

Catalyst	Light source	Irradiance /( $\text{kW m}^{-2}$ )	Au diameter /nm	Au loading /wt. %	H <sub>2</sub> :CO <sub>2</sub> ratio	Pressure /bar	Additional heating	CO activity	CO selectivity	Reference
Au/TiO <sub>2</sub>	Dolan–Jenner broadband visible light source (MI-150)	5.216	3.5	1.4	2:1	10.2	400°C	159.8 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	>99%	1
	Hg lamp (UV)	1.5	18	0.5	1:1	1	RT	4.144 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	>99%	2
	Solar simulator (AM 1.5)	14.4	1.6	3.12	1:1	3.5	RT	429 mmol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	98%	3, 4
	Solar simulator (AM 1.5)	13.9	6	3.9	1:1	3.5	RT	7.81 mmol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	>88%	5
	Solar simulator (AM 1.5)	13.9	16	3.72	1:1	3.5	RT	0.44 mmol CO g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	>84%	5
Au/Al <sub>2</sub> O <sub>3</sub>	Dolan–Jenner broadband visible light source (MI-150)	5.216	10	0.7	2:1	10.2	400°C	7.08 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	>99%	1
	365 nm LED 460 nm LED 5700K white light LED	30.0	2.6	1.7	5:1	1	350°C	1.3 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	100%	6
	Green LED	2.501	4.3	3.62	4:1	1	330°C	1.06 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	/	7
	Green LED	2.501	6.7	3.58	4:1	1	330°C	1.18 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	/	7
	Green LED	2.501	31.3	3.75	4:1	1	330°C	1.36 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	/	7
Au/SiO <sub>2</sub>	Dolan–Jenner broadband visible light source (MI-150)	5.216	2	3.925	2:1	8.1	300°C	11.24 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	>99%	1, 8
Au/CeO <sub>2</sub>	Dolan–Jenner broadband visible light source (MI-150)	5.216	5	3.3	2:1	10.2	400°C	85.02 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	>99%	1
	Xe Arc lamp	32.0	15	1	4:1	1	RT	7 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	>99%	9
	Solar simulator (AM 1.5)	8.9	<2	0.41	1:1	3.5	RT	3.9 mmol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	>98%	This work
	Solar simulator (AM 1.5)	8.9	3.9	1.57	1:1	3.5	RT	1.0 mmol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	>98%	This work
	Solar simulator (AM 1.5)	8.9	3.8	3.8	1:1	3.5	RT	2.8 mmol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	>98%	This work
	Solar simulator (AM 1.5)	8.9	3.5	5.8	1:1	3.5	RT	1.8 mmol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	>98%	This work

**Table S1:** Literature overview of metal oxide supported Au plasmonic photocatalysts for rWGS.

# 1 Experimental methods

## 1.1 Synthesis

CeO<sub>2-x</sub> particles were synthesised using a hydrothermal method adapted from Zhang et al.<sup>10</sup> The synthesis method was adjusted as to obtain larger (L-HT) and smaller (S-HT) particle sizes. In a typical experiment, Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (4.071 g, 9.38 mmol, Thermo Scientific Chemicals, 99.5%) and polyvinylpyrrolidone (PVP) (2.306 g, 20.8 mmol monomer (L-HT); 4.613 g, 41.6 mmol monomer (S-HT), 8,000 average M.W., Acros Chemicals) were dissolved in a 75 ml mixture of ethanol (VWR Chemicals, 96%) and ultra-filtered water (Milli-Q Millipore, Billerica, MA, USA, 18.2 MΩ cm) with a volume ratio of 1:2 and 3:1 for L-HT and S-HT, respectively, in a 100 ml beaker. The mixture was sonicated for two minutes in an ultrasonication bath (Fisherbrand, FB15057) to facilitate PVP dissolution and subsequently stirred with a magnetic stirrer in open air while covered with a watch glass for one hour. Next, the solution was transferred to a Teflon lined autoclave (Parr autoclave, model 4748, 125 ml). The hydrothermal reaction was carried out at 160°C (Binder, ED series 53) for 20h and 14h for L-HT and S-HT, respectively. The autoclaves were left in the oven to cool down. The resulting dispersion was stirred in open air with a magnetic stirrer in a wide, open beaker on a hot plate for 16h at 80°C, and subsequently 2h at 95°C in order to evaporate the solvent. Next, the obtained L-HT and S-HT powders were thermally treated in dry air at 400°C for 2h in an alumina boat crucible, with a heating ramp rate of 3.1°C/min and 0.6 l/min flow, in order to remove organic residues, resulting in large (L) and small (S) CeO<sub>2-x</sub> powders, respectively. The samples were allowed to cool down inside the tube furnace.

Au nanoparticles were deposited on the CeO<sub>2-x</sub> support materials by means of a deposition-precipitation method as discussed in our previous work.<sup>5</sup> Urea (0.5 g, 8.33 mmol, VWR Chemicals, 99%) and CeO<sub>2-x</sub> (500 mg, 2.9 mmol, L or S) were weighed in a 100 ml round bottom flask. Ultra-filtered MilliQ water (50 ml) was added as well as 2.00 ml, 5.18 ml and 8.10 ml of an aqueous solution of HAuCl<sub>4</sub> (0.02 M, Alfa Aesar, 99.99%) to obtain catalysts with increasing gold loadings, denoted as 1.5Au/S (1.5 wt. % Au), 4Au/S (4.0 wt. % Au), 4Au/L (4.0 wt. % Au) and 6Au/S (6.0 wt. % Au). The round bottom flask was ultrasonicated in an ultrasonication bath for one minute and next stirred and heated with a heat mantle under reflux for 3h at 80°C. Subsequently, 4.00 ml, 10.36 ml and 16.20 ml of freshly prepared NaBH<sub>4</sub> solution (0.1 M, Acros Organics, 99%) was added dropwise under continuous stirring, for 1.5Au/S, 4Au/S, 4Au/L and 6Au/S respectively, and left to stir for 1h at 80°C under reflux. Then, the samples were centrifugated and washed three times with ultra-filtered water and once with ethanol. Finally, the catalysts were allowed to dry overnight in a fume hood.

An alternative deposition-precipitation method was utilised for synthesis of a 0.4 wt. % Au sample in order to achieve a smaller Au NP size, denoted 0.4Au/S.<sup>3, 4, 11, 12</sup> HAuCl<sub>4</sub>·3H<sub>2</sub>O (7.8 mg, 0.020 mmol, Alfa Aesar, 99.99%) was dissolved in ultra-filtered MilliQ water (100 ml) in a 100 ml round bottom flask. NaOH (50% m/m, Sigma-Aldrich, 98%) was diluted to a concentration of 0.02 M and added dropwise under continuous stirring and pH monitoring until a stable pH of 9 was obtained, under ambient conditions. Next, 1g of S CeO<sub>2-x</sub> was added to the mixture, and subsequently the pH was readjusted to 9 by dropwise addition of NaOH. The dispersion was allowed to stir for 48 hours and subsequently centrifuged and washed three times with ultra-filtered MilliQ water and once with ethanol and dried overnight in a fume hood. Finally, the sample was thermally treated at 200°C in flow rate dry air (0.6 l/min) for 4 hours, with a heating ramp rate of 2°C/min. The sample was allowed to cool down inside the tube furnace.

Catalysts 4Au/L and 4Au/S were thermally oxidized in dry air (0.6 l/min) at 500°C for 2h, with a heating ramp rate of 4.0°C/min, resulting in samples denoted 4Au/L-O and 4Au/S-O. The 4Au/L and

4Au/S catalysts were also thermally reduced in forming gas (5% H<sub>2</sub> in N<sub>2</sub>; stationary atmosphere) at 500°C for 2h, with a heating ramp rate of 7.9°C/min. Resulting in samples denoted 4Au/L-R and 4Au/S-R. The samples were allowed to cool down inside the tube furnace.

In order to minimise the impact of possible batch to batch variations, samples of repetitive batches were mixed before carrying out subsequent synthesis steps.

## 1.2 Characterisation

Transmission electron microscopy (TEM) studies of the CeO<sub>2-x</sub> support particles were carried out on a FEI Tecnai Spirit operated at 120 kV. At least 90 particles were analysed per sample.

TEM studies of Au/CeO<sub>2-x</sub> catalysts were carried out at 200 kV with a JEOL ARM 200F probe corrected TEM. Particle imaging was performed in high-angle annular dark field scanning TEM (HAADF-STEM) mode. Energy dispersive X-ray spectroscopy (EDX) spectra were recorded using a 100 mm<sup>2</sup> Centurio SDD detector. EDX mappings were obtained in STEM mode by acquiring full spectra in grids of 256 x 256 pixels for all magnifications. All mappings were obtained by summation of 50-100 frames, each having 0.1 ms acquisition time per pixel per frame. In this way, the material remained unaffected by the impact of the incident electron beam. EDX mappings were used for material identification, particle size analysis was performed on the corresponding HAADF-STEM images at a consistent magnification level. For particle size distributions at least 90 particles were analysed per sample, unless noted otherwise.

Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) analysis was performed using a PerkinElmer Frontier (32 scans, scan range 4000-400 cm<sup>-1</sup>, resolution 4 cm<sup>-1</sup>).

Thermogravimetric analysis (TGA Q500, TA instruments, High-T Pt sample pan) was carried out from room temperature up to 900°C with a heating rate of 10°C/min in a dry air atmosphere (90 ml min<sup>-1</sup>).

Dynamic light scattering (DLS) was performed with a Brookhaven ZetaPals. To this end dispersed CeO<sub>2-x</sub> samples from hydrothermal synthesis were diluted with ultrapure water for measurement. Five measurements (two minutes each) were carried out per sample.

Raman spectra were collected using a Renishaw InVia Qontor Confocal Raman Microscope with a 100x objective and a 785 nm laser excitation source (100 mW). Calibration of the Raman shift scale was performed with Silicon. Measurements were performed at room temperature in air with a low laser power (0.05 %) to guarantee the sample to be unaffected during laser exposure. An exposure time of 30 seconds (60 summations) was performed using a 1200 l/mm grating. Processing of Raman spectra, background subtraction and cosmic ray removal, was carried out in the Renishaw WiRe software.

Powder X-ray diffraction was carried out using a Bruker D8 Discover (Cu K- $\alpha$  radiation, LynxEye detector). 100 mg of LaB<sub>6</sub> (Alfa Aesar, 99.5%) was added as an internal standard to 100 mg sample. Measurements were carried out from 2 $\theta$  value of 10° to 130° with a step size of 0.01° and step time of 3 seconds. Le Bail refinement was carried out in the JANA2006 software to obtain cell parameters.<sup>13</sup>

UV-Visible diffuse reflectance spectrometry was performed with a Cary UV-Vis-NIR spectrometer, Agilent Technologies. The sample (500 mg) was added to the powder holder and reflectance was measured in scan mode with a scan rate of 10 nm/s, with a range between 300 nm and 800 nm. A sample holder containing PTFE was used to construct a baseline (100% reflectance) while a zero-reference point was constructed in absence of a sample holder (0% reflectance).

Brunauer-Emmett-Teller (BET) theory was applied on N<sub>2</sub> physisorption isotherms (Micromeritics, Tristar II, -196°C) of the photocatalysts in order to determine the specific surface area. Samples were flushed with nitrogen gas at 150°C for 16h prior to the measurement in order to remove possible residual adsorbed components.

Au content in the Au/CeO<sub>2-x</sub> photocatalysts was determined with inductively coupled plasma-optical emission spectrometry (ICP-OES), Perkin Elmer Optima 330 dv simultaneous spectrometer, PerkinElmer, Waltham, MA, USA. Sample digestion was carried out in a 10 ml mixture of mineral acids (HCl (≥37%, TraceSELECT, for trace analysis, Honeywell chemicals):HNO<sub>3</sub> (69.0-70.0%, J.T.Baker, for trace metal analysis):HF (40%, AnalaR NORMAPUR® analytical reagent, VWR) in a 3.17:1:1.71 ratio) in a Milestone microwave setup. For ICP-OES measurements, 1000 ppm Au standard (Merck) and the sample solutions were diluted by 5% HNO<sub>3</sub> to 1-2-5-10 ppm and 1-10 ppm concentrations, respectively. All ICP analyses were carried out *in duplo*.

Hydrogen-temperature programmed reduction (H<sub>2</sub>-TPR) was performed with a Chemstar TPX Chemisorption Analyzer (Quantachrome). First the sample was degassed (typically 50 mg) at 300°C for 2h with 40 ml min<sup>-1</sup> He flushing, after which the sample was cooled down to 50°C. H<sub>2</sub>-TPR was performed from 50°C to 900°C at a heating rate of 10°C/min under 40 ml min<sup>-1</sup> 5% H<sub>2</sub>/Ar flow.

### 1.3 Photocatalytic experiments

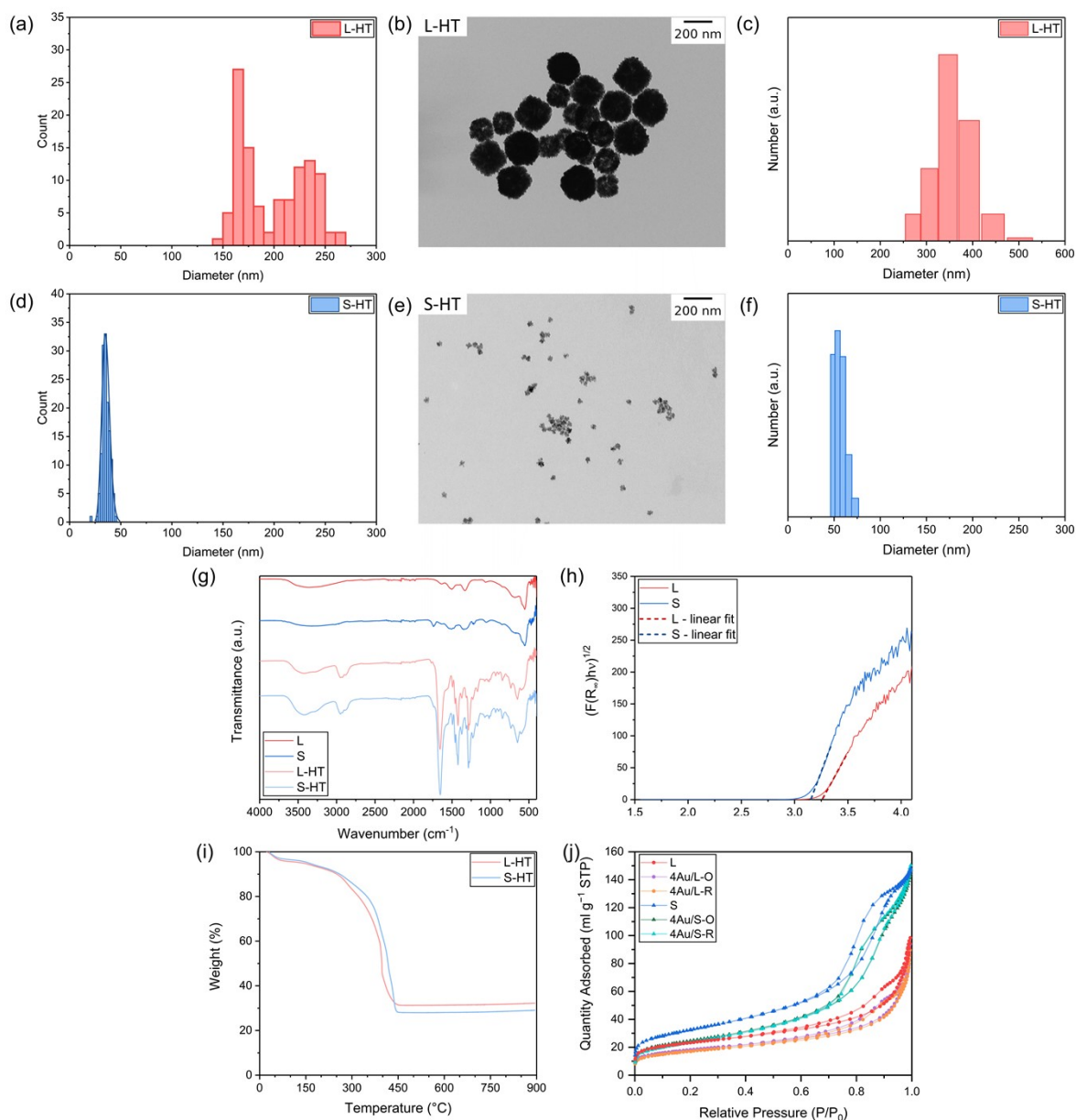
The catalytic CO<sub>2</sub> conversion tests were carried out in a custom-made reactor, a quartz window at the top allows for light irradiation, as described by Sastre et al.<sup>14</sup> Light for photocatalysis was supplied by a solar simulator (Newport Sol3A) situated above the reactor and was equipped with a high flux beam concentrator (Newport 81,030), and AM1.5 filter. Intensity of the irradiated light was calibrated with a thermopile sensor. For experiments without UV component, an additional filter was mounted cutting off wavelengths below 395 nm. The irradiated area was about 3.14 cm<sup>2</sup>, which was fully covered by the sample catalyst. Temperature during reaction was monitored by three thermocouples: top of the reactor, bottom of reactor, bottom of the catalyst bed. In addition, temperature inside the catalyst bed was monitored by four optical Fibre Bragg Gratings (FBG) as described by Xu et al.<sup>15</sup> at depths of 0 mm, 0.15 mm, 0.30 mm and 0.50 mm. A fifth FBG was placed on the rim of the catalyst holder as a reference. In a typical experiment, 200 mg of the catalyst was loaded in the catalyst holder and flattened homogeneously for accurate FBG measurements. The reactor was then vacuum purged and filled with N<sub>2</sub> in three cycles. Next, a constant flow of a mixture of H<sub>2</sub> (Linde 6.0), CO<sub>2</sub> (Linde 4.5) and N<sub>2</sub> (Linde 5.0), with flow rates of 8 ml min<sup>-1</sup>, 8 ml min<sup>-1</sup> and 4 ml min<sup>-1</sup>, respectively, was allowed through the catalyst bed. A reactor pressure of 3.5 bar was maintained by a backpressure regulator. The lamp was switched on after 20 minutes of flow. In dark reaction conditions, the reactor vessel was heated to 180°C under vacuum, once the temperature stabilised the gas flow was initiated. The reaction products were analysed by a gas chromatograph (Compact GC, Global Analyzer Solutions), and injections were automatically taken every 2.5 min from the outgoing flow. The GC was equipped with three channels, two microthermal conductivity detectors (TCD) and one flame ionisation detector (FID). The peak areas were used to determine the ratio of all components based on calibration, N<sub>2</sub> being used as an internal standard. If any products were present in the time zero analysis, this value was subtracted from the following results.

Catalytic tests with varied catalyst loading were performed with a custom-made reactor, a quartz window at the top allows for light irradiation. Light for catalysis was supplied by a 300 W Xe Arc lamp (LOT-Quantum Design, LSB531). The irradiated area was about 2.14 cm<sup>2</sup>, where the sample catalyst homogeneously covered the area. In a typical experiment, the catalyst was loaded in the reactor, the reactor was then vacuum purged and filled with a mixture of H<sub>2</sub> (Air Liquide, P0232), CO<sub>2</sub> (Air Liquide,

P1209) and N<sub>2</sub> (Air Liquide, P0271) at constant flow rates of 8 ml min<sup>-1</sup>, 8 ml min<sup>-1</sup> and 4 ml min<sup>-1</sup>, respectively. A reactor pressure of 3.5 bar was maintained by a backpressure regulator. The lamp was switched on after 30 minutes of flow. The reaction products were analysed by a gas chromatograph (Agilent, 990 Micro GC) with two TCD channels (MS5A SS column for H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO and PORAPLOT U column for CO<sub>2</sub> and C<sub>2</sub>+ components). The peak areas were used to determine the ratio of all components based on calibration, N<sub>2</sub> being used as an internal standard. If any products were present in the time zero analysis, this value was subtracted from the following results.

Sample	CeO <sub>2</sub> size /nm	Au size /nm	Au loading /wt. %	Thermal treatment
L-HT	200 ± 7	/	/	/
L	196 ± 13	/	/	400°C (Dry Air)
4Au/L	/	3.5 ± 0.2	4.0 ± 0.8	/
4Au/L-O	/	5.1 ± 0.3	4.0 ± 0.8	500°C (Dry Air)
4Au/L-R	/	3.0 ± 0.3	4.0 ± 0.8	500°C (5% H <sub>2</sub> )
S-HT	35.5 ± 0.7	/	/	/
S	37 ± 2	/	/	400°C (Dry Air)
4Au/S	/	3.6 ± 0.3	3.8 ± 0.9	/
4Au/S-O	/	4.9 ± 0.4	3.8 ± 0.9	500°C (Dry Air)
4Au/S-R	/	3.8 ± 0.4	3.8 ± 0.9	500°C (5% H <sub>2</sub> )
0.4Au/S	/	<2	0.41 ± 0.02	/
1.5Au/S	/	3.9 ± 0.3	1.57 ± 0.08	/
6Au/S	/	3.5 ± 0.3	5.8 ± 0.4	/

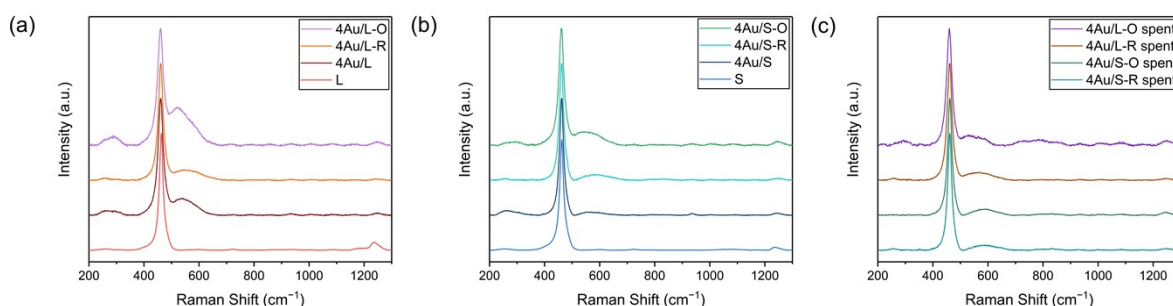
**Table S2:** Summary of synthesised samples and their characterisation, 98% confidence intervals are reported



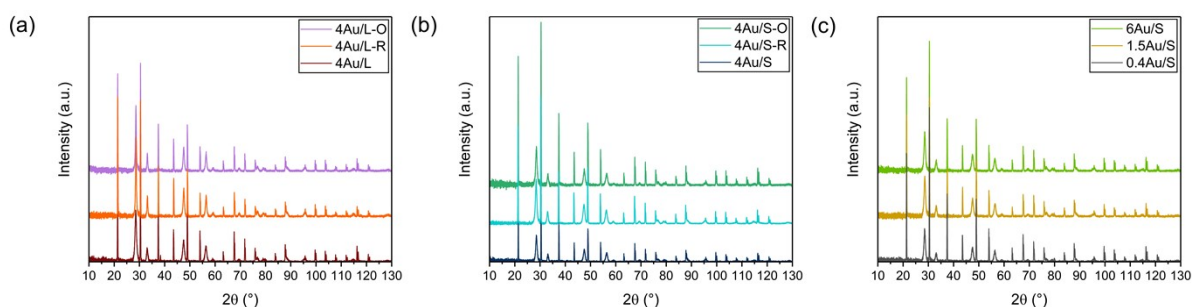
**Fig. S1:** (a) Particle size distribution of L-HT CeO<sub>2</sub> support from TEM analysis; (b) representative TEM image of L-HT CeO<sub>2</sub> particles; (c) particle size distributions of L-HT CeO<sub>2</sub> sample from DLS; (d) particle size distribution of S-HT CeO<sub>2</sub> support from TEM analysis with lognormal fit; (e) representative TEM image of S-HT CeO<sub>2</sub> particles; (f) particle size distributions of L-HT CeO<sub>2</sub> sample from DLS; (g) ATR-FTIR spectrograms of L, S L-HT and S-HT CeO<sub>2</sub> particles, graphs have been stacked for visual clarity; (h) Tauc analysis of diffuse reflectance UV-Vis measurements of L and S CeO<sub>2</sub> particles, band gap energy is determined by intercept of the linear fit with the x-axis; (i) TGA analysis of L-HT and S-HT samples; (j) N<sub>2</sub> adsorption isotherms of L, 4Au/L-O, 4Au/L-R, S, 4Au/S-O and 4Au/S-R samples.

L		S	
Wavenumber /cm <sup>-1</sup>	Origin	Wavenumber /cm <sup>-1</sup>	Origin
>3000	H <sub>2</sub> O	>3000	H <sub>2</sub> O
		1741, 1727	Bridged carbonate
1640	H <sub>2</sub> O	1636	H <sub>2</sub> O
1500	Bidentate carbonate	1506	Bidentate carbonate
1330	Unidentate carbonate	1473, 1352	Unidentate carbonate
		1230, 1217	Bridged carbonate
1063, 845	Unidentate carbonate	1057, 843	Unidentate carbonate
686, 590, 550	CeO <sub>2</sub>	674, 583, 552	CeO <sub>2</sub>

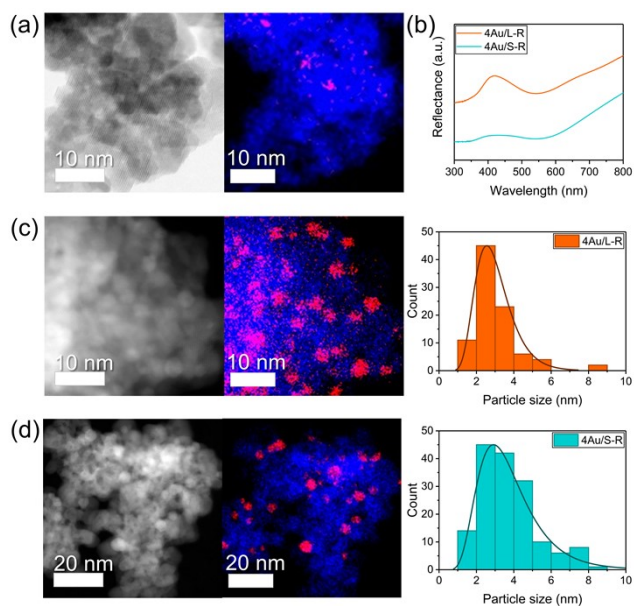
**Table S3:** Assignment of main peaks found in the ATR-FTIR of L and S following Li et al. <sup>16</sup>.



**Fig. S2:** Raman spectra of (a) 4Au/L-O, 4Au/L-R, 4Au/L, and L, (b) 4Au/S-O, 4Au/S-R, 4Au/S and S, (c) 4Au/L-O spent catalyst, 4Au/L-R spent catalyst, 4Au/S-O spent catalyst and 4Au/S-R spent catalyst. Intensity has been normalised on the intensity of the F<sub>2g</sub> peak, graphs have been stacked for visual clarity.



**Fig. S3:** XRD diffractograms of (a) 4Au/L-O, 4Au/L-R and 4Au/L, (b) 4Au/S-O, 4Au/S-R and 4Au/S, (c) 6Au/S, 1.5Au/S and 0.4Au/S with LaB<sub>6</sub> as internal standard, intensity is normalised on the wt% of sample in the sample/LaB<sub>6</sub> mixture, graphs have been stacked for visual clarity.



**Fig. S4:** (a) Representative annular bright field-STEM image and EDX mapping in STEM mode of 0.4Au/S, CeO<sub>2</sub> is coloured blue and Au is coloured red in the EDX mapping; (b) diffuse reflective UV-Vis spectra of 4Au/L-R and 4Au/S-R, graphs have been stacked for visual clarity; Representative HAADF-STEM image, EDX mapping in STEM mode and Au particle size distribution from TEM analysis with lognormal fit of (c) 4Au/L-R and (d) 4Au/S-R, CeO<sub>2</sub> is coloured blue and Au is coloured red in the EDX mapping.

Sample	TPR: %H <sub>2</sub> uptake CeO <sub>2-x</sub> surface
L	41.8
4Au/L	18.7
4Au/L-O	25.7
4Au/L-O spent	16.7
4Au/L-R	16.0
4Au/L-R spent	18.2
S	55.2
4Au/S	31.7
4Au/S-O	30.6
4Au/S-O spent	24.3
4Au/S-R	20.6
4Au/S-R spent	22.5

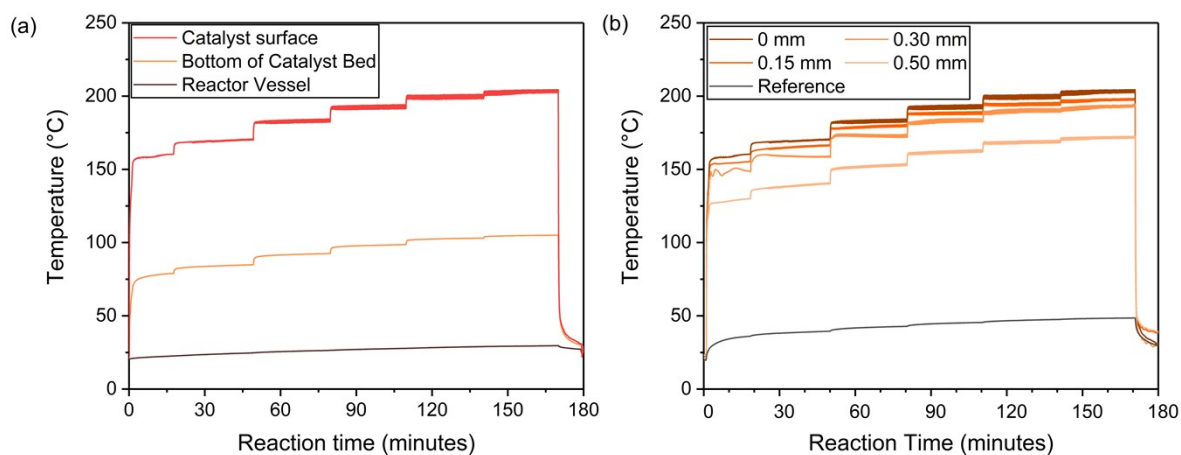
**Table S4:** %H<sub>2</sub> uptake at the surface of CeO<sub>2-x</sub> normalised on the total H<sub>2</sub> uptake in the sample in H<sub>2</sub>-TPR. H<sub>2</sub> uptake peaks under 500°C are considered originating from the CeO<sub>2-x</sub> surface.

Sample	9 kW m <sup>-2</sup> illumination and no external heating			No illumination and external heating to 180°C		
	CO production /mmol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	CH <sub>4</sub> production /mmol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	CO selectivity /%	CO production /mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	CH <sub>4</sub> production /mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	CH <sub>4</sub> selectivity /%
L	0	0	/	0	2.22 ± 0.02	100
4Au/L-O	1.06 ± 0.09	0.0014 ± 0.0005	99.8	0.017 ± 0.005	2.156 ± 0.003	99.2
4Au/L-R	2.2 ± 0.2	0.0025 ± 0.0006	99.9	0.061 ± 0.006	1.990 ± 0.003	97.0
S	0	0	/	0	2.620 ± 0.004	100
4Au/S-O	1.4 ± 0.4	0.0054 ± 0.0009	99.6	0.010 ± 0.002	1.767 ± 0.003	97.8
4Au/S-R	2.8 ± 0.2	0.039 ± 0.002	98.6	0.032 ± 0.005	1.435 ± 0.002	97.8
0.4Au/S	3.9 ± 0.7	0.08 ± 0.02	99.4	/	/	/

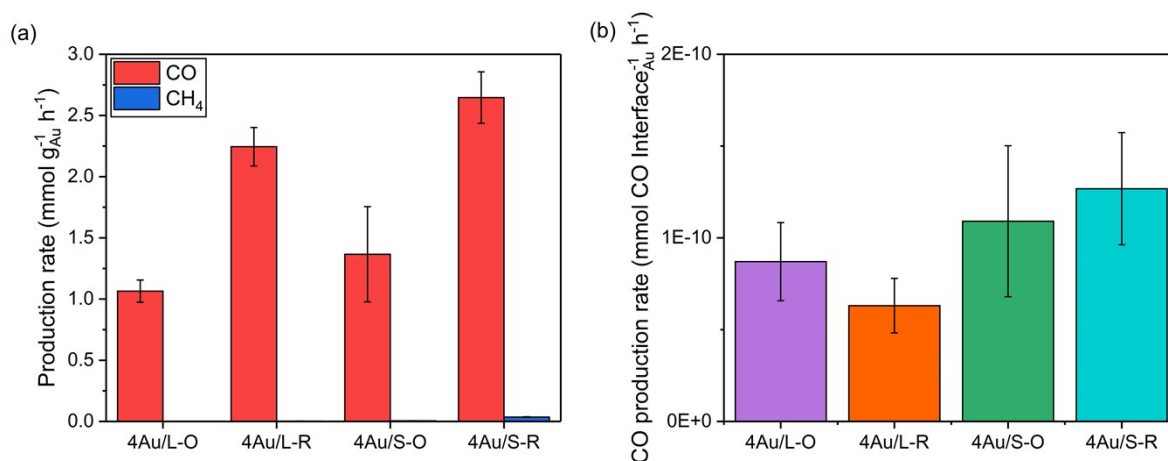


1.5Au/S	$1.0 \pm 0.1$	$0.017 \pm 0.003$	98.3	/	/	/
6Au/S	$1.8 \pm 0.2$	$0.0054 \pm 0.0004$	99.7	/	/	/

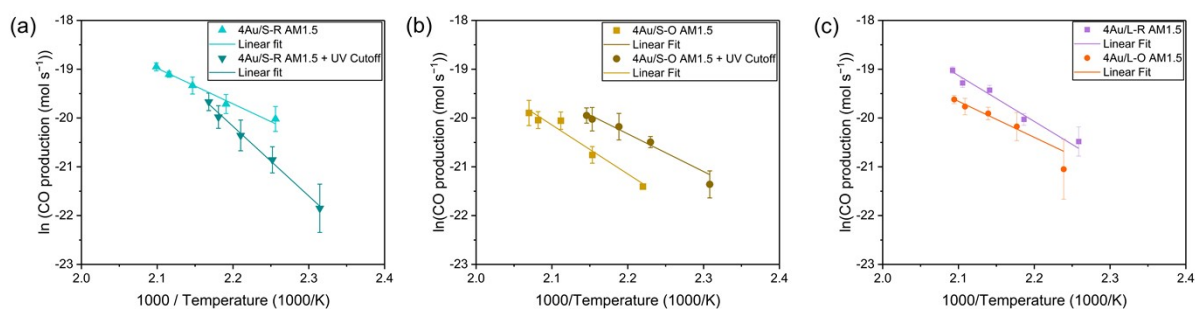
**Table S5:** Summary of catalysis results, confidence intervals of 98% are shown.



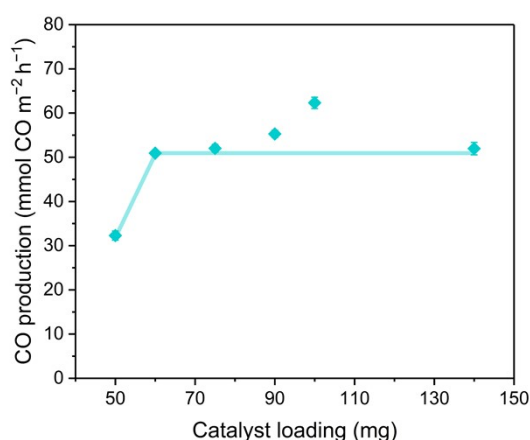
**Fig. S5:** (a) Temperature of reactor vessel, bottom of the catalyst bed and top of the catalyst of 4Au/S-R light variation experiments. (b) Temperature gradient inside the catalyst bed determined by FBGs at the catalyst surface, 0.15 mm depth, 0.30 mm depth and 0.50 mm depth during 4Au/S-R light variation experiment. Additionally, a reference FBG was present on the catalyst holder.



**Fig. S6:** (a) CO and CH<sub>4</sub> production rates of 4Au/L-R, 4Au/L-O, 4Au/S-R and 4Au/S-O under illumination (b) CO production rates of 4Au/L-R, 4Au/L-O, 4Au/S-R and 4Au/S-O under illumination normalised on circumference of Au particles. Reaction conditions: mixture of CO<sub>2</sub>:H<sub>2</sub>:N<sub>2</sub> (8 ml min<sup>-1</sup> :8 ml min<sup>-1</sup>:4 ml min<sup>-1</sup>) at 3.5 bar pressure, 200 mg Au/CeO<sub>2</sub> photocatalyst, 9 kW m<sup>-2</sup> illumination from solar simulator (AM1.5).



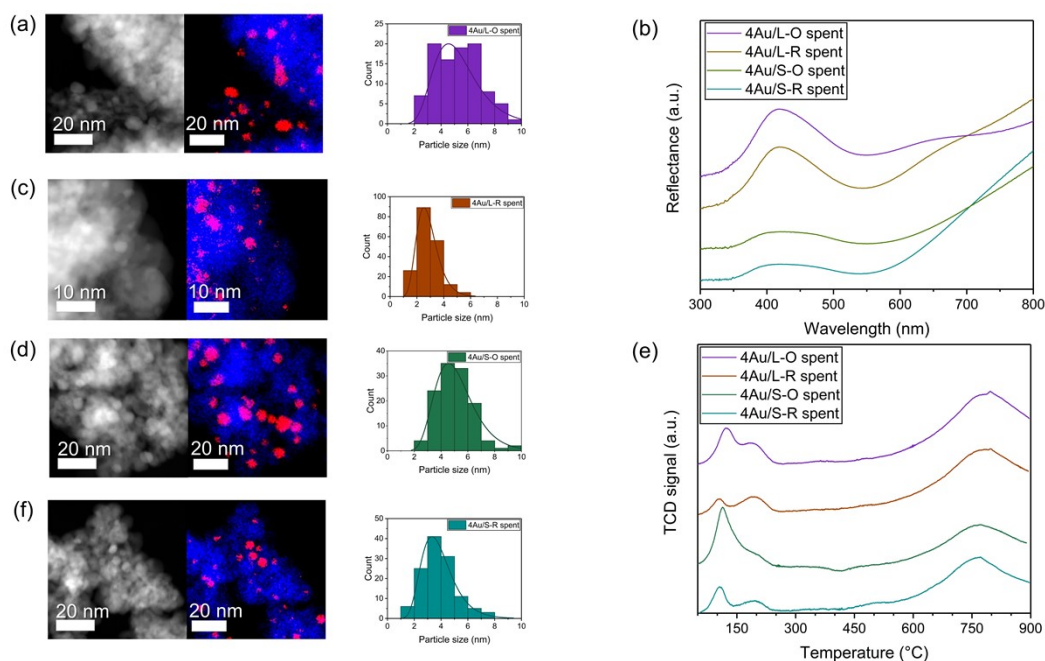
**Fig. S7:** Arrhenius plots of (a) 4Au/S-R and (b) Au/S-O under varied illumination using AM1.5 filter and AM1.5 + UV cutoff filter and (c) 4Au/L-R and 4Au/L-O under varied illumination using AM1.5 filter. Confidence intervals of 98% are reported.



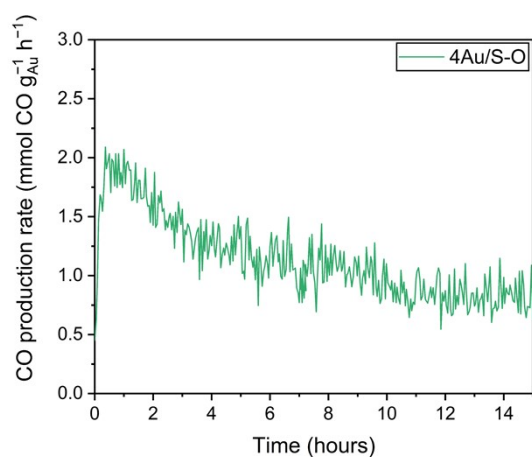
**Fig. S8:** CO production normalised on illuminated area in function of catalyst loading of 4Au/S-R. Confidence intervals of 98% are reported. Reaction conditions: mixture of CO<sub>2</sub>:H<sub>2</sub>:N<sub>2</sub> (8 ml min<sup>-1</sup>:8 ml min<sup>-1</sup>:4 ml min<sup>-1</sup>) at 3.5 bar pressure, varied loading of Au/CeO<sub>2</sub> photocatalyst, 8.4 kW m<sup>-2</sup> illumination from 300W Xe Arc lamp.

Sample	CO production		
	/mmol g <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	/10 <sup>-11</sup> mmol C <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>	/10 <sup>-19</sup> mmol #particles <sub>Au</sub> <sup>-1</sup> h <sup>-1</sup>
0.4Au/S	3.9 ± 0.7	1.8 ± 0.7	1.0 ± 0.5
1.5Au/S	1.0 ± 0.1	2.3 ± 0.4	2.9 ± 0.7
6Au/S	1.8 ± 0.2	3.5 ± 0.7	4 ± 1

**Table S6:** Summary of calculated values in order to correlate CO production rate to Au size and loading. C is the circumference of the circle at the interface between metal and support. The size of Au in 0.4Au/S was assumed to be 1.7 ± 0.3 nm for the calculations. Confidence intervals of 98% are reported on these values.



**Fig. S9:** Representative HAADF-STEM image, EDX mapping in STEM mode and Au particle size distribution from TEM analysis with lognormal fit of (a) 4Au/L-O spent catalyst, (c) 4Au/L-R spent catalyst, (d) 4Au/S-O spent catalyst and (f) 4Au/S-R spent catalyst, CeO<sub>2</sub> is coloured blue and Au is coloured red in EDX mapping; (b) reflective diffuse UV-Vis spectra of 4Au/L-O, 4Au/L-R, 4Au/S-O and 4Au/S-R spent catalysts, graphs have been stacked for visual clarity; (e) H<sub>2</sub>-TPR profiles of 4Au/L-O, 4Au/L-R, 4Au/S-O and 4Au/S-R spent catalysts, graphs have been stacked for visual clarity.



**Fig.S10** CO production of 4Au/S-O over 15h. Reaction conditions: mixture of CO<sub>2</sub>:H<sub>2</sub>:N<sub>2</sub> (8 ml min<sup>-1</sup> :8 ml min<sup>-1</sup>:4 ml min<sup>-1</sup>) at 3.5 bar pressure, 200 mg Au/CeO<sub>2</sub> photocatalyst, 9 kW m<sup>-2</sup> illumination from solar simulator (AM1.5).

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