

Supporting Information

Unraveling the light-promoted synergy between highly dispersed Ni and Ni nanoparticles for efficient photothermocatalytic cellulose steam reforming to syngas

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Experimental

Catalyst preparation

NaOH (1.0 g) and Na₂CO₃ (2.6498 g) were dissolved into 18 mL of distilled water in a beaker. Ethanol (5.0 mL) was dropped into the above alkaline aqueous solution under magnetic stirring. MgCl₂·6H₂O (7.6238 g) was dissolved into 18 mL of distilled water in a beaker and added dropwise to the alkaline solution under magnetic stirring. The solution was heated to 70 °C for 2 h. The resultant precipitate was filtered, washed with deionized water, and dried at 110 °C for 10 h. The solid powder obtained was calcined at a rate of 5 °C min⁻¹ to 500 °C for 3h in a muffle furnace, labeled as MgO_{ET}.

The prepared MgO was loaded with Ni using the impregnation method. Ni(NO₃)₂·6H₂O was dissolved into 5.0 g of distilled water in a beaker. This solution was mixed with MgO in an evaporating dish. The evaporating dish was heated to 180 °C until the water was completely evaporated. The obtained powder was heated at 5 °C min⁻¹ to 500 °C and calcined at 500 °C for 3 h in a muffle furnace. Catalysts with different Ni molar loadings (Ni: Mg = 5:100, 10:100, and 15:100) were obtained by reducing in a quartz tubular reactor at 700 °C for 1 h with a 15 mL min⁻¹ flow of pure H₂, denoted as 5Ni/MgO_{ET}, 10Ni/MgO_{ET}, and 15Ni/MgO_{ET}.

The 10Ni_{NPs}/MgO catalyst preparation: 4.1000 g MgCl₂·6H₂O and 0.7300 g urea were dissolved into

65 mL of distilled water in a beaker. Then, the mixed sol-gel solution was transferred to a 100 mL Teflon bottle. The Teflon bottle was sealed in a stainless autoclave, and heated at 160 °C for 24 h in an electric oven. The resultant precipitate was filtered, washed with deionized water, and dried at 100 °C for 12 h. The resultant was heated at 5 °C min⁻¹ to 500 °C and calcined at 500 °C for 3 h in a muffle furnace, labeled as MgO. Load 10 mol% Ni using the impregnation method and follow the same subsequent treatment as Ni/MgO_{ET}, labeled as 10Ni_{NPs}/MgO.

Characterization

XRD patterns were acquired using a Cu K α radiation source on an Empyrean diffractometer. Sample compositions were analyzed via ICP-OES on an Optima 4300DV instrument from PerkinElmer. Transmission electron microscopy (TEM) images were captured using a Talos F200S electron microscope. Agricultural feedstock compositions were determined with a CHNS elemental analyzer (Vario EL cube, Elementar), as detailed in Table S1. *In situ* XPS spectra were recorded on an X-ray photoelectron spectrometer (ESCALAB 250Xi) using Mg K α radiation following pre-reduction at 5% H₂/Ar at 700 °C and cooling to room temperature in pure Ar. Char and organic compound content in reaction residues and agricultural wastes were quantified through muffle furnace calcination. Raman spectra were obtained using a LABHRev-UV microscope with a 532 nm laser. Diffuse reflectance UV–vis–infrared absorption spectra were measured on a Lambda 750S spectrophotometer. Fourier transform infrared spectra (FTIR) was recorded on a Nicolet 6700 infrared spectrometer.

Photothermocatalytic and photocatalytic tests

Photothermocatalytic steam cellulose reforming on the samples was assessed in a homemade reactor (Scheme S1)⁴⁰. Cellulose was mixed with the catalyst according to a weight ratio of 18:1 and ground in an agate mortar. Deionized water, at a 1.9:1 weight ratio to cellulose, was added to the mixture. A measured amount of the paste, containing 0.05 g of cellulose, was placed in a corundum crucible on aluminum silicate insulation cotton. The reaction details and gas analysis are described in our prior study (Scheme S2)⁴⁰. The reactor received focused illumination from UV–vis–IR light sources with wavelengths $\lambda > 420$ nm and $\lambda > 560$ nm, with power densities of 181.9, 151.3, and 131.1 kW m⁻², respectively. The irradiated area was 7.0 mm in diameter, matching the crucible size. Equilibrium temperatures (T_{eq}) were recorded using a thermocouple in contact with the sample center (Scheme 1).

For the catalytic durability was tested, the residual catalyst and char mixture in the alumina crucible was collected. The char content was determined by calcining the residue, allowing for the calculation of

the residual catalyst amount. This residual was then mixed with cellulose at the same 18:1 ratio, and deionized water was added as before. The mixture was ground uniformly and tested in the reactor under identical conditions to the initial photothermal test.

Dry cellulose pyrolysis was conducted by compressing 0.05 g of cellulose and catalyst into tablets at an 18:1 weight ratio.

For biomass steam reforming, rice straw, wheat straw, or corn stalk powder replaced cellulose (Table S1). Specific reactant amounts for cellulose/biomass reforming are detailed in Table S2.

Photocatalytic reactions were carried out with the mixture placed on the reactor bottom, maintained at room temperature using an ice-water bath.

Experimental calculation

Light-driven cellulose steam reforming on catalysts under concentrated UV–vis–IR illumination accomplishes efficient light-to-fuel conversion. The following equation was applied to calculate the light-to-fuel efficiency (η)³⁹.

$$\eta = (r_{\text{H}_2} \times \Delta_c H^0_{\text{H}_2} + r_{\text{CO}} \times \Delta_c H^0_{\text{CO}} + r_{\text{CH}_4} \times \Delta_c H^0_{\text{CH}_4} - r_{\text{C}_6\text{H}_{10}\text{O}_5} \times \Delta_c H^0_{\text{C}_6\text{H}_{10}\text{O}_5}) * m_{\text{catalyst}} / (P * 3600)$$

$\Delta_c H^0_{\text{H}_2}$, $\Delta_c H^0_{\text{CO}}$, $\Delta_c H^0_{\text{CH}_4}$, and $\Delta_c H^0_{\text{C}_6\text{H}_{10}\text{O}_5}$ are the standard combustion heats (298.15 K) of H₂, CO, CH₄, and cellulose as fuels, respectively. r_{CO} , r_{H_2} , and r_{CH_4} are the specific production rates of H₂, CO, and CH₄ as fuels, respectively. $r_{\text{C}_6\text{H}_{10}\text{O}_5}$ is the reaction rate of cellulose that is consumed in producing gas. P is the power of concentrated illumination.

After the photothermocatalytic test, a solid residue of the catalyst and char remained in an alumina crucible in the reactor. The weight of char in the residue was measured by calcining the residual solid after the reaction in a muffle furnace⁴⁰.

The yield of char (y_{char}) was calculated according to the following equation.

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

Where m_{char} is the weight (g) of char. m_i is the weight (g) of the cellulose/biomass (i) used for the catalytic test. $c_{i,C}$ is the weight ratio of carbon in the biomass.

m_{char} was determined according to the following equation by measuring the weight loss ratio (r_{wl}) of the remaining solid after the reaction.

$$m_{\text{char}} = m_{\text{catalyst}} \times (r_{\text{wl}} + c_{\text{Ni}} \times m_{\text{O}} / m_{\text{Ni}}) / (1 - r_{\text{wl}})$$

Where c_{Ni} is the weight ratio of Ni in the catalyst. m_{O} and m_{Ni} are the atomic weights of O and Ni, respectively.

The yield of tar (y_{tar}) was obtained by the calculation according to the following equations based on the mass conversation of carbon.

$$y_{\text{tar}} (\%) = 100 - (c_{\text{CO}} + c_{\text{CO}_2} + c_{\text{CH}_4}) \times V \times 12 / (24450 \times m_i \times c_{\text{v,C}}) \times 100 - y_{\text{char}}$$

Controlled catalytic tests.

Controlled cellulose steam reforming tests in a fixed bed reactor with illumination or in the dark under varying conditions were evaluated on a set-up, as detailed in our previous work (Scheme S3)⁴⁰. The reactor was heated at 5 °C min⁻¹ to 700 °C with concentrated illumination or in the dark. The mixture, prepared similarly to the photothermocatalytic cellulose steam reforming, was loaded into a tubular quartz reactor (Scheme S3). The system was purged with high-purity Ar before each reaction.

For dry cellulose pyrolysis, the mixture was prepared as described for photothermocatalytic cellulose pyrolysis but without tablet compression. The mixture was dried at 120 °C for 1 hour in a high-purity Ar flow before the reaction.

For adsorbed H₂O reaction with pre-formed char, 1 g of the mixture was heated to 700 °C in a high-purity Ar flow to form char (Scheme S3). After cooling, the residue containing 0.01 g of char was placed in the reactor, purged with Ar, and then passed through deionized H₂O for 20 minutes, followed by drying with Ar for 2 h.

The isotope labeling experiment of the reaction between cellulose and H₂¹⁸O on 10Ni/MgO_{ET} was performed in the homemade photothermocatalytic reactor. The produced CO₂ and CO were analyzed by FTIR, following the same procedure as for cellulose steam reforming under concentrated illumination.

H₂ temperature-programmed reduction (H₂-TPR) was performed on TP5080 with a thermal conductivity detector (TCD) multifunctional adsorption apparatus using a tubular quartz reactor linked to a quartz window. The sample (0.0050g) was pretreated at 500 °C in a pure Ar atmosphere for 1 h with a flow of 30 mL min⁻¹, followed by cooling to 25 °C. Then, the gas was switched to 5 vol% H₂/Ar with a flow rate of 24.5 mL min⁻¹. Afterward, the sample was heated from RT to 775 °C with a heating rate of 10 °C min⁻¹.

H₂ temperature-programmed reduction of the pre-chemisorbed oxygen (H₂-TPR-O₂) on the surface of Ni sites with paralleled illumination or in the dark was conducted on a TP5080 apparatus. 0.0050 g catalyst was heated to 700 °C with a 25 mL min⁻¹ pure H₂ flow at a rate of 10 °C min⁻¹ and held for 10 min, and switched to high pure Ar for 30 min. After cooling to RT, the gas was switched to 5 vol% O₂/He with a flow rate of 25 mL min⁻¹ for 30 min. Switch to high pure Ar for 30 min with a flow rate of 30 mL

min⁻¹. After that, the gas was switched to 5 vol% H₂/Ar with a flow rate of 25 mL min⁻¹ and heated from RT to 700 °C with a rate of 10 °C min⁻¹.

H₂O temperature-programmed dissociation (H₂O-TPD) was carried out by 0.02 g of the sample put in a tubular quartz reactor of the TP5080 apparatus. Then the sample was in-situ reduced at 700 °C for 1 h in a 24 mL min⁻¹ pure H₂ and then switched to high pure Ar for 20 min. After cooling to RT, the flow of pure Ar was connected to a bubbler to introduce saturated steam for 25 min to adsorb H₂O. The gas was switched to a flow of high pure Ar (50 mL min⁻¹) for 60 min. Finally, the outlet was linked to a thermal conductivity detector (TCD) without passing the NaOH drier. Pending the stability of the TCD baseline (~ 2 h), the sample was heated from RT to 700 °C.

For the photothermocatalytic tar steam reforming, 0.2 g of cellulose was irradiated under focused light for 4 min and the tar product was collected. 0.03 g of tar was taken and blended with 0.01 g fresh catalyst in a stirring mixture, after adding 0.1 g of H₂O and exposed to focused light irradiation for 7 min.

Temperature-programmed tar oxidation by pre-adsorbed H₂O on the Ni/MgO sample was conducted during the set-up. It was linked via a micro pump to a tubular FTIR cell placed in the chamber of an infrared spectrometer (Nicolet 6700). 0.2 g of cellulose was irradiated under focused light for 4 min and the tar product was collected. 0.03 g of tar was taken and blended with 0.01 g of catalyst. 0.0025 g of the mixture sample, placed in the quartz tube, was heated at 10 °C min⁻¹ to 100 °C and kept at 100 °C for 30 min in a flow of high pure Ar (30 mL min⁻¹) purified by a tube of deoxidant. After cooling to RT, the flow of pure Ar was connected to a bubbler to introduce saturated steam for 10 min for the adsorption of H₂O on the sample. The feed gas was switched to a flow of high pure Ar for 60 min. Finally, the blower is interrupted, and the micropump is turned on to enable the gases to circulate in the system. The FTIR spectra were recorded at a known temperature.

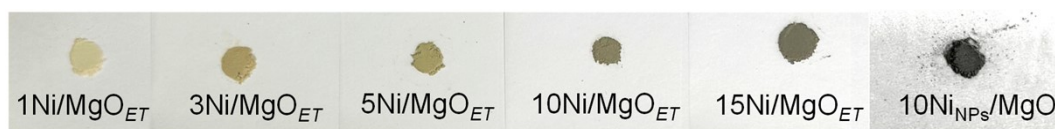


Figure S1. Photograph of the as-obtained samples.

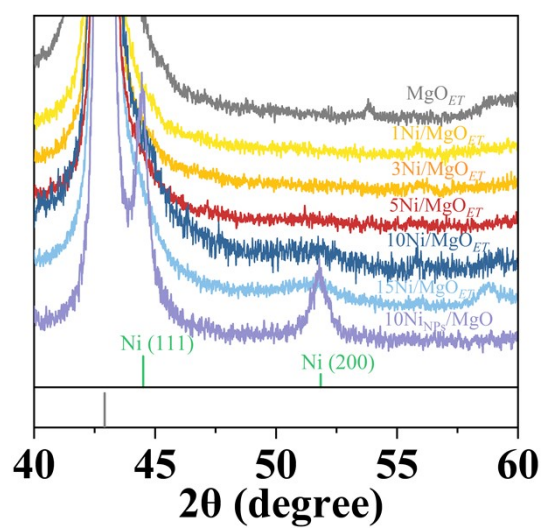


Figure S2. XRD patterns of magnified 40° to 60° for Ni/MgO_{ET} and 10Ni_{NPs}/MgO catalyst.

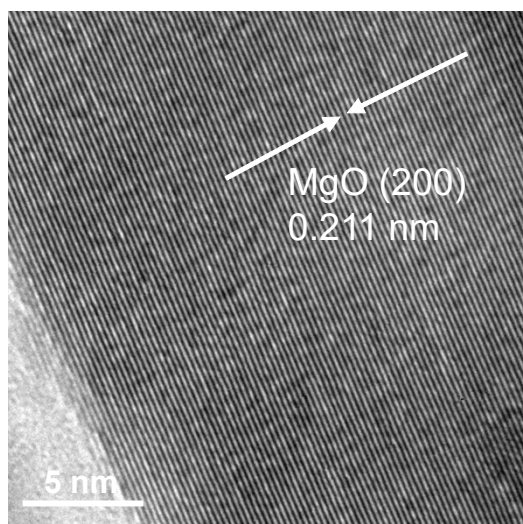


Figure S3. HRTEM images of 5Ni/MgO_{ET}.

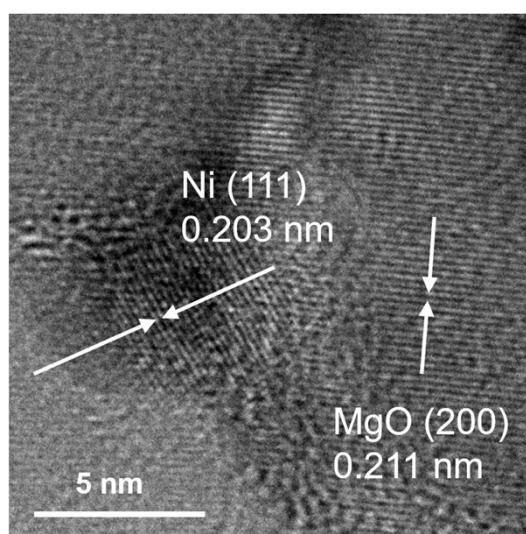


Figure S4. HRTEM images of 10Ni/MgO_{ET}.

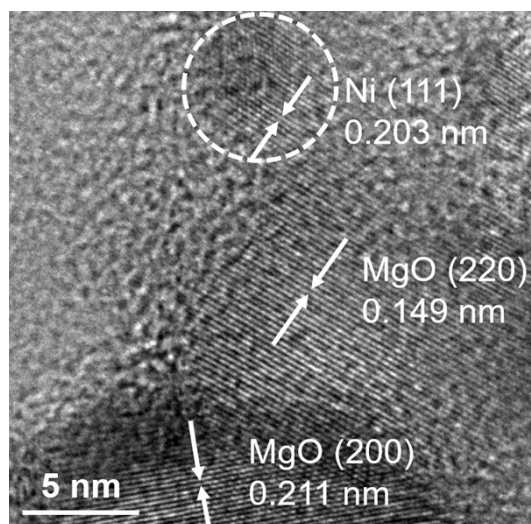


Figure S5. HRTEM images of 10Ni_{NPs}/MgO.

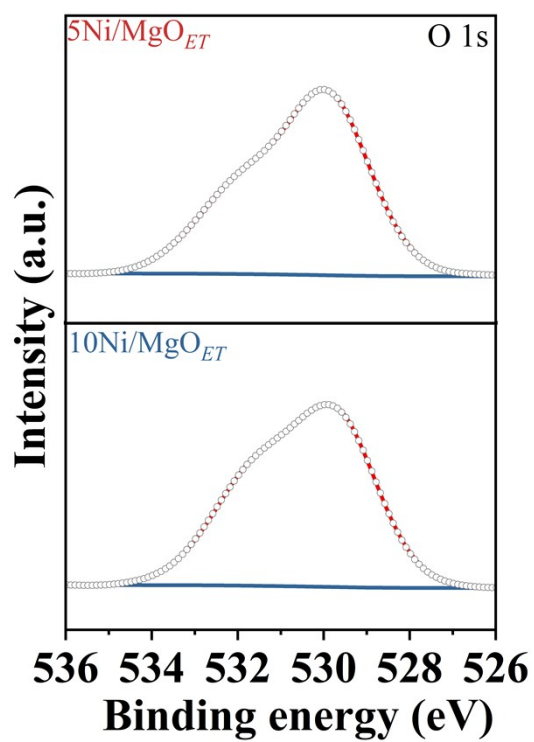


Figure S6. *In situ* XPS spectra obtained of O 1s for pre-reduced 5Ni/MgO_{ET} and 10Ni/MgO_{ET}.

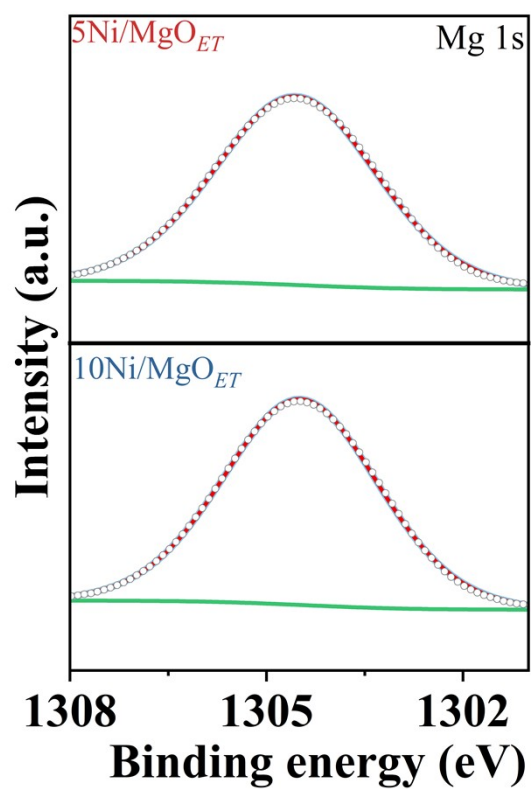


Figure S7. *In situ* XPS spectra obtained of Mg 1s for pre-reduced 5Ni/MgO_{ET} and 10Ni/MgO_{ET}.

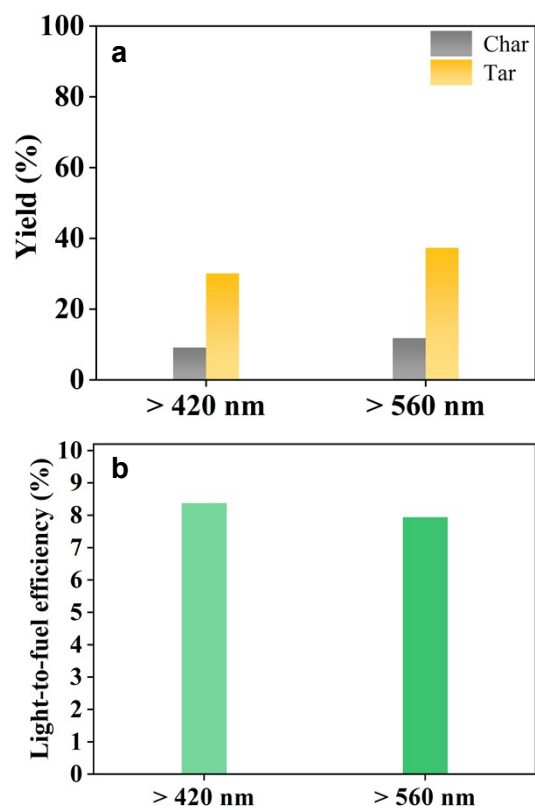


Figure S8. a) The carbon selectivities of char and tar, and b) light-to-fuel efficiencies of cellulose steam reforming on 10Ni/MgO_{ET} under concentrated $\lambda > 420$ nm vis-IR, and $\lambda > 560$ nm vis-IR illumination. The light density are 151.3 and 131.1 kW m⁻², respectively.

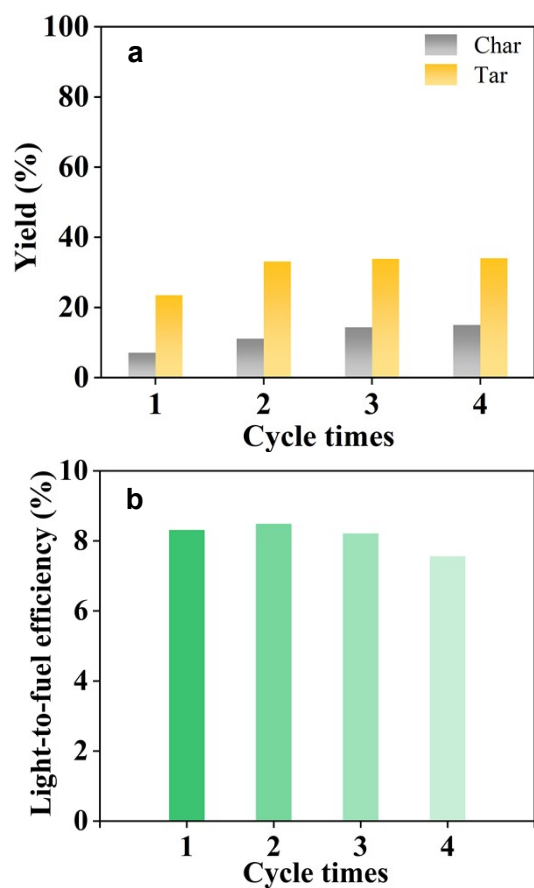


Figure S9. a) Durability test (1~4 cycles) on 10Ni/MgO_{ET} of a) the carbon selectivities of char and tar, b) light-to-fuel efficiencies under concentrated UV-vis-IR illumination.

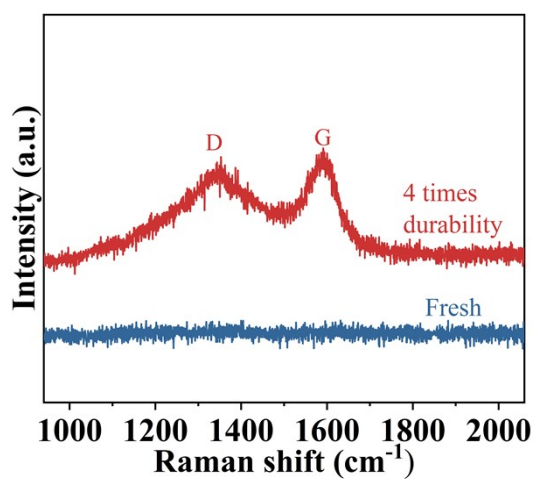


Figure S10. Raman spectra of the fresh reduced 10Ni/MgO_{ET} and the used 10Ni/MgO_{ET} after 4 cycles of photothermocatalytic durability test.

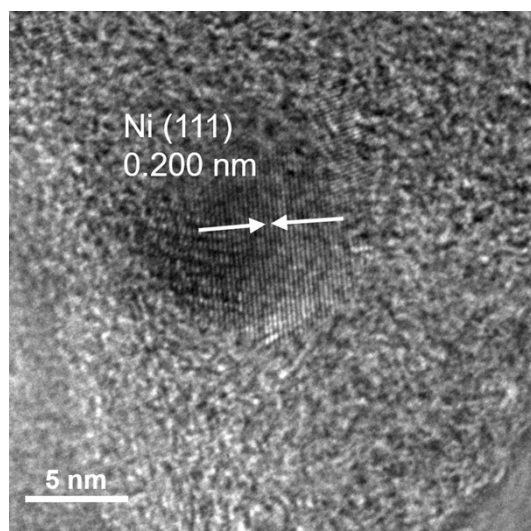


Figure S11. The HRTEM image of 10Ni/MgO_{ET} after 4 cycles of photothermocatalytic durability test.

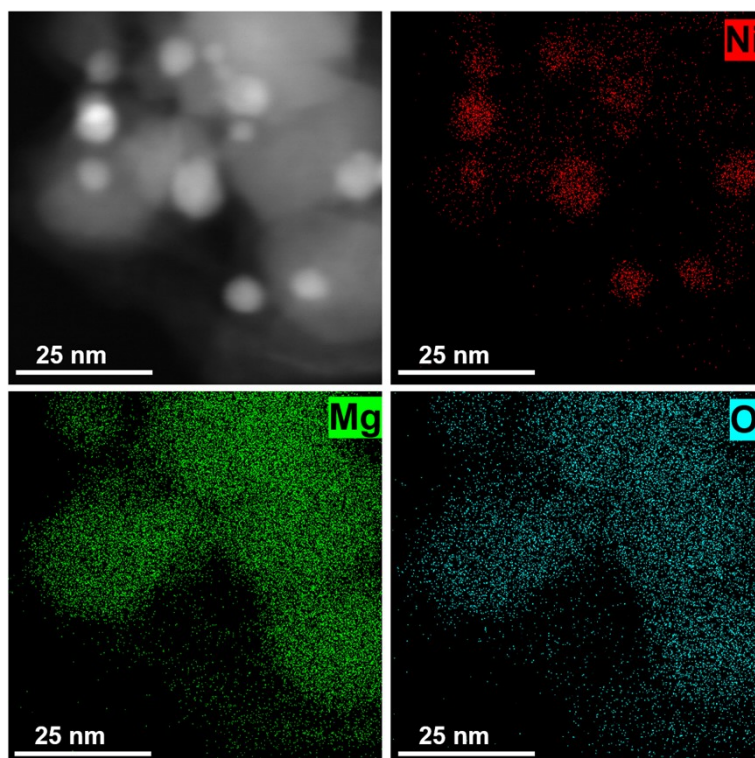


Figure S12. The HAADF image and EDS images of 10Ni/MgO_{ET} after 4 cycles of photothermocatalytic durability test.

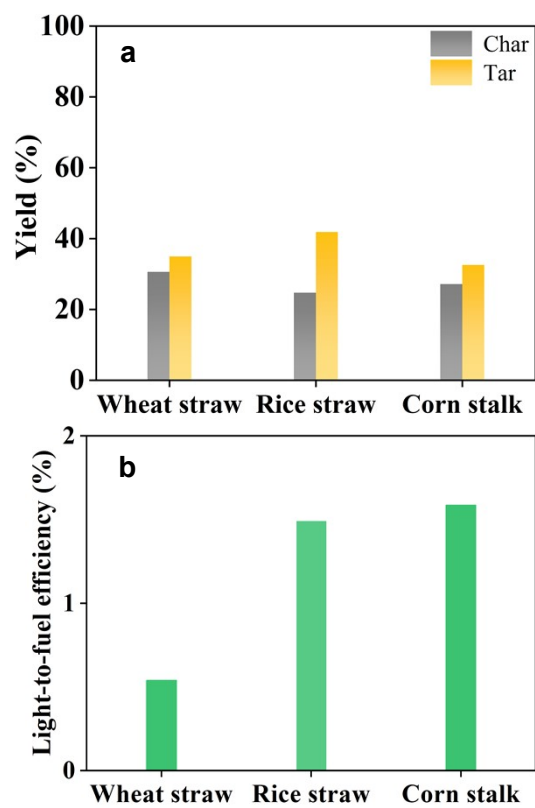


Figure S13. a) Carbon selectivity of char and tar and b) light-to-fuel efficiencies on 10Ni/MgO_{ET} for photothermocatalytic biomass steam reforming.

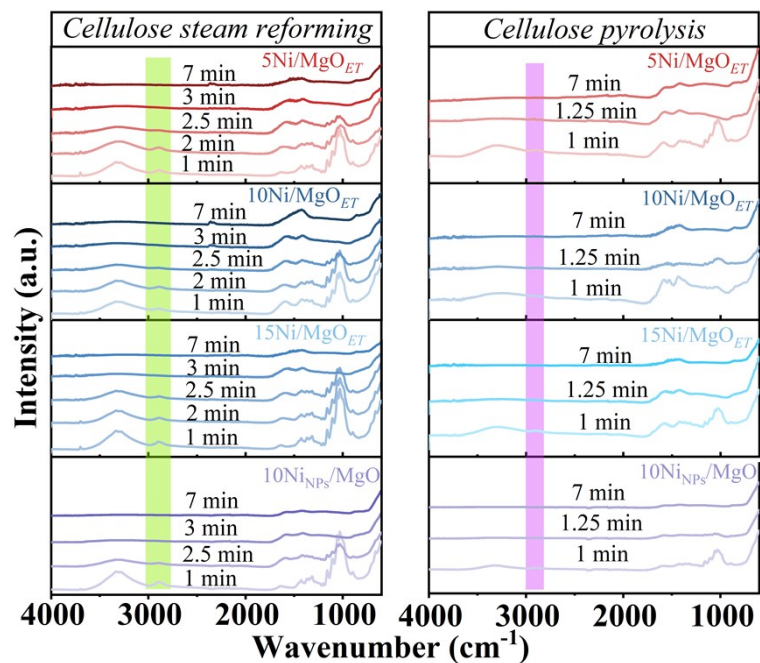


Figure S14. FTIR spectra and the time-based residual solids after cellulose steam reforming and dry cellulose pyrolysis for 5Ni/MgO_{ET}, 10Ni/MgO_{ET}, 15Ni/MgO_{ET}, and 10Ni/MgO under concentrated UV-vis-IR illumination.

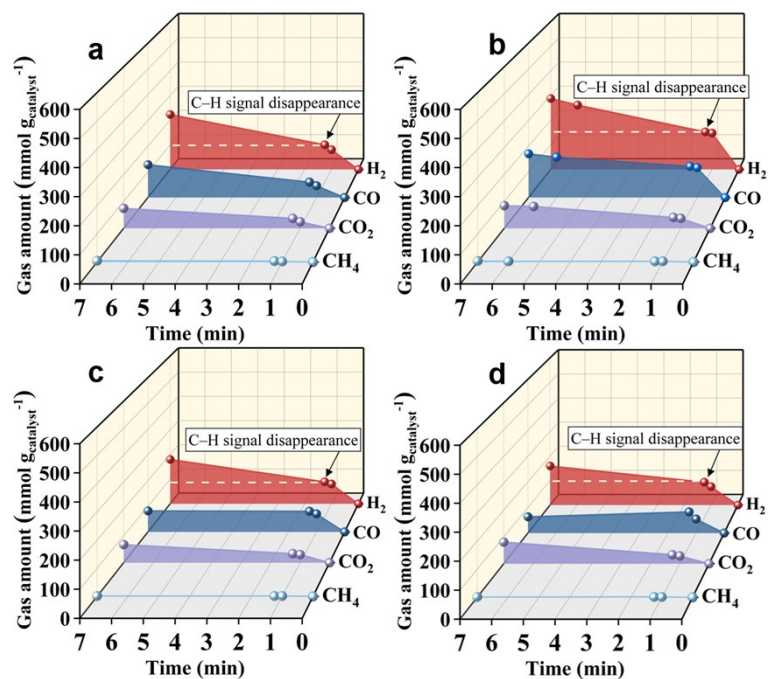


Figure S15. The product amounts for cellulose pyrolysis on a) 5Ni/MgO_{ET}, b) 10Ni/MgO_{ET}, c) 15Ni/MgO_{ET}, and d) 10Ni_{NPs}/MgO with time on stream.

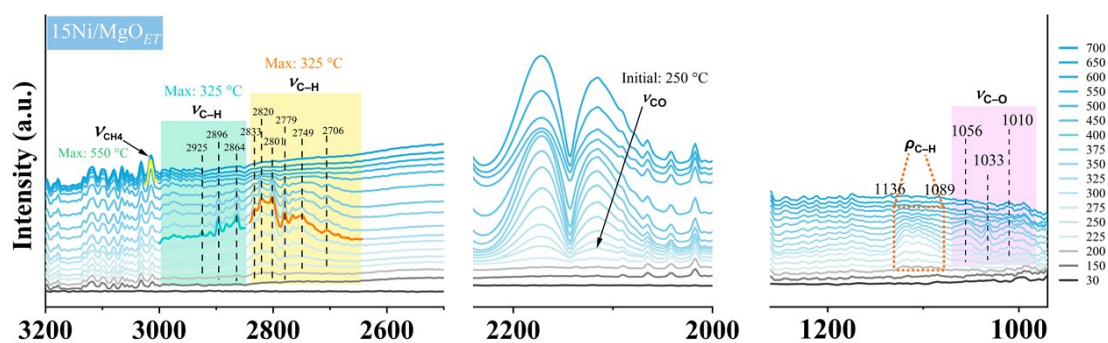


Figure S16. Evolution of FTIR spectra of the gaseous products obtained during catalytic reforming of tar for 15Ni/MgO_{ET}.

Table S1. The compositions of the agricultural biomass.

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

Table S2. The amounts of biomass, catalyst, and H₂O in the mixture, and the amounts of the mixture used for photothermocatalytic biomass steam reforming tests.

	Amounts in the mixture (g)			Amounts of the mixture (g)
	Biomass	10Ni/MgO _{ET}	H ₂ O	
Cellulose	0.4935	0.0274	0.9377	0.1478
Rice straw	0.4016	0.0156	0.9934	0.1756
Wheat straw	0.3417	0.0133	0.8764	0.1799
Corn stalk	0.3676	0.0164	0.9113	0.1762

Table S3. Physicochemical properties and Rietveld refinement results obtained from the diffraction data of reduced samples.

	Ni loading (mol.%) ^a	Ni particle size (nm) ^b
MgO _{ET}	--	--
5Ni/MgO _{ET}	5.3	--
10Ni/MgO _{ET}	10.5	4.3
15Ni/MgO _{ET}	15.3	6.3
10Ni _{NPs} /MgO	10.2	8.0

^a Ni loading was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

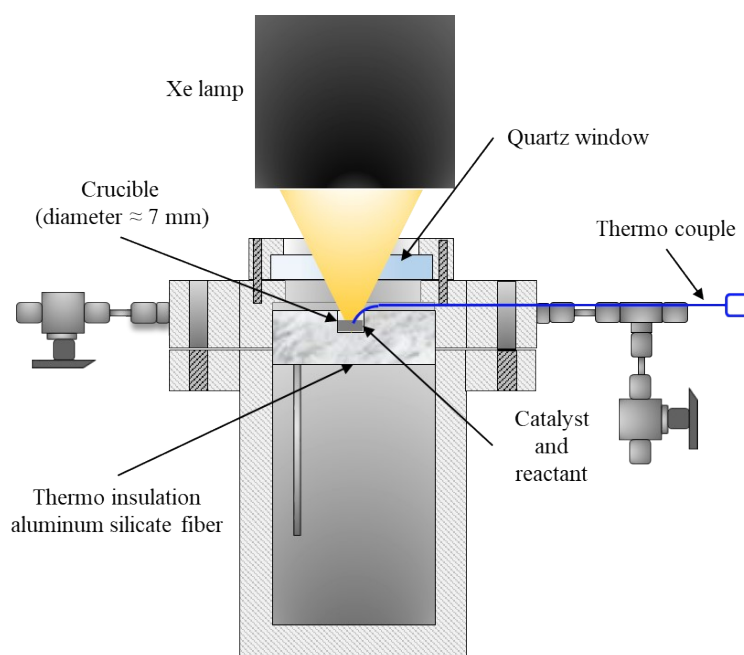
^b Mean particle size of Ni was determined by HAADF-TEM.

Table S4. The performance of catalysts in cellulose steam reforming.

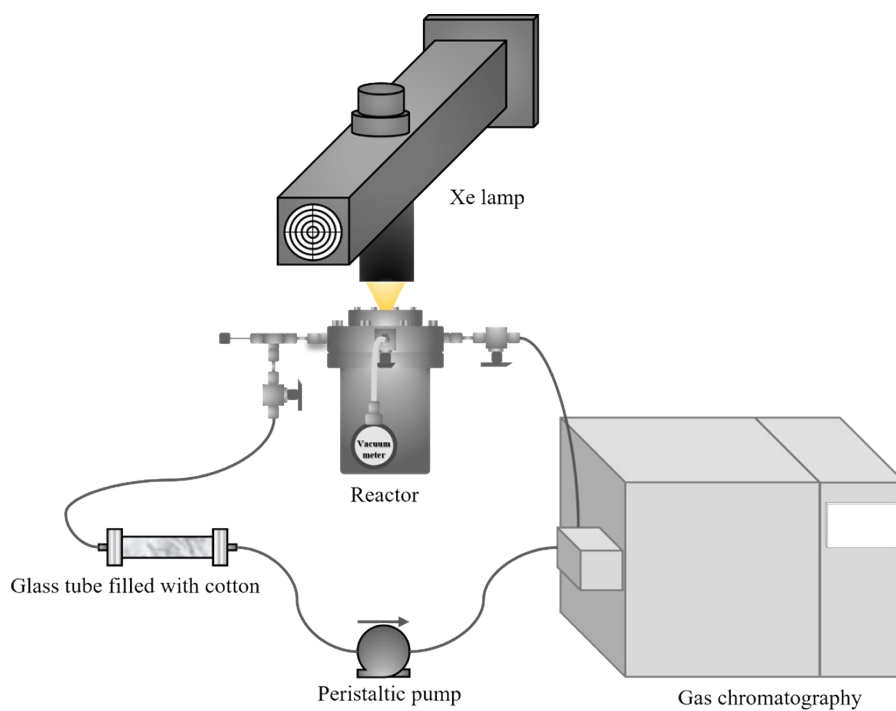
	H ₂ production rate (mmol g ⁻¹ catalyst h ⁻¹)	CO production rate			
		CO production rate (mmol g ⁻¹ catalyst h ⁻¹)	Char yield (%)	Tar yield (%)	η value (%)
MgO _{ET}	437.0	779.8	27.3	51.0	-0.14
1Ni/MgO _{ET}	1220.1	1306.9	21.5	45.5	1.7
3Ni/MgO _{ET}	2936.	1712.1	16.7	36.3	4.2
5Ni/MgO _{ET}	3450.2	1881.8	6.0	43.9	5.6
10Ni/MgO _{ET}	4986.6	2752.7	6.8	23.7	8.3
15Ni/MgO _{ET}	4291.5	2377.2	15.5	23.1	7.1
10Ni _{NPs} /MgO	2789.3	1328.5	14.7	39.7	4.0

Table S5. The performance of catalysts in cellulose pyrolysis.

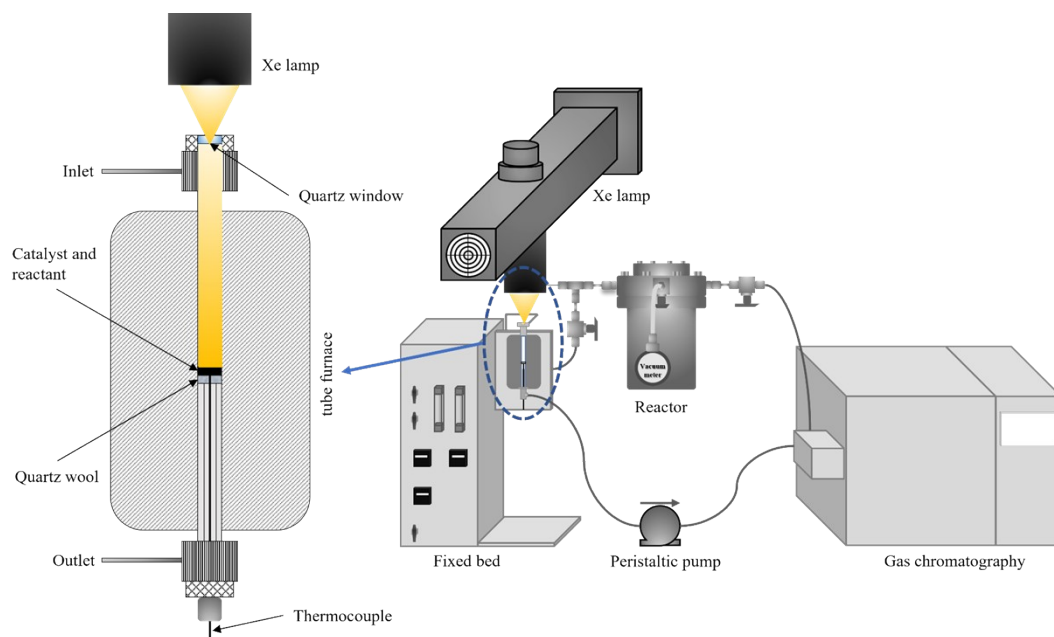
	H₂ production rate (mmol g⁻¹ catalyst h⁻¹)	CO production rate (mmol g⁻¹ catalyst h⁻¹)	Char yield (%)	Tar yield (%)	η value (%)
MgO _{ET}	225.0	320.8	13.0	72.0	--
1Ni/MgO _{ET}	601.1	469.9	10.6	70.5	--
3Ni/MgO _{ET}	1490.3	781.1	10.0	62.1	--
5Ni/MgO _{ET}	1911.1	1092.8	10.9	58.3	2.5
10Ni/MgO _{ET}	2467.7	1457.4	10.1	51.2	3.2
15Ni/MgO _{ET}	1542.8	700.9	11	65.49	1.9
10Ni _{INPs} /MgO	1365.2	544.0	10.2	77.0	0.95



Scheme S1. Schematically illustrated homemade reactor for measuring the photothermocatalytic activity of the samples merely under concentrated illumination from a 500 W Xe lamp.⁴⁰ (Just for review)



Scheme S2. Schematically illustrated set-up for measuring the photothermocatalytic activity of the samples merely under concentrated illumination from a 500 W Xe lamp.⁴⁰ (Just for review)



Scheme S3. Schematically illustrated set-up for measuring the thermocatalytic activity of catalysts in the fixed bed at different temperatures with concentrated illumination or in the dark. *Note:* The reactor in which no catalyst and cellulose were put, was used as a container for storing the gases produced by the reaction in the tubular quartz reactor.⁴⁰ (Just for review)