunction photoanode.

X. CV curves

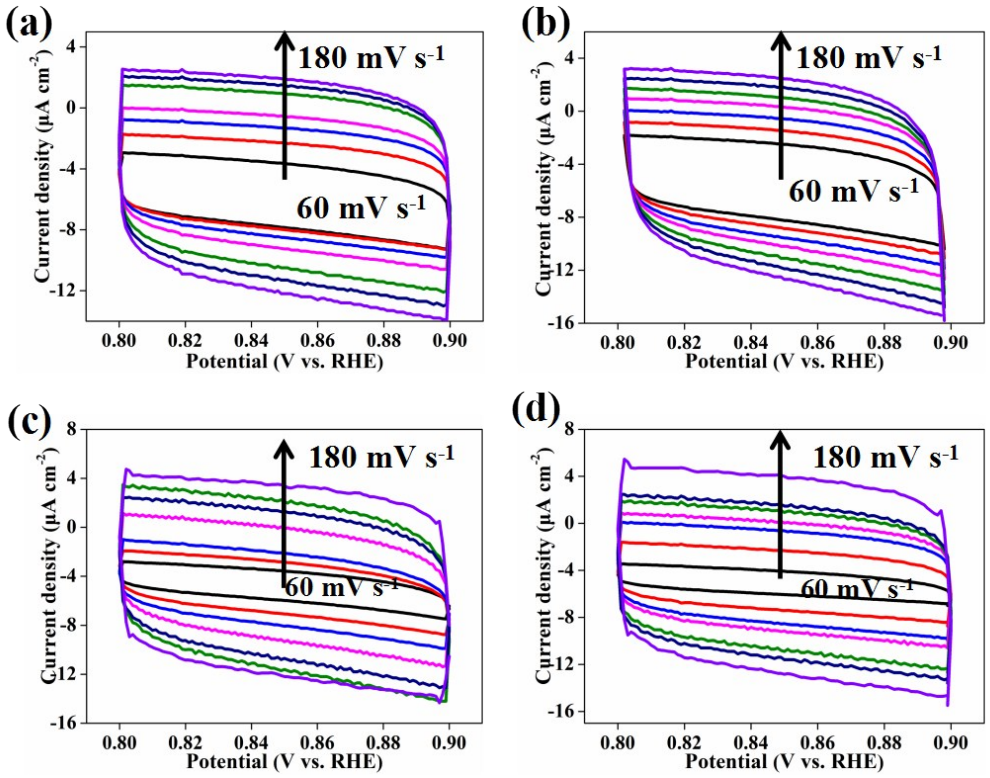


Fig. S9 CV curves measured in a non-Faradaic region of 0.8-0.9 V at various scan rates for (a) PANI/$BiVO_4$. (b) PANI/$BiVO_4$-NIR. (c) CPB and (d) CPB-NIR photoanode with a geometric area of 1 cm^2, respectively.

XI. Tests related to charge separation efficiency

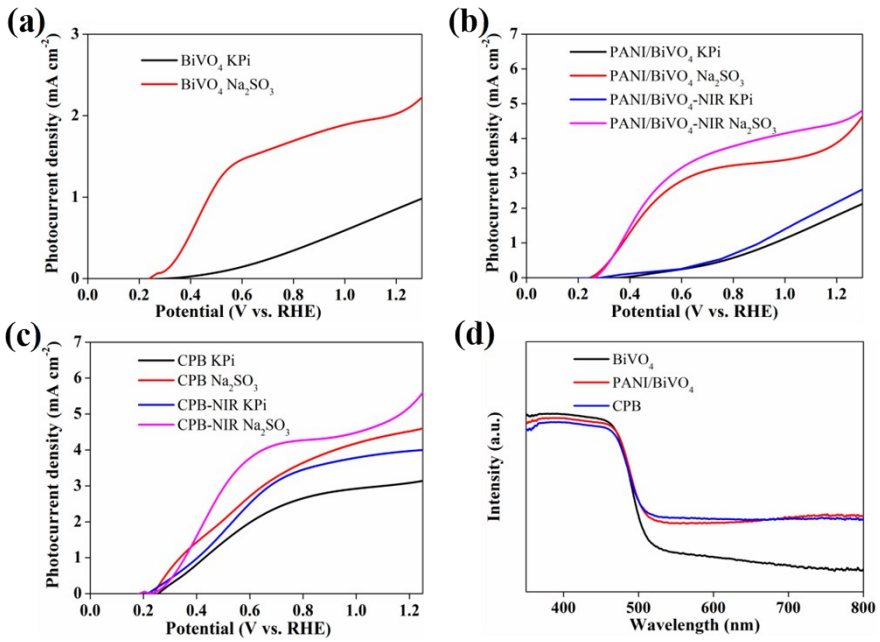


Fig. S10 (a-c) LSV curves measured with 0.5 M KPi solution and 1M Na_2SO_3 solution of $BiVO_4$, PANI/$BiVO_4$ and CPB photoanodes at 1.23 V_{RHE} with or without NIR laser and (d) UV-Vis absorptance spectra of $BiVO_4$, PANI/$BiVO_4$ and CPB photoanodes.

XII. Charge separation of different photoanodes

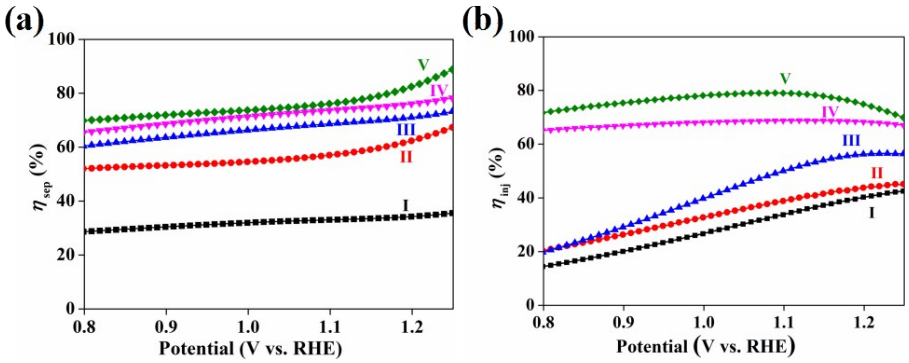


Fig. S11 (a) Bulk (η_{sep}) charge separation of $BiVO_4$, PANI/$BiVO_4$, PANI/$BiVO_4$-NIR, CPB and CPB-NIR photoanodes. (b) Surface (η_{inj}) charge separation of $BiVO_4$, PANI/$BiVO_4$, PANI/$BiVO_4$-NIR, CPB and CPB-NIR photoanodes. I, II, III, IV, V represent $BiVO_4$, PANI/$BiVO_4$, PANI/$BiVO_4$-NIR, CPB, CPB-NIR, respectively.

XIII. Summary of PEC performance of some $BiVO_4$ based photoanodes

Tab. S1. Comparison of the solar-driven photoactivity for water oxidation of the reported most active $BiVO_4$-based photoanodes.

Photoanode	Electrolyte	J (mA cm^{-2})	Stability (s)	Ref.
FTO/$BiVO_4$/PANI/Co-Pi	**0.5 M KPi (pH 7)**	**4.05**	7500	This paper
FTO/Zn-$BiVO_4$/GQDs	**0.1 M KPi (pH 7)**	**3.06**		1
FTO/Mo:$BiVO_4$/Co:$BiVO_4$	**0.1 M KPi (pH 7)**	**2.09**		2
FTO/W:Mo-$BiVO_4$	**0.1 M KPi (pH 7)**	**1.28**	3600	3
FTO/$BiVO_4$/Co_3O_4	**0.1 M KPi (pH 7)**	**2.71**		4
FTO/Zn:$BiVO_4$/Mo:$BiVO_4$/Ni:FeOOH	**0.1 M KPi (pH 7)**	**2.70**	3000	5
FTO/$BiVO_4$/FeOOH	**0.2 M Na_2SO_4 (pH 7)**	**4.30**	7200	6
FTO/Co-Pi/$BiVO_4$/SnO_2	**0.1 M KBi (pH 7)**	**2.02**	3600	7
FTO/$BiVO_4$/PANI/Ni:FeOOH	**0.1 M KPi (pH 7)**	**3.31**	10800	8
FTO/SnO_2/$BiVO_4$/Co-Pi	**0.1 M PBS (pH 7)**	**2.63**	6000	9
FTO/$BiVO_4$/Cu_2S/$Co(OH)_x$	**0.1 M KPi (pH 7)**	**3.51**	3600	10
FTO/BiOI/$BiVO_4$	**0.5 M KPi (pH 7)**	**3.27**	36000	11
FTO/$BiVO_4$/FeOOH/NiOOH	**0.2 M Na_2SO_4 (pH 9.5)**	**5.87**	6000	12
ITO/WO_3-NRs/$BiVO_4$/Co-Pi	**0.5 M Na_2SO_4 (pH 7)**	**5.10**	6000	13

XIV. References

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