

Supporting Information

Bioinspired Floatable System with 3D Sandwich-type Triphase Interface for Highly Efficient Nitrogen Fixation

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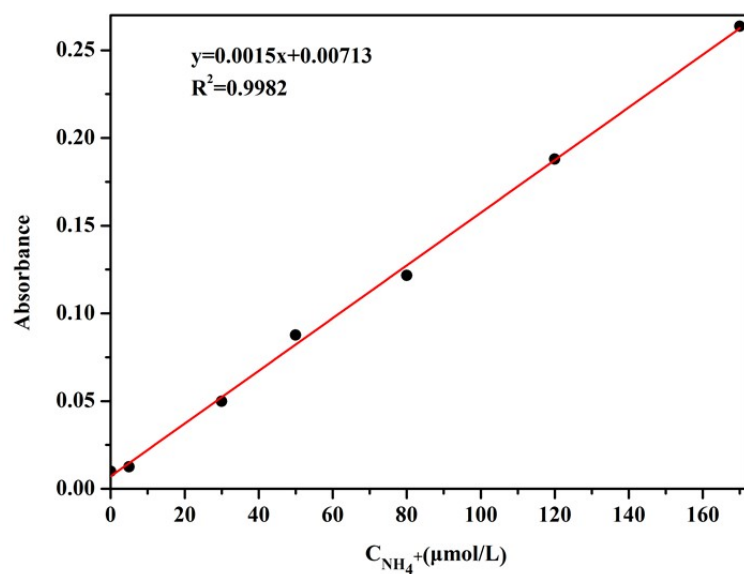


Fig. S1 Standard curve of ammonia measured by colorimetric with Nessler's reagent.

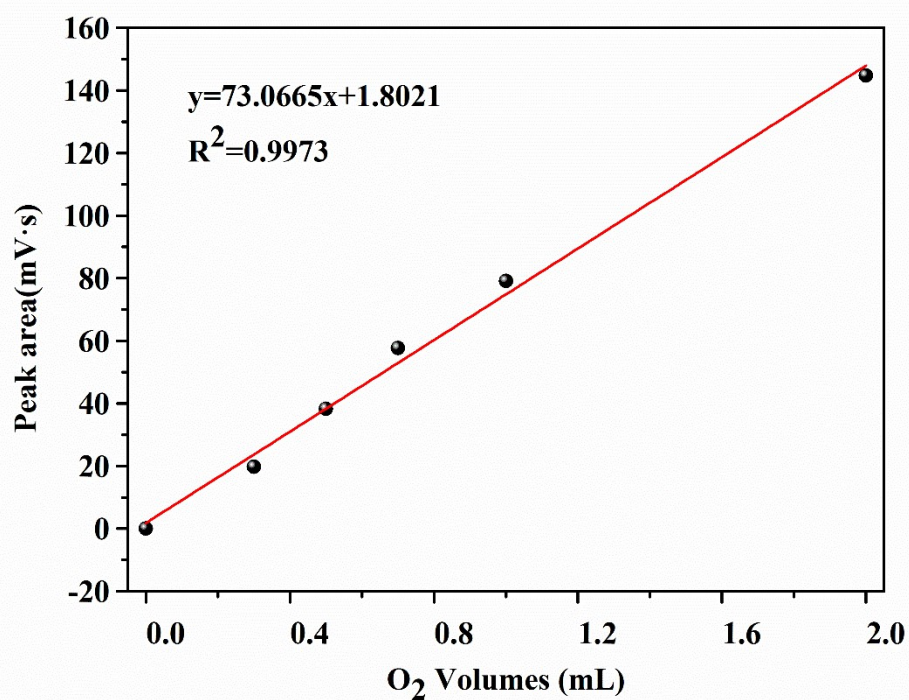


Fig. S2 Standard curve of oxygen measured by gas chromatography analysis.

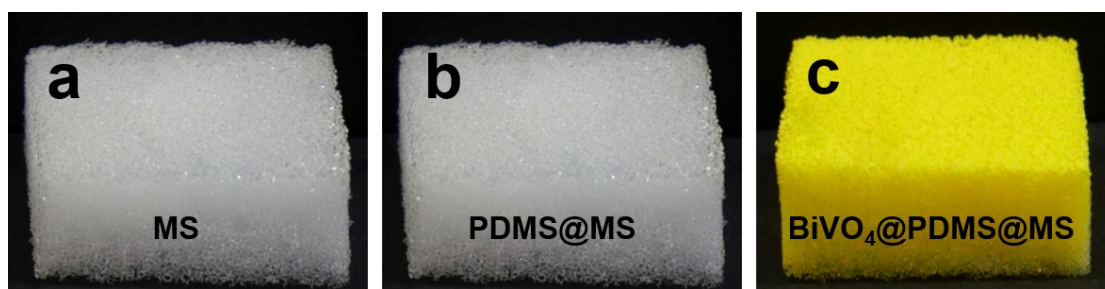


Fig. S3 The digital picture of (a) MS, (b) PDMS@MS, (c) BiVO₄@PDMS@MS.

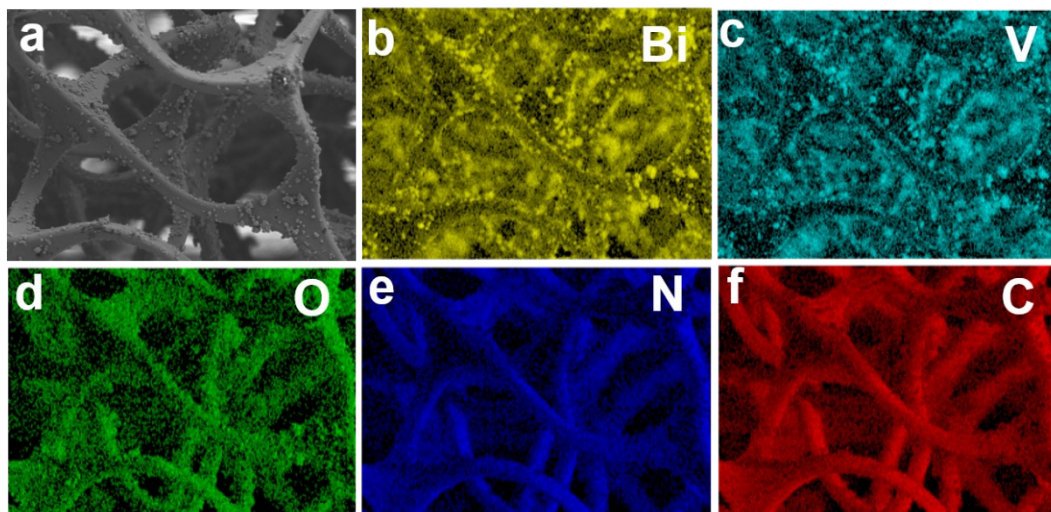


Fig. S4 (a) SEM image of BiVO₄@ MS-l and corresponding EDX elemental mapping profiles of (i) Bi (yellow), (j) V (blue-green), (l) O (green), (m) N (blue), and (n) C (red).

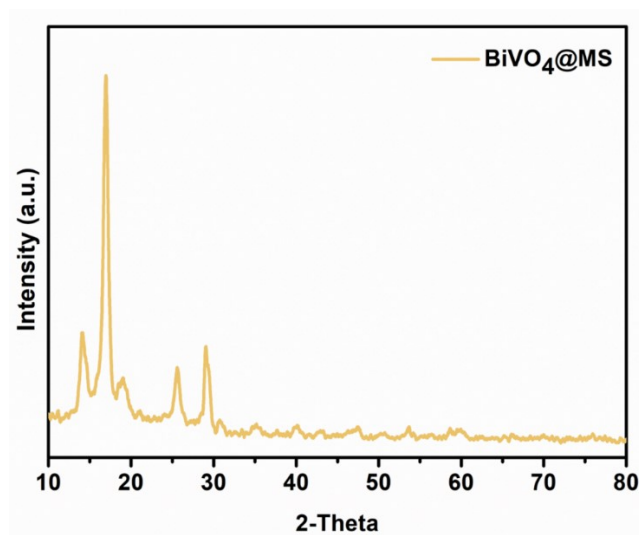


Fig. S5 XRD pattern of BiVO₄@ MS.

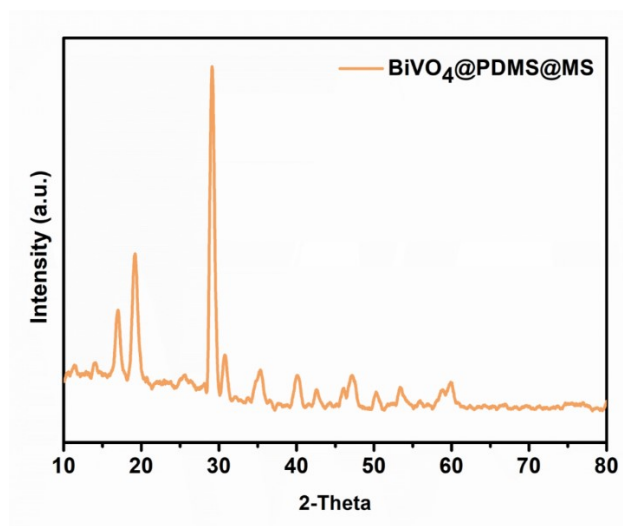


Fig. S6 XRD pattern of $\text{BiVO}_4\text{@PDMS@MS}$ after 3 cycles of reaction.

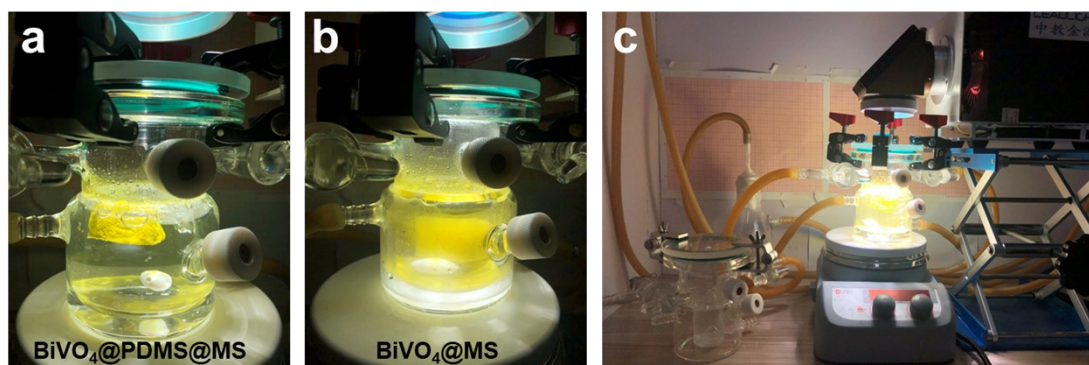


Fig. S7 The digital picture of reaction system $\text{BiVO}_4\text{@MS}$ (a) and $\text{BiVO}_4\text{@PDMS@MS}$ (b) and overall reaction equipment (c).

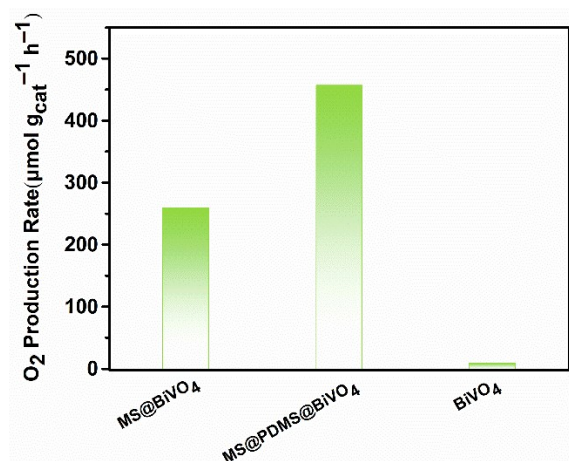


Fig. S8 (a) Comparison of photocatalytic O_2 generation activity of as prepared $\text{BiVO}_4\text{@PDMS@MS}$ catalysts and control experiments.

Table S1. Summary of previously-reported catalysts BiVO₄ for photo/electrocatalytic nitrogen fixation in aqueous solution under mild conditions

Catalyst	Scavenger	Light Source power(wavelength)	NH ₃ Yield ($\mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$)	Testing method	Ref.
BP-BiVO ₄	30 mL ethanol and 70 mL water	350 W Xe arc lamp visible light	208	Nessler's reagent	1
BiVO ₄ /ZnIn ₂ S ₄	No	300 W Xe arc lamp ($\lambda > 400 \text{ nm}$)	80.6	Nessler's reagent and ion chromatography	2
BiVO ₄	No	300 W Xe arc lamp ($\lambda > 400 \text{ nm}$)	103.4	Nessler's reagent	3
p-BiVO ₄	No	300 W Xe arc lamp ($\lambda > 400 \text{ nm}$) PEC NRR	$11.6 \times 10^{-8} \text{ mol h}^{-1} \text{ cm}^{-2}$	Nessler's reagent	4
BiVO ₄ /MnCO ₃ /C	No	($\lambda > 400 \text{ nm}$) PEC NRR	$2.426 \text{ mmol m}^{-2} \text{ h}^{-1}$	Nessler's reagent	5
Ag-OVs-BVO	5% methanol	300 W Xe arc lamp ($\lambda > 400 \text{ nm}$)	50.7	indophenol blue	6
BiVO ₄ -0.50	No	300 W Xe arc lamp ($\lambda > 400 \text{ nm}$)	$15.5 \text{ mmol g}^{-1} \text{ L}^{-1} \text{ h}^{-1}$	Nessler's reagent	7
Au/BiVO ₄	H ₂ O:CH ₃ OH=4:1	300 W Xe arc lamp ($\lambda > 400 \text{ nm}$)	0.419 mg·L ⁻¹	Nessler's reagent	8

BiVO ₄ (pH=7)	Na ₂ SO ₄	PEC NRR	8.60 μg h ⁻¹ mg ⁻¹ _{cat.}	indophenol blue	⁹
BiVO ₄ @ PDMS@ MS	No	300 W Xe arc lamp (λ > 400 nm)	624.87	Nessler's reagent	This work

Table S2. Photocatalytic N₂ fixation over the catalyst under various reaction conditions.^a

Entry	Catalyst	Light (> 400 nm)	Atmosphere	Solvent	NH ₃ production rate (μmol g _{cat} ⁻¹ h ⁻¹)
1	BiVO ₄ @PDMS@MS	√	N ₂	H ₂ O	624.87
2	BiVO ₄ @MS	√	N ₂	H ₂ O	373.25
3	BiVO ₄	√	N ₂	H ₂ O	1.77
4	BiVO ₄ @PDMS@MS	√	Ar	H ₂ O	N.D. ^b
5	PDMS@MS	√	N ₂	H ₂ O	N.D. ^b
6	×	√	N ₂	H ₂ O	N.D. ^b
7	BiVO ₄ @PDMS@MS	×	N ₂	H ₂ O	N.D. ^b
8	BiVO ₄ @PDMS@MS _{1/3}	√	N ₂	H ₂ O	524.56

^a Reaction condition: light intensity (200 mW cm⁻²), H₂O (100 mL), reaction time (4 h). ^b N.D. = not detected.

Reference

1. R. Zha, C. Li, L. He and M. Zhang, *J. Colloid Interface Sci.*, 2022, **628**, 378-388.
2. G. Zhang, X. Yuan, B. Xie, Y. Meng, Z. Ni and S. Xia, *Chem. Eng. J.*, 2022, **433**, 133670.
3. G. Zhang, Y. Meng, B. Xie, Z. Ni, H. Lu and S. Xia, *Appl. Catal. B*, 2021,

296,120379.

4. Y. Bai, J. Lu, H. Bai, Z. Fang, F. Wang, Y. Liu, D. Sun, B. Luo, W. Fan and W. Shi, *Chem.Eng. J.*, 2021, **414**,128773.
5. D. Sun, H. Bai, Y. Zhao, Q. Zhang, Y. Bai, Y. Liu, X. Pang, F. Wang, J. Ding, D. Xu, W. Fan and W. Shi, *ACS Appl. Mater. Interfaces*, 2020, **12**, 52763-52770.
6. L. Wang, M. Li, S. Wang, T. Zhang, F. Li and L. Xu, *New J. Chem.*, 2021, **45**, 22234-22242.
7. H. Chu, S. Zheng, Y. Li, K. Xu, Q. Hong, T. Li, W. Ren, S. Li, Z. Mei and F. Pan, *RSC Adv.*, 2021, **11**, 28908-28911.
8. M. Sui and X. Gu, *Optoelectronics Lett.*, 2022, **18**, 24-28.
9. J. X. Yao, D. Bao, Q. Zhang, M. M. Shi, Y. Wang, R. Gao, J. M. Yan and Q. Jiang, *Small Methods*, 2018, **3**, 1800333.