Supplementary Material

Photocatalyst with metal-free electron-hole pair double transfer mechanism for pharmaceutical and personal care products degradation

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Additional Details on Methods

Text S1. Electrochemical measurements

Photoelectrochemical measurements were analyzed using a CHI-660 electrochemical system (Shanghai, China), which was equipped with a conventional three-electrode electrochemical cell. The as-prepared catalysts on ITO served as the working electrode, while a saturated calomel electrode (SCE) and platinum (Pt) wire were employed as the reference electrode and the counter electrode, respectively. A 450 nm LED lamp (3 x 3 W, Shenzhen lamplic co., LTD, China) was used for illumination. The photocurrent was recorded in a 0.1 M sodium sulfate solution (Na₂SO₄).

Text S2. Transformation products identification

The photocatalytic degradation intermediates of ENR were identified by HRLC-MS-MS (Thermo Scientific Ultimate 3000 RSLC and Q Exactive Orbitrap). Separation was accomplished using a Hypersil GOLD C18 (100 x 2.1 mm, 1.9 μ m) with column temperature 40 °C. Elution was performed at a flow rate of 0.3 mL/min with water that contained 0.1 % (v/v) formic acid as eluent A, and methanol as eluent B. Mass spectral analysis was conducted in positive mode.

Text S3. Determination of ENR concentration

The concentration of ENR were determined by an HPLC system HPLC was carried out by a Waters e2968 instrument which outfit a UV detector, and a 4.6×250 mm Zorbax Eclipse XDB C18 reverse-phase column (Agilent, USA) at 40 °C. Other conditions of the detection are listed as follow: mobile phase: methanol/Milli-Q water containing 0.2% formic acid (78:22 v/v); flow rates: 1 mL/min; injection volume: 20μ L; and determine wavelength: 278 nm.

Potential	parameters
Init E (V)	-1
Final E (V)	-0.2
Incr E (V)	0.001
Amplitude (V)	0.01
Cycles (below 10	5
Quiet time (sec)	2
Bias DC Current	Below 1
Sensitivity (A/V)	Automation

Table S1. The characterization details of the Mott-Schottky plots.

Table 52. DET sufface aleas of materials.

Commits.	BET surface area	Pore volume	Pore size
Sample	$(m^2 g^{-1})$	$(cm^2 g^{-1})$	(nm)
g-C ₃ N ₄	9.09	0.05	21.12
CN3	15.25	0.08	19.87
0.1CCN3	14.80	0.06	16.49
BN	23.36	0.06	9.44

(numl	oer)	FED ² _{HOMO} +	Point	(number) FED ² _{HOMO} +	Point
Ato	m	FED ² LUMO	charge	Atom	FED ² LUMO	charge
1	С	0.561056	0.236645	18 N	N 0.331536	-0.470913
2	C	0.353475	-0.080719	19 C	0.002984	-0.077043
3	C	0.171301	-0.257861	20 0	C 0.000522	-0.201856
4	C	0.022062	0.311741	21 0	C 0.003470	-0.24548
5	C	0.437277	-0.165586	27 F	F 0.068178	-0.251128
6	C	0.064631	0.224907	28 N	N 0.528481	-0.479031
8	C	0.287490	0.385029	29 0	C 0.004798	-0.153217
10	C	1.059679	0.270456	30 C	0.026412	-0.009355
11	C	0.136015	-0.40379	31 (C 0.048020	0.007165
13	C	0.086737	0.424413	33 (0.005152	-0.134821
14	0	0.056114	-0.402367	35 N	N 0.073888	-0.404359
15	0	0.040053	-0.324889	42 0	C 0.003247	-0.120203
17	0	0.251619	-0.401878	43 (C 0.010025	-0.308064

Table S3. Frontier electron densities on atoms of ENR was calculated via usingGaussian 09 program at the B3LYP/6-311 + g(d, p) level.

 Table S4 Compounds (ENR) identified by HPLC–MS-MS during the photocatalytic

 degradation of ENR under blue LED light irradiation.

Products	Rt(min)	m/z	Probable Structure
ENR	7.79	359	
TP1	9.52	265	F COOH N H
TP2	7.87	357	
TP3	9.76	389	
TP4	8.92	361	
TP5	7.44	375	
TP6	6.89	373	
TP7	7.71	331	





Fig. S1. Photocatalytic degradation of ENR with different photocatalysts (CN-x)

under blue LED light irradiation



Fig. S2. Irradiation of the homemade photocatalytic reactor system: 1 = blue LED lamps, 2 = quartz breaker reaction vessel, 3 = magnetic stirrer



Fig. S3. XPS survey spectrum of CN3 and 0.1CCN3 and their corresponding high-

resolution XPS spectrum of O1s regions.



Fig. S4. The adsorption capacity of enrofloxacin over different photocatalysts before

photoirradiation.





Fig. S5. Mott-Schottky plots for $g-C_3N_4$ (a), CN3 (b) and 0.1CCN3 (c).

Decay2 (Em) Reconvolut	tion Fit			X
Fit Range Fitting Rang	e: 1	o 511 char	15	*
Instrument Response				
Use Measuremer	it: IR8 (Em)			Select
Fit With Backgroun	d: 1.896			
$R(t) = B_1$	$e^{\left(\frac{-t}{\tau_1}\right)} + B_2$	$e^{\left(\frac{-t}{\tau_2}\right)} + B_3 e^{\left(\frac{-t}{\tau_2}\right)} $	$e^{(-t/\tau_2)} + B_4$	$_{1}e^{(-t/\tau_{4})}$
Fix Value / ns	Std. Dev / ns	Fix Value	Std. Dev	Rel %
τ ₁ 🗌 0.4680	0.05980	B ₁ 0.040	0.0021	14.82
τ ₂ 2.0541	0.18082	B ₂ 0.026	0.0015	42.13
τ ₃ 🗌 8.2964	0.75875	B ₃ 🗌 0.007	0.0010	43.05
τ4		B ₄		
δt [] 0.0147	0.0076	A 🗌 8.715		
		χ ² : 1.031		
Copy Results To Clipboa	rd	Results Window		
Copy As Text Copy	As Image	◯ Add to existing	g window 💿 Crea	ate new window
Print			Close	Apply

Fig. S6. Detailed fitting data of $g-C_3N_4$.

Decay3 (Em) Reconvolut	ion Fit			X
Fit Range Fitting Range	: 1	to 511 cha	ns	*
Instrument Response Use Measuremen Fit With Background	t: IR9 (Em) t: 1.667			Select
$R(t) = B_1 \epsilon$	$e^{(-t/\tau_1)} + B_2$	$_{2}e^{(-t/\tau_{2})}+B_{3}e^{(-t/\tau_{2})}$	$e^{(-t/\tau_3)} + B_4$	$_{1}e^{(-t/\tau_{4})}$
Fix Value / ns	Std. Dev / ns	Fix Value	Std. Dev	Rel %
τ ₁ 🗌 0.3016	0.03438	B ₁ 0.067	0.0044	22.43
τ ₂ [1.4737	0.08518	B ₂ 0.027	0.0016	43.39
τ ₃ □ 6.0093	0.28161	B ₃ 0.005	0.0005	34.18
τ4 🗆		B ₄		
δt [] 0.0437	0.0079	A 🗌 3.718		
		χ ² : 1.156		
Copy Results To Clipboar Copy As Text Copy /	d As Image	Results Window	g window 💿 Crea	ate new window
Print		luli:	Close	Apply

Fig. S7. Detailed fitting data of CN3.

Fit Range				
- Fitting Rang	ge: 1	o 511 char	18	
Instrument Response				
Use Measureme	nt: IR1 (Em)			Select
Fit With Backgrour	nd: 1.875			
P(t) = P	$a^{\left(-t/\tau_{t}\right)} + P$	$a\left(\frac{-t}{\tau_{2}}\right) + P$	$\left(\frac{-t}{\tau_{n}}\right) + p$	$a^{\left(-t/\tau_{t}\right)}$
$\Lambda(\iota) = D_1$	$e^{-1} + D_2$	$2e^{-7} + D_3e^{-7}$	$+ D_2$	40 4
				D 1 %
Fix Value / ns	Std. Dev / ns	Fix Value	Std. Dev	Hel Z
Fix Value / ns T₁ [] 0.3408	Std. Dev / ns 0.02878	Fix Value B₁ 0.073	0.0030	30.86
Fix Value / ns T ₁ 0.3408 T ₂ 1.4260	Std. Dev / ns 0.02878 0.07907	Fix Value B₁ 0.073 B₂ 0.026	0.0030	30.86 45.18
Fix Value / ns T ₁ 0.3408 T ₂ 1.4260 T ₃ 6.3906	Std. Dev / ns 0.02878 0.07907 0.38623	Fix Value B1 0.073 B2 0.026 B3 0.003	Std. Dev 0.0030 0.0018 0.0003	30.86 45.18 23.95
Fix Value / ns T ₁ 0.3408 T ₂ 1.4260 T ₃ 6.3906 T ₄ 0	Std. Dev / ns 0.02878 0.07907 0.38623	Fix Value B ₁ 0.073 B ₂ 0.026 B ₃ 0.003 B ₄ 0	Std. Dev 0.0030 0.0018 0.0003	Hel Z 30.86 45.18 23.95
Fix Value / ns 1 0.3408 1/2 1.4260 1/3 6.3906 1/4 0.0532	Std. Dev / ns 0.02878 0.07907 0.38623 0.00064	Fix Value B1 0.073 B2 0.026 B3 0.003 B4 2.530	Std. Dev 0.0030 0.0018 0.0003	Hei Z 30.86 45.18 23.95
Fix Value / ns T 1 0.3408 T 2 1.4260 T 3 6.3906 T 4	Std. Dev / ns 0.02878 0.07907 0.38623 0.0064	Fix Value B_1 0.073 B_2 0.026 B_3 0.003 B_4	Std. Dev 0.0030 0.0018 0.0003	Hel Z 30.86 45.18 23.95
Fix Value / ns T 1 0.3408 T 2 1.4260 T 3 6.3906 T 4 0.0532	Std. Dev / ns 0.02878 0.07907 0.38623 0.00064	Fix Value B_1 0.073 B_2 0.026 B_3 0.003 B_4	Std. Dev 0.0030 0.0018 0.0003	Hei Z 30.86 45.18 23.95
Fix Value / ns T ₁ 0.3408 T ₂ 1.4260 T ₃ 6.3906 T ₄ 0 D 0.0532 Copy Results To Clipboo	Std. Dev / ns 0.02878 0.07907 0.38623 0.0064 ard	Fix Value B_1 0.073 B_2 0.026 B_3 0.003 B_4	Std. Dev 0.0030 0.0018 0.0003	Hel Z 30.86 45.18 23.95

Fig. S8. Detailed fitting data of 0.1CCN3.