Supporting Information

Construction of Janus-structured ZnO@ZIF-8(-NH_2)/Cellulose Nanofiber Foam for Highly Efficient Adsorption and Photo-catalytic Assisted Desorption of Tetracycline

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1. Experimental

1.1. Experimental material

Cellulose nanofibers (CNF) were synthesized according to a previously reported method.[1] Tetracycline (TC, $C_{22}H_{24}N_2O_8$, 98%) was acquired from Solarbio (Beijing, China). 2-methylimidazole (2-MeIM, $C_4H_6N_2$, 98%) was received from Sigma-Aldrich (Shanghai, China). Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 98%) and 5-amino-4-imidazolamide (AICA, $C_4H_6N_4O$, 98%) were provided by Aladdin Reagents (Shanghai, China) Co., Ltd. Sodium hydroxide (NaOH, 96.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd. China. All chemicals were used as received without further purification.

1.2. Preparation of CNFs suspension

Briefly, 2g of CNFs were placed in 250 mL Erlenmeyer flasks, and then deionized water was added to dilute the solution concentration to 2 wt.%. Finally, a high pressure homogenizer (M-110EH-30, Netherlands) was used for homogenization.

1.3. Characterization methodology

The materials were characterized using a scanning electron microscope (SEM, SU8020). Before analysis, the sample was coated with gold in a high vacuum. Powder X-ray diffraction (PXRD) patterns were recorded (5° to 50°) at a 0.03 °/min scanning rate. Bruker Vector instrument was employed to obtain Fourier Transform Infrared Spectrometry (FTIR) data in the 400-4000 cm^{-1} range. METTLER TOLEDO (TGA/DSC 3+) instrument was used to acquire thermogravimetric analysis (TGA) data from 303-1273 K at a 10 K/min ramping rate under an N_2 condition. XPS investigations to analyze the surface elemental composition and their states were carried out by an

Escalab 250Xi X-ray photoelectron spectrometer (Thermo Fisher, USA). The pore size distribution and texture of samples were analyzed *via* N_2 adsorption-desorption isotherms on a surface area analyzer (ASAP-2460, Micromeritics). Prior to each adsorption test, the materials were vacuum dried at 353 K for 10 h under a vacuum pressure of < 0.05 Pa. A UV-vis spectrophotometer (TU-1901, Beijing Persee General Instrument Co., Ltd.) was used to record the UV-vis diffuse reflectance spectra (DRS) of the adsorbents.

2. Figures

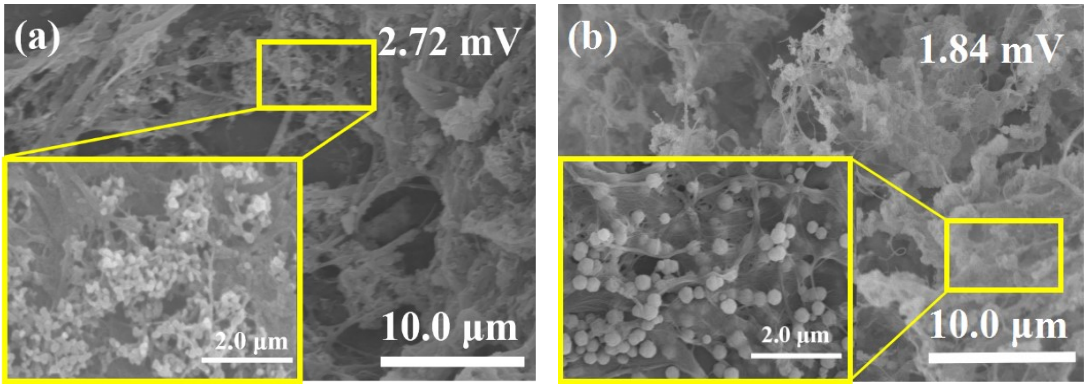

Fig. S1. SEM images of (a) C-ZnO foam, (b) C-ZIF foam.

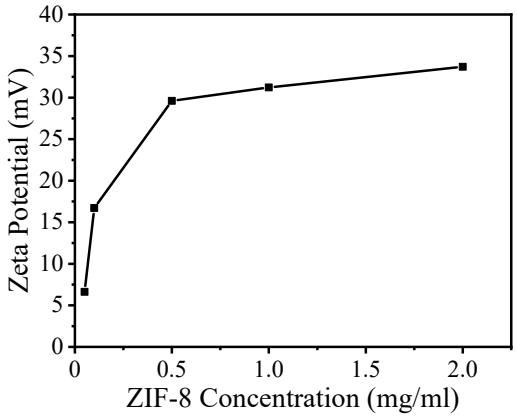

Fig. S2. Dependence of zeta potential values and concentration of pure ZIF-8 solution.

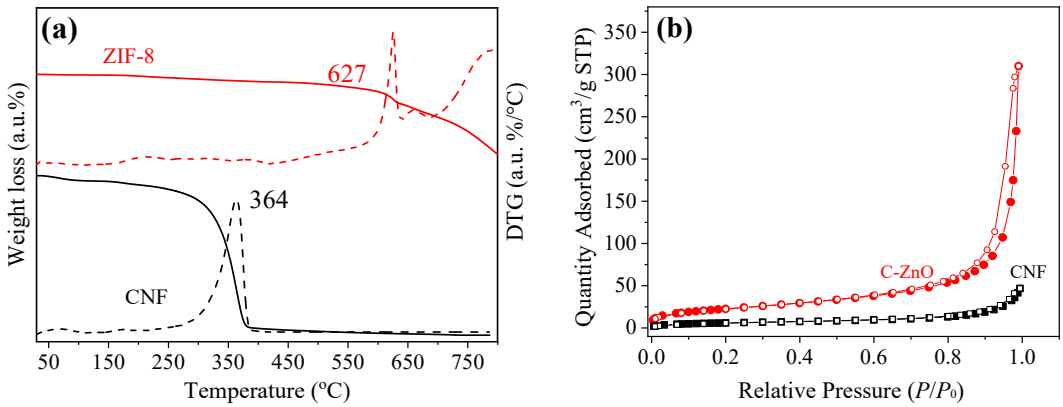

Fig. S3. (a) TG and DTG curves of CNF foam and ZIF-8; (b) N_2 adsorption-desorption isotherms of CNF foam and C-ZnO foam.

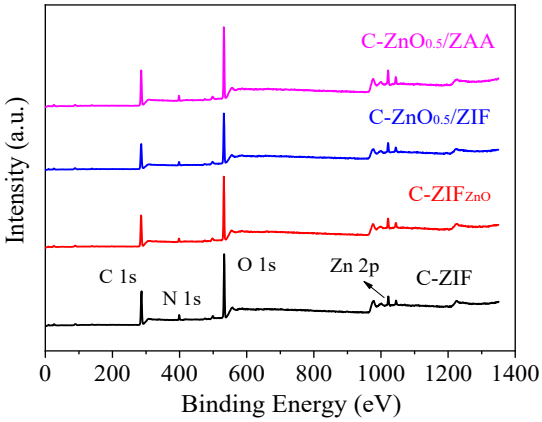

Fig. S4. XPS survey spectra of C-ZIF, C-ZIF_{ZnO}, C-$ZnO_{0.5}$/ZIF and C-$ZnO_{0.5}$/ZAA foams.

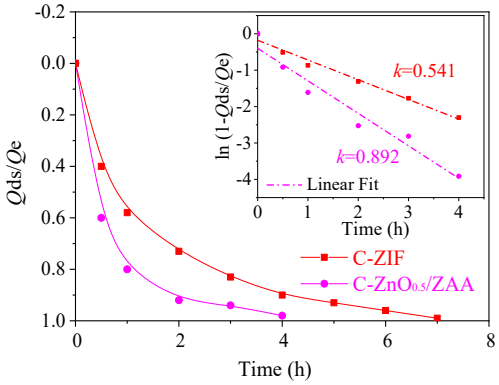

Fig. S5. TC desorption rate curves of C-$ZnO_{0.5}$/ZAA foam and C-ZIF foam (inset is the corresponding linear relation between ln (1-Q_{ds}/Q_e)).

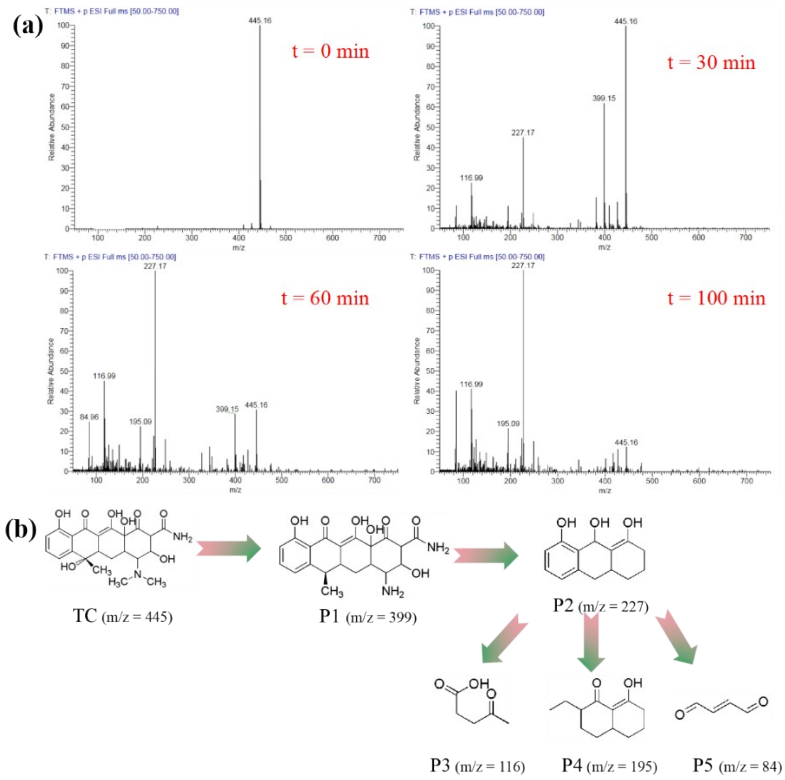

Fig. S6. (a) HPLC-MS peaks for photodegradation products of TC after different photocatalytic time (dosage: 0.05 g/L, initial TC concentration = 20 mg/L, V = 200 mL, *T* = 25 ℃), (b) Possible routes for tetracycline degradation during photocatalytic desorption.

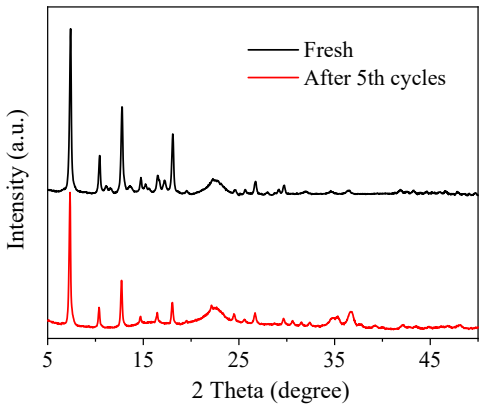

Fig. S7. XRD of C-$ZnO_{0.5}$/ZAA foam after 5th cyclic adsorption experiments.

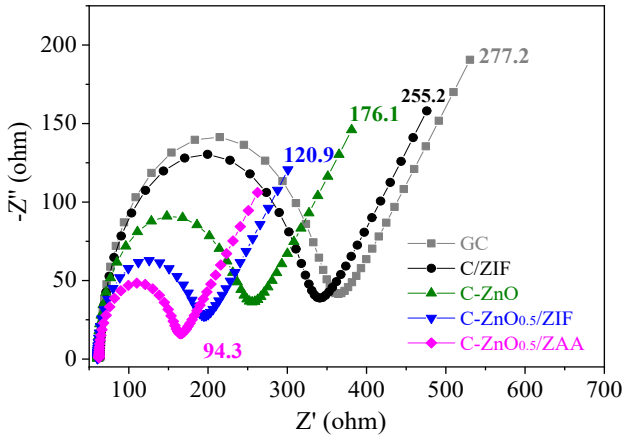

Fig. S8. EIS spectra of C-ZIF, C-ZnO, C-$ZnO_{0.5}$/ZIF, C-$ZnO_{0.5}$/ZAA foams.

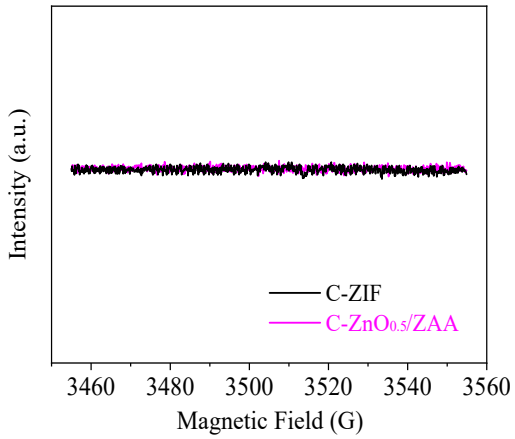

Fig. S9. ESR spectra of DMPO-·O_2^- after 10 min on C-ZIF foam and C-$ZnO_{0.5}$/ZAA foam in dark environment.

3. Tables

Table S1. Pore structure parameters of CNF, C-ZnO, C-ZIF, C-ZIF_{ZnO}, C-$ZnO_{0.5}$/ZIF and C-$ZnO_{0.5}$/ZAA foams.

Sample	S_{BET}* (m²/g)	S_{Micro}* (m²/g)	S_{Meso}* (m²/g)	V_{Meso}* (cm³/g)	V_{Micro}* (cm³/g)
CNF	21.8	-	21.8	0.07	-
C-ZnO	81.8	-	81.8	0.47	-
C-ZIF	259.4	209.4	50.0	0.16	0.08
C-ZIF_{ZnO}	304.4	195.8	108.6	0.50	0.08
C-$ZnO_{0.5}$/ZIF	340.3	288.7	51.6	0.17	0.11
C-$ZnO_{0.5}$/ZAA	555.7	440.0	115.7	0.25	0.17

*S_{BET}, S_{Micro} and S_{Meso} (m^2/g) : BET specific surface area, surface area supplied from micropores (<2.0 nm), and surface area supplied from micropores (> 2.0 nm).

*V_{micro} and V_{Meso} (cm^3/g) : pore volume supplied from micropores (< 2.0 nm) and mesopores (>2.0 nm).

Table S2. Distribution of surface element (C, O, Zn and N) of C-ZIF, C-ZIF_{ZnO}, C-$ZnO_{0.5}$/ZIF and C-$ZnO_{0.5}$/ZAA foams determined from XPS.

Sample	Atomic content (%)			
	C	O	Zn	N
C-ZIF	57.69	37.88	1.39	3.04
C-ZIF_{ZnO}	57.58	38.08	1.51	2.83
C-$ZnO_{0.5}$/ZIF	56.63	38.18	1.77	3.42
C-$ZnO_{0.5}$/ZAA	56.35	37.91	1.92	3.81

Table S3. Langmuir and Freundlich isotherm parameters of C-ZIF, C-ZIF_{ZnO}, C-$ZnO_{0.5}$/ZIF and C-$ZnO_{0.5}$/ZAA foams.

Sample	Langmuir isotherm			Freundlich isotherm		
	Q_{max} (mg/g)	R^2	k_L (L/mg)	n	R^2	k_F
C-ZIF	217.45	0.995	1.98	3.71	0.920	70
C-ZIF_{ZnO}	246.47	0.992	2.29	3.79	0.926	82
C-$ZnO_{0.5}$/ZIF	279.83	0.990	2.19	3.83	0.903	95
C-$ZnO_{0.5}$/ZAA	418.81	0.996	2.01	3.37	0.919	125

Table S4. The distribution coefficient of C-$ZnO_{0.5}$/ZAA foam and other adsorbents at low concentration.

Adsorbents	m (mg)	C_0 (mg/L)	V (ml)	Q_e (mg/g)	K_d (L/mg)	Reference
MIL-68(Al)/GO	20	50	100	203.3	21.1	[2]
N-doped carbon	400	25	1000	47.8	8.1	[3]
ZIF-8-chitosan composite beads	50	50	100	86.2	12.5	[4]
ZIF-8-derived carbon	25	20	150	72.4	9.1	[5]
Carbon aerogel	10	50	25	112.6	22.7	[6]
C-$ZnO_{0.5}$/ZAA foam	10	20	200	257.0	36.0	This work

Table S5. Pseudo-first-order model and Pseudo-second-order model constants for tetracycline adsorption on composite foams.

Sample	Q_e,exp (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		k_1* (min^{-1})	Q_e,cal (mg/g)	R^2	k_2* (10^{-5} g/mg·min)	Q_e, cal (mg/g)	R^2
C-ZIF	130.49	0.011	138.37	0.997	5.05	186.59	0.993
C-ZIF_{ZnO}	162.15	0.019	167.54	0.996	9.84	205.42	0.981
C-$ZnO_{0.5}$/ZIF	190.09	0.023	197.59	0.985	11.14	236.62	0.963
C-$ZnO_{0.5}$/ZAA	257.02	0.048	263.35	0.993	24.55	291.78	0.965

References:

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