Supplementary Information

Water pretreatment promoting the removal of indoor formaldehyde over nano-CeO₂ at ambient temperature

Meng Zhang,^{†ab} Jiaqi Chen,^{†ab} Zhihua Xu,^{*ab} Yingjie Ding,^a Zhaoxiong Yan,^{*ab} Lin Yue^{ab} and Ling Shi^{ab}

^a Hubei Key Laboratory of Industrial Fume and Dust Pollution Control, Jianghan University, Wuhan 430056, China

^b School of Environment and Health, Jianghan University, Wuhan 430056, China

*Corresponding authors

E-mail addresses: xuzhihua78@sina.com; zhaoxiongyan75@163.com

† These authors (Meng Zhang and JIaqi Chen) contributed equally to this work.

1. Experimental

1.1 Materials

Cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O), was purchased from Shanghai Maclean's Biochemical Co.,Ltd (Shanghai,China). Ammonium carbonate ((NH₄)₂CO₃) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

1.2 HCHO removal measurements

HCHO removal experiments at ambient temperature were carried out in a Plexiglass chamber with a 5 W fan at the bottom. The sample (0.1 g) was spread on a glass plate and placed in the chamber covered with a glass lid. A specified volume of HCHO solution (38%) was introduced into the chamber, which turned into gaseous HCHO to achieve a stable level with the assistance of the fan. A photoacoustic IR multigas monitor (INNOVA Model 1412, INNOVA air Tech Instrument, Denmark) was used for online detection of the concentration changes of HCHO, CO₂, CO and water vapor. The lid on the glass plate was removed to start the measurement after the gaseous HCHO reached adsorption/desorption equilibrium, and simultaneously the fluorescent lamp was turned on as needed. The concentration changes of HCHO and CO_2 were used to evaluate the catalysts' activity.

1.3 Toluene catalytic test

In this paper, catalyst activity evaluation experiments were conducted in a fixed bed reactor (6 mm inner diameter) at atmospheric pressure. For each test, 0.3 g of catalyst sample (40~60 mesh) was weighed and placed in the reactor, and air as carrier gas was passed through the volatile organic compound (VOC) bubbler reactor to bring out a high concentration of VOCs, and then mixed with the other air to enter the fixed bed reactor. The mixed gas flow rate was controlled at 40 mL min⁻¹, and the toluene flow rate was 150 mL min⁻¹. Before the experiment, the temperature of the reactor was raised to 100 °C, and the VOCs gas flow was stabilized for 30 min before the initial concentration of toluene was measured. The initial concentration of toluene was measured. Then the reactor was warmed up and the temperature was kept constant for 20 min at each measured temperature point, and the conversion rate at that temperature point was determined from the change in VOCs concentration. The conversion rate at that temperature point was determined according to the change of VOCs concentration. The gas chromatograph (GC-7806, FID detector) was used for the quantitative analysis of VOCs gas components online.

1.4 Active species capture

In order to detect the active species formed under visible light, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), isopropanol (IPA) and silver nitrate (AgNO₃) were selected as scavengers for h⁺, \cdot OH, and e⁻ species, respectively. In a typical measurement, 50 mL of methylene blue (MB) solution (10 mg L⁻¹) is first transferred to a beaker with 100 mL. Then, 50 mg of the prepared sample was put into the above beaker under magnetic stirring. The distance between the lamp and the solution is 10 cm. Before illumination, the suspension was stirred in the dark for 30 minutes to achieve the adsorption-desorption equilibrium between the catalyst and MB. At the next moment, 1 mmol of scavenger was injected into the above solution and the mixture was exposed to the visible light. The concentration change of MB in the solution was analyzed by UV-Vis spectrophotometer (UV-2600i, Shimadzu, Japan) with the maximum absorbance wavelength at 662 nm. The distance between the lamp and the solution is 50 cm.

1.5 Electrochemical measurements

The electrochemical impedance spectroscopy (EIS) \cdot the transient photocurrent response and Mott-Schottky tests were conducted on the CHI760E electrochemical work station. The frequency of EIS ranged from 0.01 Hz to 10⁵ Hz and the alternating current amplitude was 10 mV. The detailed fabrication of the working electrode was as follows: 50 mg of catalyst and 20 mg of polyethylene glycol (PEG20000) were mixed into slurry together with 1 mL of deionized water. The slurry was then coated onto an ITO glass electrode with 1 cm \times 1 cm and dried at 80 °C for 3 h. The asprepared catalyst was served as the working electrode, respectively. The electrolyte was 0.5 mol L⁻¹ of Na₂SO₄ solution. In the active species and electrochemical tests, a 350 W Xe lamp (Changzhou Siyu Technic Co., China) was employed as the light source.



Fig. S1 Top view and front view for H_2O molecule adsorbed on top Ce (a,b), bridged Ce-Ce (c,d), and bridged Ce-O (e,f) of CeO₂ (111).

Adsorption sites		E _{ads} (eV) -	Bond length (Å)	Angle (°)	
			О-Н	НОН	
Free H ₂ O		_	0.96	104.5	
CeO ₂ (111)	top Ce	-0.43	0.97	105.4	
	bridged Ce-Ce	-0.27	0.98	104.5	
	bridged Ce-O	-0.28	0.99	104.6	
CeO ₂ (220)	top Ce	-0.43	0.97	105.4	
	bridged Ce-Ce	-0.55	1.01	102.5	
	bridged Ce-O	-0.71	1.03	107.5	

Table S1 Comparison of H₂O molecule adsorbed on CeO₂ (111) and CeO₂ (220).



Fig. S2 HCHO degradation (a) and the corresponding CO₂ yielding (b) over p-CeO₂, CeO₂-10-80, CeO₂-20-80, CeO₂-30-80, CeO₂-20-50 and CeO₂-20-100 under indoor light irradiation.



Fig. S3 (a) XRD patterns, (b) FTIR spectra (c) O 1s and (d) Ce 3d XPS spectra of

CeO₂-20-80 before and after 5 cycles.



Fig. S4 Comparison of toluene conversion over CeO₂-20-80 and p-CeO₂.

Samples	$T_{50}/^{\circ}C$	T ₉₀ /°C
p-CeO ₂	210	250
CeO ₂ -20-80	~190	200

Table S2 T_{50} and T_{90} of synthesized catalysts for toluene oxidation.

 T_{50} -the temperature of 50% toluene conversion; T_{90} -the temperature of 90% toluene

conversion.



Fig. S5 Top view and front view for HCHO molecule adsorbed on top Ce (a,b), bridged Ce-Ce (c,d), and bridged Ce-O (e,f) of CeO₂ (220).

Adsorption sites		E _{ads} (eV)	Bond length (nm)		Angle (°)	
			С-Н	С=О	НСН	НСО
Free HCHO			0.111	0.121	116.1	121.2
CeO ₂ (111)	top Ce	-0.20	0.111	0.122	118.8	120.9
	bridged Ce-Ce	-0.04	0.111	0.121	116.9	122.1
	bridged Ce-O	-0.75	0.111	0.136	107.8	110.8
CeO ₂ (220)	top Ce	-0.18	0.111	0.123	119.0	120.7
	bridged Ce-Ce	-0.06	0.112	0.122	117.2	121.1
	bridged Ce-O	-0.2	0.111	0.125	115.7	121.1

Table S3 Comparison of HCHO molecule adsorbed on CeO₂ (111) and CeO₂ (220).



Fig. S6 O_2 -TPD-MS for (a) p-CeO₂ and (b) CeO₂-20-80.



Fig. S7 The transient photocurrent response under visible light irradiation of p-CeO₂ and CeO₂-20-80.