Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Enhanced photocatalytic ammonia synthesis over a Bi/carbon cloth float: triphase reaction system assisted N_2 supply and photothermal co-activation

Yaru Li, [a] Jianxin Liu,*[a] Zijun Sun, [a] Rui Li, [b] Lijun Guo, [a] Xiaochao Zhang, [a] Yawen Wang, [a] Yunfang Wang, [a] Zhuobin Yu [c] and Caimei Fan*[a]

[a]*College of Chemical Engineering and Technology, Taiyuan University of Technology, Taiyuan 030024, PR China*

[b]*College of Environmental Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, PR China*

[c]*Instrumental Analysis Center, Taiyuan University of Technology, Taiyuan 030024, PR China*

**Correspondence to: liujx0519@163.com; fancm@163.com*

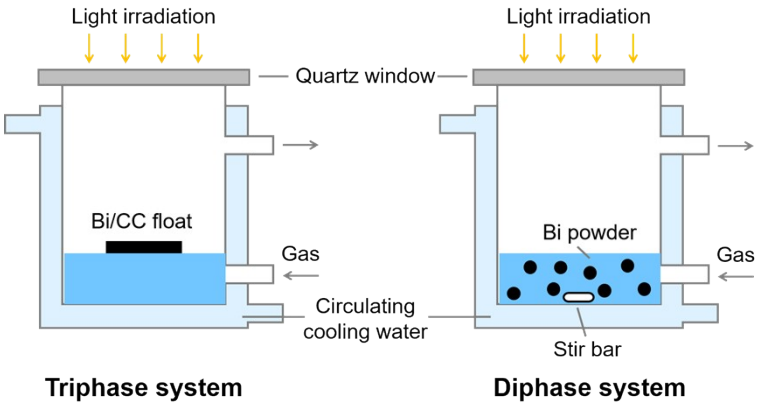

Fig. S1 The schematic diagrams of the photocatalytic NRR experiment performed in the triphase and diphase systems. The circulating cooling water is used when the controlled temperature condition is explored.

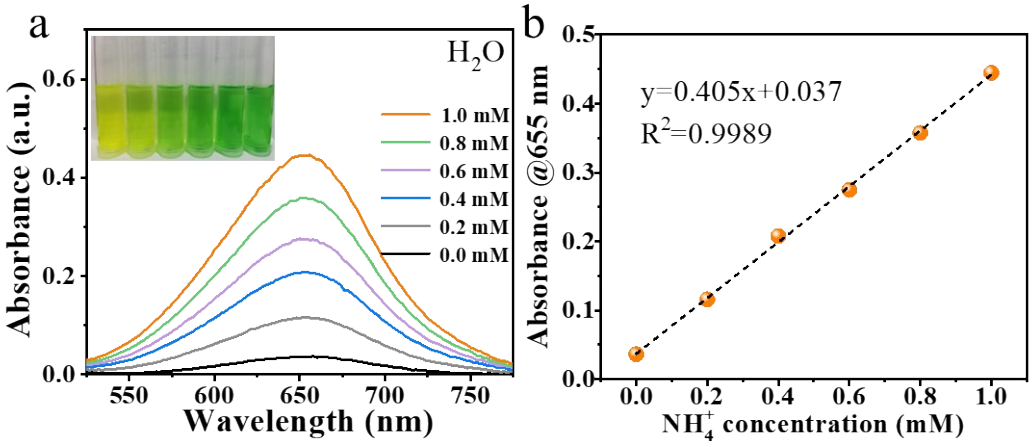

Fig. S2 (a) UV-Vis absorption spectra of indophenol assays with NH_4^+ ions after incubated for 2 h at room temperature and (b) Calibration curve used for calculation of NH_4Cl concentrations in deionized water.

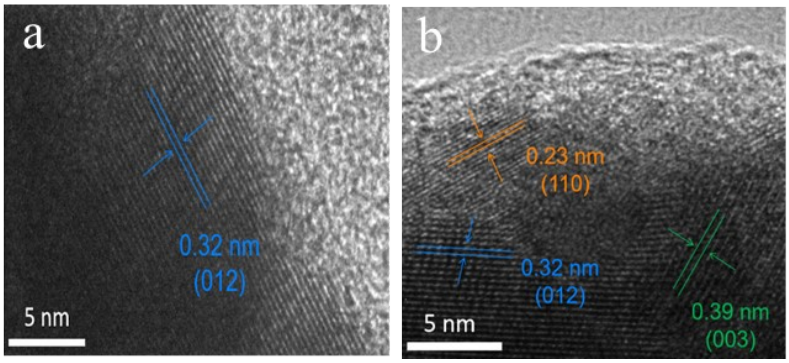

Fig. S3 The HRTEM images of (a) the solid sphere in *s*-Bi and (b) the hollow sphere in typical *h*-Bi2 samples.

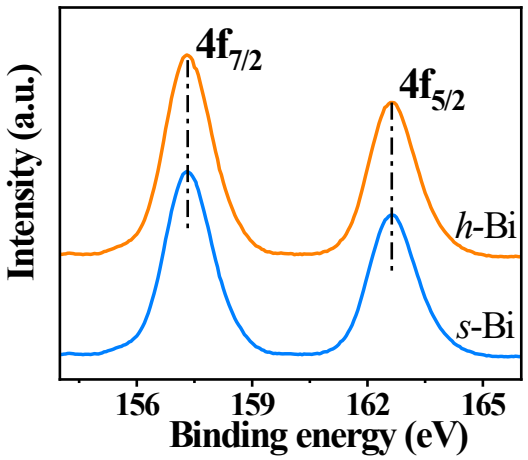

Fig. S4 High-resolution XPS spectra for Bi 4f of *s*-Bi and typical *h*-Bi2.

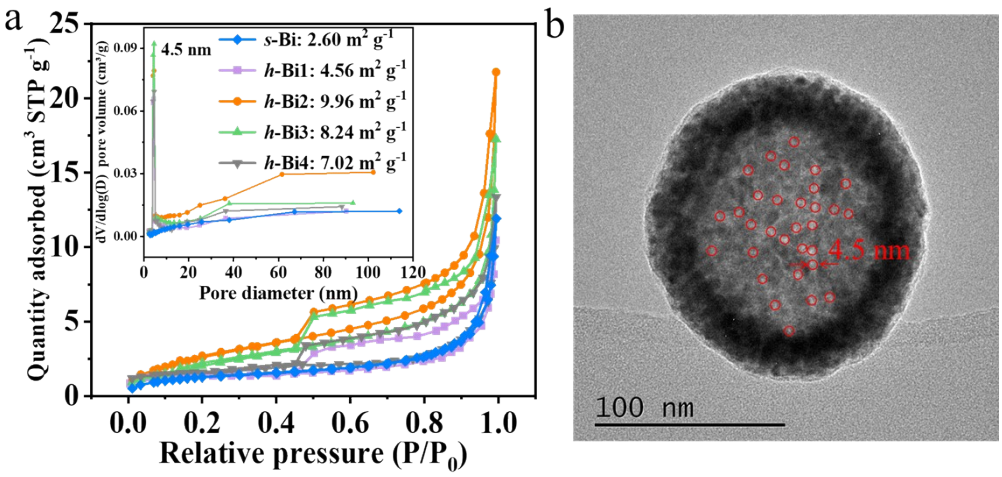

Fig. S5 (a) The N_2 adsorption-desorption isotherms and pore size distribution (inset) of all Bi samples, and (b) The HRTEM images of the hollow structure in *h*-Bi.

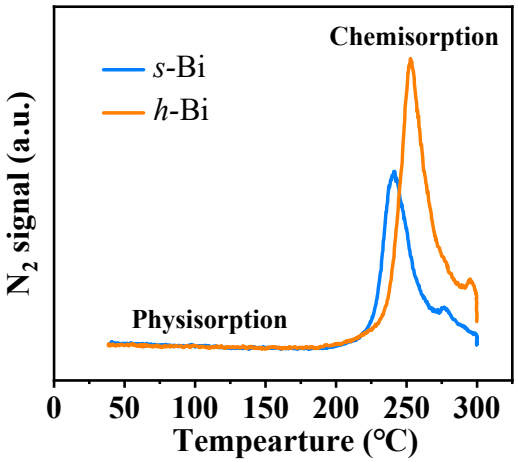

Fig. S6 The N_2-TPD spectra of *s*-Bi and typical *h*-Bi2.

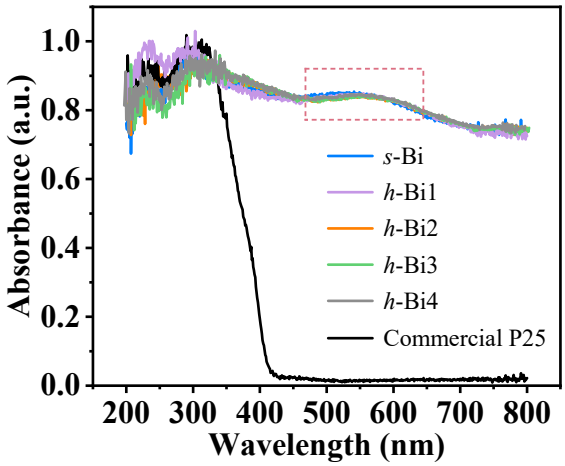

Fig. S7 The DRS spectra of all Bi samples and commercial P25 samples.

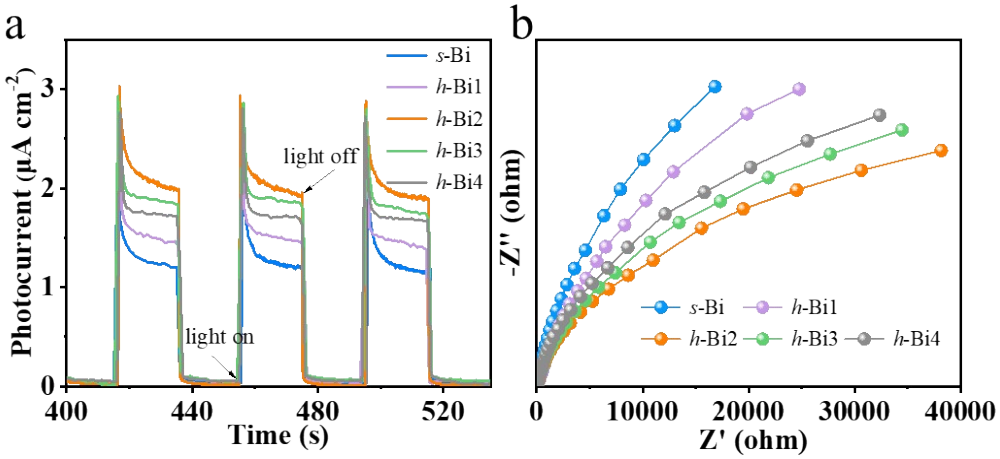

Fig. S8 (a) Photocurrent and (b) EIS spectra of all Bi samples coated on ITO substrate.

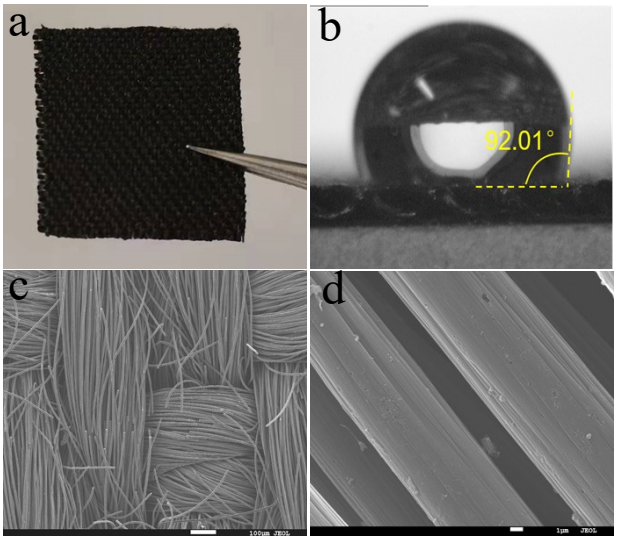

Fig. S9 (a) The photograph, (b) Water droplet, and (c) (d) SEM images of the hydrophilic carbon cloth (CC_l, 2 cm×2 cm).

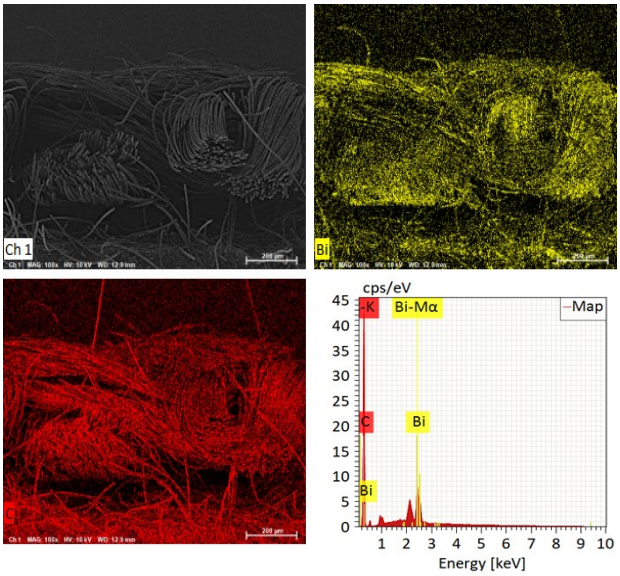

Fig. S10 SEM and related EDX mapping images of sectional view for Bi/hydrophilic carbon cloth (Bi/CC_l) float.

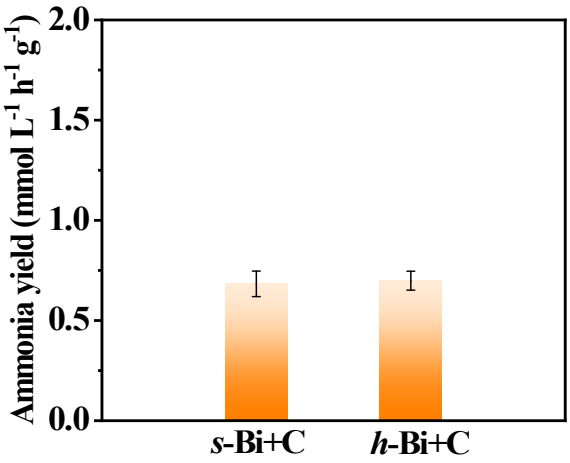

Fig. S11 The ammonia yields of *s*-Bi and typical *h*-Bi2 mixed with C powders in diphase system.

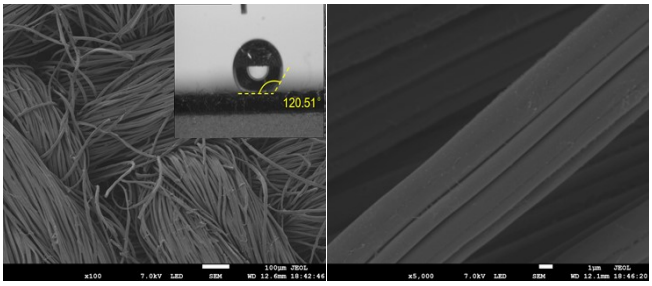

Fig. S12 SEM images and inset of the photograph of water droplet of the hydrophobic carbon cloth (CC_b).

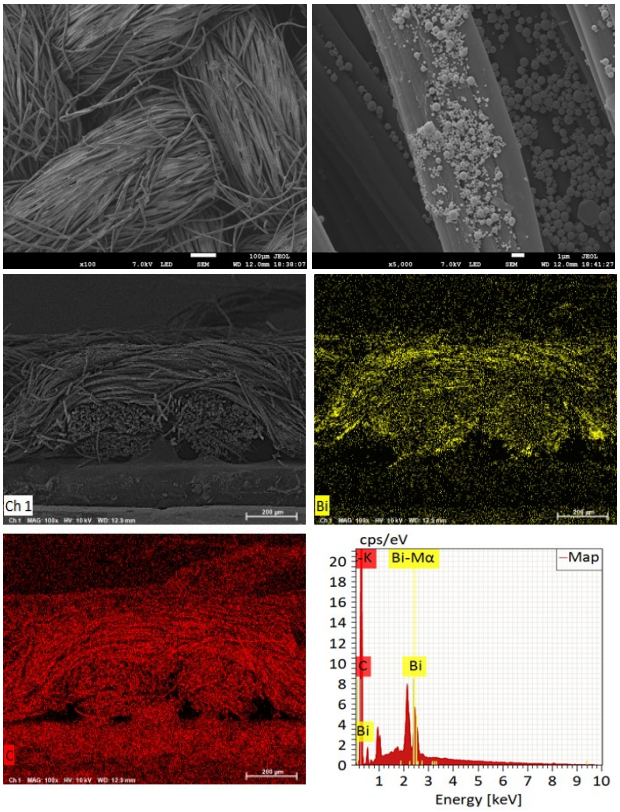

Fig. S13 SEM and related EDX mapping images of Bi/hydrophobic carbon cloth (Bi/CC_b) float.

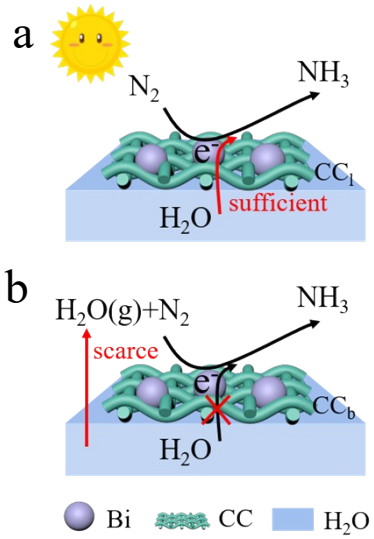

Fig. S14 Schematic H_2O reactant supply diagrams of (a) Bi/CC_l and (b) Bi/CC_b float triphase systems, respectively. CC_b and CC_l represent hydrophobic and hydrophilic carbon cloth, respectively.

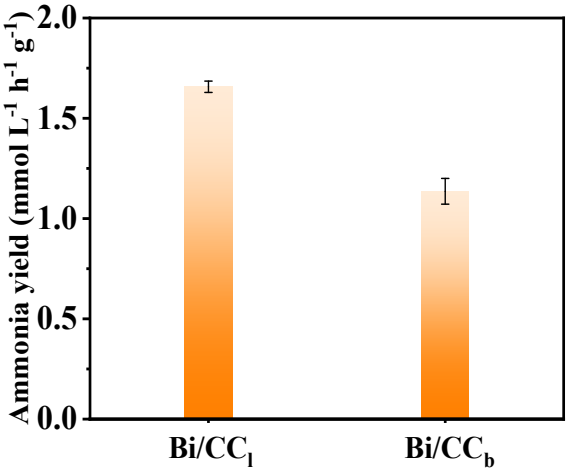

Fig. S15 Photocatalytic N_2 reduction to ammonia yield of Bi/CC_l and Bi/CC_b. CC_b and CC_l represent hydrophobic and hydrophilic carbon cloth, respectively.

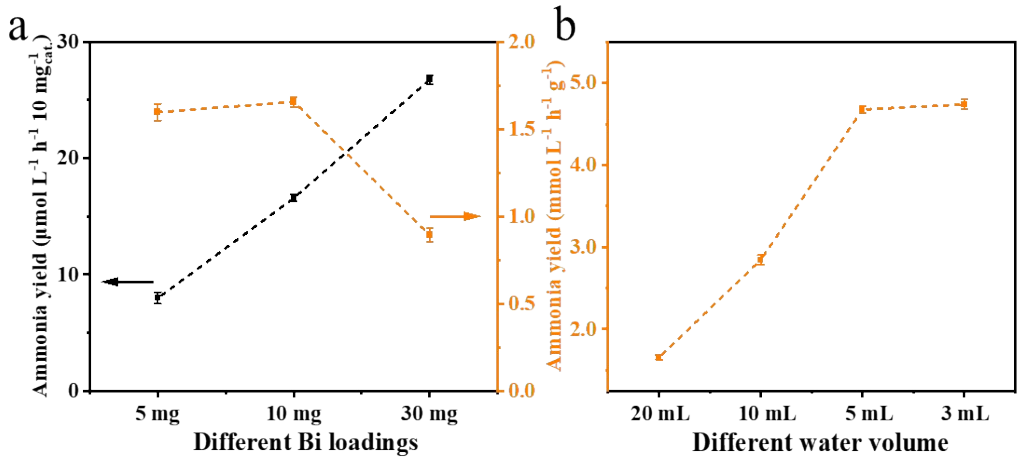

Fig. S16 The photocatalytic N_2 reduction to ammonia yield of Bi/CC float (a) with different Bi photocatalyst loadings and (b) deionized water volume.

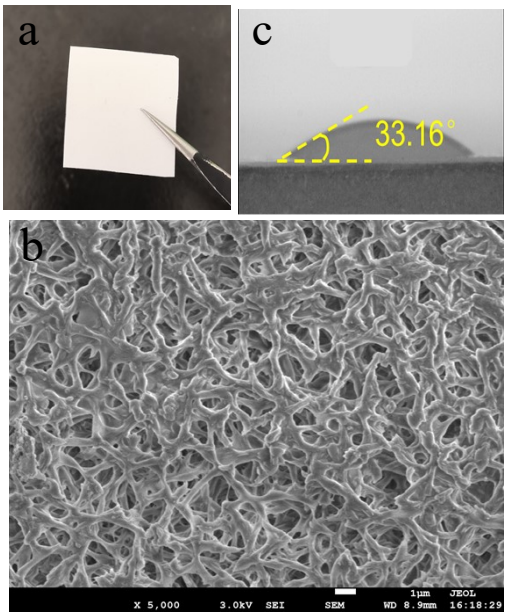

Fig. S17 (a) The photograph, (b) SEM, and (c) Water droplet images of the Nylon66 membrane (2 cm×2 cm).

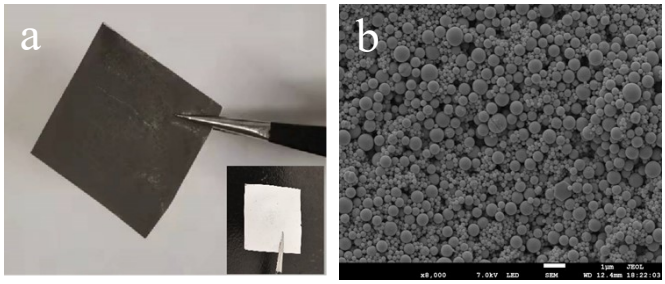

Fig. S18 (a) The photographs of the front and back (inset) views, (b) SEM images of the Bi/Nylon66 float (2 cm×2 cm).

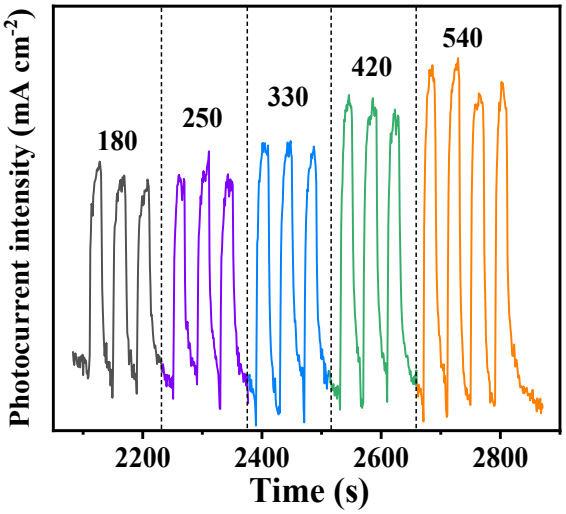

Fig. S19 The photocurrent spectrum of Bi under different photo intensity: 180, 250, 330, 420, and 540 mW cm^{-2}, respectively.

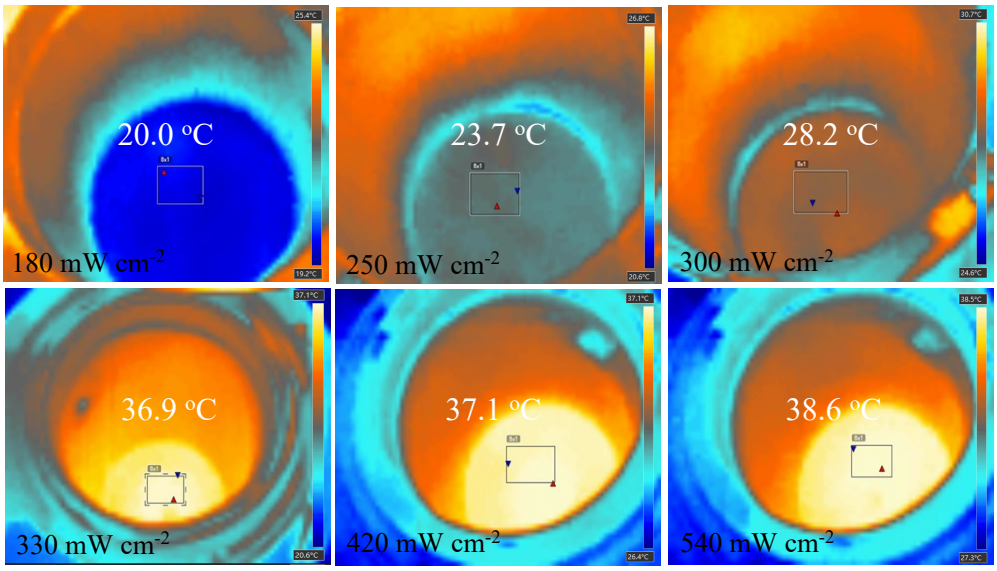

Fig. S20 The infrared imaging photographs of the powders diphase system with different photo intensity: 180, 250, 300, 330, 420, and 540 mW cm^{-2}, respectively.

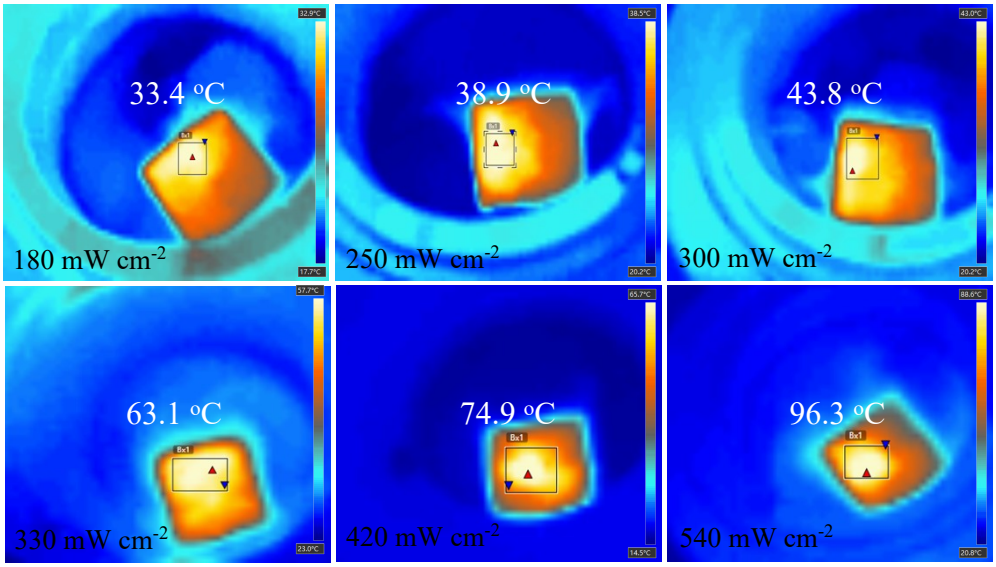

Fig. S21 The infrared imaging photographs and corresponding surface temperatures of the Bi/CC float triphase system under different photo intensity: 180, 250, 300, 330, 420, and 540 mW cm^{-2}, respectively.

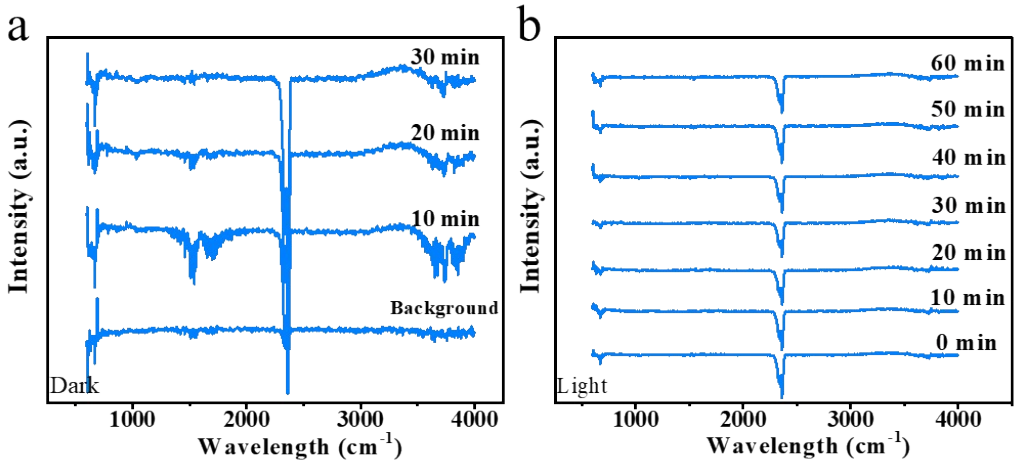

Fig. 22 The in-situ FTIR spectra recorded from CC sample in the (a) dark and (b) light conditions during the photocatalytic N_2 reduction to ammonia progress.

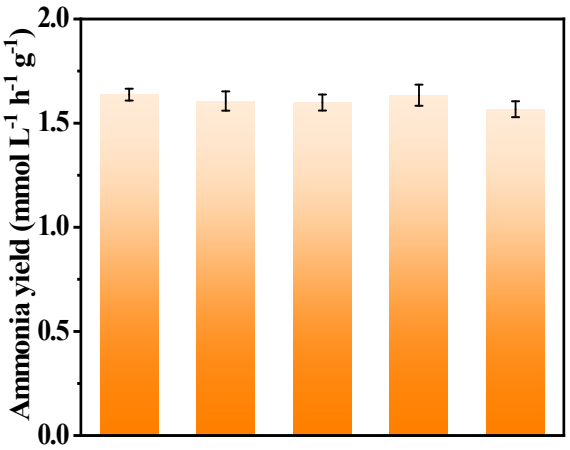

Fig. S23 The cycle tests of Bi/CC float triphase system for photocatalytic N_2 reduction to ammonia.

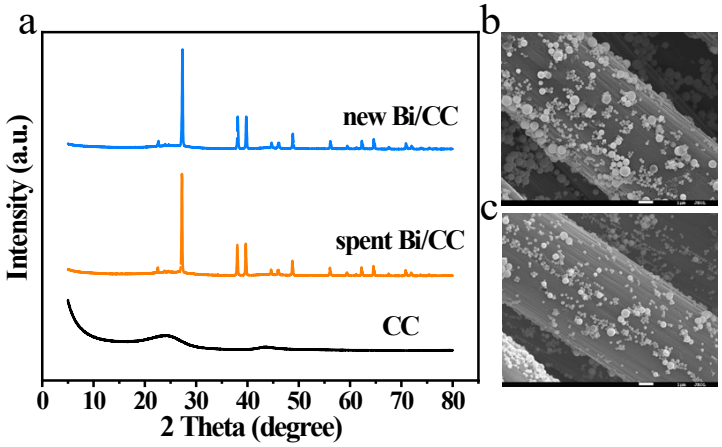

Fig. S24 (a) XRD spectra and correspondent SEM images of Bi/CC (b) before and (c) after five cycles PNRR reactions.

Table S1 The reported results for PNRR using water and nitrogen as feedstocks at ambient conditions.

Catalysts	Reaction systems	Light source: 300 W Xe lamp		Hole scavenger	NH_3 yield (mmol L^{-1} h^{-1} g^{-1})	References
		Wavelength (λ)	Photo intensity (mW cm^{-2})			
s-Bi	Liquid-Solid	320-780 nm	330	/	0.65	This work
h-Bi					0.70	
s-Bi/CC	Gas-Solid-Liquid				0.91	
h-Bi/CC					1.66	
			540		2.85	
		Real sunlight			1.22	
BiOBr	Liquid-Solid	Full spectrum	-	/	0.06	S1
OVs-BiOBr	Liquid-Solid				0.55	
MOF-76(Ce)	Liquid-Solid	Full spectrum	-	/	0.34	S2
In_2O_3/In_2S_3	Liquid-Solid	Full spectrum	200	/	0.40	S3
$AgBr/Ag/Bi_4O_5Br_2$	Liquid-Solid	Full spectrum	-	ethanol	0.18	S4
SiW_9Co_3 /PDA/OVs-Bi_2WO_6	Liquid-Solid	Simulated sunlight	400	/	0.35	S5
OVs-TiO_2	Liquid-Solid	＞420 nm	-	methanol	0.46	S6
V_O-S-rich $TiO_{2-x}S_y$	Liquid-Solid	Full spectrum	-	/	1.90	S7
SVs-Bi_2S_3	Liquid-Solid	200-1100 nm	200	/	0.51	S8
PCON	Liquid-Solid	＞420 nm	-	/	0.49	S9

References

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(S9) S. Yang, X. Deng, P. Chen, T. Zhao, F. Liu, C. Deng and S. Yin, *Appl. Catal. B-Environ.*, 2022, 121370.