

## Supplementary Information:

**Table SI1.** CH<sub>4</sub> production rate, reaction temperature and Cu content of Cu<sub>2</sub>O/G, c-Cu NPs, hm-Cu<sub>2</sub>O NPs and G samples at 250 °C under illumination with a Xe lamp of 300 W after 4 h reaction time. P<sub>H<sub>2</sub></sub> = 1.05 bar, P<sub>CO<sub>2</sub></sub> = 0.25 bar.

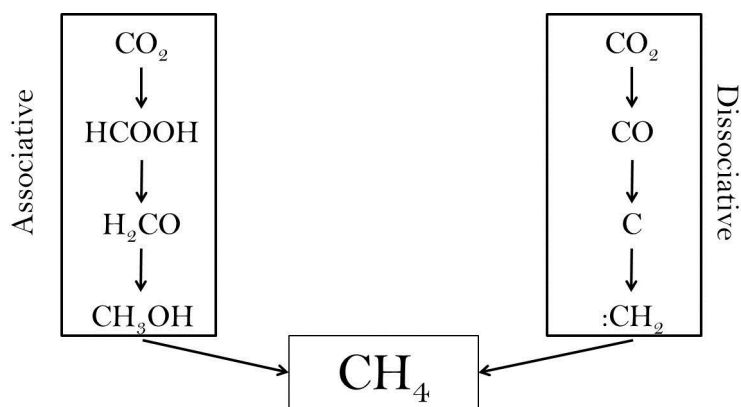
Samples	Cu content (mg)	Temperature (°C)	CH <sub>4</sub> production (mmol/g <sub>Cu</sub> ·h)
Cu <sub>2</sub> O/G	0.56	250	14.93
G	28.1 <sup>a</sup>	250	< 0.01
c-Cu <sub>2</sub> O NPs	0.5	250	2.69
hm-Cu <sub>2</sub> O NPs	30	250	0.01
c-Cu <sub>2</sub> O NPs <sup>b</sup>	0.5	250	< 0.01
Cu <sub>2</sub> O/G	0.55	225	11.79
Cu <sub>2</sub> O/G	0.55	200	7.73
Cu <sub>2</sub> O/G	0.39	150	2.56
Cu <sub>2</sub> O/G <sup>b</sup>	0.34	250	< 0.01
Cu <sub>2</sub> O/G <sup>c</sup>	10.0	250	0.81 <sup>d</sup>

<sup>a</sup> Corresponds to the amount of G used in this run. <sup>b</sup> Irradiated only with visible light using a cut-off filter of 360 nm. <sup>c</sup> Irradiated with monochromatic light (at 254 nm) from a Hg lamp of 24 W. <sup>d</sup> Value obtained after 24 h reaction.

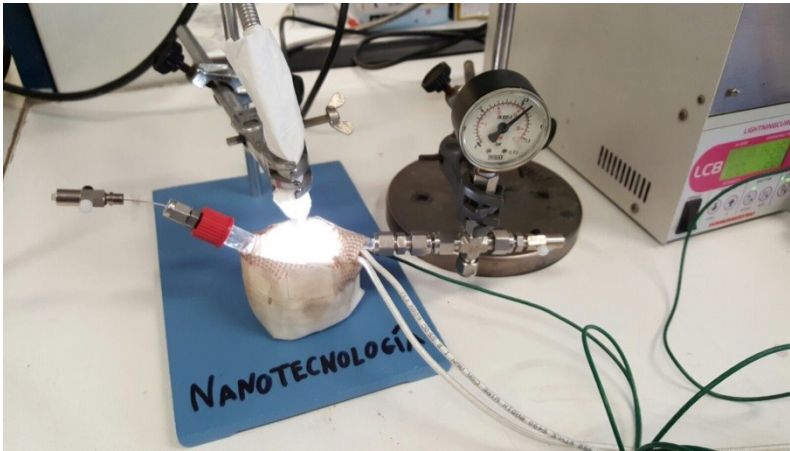
**Table SI2.** Photocatalytic CH<sub>4</sub> production and reaction conditions

Photocatalyst	Light	Reductant	CH <sub>4</sub> production (μmol/g <sub>cat</sub> ·h)	Ref.
(Au/Cu)-TiO <sub>2</sub>	1000 W Xe-lamp	H <sub>2</sub> O Vapor	2200	J. Am. Chem. Soc., <b>2014</b> , 136(45), 15969-15976.
(Cu/Pt)-TiO <sub>2</sub> nanotubes	1000 W/m <sup>2</sup> AM1.5 lamp	H <sub>2</sub> O Vapor	6100 (μmol/m <sup>2</sup> ·h)	Angew. Chem., Int. Ed. <b>2012</b> , 51(51), 12732-12735.
Pt-TiO <sub>2</sub>	400 W Xe-lamp	H <sub>2</sub> O Vapor	1361	J. Am. Chem. Soc., <b>2012</b> , 134(27), 11276-11281.
In-TiO <sub>2</sub>	500 W Hg lamp (365 nm)	H <sub>2</sub> O Vapor	1156	Appl. Catal., B <b>2015</b> , 162, 98-109.
G-TiO <sub>2</sub>	100 W Hg lamp (365 nm)	H <sub>2</sub> O Vapor	8.3 (μmol/m <sup>2</sup> ·h)	Nano Lett. <b>2011</b> , 11(7), 2865-2870.
Pd-TiO <sub>2</sub>	Two UV-LEDs 90 mW/cm <sup>2</sup> (365 nm)	H <sub>2</sub> O Vapor (140 °C)	64	Photochem. Photobiol. Sci., <b>2015</b> , 14, 550-555.
GaN nanowire	300 W UV-enhanced Xe-lamp	H <sub>2</sub> O Vapor	994 (μmol/cm <sup>2</sup> ·h·g <sub>cat</sub> )	Int. J. Photoenergy <b>2014</b> , 2014, 894396.
Pt-g-C <sub>3</sub> N <sub>4</sub>	15 W energy-saving daylight bulb	H <sub>2</sub> O Vapor	13	Dalton Trans. <b>2015</b> , 44, 1249-1257.
Au <sub>3</sub> Cu-	300 W Xe lamp	CO <sub>2</sub> -saturated	421	Angew. Chem. Int.

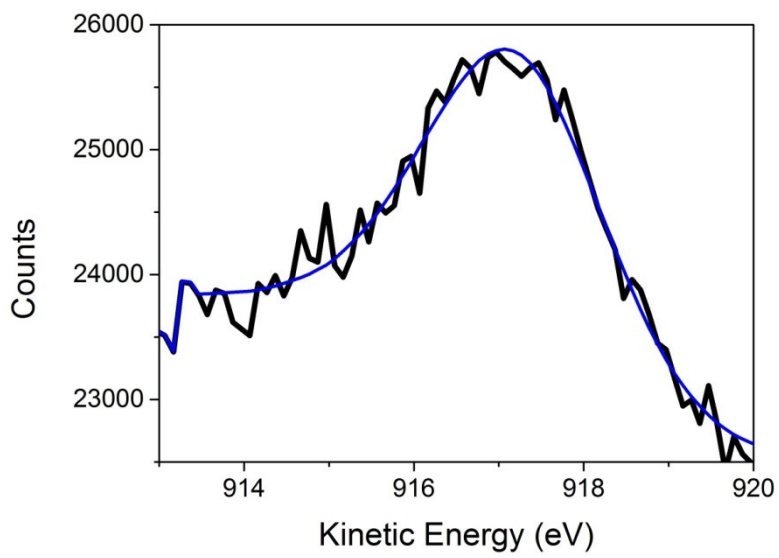
SrTiO <sub>3</sub> /TiO <sub>2</sub>		N <sub>2</sub> H <sub>4</sub>		Ed. <b>2015</b> , 54, 841-845,
Ag@Cu-TiO <sub>2</sub> /PU	Two 20 W bulbs	H <sub>2</sub> O Vapor	880	Appl. Catal. A: General, <b>2017</b> , 529, 40-48
Pd/TiO <sub>2</sub>	150 W Hg lamp	H <sub>2</sub>	120	J. Phys. Chem. C, <b>2017</b> , 121(5), 2923-2932
Ru/Al <sub>2</sub> O <sub>3</sub>	300 W Xe lamp (370 °C)	H <sub>2</sub>	300000	Angew. Chem. Int. Ed. <b>2014</b> , 53, 11478-11482.
Rh/Al <sub>2</sub> O <sub>3</sub>	300 W Xe lamp (370 °C)	H <sub>2</sub>	156000	Angew. Chem. Int. Ed. <b>2014</b> , 53, 11478-11482.
Ni/Al <sub>2</sub> O <sub>3</sub>	300 W Xe lamp (380 °C)	H <sub>2</sub>	48000	Angew. Chem. Int. Ed. <b>2014</b> , 53, 11478-11482.
Co/Al <sub>2</sub> O <sub>3</sub>	300 W Xe lamp (350 °C)	H <sub>2</sub>	21000	Angew. Chem. Int. Ed. <b>2014</b> , 53, 11478-11482.
Ni/Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	AM 1.5 100mW/cm <sup>2</sup> (150 °C)	H <sub>2</sub>	54600	J. Am. Chem. Soc. <b>2014</b> , 136(19), 6798-6801.
Ru/Si(nanowires)	320 W Xe lamp (150 °C)	H <sub>2</sub>	990	Adv. Sci. <b>2014</b> , 1(1), 1400001



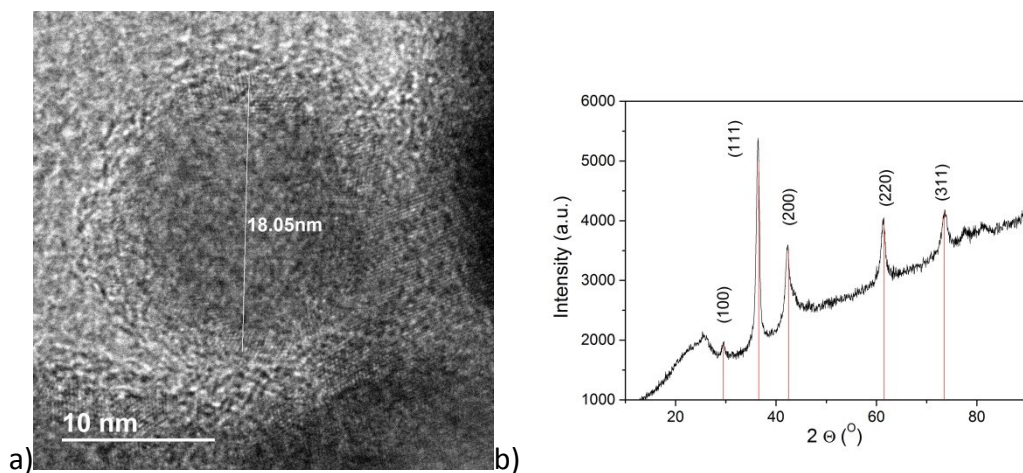
**Scheme SI1.** Proposed reaction pathways for the CO<sub>2</sub> methanation.



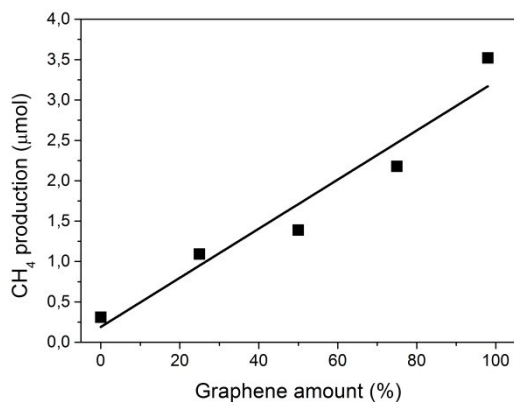
**Fig. S11.** Photograph of the photoreactor under illumination from typical reaction.



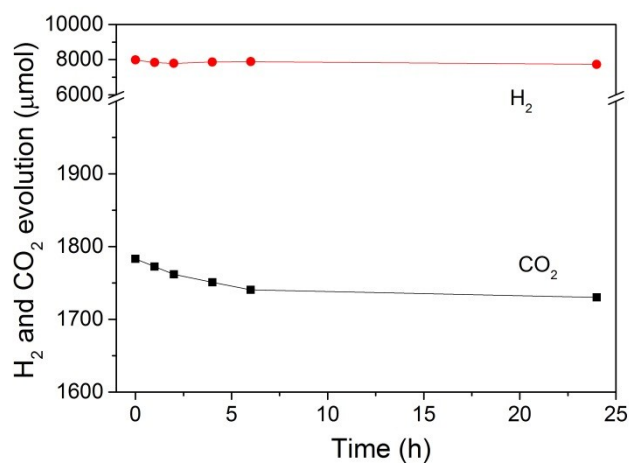
**Fig S12.** Cu<sub>2</sub>p Auger spectrum of a Cu<sub>2</sub>O/G sample.



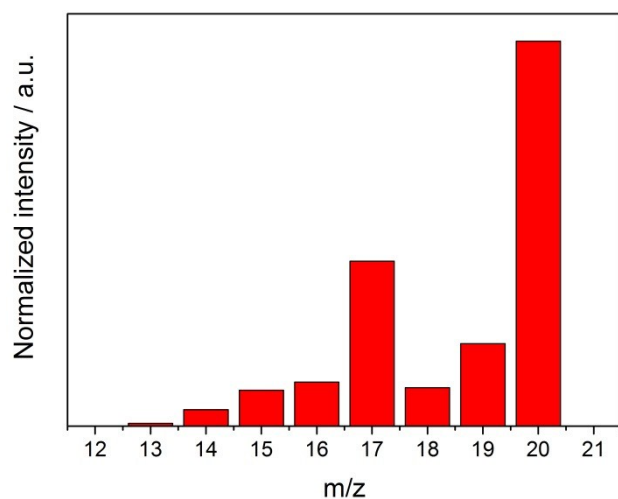
**Fig S13.** HRTEM (a) and XRD (b) of hm-Cu<sub>2</sub>O NPs.



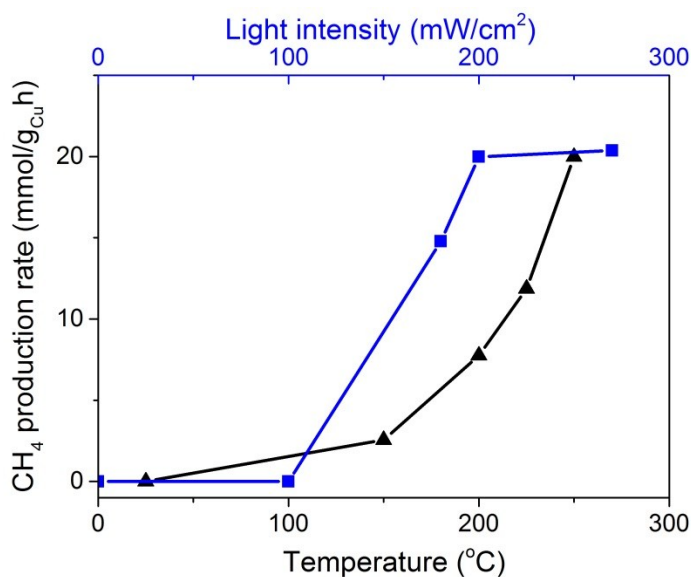
**Fig S14.** CH<sub>4</sub> production as function of the G content in the mixed hm-Cu<sub>2</sub>O NPs with G, measured at 1 h reaction time under constant light intensity of 200 mW/cm<sup>2</sup> from a 300 W Xenon lamp, and 200 °C. P<sub>H<sub>2</sub></sub> = 1.05 bar, P<sub>CO<sub>2</sub></sub> = 0.25 bar. The amount of hm-Cu<sub>2</sub>O NPs was constant (30 mg) in all experiments. The amount of G was adjusted to the desired proportions.



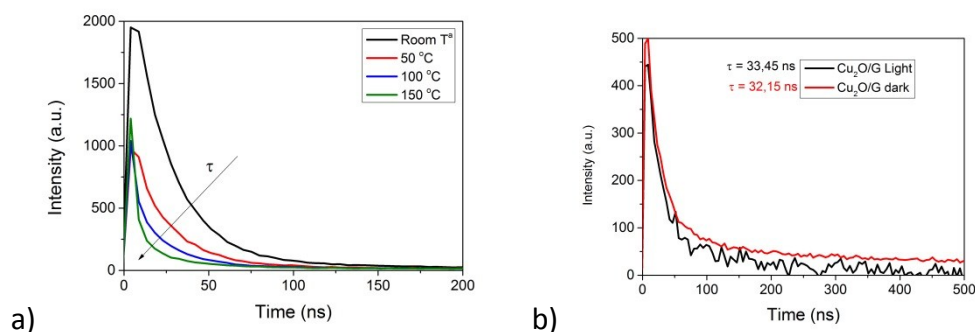
**Fig. S15.** H<sub>2</sub> and CO<sub>2</sub> temporal profiles (μmol) at 250 °C for 24 h under illumination with a Xenon lamp of 300 W Reaction conditions: Cu content 0.56 mg. P<sub>H<sub>2</sub></sub> = 1.05 bar, P<sub>CO<sub>2</sub></sub> = 0.25 bar.



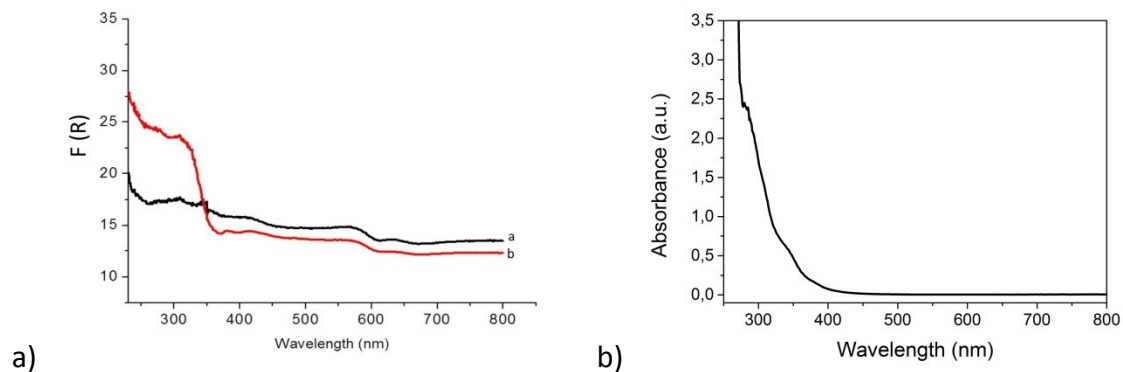
**Fig. S16.** Mass spectra of the reaction product from <sup>13</sup>C<sup>18</sup>O<sub>2</sub> and H<sub>2</sub> on Cu<sub>2</sub>O/G showing that <sup>13</sup>CH<sub>4</sub> and H<sub>2</sub><sup>18</sup>O are the main reaction products, as revealed by the peak at *m/z* = 17 (further fragmentation results in peaks at 16 and 15) and *m/z* = 20 (fragmentation 19), respectively.



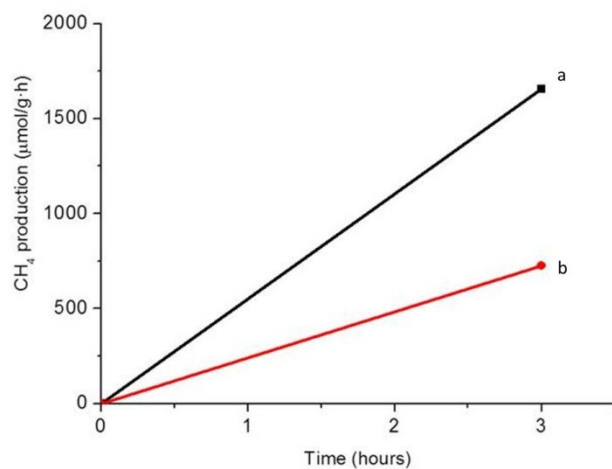
**Fig. S17.** CH<sub>4</sub> production rate as a function of the temperature (black triangles) and light intensity (blue squares). The CH<sub>4</sub> production rate as temperature function was measured under constant light intensity of 200 mW/cm<sup>2</sup>, and the light intensity dependence measurements were performed at 250 °C. Reaction time in the temperature and light intensity experiments was 4 h and 2 h, respectively. Photocatalyst Cu content was 0.55 mg and 0.69 mg in the temperature and light intensity measurements, respectively. P<sub>H<sub>2</sub></sub> = 1.05 bar, P<sub>CO<sub>2</sub></sub> = 0.25 bar.



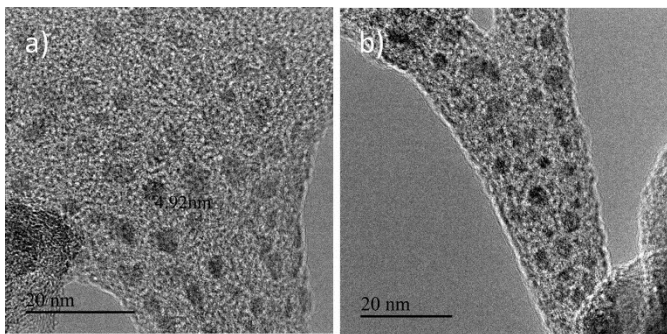
**Fig. S18.** Time correlated emission decay of a thin film of commercial CdSe@ZnS quantum dots onto a quartz substrate at different temperatures (a) and CdSe@ZnS quantum dots thin film of a Cu/G film in dark and illumination conditions.



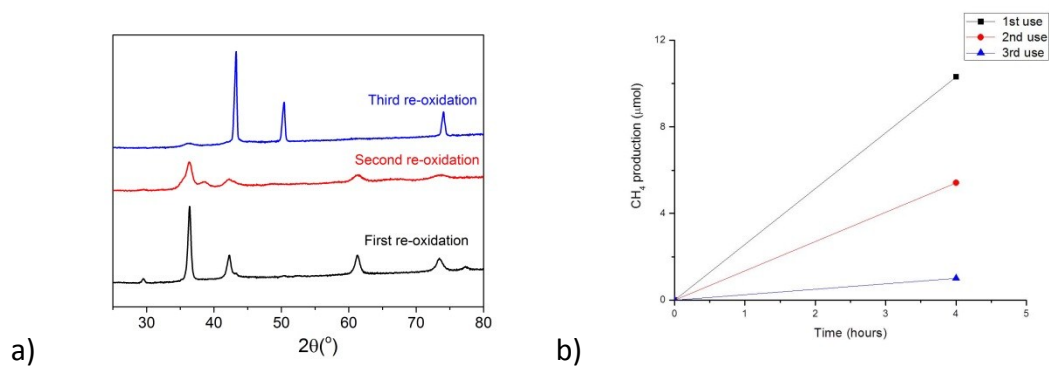
**Fig. S19.** (a) Diffuse reflectance UV-Vis spectra, plotted as the Kubelka-Munk function ( $F$ ) of the reflectance ( $R$ ) of G (a) and  $\text{Cu}_2\text{O}/\text{G}$  (b) samples; (b) UV-Vis spectrum of the  $c\text{-Cu}_2\text{O}$  NPs in ethanol at 1.5 wt.%.



**Fig. S110.**  $\text{CH}_4$  production rate using CO (a) or  $\text{CO}_2$  (b) as initial reactants. Measured under constant light intensity of  $200 \text{ mW}/\text{cm}^2$  from a 300 W Xenon lamp, and  $250 \text{ }^\circ\text{C}$ .



**Fig. S111** HRTEM images of fresh (a) and used (b)  $\text{Cu}_2\text{O}/\text{G}$  photocatalysts.



**Fig. S112** (a) XRD of  $\text{Cu}_2\text{O}/\text{G}$  photocatalyst after three consecutive reaction-oxidation processes. (b)  $\text{CH}_4$  production using 3 times  $\text{Cu}_2\text{O}/\text{G}$  reused after successive oxidation cycles.