A solar-driven heterojunction hydrogel with reversible phase transition for efficient photocatalytic decontamination and freshwater generation

Jiangyang Mei [a,b], *Yong Jin* [a,b,]*, *Haonan Chen* [a,b], *RongZhou* [a,b], *Zhexian Mao* [a,b], *Kun Huang*[a,b], *Hailong Yang*[a,b]

[a] National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University, Chengdu 610065, PR China

[b] Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, PR China

* E-mail: jinyong@cioc.ac.cn (Yong Jin)

Corresponding author: Yong Jin; E-mail: jinyong@cioc.ac.cn

1. Experimental section

1.1. Materials

All chemicals were purchased from commercial sources and used without further treatment. Graphite, ethyl alcohol (≥99.7%) and hydrogen peroxide (30 wt%) were purchased from Sinopharm Chemical Reagent Co. Ltd. N, N'-Methylenebisacrylamide (Bis, 99.0%) and Potassium peroxodisulfate (PPS, 99.5%) were purchased from Aladdin. N, N-Diethylacrylamide (DEAAm, 98%) and N, N, N', N'-tetramethyl-ethylenediamine (TEMED, 99.5%) were bought from Maclin. Potassium permanganate (99.5%), and concentrated sulfuric acid (98.3%) were derived from Chengdu Kelong Chemical.

2.2. Sample preparation

Graphene oxide (GO) was obtained through a modified Hummers' method as the literature reported. The complex catalysts(RGO (R), RGO-TiO_2 (RT), RGO-TiO_2-ZnS (RTZ)) were prepared via coprecipitation and the hydrothermal method. The PDEAAm@RTZ hydrogel (PRTZ hydrogel) was synthesized via a one-step polymerization process.

1) Preparation of the RGO

Reduced graphene oxide (RGO) was synthesized according to the procedure outlined in Figure S1. Initially, concentrated sulfuric acid and graphite powder were mixed in a three-necked flask and allowed to react for 48 hours. The resulting mixture was then subjected to ultrasonic dispersion for 6 h. Subsequently, KMnO4 was slowly added to the reaction system on an ice bath, leading to the formation of GO. The GO was then obtained after neutralizing the reaction and washing the product. Meanwhile, RGO was prepared from GO by hydrothermal treatment (120°C, 12 h).

2) Preparation of the RGO-TiO_2 (RT)

At room temperature, 15 mg of GO was added to 60 mL of diethylene glycol (DEG) and stirred magnetically for 1 hour to form a homogeneous brown solution.

Under magnetic stirring, 2.63 mmol of tetrabutyl titanate (TNBT) was added dropwise. After sealing the container, the stirring speed was adjusted to 950 r/min, and stirring was continued for 12 hours. The resulting solution was slowly added to 180 mL of acetone under vigorous stirring, and then 600 μL of deionized water was added to the acetone solution at a rate of 10 μL/s. After stirring for an additional 90 minutes, the product was washed by centrifugation three times with deionized water and anhydrous ethanol, yielding the precursor product, referred to as GO-TiO_2. Disperse the precursor product GO-TiO_2 in 80 mL of deionized water and stir at room temperature for 10 minutes. Then transfer it to a 100 mL hydrothermal reactor and react at 120° C for 12 hours. Allow it to cool naturally to room temperature. Remove the supernatant, and wash the solid product by centrifugation with ethanol and deionized water three times each. Finally, freeze-dry the product, which is referred to as RGO-TiO_2.

3) Preparation of the RGO-TiO_2-ZnS (RTZ) heterojunction catalyst

The precursor product GO-TiO_2 was dispersed in 80 mL of deionized water, and under magnetic stirring, 0.1 mmol of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.3 mmol of L-cysteine were added. The resulting solution was transferred to a 100 mL hydrothermal reactor and reacted at 120°C for 12 hours, followed by natural cooling to room temperature. The product was washed by centrifugation with ethanol and deionized water three times each, and then freeze-dried to obtain the ternary nanocomposite, referred to as RGO-TiO_2-ZnS (RTZ).

4) Synthetic PRTZ heterojunction hydrogel

The heterojunction hydrogel (PRTZ) was prepared by radical polymerization. Specifically, DEAAm (2 g), PPS (20 mg), and Bis (20 mg) dissolved in 8mL of deionized water, and then added 2mL RTZ (0.02g/mL). Finally, a drop of TEMED was added to obtain the PRTZ heterojunction hydrogel.

2.3. Characterization

Fourier transform infrared spectrums (FT-IR) were obtained by Fourier infrared spectrometer (FT-IR Spectrometer 3, PerkinElmer). Hydrogels (1.5 mm thick) were attached to the inner wall of an ultraviolet-visible spectrophotometer (U-3900, PerkinElmer) to measure the transmittance of materials. The surface temperature of hydrogels at different illumination times was taken by a camera with an infrared thermal imager (FLIR E5 Systems). Thermogravimetric Analysis (TGA, TG209F3) was employed to analyze the thermostability of materials with different structures, ranging from 80-800 ℃ at a heating rate of 10 ℃/min. The optical microscopy photograph was obtained by Novel Optics BM2000 (LTD). A scanning electron microscope (SEM, Helios G4 UC) was employed to observe the microstructure of the SSH hydrogels. The crystallinity of photocatalysts was detected by Panalytic XRD. The diffracted intensities were collected in step-scan mode (step size 0.02°) in the angular (2θ) range 5°-80°. CKX53 inverted microscope was used to obtain optical picture of photocatalysts. Confocal laser scanning microscopy (CLSM) with an inverted microscope (Fluoview FV3000, Olympus) was used to visualise live and dead bacterial cells attached to the surfaces after incubation.

2.4. Surface temperature and water collection test of PRTZ hydrogel

The surface temperature of the PRTZ hydrogel was measured using a photochemical reactor (CEL-HXF300, CEAULIGHT) equipped with a xenon arc lamp emitting a simulated radiation intensity of 1 kW/m^2 (equivalent to one sun, 300 W). The water collection performance was evaluated using a water purification system made from PRTZ hydrogel in the form of a cylinder (r=1 cm), with mass loss measured after exposure to simulated sunlight at 1 kW/m^2 (300 W).

2.5. Photocatalytic performance to produce clear water test

The photocatalytic performances of different samples were evaluated under simulated solar irradiation (200-2500 nm, light intensity 100 mW cm^{-2}) by using Rhodamine B (R6G), methyl orange (MO), Eosin Y and Giemsa solution as models. The photocatalytic test was carried out using a lab-assembled closure device equipped with a funnel for containing the hydrogel and a container for collecting the purified water. The hydrogels were mixed with pollutant solutions (0.05 mg/m L), and then placed the above mixtures in dark for 2 h to reach adsorption desorption equilibrium prior to light exposure. The fully absorbent hydrogel was then placed into a lab-assembled closure device and exposed to solar simulator illumination for photocatalytic degradation. The water that was released from the hydrogels was collected and its absorbance was measured using a UV-vis spectrophotometer.

2. Supplementary Figures

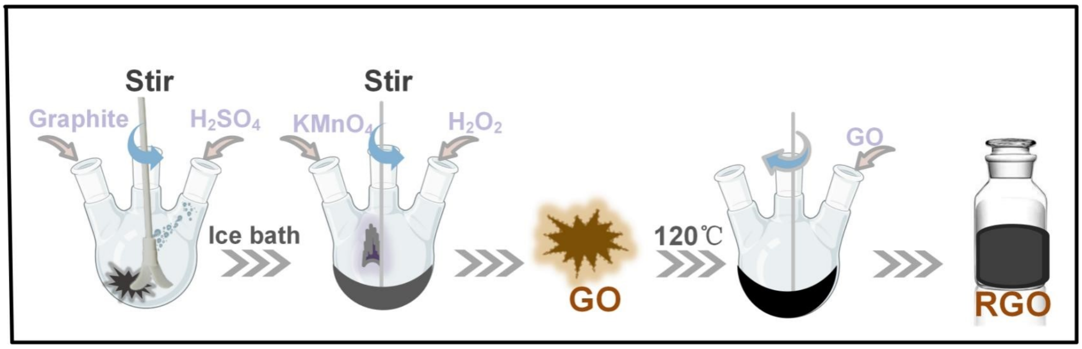
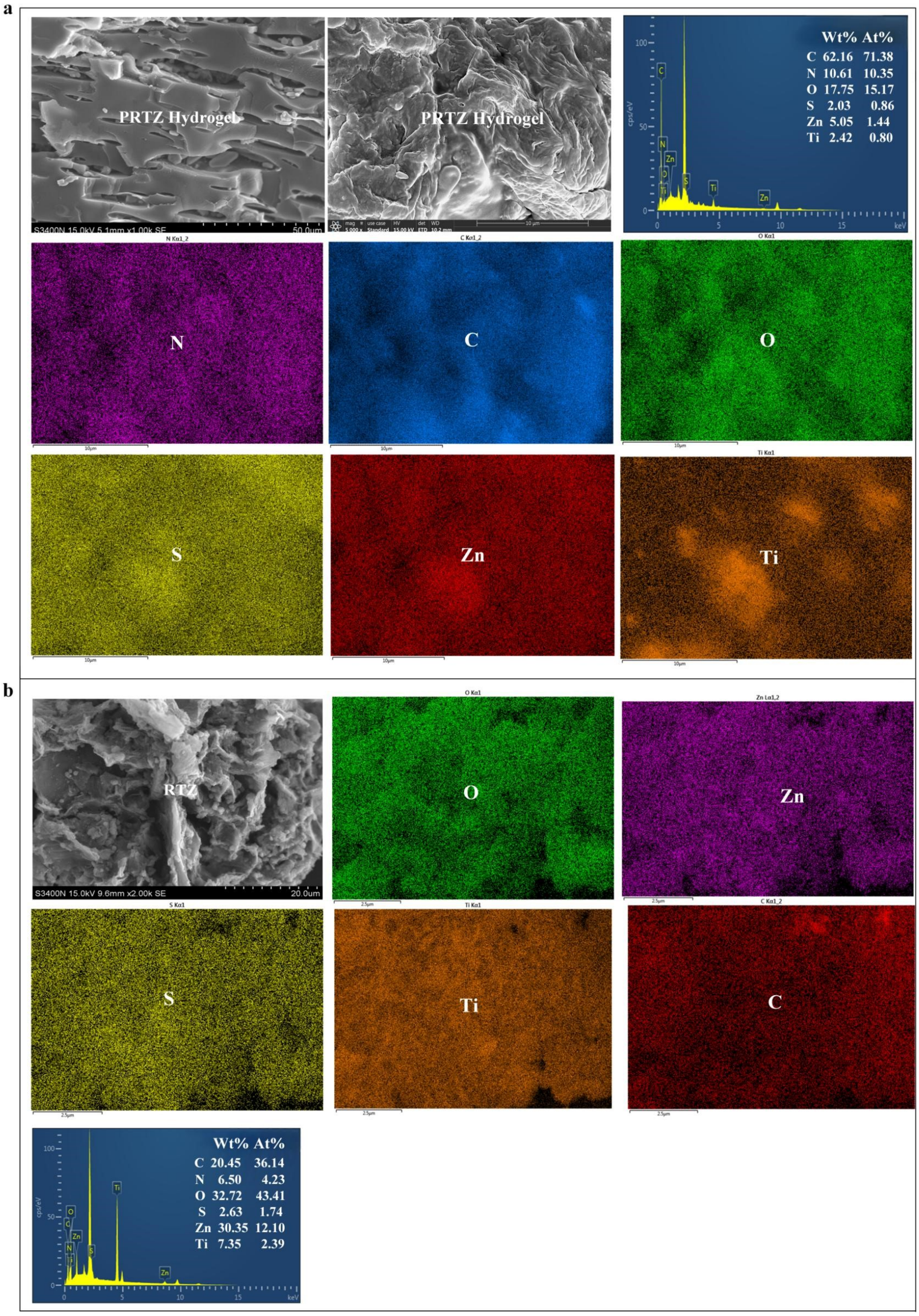


Fig. S1. Preparation of GO and RGO materials



	Wt%	At%
C	62.16	71.38
N	10.61	10.35
O	17.75	15.17
S	2.03	0.86
Zn	5.05	1.44
Ti	2.42	0.80

	Wt%	At%
C	20.45	36.14
N	6.50	4.23
O	32.72	43.41
S	2.63	1.74
Zn	30.35	12.10
Ti	7.35	2.39

Fig. S2. SEM,EDS and distribution diagram total spectrum diagram of (a) PRTZ hydrogel and (b) RTZ composite material.

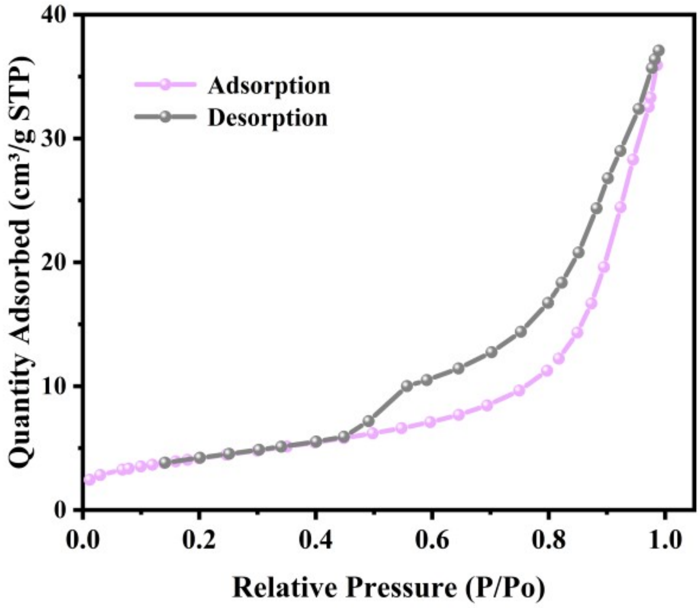


Fig. S3. Isotherm linear plot (adsorption and desorption) of T

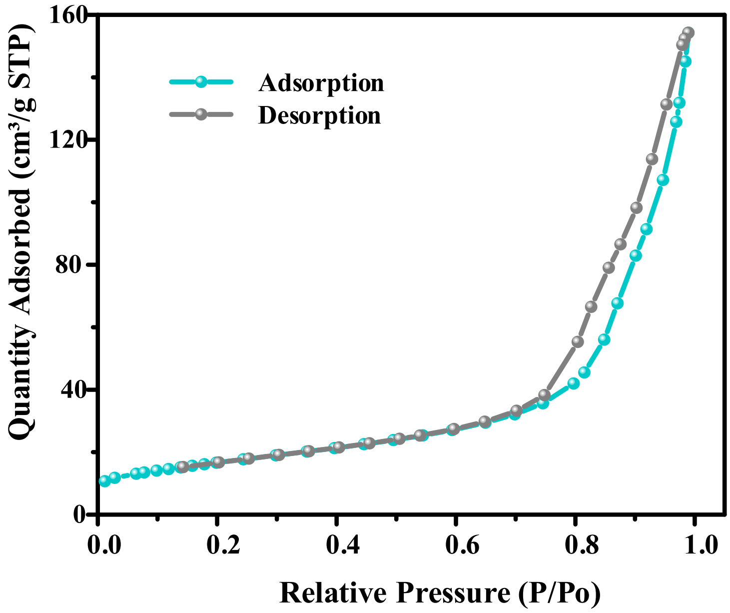


Fig. S4. Isotherm linear plot (adsorption and desorption) of Z

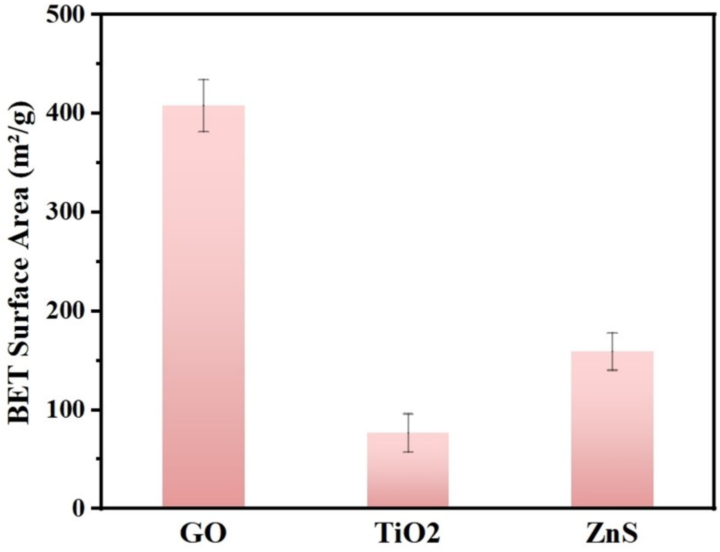


Fig. S5. Surface area of GO, TiO2 and ZnS

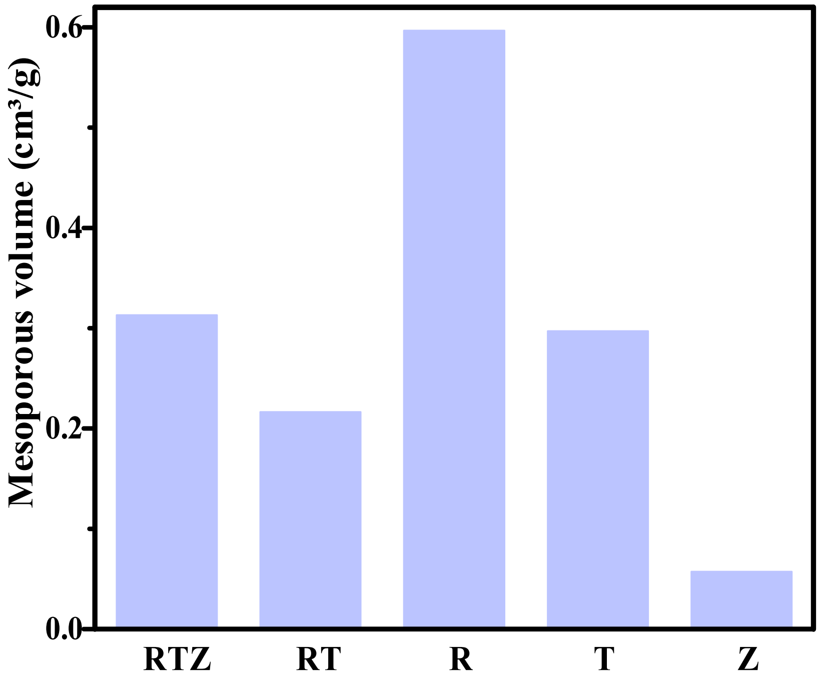


Fig. S6. Mesoporous volume of materials

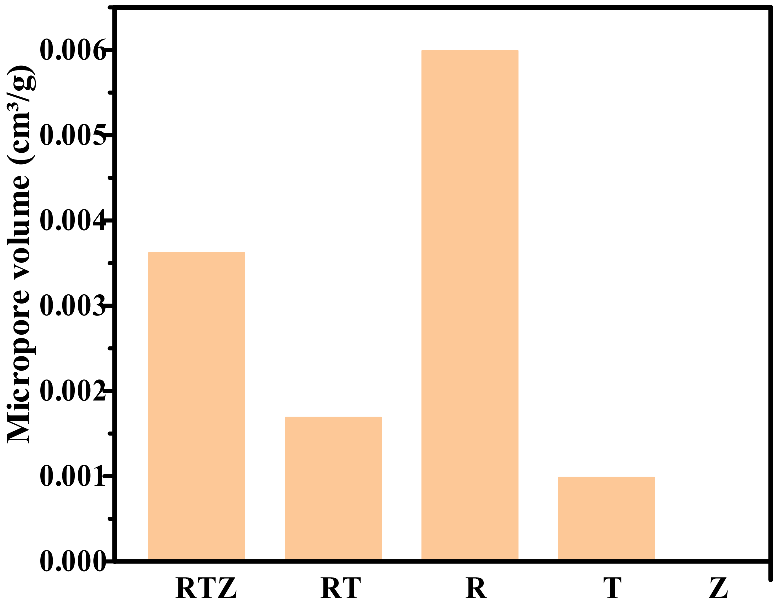


Fig. S7. Microporous volume of materials

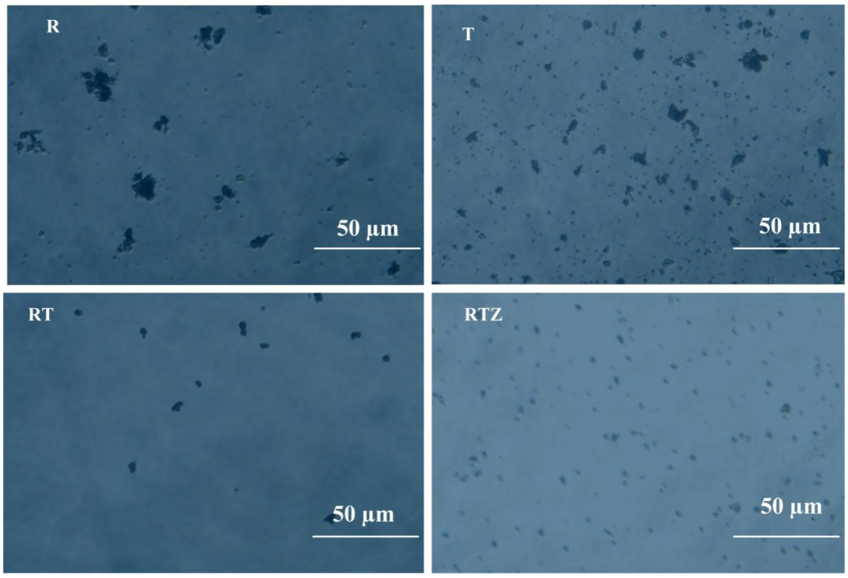


Fig. S8. Optical photograph of materials

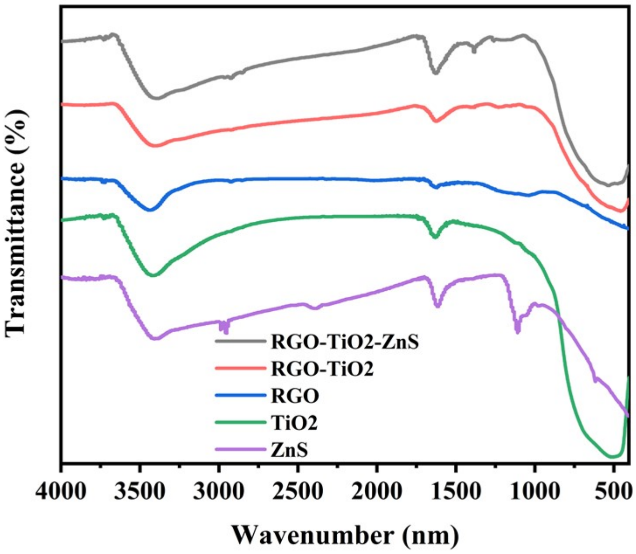


Fig. S9. FTIR spectrum of materials

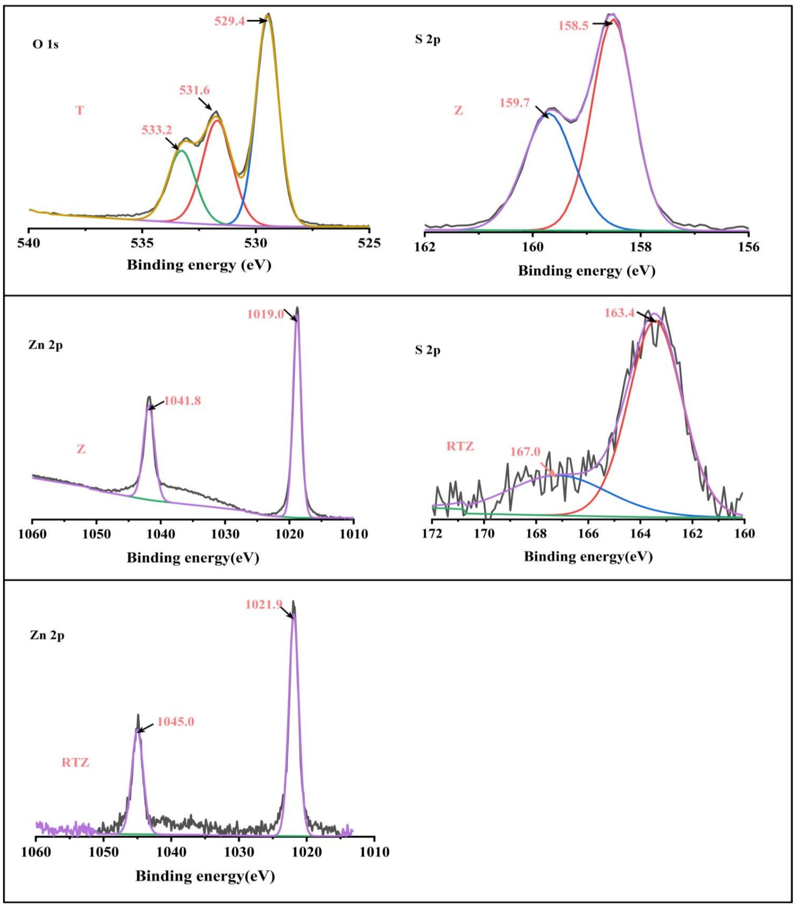


Fig. S10. XPS of materials.

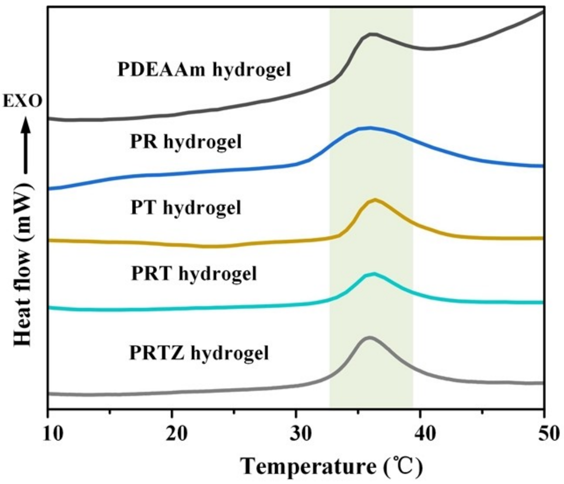


Fig. S11 DSC thermogram of swollen hydrogels.

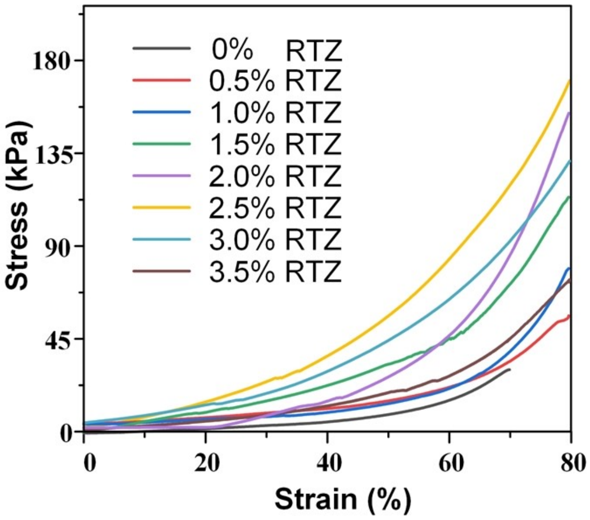


Fig. S12 Compress stress of hydrogels with varying concentrations of RTZ

Table S1. Photocatalytic degradation of methylene blue solution by PRTZ hydrogel with varying amounts of RTZ added.

Hydrogels	0	0.5%	1.0%	1.5%	2.0%	2.5%
Removal rate	38.11%	65.80%	74.22%	86.54%	96.09%	98.89%

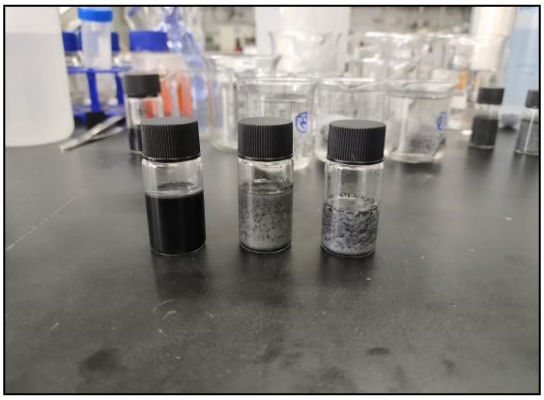


Fig. S13 PRTZ hydrogel with varying amounts of RTZ added (2.5%, 3.0%, 3.5% from left to right)

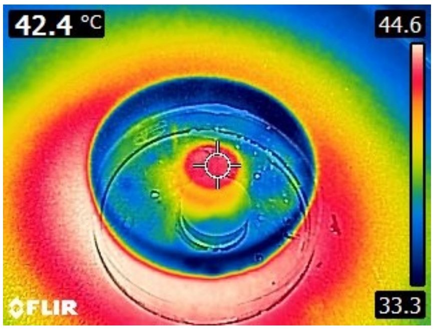


Fig. S14. IR images of PRTZ hydrogel during different exposure times under 0.8 sun irradiation.

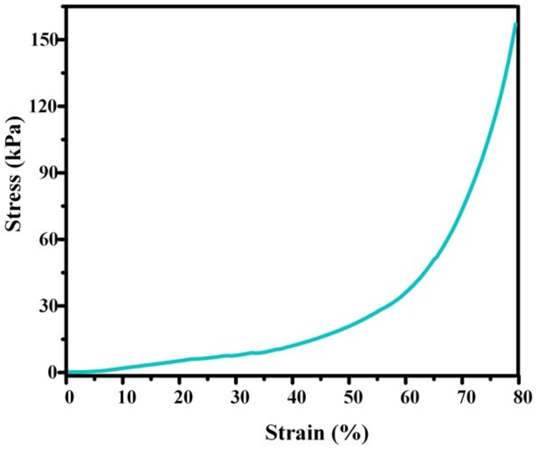


Fig. S15 Compress stress of the PRTZ hydrogel after 15 cycles resue

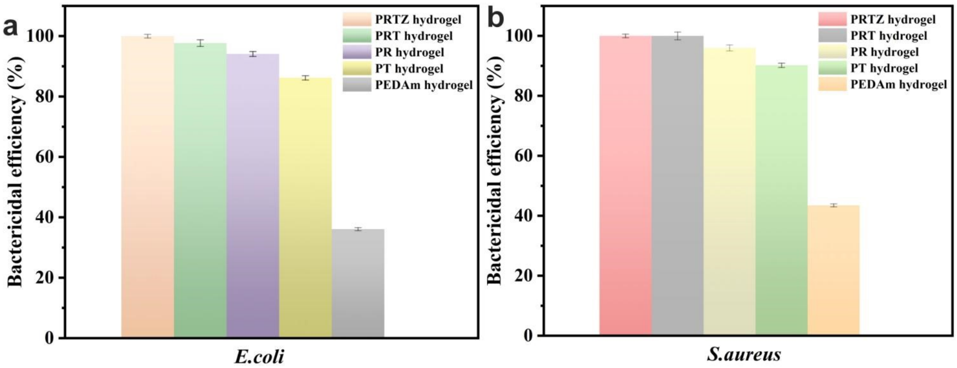


Fig. S16. Bactericidal efficiency of (b) *E. coli* and (c) *S. aureus*.

Table S2. Photocatalytic degradation of methylene blue solution by hydrogels

Hydrogels	PRTZ	PRT	PT	PR	PDEAm
Removal rate	98.89%	88.77%	71.85%	45.74%	38.11%

Table S3. Photocatalytic degradation of Eosin Y solution by PRTZ hydrogel under different sunlight illumination intensity

Illumination intensity	0.8 sun	1.0 sun	1.5 sun	2.0 sun	2.5 sun
Removal rate	99.19%	98.77%	85.42%	58.28%	31.15%

Table S4. Photocatalytic degradation of Giemsa solution by PRTZ hydrogel under 0.8 sun

Cycle times	1	2	3	4	5	6	7	8	9	10	15
Degradation rate (%)	97.93	96.74	95.18	90.49	89.96	85.42	84.85	82.83	80.81	79.71	53.33

Table S5. PRTZ hydrogel compared with the existing catalyst materials with different types

Ref.	**Raw materials**	**Degradation rate**	**Manifold cycles**
This work	PDEAAm/RTZ	99.19%	Yes
[1]	PVA/MIL-88A/CNTs	93%	No
[2]	C3N4/chitosan	82.5%	No
[3]	β-FeOOH/FP	94.1%	No
[4]	ZIF-67/CoFe	95%	No
[5]	TiO/iron tailings	98.37%	No
[6]	RGO/PPy	94.8%	No

Table S6. PRTZ hydrogel compared with the existing catalyst materials with different types

Ref.	**Water production rate/kg·m^{-2}·h^{-1}**	**Raw materials**	**Types**	**Removal contaminant**	**Bactericidal function**
This work	8.87	PDEAAm/ RGO-TiO_2-ZnS	Passive hydrogel	96.09% in 50 mins	100%
[7]	/	(P(HEA/NMMA)-CuS	Catalyst	95.91% in 24 h	/
[8]	/	PNIPAM/OCN	Catalyst	95% in 70 mins	/
[9]	/	Bi_2WO_6/graphene	Catalyst	36.1% in 74 h	/
[10]	/	P(HEA-co-HAM)-CdS)	Catalyst	92% in 3 h	/
[6]	2.08	RGO/PPy	Evaporation haydrogel	94.8%	/
[11]	/	PAM/ZnO	Separating membranes	90%	/

Fig. S17. Water intake point and sunlight-driven release clear water

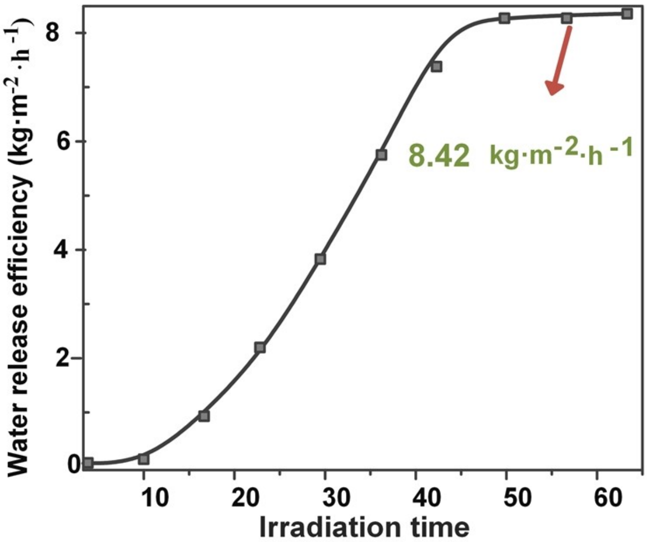


Fig. S18. Light-trigged water release performance under natural sunlight

References

[1] L. K. Rathore, A. Bera. ACS Appl. Mater. Interfaces., 2024, 16, 12.

[2] Z. Chen, LJN. Kuate, H. Zhang, J. Hou, H Wen, C. Lu, C. Li, W. Shi, Sep. Purif. Technol., 2025, 355, 129751.

[3] T. T. Xi, C. J. Li, Y. Q. Yu, W.Q. Wei, S. Wang, T. T. Xu, H. N Xiao, H. Q. Dai, X. L. Zhou, H. Y. Bian, Adv. Compos. Hybrid Ma., 2025, 8, 196.

[4] Z. W. Wang, L. S. Gao, X. F. Chen, H. B. Jin, H. Z. Wei, L. Ma, Q. Y. Gu, X. W. Liu, J. Colloid. Interf. Sci., 2025, 2, 213.

[5] B. Sun, Z. Y. Guo, F. F. Ren, X. N. Pan, C. J. Lyu, X. X. Qiao, W. L. Bi, F. W. Liu, Q. J. Hou, J. Clean. Prod., 2023, 427, 139241.

[6] S. W. Yan, H. J Song, Y. Li, J. Yang, X. H. Jia, S. Z. Wang, X. F. Yang, App. Catal. B-Environment. Energy., 2022, 301, 120820.

[7] J.H. Yang, Z.k. Li, H.j. Zhu, Adsorption and photocatalytic degradation of sulfamethoxazole by a novel composite hydrogel with visible light irradiation[J]. Applied Catalysis, B. Environmental 217(2017).

[8] W.H. Chen, W. Mao, Z.Q. Liu, W, Hou, N. Kumar, J.Sun, X. W Cai, C. Huang, W. Shen, F. Yang, Y.Y. Cui, H.K. Lee, S. Tang, Photocatalytic degradation of bisphenol A by temperature-sensitive magnetic hydrogel with enhanced service life[J]. Journal of Hazardous Materials 459(2023).

[9] J.J. Yang, D. Chen, Y. Zhu, Y.M Zhang, Y.F. Zhu, 3D-3D porous Bi2WO6/graphene hydrogel composite with excellent synergistic effect of adsorption-enrichment and photocatalytic degradation[J]. Applied Catalysis, B. Environmental 205(2017).

[10] H.J. Zhu, Z.K Li, J.H. Yang, A novel composite hydrogel for adsorption and photocatalytic degradation of bisphenol A by visible light irradiation[J]. Chemical Engineering Journal 334(2018).

[11] C.X. Li,1 B.L. Jiangli, B. Lee, G.H. Yu, W. Zhang, H.X. Chen, S. Sanders, M. Al-Hashimi, S. Banerjee, L. Fang, Versatile and efficient photopolymerization approach to zinc oxide-composed dual functional membranes for sustainable water treatment[J]. Matter 7(2024).