Supplementary Materials

Molten salt-assisted synthesis of nitrogen-doped biochar catalyst at low temperature for enhanced degradation of acetaminophen

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Text S1. The morphology and microstructure of the samples were observed using a scanning electron microscope (SEM). The pore structure and Brunauer-Emmett-Teller specific surface area (SSA) of biochar were obtained by N2 adsorption–desorption isotherms at 77 K (ASAP 2460). The crystal structure of AL@NX was analyzed using an X-ray diffractometer (model Bruker AXS D8 Advance) equipped with a high-intensity monochromatic Cu-Kα light source with $\lambda = 1.5218$ Å, and the 2θ angle was between 10◦ and 90◦. The interaction between AL@NX and PMS and the carbon structure of AL@NX were monitored by Raman spectroscopy (Horiba JobinYvon). The surface elemental composition of biochar was analyzed using X-ray photoelectron spectroscopy (XPS) (Escalab 250Xi, Thermo Fisher). Binding energy of C1s at 284.8 eV was used for correction. Fourier Transform Infrared (Nicolet iS10, Thermo Fisher) was used to observe the functional groups of AL@NX.

Text S2. The reactive species produced in the AL@NX/PMS system were analyzed using the Electron paramagnetic resonance (EPR, Bruker EMXPlus-10/12) spectrometer. DMPO and TEMP were employed as spin-trapping reagents for free radicals and singlet oxygen, respectively. The experimental parameters of the spectrometer included a resonant frequency of 9.85 GHz, a microwave power of 20.00 mW, a modulation frequency of 100 kHz, a modulation amplitude of 1.00 G, a sweep width of 100 G, a time constant of 0.01 ms, and a sweep time of 40.00 s.

Text S3. Electrochemical analysis was conducted using a three-electrode system on an electrochemical workstation (CHI 650e, Chenhua, China). The experiment was carried out using the timing current method with the study sample as the working electrode, platinum electrode as the counter electrode, and Ag/AgCl electrode as the reference electrode in a 0.1M sodium sulfate solution. A bias voltage of +0.5V was applied during the experiment. Initially, at 200s, 2mM of PMS was added to the electrolyte, and the subsequent current change was recorded. Subsequently, at 400s, the pollutant APAP was introduced into the electrolyte at a concentration of 50mg/L, and the resulting current change was monitored at 600s. The LSV test began by utilizing a platinum electrode matched with an Ag/AgCl electrode in a 0.1M sodium sulfate solution as the electrolyte. The voltage window ranged from 0V to +1.6V, with a scan rate of 20mV/s. Following the addition of the corresponding reagent to the electrolyte, the test was initiated. Four different systems were tested: the first with pure electrolyte, the second with electrolyte containing only 2mM PMS, the third containing only 50mg/L APAP, and the fourth with electrolyte containing both 2mM PMS and 50mg/L APAP.

Text S4. To assess the cycling stability of the materials, four degradation experiments were conducted on the same batch of materials. After each experiment, the samples were filtered, washed several times with ultrapure water and anhydrous ethanol, dried in an oven at 80°C for 12 hours, and then subjected to catalyst recovery by placing them in a tubular furnace with an argon atmosphere (40 ml/min), a pyrolysis temperature of 350°C, and a retention time of 1 hour.

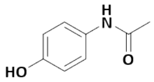
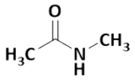
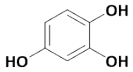
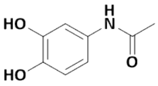
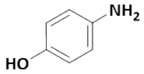
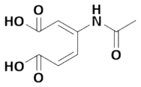
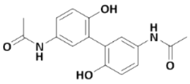
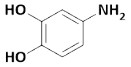
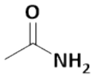
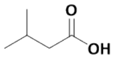
Table S1. Other catalysts reported in literatures. [1-4]

Catalyst type	Catalyst doage (g L^{-1})	Concentration of APAP (ppm)	PMS dosage (mM)	Degradation time (min)	Ref.
CM	0.1	10	0.662	15	[1]
CoFe-C_3N_4	0.2	10	0.5	20	[2]
Fe-N-C	0.1	10	0.5	25	[3]
MX@N-800	0.1	50	0.5	15	[4]
AL@NX	**0.1**	**50**	**0.5**	**5**	**This work**

Table S2. Percentages of different forms of nitrogen in fresh and used AL@N and AL@NX.

Samples	pyridinic N (%)	pyrrolic N (%)	graphitic N (%)
AL@N	51.54	42.77	5.69
AL@NX	54.05	36.58	9.37
AL@NX-2nd	40.25	44.55	15.19
AL@NX-3rd	32.97	52.67	14.36

Table S3. Identified degradation intermediates of APAP in AL@NX/PMS system.

Formula	Retention time	Theoretical m/z $[M-H]^-$	Experimental m/z $[M-H]^-$	DE[1] (ppm)	Structural formula
$C_8H_9NO_2$	3.395	151.0632	152.0705	-0.94	
C_3H_7NO	1.26	73.0527	74.0600	-0.9	
$C_3H_6O_3$	0.533	126.0316	127.0389	-0.78	
$C_8H_9NO_3$	1.809	167.0581	168.0654	-1	
C_6H_7NO	3.513	109.0527	110.0600	-0.6	
$C_8H_9NO_5$	2.861	199.0479	200.0552	-0.87	
$C_{16}H_{16}N_2O_4$	8.601	300.1105	301.1177	-1.57	
$C_6H_7NO_2$	0.565	125.0476	126.0548	-0.92	
C_2H_5NO	0.945	59.0373	60.0446	3.05	
$C_5H_{10}O_2$	10.833	102.0680	103.0752	-1.13	

DE[1] represented the relative error between theoretical m/z value and experimental m/z value.

Table S4. Water quality indexes of actual water.

pH	TOC (mg/L)	COD (mg/L)	Conductivity (µS/cm)	HCO_3^- (mg/L)	Cl^- (mg/L)	reactive phosphate (mg/L)	HA (mg/L)
7.57	19.39	1.92	15770	60.05	37.66	0.046	10.43

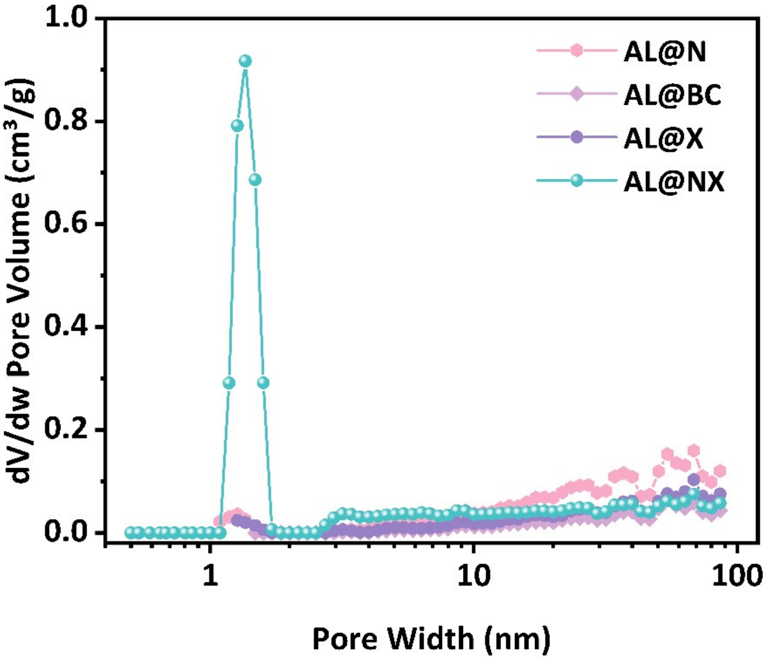


Fig. S1. Pore distribution maps of four catalysts.

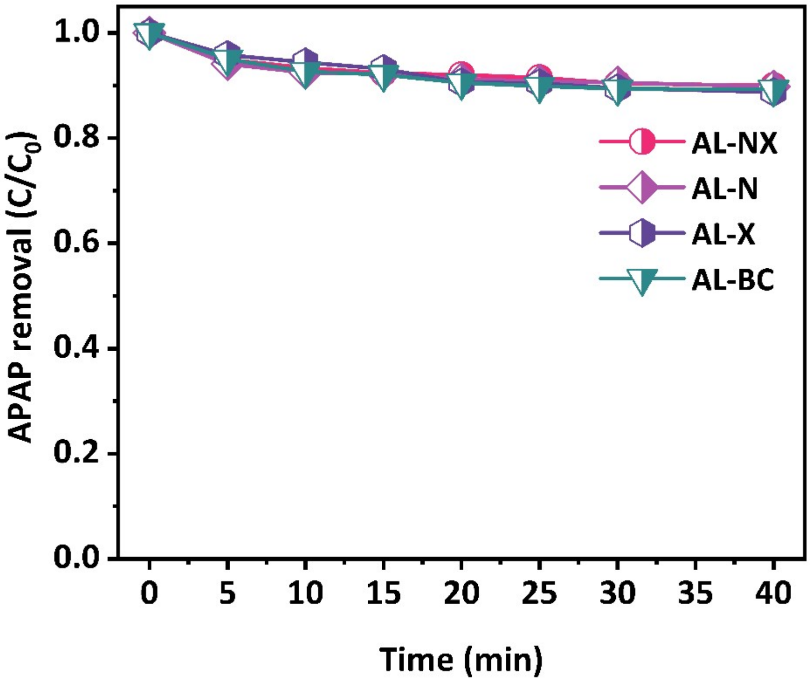


Fig. S2. Comparison of adsorption properties of four catalysts. Conditions: $[\text{catalyst}]_0 = 0.1$ g L^{-1}, $[\text{APAP}]_0 = 50$ mg L^{-1}, $[\text{PMS}]_0 = 1$ mM, Temperature = 25 ℃.

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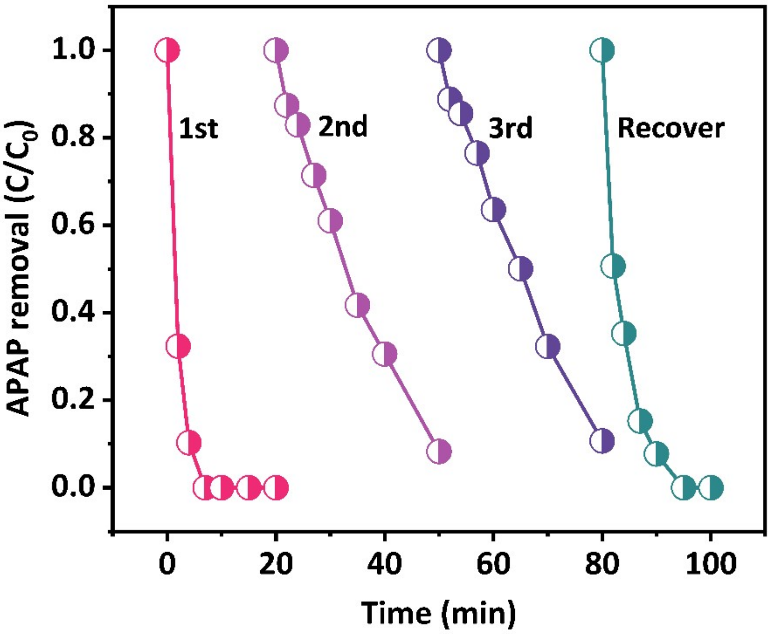

Fig. S3. Cyclic degradation experiments by AL@NX/PMS system. Conditions: $[\text{catalyst}]_0$ = 0.1 g L^{-1}, $[\text{APAP}]_0$ = 50 mg L^{-1}, $[\text{PMS}]_0$ = 1 mM, Temperature = 25 ℃.

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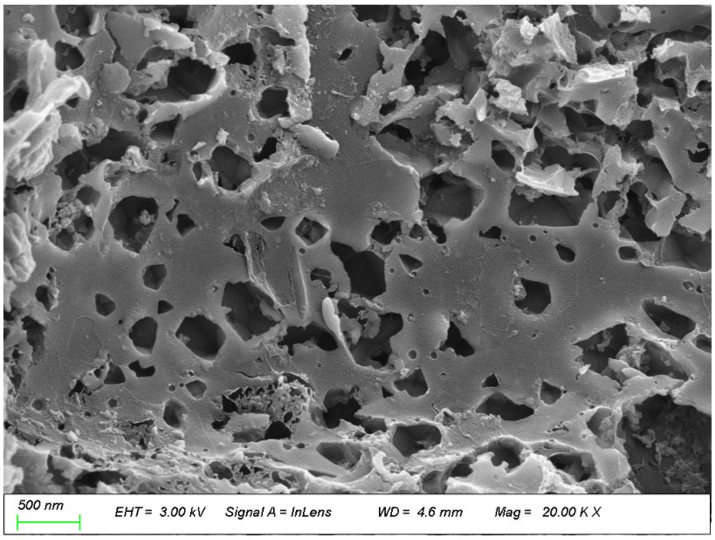

Fig. S4. SEM images of AL@NX-2nd.

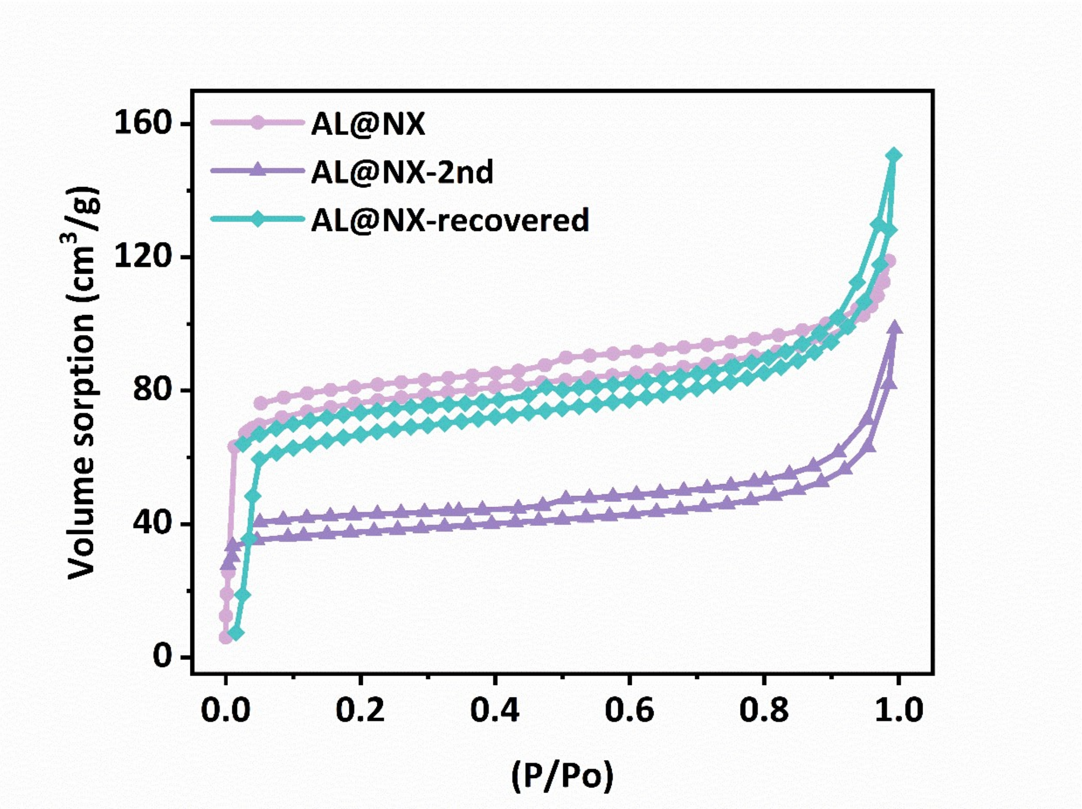

Fig. S5. N_2 adsorption isotherm of fresh, used and recovered AL@NX.

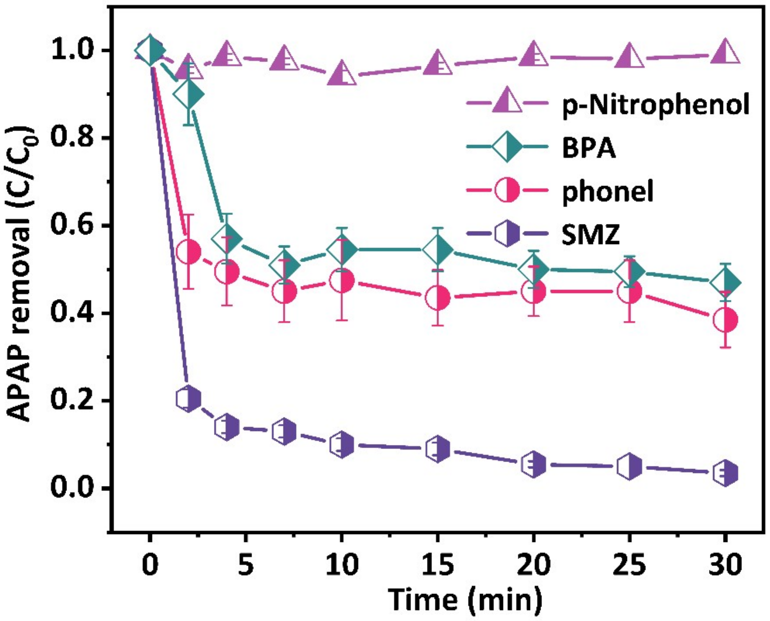

Fig. S6. Degradation experiments on different pollutants. Conditions: $[\text{catalyst}]_0 = 0.1$ g L^{-1}, $[\text{APAP}]_0 = 50$ mg L^{-1}, $[\text{PMS}]_0 = 1$ mM, Temperature = 25 ℃.

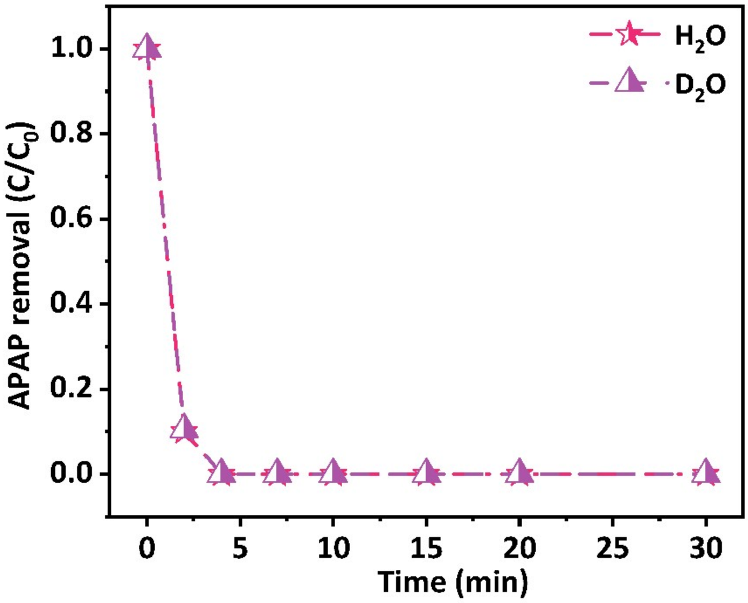

Fig. S7. APAP removal performance of AL@NX/PMS system in D_2O and regular water. Conditions: $[\text{catalyst}]_0 = 0.1$ g L^{-1}, $[\text{APAP}]_0 = 50$ mg L^{-1}, $[\text{PMS}]_0 = 1$ mM, Temperature = 25 ℃.

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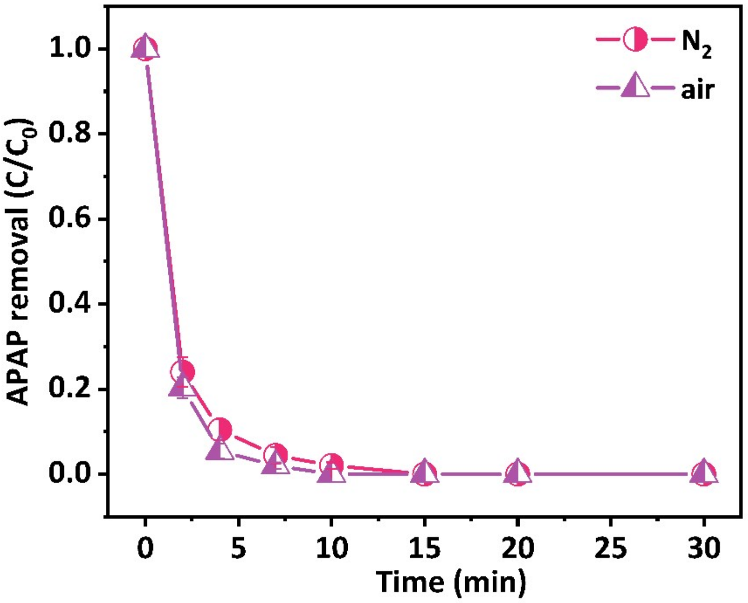

Fig. S8. Degradation of APAP in the AL@NX/PMS system under air and N_2-saturated conditions. Conditions: $[\text{catalyst}]_0$ = 0.1 g L^{-1}, $[\text{APAP}]_0$ = 50 mg L^{-1}, $[\text{PMS}]_0$ = 1 mM, Temperature = 25 ℃.

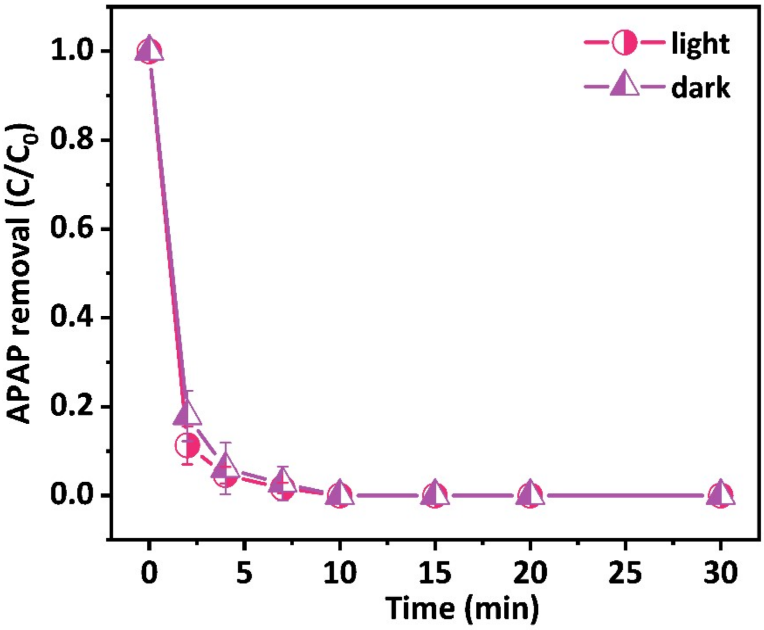

Fig. S9. Degradation of APAP in the AL@NX/PMS system under photoirradiation and dark conditions. Conditions: $[\text{catalyst}]_0 = 0.1$ g L^{-1}, $[\text{APAP}]_0 = 50$ mg L^{-1}, $[\text{PMS}]_0 = 1$ mM, Temperature = 25 ℃.

References

1. S. Liu, P. Qi, S. Xu, P. Jin, B. Li, W. Yu and B. Young, *Journal of Environmental Chemical Engineering*, 2022, **10**.
2. Y. Shen, M. J. M. d. De Vidales, G. Gorni, A. Gomez-Herrero, F. Fernandez-Martinez and A. J. Dos santos-Garcia, *Chemical Engineering Journal*, 2022, **444**.
3. L. Peng, X. Duan, Y. Shang, B. Gao and X. Xu, *Applied Catalysis B-Environmental*, 2021, **287**.
4. W. Li, C. Nie, X. Wang, H. Ye, D. Li and Z. Ao, *Separation and Purification Technology*, 2023, **323**.