Supplementary Material

Synchronous removal of antibiotics in sewage effluent by surface-anchored photocatalytic nanofiltration membrane in a continuous dynamic process

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Supplementary content:

Table S1. The main physicochemical properties of both antibiotics used in this study.

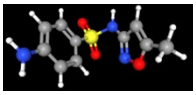
Compound	Sulfamethoxazole	Trimethoprim
Molecular structure		
Molecular formula	$C_{10}H_{11}N_3O_3S$	$C_{14}H_{18}N_4O_3$
Molecular weight (g/mol)	253.28	290.32
Chemical safety		
Log K_{ow}	−0.56	1.28
pK_a	10.4	7.16
Density (g/cm^3)	1.39	1.252
Isoelectric point	4.62	9.58
Diffusion coefficient (10^{-10} m^2/s)	6.01	5.65
Stokes radius (nm)	0.396	0.459
K_d (L/Kg)	4.3-20.1	85.5-367.2
Water-solubility	Sparingly soluble	
Charge (pH 7.4)	Negative	Positive
CAS	723-46-6	738-70-5

Table S2. Water quality before and after ultrafiltration of secondary effluent from Xiaoshangzhuang Sewage Treatment Plant in Xinxiang city and related discharge standard of pollutants for municipal wastewater treatment plant.

Parameters	Unit	Secondary effluent	UF filtrate	GB 18918-2002[a]
BOD_5		9.13	6.7	10
COD		35.1	30.1	50
TN		2.21	2.19	15
NH_3-N		1.43	1.41	5 (8)[b]
TP		0.44	0.43	0.5
TSS	mg/L	9.22	0.58	10
DOC		28.4	16.4	-
TDS		697	682	-
Na^+		118.6	109.5	-
Ca^{2+}		74.9	72.4	-
Cl^-		99.5	97.6	-
pH	-	8.37	8.29	6.0-9.0
UV_{254}	cm^{-1}	0.109	0.054	-
Turbidity	NTU	0.68	0.02	-
Conductivity	μS/cm	1398	1338	-

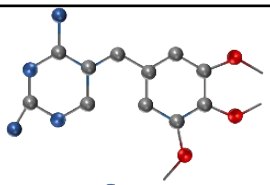
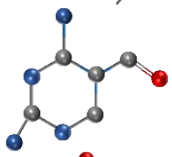
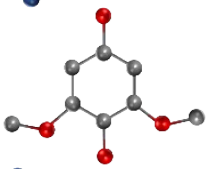
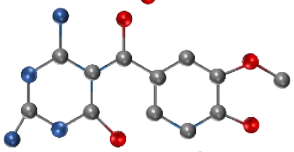
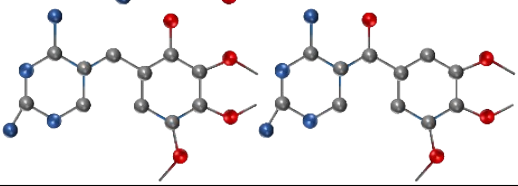
[a] GB 18918-2002: Grade I-A in discharge standard of pollutants for municipal wastewater treatment plant in China.

[b] The value outside the parenthese is water temperature > 12℃; The value in bracket is the control indicator when the water temperature is ≤ 12℃.

Table S3. BET characterization of pristine g-C_3N_4, NCN, the optimal HNCN-2.

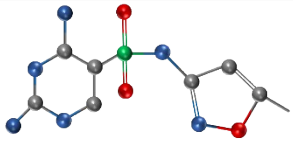
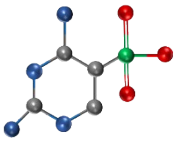
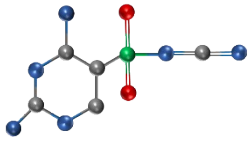
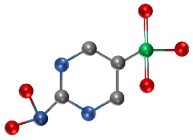
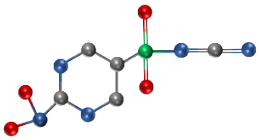
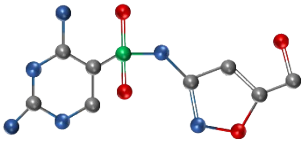
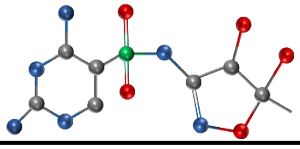
Sample	g-C_3N_4	NCN	HNCN-2
Specific surface area (m^2/g)	76.66	67.31	177.8
Pore volume (cm^3/g)	0.18	0.149	0.358

Table S4. The main degradation intermediates of trimethoprim in PNF-2-light scheme.

Compound	m/z	Molecular structures
Trimethoprim	291	
A	139	
B	171	
C	279	
D_1, D_2	307	

C N O

Table S5. The major degradation intermediates of sulfamethoxazole in PNF-2-light scheme.

Compound	m/z	Molecular structures
Sulfamethoxazole	253	
A	174	
B	198	
C	201	
D	226	
E	266	
F	288	

C N O S

Additional details on experimental section

Text S1 Auxiliary reagents

Graphene oxide, glycidyltrimethylammonium chloride (GDTMAC) and 3-aminopropyltriethoxysilane (APTES) for the synthesis of quaternized graphene oxide (QGO), trimesoyl chloride (TMC, 98.0%), fluorescein isothiocyanate isomer I and dimethyl sulfoxide were supplied by Macklin (China). Furthermore, peptone, yeast extract, glycerin were obtained from Beijing Aoboxing Bio-Tech Co., Ltd (China).

Text S2 Synthesis processes of QGO precursor and HNCN photocatalysts

QGO was synthesized as follows: Specifically, 150 mL APTES and 500 g GO nanosheets were first dissolved in DI water assisted by ultrasonication. Then, the homogeneous mixture was stirred at 333 K for 8 h, and the suspension was centrifuged and washed thoroughly with DI water and ethanol, respectively. Finally, 0.25 g obtained intermediate product and 0.50 g GDTMAC were put in 250 mL DI water, and the formed black mixture was again stirred firstly at 298 K for 3 h and then at 353 K for 6 h, followed by cooling, centrifugation and washing with DI water and ethanol, respectively.

Based on a modified hydrothermal method in previous studies, [1] for the fabrication of NCQDs precursor, urea and citric acid with the mass ratio of 1:3 were highly dispersed into a certain amount of DI water at first. Then, the resultant mixture was added into an autoclave for hydrothermal treatment at 453 K for 5 h. Subsequently, the obtained tan suspension was naturally cooled down and adjusted to pH=7, closely followed by centrifuging at 5000 rpm for 0.5 h to remove impurities. After that, a certain amount of the gained NCQDs solution and 5 g of urea were completely mixed into 20 mL DI water, which was then maintained at 343 K to remove the solvent. [2] Hereafter, the obtained brown powder was heated for 3h at 823 K (first high temperature calcination) to obtain the intermediate of NCQDs modified carbon nitride (namely NCN). For the remaining step, this intermediate was calcined at high temperature again involving a heating rate of 278 $K \cdot min^{-1}$ lasting for different periods of time (2 h, 4 h, 6 h), [3] and thus the synthesized photocatalysts were briefly labeled as HNCN-1, HNCN-2 and HNCN-3, respectively. Besides, the pure g-C_3N_4 was prepared by the same synthetic process without NCQDs and secondary high temperature calcination.

Text S3 Photocatalyst characterization

The chemical compositions, structure, surface morphologies, surface hydrophilicity, crystal structure and photoluminescence (PL) spectra of the relevant photocatalysts were obtained from XPS (ESCALAB 250Xi, USA), ATR-FTIR (NEXUS, USA), FE-SEM (JSM-6390LV, Japan), goniometer (Theta, Finland), XRD (X' Pert3 Powder, Netherlands) and HORIBA FRANCE SAS (LabRAM HR Evolution, France) respectively. In addition, the pore distribution and specific surface area of these nanomaterials were analyzed by N_2 adsorption-desorption isotherms at a fully automated multi-station surface, micropore and mesoporous pore analyzers (BELSORP series, Japan). The visible light absorption range and band gap value were recorded by using an ultraviolet-visible spectrophotometer (UV-3600 plus, China) over the range of 300–600 nm, and $BaSO_4$ as the reference material.

Text S4 Radical species trapping experiment

The radical species generated during sulfamethoxazole photocatalysis degradation were detected through trapping test. Under the same conditions as the photocatalysis experiment, 1 mM of methanol (MeOH), isopropanol (IPA) and ammonium oxalate (AO) were added into the sulfamethoxazole aqueous solution containing the HNCN-2 photocatalyst to quench the ❿O_2^-, ❿OH and hole h^+ radicals, respectively. The results are plotted in Fig. S9, which shows that the degradation of target antibiotics by HNCN-2 was dominated by ❿O_2^- reduction, followed by ❿OH.

Text S5 Determination of photocatalytic degradation by-products

High-performance liquid chromatography-triple quadrupole mass spectrometer (HPLC-MS, Agilent) was used to identify the transformation products of sulfamethoxazole and trimethoprim. The initial concentration of each target antibiotic was set at 1 ppm, and the permeate samples collected at 2 h of irradiation for HPLC-MS analysis. Full-scan MS and MS/MS spectra were obtained by scanning m/z from

50 to 500. Ten major transformation products were confirmed (Tables S(4-5)).

Overall, the peak intensities of sulfamethoxazole and trimethoprim molecules (m/z = 253 and 291) gradually decreased with the illumination time, while the peak intensities of the substances with smaller or several bigger m/z values were first increased with irradiation time and then slowly decreased upon further irradiation within 2 h, which means that both target antibiotics were gradually degraded into more hydrophilic molecules by HNCN-2, and further illumination mineralized these products to a certain extent.

Text S6 Water quality analysis

Total dissolved solids (TDS), turbidity, pH, total organic carbon (TOC), chromaticity and NH_3-N of both influent and effluent samples of each treatment unit were determined by conductivity meter (DDS-307A, China), digital turbidimeter (HI83414, Italy), pH-meter (PHSJ-3F, China), TOC/TNb analyzer (Vario, Germany), dilution multiple (GB 11903-89) and Nessler's reagent colorimetric methods, respectively. Ionic type and content were recorded by inductively coupled plasma mass spectrometer (ICP-MS, ELAN DRC-e, USA). Other indexes including BOD_5, COD, TP, TN were measured according to the standard methods of State Environmental Protection Administration of China. [4]

Text S7 Acute and chronic toxicity tests

The liquid culture media of Q67 were prepared according to the method in previous studies. [5, 6] Briefly, luminescent bacteria Q67 were cultured in liquid medium containing the desired nutrients for 12-16 h (120 rpm, 295 K) to reach the logarithmic growth phase. Then, the bacterial suspension and each permeate/Milli-Q water (as the control) were added to the sterilized centrifuge tubes at a volume ratio of 1:1, after which they were placed in a shaker for 0.25 h incubation. Afterwards, 200 μL of each

mixture was pipetted into a 96 micro-porous plate (MilliQ water was added in the 36 wells at the edge to prevent edge effects), the relative light units (RLU) of Q67 in the test microplate were then measured using the multi-mode microplate detection system (PerkinElmer Ensight, Singapore). At the same time, after the remaining mixtures were incubated for 12h, their RLU were determined according to the same procedure.

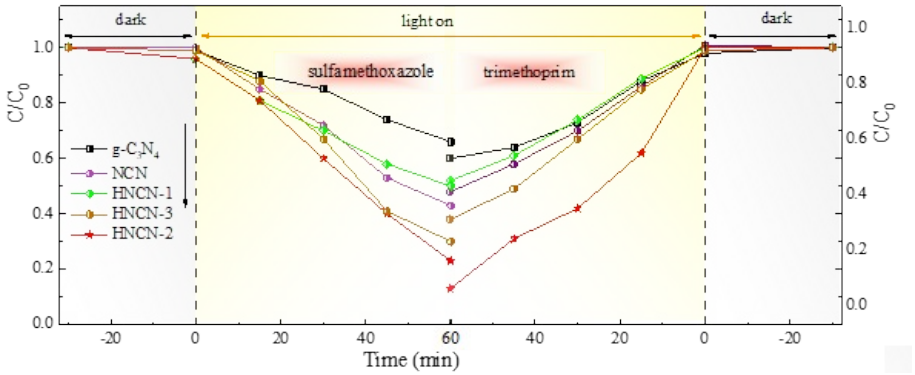


Fig. S1. Effect of different photocatalysts on the degradation performance of sulfamethoxazole and trimethoprim in the static state. (Initial sulfamethoxazole / trimethoprim concentration = 2 mg·L^{-1}, photocatalyst dosage = 200 mg·L^{-1}).

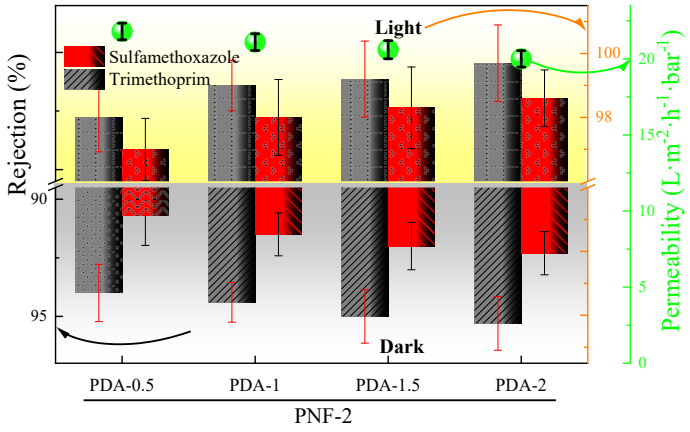


Fig. S2. Effects of different concentrations of PDA on the resultant PNF-2 membranes removal performance in darkness and visible light irradiation.

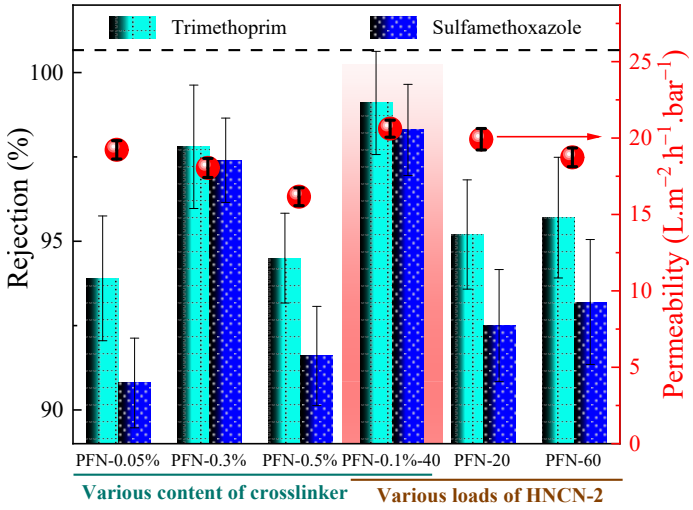


Fig. S3. Effects of different concentrations of crosslinker and HNCN-2 on the resultant PNF membranes removal performance.

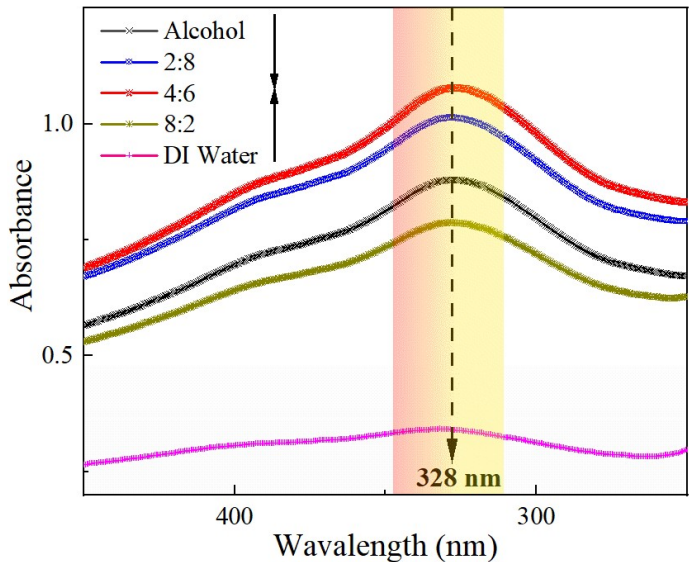


Fig. S4. UV-vis spectra of HNCN-2 supernatant samples derived from water and ethanol solution with various volume ratios.

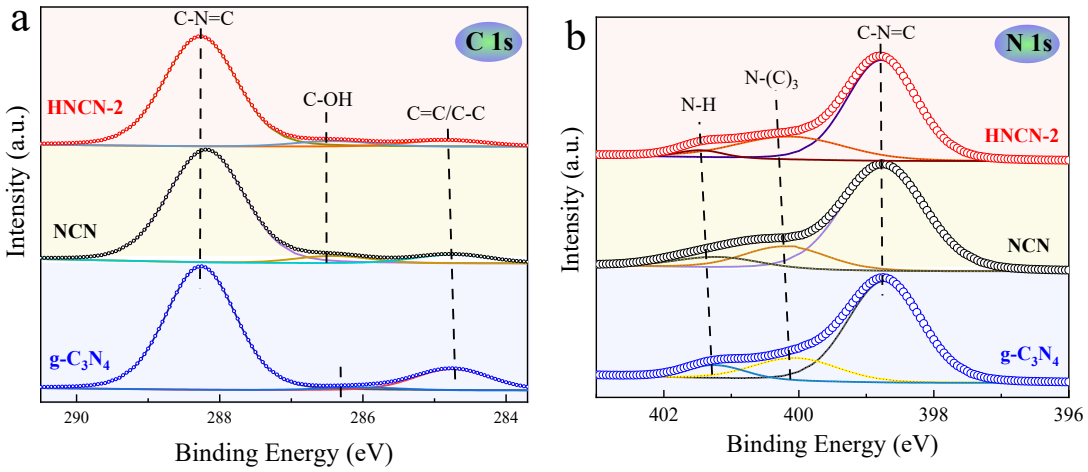


Fig. S5. High resolution XPS spectra of C 1s (a) and N 1s (b) of g-C_3N_4, NCN and HNCN-2 photocatalysts.

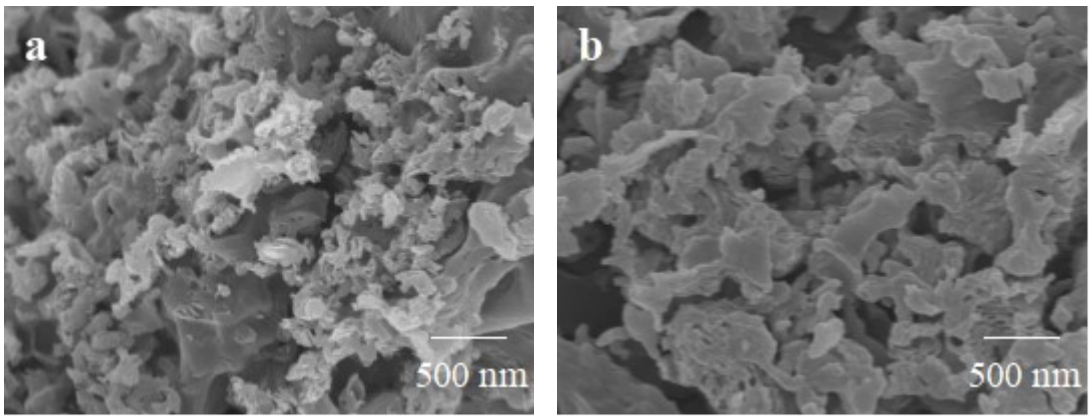


Fig. S6. FE-SEM images of g-C_3N_4 (a) and NCN (b) photocatalysts.

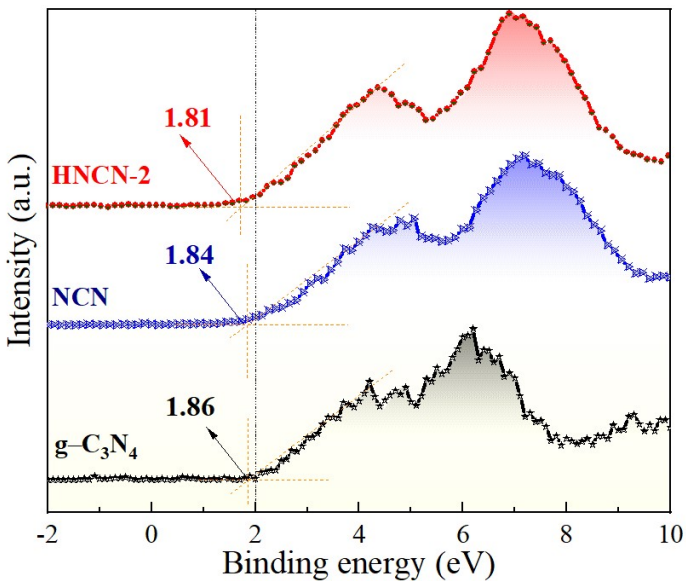


Fig. S7. VB-XPS spectra of pristine g-C_3N_4, NCN and HNCN-2.

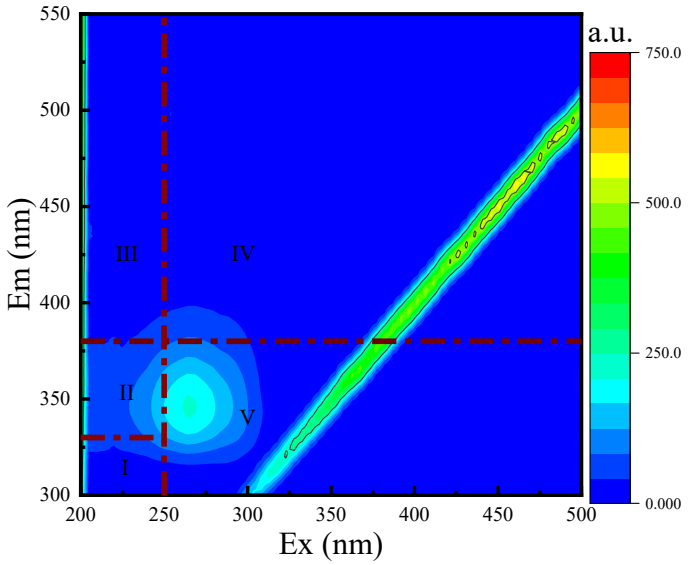


Fig. S8. 3DEEM fluorescence spectra of the influent only containing selected antibiotics.

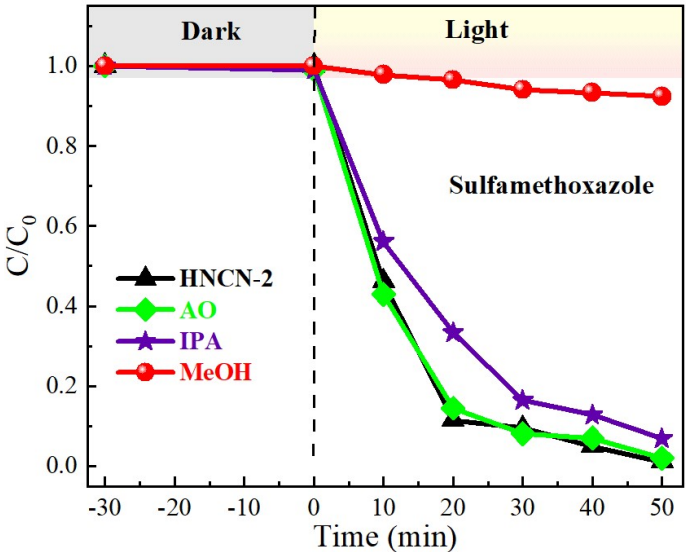


Fig. S9. Effects of different scavengers (1 mM MeOH, IPA, AO) on the degradation kinetics towards sulfamethoxazole.

References

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