Unravelling the facets-dependent behavior among H_2O_2, O_3 and oxygen vacancies on CeO_x and the promotion of peroxone reaction at acidic condition

Weirui Chen[a,b,c,d], Hengxi He[†,a,b,c,d], Ruini Zou[a], Yidan Chen[a], Xukai Li[a,b,c,d], Jing Wang[a,b,c,d*], Yiming Tang[a,b,c,d], Laisheng Li[a,b,c,d*]

a School of Environment, South China Normal University, Guangzhou 510006, China

b Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Guangzhou 510006, China

c Guangdong Provincial Engineering Technology Research Center for Drinking Water Safety, Guangzhou 510006, China

d Guangdong Provincial Key Lab of Functional Materials for Environmental Protection, Guangzhou 510006, China

Tel: +86-20-39310185, Fax: +86-20-39310187

† Both authors contributed equally to this work

* Corresponding author, E-mail: jing.wang@m.scnu.edu.cn (J. Wang)

* Corresponding author, E-mail: llsh@scnu.edu.cn (L. Li)

Table S1 HPLC condition for detecting selected PPCPs

Compound	Mobile phase (v/v)	Wavelength (nm)
Ketoprofen	Ultra-pure water: acetonitrile =55:45	220
Sulfamethoxazole	0.1% Acetic acid solution: methanol=70:30	272
Ibuprofen	0.1% formic acid : acetonitrile=75:25	220
Ciprofloxacin	5% Acetic acid solution: methanol 68:32	278
Lincomycin	0.02 M KH_2PO_4:acetonitrile:methanol=70:15:15	206
Chlortetracycline	0.01 M oxalic acid:acetonitrile:methanol=67:22:11	274
Sulfadimethoxine	Acetonitrile:water=60:40	270
Clofibric acid	Methanol and 0.1% acetic solution =65:35	232
Bezafibrate	Methanol: acetonitrile:0.02% acetic solution =5:40:55	228
Chloramphenicol	Methanol: water=65:35	275
Sulpiride	Acetonitrile: ultra-pure water=5:95	290
Norfloxacin	0.01 M oxalic acid:acetonitrile:methanol=67:22:11	268
Trimethoprim	Acetonitrile: 0.1% formic solution=30:70	210
Tetracycline	Acetonitrile: 0.1 M oxalic acids =20:80	375
Carbamazepine	Methanol: ultra-pure water =80:20	280
Erythromycin	0.025 M phosphate: acetonitrile=40:60	210
Sulpiride	Acetonitrile: 0.1% formic solution =5:95	210
Ofloxacin	Methanol: 0.1% formic solution =5:95	278
Indomethacin	Methanol: ultra-pure water =65:35	265
Nalidixic acid	Acetonitrile: 0.1% formic solution=40:60	258
Diclofenac	Methanol:1% acetic solution=80:20	280

Table S2 Peaks information for Ce 3d

Samples	Peak	Fresh		Used	
		Position (eV)	Area	Position (eV)	Area
(100) CeO_x	v_0	880.204	50775.45	880.204	87772.99
	v'	885.043	82871.38	885.043	140447.1
	u_0	897.37	114700.1	897.37	103968.3
	u'	903.309	26068.37	903.309	43496.35
	v	882.058	195758.1	882.058	194512.2
	v''	888.121	34742.64	888.121	29644.68
	v'''	898.39	69984.29	898.39	115349.5
	u	900.502	97114.5	900.502	110819.6
	u''	906.808	34826.61	906.808	29504.58
	u'''	915.976	128004.6	915.976	151754.2
(110) CeO_x	v_0	880.204	41127.36	880.204	78842.38
	v'	885.043	95141.88	885.043	93804.52
	u_0	897.37	79611.05	897.37	94481.77
	u'	903.309	25721.39	903.309	29594.04
	v	882.058	141029.3	882.058	120803.6
	v''	888.121	25115.85	888.121	13808.67
	v'''	898.39	70154.78	898.39	63511.02
	u	900.502	76569.78	900.502	66263.52
	u''	906.808	31571.45	906.808	23748.45
	u'''	915.976	106440.6	915.976	93835.12
(111) CeO_x	v_0	880.204	49674.59	880.204	0.101
	v'	885.043	71197.57	885.043	65945.88
	u_0	897.37	69796.09	897.37	21184.06
	u'	903.309	18121.91	903.309	16354.01
	v	882.058	118140.1	882.058	137444.8
	v''	888.121	17662.12	888.121	22328.07
	v'''	898.39	69883	898.39	61756.55
	u	900.502	62171.24	900.502	81088.28
	u''	906.808	19654.78	906.808	19171.81
	u'''	915.976	100347.5	916.5	74319.62

Table S3 Peaks information for O 1s

Samples	Peak	Fresh		Used	
		Position (eV)	Area	Position (eV)	Area
(100) CeO_x	O_I	528.855	192164.5	529.001	244242.5
	O_{II}	531.593	26482.17	531.693	32091.54
(110) CeO_x	O_I	529.102	163541.8	529.156	181440.7
	O_{II}	531.364	40216.72	531.439	75884.52
(111) CeO_x	O_I	529.319	115716.5	529.405	158835.7
	O_{II}	531.834	25035.03	531.834	26089.17

Table S4 Reaction rate constants from first order kinetics fitting

	$k(CeO_x/O_3)$	$k(H_2O_2)$	$k(CeO_x/O_3/H_2O_2)$	η
Ketoprofen	0.015	0.001	0.074	4.43
Sulfamethoxazole	-0.112	-0.004	-0.264	2.27
Ibuprofen	-0.019	0.001	-0.039	2.21
Ciprofloxacin	-0.184	-0.010	-0.394	2.04
Lincomycin	-0.704	-0.010	-1.242	1.74
Chlortetracycline	-0.391	0.001	-0.554	1.42
Sulfadimethoxine	-0.119	-0.007	-0.176	1.40
Clofibric acid	0.024	0.002	0.036	1.39
Bezafibrate	0.059	0.000	0.081	1.36
Chloramphenicol	-0.068	-0.003	-0.085	1.21
Norfloxacin	-0.126	-0.010	-0.153	1.12
Trimethoprim	-0.137	-0.002	-0.153	1.10
Tetracycline	-0.395	-0.009	-0.422	1.05
Carbamazepine	-0.100	-0.011	-0.110	0.99
Erythromycin	-0.302	-0.001	-0.292	0.96
Sulpiride	-0.130	-0.002	-0.109	0.82
Ofloxacin	-0.096	-0.009	-0.096	0.91
Indomethacin	-0.092	-0.025	-0.101	0.86
Nalidixic acid	-0.031	-0.005	-0.032	0.88
Diclofenac	-0.216	0.000	-0.163	0.76

Figure captions

Fig.S1 XRD pattern of different CeO_x;

Fig.S2 TGA of different CeO_x;

Fig.S3 Influence of calcination temperature on activity of (111) CeO_x;

Fig.S4 N_2 adsorption-desorption isotherm of different CeO_x;

Fig.S5 Heterogeneous peroxone of OA by different CeO_x with same S_{BET} dosage;

Fig.S6 •OH concentration in different $CeO_x/O_3/H_2O_2$ processes;

Fig.S7 Influence of PO_4^{3-} on heterogeneous peroxone process;

Fig.S8 Change of Ramen pattern of (100) and (110) during peroxone process;

Fig.S9 Atomic coordination of (100), (110) and (111) CeO_x;

Fig.S10 Degradation of PPCPs by (111) $CeO_x/H_2O_2/O_3$ with promotion effect; Reaction condition: pollutants concentration: 10 mg/L; catalyst dosage: 0.1 g/L; initial pH=4.2; reaction temperature: 298 K; ozone output: 100 mg/h; H_2O_2 dosage: 3.3 mg/L;

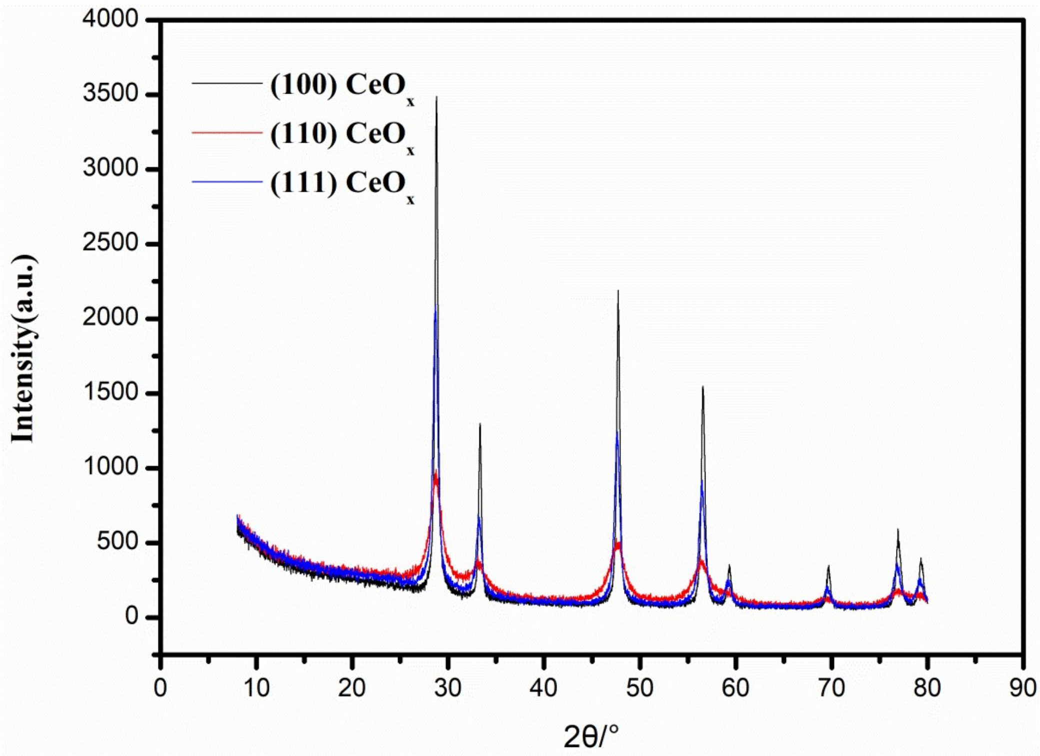
Fig.S11 Degradation of PPCPs by (111) $CeO_x/H_2O_2/O_3$ with similar effect;

Reaction condition: pollutants concentration: 10 mg/L; catalyst dosage: 0.1 g/L; initial pH=4.2; reaction temperature: 298 K; ozone output: 100 mg/h; H_2O_2 dosage: 3.3 mg/L;

Fig.S12 Degradation of PPCPs by (111) $CeO_x/H_2O_2/O_3$ with inhibition effect;

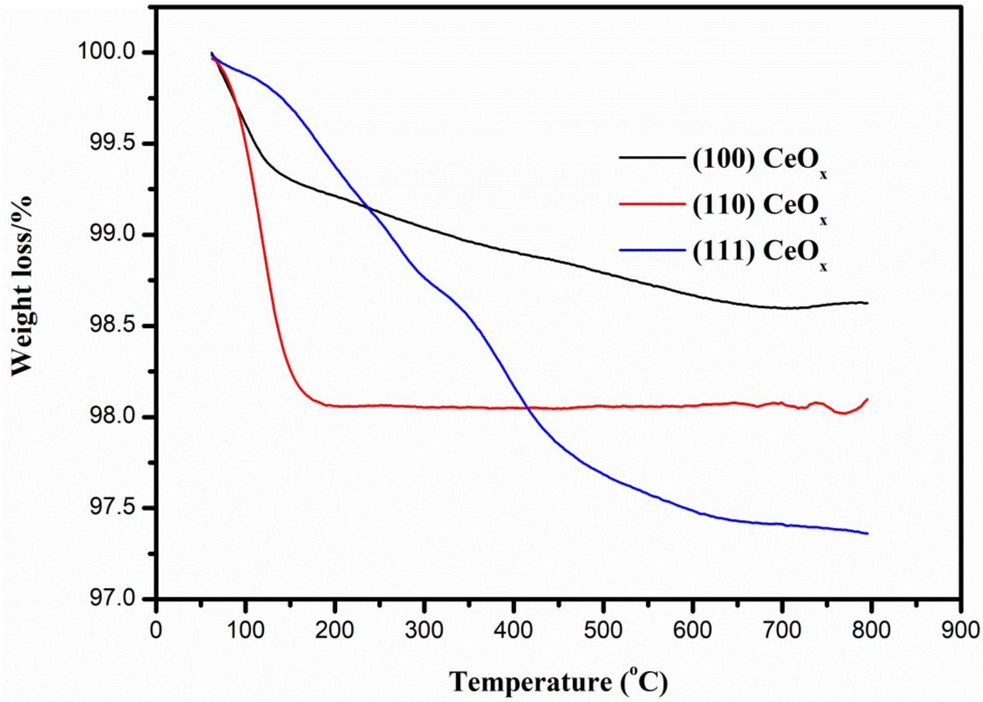
Reaction condition: pollutants concentration: 10 mg/L; catalyst dosage: 0.1 g/L; initial pH=4.2; reaction temperature: 298 K; ozone output: 100 mg/h; H_2O_2 dosage: 3.3 mg/L;

Fig.S1



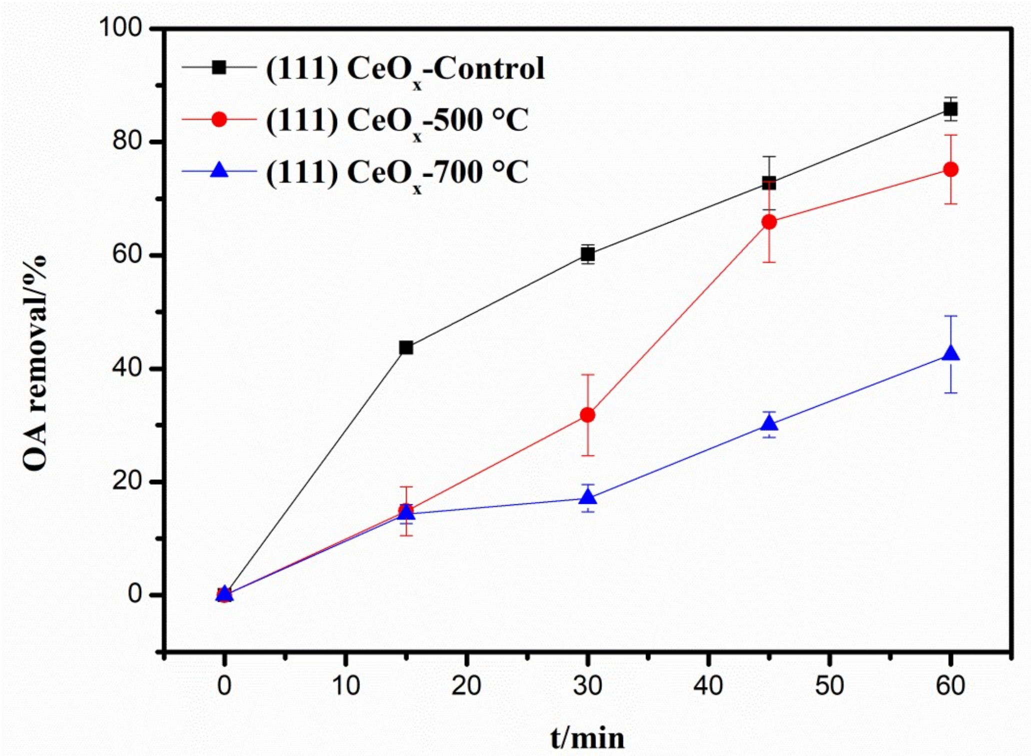
(100) CeO$_x$
(110) CeO$_x$
(111) CeO$_x$
Intensity(a.u.)
2θ/°
4000
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
80
90

Fig.S2



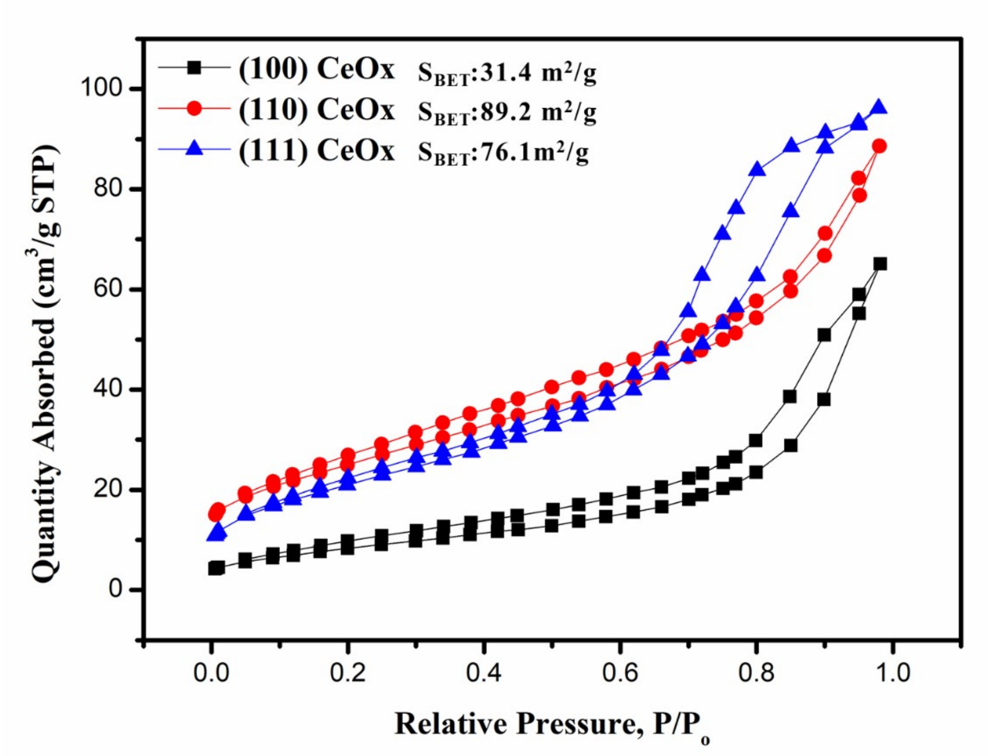
100.0
99.5
99.0
98.5
98.0
97.5
97.0
Weight loss/%
0
100
200
300
400
500
600
700
800
900
Temperature (°C)
(100) CeO$_x$
(110) CeO$_x$
(111) CeO$_x$

Fig.S3



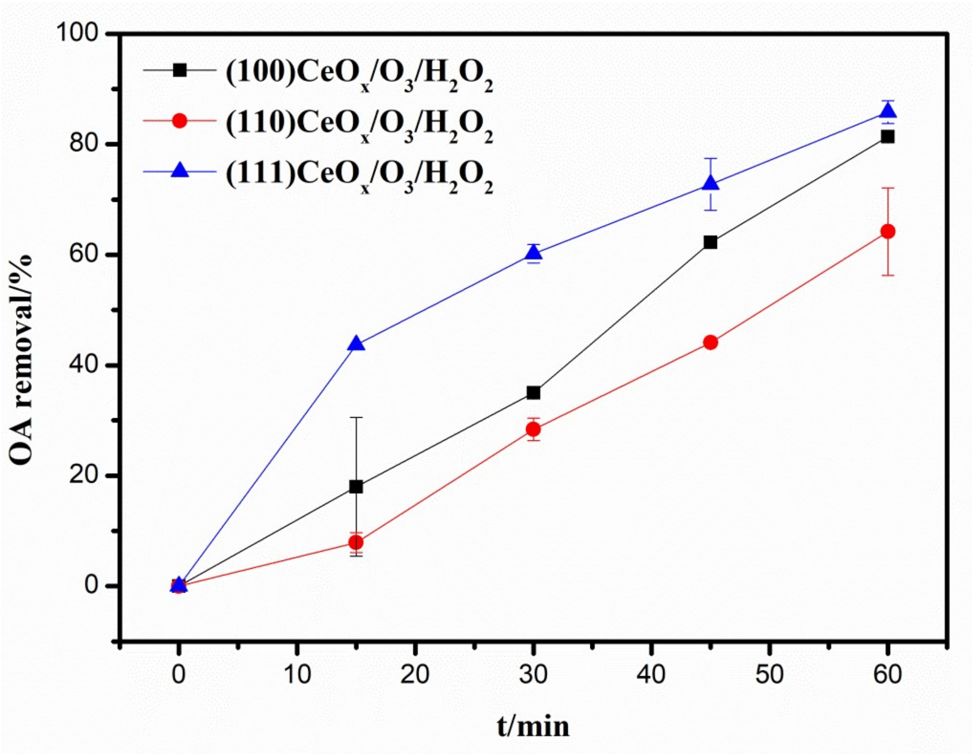
(111) CeOx-Control
(111) CeOx-500 °C
(111) CeOx-700 °C
OA removal/%
t/min
0
20
40
60
80
100
0
10
20
30
40
50
60

Fig.S4



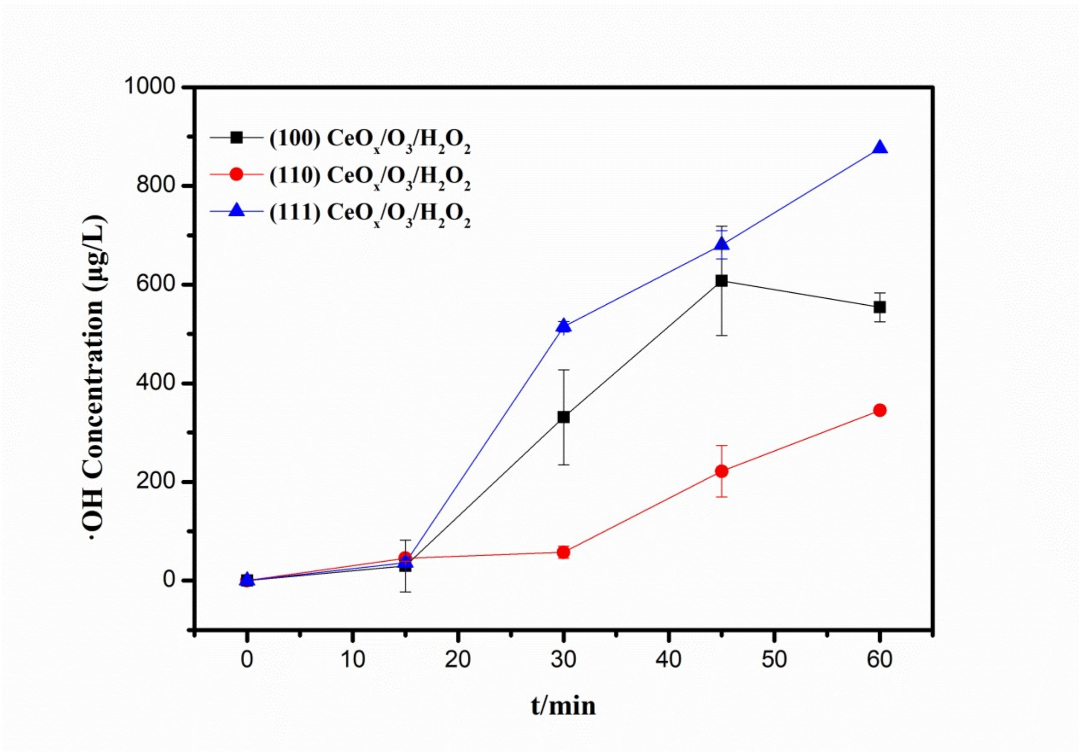
(100) CeOx S$_{BET}$:31.4 m^2/g
(110) CeOx S$_{BET}$:89.2 m^2/g
(111) CeOx S$_{BET}$:76.1m^2/g
Quantity Absorbed (cm^3/g STP)
Relative Pressure, P/P$_o$
0
20
40
60
80
100
0.0
0.2
0.4
0.6
0.8
1.0

Fig.S5



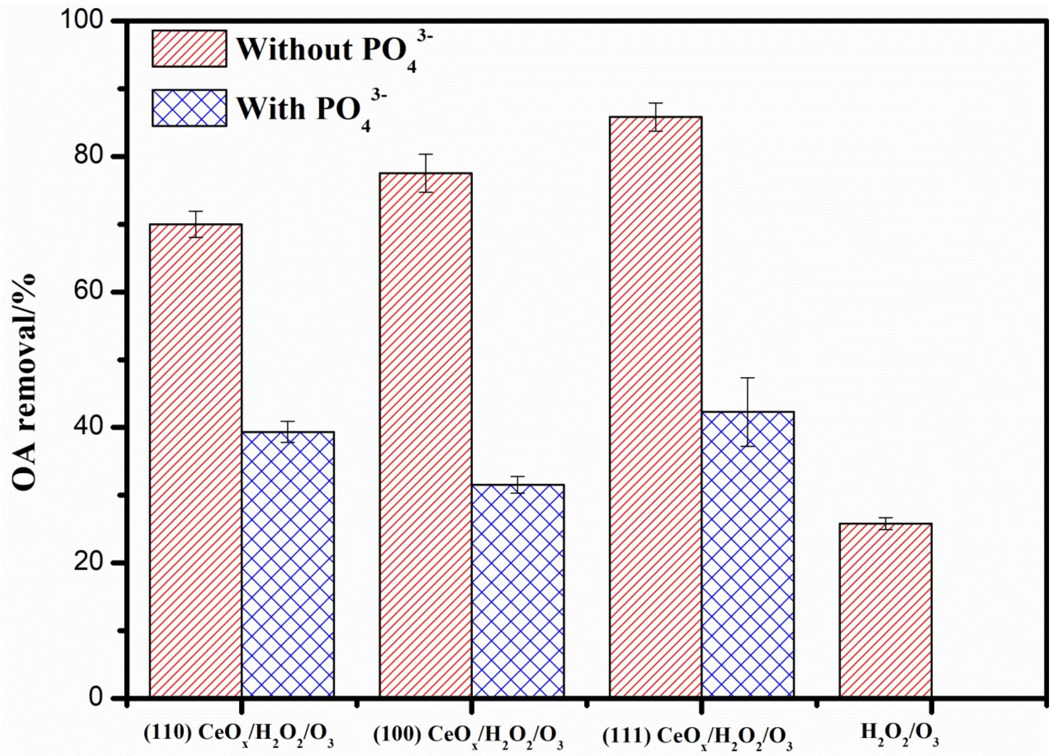
100
80
60
40
20
0
0
10
20
30
40
50
60
OA removal/%
t/min
(100)CeOx/O3/H2O2
(110)CeOx/O3/H2O2
(111)CeOx/O3/H2O2

Fig.S6



1000
800
600
400
200
0
0
10
20
30
40
50
60
·OH Concentration (μg/L)
t/min
(100) CeOx/O3/H2O2
(110) CeOx/O3/H2O2
(111) CeOx/O3/H2O2

Fig.S7



Without PO_4^{3-}
With PO_4^{3-}
OA removal/%
100
80
60
40
20
0
(110) $CeO_x/H_2O_2/O_3$
(100) $CeO_x/H_2O_2/O_3$
(111) $CeO_x/H_2O_2/O_3$
H_2O_2/O_3

Fig.S8

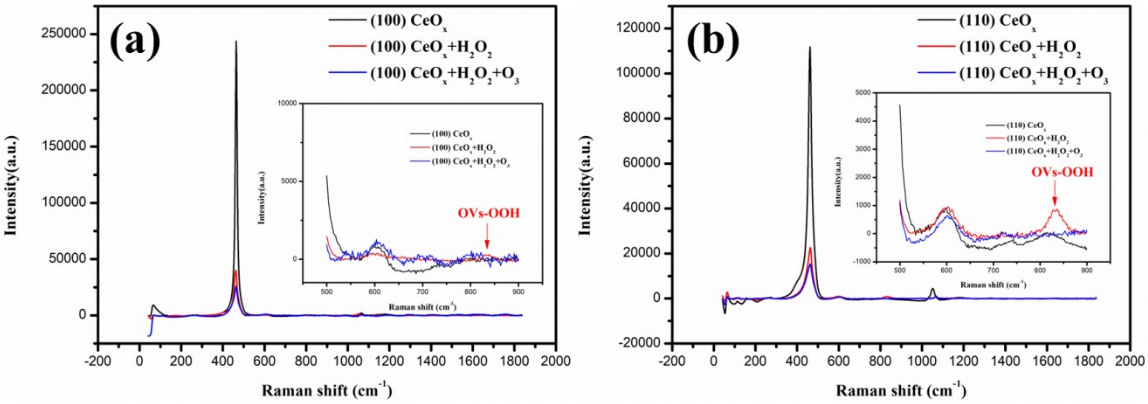

(a)
(100) CeOx
(100) CeOx+H2O2
(100) CeOx+H2O2+O3
Intensity(a.u.)
Raman shift (cm-1)
OVs-OOH
(b)
(110) CeOx
(110) CeOx+H2O2
(110) CeOx+H2O2+O3
Intensity(a.u.)
Raman shift (cm-1)
OVs-OOH

Fig.S9

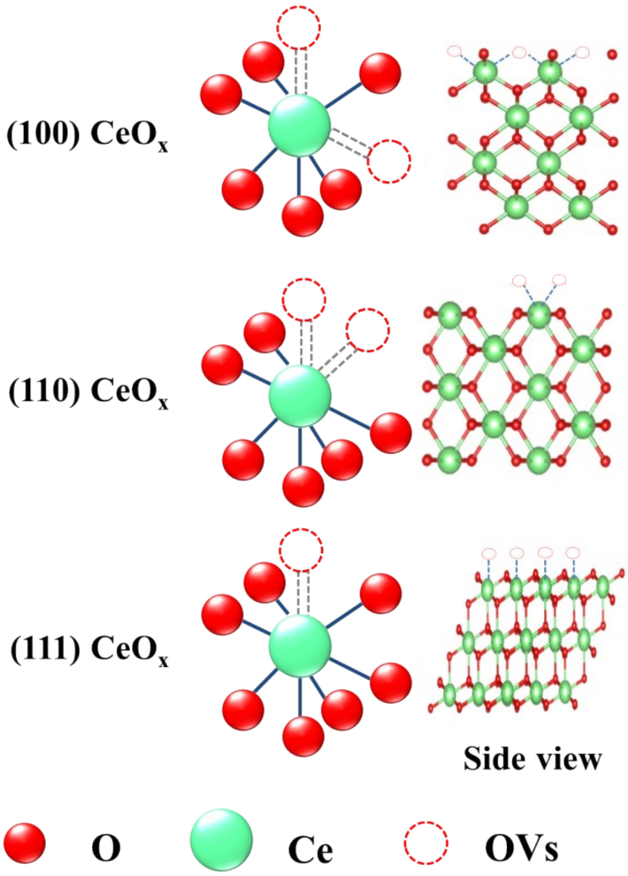


Fig.S10

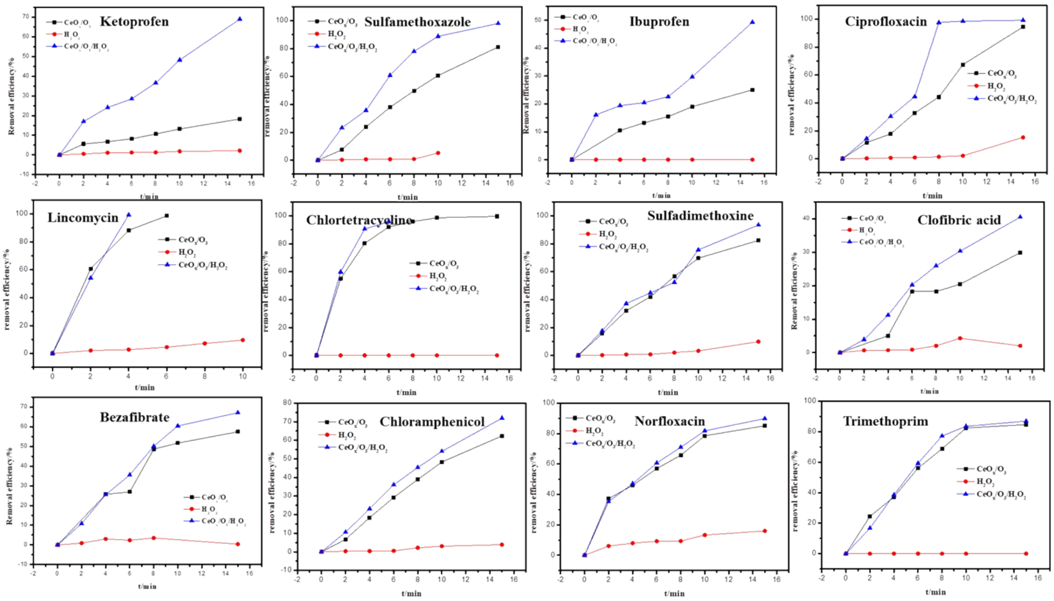

Ketoprofen
Sulfamethoxazole
Ibuprofen
Ciprofloxacin
Lincomycin
Chlortetracycline
Sulfadimethoxine
Clofibric acid
Bezafibrate
Chloramphenicol
Norfloxacin
Trimethoprim
CeO_x/O_3
H_2O_2
$CeO_x/O_3/H_2O_2$
Removal efficiency/%
t/min

Fig.S11

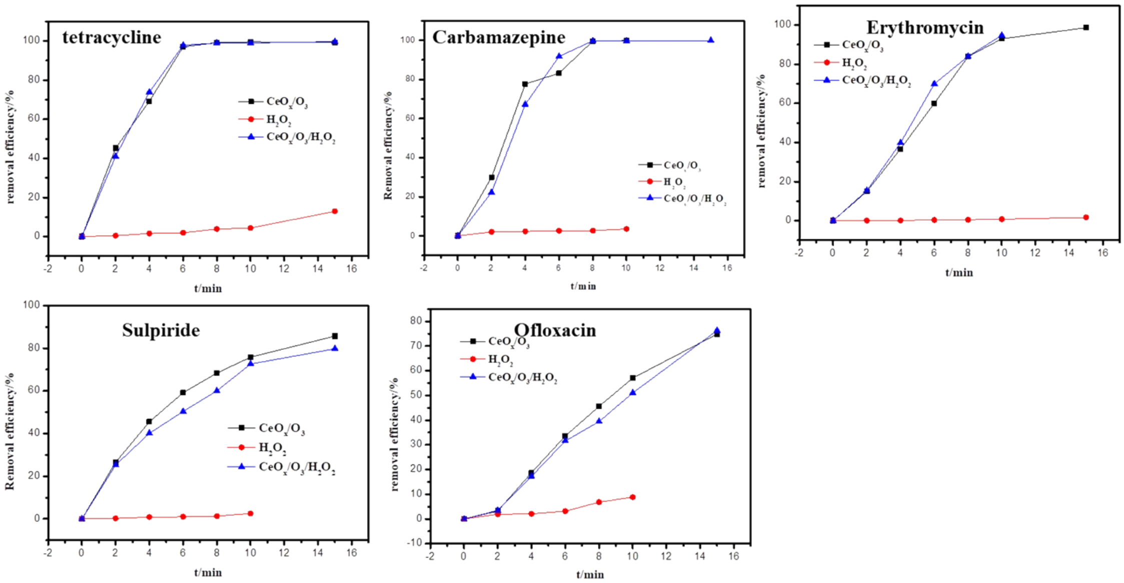
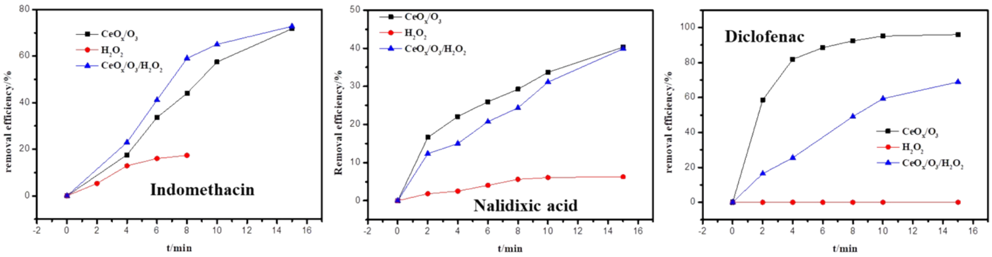

tetracycline
Carbamazepine
Erythromycin
Sulpiride
Ofloxacin
removal efficiency/%
Removal efficiency/%
t/min
CeOx/O3
H2O2
CeOx/O3/H2O2

Fig.S12



Indomethacin
Nalidixic acid
Diclofenac
CeOx/O3
H2O2
CeOx/O3/H2O2
removal efficiency/%
Removal efficiency/%
t/min