Electronic Supplementary Information (ESI)

Constructing multivalent Co-confined N-doped C-Si hybrid hollow nanoreactor for synchronous pollutant mineralization and solar-driven interfacial water regeneration

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Detailed experimental section

Characterizations information

Transmission electron microscopy (TEM, JEM-2100F by JEOL) was employed to examine the microscale morphology of the samples. Wide-angle X-ray diffraction (XRD, XRD-6000 X by Shimadzu) was utilized to discern the crystal state of material and potential phases of active Co and carbon materials. Raman spectra were employed to validate the atomic structure of the acquired material. X-ray photoelectron spectroscopy (XPS, 5000 VP by ULVAC-PHI) facilitated the determination of the surface elemental composition and chemical state of material. The photothermal conversion capability of the materials was assessed using a solar simulator, a 360° optical path converter, and an infrared thermal imager, capturing infrared images of the materials under simulated sunlight. For comparative analysis, the photothermal imaging of the reference samples was conducted on a polymer membrane placed on dust-free paper submerged in water, utilizing the UTi260B thermal imager (UNI-T by Yulide Technology (China) Co., LTD). A sunlight solar simulator (Solar-500T, Beijing Newbit Technology) was employed to provide simulated sunlight during the imaging process.

Preparation of photothermal membrane

An appropriate quantity of the prepared photothermal material Co-SiCNO-6 was poured into a beaker containing deionized water, and the above mixtures were ultrasonically oscillated until they were completely and uniformly dispersed in the deionized water, resulting in a uniform black solution. A hydrophilic polytetrafluoroethylene filter membrane was placed in the center of the funnel, and the uniform black solution was slowly dropped onto the filter membrane with a dropper. Under the strong extraction of the vacuum pump, the photothermal material was evenly spread on the filter membrane surface. This process obtained a sample of the photothermal membrane for the interface evaporation material. The advantage of the photothermal membrane made by the hydrophilic PTFE membrane was that the photothermal material on the upper surface was not lost and did not pollute the lower body water. The lower body water passed through the hydrophilic PTFE membrane to reach the surface of the photothermal film and completed the water evaporation.

Preparation of catalytic degradation-photo-thermal water evaporation integrated device

7 mg of SA was dissolved in 15 ml of deionized water, and then the 30 mg of catalyst got dispersed in the SA solution. Following this, a circular sponge with a 3 cm diameter was taken and placed in this dispersion to absorb the liquid. The sponge was then placed in a CaCl₂ solution for cross-linking, and this procedure was repeated to finally obtain a sponge embedded with the catalyst. This device had the advantage of not only receiving light and heat for the evaporation of interfacial water but also being used for pollutant degradation and recycling.

Photothermal experiment operation description:

Initially, an appropriate amount of water was poured into a flat beaker. To prevent radiative heat loss from the evaporating heat to the water body, the interface evaporation method was employed, using thermal insulation foam to isolate the lower water body and the upper evaporation layer. A root system was utilized to pump water upwards. The top evaporation layer and the photothermal membrane were placed at the center of the top evaporation layer. To minimize heat radiation loss from the water body to the surroundings, the beaker was encased with thermal insulation foam, effectively isolating it from the surrounding environment. Subsequently, the light intensity of the simulated sunlight device was adjusted to match sunlight intensity, covering the top of the evaporation device. This device was placed on a precise balance. As the membrane materials' surface temperature rapidly rose, steam began to overflow gradually, and evaporation increased over time, resulting in a gradual decrease in the overall evaporation device's weight. The device's weight was recorded at specified intervals, and the weight loss was calculated to determine the photothermal membrane evaporation efficiency. The solar steam experiment, assembling a solar evaporator in the laboratory, involved a system that simulated sunlight illumination using a solar light

simulator. An analytical balance tracked steam production, while an infrared camera monitored temperature changes. Additionally, a light meter measured light intensity. Throughout each test, the room temperature remained between 20 ± 5 °C, with humidity levels maintained at 60 ± 10 %.

The heat loss during solar steam generation consists of three components: radiation, convection, and conduction, each contributing uniquely to the overall heat loss. A detailed analysis of these components is as follows:

Radiation:

Thermal radiation losses are calculated by the Stefan-Boltzmann equation:

$$\emptyset = \varepsilon \ A \ \mathcal{B}_1^4 - (\mathcal{T}_2^4)$$

 Φ represents the heat flux, ε is the emissivity (value is 1), A is the effective evaporation surface area (490 mm²), σ is the Stephen Boltzmann constant (value is 5.67×10⁻⁸ W m⁻² K⁻⁴), And the surface temperature of the membrane after T₁ is stably evaporated under sunlight (about 40.7 °C, 314 K), and T₂ is the ambient temperature above the membrane, so the thermal radiation of Co-SiCNO-6 membrane is calculated. The losses are calculated to be 5.4%.

In the same way as above the losses of the catalytic degradation-photothermal water

evaporation integrated device are calculated to be 8.0%.

Convection:

Convective heat loss is defined by Newton's law of cooling:

$$Q = hA\Delta T$$

where Q is the convective heat flux, and h is the convective heat transfer coefficient, which is about 5 W m⁻² K⁻¹. A is the effective evaporation surface area, about 490 mm². Δ T is the difference between the surface temperature of the prepared solar evaporation material and the ambient temperature. Therefore, the convective heat loss of the Co-SiCNO-6 membrane is calculated by a formula, yielding values of 4.2%.

In the same way as above the convective heat loss of the catalytic degradation-photothermal water evaporation integrated device is calculated to be 6.4%.

Conduction:

The thermal conduction heat loss is caused by the heat transferred from the prepared material to the water, and its calculation formula is:

$$q = kA \frac{(T_1 - T_2)}{L}$$

In the formula, q is the heat transfer and heat transfer, because it is made of PC foam for thermal insulation, so k is the thermal conductivity of PC foam about 0.03 W m⁻¹ K⁻¹, A is the heat exchange surface area, about 490 mm², where T₁ and T₂ are the surface temperature of the prepared solar evaporation material and the ambient temperature after the steady-state temperature, L is the thickness of the PC foam support (13 mm). Therefore, according to the formula, the thermal conduction heat loss of Co-SiCNO-6 membrane is calculated to be 1.9%.

In the same way as above the thermal conduction heat loss of the catalytic degradationphoto-thermal water evaporation integrated device is calculated to be 0.1%.

$$\eta = m \times h_{LV} / 3600 P_{in}$$

$$EF = m(absorber)/m(blank)$$

where m' is the evaporation rate after subtracting the evaporation rate in the dark (kg m⁻² h⁻¹), h_{Lv} is the evaporation enthalpy of water (J g⁻¹), Pin is the light intensity (1 kW m⁻²), m (Blank) is the evaporation rate without absorbent. As a result, the photothermal conversion rates of the Co-SiCNO-6 membrane and the catalytic degradation-photothermal water evaporation integrated device are 93.14% and 123.95% respectively.



Fig. S1 N₂ adsorption desorption isotherms (a) and BJH pore size distribution curves (b), HK pore size distribution curves (c) of Co-SiCNO-6, Co-SiNO-6, Co-CNO-6, and Co-NO-6.



Figure S2 Wide-angle XRD patterns of Co-SiCNO-5, Co-SiCNO-6, and Co-SiCNO-7.



Figure S3 XPS spectra of survey scans of Co-SiCNO-6, Co-CNO-6, Co-SiNO-6, and Co-NO-6



Figure S4 Reaction time dependent NFX degradation course (a) and $\ln(C_0/C)$ versus reaction time of NFX degradation (b) over catalysts with different calcination temperatures; Reaction conditions: [NFX]=20 mg·L⁻¹, [PMS]=0.1 g·L⁻¹, [catalyst]=0.2 g·L⁻¹.



Figure S5 3D fluorescence spectra during NFX degradation process with Co-SiCNO-6. Reaction condition: $[NFX] = 20 \text{ mg} \cdot \text{L}^{-1}$, $[PMS] = 0.1 \text{ g} \cdot \text{L}^{-1}$, $[catalyst] = 0.3 \text{ g} \cdot \text{L}^{-1}$.



Figure S6 (a) Time-dependent NFX degradation course curves over Co-SiCNO-6 using different reaction temperatures, and (b) corresponding kinetic fitting curves: $\ln(C_0/C)$ v.s. reaction time. Reaction condition: $[NFX] = 20 \text{ mg} \cdot \text{L}^{-1}$, $[PMS] = 0.1 \text{ g} \cdot \text{L}^{-1}$, $[catalyst] = 0.3 \text{ g} \cdot \text{L}^{-1}$. (f) Arrhenius plots derived from corresponding kinetic curves of Co-SiCNO-6: $\ln(k)$ v.s. T^{-1} .



Figure S7 Time-dependent NFX degradation course curves over Co-SiCNO-6 with different anionic interferents. Reaction condition: $[NFX] = 20 \text{ mg} \cdot \text{L}^{-1}$, $[PMS] = 0.1 \text{ g} \cdot \text{L}^{-1}$, $[catalyst] = 0.3 \text{ g} \cdot \text{L}^{-1}$, $[anionic] = 1 \text{ mmol} \cdot \text{L}^{-1}$.



Figure S8 (a) NFX degradation course curves by Co-SiCNO-6 system in actual water samples. Reaction condition: [NFX] = 20 mg·L⁻¹, [PMS] = 0.1 g·L⁻¹, [catalyst] = 0.3 g·L⁻¹. (b) The cycling experiment results of Co-SiCNO-6 in activation of PMS for NFX degradation; Reaction condition: [NFX] = 20 mg·L⁻¹, [PMS] = 0.1 g·L⁻¹, [catalyst] = 0.3 g·L⁻¹. (c) Time-dependent degradation course of different pollutants over Co-SiCNO-6; Reaction condition: [NFX] = 20 mg·L⁻¹, [PMS] = 0.1 g·L⁻¹, [catalyst] = 0.3 g·L⁻¹.



Fig. S9 Infrared thermograms of dried membrane (a) and wetting membrane for deionized water (b), norfloxacin (c) and carbamazepine (d), respectively composed of Co-SiCNO-6.



Fig. S10 UV-vis-NIR absorption spectrum of Co-SiCNO-6 nanocomposite with AM 1.5 solar irradiance as a reference in red marking and natural light.



Fig. S11 Cyclic evaporation experiment for NFX solution and CBZ solution using 2D separated membrane. Operation condition: temperature: 20 ± 5 °C, relative humidity: 60 \pm 10 %.

Sample	a _{s,BET} (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (nm) 5.82		
Co-SiCNO-6	392.42	0.57	5.82		
Co-SiNO-6	546.02	0.68	4.95		
Co-CNO-6	218.27	0.68	12.12		
Co-NO-6	201.38	0.57	11.63		

Table S1. Detailed structural properties of Co-SiCNO-6, Co-SiNO-6, Co-CNO-6, and Co-NO-6.

Table S2 The Co contents of catalysts of Co-SiCNO-6, Co-SiNO-6, Co-CNO-6, and Co-NO-6.

Sample	Co content (wt%)	Co leaching content (wt%)
Co-SiCNO-6	5.69%	5.50%
Co-SiNO-6	9.73%	5.64%
Co-CNO-6	67.45%	17.97%
Co-NO-6	21.74%	14.65%

Table S3 Total organic carbon (TOC) content before and after NFX degradation reaction by Co-SiCNO-6, Co-SiNO-6, Co-CNO-6, and Co-NO-6 catalysts. Reaction conditions: $[NFX] = 20 \text{ mg} \cdot \text{L}^{-1}$, $[PMS] = 0.1 \text{ g} \cdot \text{L}^{-1}$, [Reaction Time] = 60 min.

Sample	TOC (m	Removal Rate (%)	
	Before	After	
Co-SiCNO-6	21.45	10.52	50.96
Co-SiNO-6	21.45	14.29	33.36
Co-CNO-6	21.45	13.41	37.48
Co-NO-6	21.45	14.62	31.84

NEV						Rate	
NFX (mg·L ⁻ ¹)	Time (min)	Conv. (%)	Catalyst	Dosage (g·L ⁻¹)	PMS (g·L ⁻¹)	constant k (min ⁻ ¹)	Ref.
20	17	89.9	Co-SiCNO-6	0.3	0.1	0.917	This work
3	45	95~	Co ₃ O ₄ @Fe ₂ O ₃	0.2	0.03	0.140	[1]
32	20	100	Fe/Fe ₃ C@NG	0.1	0.15	0.22	[2]
5	60	94.8	Co ₃ O ₄ @CNT	0.12	0.076	0.044	[3]
10	30	99.1	β -CD@Fe ₃ O ₄	0.4	0.608	0.158	[4]
30	30	100	Fe ₂ O ₃ @CoFe ₂ O	0.3	0.061	0.188	[5]
5	30	80	CuNiN@C	0.2	0.304	-	[6]

Table S4. Comparison of NFX degradation based on optimal Co-SiCNO-6 and several comparative catalysts.

Table S5 Statistics results for evaporation rate and corresponding conversion efficiency

 of the Co-SiCNO-6 and reported catalysts.

Photothermal Materials	Water Evaporation Rate (kg m ⁻² h ⁻¹)	PTCE (%)	References
Co-SiCNO-6	1.50	93.14	This work
Janus MXene-based	1.34	90.81	[7]
rGO-MWCNT	1.22	80.4	[8]
SiO ₂ /MWCNTs-COOH/PAN	1.28	85.52	[9]
CR-TPE-T	1.27	72.7	[10]
FeS2-Mo2S3/GF@PDA@STA	1.34	89	[11]
CNF/CNT aerogel	1.11	76.3	[12]
PVA-CNP/PDMS foams	1.26	80	[13]
Fe ₂ O ₃ /CNT/Ni foam	1.48	81.3	[14]

Table S6 The energy	loss of the	photothermal	membrane and	l the sponge	evaporator.
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Energy loss	Radiation loss	Convection loss	Conduction loss	Total
The separated 2D membrane	5.4%	4.2%	1.9%	11.5%
The sponge evaporator	8.0%	6.4%	0.1%	14.5%

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