

Supplementary Material

A multi-functional photothermal-catalytic foam for cascade treatment of saline wastewater

Binrong Li ^{a,d}, Zhiwei Guo ^b, Yonghai Feng ^{c*}, Minjia Meng ^{c*}

^a *School of Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China*

^b *School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China*

^c *Institute for Advanced Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China*

^d *Department of Materials Science and Engineering, National University of Singapore, Singapore 117575*

*Corresponding authors: M.J. Meng (mmj@ujs.edu.cn), Y.H. Feng (fengyonghai@ujs.edu.cn)

1.1 Characterization

X-ray diffraction (XRD, XRD-6100) with Cu K α radiation was conducted to confirm the crystal structure of composites foam. The surface chemical state and composition were studied by x-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi). Scanning electron microscope (SEM, JSM-6010 PLUS/LA) and transmission electron microscope (TEM, JEM-2100(HR)) were used to observe the microstructure and morphology of composites foams. The corresponding element mapping was also tested for studying element distribution. Fourier transform infrared spectroscopy (FTIR) spectrum was recorded on a Nicolet Nexus 470 spectrometer (America thermo-electricity Company). Water contact angle (optical surface analyzer, OSA60) was used to test the hydrophilicity of LDHs based PVDF foam. The concentrations of pollutants were measured by UV–Vis spectrophotometer. Total organic carbon analyzer (TOC, Shimadzu TOC-vcv) was used to test the mineralization performance of the optimal foam. EPR spectra were collected on a Bruker A300 EPR spectrometer to detect reactive oxygen species (ROS) during the catalytic degradation in the presence of PMS. Typically, 20 μ L of DMPO was added into 80 μ L of the LDHs based foam-soaked water solution to detect reactive radicals (SO₄ \cdot^- , \cdot OH).

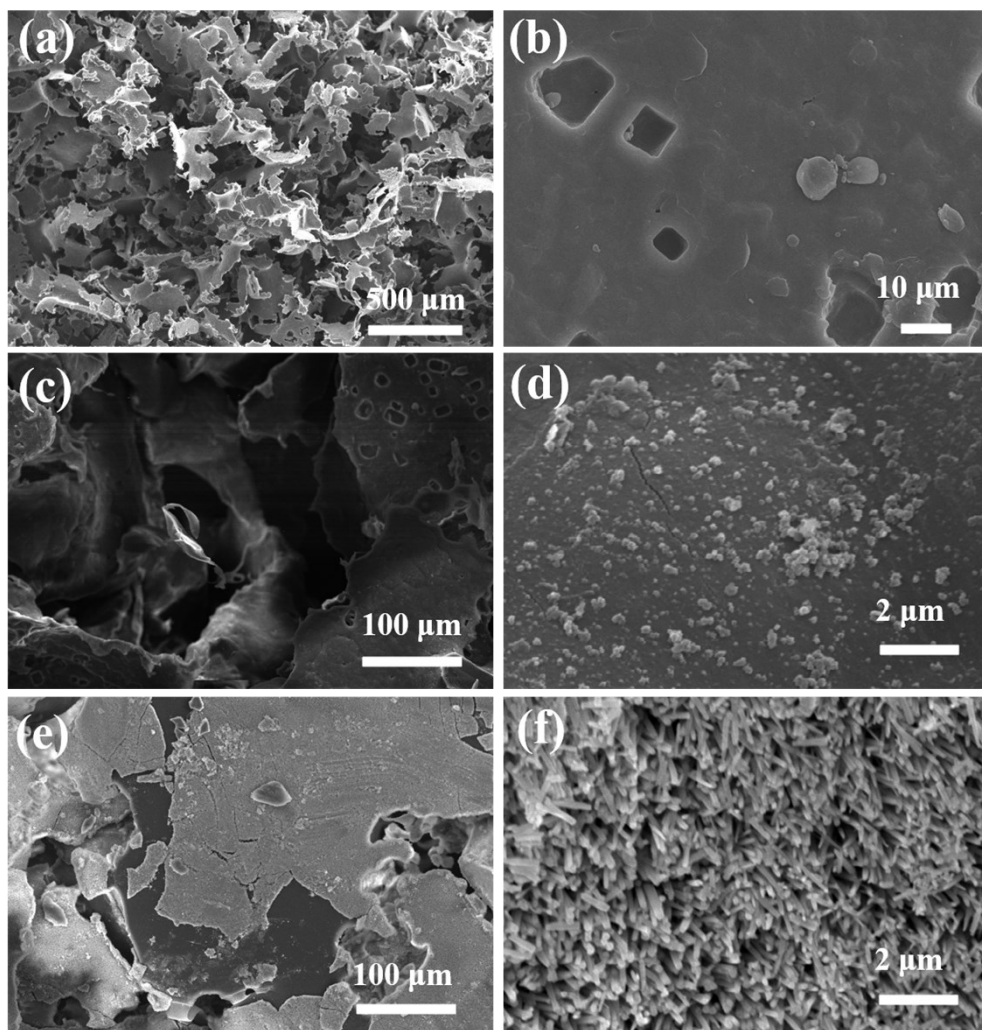


Fig.S1. SEM image of (a-b) PVDF foam, (c-d) pDA/PVDF foams and (e-f) $\text{Co}_5\text{Ni}_{2.5}\text{LDH-pDA/PVDF}$.

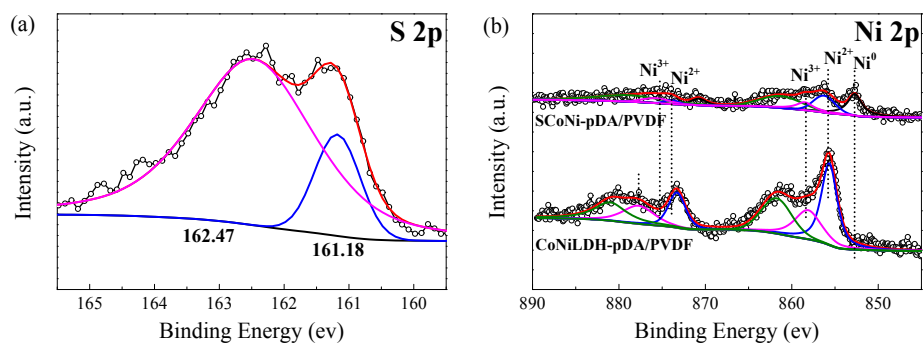


Fig.S2. XPS spectrum: (a) S 2p and (b) Ni 2p.

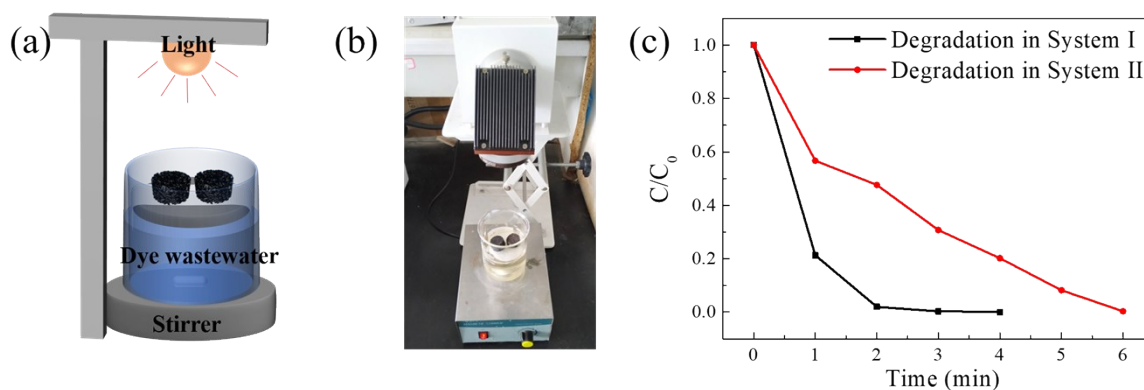


Fig.S3. (a) Schematic illustration and (b) physical photos of one-unit system for degradation and evaporation. (c) degradation efficiency in different system.

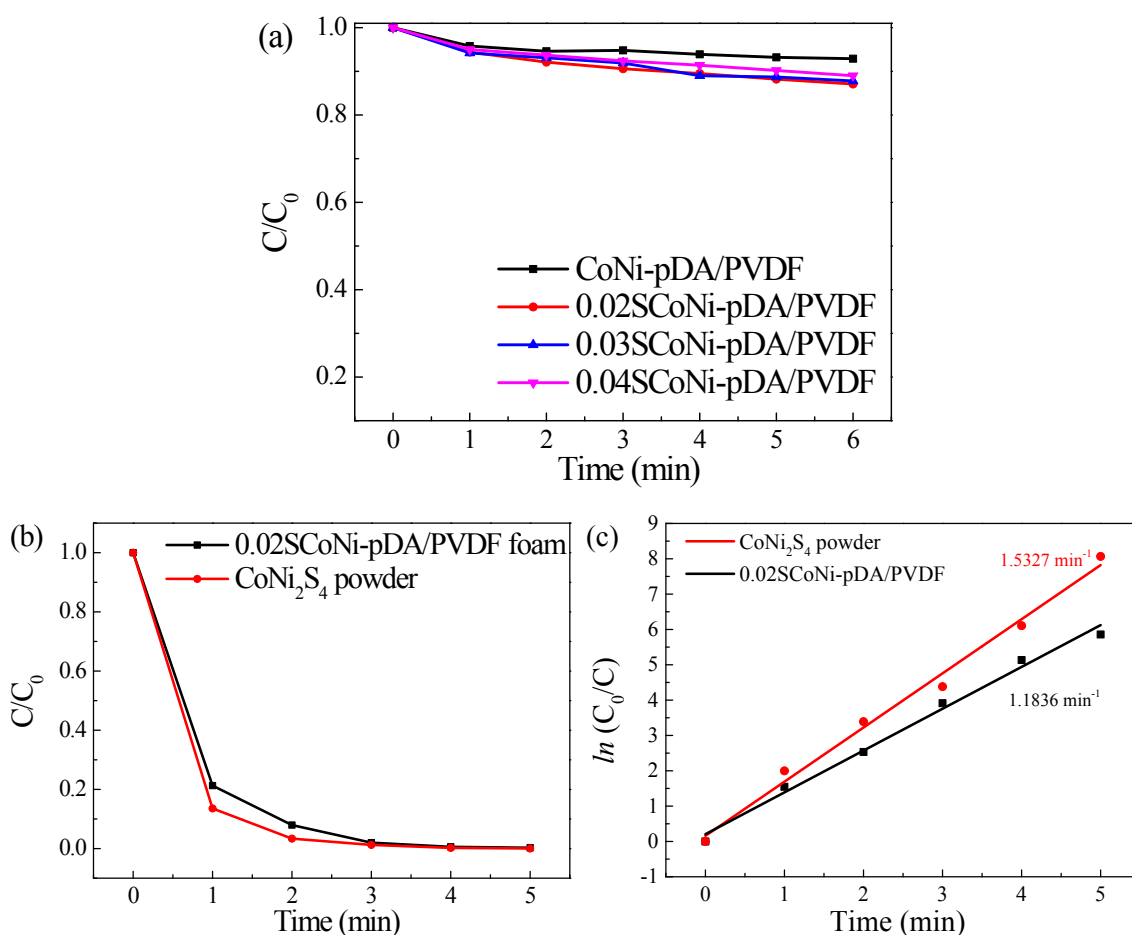


Fig.S4. (a) The adsorption capacity of different composite foams. (b-c) Comparison of catalytic performance between SCoNi-pDA/PVDF foams and powdered CoNi₂S₄.

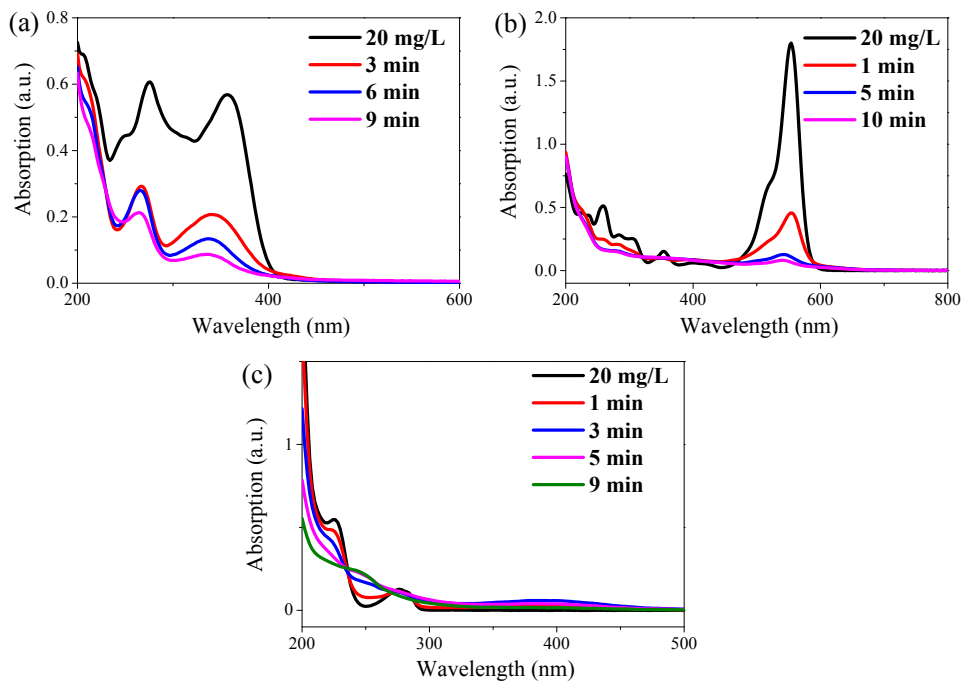


Fig.S5. Degradation efficiency of different organic pollution: (a) TC, (b) RhB and (c) BPA.

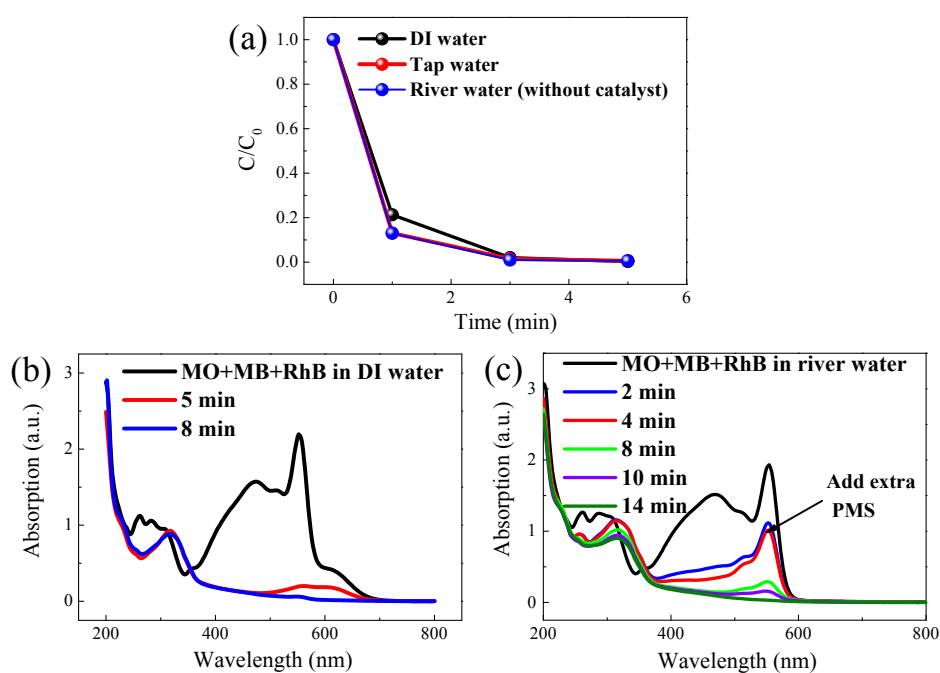


Fig.S6. Degradation of mixed dyes in (c) DI water and (d) river water. Catalytic condition: 250 mL of wastewater, pH=6.8, PMS concentration: 0.5 M, room temperature and flow velocity= 1.2 L/h.

Different background solvents such as tap water and river water were used to study the catalytic degradation process. As shown in Fig.S6a, the tap water can accelerate MB solution degradation probably due to the improvement effect of Cl^- mentioned above. Another interesting phenomenon is that 20 mg/L of MB solution dissolved in river water is gradually change to colorless without PMS and catalysts, which may be due to adsorption of MB molecular by natural organic matters and impurities. To further simulate the actual situation, the degradation of the mixed dye solution was used to explore the performance of SCoNi-pDA/PVDF foam in a complex water environment. As shown in Fig.S6b-c, mixed dyes (RhB +MO +MB) were dissolved in DI water and Yudai river water (from Jiangsu University) as target pollutants.

Characteristic absorption peaks from these three dyes were observed clearly and rapidly weaken after 5 min (Fig.S6b). After degradation for 8 min, the mixture solution becomes almost colorless, and the absorption peak of the dye disappears. When river water is selected as background solvent, the mixed solution only shows two characteristic peaks of RhB and MO, which consistent with above results. Different with DI water, the decolorization slowed down after 2 minutes. By adding an equal amount of PMS, the mixed dye can quickly decolorize and become almost colorless after 14min, which may be due to the natural organic matters (a ubiquitous substance containing carboxyl and phenolic hydroxyl groups) in river water restrain degradation process by blocking active sites on catalysts surface and quenching radicals [1, 2]. These results show that SCoNi-pDA/PVDF foams exhibit strong PMS activation activity in complex water environment and has potential in treating actual water polluted by dyes.

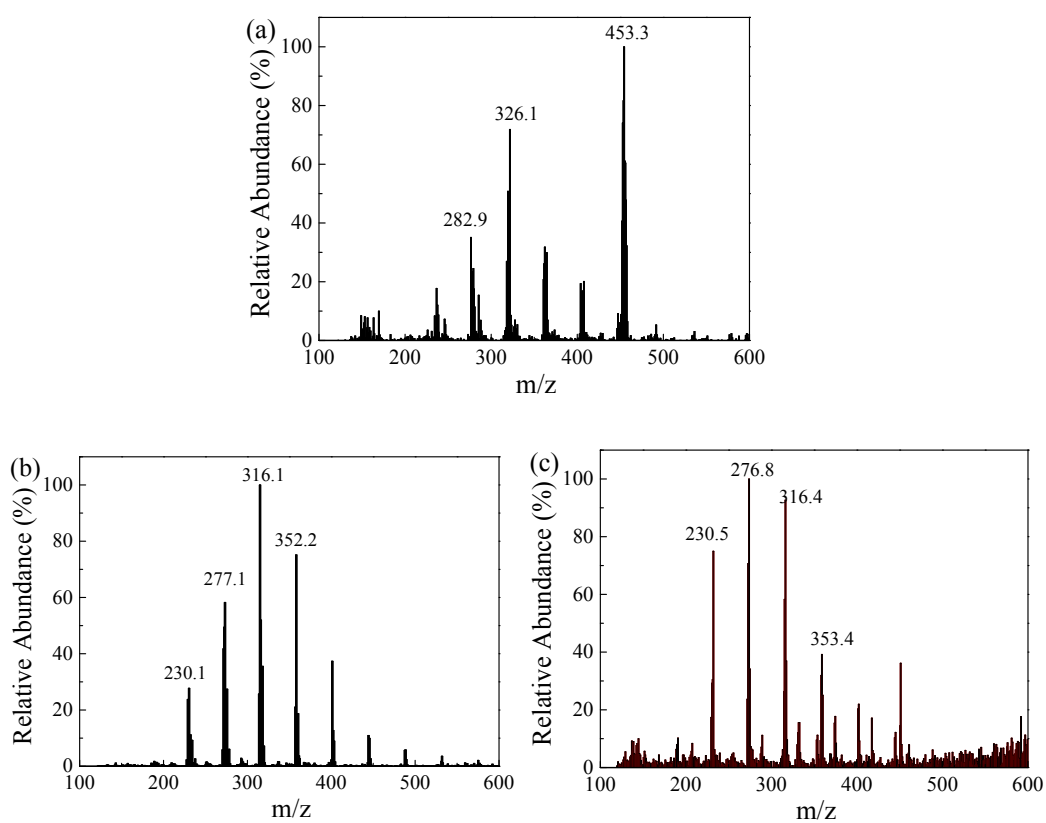


Fig.S7. LC-MS of mixed dyes wastewater after (a) 0 min, (b) 10 min and (c) 20 min of degradation.

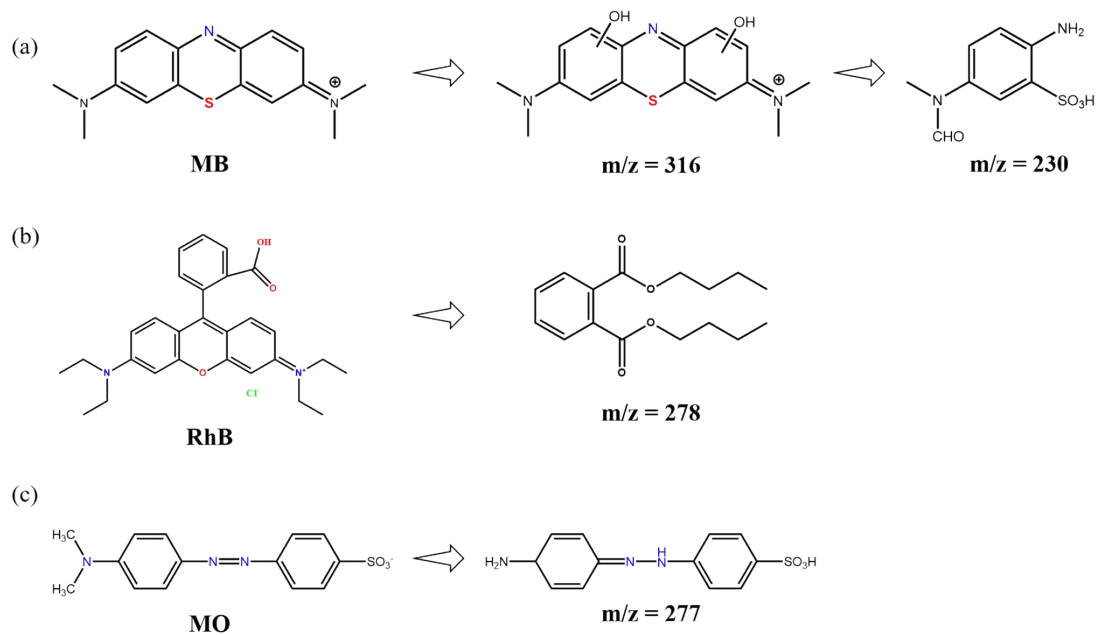


Fig.S8. The possible degradation production and pathways of mixed dyes wastewater.

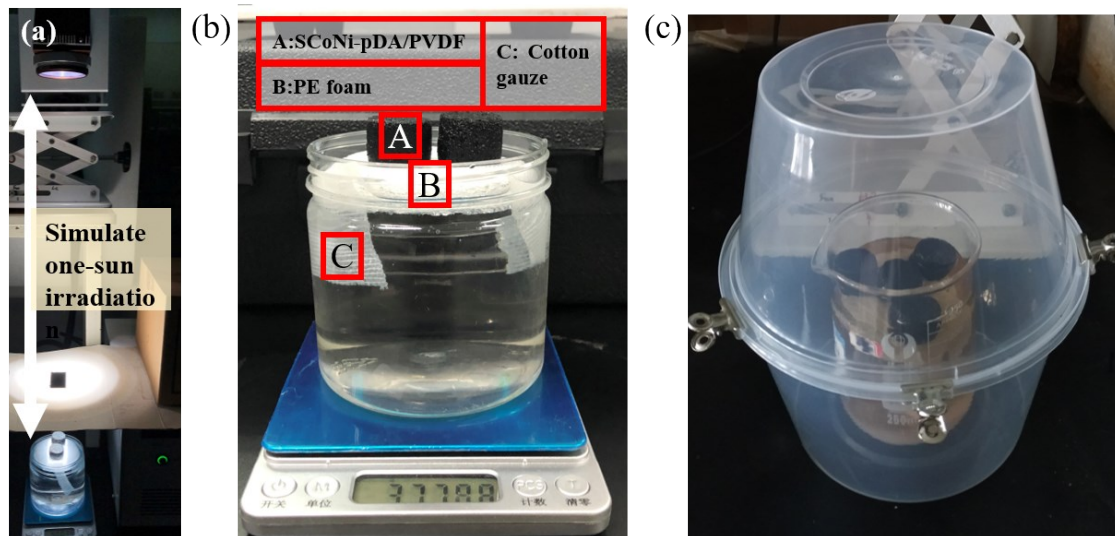


Fig.S9. (a-b) Digital photographs of evaporator setup.

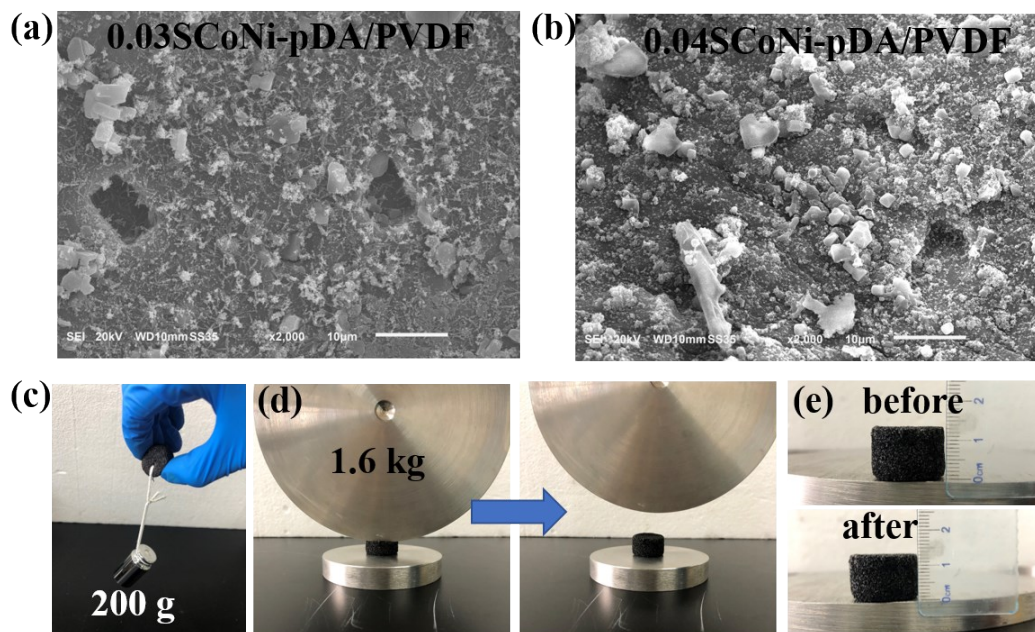


Fig.S10. (a-b) SEM images of samples. (c) The SCoNi-pDA/PVDF foams after 7 h of solar evaporation can also hold a weight of about 200 g. (d-e) SCoNi-pDA/PVDF foams also exhibits excellent flexibility.

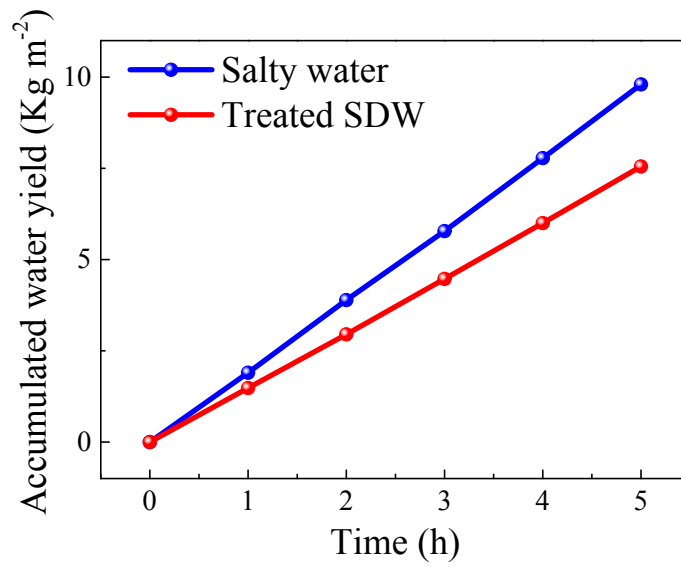


Fig.S11. The accumulated water yield during evaporation from DI water or treated SDW under simulated one-sun irradiation.

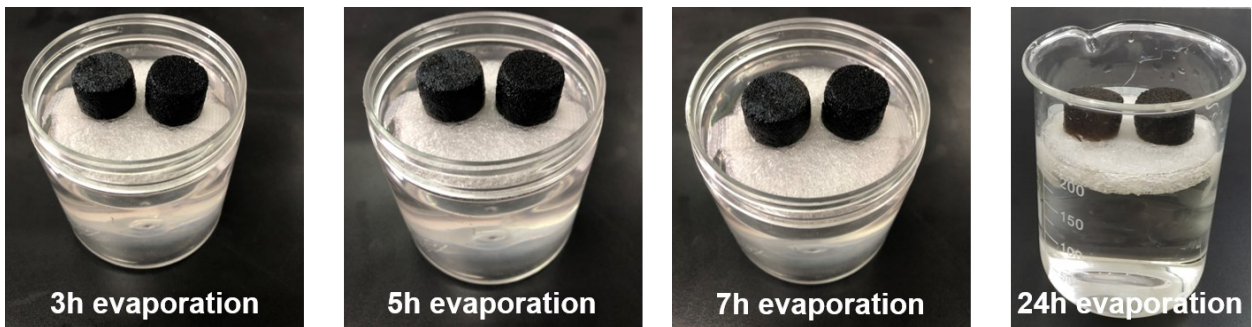


Fig.S12. The picture of SCoNi-pDA/PVDF foams after solar evaporation with different hours.

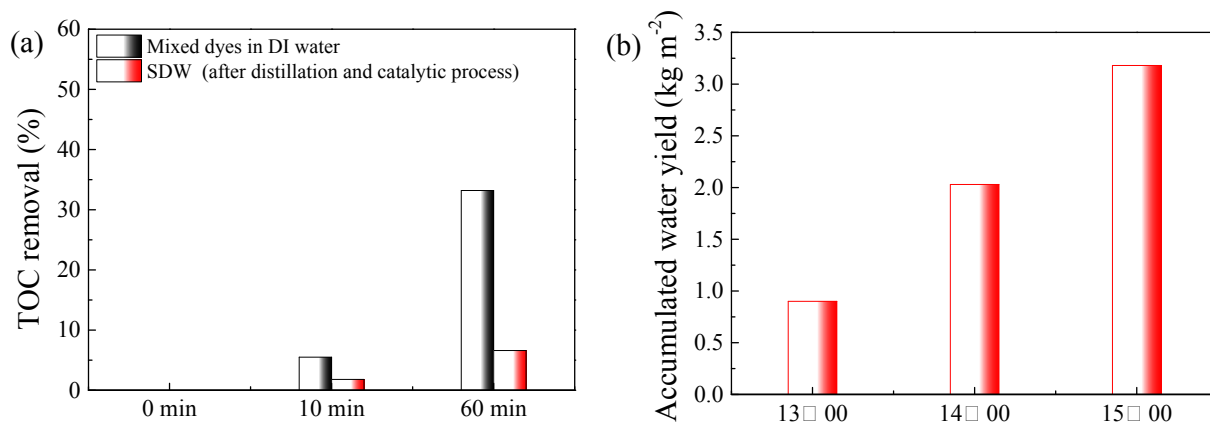


Fig.S13. (a) TOC removal of mixed dyes (after catalytic process) and the high salty dyeing wastewater (after distillation and catalytic process). (b) Collection of distilled water from treated SDW by using SCoNi-pDA/PVDF foams under natural sun irradiation.

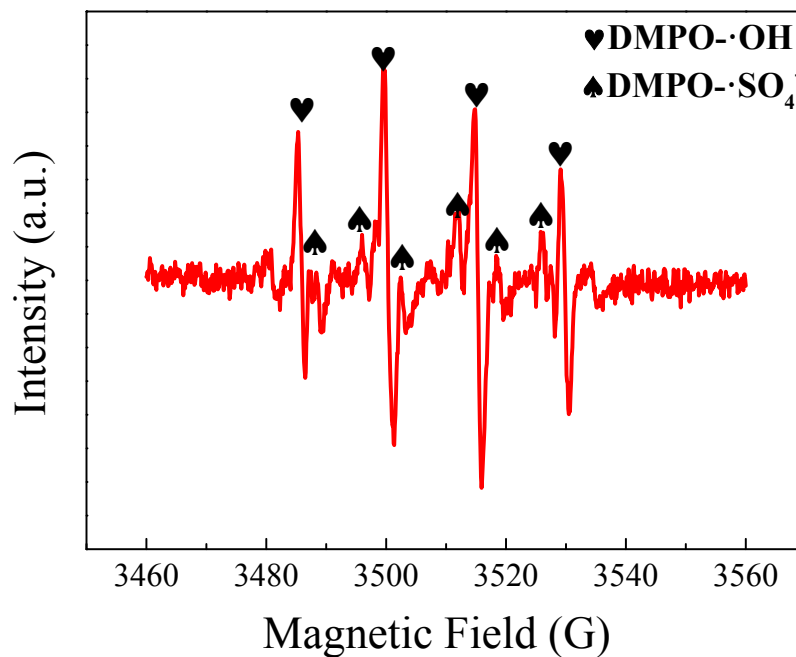


Fig.S14. The ESR signals of SO₄⁻ and ·OH produced by SCoNi-pDA/PVDF foams.

Table S1. The porosity of PVDF foams with different mass ratio of salt template.

Samples	Porosity (%)	CoNi ₂ S ₄ loading (g) (calculated by weight method)
PVDF (1:3)	77.66	--
PVDF (1:5)	83.15	--
PVDF (1:7)	88.08	--
PVDF (1:9)	88.62	--
0.02SCoNi-pDA/PVDF	88.13	0.0465
0.03SCoNi-pDA/PVDF	88.08	0.0458
0.04SCoNi-pDA/PVDF	88.16	0.0473

Table S2. The water-quality indexes of distilled water and treated feedwater.

Water-quality indexes	Distilled water (mg/L)	Feedwater (after distillation and catalytic process) (mg/L)	Integrated wastewater discharge standard- Class I (GB8978-1996)
pH (non-dimensional)	7.2	6.2	6-9
Color (dilution ratio)	8	32	50
Suspended solids	8	16	70
Na ⁺	19.72	70500	--
COD _{Cr}	56	219	100
Ammonia nitrogen	0.924	1.16	15
Total phosphorus	<0.01	<0.01	0.1
Total chromium (Cr)	<0.03	<0.03	1.5
Total cobalt	0.0067	9.2356	--
Total nickel	0.0069	2.6817	1.0

References

- [1] X. Zhou, M. Luo, C. Xie, H. Wang, J. Wang, Z. Chen, J. Xiao, Z. Chen, Tunable S doping from Co_3O_4 to Co_9S_8 for peroxymonosulfate activation: Distinguished Radical/Nonradical species and generation pathways, *Appl. Catal. B-Environ.*, 282 (2021) 119605.
- [2] W. Ma, N. Wang, Y. Fan, T. Tong, X. Han, Y. Du, Non-radical-dominated catalytic degradation of bisphenol A by ZIF-67 derived nitrogen-doped carbon nanotubes frameworks in the presence of peroxymonosulfate, *Chem. Eng. J.*, 336 (2018) 721-731.