Ultrahigh efficiency CH_4 photocatalytic conversion to C1 liquid products over cheap and plentiful CeO_2 at 30 °C

Hailong Tang [a], Tangtong Ju [a], Yue Dai [a], Meiling Wang [a,], Yongqing Ma [a, b,] *, Min Wang [c] and Ganhong Zheng [a]*

[a] *School of Materials Science and Engineering, Anhui University, Hefei, 230601, China*

[b] *Institute of Physical Science and Information Technology, Anhui University, Hefei 230601, China*

[c] *School of Physics and optoelectronics engineering, Anhui University, Hefei, 230601, China*

*To whom correspondence should be addressed.

Tel: (86) 13856996630, E-mail: mlw@ahu.edu.cn, yqma@ahu.edu.cn

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Fig. S1-S8, Table S1-S4

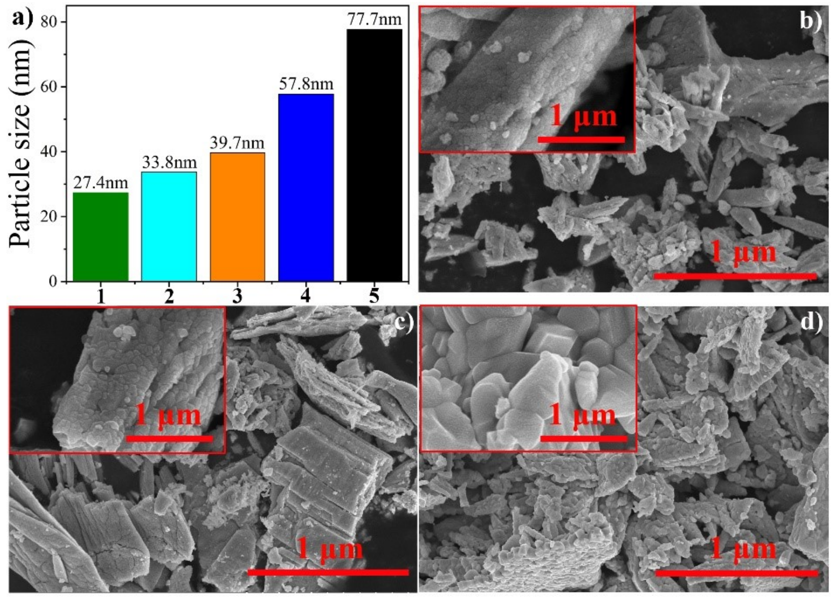

Fig. S1 a) Particle size distributions of different catalysts calculated using Scherrer equation, b-d) Low- and high-magnification SEM images of representative samples.

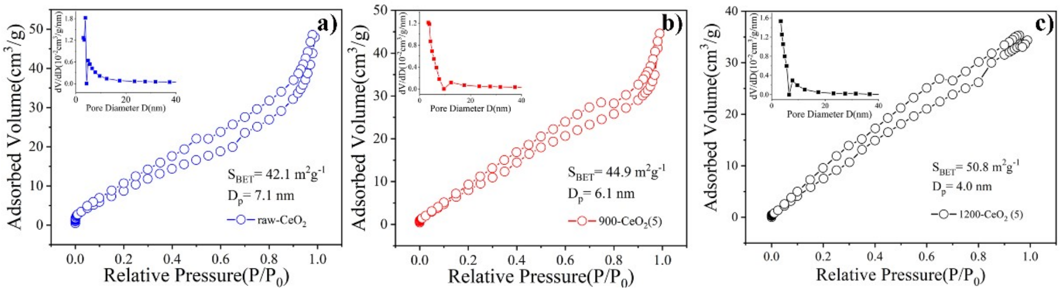

Fig. S2 The nitrogen adsorption-desorption isotherms and pore size distributions of raw-CeO_2, 900-CeO_2(5) and 1200-CeO_2(5) respectively.

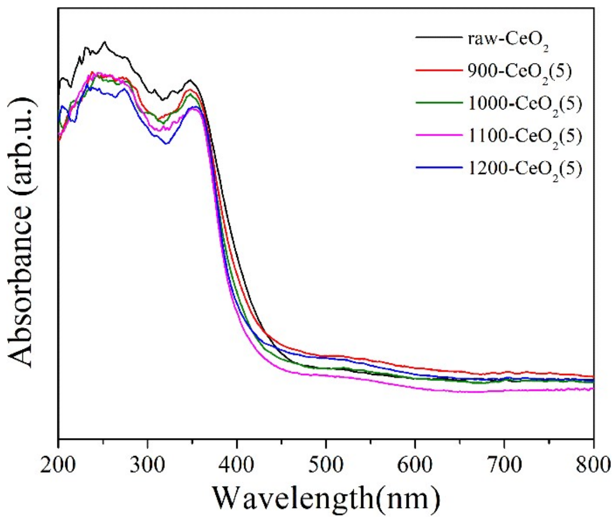

Fig. S3 UV–vis absorption spectra of different samples.

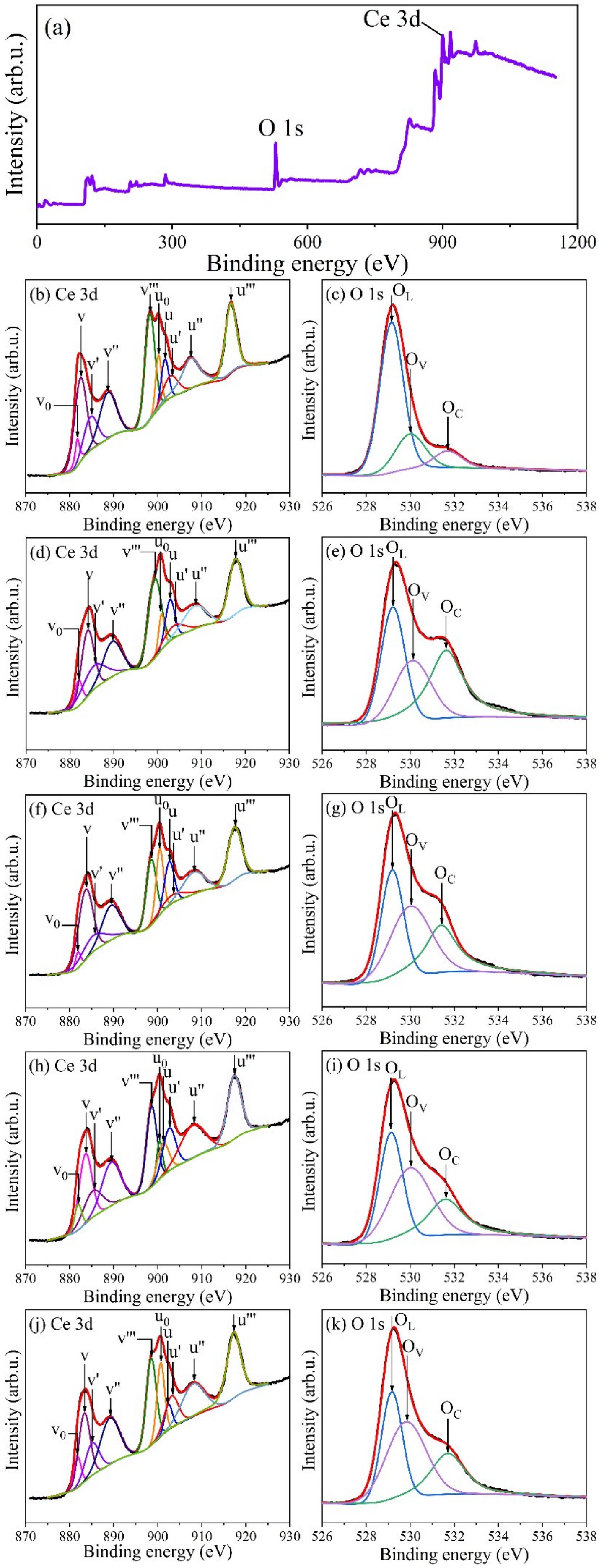
(a)
Ce 3d
O 1s
Intensity (arb.u.)
0 300 600 900 1200
Binding energy (eV)
(b) Ce 3d
(c) O 1s
(d) Ce 3d
(e) O 1s
(f) Ce 3d
(g) O 1s
(h) Ce 3d
(i) O 1s
(j) Ce 3d
(k) O 1s
v
v'
v''
v'''
v0
u
u'
u''
u'''
u0
OL
OV
OC
870 880 890 900 910 920 930
526 528 530 532 534 536 538

Fig. S4 a) XPS survey spectra of sample 1200-CeO_2, and high resolution Ce 3d and O 1s XPS spectra of sample b, c) raw-CeO_2, d, e) 900-CeO_2(5), f, g) 1000-CeO_2(5), h, i) 1100- CeO_2(5) and j, k) 1100- CeO_2(5) respectively.

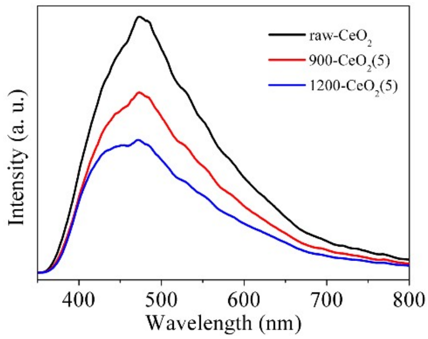

Fig. S5 Photoluminescence spectra of raw-CeO_2, 900-CeO_2(5) and 1200-CeO_2(5).

Catalyst	**Main Products**	**Oxidant**	**Temperature**	**Pressure**	**References**
Fe/TiO_2	**alcohol**	**H_2O_2**	**Room temperature**	**Atmospheric pressure**	**17**
Cu/C_3N_4	**ethanol**	**H_2O**	**Room temperature**	**Atmospheric pressure**	**19**
Au-CoO_x/TiO_2	**CH_3OOH and CH_3OH**	**O_2**	**25 °C**	**0.1 MPa O_2 and 2.0 MPa**	**21**
ZnO nanosheets	**CH_3OOH, CH_3OH, HCHO and HCOOH**	**H_2O_2**	**50 °C**	**Atmospheric pressure**	**22**
CeO_2	**ethanol and aldehyde**	**water**	**25 °C**	**0.2 MPa**	**34**
IrFe supported on ZSM-5	**CH_3COOH, CH_3OH, and HCOOH**	**H_2O_2**	**50 °C**	**3 MPa**	**41**

RGO-TiO_2	**Aldehyde and acetone**	**Water vapor**	**60 ℃**	**Atmospheric pressure**	**42**
BiOCl	**CH_3OH**	**O_2**	**40 ℃**	**Normal**	**43**
CeO_2	**HCHO, CH_3OH, CH_3OOH and HCOOH**	**H_2O_2**	**30 ℃**	**2 MPa**	**Our work**

Table S1 Catalysts referenced in Fig. 4f and their photocatalytic experimental conditions.

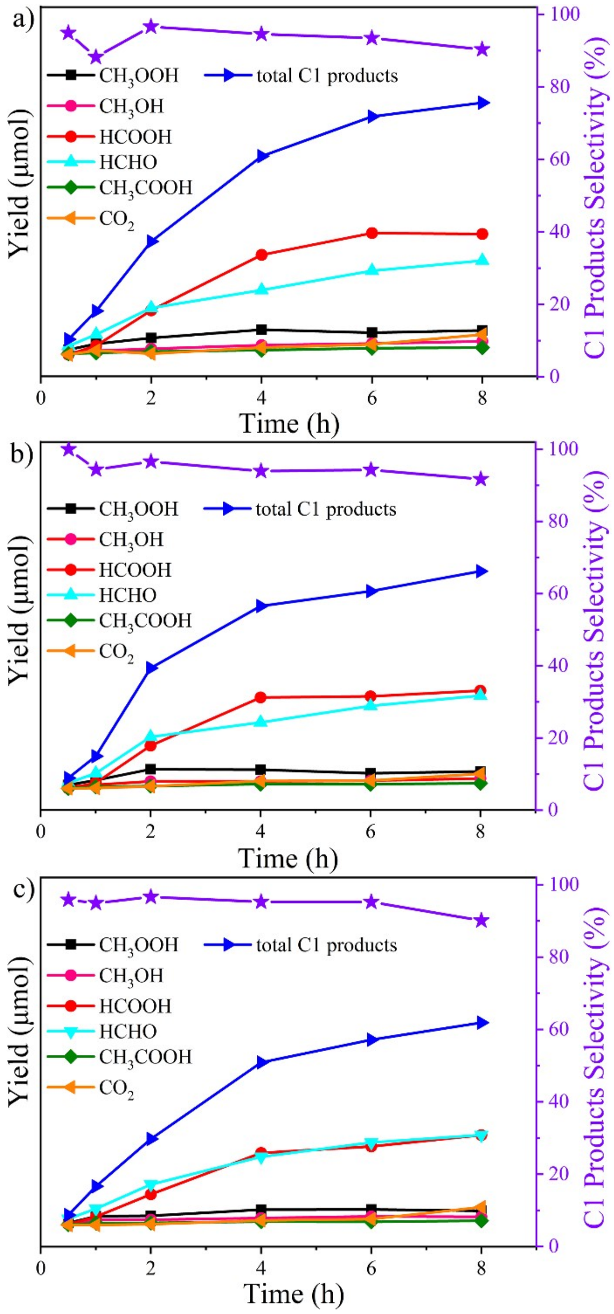

Fig. S6 Different products yields and C1 products selectivity over a) 5 mg, b) 10 mg and c) 20 mg 1200-CeO_2(5) obtained as a function of photoexcitation time (2 MPa CH_4, 30 °C, 165 μL H_2O_2).

C1 liquid products	e^- transfered	C1 selectivity	HCHO and HCOOH selectivity	H_2O_2 conversion rate	Gain factor
67.31	348.1	1	0.92	0.1	0.39

Table S2 Photocatalytic performance of 1200-CeO_2(5), experimental condition: (20 mg catalyst, 2 MPa CH_4, 70 °C, 165 μL H_2O_2, 2 h).

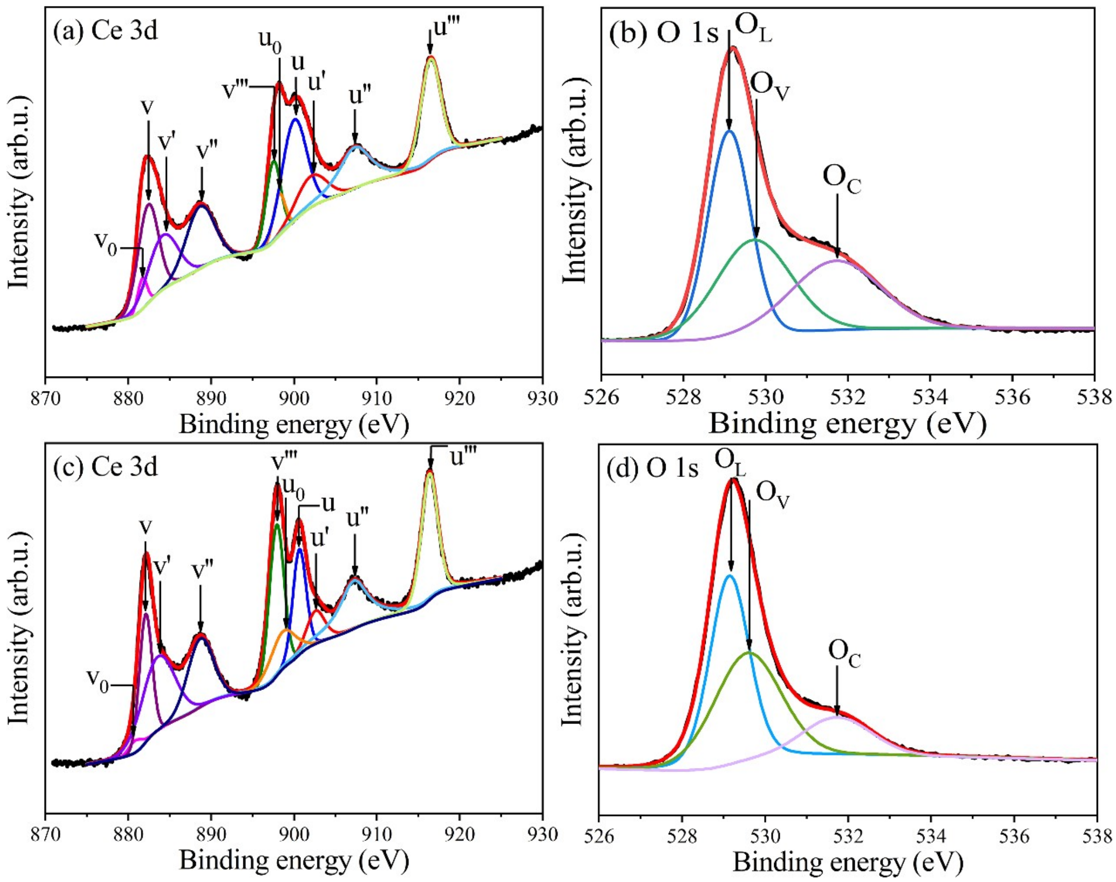

Fig. S7 High resolution Ce 3d and O 1s XPS spectra of sample 1200-CeO_2(5) a) after photocatalysis and b) regenerated via reannealing treatments.

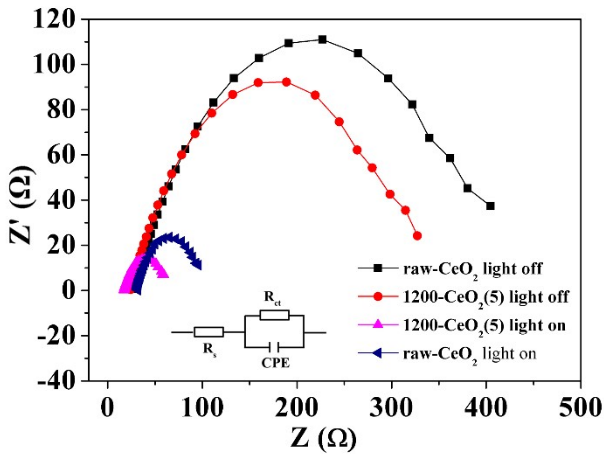

Fig. S8 Electrochemical impedance spectra of raw-CeO_2 and 1200-CeO_2(5) in 1 M Na_2SO_4 aqueous solution at 1.8 V vs reversible hydrogen electrode.

1200-CeO_2(5)	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$ (%)	O_v ratios (%)
After 4th cycle	23.13	32.83
Regenerated	27.4	41.45

Table S3 $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ and O_v ratios of 1200-CeO_2(5) after 4th cycle and regeneration via the relative intensity ratios in XPS spectra.

radical scavengers	CH_3OH	HCHO	HCOOH	CH_3COOH	CH_3OOH	CO_2	C1 products
Without radical scavengers	2.2	11.5	15.9	0.5	4.8	0.5	34.9
isopropanol	0.7	4.1	16.9	3.6	0.6	0	25.9
benzoquinone	0	0	0		0	3.2	0

Table S4 Yields of C1 products without and with radical scavengers.

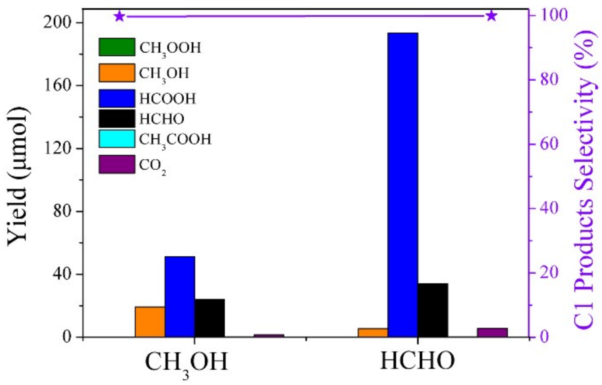

Fig. S9 Yields of various products using CH_3OH and HCHO as the starting reactants respectively.