

Ag–O–Ce³⁺ Atomic Interface and Surface Oxygen Vacancies on CeO₂ Synergistically Promoted Selective Visible Photocatalytic Reduction of Carbon Dioxide

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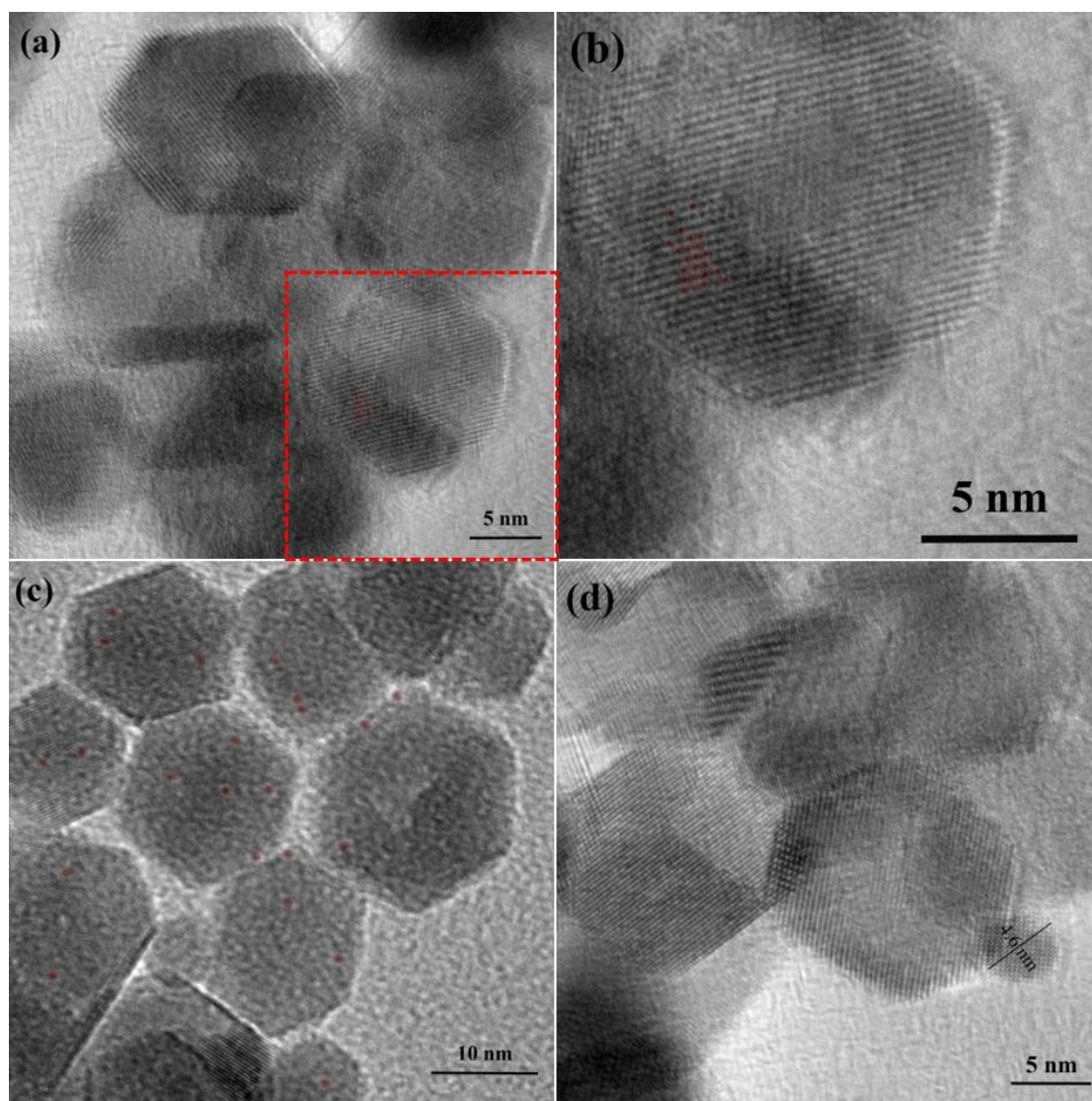


Fig. S1 (a, b) HRTEM image of 0.5% Ag/H-CeO₂, (c) 1.0% Ag/H-CeO₂, and (d) 3.0% Ag/H-CeO₂.

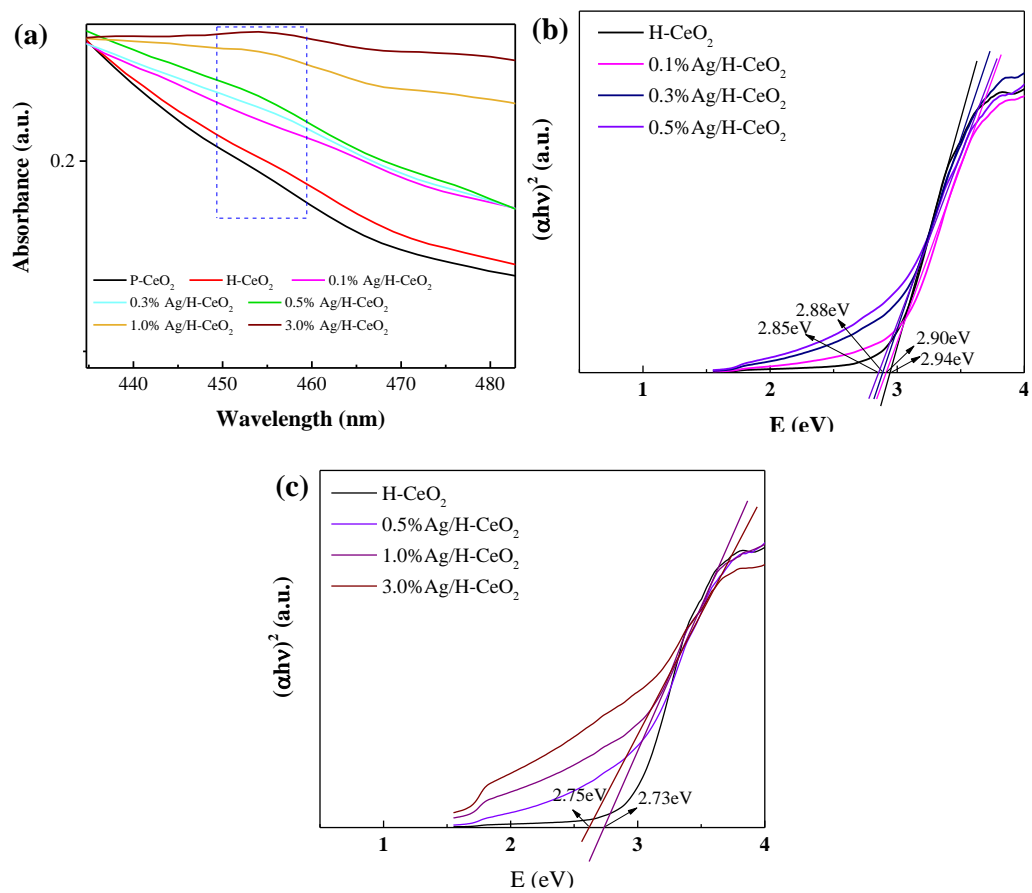


Fig. S2 Enlarged region of ultraviolet visible diffuse reflectance spectroscopy (a), and Tauc-plots of different photocatalysts (b, c).

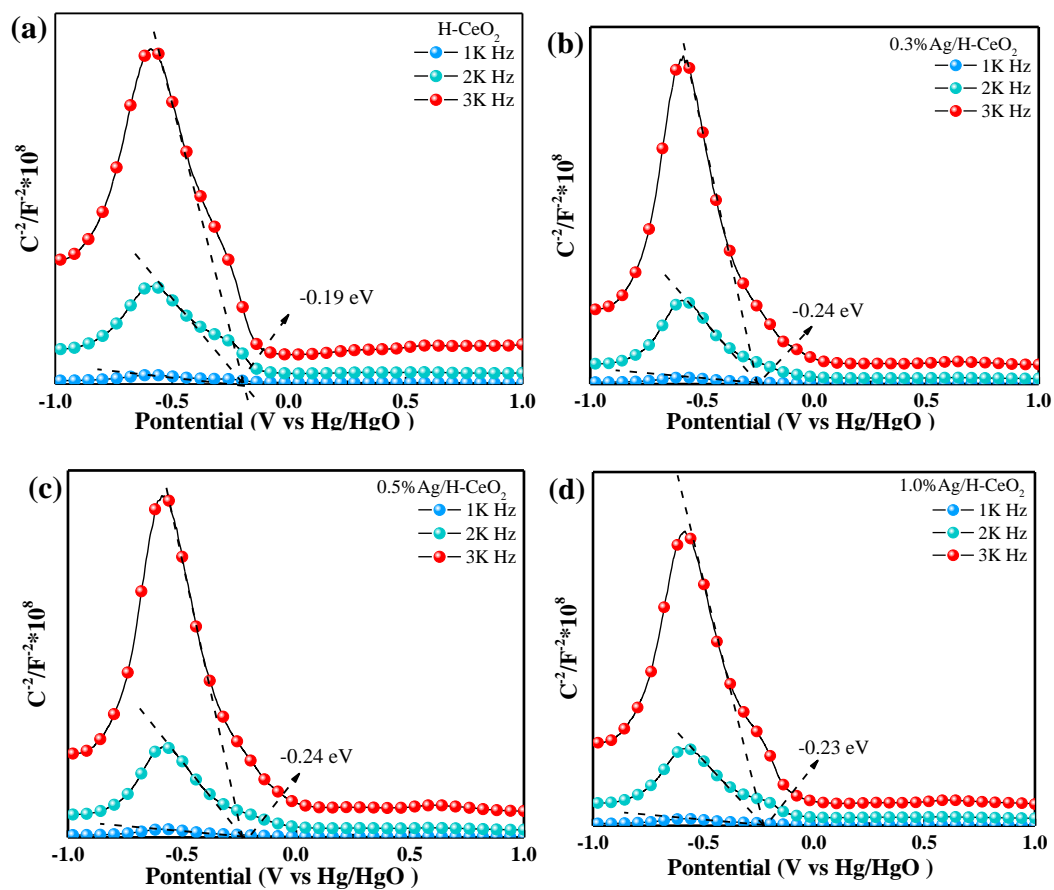


Fig. S3 Mott-Schottky plots of the photocatalysts.

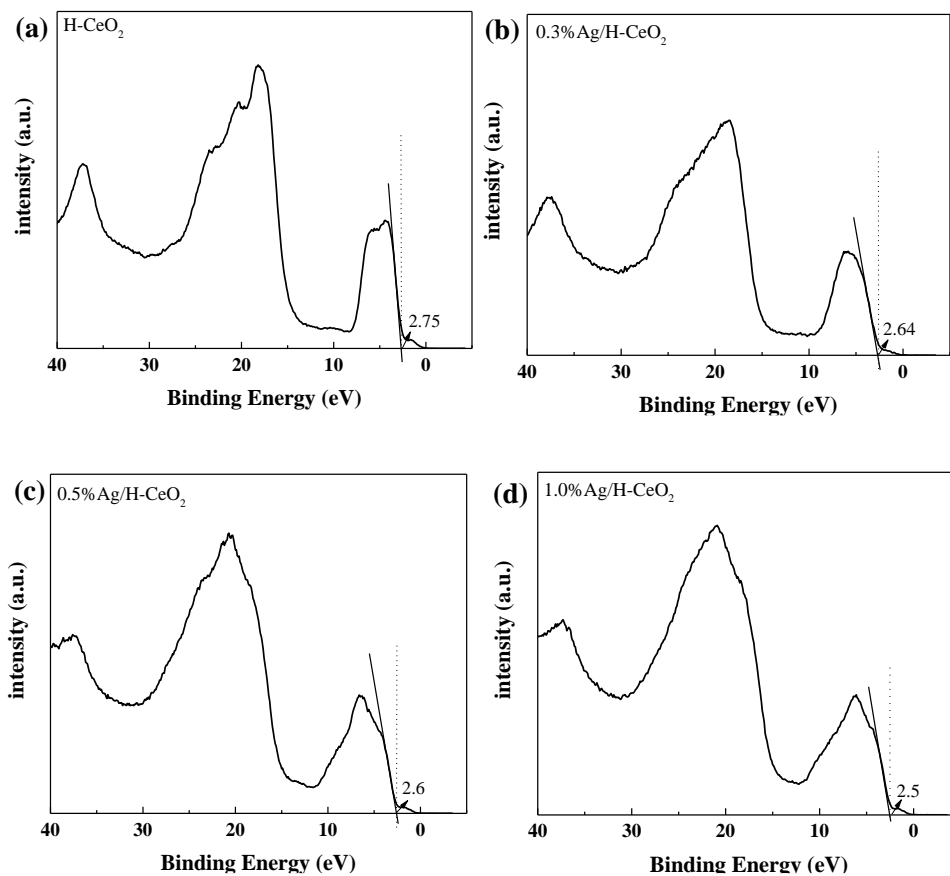


Fig. S4 XPS Valence band spectrum of the photocatalysts.

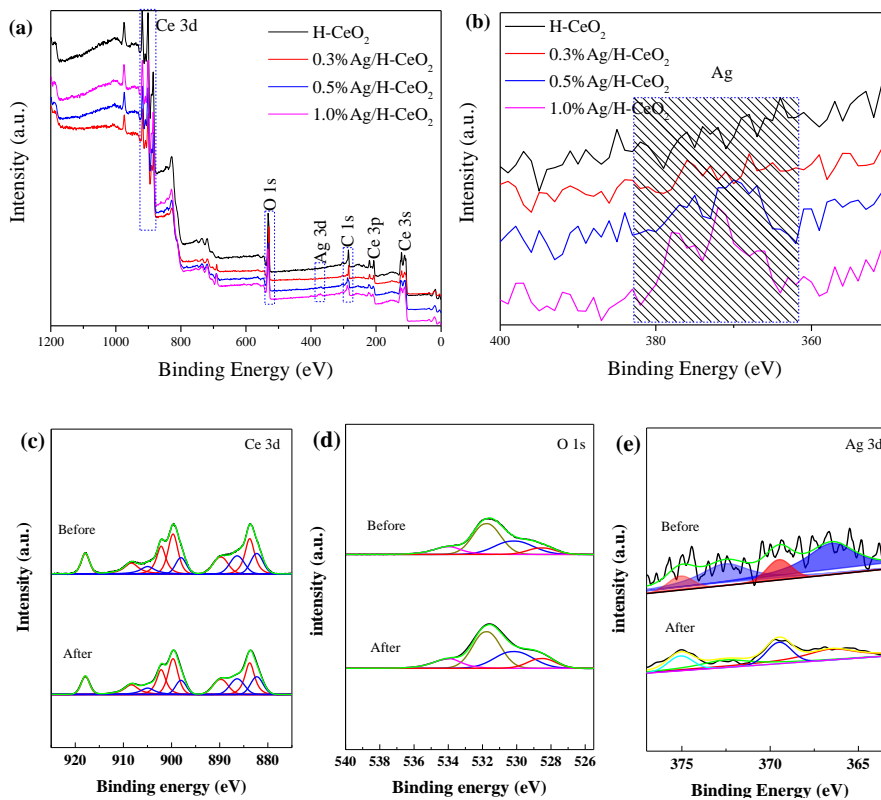


Fig. S5 Survey XPS spectra of photocatalysts (a), enlarged area of survey spectra (b) of the photocatalysts, and comparison of the species over 0.3% Ag/CeO₂ photocatalyst before and after photocatalytic reaction (c-e).

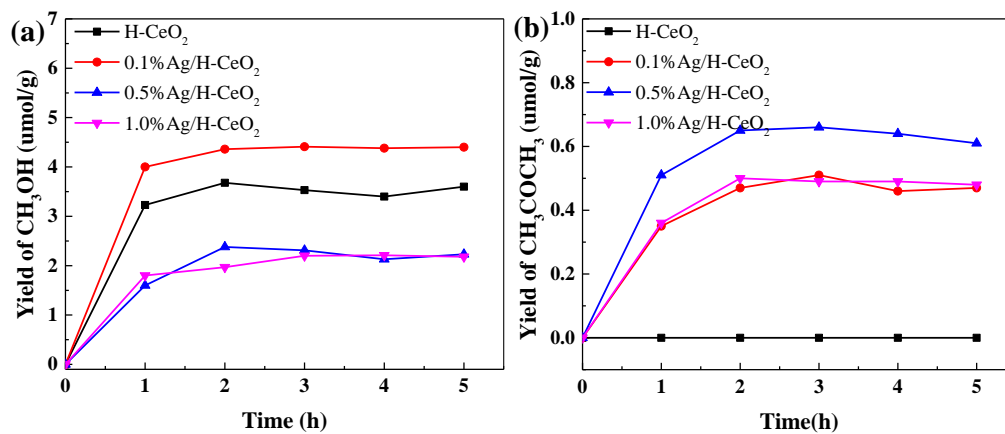


Fig. S6 Photocatalytic reduction of carbon dioxide in anhydrous conditions using various photocatalysts to different products: (a) CH₃OH, (b) CH₃COCH₃.

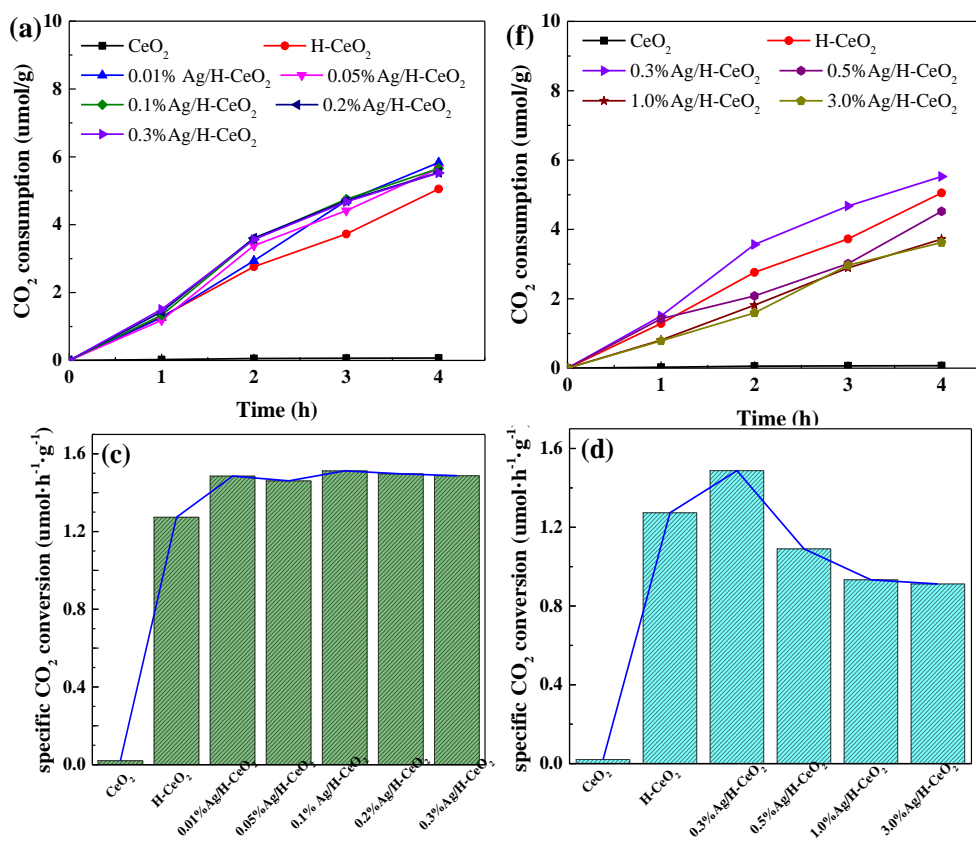


Fig. S7 (a, b) CO₂ consumption, (c, d) normalized apparent rate constant of the CO₂ conversion.

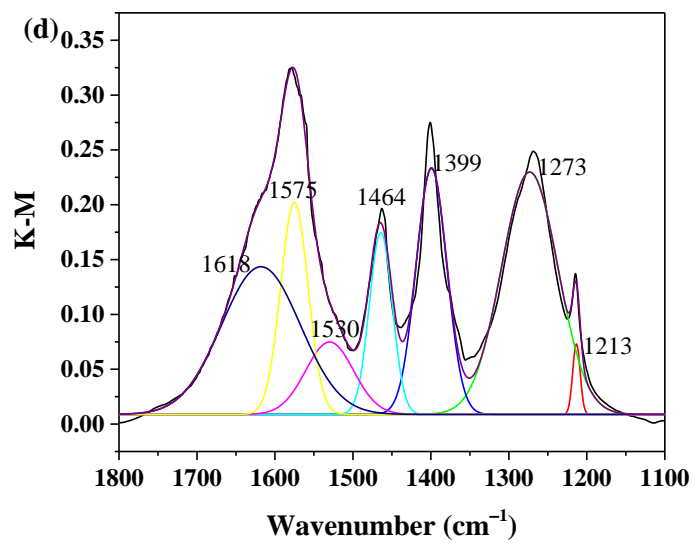


Fig. S8 Devaluated peaks of DRIFTS spectra of CO₂ adsorbed on 0.3% Ag/H-CeO₂.

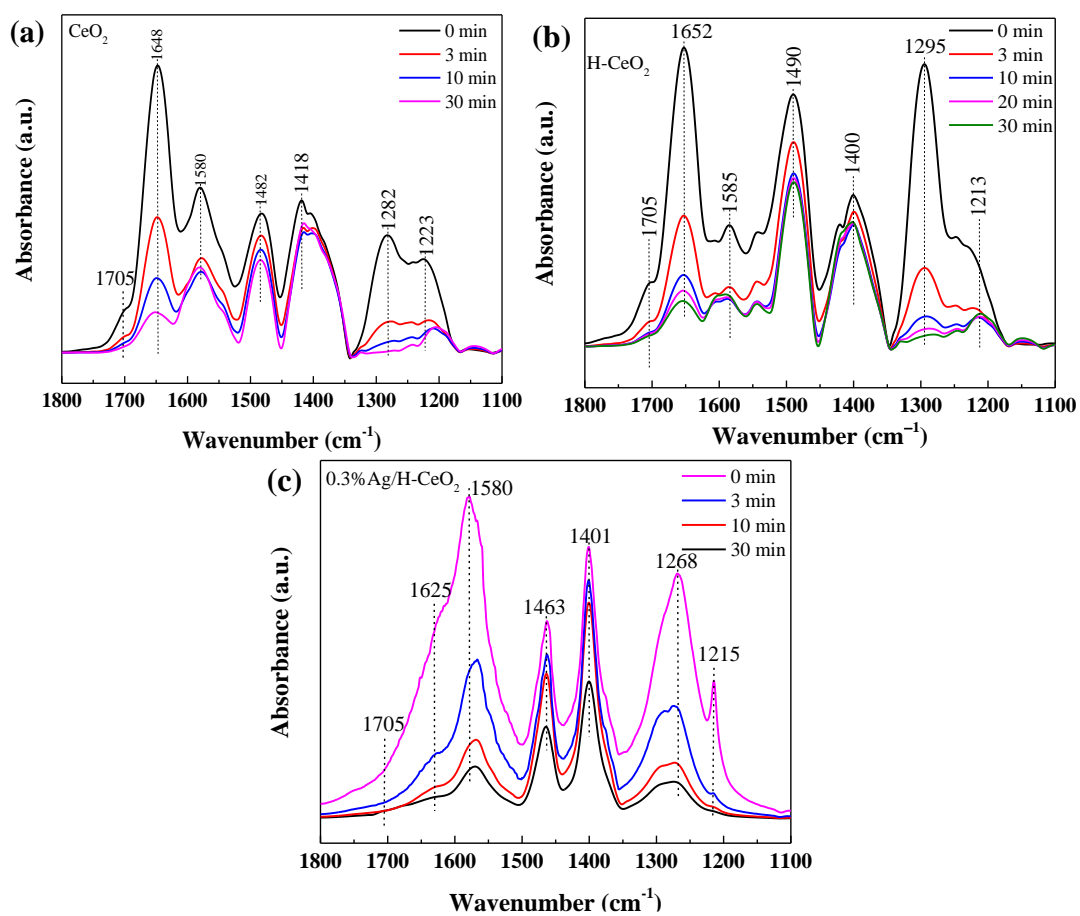


Fig. S9 In-situ DRIFTS spectra of CO_2 desorbed on the different photocatalysts, (a) CeO_2 , (b) H-CeO_2 , (c) 0.3%Ag/ H-CeO_2 .

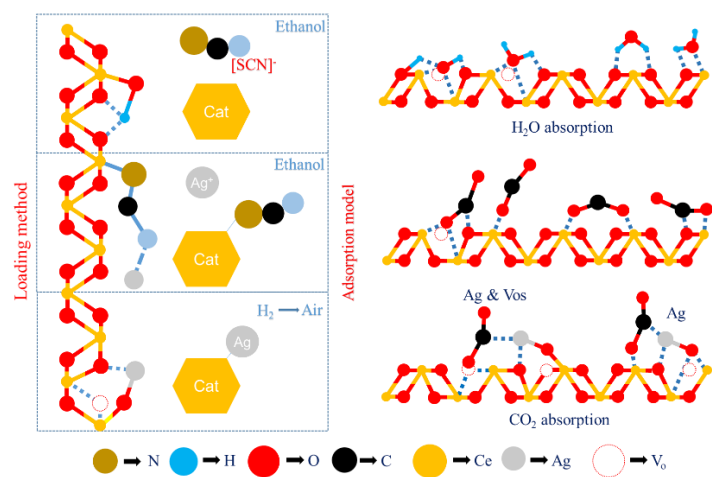


Fig. S10 Diagram of Ag load mode and CO₂ adsorption in H-CeO₂.

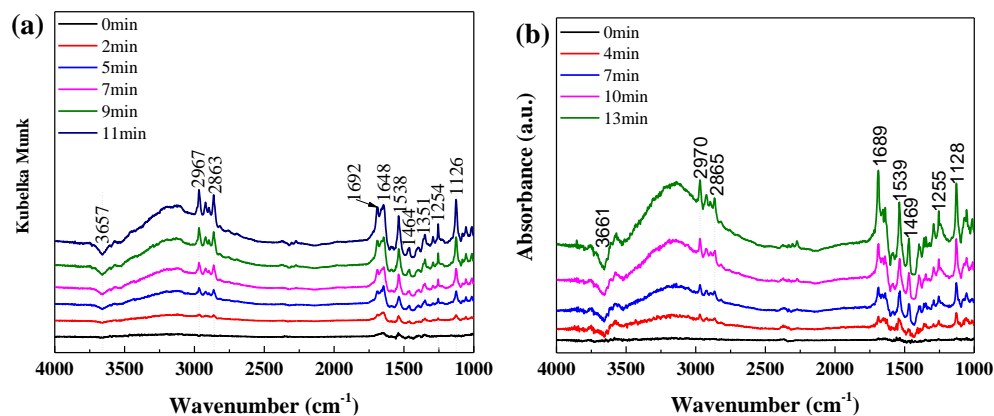


Fig. S11 IR spectroscopy of (a) methanol and (b) acetone absorbed in-situ on H-CeO₂.

Fig. S11a presents a broad absorption band centered at 1692 cm⁻¹ that can be assigned to the hydroxyl in methanol, the band at 1128 cm⁻¹ can be due to the stretching vibration of hydroxyl of methanol, and the band at 1648 cm⁻¹ can be attributed to the stretching vibration of C–O bond. The bands in 2860~2970 cm⁻¹ and 1351 cm⁻¹ are the characteristic of methyl (–CH₃).^[1] Generally, the IR vibration of carbonyl in acetone lies at 1720 cm⁻¹,^[1] here the band at 1689 can be assigned to the carbonyl of acetone, the shift of this band to lower wavenumber due to the strong interaction of carbonyl and H-CeO₂, which weakens the strength of C=O bond.

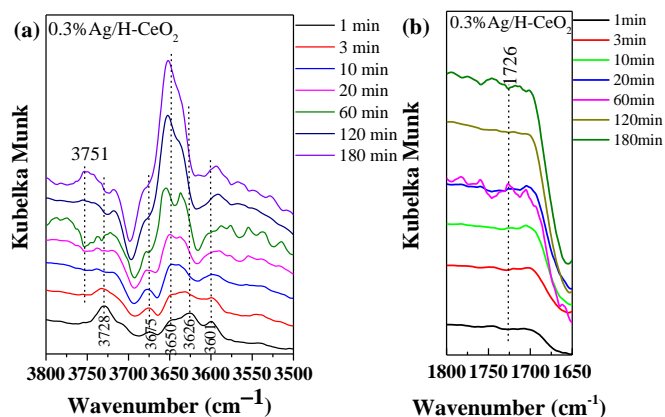


Fig. S12 Alteration of in-situ IR spectra of photocatalytic CO₂ reduction performed on 0.3% Ag/H-CeO₂.

The DRIFTS of 0.3% Ag/H-CeO₂ sample that adsorbed CO₂ and H₂O in dark for 30 min and subsequently were irradiated with visible light for 1, 3, 10, 20, 60, 120, and 180 min. The absorption band in 3500~3800 cm⁻¹ can be ascribed to a joint stretching vibration coupling the H-bound OH groups with the physically adsorbed water molecules.^[2] Significant reduction of the band at 3728 assigned to surface hydroxyl was observed in the reactions, which can be due to the elimination of hydroxyl that take part in the photocatalytic reactions. A new peak at 3751 appears, which can be assigned to the hydroxyl in methanol, indicating the formation of methanol.

A new band at 1726 cm⁻¹, assigned to the H-C=O group, appears as the reaction prolonged, which confirms the formation of intermediate, aldehyde.^[2] The amount of aldehyde formed in the reaction increases first and then decrease, indicating the formed aldehyde further takes part in the following reaction for the production of acetone.

Table S1 element content obtained from XPS

Sample	XPS spectra	Peak	Position (eV)	Area	Peak/XPS spectra (%)
H-CeO ₂	Ce3d	Ce ³⁺	-	684688.2	31.9
		Ce ⁴⁺	-	1,461,350.1	68.1
0.3% Ag/H-CeO ₂		Ce ³⁺	-	371283.03	32.4
		Ce ⁴⁺	-	774515.2	67.6
0.5% Ag/H-CeO ₂		Ce ³⁺	-	527989.5	32.9
		Ce ⁴⁺	-	1078249	67.1
1.0% Ag/H-CeO ₂		Ce ³⁺	-	575563.1	34.1
		Ce ⁴⁺	-	1114057	65.9
H-CeO ₂	Ag3d	Ag ⁺	-	-	-
		Ag	-	-	-
0.3% Ag/H-CeO ₂		Ag ⁺	372.5/366.5	3,579.8	82.1
		Ag	375/369	780.53	17.9
0.5% Ag/H-CeO ₂		Ag ⁺	372.5/366.5	3,862.64	69.66
		Ag	375/368.8	1,682.36	30.34
1.0% Ag/H-CeO ₂		Ag ⁺	372.3/366.3	7,393.67	38.8
		Ag	375/369	11,662.19	61.2
H-CeO ₂	O1s	O ₁ (lattice oxygen)	528.6	97705.00	25.3
		O ₂ (V _{os})	530	111,205.26	28.8
		O ₃ (Surface hydroxyl)	531.9	141717.90	36.7
		O ₄ (Absorbed H ₂ O)	534	35442.21	9.2
0.3% Ag/H-CeO ₂		O ₁ (lattice oxygen)	528.6	20253.62	10.1
		O ₂ (V _{os})	530	57387.73	28.7
		O ₃ (Surface hydroxyl)	531.9	95830.42	47.9
		O ₄ (Absorbed H ₂ O)	534	26560.87	13.3
0.5% Ag/H-CeO ₂		O ₁ (lattice oxygen)	528.6	28192.17	9.3
		O ₂ (V _{os})	530	88,041.57	28.9
		O ₃ (Surface hydroxyl)	531.9	129,777.53	42.6
		O ₄ (Absorbed H ₂ O)	534	47915.38	15.7
1.0% Ag/H-CeO ₂	O ₅ (Ag-O)	527.3	10805.78	3.5	
	O ₁ (lattice oxygen)	528.6	36,026.10	10.3	
	O ₂ (V _{os})	530	101487.8	29.0	
	O ₃ (Surface hydroxyl)	531.9	157,745.37	45.1	
	O ₄ (Absorbed H ₂ O)	534.2	28893.12	8.2	
	O ₅ (Ag-O)	527	25887.51	7.4	

Table S2 Control experimental results under different conditions.

Conditions		Typical experiment: visible light, 80 °C, photocatalyst, H ₂ O+CO ₂					
Samples	No light	30 °C	No photocatalyst	No H ₂ O	No CO ₂	No H ₂ O Add CH ₃ OH	No CO ₂ Add CH ₃ OH
P25	None	None	None	None	None	None	None
CeO ₂	None	CH ₃ OH	None	CH ₃ OH	None	-	None
Ag/ H-CeO ₂	None	CH ₃ OH CH ₃ COCH ₃	None	CH ₃ OH CH ₃ COCH ₃	None	-	None

Notes: "None" is designated that no product was detected.

The controlled experiments were carried out on a CEL-GPPCN system designed by CEALIGHT (Beijing China), with a flame ionization detector (FID) and thermal conductive detector (TCD), which was equipped with a TDX-01 and SE-54 column, respectively, using argon as a carrier. The possible products were identified by a standard external method and detailed as follows. Firstly, the standard gas with concentration of 10, 20, 50 and 100 ppm were injected into the detector. Secondly, the standard curves were made by the abundance of the peaks and then the unique characteristic retention peak was used to identify the possible products (CO, CH₄, C₂H₄, CH₃O, CH₃OH, HCOOH, C₂H₅OH).

Different with typical run, it changes reaction condition as shown in the table, and all control experiments use Ar to clean the reactor before the dark treatment to avoid impact that the impurity gas adsorbed by catalyst. After reaction, 1.0 mL gas was sampled at a regular interval (1 h) through the septum, and analyzed by the gas chromatograph.

Table S3 Adsorption energy of different molecules on various photocatalysts.

	CO ₂ /CeO ₂ -Ag-V _o (eV)	CeO ₂ -Ag-V _o (eV)	CO ₂ (eV)	Adsorption Energy (eV)
Ag-O=C=O	-47209.61	-46172.96	-1034.53	-2.12
Ag-CO ₂	-47210.53	-46173.48	-1034.78	-2.26
	CH ₃ OH/CeO ₂ -Ag(SA)-V _o -46834.28	CeO ₂ -Ag-V _o -46173.48	CH ₃ OH -660.48	-0.32
	HCHO/CeO ₂ -Ag(SA)-V _o -46802.34	CeO ₂ -Ag-V _o -46173.48	HCHO -627.12	-1.73
	HCHO/CeO ₂ -V _o -42798.16	CeO ₂ -V _o -42168.45	HCHO -627.35	-5.55
	CH ₃ OH/CeO ₂ -V _o -42831.95	CeO ₂ -V _o -42168.45	CH ₃ OH -657.96	-2.36
Adsorption Energy (eV)	CH ₃ COCH ₃ /CeO ₂ -Ag(SA)-V _o -42768.30	CeO ₂ -V _o -42168.45	CH ₃ COC H ₃ -596.38	-3.47
	CH ₃ COCH ₃ /CeO ₂ - Ag(SA+NC)-V _o -46781.92	CeO ₂ -Ag(SA+NC)- V _o -46182.48	CH ₃ COC H ₃ -596.38	-3.06
	CH ₃ OH/CeO ₂ -Ag(SA+NC)-V _o 46,846.60	CeO ₂ -Ag(SA+NC)- V _o -46182.48	CH ₃ OH -660.48	-3.64

Note: SA: single atom, NC: nanocluster.

References

- [1] Xing Qiyi, Pei Weiwei, Xu Ruiqiu, Pei Jian, Basic Organic Chemistry (I), 4th edition, Peking University Press, 2018.
- [2] N. Li, B. Wang, Y. Si, F. Xue, J. Zhou, Y. Lu, M. Liu, Toward high-value hydrocarbon generation by photocatalytic reduction of CO₂ in water vapor, ACS Catal. 2019, 9, 5590-5602.