Supplementary Information

Key role of light on highly efficient photothermocatalytic steam cellulose reforming on Co/CeO_2-$Al_1Mg_3O_{4.5}$

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1. Characterization.

X-ray diffraction (XRD) patterns of different catalysts were tested using Cu Kα radiation on an X-ray diffractometer (Rigaku D/max). A transmission electron microscope (JEM-ARM200F) was used to obtain TEM images and EDS images. The HRTEM images and HAADF images were obtained using a transmission electron microscope (JEM-ARM200F). The specific surface area and pore volume of the samples were measured at 77.15 K using N_2 adsorption on an ASAP2020 instrument. The composition of biomass was analyzed using a cube elemental analyzer (Vario EL) (Table S1). Fourier-transform infrared spectroscopy (FTIR) spectra were obtained using an infrared spectrometer (Nicolet 6700). Lambda 750S spectrophotometer was used to get their diffuse reflectance absorption spectra. Raman spectra were measured using a Raman microscope (LABHRev-UV) with an excitation source of 532 nm.

2. Photothermocatalytic or photocatalytic performance tests.

Only using the illumination from a 500 W Xe lamp, the photothermalcatalytic steam cellulose or biomass reforming and cellulose pyrolysis without adding H_2O experiments were conducted in a setup (Scheme S1 and S2). The focused UV-vis-IR illumination had a power (*P*) of 6849.8 mW, with a spot size (*d*) of approximately 7 mm (the diameter of crucible), corresponding to a light intensity value of 178.0 kW m^{-2}. According to a weight ratio of 13:1, 0.4126 g of cellulose and 0.0318 g of the sample were ground in an agate mortar to obtain a homogeneous mixture. The mixture was then mixed evenly with 0.7242 g of H_2O to get a paste. 0.1414 g of the paste was placed in an alumina crucible supported by insulation aluminum silicate fibers in the reactor. Prior to the reaction, the reactor was evacuated using a vacuum pump. Then, the paste was illuminated with the focused light of the Xe lamp for 7 minutes. Purity Ar was then filled into the reactor until the internal pressure reached atmospheric pressure. The H_2, CO, CO_2, and CH_4 produced by the photothermocatalytic process were analyzed by a GC9560 gas chromatograph. The detailed procedures for gas chromatography analysis and measurement of light intensity have been reported in previous work[25]. The experiments were repeated three times, and the average values were taken as the photothermocatalytic activity of the sample. To test the photothermocatalytic activity of the samples with the focused vis-IR illumination, a long-wave pass cut-off filter with $\lambda > 420$, > 560, or > 690 nm was placed on the quartz window of the reactor. The corresponding powers for the filters were 5747.9 mW, 4982.2 mW, and 3957.5 mW, respectively, with corresponding light intensity values of 149.4 kW m^{-2}, 129.5 kW m^{-2}, and 102.8 kW m^{-2}.

The paste for photothermocatalytic steam biomass reforming was prepared by grinding the biomass, catalyst, and H_2O in the same steps above according to a certain proportion. The amounts of the paste for photothermocatalytic steam biomass reforming and the contents of biomass, catalyst, and H_2O in the mixture are presented in Table S2.

The durability test of photothermocatalytic steam cellulose reforming on Co/CeO_2-$Al_1Mg_3O_{4.5}$ was as follows. The residual solid of steam cellulose reforming (without any treatment) was added at the ratio of cellulose: catalyst 13:1. After mixed it evenly, we added 1.75 times water and mix it into paste to continue the photothermocatalytic steam cellulose reforming. A total of four experiments were conducted.

The mixture for cellulose pyrolysis experiment was prepared by the same steps as that for steam cellulose reforming, except for adding H_2O, and the experimental procedure is identical to steam cellulose reforming.

For isotope labeling experiments of photothermocatalytic cellulose reforming with $H_2{}^{18}O$, the preparation method of the paste is the same as the steam cellulose reforming above, except that 0.8047 g of $H_2{}^{18}O$ was used to replace $H_2{}^{16}O$. The gases produced by the photothermocatalytic process were analyzed using an infrared spectrometer (Nicolet 6700) to get the Fourier-transform infrared spectroscopy (FTIR) spectra. After the isotope labeling experiment, 0.0324 g of the remained solid was ground to be a paste with 0.0324 g cellulose and 0.0561 g $H_2{}^{16}O$. Then, the photothermocatalytic experiment is performed as the same procedure of steam cellulose reforming above. The gases produced by the photothermocatalytic process were also analyzed by the FTIR.

For without isotope labeling experiments of photothermocatalytic cellulose reforming with $H_2{}^{16}O$, the preparation method of the paste is the same as the steam cellulose reforming above. After without the isotope labeling experiment, 0.0324 g of the remained solid was ground to be a paste with 0.0324 g cellulose and 0.0561 g $H_2^{16}O$. Then, the photothermocatalytic experiment is performed as the same procedure of steam cellulose reforming above. The gases produced by the photothermocatalytic process were also analyzed by the FTIR.

For the photocatalytic steam cellulose reforming experiment on the $Co/CeO_2\text{-}Al_1Mg_3O_{4.5}$, the paste was directly placed on the stainless bottom of the reactor. The reactor was placed in an ice-water bath to maintain the temperature close to room temperature (RT) when with the focused UV-vis-IR illumination.

The byproducts of photothermocatalytic steam biomass reforming are char and tar, resulting in lower yields of the targeted gas products of H_2 and CO. Due to the complete pyrolysis of biomass (such as the complete pyrolysis of cellulose: $(C_6H_{10}O_5)_n = 6nC + 5nH_2O$), amorphous char was generated. Therefore, after the photothermocatalytic experiment, the solid mixture of catalyst was retained in the alumina crucible in the reactor. The weight difference before and after calcining in the Muffle furnace was used to calculate the weight of char in the solid mixture.

The light-to-fuel efficiency (η) was calculated as follows[25] (*just for review*):

$$\eta = (r_{H2}\times\Delta_cH^0_{H2} + r_{CO}\times\Delta_cH^0_{CO} + r_{CH4}\times\Delta_cH^0_{CH4} - r_{C6H10O5,\ gas}\times\Delta_cH^0_{C6H10O5}) \times m_{catalyst}/(P\times3600)$$

Where $\Delta_cH^0_{H2}$, $\Delta_cH^0_{CO}$, $\Delta_cH^0_{CH4}$ and $\Delta_cH^0_{C6H10O5}$ are the standard combustion heats (298.15 K) of CO, H_2, CH_4, and cellulose as fuel, respectively. r_{H2}, r_{CO} and r_{CH4} (mmol $g^{-1}_{catalyst}$ h^{-1}) are the production rates of CO, H_2, and CH_4 as fuels, respectively. $r_{C6H10O5,\ gas}$ is the reaction rate of cellulose consumption to produce gases. P (mW) is the illumination power.

The energy cost of H_2 and CO production (E_{cost}) was calculated as follows:

$$E_{cost} = P \times 10^{-6} \times T / n_i \times 10^{-6} \times M_i$$

Where P (mW) is the illumination power. T (h) is reaction time. n_i (umol) is amount of substance of the H_2 or CO. M_i (g mol^{-1}) is relative molecular mass of H_2 or CO.

The TOF (turnover frequency) was calculated as follows:

$TOF = r_i \times 10^{-3} \times N_A / (m_{1gcatalyst} \times(m_{Co} / M_{Co}) \times N_A \times D)$

Where r_i is the production of H_2 or CO (mmol g^{-1} h^{-1}). N_A is the Avogadro constant. $m_{1gcatalyst}$ is the mass of the catalyst (1g). m_{Co} is the mass percentage of Co atoms in the catalyst. M_{Co} is the atomic weight of Co (58.93 g mol^{-1}). D is Co dispersion of the catalyst, which is calculated according to formula[s1] (D = 1.21/d), d is the average crystal size of metallic Co (the d of the catalyst are estimated using the Scherrer formula ($0.89\lambda/(\beta\cos\theta) = L$) at the peak position corresponding to the (111) facet in the XRD pattern).

The yield of char (y_{char}) was calculated as follows[25] (*just for review*):

$y_{char}(\%)=m_{char}/(m_i \times c_{i,c}) \times 100$

Where m_{char} is the weight (g) of the char. m_i is the weight (g) of the biomass (i). $c_{i,c}$ is the weight ratio of carbon in the biomass.

The m_{char} was determined according to the following formula[25] (*just for review*):

$m_{char}= m_{catalyst} \times (r_{wl} + c_{Co} \times m_O/m_{Co})/(1 - r_{wl})$

Where r_{wl} is the weight loss ratio (r_{wl}) between the catalyst and the remaining solid mixture to produce char, c_{Co} is the weight ratio of Co in samples. m_O and m_{Co} are the atomic weights of O and Co, respectively.

The tar yield (y_{tar}) was calculated according to the formula below[25] (*just for review*):

$y_{tar}(\%)=100 - (c_{CO} + c_{CH4} + c_{CO2}) \times V \times 12/(24450 \times m_i \times c_{i,c}) \times 100 - y_{char}$

3. Controlled catalytic test.

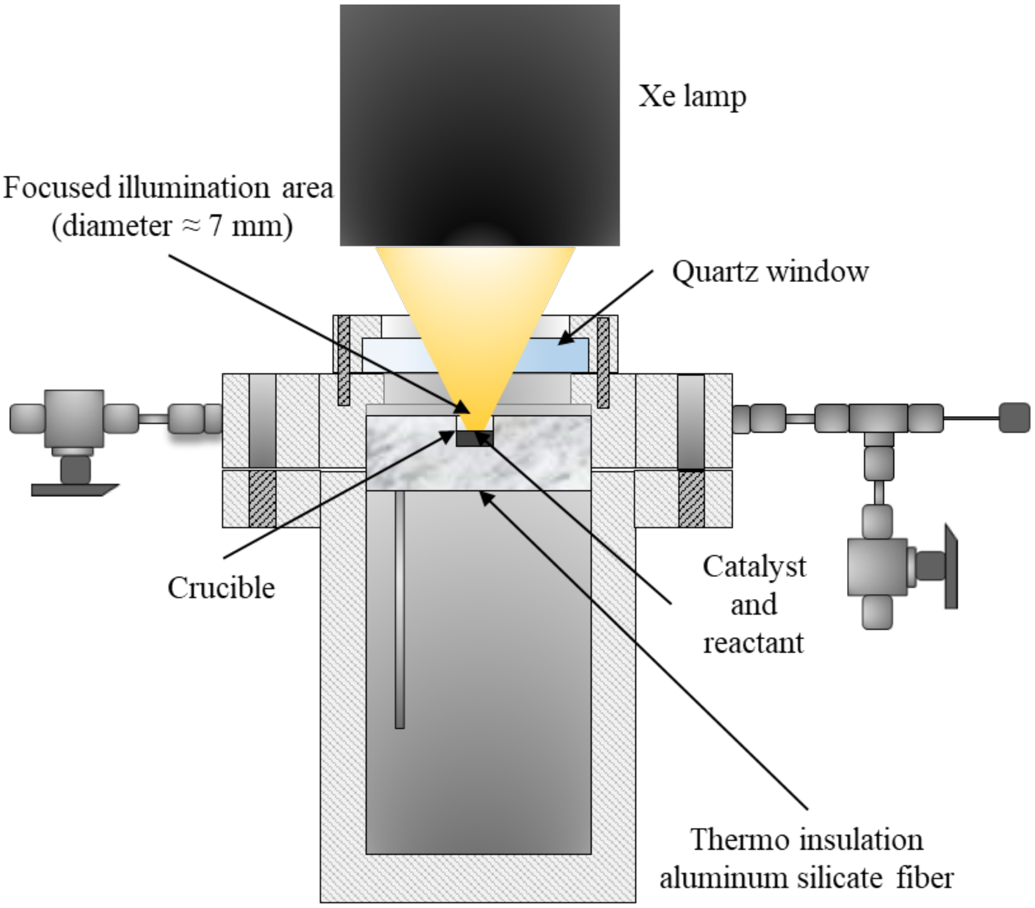
The thermocatalytic steam cellulose reforming experiments with illumination or in the dark at different temperatures were conducted on a set-up using a tubular quartz reactor attached to a quartz window (Scheme S3). The reaction temperature was controlled by an electric tubular furnace. A paste of 0.1414 g of cellulose, catalyst, and H_2O (prepared using the same steps as the photothermocatalytic steam cellulose reforming mentioned above) was placed in the tubular quartz reactor. Prior to the catalytic reaction, the reaction system was purged with high purity Ar flow. With the focused UV-vis-IR illumination or in the dark, the reactor was heated to 725 °C at a rate of 5 °C $\min^{-1}$. The H_2, CO, CO_2, and CH_4 produced were also analyzed by a GC9560 gas chromatograph.

To conduct thermocatalytic cellulose pyrolysis without adding H_2O on $Co/CeO_2-Al_1Mg_3O_{4.5}$ at different temperatures, 0.0538 g mixture of cellulose and catalyst (prepared using the same steps as the cellulose pyrolysis without adding H_2O mentioned above) was placed in the tubular quartz reactor. Prior to the catalytic reaction, the reactor was heated to 100 °C at a rate of 5 °C $\min^{-1}$ and maintained at 100 °C for 60 minutes to dry the mixture. After the reactor cooled to room temperature, the reaction was conducted the same as the thermocatalytic steam cellulose reforming mentioned above.

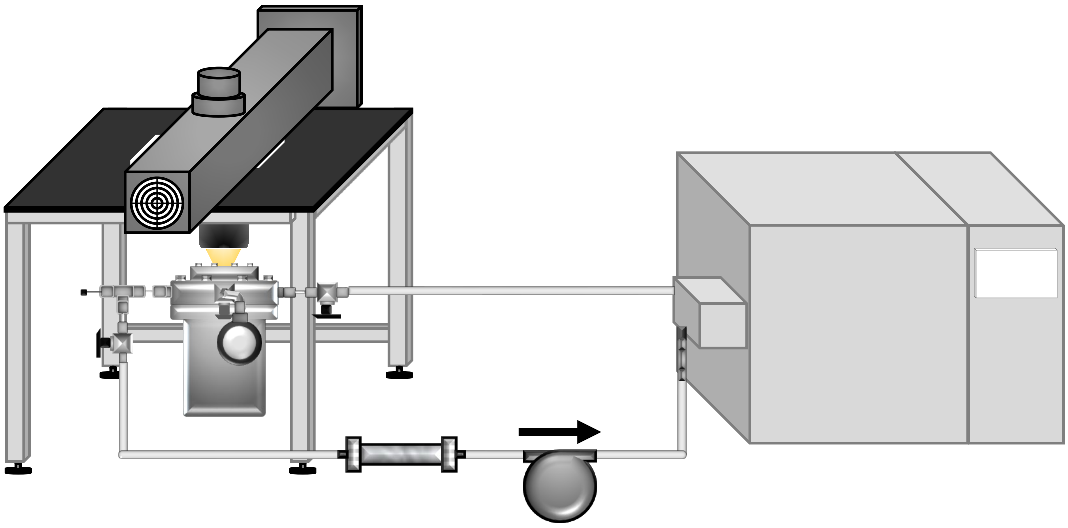
With the focused UV-vis-IR illumination or in the dark, thermocatalytic reactions of H_2O and pre-deposited carbon on the catalysts were conducted at different temperatures using the following steps. 0.5 g homogeneous mixture of cellulose and catalyst with a weight ratio of 13:1 was placed in the reactor. Prior to the catalytic reaction, the reaction system was purged with high purity Ar flow. The reactor was heated to 700 °C at a rate of 5 °C $\min^{-1}$ and maintained at 700 °C for 30 minutes. After the reactor cooled to room temperature, 0.02 g of residual solid was placed in the quartz reactor before adding 0.02 g of H_2O. The subsequent steps were the same as the thermocatalytic steam cellulose reforming above.

4. H_2-TPR.

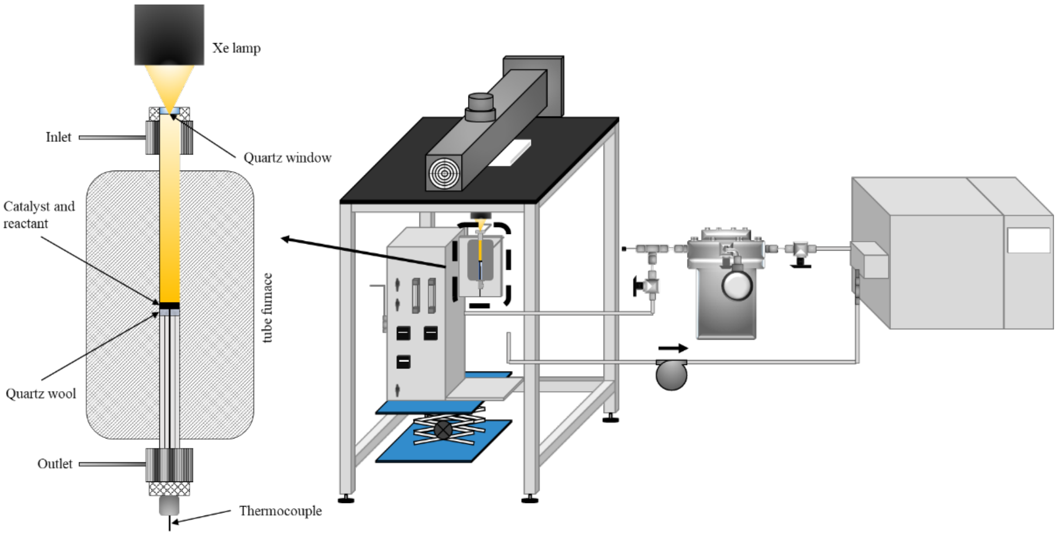
The H_2 temperature programmed reduction (H_2-TPR) experiments were conducted in a photothermal adsorption instrument (TP-5080F). Firstly, 0.0050 g of the sample was placed in a quartz tube reactor with a quartz window attached at one end. Then the sample was reduced at 700 °C for 2 hours in a 30 ml min^{-1} pure H_2 flow. After the reactor cooled to room temperature, the H_2 flow was switched to 5 vol% O_2/He for 30 minutes adsorption at room temperature. Finally, the sample was heated from room temperature to 700 °C at 10 °C min^{-1} in a 24 ml min^{-1} 5 vol% H_2/Ar flow with UV-vis-IR illumination or in the dark. The H_2 consumption curve during the last process was recorded.



Scheme S1. The reactor for evaluating photothermocatalytic steam cellulose reforming on the samples with the focused illumination from a 500 W Xe lamp[26] (*just for review*).



Scheme S2. The set-up for measuring the photothermocatalytic activity of samples for steam cellulose reforming merely with the focused illumination from a 500 W Xe lamp[26] (*just for review*).



Scheme S3. The set-up for testing the catalytic activity of samples for steam cellulose reforming at the same temperature with the focused illumination from 500 W Xe lamp or in the dark[26] (*just for review*).

Table S1. The compositions of the biomass.

Substrates	The weight ratio （wt%)				
	C	H	N	S	Organic compounds
Corn stalk	39.08	5.807	1.09	0.246	80.31
Wheat straw	38.47	5.948	1.18	0.342	70.20
Rice straw	39.83	6.273	0.95	0.279	69.92

Table S2. The contents of biomass, the catalyst, and water in the paste like mixture, and the amounts of the mixture used for photothermocatalytic steam biomass reforming tests.

	Contents in the mixture (g)			
	Biomass	Co/CeO_2-$Al_1Mg_3O_{4.5}$	H_2O	Amount of the mixture (g)
Cellulose	0.4126	0.0138	0.7242	0.1414
Corn stalk	0.3564	0.0222	0.7202	0.1533
Wheat straw	0.4630	0.0250	0.9269	0.1528
Rice straw	0.4946	0.0266	0.9914	0.1529
lignin	0.4823	0.0371	0.8457	0.1415

Table S3. Comparison of light-driven H_2 production from biomass

Catalyst	Substrate	Light source	Light Intensity (kW m^{-2})	Conditions	H_2 production rate (mmol g^{-1} h^{-1})	Quantum efficiency (%)[a]	Light-to-fuel efficiency (%)	Ref.
Co/CeO$_2$-Al$_1$Mg$_3$O$_{4.5}$	cellulose	Xe lamp	178.0		3374.4		7.8	This work
	rice straw				1526.7		1.2	
	wheat straw				1600.2		1.1	
	corn stalk				1967.4		1.9	
Ni/m-SiO$_2$	cellulose	Xe lamp	361.0		1966.2		5.5	25
	rice straw				1488.1			
	wheat straw				728.4			
	corn stalk				1036.5			
	kitchen waste				760.4			
SiF/Ni-NGQD	cellulose	Solar simulator	1.0	Water	5.735			4
	lignin				14.270	37 (400 nm)		
Pt NCs/TiO2	cellulose	Xe lamp		aqueous solution	0.54	4.1 (380 nm)		5
Pt/TiO2 NSs	cellulose	Xe lamp		aqueous solution	0.275	1.89 (380 nm)		20

Pt/CdOx/CdS/SiC	poplar wood cellulose	Xe lamp		10M NaOH 70 °C	0.026 0.362		6
CdS/CdOx	lignin cellulose	AM 1.5G	1.0	10 M KOH	0.072 2.57	1.2 (430 nm)	3
Ru–$ZnIn_2S_4$	Wooden branch methylfurans	LEDs (455 nm)		CH_3CN Ar	5.59 6.0	15.2 (452 nm)	10
NiP/carbon nitride	cellulose	AM 1.5G	1.0	K_3PO_4 (pH 4.5)	1.69		7
NiP/carbon dots	cellulose	AM 1.5G	1.0	K_3PO_4 (pH 6.0)	0.021		15
Pt/S,N doped graphene oxide	lignin cellulose	AM 1.5G	1.0	NaOH (pH 12.5)	0.033 0.5	23.3 (420 nm)	23
NiS/TiO_2	cellulose	Xe lamp	4.0	H_2O	3.02		8

Table S4. Summarization of the experimental results.

Reaction condition				Sample	Production rates (mmol g^{-1} h^{-1})				Yield (%)		Light-to-fuel efficiency (%)
Reactant	H_2O	Light	Reaction time		H_2	CO	CO_2	CH_4	Char	Tar	
cellulose	√	UV-vis-IR	7 min	$Co/CeO_2-Al_1Mg_3O_{4.5}$	3374.4	1872.1	792.7	24.2	9.4	25.5	7.8
cellulose	√	UV-vis-IR	7 min	$Co/Al_1Mg_3O_{4.5}$	2556.5	1493.7	663.5	36.8	14.4	32.5	5.6
cellulose	√	UV-vis-IR	7 min	$CeO_2-Al_1Mg_3O_{4.5}$	601.2	694.6	332.0	86.6	18.8	54.2	0.4
cellulose	√	UV-vis-IR	7 min	$Al_1Mg_3O_{4.5}$	380.8	633.4	276.2	83.2	19.1	56.9	*Negligible*
cellulose	√	UV-vis-IR	7 min	Co/CeO_2	1630.9	838.8	676.1	15.9	3.91	59.0	2.2
cellulose	√	UV-vis-IR	7 min	$1.5Co/CeO_2-Al_1Mg_3O_{4.5}$	3482.4	1649.2	1023.8	34.1	12.0	22.4	7.4
cellulose	√	UV-vis-IR	7 min	$0.5Co/CeO_2-Al_1Mg_3O_{4.5}$	2403.0	1436.9	744.4	47.1	14.2	31.8	4.6
cellulose	√	$\lambda > 420$ nm	7 min	$Co/CeO_2-Al_1Mg_3O_{4.5}$	3073.1	1594.5	821.1	30.6	9.2	31.5	8.0
cellulose	√	$\lambda > 560$ nm	7 min		2767.5	1351.8	849.6	32.4	13.0	32.8	7.6
cellulose	√	$\lambda > 690$ nm	7 min		2202.6	1034.7	735.7	31.3	14.0	42.4	7.2
rice straw	√	UV-vis-IR	7 min		1526.7	1252.8	476.8	99.4	28.8	36.7	2.1
wheat straw	√	UV-vis-IR	7 min		1600.2	1194.6	486.1	87.7	22.7	42.5	2.3
corn stalk	√	UV-vis-IR	7 min		1967.4	1486.9	536.0	89.6	29.6	23.6	3.3
lignin	√	UV-vis-IR	7 min		1962.3	225.6	935.4	75.2	7.4	68.6	5.0
cellulose	×	UV-vis-IR	7 min		2144.2	1367.6	473.5	16.4	7.1	47.9	4.9
cellulose	×	UV-vis-IR	7 min	$Co/Al_1Mg_3O_{4.5}$	2017.2	1524.8	405.4	22.6	8.1	44.6	4.5

Table S5. Mass efficiency (per gram of cellulose/lignin)..

Reaction condition				Sample	mass efficiency $g/g_{cellulose/lignin}$				
Reactant	H_2O	Light	Reaction time		H_2	CO	CO_2	CH_4	Char
cellulose	√	UV-vis-IR	7 min	$Co/CeO_2-Al_1Mg_3O_{4.5}$	0.0605	0.4702	0.3129	0.0035	0.0418
cellulose	√	UV-vis-IR	7 min	$Co/Al_1Mg_3O_{4.5}$	0.0459	0.3752	0.2619	0.0053	0.0639
cellulose	√	UV-vis-IR	7 min	$CeO_2-Al_1Mg_3O_{4.5}$	0.0108	0.1745	0.1311	0.0124	0.0836
cellulose	√	UV-vis-IR	7 min	$Al_1Mg_3O_{4.5}$	0.0068	0.1591	0.1090	0.0119	0.0848
cellulose	√	UV-vis-IR	7 min	Co/CeO_2	0.0293	0.2108	0.2670	0.0023	0.0174
cellulose	√	UV-vis-IR	7 min	$1.5Co/CeO_2-Al_1Mg_3O_{4.5}$	0.0625	0.4144	0.4043	0.0049	0.0534
cellulose	√	UV-vis-IR	7 min	$0.5Co/CeO_2-Al_1Mg_3O_{4.5}$	0.0431	0.3611	0.2939	0.0068	0.0633
cellulose	√	$\lambda > 420$ nm	7 min	$Co/CeO_2-Al_1Mg_3O_{4.5}$	0.0551	0.4005	0.3241	0.0044	0.0438
cellulose	√	$\lambda > 560$ nm	7 min		0.0497	0.3396	0.3353	0.0047	0.0592
cellulose	√	$\lambda > 690$ nm	7 min		0.0395	0.2599	0.2904	0.0045	0.0650
rice straw	√	UV-vis-IR	7 min		0.0192	0.2201	0.1316	0.0100	0.1145
wheat straw	√	UV-vis-IR	7 min		0.0202	0.2107	0.1347	0.0088	0.0874
corn stalk	√	UV-vis-IR	7 min		0.0278	0.2999	0.1678	0.0104	0.1158
lignin	√	UV-vis-IR	7 min		0.0352	0.0567	0.3694	0.0108	0.0413
cellulose	×	UV-vis-IR	7 min		0.0385	0.3437	0.1870	0.0024	0.0316
cellulose	×	UV-vis-IR	7 min	$Co/Al_1Mg_3O_{4.5}$	0.0362	0.3831	0.1601	0.0032	0.0360

Table S6. Mass efficiency (per gram of H_2O).

Reaction condition				Sample	mass efficiency g/g_{H2O}				
Reactant	H_2O	Light	Reaction time		H_2	CO	CO_2	CH_4	Char
cellulose	√	UV-vis-IR	7 min	Co/CeO_2-$Al_1Mg_3O_{4.5}$	0.0346	0.2685	0.1787	0.0020	0.0239
cellulose	√	UV-vis-IR	7 min	$Co/Al_1Mg_3O_{4.5}$	0.0262	0.2143	0.1496	0.0030	0.0365
cellulose	√	UV-vis-IR	7 min	CeO_2-$Al_1Mg_3O_{4.5}$	0.0062	0.0996	0.0748	0.0071	0.0477
cellulose	√	UV-vis-IR	7 min	$Al_1Mg_3O_{4.5}$	0.0039	0.0908	0.0622	0.0068	0.0484
cellulose	√	UV-vis-IR	7 min	Co/CeO_2	0.0167	0.1203	0.1524	0.0013	0.0099
cellulose	√	UV-vis-IR	7 min	$1.5Co/CeO_2$-$Al_1Mg_3O_{4.5}$	0.0357	0.2365	0.2307	0.0028	0.0305
cellulose	√	UV-vis-IR	7 min	$0.5Co/CeO_2$-$Al_1Mg_3O_{4.5}$	0.0246	0.2060	0.1677	0.0039	0.0361
cellulose	√	$\lambda > 420$ nm	7 min	Co/CeO_2-$Al_1Mg_3O_{4.5}$	0.0313	0.2276	0.1842	0.0025	0.0249
cellulose	√	$\lambda > 560$ nm	7 min		0.0285	0.1946	0.1922	0.0027	0.0339
cellulose	√	$\lambda > 690$ nm	7 min		0.0226	0.1489	0.1664	0.0026	0.0372
rice straw	√	UV-vis-IR	7 min		0.0096	0.1098	0.0657	0.0050	0.0571
wheat straw	√	UV-vis-IR	7 min		0.0101	0.1053	0.0673	0.0044	0.0437
corn stalk	√	UV-vis-IR	7 min		0.0139	0.1497	0.0837	0.0052	0.0578
lignin	√	UV-vis-IR	7 min		0.0201	0.0323	0.2106	0.0062	0.0235
cellulose	×	UV-vis-IR	7 min		\	\	\	\	\
cellulose	×	UV-vis-IR	7 min	$Co/Al_1Mg_3O_{4.5}$	\	\	\	\	\

Table S7. Mass efficiency (per gram of catalyst).

Reaction condition				Sample	mass efficiency $g/g_{catalyst}$				
Reactant	H_2O	Light	Reaction time		H_2	CO	CO_2	CH_4	Char
cellulose	√	UV-vis-IR	7 min	$Co/CeO_2\text{-}Al_1Mg_3O_{4.5}$	0.7874	6.1156	4.0694	0.0453	0.5442
cellulose	√	UV-vis-IR	7 min	$Co/Al_1Mg_3O_{4.5}$	0.5965	4.8795	3.4059	0.0686	0.8314
cellulose	√	UV-vis-IR	7 min	$CeO_2\text{-}Al_1Mg_3O_{4.5}$	0.1403	2.2689	1.7041	0.1617	1.0874
cellulose	√	UV-vis-IR	7 min	$Al_1Mg_3O_{4.5}$	0.0888	2.0691	1.4177	0.1554	1.1030
cellulose	√	UV-vis-IR	7 min	Co/CeO_2	0.3805	2.7402	3.4705	0.0296	0.2257
cellulose	√	UV-vis-IR	7 min	$1.5Co/CeO_2\text{-}Al_1Mg_3O_{4.5}$	0.8126	5.3874	5.2557	0.0636	0.6947
cellulose	√	UV-vis-IR	7 min	$0.5Co/CeO_2\text{-}Al_1Mg_3O_{4.5}$	0.5607	4.6937	3.8212	0.0880	0.8230
cellulose	√	$\lambda > 420$ nm	7 min	$Co/CeO_2\text{-}Al_1Mg_3O_{4.5}$	0.7168	5.2069	4.2134	0.0572	0.5691
cellulose	√	$\lambda > 560$ nm	7 min		0.6455	4.4143	4.3595	0.0605	0.7699
cellulose	√	$\lambda > 690$ nm	7 min		0.5137	3.3789	3.7754	0.0583	0.8445
rice straw	√	UV-vis-IR	7 min		0.3562	4.0924	2.4478	0.1855	2.1294
wheat straw	√	UV-vis-IR	7 min		0.3734	3.9024	2.4953	0.1638	1.6192
corn stalk	√	UV-vis-IR	7 min		0.4497	4.8552	2.7161	0.1679	1.8748
lignin	√	UV-vis-IR	7 min		0.4579	0.7371	4.8016	0.1403	0.5364
cellulose	×	UV-vis-IR	7 min		0.5003	4.4675	2.4304	0.0306	0.4111
cellulose	×	UV-vis-IR	7 min	$Co/Al_1Mg_3O_{4.5}$	0.4707	4.9809	2.0810	0.0421	0.4674

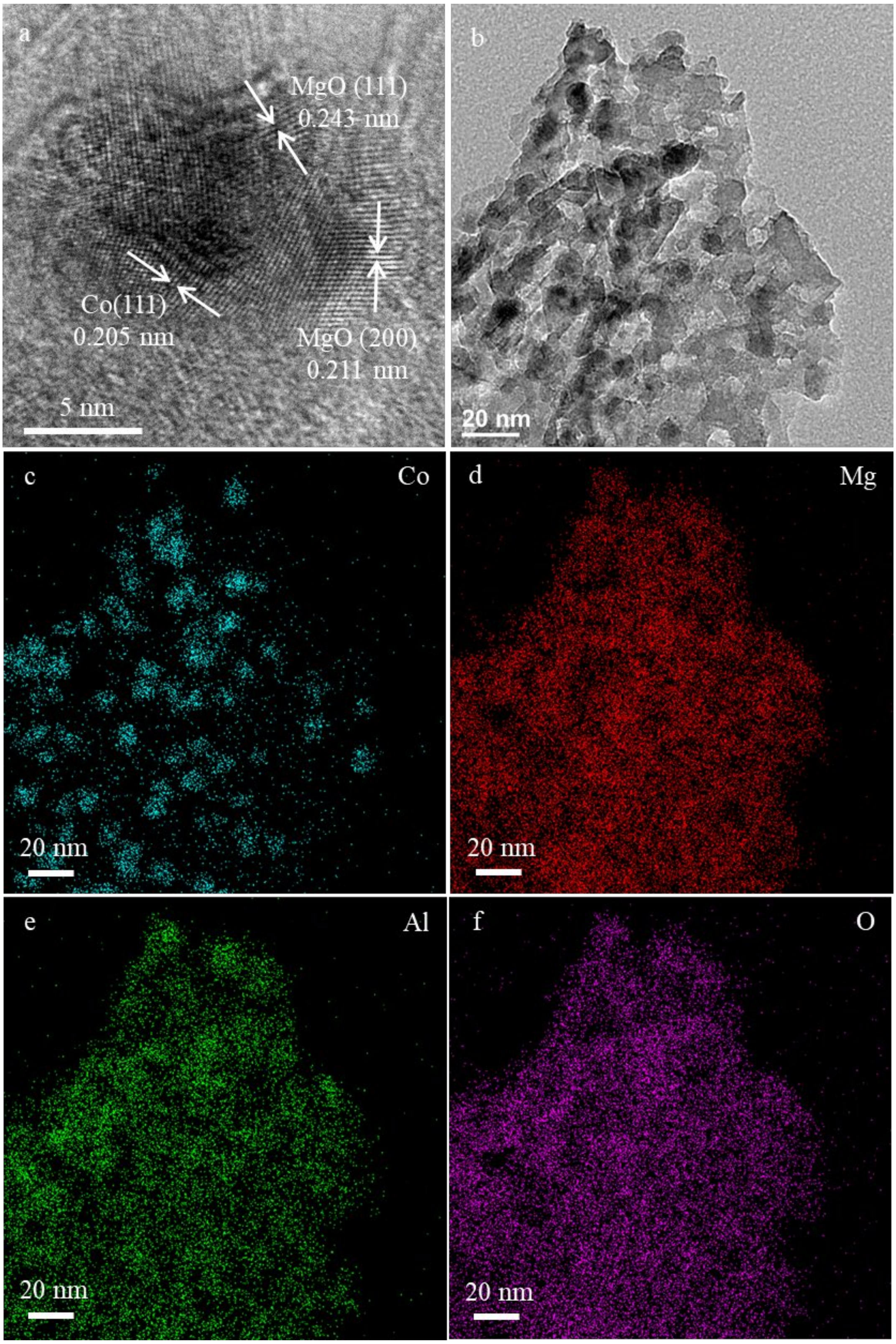


Fig. S1. (a) HRTEM image, (b) TEM image and the corresponding element mappings of (c) Co, (d) Mg, (e) Al, and (f) O of Co/$Al_1Mg_3O_{4.5}$.

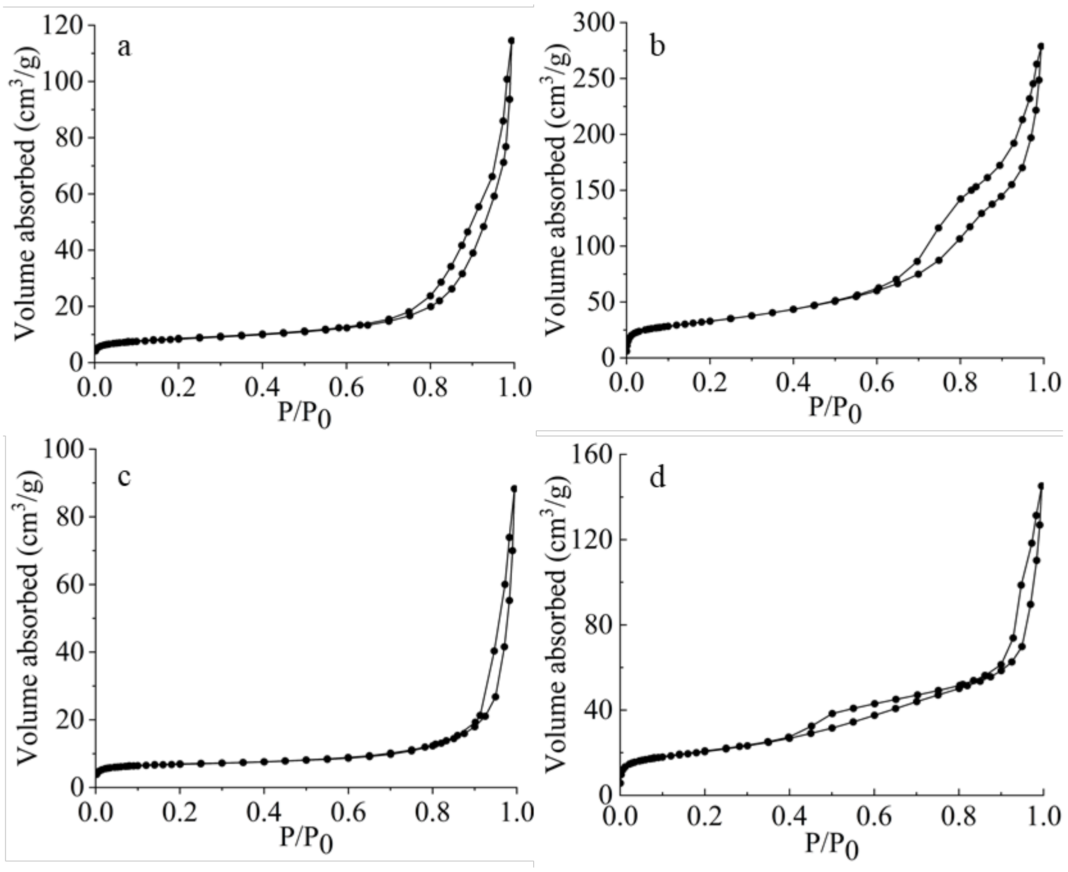


Fig. S2. N_2 adsorption and desorption of (a) Co/CeO_2-$Al_1Mg_3O_{4.5}$, (b) Co/$Al_1Mg_3O_{4.5}$, (c) CeO_2-$Al_1Mg_3O_{4.5}$ and (d) $Al_1Mg_3O_{4.5}$.

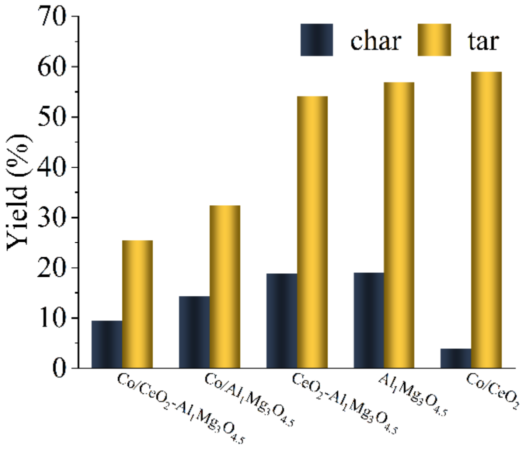


Fig. S3. The char and tar yields for photothermocatalytic steam cellulose reforming on Co/CeO_2-$Al_1Mg_3O_{4.5}$, Co/$Al_1Mg_3O_{4.5}$, CeO_2-$Al_1Mg_3O_{4.5}$, $Al_1Mg_3O_{4.5}$, Co/CeO_2 with the focused UV-vis-IR illumination.

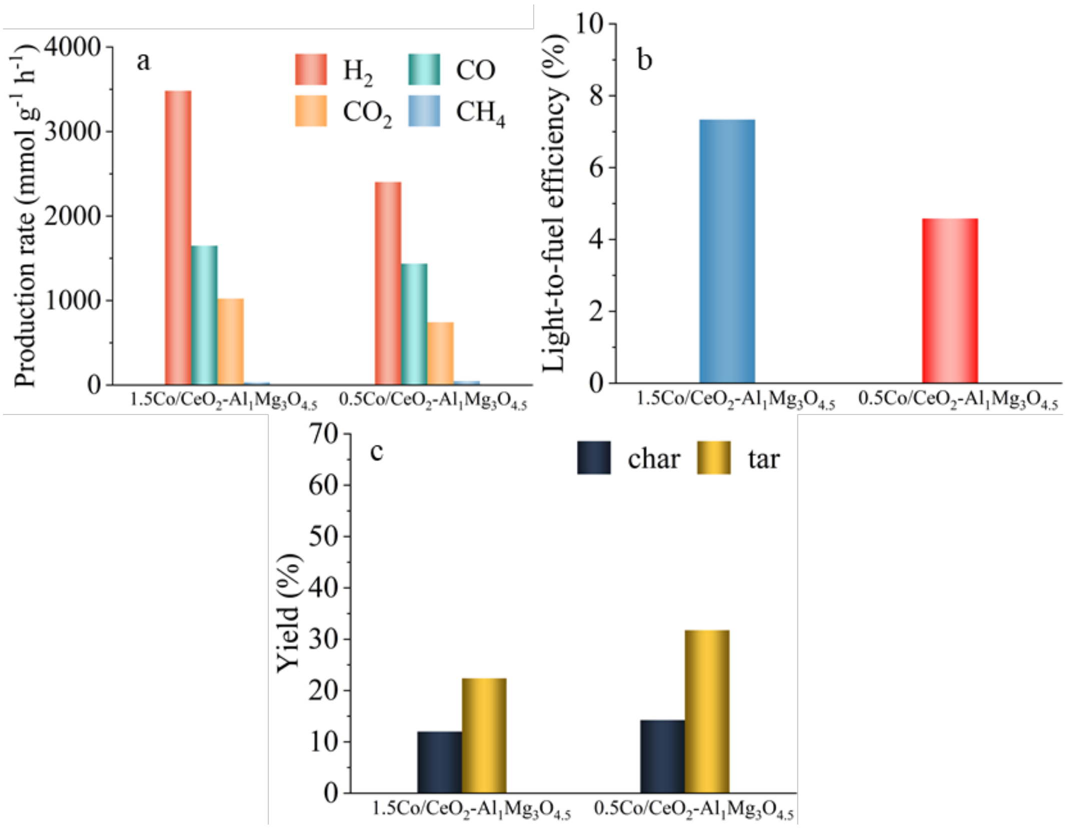


Fig. S4. The (a) gases average production rates, (b) light-to-efficiencies and (c) the char and tar yields for photothermocatalytic steam cellulose reforming on 1.5Co/CeO_2-$Al_1Mg_3O_{4.5}$ and 0.5Co/CeO_2-$Al_1Mg_3O_{4.5}$ with the focused UV-vis-IR illumination.

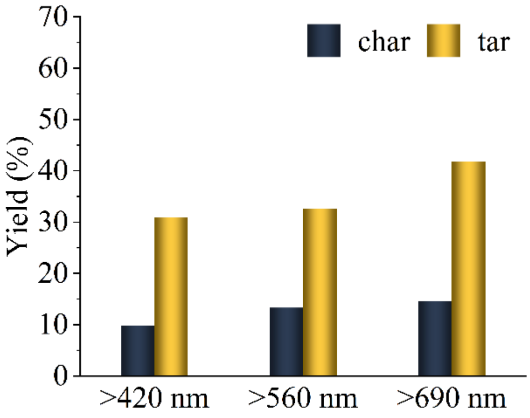


Fig. S5. The char and tar yields on Co/CeO_2-$Al_1Mg_3O_{4.5}$ for photothermocatalytic steam cellulose reforming with the focused λ > 420 nm, > 560 nm, and > 690 nm vis-IR illumination.

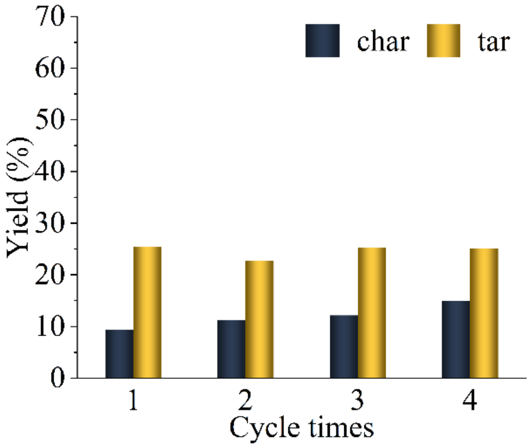


Fig. S6. The char and tar yields with recycling times (1~4 cycles) on Co/CeO_2-$Al_1Mg_3O_{4.5}$ for photothermocatalytic steam cellulose reforming.

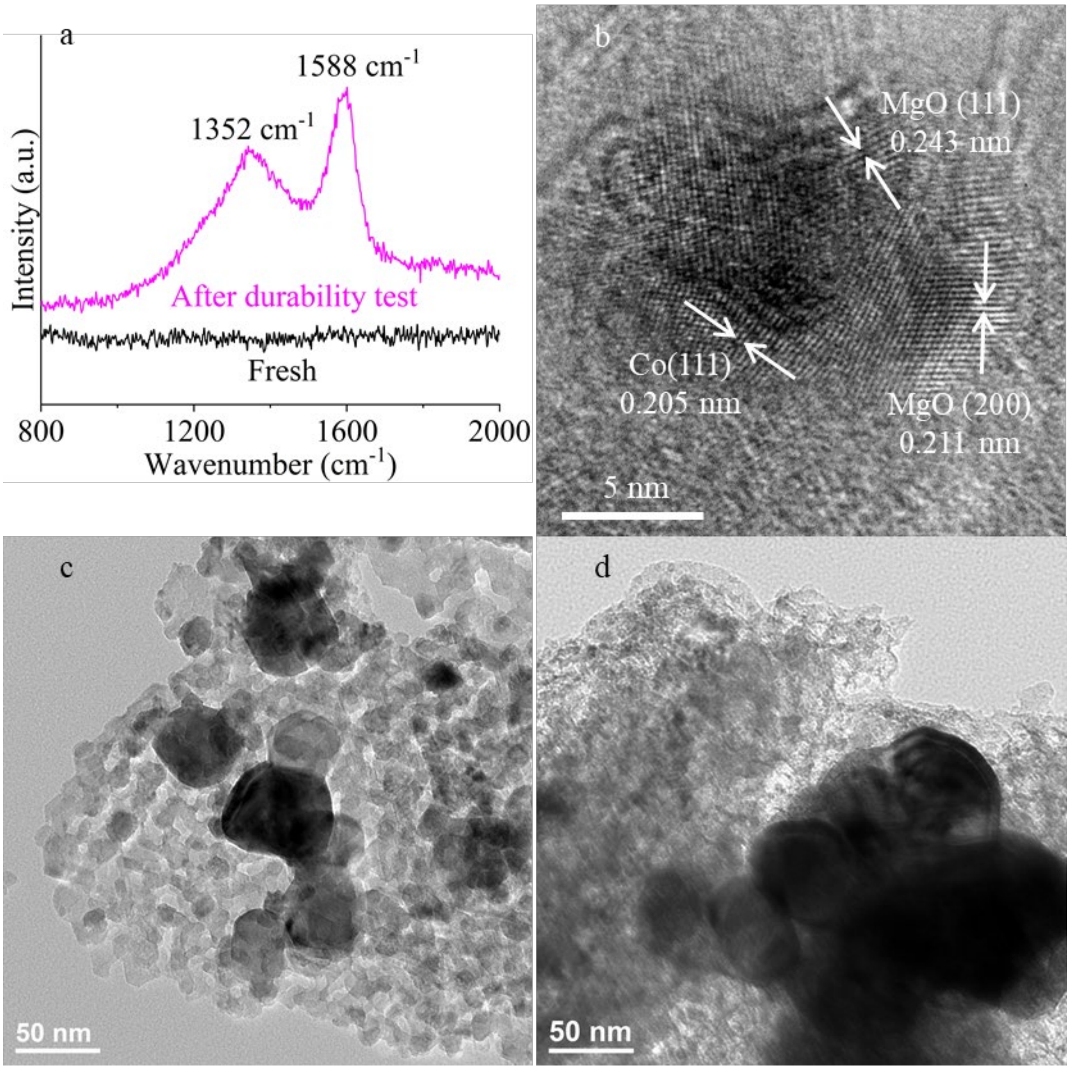


Fig. S7. (a) Raman spectra of fresh Co/CeO_2-$Al_1Mg_3O_{4.5}$ and the residual solid after durability test. (b) HRTEM image of the used sample after durability. TEM images of (c) fresh Co/CeO_2-$Al_1Mg_3O_{4.5}$ and (d) the residual solid after durability test.

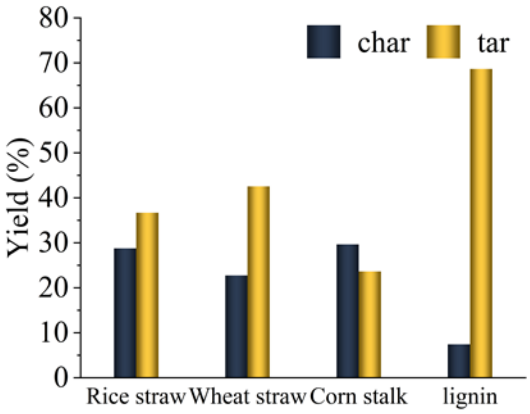


Fig. S8. The char and tar yields on Co/CeO$_2$-Al$_1$Mg$_3$O$_{4.5}$ for photothermocatalytic steam reforming of rice straw, wheat straw, corn stalk and lignin with the focused UV-vis-IR illumination.

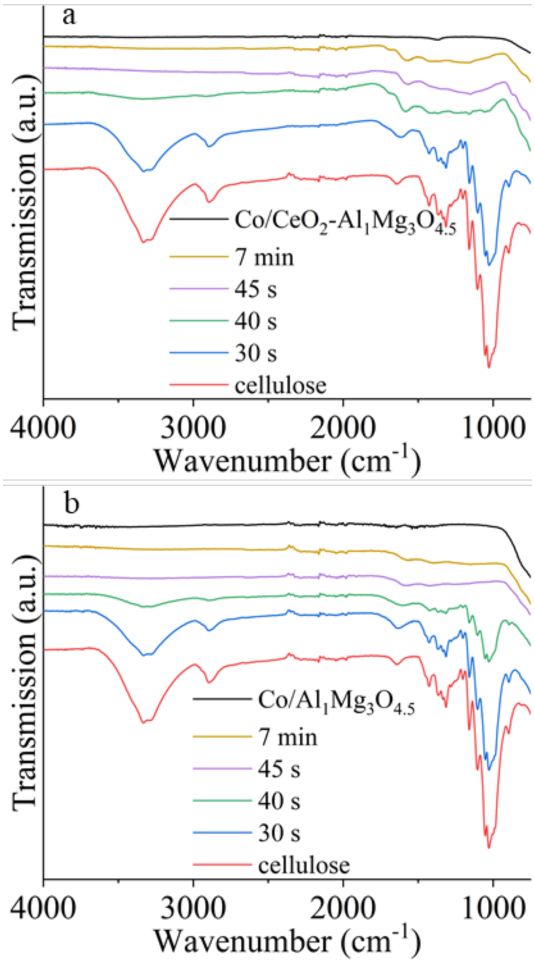


Fig. S9. FTIR spectra of the residual solid after photothermocatalytic cellulose pyrolysis without H$_2$O for certain times on (a) Co/CeO$_2$-Al$_1$Mg$_3$O$_{4.5}$ and (b) Co/Al$_1$Mg$_3$O$_{4.5}$ with the focused UV-vis-IR illumination.

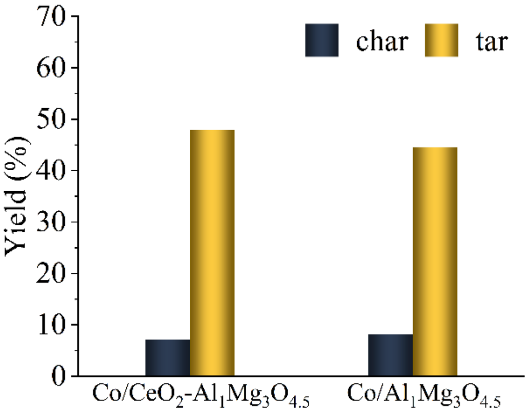


Fig. S10. The char and tar yields on $Co/CeO_2-Al_1Mg_3O_{4.5}$, $Co/Al_1Mg_3O_{4.5}$ for photothermocatalytic cellulose pyrolysis without adding H_2O for 7 min with the focused UV-vis-IR illumination.

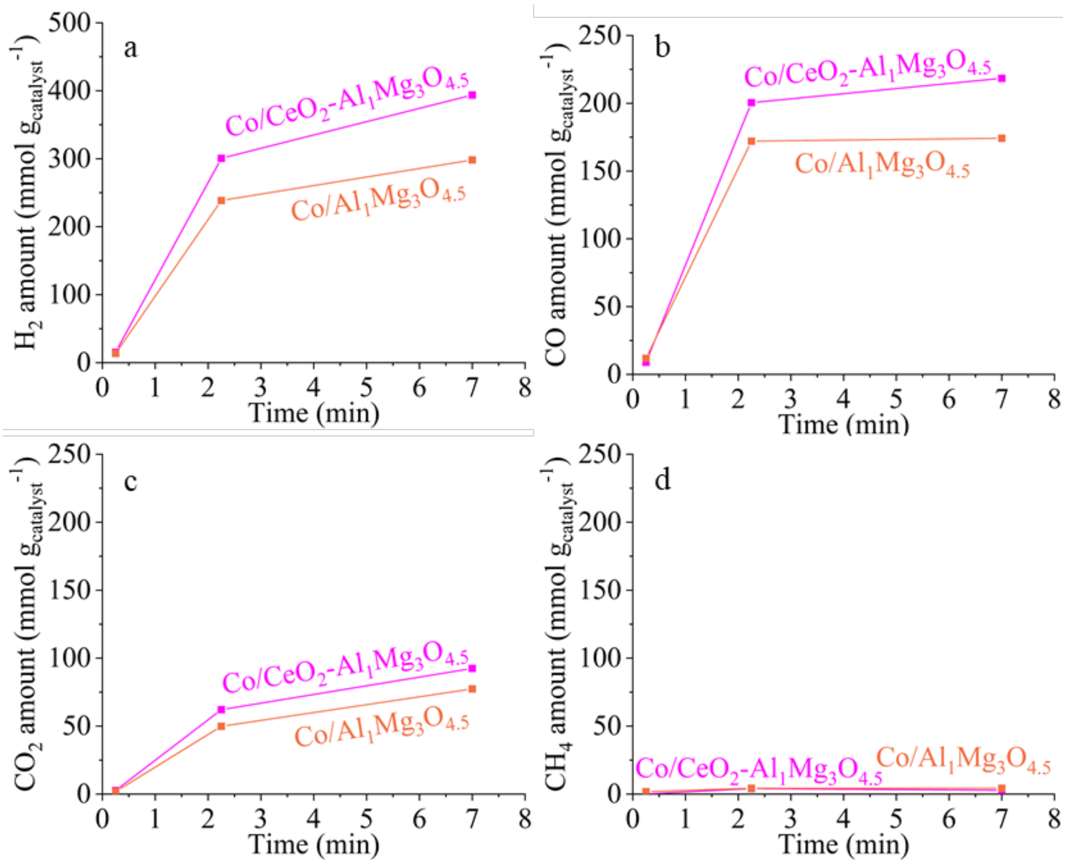


Fig. S11. The gas amounts of (a) H_2, (b) CO, (c) CO_2, and (d) CH_4 on $Co/CeO_2-Al_1Mg_3O_{4.5}$ and $Co/Al_1Mg_3O_{4.5}$ for photothermocatalytic steam cellulose reforming for different times with the focused UV-vis-IR illumination.

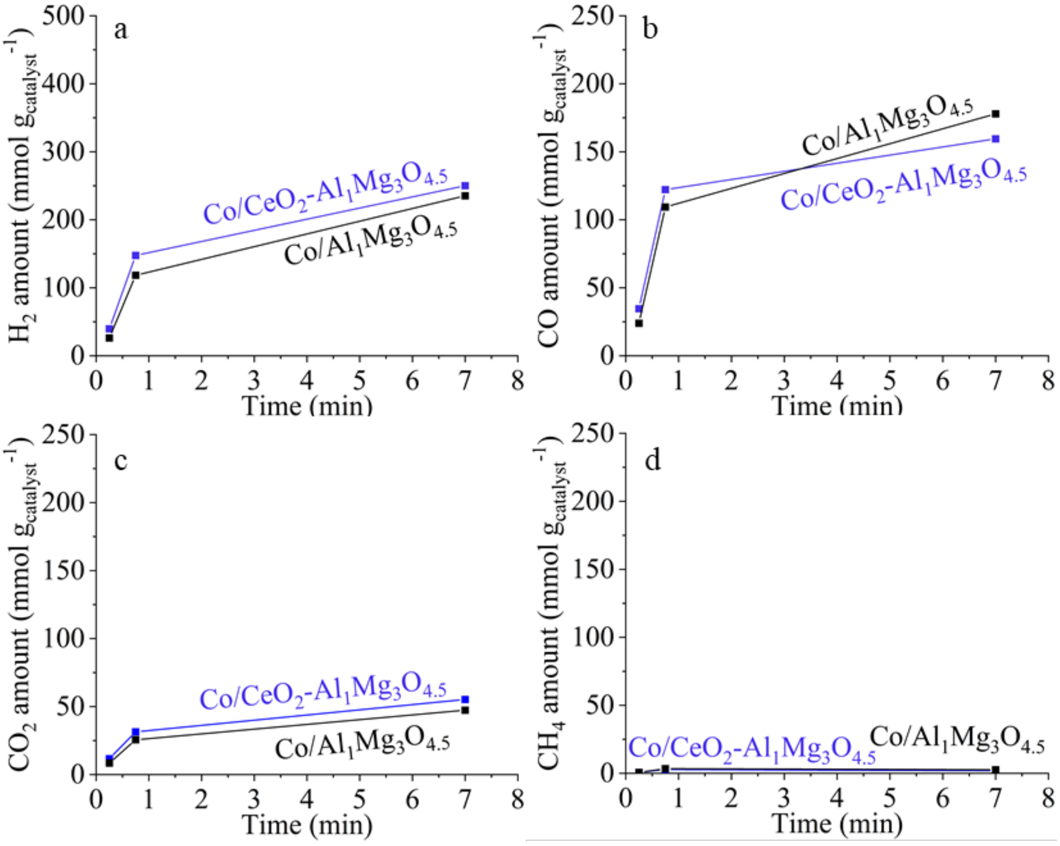


Fig. S12. The gas amounts of (a) H_2, (b) CO, (c) CO_2, and (d) CH_4 on Co/CeO_2-$Al_1Mg_3O_{4.5}$ and Co/$Al_1Mg_3O_{4.5}$ for photothermocatalytic cellulose pyrolysis without adding H_2O for different times with the focused UV-vis-IR illumination.

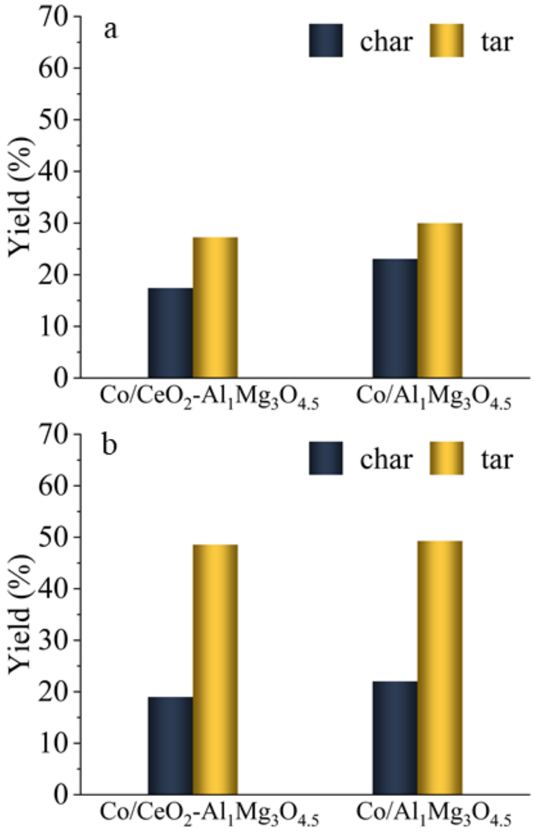


Fig. S13. The char and tar yields for photothermocatalytic (a) steam cellulose reforming of 135 s and (b) cellulose pyrolysis without adding H_2O of 45 s photothermocatalytic on Co/CeO$_2$-Al$_1$Mg$_3$O$_{4.5}$ or Co/Al$_1$Mg$_3$O$_{4.5}$ with the focused UV-vis-IR illumination.

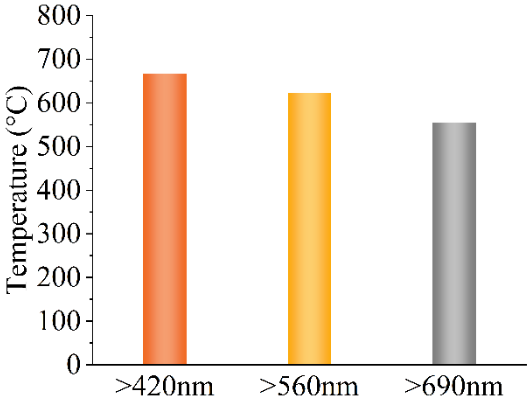


Fig. S14. The T_{eq} values of Co/CeO$_2$-Al$_1$Mg$_3$O$_{4.5}$ with the focused λ > 420 nm, > 560 nm, and > 690 nm vis-IR illumination.

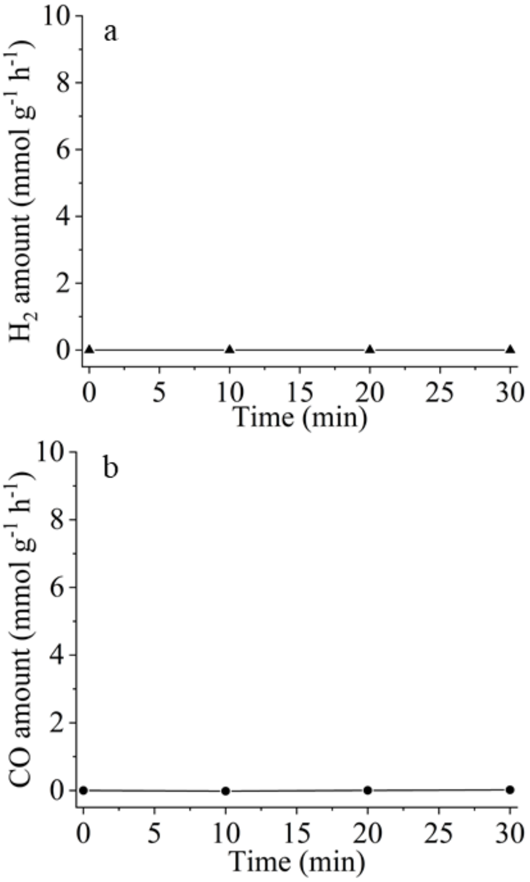


Fig. S15. The amounts of (a) H_2 and (b) CO for photocatalytic steam cellulose reforming on Co/CeO_2-$Al_1Mg_3O_{4.5}$ with the focused UV-vis-IR illumination at near room temperature.

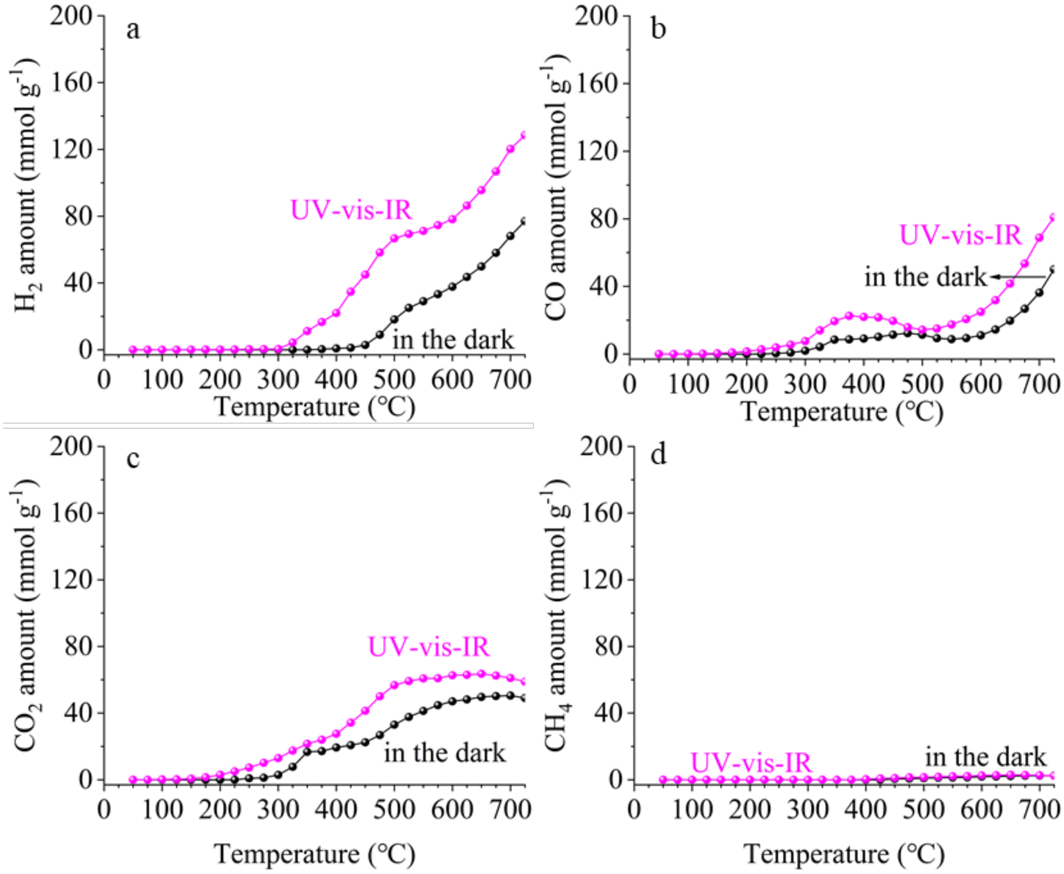


Fig. S16. The amounts of (a) H_2, (b) CO, (c) CO_2, and (d) CH_4 produced by cellulose pyrolysis without adding H_2O on Co/CeO_2-$Al_1Mg_3O_{4.5}$ at different temperatures with the focused UV-vis-IR illumination or in the dark.

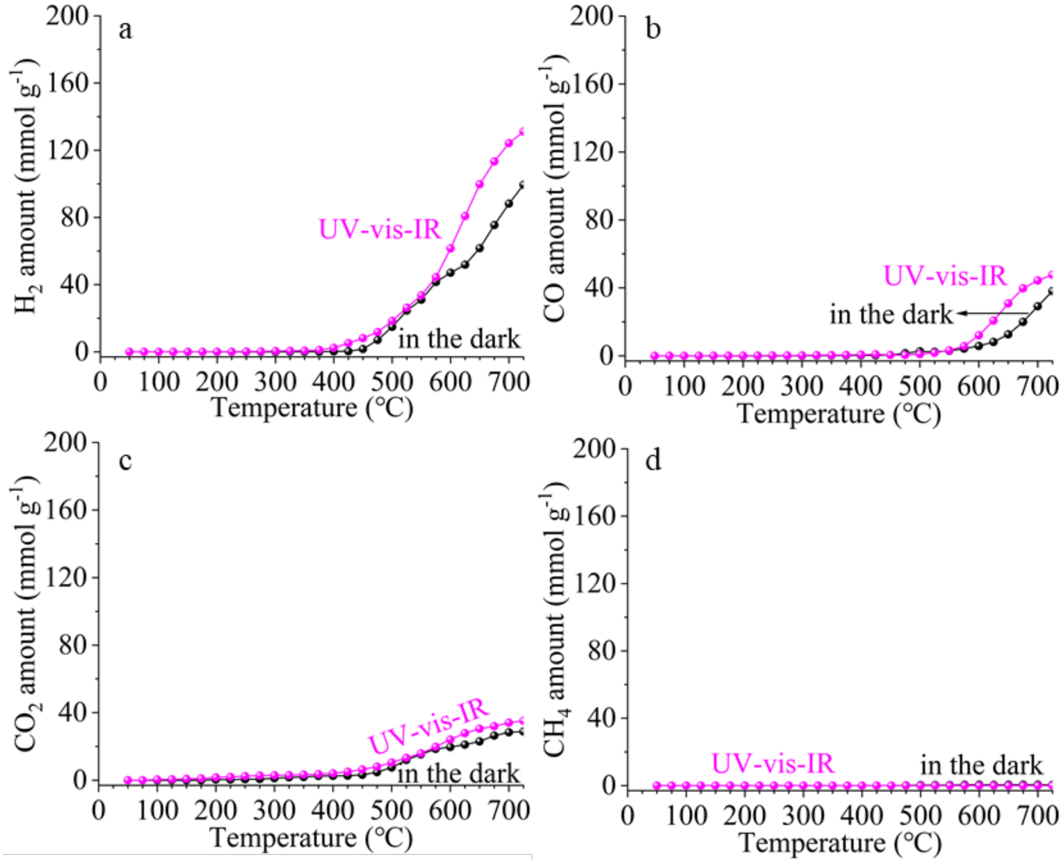


Fig. S17. The amounts of (a) H_2, (b) CO, (c) CO_2, and (d) CH_4 produced by the reaction between H_2O and pre-deposited C* on $Co/Al_1Mg_3O_{4.5}$ at different temperatures with the focused UV-vis-IR illumination or in the dark.

References

s1. Gérard Bergeret, Pierre Gallezot. Particle Size and Dispersion Measurements. Handbook of Heretogeneous Catalysis, 2, Wiley-VCH, 738-765, 2008.