Supplementary data for Dalton Transations

Generation of singlet oxygen over CeO_2/K, Na-codoped g-C_3N_4 for tetracycline hydrochloride degradation in a wide pH range

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1. Results

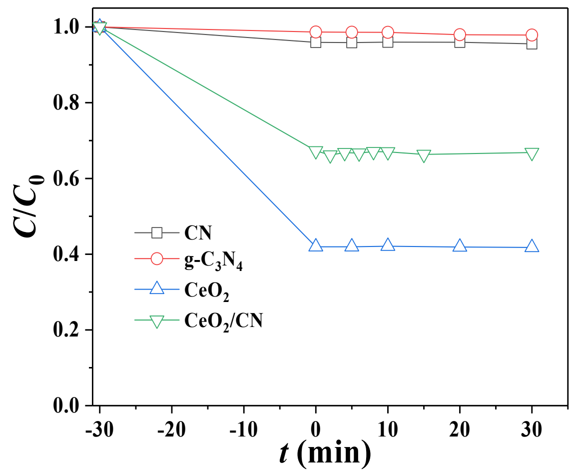


Fig. S1 Adsorption curves of TCH over the CN, g-C_3N_4, CeO_2 and CeO_2/CN catalysts in absence of H_2O_2

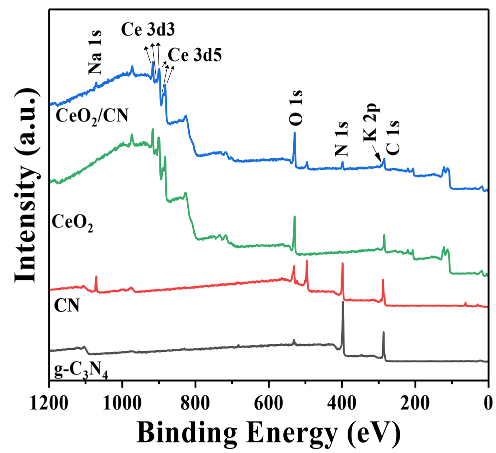
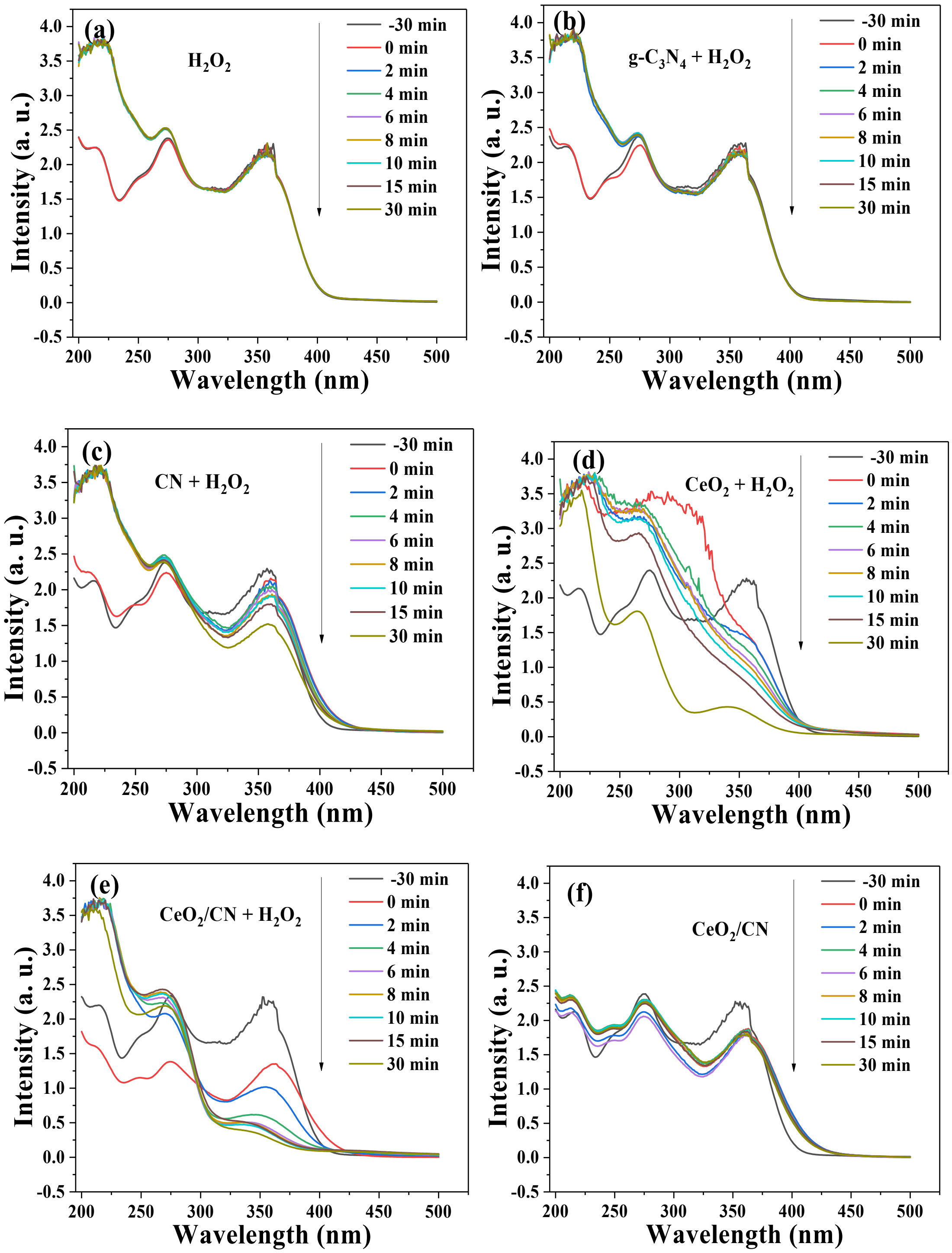


Figure S2 XPS survey spectra for the g-C_3N_4, CN, CeO_2 and CeO_2/CN.


(a)
H2O2
(b)
g-C3N4 + H2O2
(c)
CN + H2O2
(d)
CeO2 + H2O2
(e)
CeO2/CN + H2O2
(f)
CeO2/CN
-30 min
0 min
2 min
4 min
6 min
8 min
10 min
15 min
30 min
Intensity (a. u.)
Wavelength (nm)

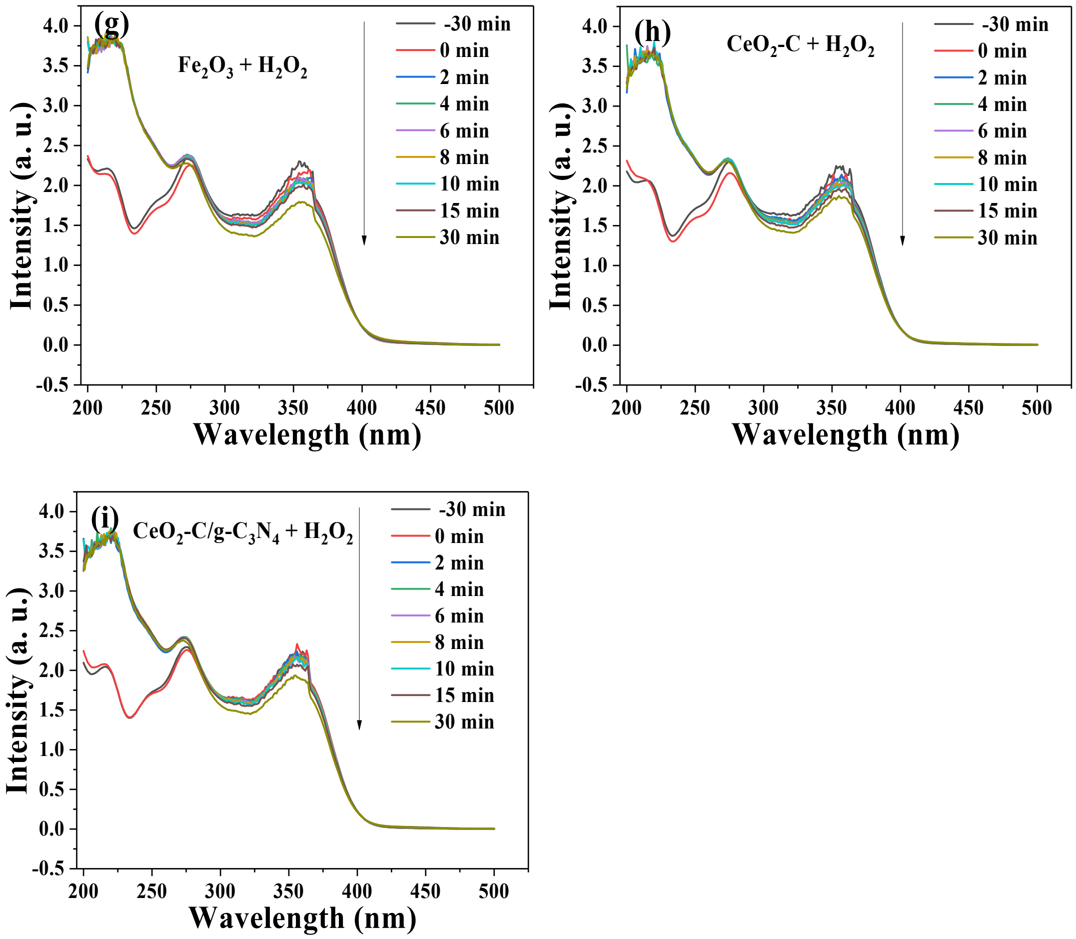


Fig. S3 the UV-vis spectra of TCH dependent on reaction time over H_2O_2 (a), g-C_3N_4 + H_2O_2 (b), CN + H_2O_2 (c), CeO_2 + H_2O_2 (d) , CeO_2/CN + H_2O_2 (e), CeO_2/CN (f), Fe_2O_3 + H_2O_2 (g), CeO_2-C + H_2O_2 (h), and CeO_2-C/g-C_3N_4 + H_2O_2 (i), respectively.

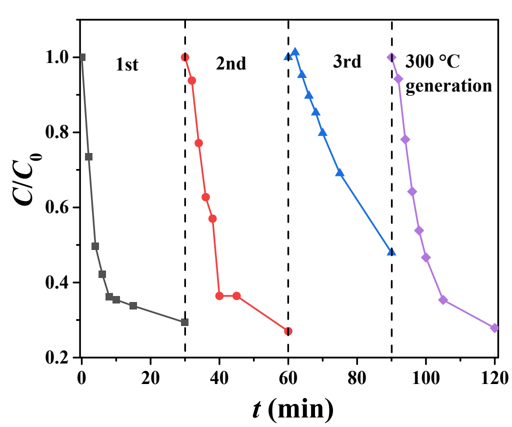


Fig. S4 The degradation curves of TCH in the recycling/regeneration experiments over CeO_2/CN in presence of H_2O_2.

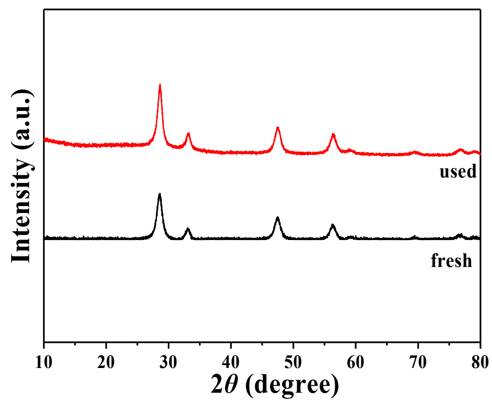


Fig. S5 XRD patterns for the fresh and used CeO_2/CN samples.

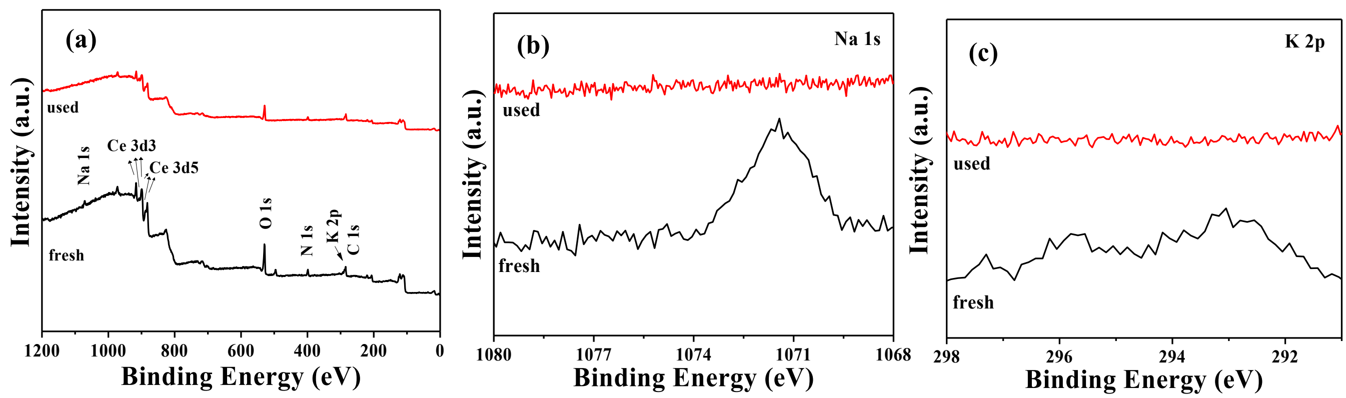


Fig. S6 XPS spectra for the fresh and used CeO_2/CN samples: survey spectra (a), high resolution spectra of Na 1s (b) and K 2p (c).

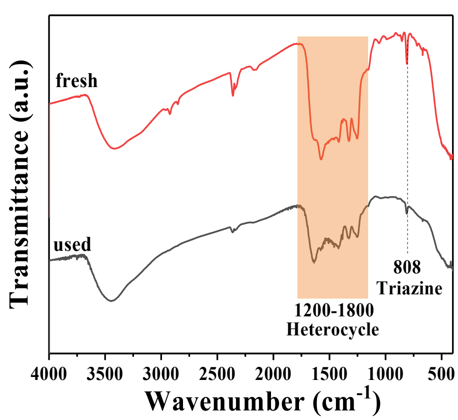


Fig. S7 FTIR spectra for the fresh and used CeO_2/CN samples.

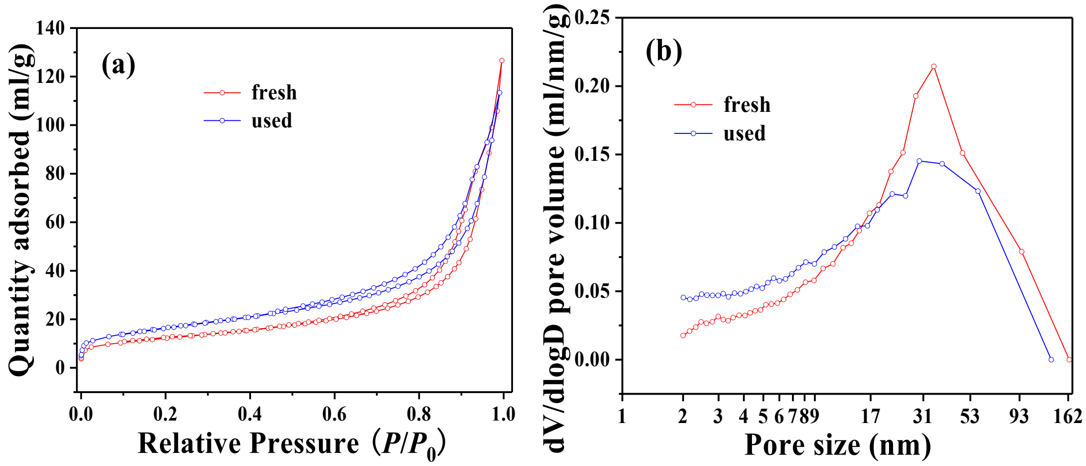


Fig. S8 Nitrogen adsorption-desorption isotherms of the fresh and used CeO_2/CN samples (a) and the corresponding pore size distribution curves (b).

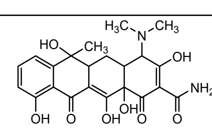
Table S1 Binding energies (B.E.) of the elements in the CeO_2, CN, and CeO_2/CN samples and the shift of the binding energies (in bracket) of the elements in CeO_2/CN compared with those in CN or CeO_2.

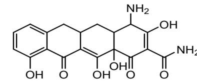
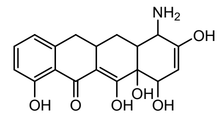
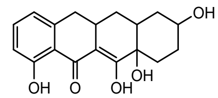
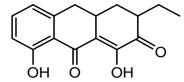
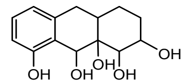
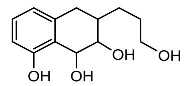
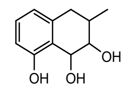
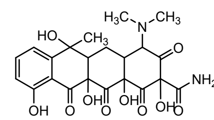
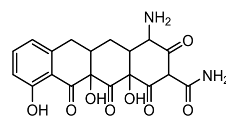
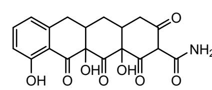
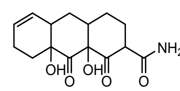
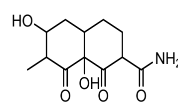
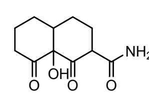
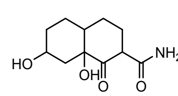
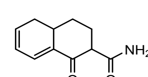
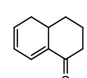
elements		CN	CeO_2	CeO_2/CN (binding energy shift)	Atomic percentage of elements		
		B.E. (eV)	B.E. (eV)	B.E. (eV)	CN	CeO_2	CeO_2/CN (fresh/used)
Na 1s		1071.4		1071.5 (+0.1)	7.1	/	4.0/0.9
K 2p	$2p_{1/2}$	292.7		293.1 (+0.4)	1.0		0.9/0.0
	$2p_{3/2}$	295.4		295.7 (+0.3)			
C 1s	C_I	284.8		284.8	42.0	/	34.1/47.7
	C_{II}	286.3		285.9 (-0.4)			
	C_{III}	288.2		288.5 (+0.3)			
N 1s	N_I	398.5		398.6 (+0.1)			
	N_{II}	399.6		399.7 (+0.1)	35.6	/	8.2/11.3
	N_{III}	401.0		401.2 (+0.2)			
	N_{IV}	404.7		406.8 (+2.1)			
Ce 3d	ν		900.9	900.8 (-0.1)			
	ν'		903.2	903.1 (-0.1)			
	ν''		907.5	907.4 (-0.1)			

	ν'''	916.8	916.6 (-0.2)	/	28.9	12.4/5.9
	μ	882.3	882.2 (-0.1)			
	μ'	884.6	884.5 (-0.1)			
	μ''	888.9	888.8 (-0.1)			
	μ'''	898.2	898.0 (-0.2)			
	O_I	529.4	529.2 (-0.3)			
O 1s	O_{II}	531.1	530.6 (-0.5)	14.5	71.1	40.3/34.2
	O_{III}	532.4	532.2 (-0.2)			

The atomic percentage of each element was supplemented in Table S1. For both CN and CeO_2/CN, the atomic percentage of Na is higher than that of K, indicating Na is easier to dope into g-C_3N_4 possibly owing to its smaller ion size. Compared with CN, the atomic percentage of Na, K, C and N in CeO_2/CN shows a decrease in different degree owing to the incorporation of CeO_2. The molar ratios of C/N for CN and CeO_2/CN are 1.8 and 4.2, respectively, indicating that N vacancies are formed in both samples and more N vacancies exist in the later. The Na contents before and after reaction (for three repeated experiments) in CeO_2/CN are 4.0 % and 0.9 % of atomic percentage by XPS, and the K contents before and after reaction in CeO_2/CN are 0.9 % and 0.0 % of atomic percentage, respectively. The decrease of the contents of Na^+ and K^+ ions in the used sample by XPS is owing to the adsorption of intermediates formed in the degradation of TCH on the surface of CeO_2/CN because the XPS technique can only analyze elemental content in the surface thin layer.

Table S2 Possible degradation intermediates identified by LC-MS.

Compounds	Retention time (min)	*m/z*	Proposed structure
TC	3.82	445	

1	6.61	387	
2	1.24	345	
3	1.03	317	
4	1.01	273	
5	7.50	267	
6	1.27	239	
7	1.19	195	
8	1.30	477	
9	2.07	403	
10	1.45	388	
11	7.67	294	
12	1.00	256	
13	2.37	226	
14	5.94	228	
15	0.92	192	
16	8.06	149	

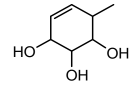
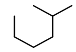
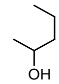
17	2.26	145	
18	5.97	101	
19	1.19	89	

Table S3 Characteristic parameters of the fresh and used CeO_2/CN samples.

Sample	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	d_{pore} (nm)
Fresh CeO_2/CN	43.4	0.17	16.4
used CeO_2/CN	59.6	0.17	11.7