Supporting information for

Sunlight-Fueled, Low-Temperature Ru-Catalyzed Conversion of CO₂ and H₂ to CH₄ with a High Photon-to-Methane Efficiency

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Table of Contents
S1. Overview of literature on photomethanation processes with correspondingly reported catalytic activities ................................................................. S6
   Table S1. Photomethanation overview ........................................................... S6
S2. Images of the support, RuO$_2$ precatalyst and the rod-like Ru catalyst during synthesis ..... S8
   Figure S1. Photographs of several stages in the preparation of the Ru catalyst .......... S8
S3. Equipment for the photomethanation reactions ..................................................... S8
   Figure S2. Photographs and schematic representation of the photoreactor ........... S8
   Figure S3. Temperature monitoring of the reaction ............................................ S9
   Figure S4. Spectrum of the Newport 20CGA-395 nm long-pass filter .................. S10
   Figure S5. Spectrum of the Newport 20CGA-495 nm long-pass filter ................. S10
S4. Temperature catalyst bed ............................................................................... S10
   Figure S6. Catalyst temperature measured by infrared camera and by the thermocouple .... S11
S5. Amount of CO$_2$, H$_2$ and CH$_4$ present during photomethanation reactions using the H$_2$ activated Ru catalyst at 150 °C ........................................... S11
   Figure S7. Photomethanation at 150 °C ............................................................. S11
S6. GC trace for a typical reaction ......................................................................... S12
   Figure S8. Typical GC traces for a photomethanation reaction ............................ S12
S7. Procedure for a typical reaction without illumination ........................................ S13
S8. $T_{\text{reactor}}$ and $T_{\text{cat}}$ for Figure 3a .................................................................... S14
   Table S2. $T_{\text{reactor}}$ and corresponding $T_{\text{cat}}$ at several light intensities ............. S14
   Figure S9. Typical temperature profile for a reaction with illumination (150 °C $T_{\text{reactor}}$ and 1 sun light intensity) ................................................................. S14
   Figure S10. Temperature profile for a reaction at $T_{\text{reactor}} = 25$ °C with 10.1 sun illumination. .. S15
   Figure S11. Temperature profile for a reaction at $T_{\text{reactor}} = 150$ °C with 5.7 sun illumination ... S15
   Figure S12. Temperature profile for a reaction at $T_{\text{reactor}} = 125$ °C with 8.5 sun illumination. .. S16
   Figure S13. Temperature profile for a reaction at $T_{\text{reactor}} = 150$ °C with 8.5 sun illumination. .. S16
S9. Details of the experiments performed for the Arrhenius plot in Figure 3b .............. S17
S2
Table S3. Light intensity, T$_{\text{cat}}$ and reaction rate for the experiments to determine the Arrhenius plot............................................................................................................................................. S17

S10. Photon to methane (PTM) efficiencies for photomethanation reactions....................... S18

Table S4. Light intensity, T$_{\text{cat}}$, reaction rate for the experiments with illumination, calculated reaction rates for reactions without illumination at T$_{\text{cat}}$ of the reactions with illumination, ratio k$_{\text{light}}$/k$_{\text{dark}}$ and PTM efficiency.................................................................................................................. S18

S11. Experimental details for TEM studies ................................................................................... S18

S12. Characterization of the RuO$_2$ precatalyst catalyst by TEM studies ............................... S20

Figure S14. TEM analysis of representative RuO$_2$ crystals..................................................... S20

S13. Experimental details for XRD analysis.................................................................................. S21

S14. Characterization of the RuO$_2$ precatalyst by XRD analysis ........................................... S21

Figure S15. XRD analyses of the RuO$_2$ precatalyst (red) and Ru catalyst (blue), both supported on γ-Al$_2$O$_3$.................................................................................................................................................. S21

S15. Characterization of the spherical Ru catalyst by XRD analysis ......................................... S22

Figure S16. XRD analyses of the spherical Ru catalyst supported on γ-Al$_2$O$_3$ .......................... S22

S16. Experimental details for and results from XPS analysis ..................................................... S22

Figure S17. XPS holder with powders....................................................................................... S23

Table S5. concentrations of the elements present at the surface of the samples..................... S23

Figure S18: Al 2p peaks of the samples..................................................................................... S23

Figure S19: O 1s peaks of the samples...................................................................................... S24

Figure S20: Ru 3d peaks of the samples................................................................................... S24

S17. Determination of the average size of nanospheres and nanorods ................................. S24

Figure S21. Histograms depicting: (a) the length (<length> = 153 ± 53 nm) and (b) width (<width> = 14 ± 13 nm) distribution of the nanorods present in a representative RuO$_2$ precatalyst sample; and (c) the diameter distribution (<diameter> = 11 ± 3 nm) of the spherical nanoparticles present in the same sample.................................................................................. S25

Figure S22. Histograms depicting: (a) the length (<length> =147 ± 50 nm) and (b) width (<width> = 15 ± 14 nm) distribution of the nanorods present in a typical activated rod-like Ru catalyst sample before photomethanation (catalyst activation was performed by reacting the RuO$_2$ precatalyst with H$_2$ at 150 °C and 1 sun light intensity for 2 h). (c) Histogram depicting
the diameter distribution ($<\text{diameter}> = 10 \pm 3 \text{ nm}$) of the spherical nanoparticles present in the same sample. 

Figure S23. Histogram depicting the diameter distribution ($<\text{diameter}> = 0.88 \pm 0.11 \text{ nm}$) of the spherical nanoparticles present in the spherical Ru catalyst.

S18. Experimental details for UV-vis-NIR spectroscopy

S19. Characterization of RuO$_2$ precatalyst with UV-vis-NIR spectroscopy

Figure S24. UV-VIS-NIR spectra of the RuO$_2$ precatalyst (red) and Ru catalyst (blue).

Figure S25. UV-VIS-NIR diffuse reflectance spectra of the RuO$_2$ precatalyst (red) and Ru catalyst (blue).

S20. Characterization of the spherical Ru catalyst with UV-vis-NIR spectroscopy

Figure S26. UV-VIS-NIR spectra of the spherical Ru catalyst.

S21. Details for the optical modeling based on the boundary element method (BEM)

Figure S27. (a) Average dielectric function of RuO$_2$, determined by fitting and averaging the parallel and perpendicular components of the real and imaginary parts of the dielectric function of single crystal rutile RuO$_2$. (b) Dielectric function of Ru, taken from Palik, E. D et al. and Cox et al. 

Figure S28. Calculated averaged cross section (comparable to the extinction cross section) of: (a) a single spherical RuO$_2$ and Ru nanoparticle (11 nm diameter) and (b) a single RuO$_2$ and Ru nanorod (length $\times$ width $= 153 \times 14 \text{ nm}$, aspect ratio=10.9) in a $\gamma$-Al$_2$O$_3$ medium. The nanorod spectra were determined by averaging over 30 angles of light incidence in order to take into account their (experimentally observed) random orientation on the $\gamma$-Al$_2$O$_3$ support.

Figure S29. Calculated extinction, absorption, and scattering cross section of a RuO$_2$ nanorod (a, c, e) and of a Ru nanorod (b, d, f) of dimensions length $\times$ width $= 153 \times 14 \text{ nm}$ (aspect ratio=10.9) in a $\gamma$-Al$_2$O$_3$ medium at different angles of light incidence with respect to the nanorod’s longitudinal axis, namely: $0^\circ$ (a, b), $45^\circ$ (c, d), and $90^\circ$ (e, f).

Figure S30. (a) Calculated extinction, absorption, and scattering cross section of a spherical Ru nanoparticle (11 nm diameter) in a $\gamma$-Al$_2$O$_3$ medium. (b) Calculated extinction, absorption, and scattering cross section of a Ru nanorod (length $\times$ width $= 153 \times 14 \text{ nm}$, aspect ratio=10.9) upon light incidence at $45^\circ$ with respect to its longitudinal axis and also embedded in the same medium.
S22. Procedure for a typical reaction using a long-pass filter.................................S32

S23. Details of the experiments performed for Figure 8b .....................................................S33

Table S6. Light intensity, $T_{\text{cat}}$ and reaction rate for the experiments to determine the difference
in photon to methane efficiency using spherical and rod-like Ru catalysts. ..................S33

S24. Experimental details for inductively coupled plasma optical emission spectroscopy (ICP-OES) ..............................................S33
St. Overview of literature on photomethanation processes with correspondingly reported catalytic activities

Table S1. Photomethanation overview.

| Paper     | Catalyst                          | Category             | Light source     | Light intensity [mW cm\(^{-2}\)] | Temperature [K] | Pressure [bar] | Activity [mmol (g cat)\(^{-1}\) h\(^{-1}\)] |
|-----------|-----------------------------------|----------------------|------------------|----------------------------------|----------------|---------------|-------------------------------------------|
| 1987      | Graetzel Ru/RuO on TiO\(_2\)      | Semiconductor        | Solar sim        | 80                               | 319.15         | 1             | 0.047                                     |
| 2001      | Anpo Ti/FSM-16                    | Semiconductor        | UV               | 100                              | 323            | n.a.          | 0.28                                      |
| 2006      | Shanthi Ru/TiO\(_2\) on SiO\(_2\) | Semiconductor        | UV               | 1000 W                           | ?              | ?             | 0.043                                     |
| 2009      | Swalus TiO\(_2\) Cu/Pt Nanotubes | Semiconductor        | Solar sim        | 100                              | 317.15         | 1.1           | 0.0065                                    |
| 2010      | Li Zou RuO\(_2\)/ZnGa\(_2\)O\(_4\)| Semiconductor        | Xe lamp           | 300 W                            | ?              | ?             | 0.0047                                    |
| 2011      | Shangguan Pt CdS TiO\(_2\) nanotube | Semiconductor        | Xe lamp           | 300 W                            | ?              | ?             | 7.8                                       |
| 2011      | Ye TiO\(_2\) ZnO                  | Semiconductor        | Xe lamp           | 60                               | ?              | ?             | 0.055                                     |
| 2012      | Biswas Pt on TiO\(_2\)            | Semiconductor        | UV                | UV: 19.6                         | 305.15         | ?             | 1.4                                       |
| 2012      | Ye W18O49                         | Semiconductor        | Xe lamp           | 30000                            | 343.15         | ?             | 0.86                                      |
| 2013      | Wang Li CeO\(_2\) TiO\(_2\)       | Semiconductor        | Xe lamp           | 300 W                            | 303.15         | 1.1           | 2.0                                       |
| 2014      | Corma Garcia Ni on TiO\(_2\)/SiO\(_2\) | Metallic            | Solar sim        | ?                                | 413.15         | ?             | 54.8                                      |
| 2014      | García Au/Cu on TiO\(_2\)        | Semiconductor        | Xe lamp           | 1000                             | ?              | 1.7           | 2.2                                       |
| 2014      | Ouyang Ye Ru on Al\(_2\)O\(_3\)   | Metallic             | Xe lamp           | 300 W on 7 cm\(^2\)              | 573.15         | ?             | 18160                                     |
| 2014      | Ozin Ru/Si nanowires              | Metallic             | Solar sim        | 320                              | 423.15         | 3.1           | 1                                         |
| 2014      | Roy Cu/Pt TiO\(_2\) membrane      | Semiconductor        | Solar sim        | 100                              | ?              | 1            | 3 nM cm\(^2\) h\(^{-1}\)                  |
| 2015      | Al-Ghouti KNbO\(_3\)              | Semiconductor        | Solar sim        | ?                                | ?              | ?            | 0.0029                                    |
| 2015      | Liu He CuO\(_2\) on TiO\(_2\)    | Semiconductor        | Solar sim        | ?                                | ?              | ?            | 0.00016                                   |
| 2015      | Zhang N-doped TiO\(_2\)           | Semiconductor        | Solar sim        | 2x 300 W                        | 298.15         | ?             | 0.050                                     |
| 2016      | Sassoye Debecker Ru on TiO\(_2\)  | Semiconductor        | ?                  | ?                                | 473.15         | ?             | 9.3                                       |
| 2016      | Yu Pt on C                        | Metallic             | ?                  | ?                                | ?              | ?            | 0.0009                                    |
| 2017      | Li Zhou Pd on TiO\(_2\)           | Semiconductor        | UV                 | ?                                | ?              | ?            | 0.11                                      |
| 2017      | Li Zhou 2 Pd/Co on TiO\(_2\)      | Semiconductor        | Solar sim        | ?                                | ?              | ?            | 0.075                                     |
| 2017      | Everett Liu Rh on Al\(_2\)O\(_3\) | Metallic             | UV                 | 3000                             | 328            | ?             | 36                                        |
| 2018      | Ozin RuO\(_2\) on SiO\(_2\)       | Metallic             | Solar sim        | 2200                             | 443.15         | 2.03         | 4.4                                       |
| 2018      | Ozin 2 Ru on SiO\(_2\)            | Metallic             | ?                  | 2470                             | 298.15         | ?             | 2.8                                       |
| 2018      | Liu Rh on TiO\(_2\)               | Semiconductor        | UV                 | 3000                             | 625.15         | ?             | 778                                       |
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S2. Images of the support, RuO$_2$ precatalyst and the rod-like Ru catalyst during synthesis

Figure S1. Photographs of several stages in the preparation of the Ru catalyst.

a) $\gamma$-Al$_2$O$_3$ support; b) Al$_2$O$_3$ support impregnated with Ru$_3$(CO)$_{12}$ before air calcination; c) the RuO$_2$ on Al$_2$O$_3$ support precatalyst; d) the Ru on Al$_2$O$_3$ support catalyst.

S3. Equipment for the photomethanation reactions

Figure S2. Photographs and schematic representation of the photoreactor.
Figure S3. Temperature monitoring of the reaction.

Concentrated light is obtained from a High Flux Beam Concentrator (Newport, 81030) consisting of various assembled fused silica lenses mounted in a tube that can be attached to the output assembly of the solar simulator.

The used long-pass filters are the Newport 20CGA-395 (a 2 inch square long-pass filter with a 395 ± 5 nm cut-on wavelength) and the Newport 20CGA-495 (a 2 inch square long-pass filter with a 495 ± 5 nm cut-on wavelength).
S4. Temperature catalyst bed

To verify the temperature of the bed catalyst, an experiment was done following the catalyst surface temperature with an Infrared camera. The IR camera (Optris PI450) was located on top of the reactor without the quartz windows. The reactor bulk temperature was 60°C. When the catalyst bed temperature stabilized, the lamp was turned on and the catalyst temperature raised until 86°C.

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i [https://www.newport.com/p/20CGA-395](https://www.newport.com/p/20CGA-395); site visited 26th of July 2018.

ii [https://www.newport.com/p/20CGA-495](https://www.newport.com/p/20CGA-495); site visited 26th of July 2018.
Figure S6. Catalyst temperature measured by infrared camera and by the thermocouple.

S5. Amount of CO\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4} present during photomethanation reactions using the H\textsubscript{2}-activated Ru catalyst at 150 °C.

![Graph showing CO\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4} amounts](image)

Figure S7. Photomethanation at 150 °C.

Reaction conditions: reaction mixture of H\textsubscript{2}:CO\textsubscript{2}:N\textsubscript{2} (5:1:1) at 3.5 bar pressure, 300 mg H\textsubscript{2}-activated Ru catalyst, 150 °C, 1 sun light intensity. Amounts of H\textsubscript{2} g\textsubscript{Ru}^{-1} (∆), CO\textsubscript{2} g\textsubscript{Ru}^{-1} (□) and methane g\textsubscript{Ru}^{-1} (○) as a function of time.
S6. GC trace for a typical reaction

Figure S8. Typical GC traces for a photomethanation reaction displaying a) H₂, N₂, and CH₄ (early stage of reaction), b) CO₂ (early stage of reaction), and c) CH₄ (advanced stage of reaction).

Reaction conditions: reaction mixture of H₂:CO₂:N₂ (5:3:1) at 3.5 bar pressure, 300 mg H₂-activated Ru catalyst, 150 °C, 1 sun light intensity, 30 min reaction time.
S7. Procedure for a typical reaction without illumination

The homemade photoreactor equipped with a solar simulator (Newport Sol3A) and reaction cell with quartz window was used for the thermal methanation reaction. \( \text{N}_2 \) was used as internal standard. The reactor was prepared by filling the reactor with catalyst (typically 300 mg) and \( \text{N}_2 \) and subsequent evacuation for 3 times. Then, the reactor was filled with the reaction mixture of \( \text{H}_2 \) (Linde 6.0) and \( \text{CO}_2 \) (Linde 4.5) and diluted with \( \text{N}_2 \) (Linde 5.0) with the ratio \( \text{H}_2: \text{CO}_2: \text{N}_2 \), (5:1:1) until the total pressure was 3.5 bar (2.5 bar overpressure). Prior to each experiment, the temperature was stabilized to desired reaction temperature in the range from 25°C to 150°C using electrical heating. When the temperature is stable the starting time of the reaction is determined \( (t=0) \), the \( \text{CH}_4 \) formation before the starting time is subtracted from the experiments. Gas samples were taken from the reactor using a gas lick tied syringe. 3 mL of gas were taken from the upper part of the reactor at different times and direct measured in the gas chromatograph (compact GC Interscience). The GC is equipped with three channels, 2 micro TCD detector and one FID detector. The first channel, used to measure \( \text{H}_2, \text{O}_2, \text{N}_2 \) and \( \text{CO} \), has a MolSieve 5 Å column and RT-Q bond precolumn and TCD detector. The second channel, used to measure \( \text{H}_2 \text{O} \) and \( \text{CO}_2 \), has a combination of TR-U bond column and RT-Q bond column and TCD detector. The third channel, used to measure methane, ethane and propane, is fitted with a Rtx-1, 2u column and FID detector.
S8. $T_{\text{reactor}}$ and $T_{\text{cat}}$ for Figure 3a

| $T_{\text{reactor}}$ (°C) | $T_{\text{cat}}$ @ dark (°C) | $T_{\text{cat}}$ @ 1.0 sun (°C) | $T_{\text{cat}}$ @ 5.7 sun (°C) | $T_{\text{cat}}$ @ 8.5 sun (°C) |
|---------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 25                        | 25.0                          |                               |                               | 118.5                        |
| 50                        | 50.0                          |                               | 110.7                         | 140.0                         |
| 75                        | 75.4                          | 92.0                          | 129.9                         |                               |
| 100                       | 100.8                         | 116.3                         | 156.6                         | 196.9                         |
| 125                       | 126.3                         | 139.9                         | 184.2                         | 220.6$^{ii}$                  |
| 150                       | 150.5                         | 164.4                         | 211.6$^{i}$                   | 230.6$^{ii}$                  |
| 175                       | 175.1                         | 188.9                         |                               |                               |

*Table S2. $T_{\text{reactor}}$ and corresponding $T_{\text{cat}}$ at several light intensities.*

Average temperature during 60 min reaction time. (i) Average temperature during first 5 min of the reaction; (ii) average temperature in first 2.5 min of the reaction.

Figure S9. Typical temperature profile for a reaction with illumination (150 °C $T_{\text{reactor}}$ and 1 sun light intensity).
Figure S10. Temperature profile for a reaction at $T_{\text{reactor}} = 25 \, ^\circ\text{C}$ with 10.1 sun illumination.

Figure S11. Temperature profile for a reaction at $T_{\text{reactor}} = 150 \, ^\circ\text{C}$ with 5.7 sun illumination.
Figure S12. Temperature profile for a reaction at $T_{\text{reactor}} = 125 \, ^\circ\text{C}$ with 8.5 sun illumination.

Figure S13. Temperature profile for a reaction at $T_{\text{reactor}} = 150 \, ^\circ\text{C}$ with 8.5 sun illumination.
Table S3. Light intensity, $T_{\text{cat}}$ and reaction rate for the experiments to determine the Arrhenius plot.

Reaction rate calculated by a linear fit of the produced CH$_4$ in the first 15 min of the reactions. (a) Linear fit of the first 5 min of the reaction; (b) Linear fit of the first 2.5 min of the reaction.
**S18. Photon to methane (PTM) efficiencies for photomethanation reactions**

| light intensity (sun) | T<sub>reactor</sub> (°C) | T<sub>cat</sub> (°C) | k (mmol CH<sub>4</sub> / h) | calculated k for dark reaction at T<sub>cat</sub> (mmol CH<sub>4</sub> / h) | k<sub>light</sub>/k<sub>dark</sub> (-) | PTM (%) |
|-----------------------|---------------------|----------------------|----------------------|-------------------------------|-------------------|--------|
| 1                     | 75                  | 92.0                 | 0.049                | 0.046                         | 1.07              | 0.0    |
| 1                     | 100                 | 116.3                | 0.235                | 0.202                         | 1.16              | 0.3    |
| 1                     | 125                 | 139.9                | 0.756                | 0.720                         | 1.05              | 0.3    |
| 1                     | 150                 | 164.4                | 2.529                | 2.336                         | 1.08              | 1.6    |
| 1                     | 175                 | 188.9                | 8.440                | 8.366                         | 1.01              | 0.6    |
| 5.7                   | 50                  | 110.7                | 0.120                | 0.146                         | 0.82              | 0.0    |
| 5.7                   | 75                  | 129.9                | 0.511                | 0.427                         | 1.19              | 0.1    |
| 5.7                   | 100                 | 156.6                | 1.669                | 1.631                         | 1.02              | 0.1    |
| 5.7                   | 125                 | 184.2                | 6.439                | 5.498                         | 1.17              | 1.4    |
| 5.7                   | 150                 | 211.6                | 30.899<sup>a</sup>   | 16.040                        | 1.93              | 22.3   |
| 8.5                   | 25                  | 118.5                | 0.279                | 0.229                         | 1.22              | 0.1    |
| 8.5                   | 50                  | 140.0                | 0.869                | 0.723                         | 1.20              | 0.1    |
| 8.5                   | 100                 | 196.9                | 10.785               | 9.165                         | 1.18              | 1.6    |
| 8.5                   | 125                 | 220.6                | 47.139<sup>a</sup>   | 22.249                        | 2.12              | 25.0   |
| 8.5                   | 150                 | 230.6                | 85.943<sup>b</sup>   | 31.467                        | 2.73              | 54.8   |

Table S4. Light intensity, T<sub>cat</sub>, reaction rate for the experiments with illumination, calculated reaction rates for reactions without illumination at T<sub>cat</sub> of the reactions with illumination, ratio k<sub>light</sub>/k<sub>dark</sub> and PTM efficiency.

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PTM = 100\% \frac{k_l-k_d}{\Phi A} \] with \( k_l \) = reaction rate upon illumination, \( k_d \) = reaction rate in dark at same catalyst temperature as in the illumination reaction, \( \Phi \) = photon flux and \( A \) = illuminated area. Reaction rate calculated by a linear fit of the produced CH<sub>4</sub> in the first 15 min of the reactions. (a) Linear fit of the first 5 min of the reaction; (b) Linear fit of the first 2.5 min of the reaction.

**S11. Experimental details for TEM studies**

Transmission Electron Microscopy (TEM) studies were performed using a JEOL ARM 200F Transmission Electron Microscope, probe corrected, equipped with a 100 mm<sup>2</sup> Centurio SDD EDX detector, operated at 200 kV. Imaging was performed both in Bright Field (BF) TEM mode as well as in High Angle Annular Dark Field (HAADF) Scanning TEM mode. The HAADF detector uses the electrons scattered over large angles for imaging. The HAADF detector is therefore mass sensitive, which means that higher brightness in the image corresponds to the presence of (a larger concentration of) heavier atoms. This allows for a fast and accurate inventory of the Ru loading and particle size on the alumina support.
Samples were prepared by preparing a suspension of the material in ethanol and suspending a drop onto a carbon-coated copper TEM grid and drying at room temperature. The EDX detector was used to detect element characteristic X-rays. In the EDX spectrum the detected signal is plotted as a function of the (characteristic) energy. Chemical compositions can be obtained by quantification of the data.
**Figure S14. TEM analysis of representative RuO$_2$ crystals.**

a) BFTEM micrograph of an Al$_2$O$_3$ cluster containing several elongated RuO$_2$ crystals; b) HAADF-STEM micrograph of the two RuO$_2$ crystals indicated in figure a); c) EDX spectrum of the dashed area in figure b), showing strong Ru and O peaks; d-f) EDX mappings of Ru, O and Al; g) High resolution TEM micrograph of the crystalline RuO$_2$ needle; h) corresponding fast Fourier transform (FFT) pattern, referring to the a $<111>$ zone axis of tetragonal RuO$_2$. 
S13. Experimental details for XRD analysis

The powder X-ray diffraction patterns were recorded using a Bruker AXS D8 Discover diffractometer (Cu Kα radiation, LynxEye detector).

S14. Characterization of the RuO$_2$ precatalyst by XRD analysis

![XRD analysis graph](image)

*Figure S15. XRD analyses of the RuO$_2$ precatalyst (red) and Ru catalyst (blue), both supported on γ-Al$_2$O$_3$.*

The X-ray diffraction analysis identifies the Ru containing nanodomains as RuO$_2$ nanocrystals. The diffractogram consists of reflections corresponding to RuO$_2$ at 2θ = 28.09°, 35.19° and 54.48°. The two remaining reflections at 2θ = 39.48° and 46.08° correspond to the crystalline γ-Al$_2$O$_3$ support material.

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*iii* JCPDS reference patterns: Ru 00-006-0663; RuO$_2$ 00-040-1290; Al$_2$O$_3$ 00-10-0425.
S15. Characterization of the spherical Ru catalyst by XRD analysis

![XRD analysis](image)

**Figure S16.** XRD analyses of the spherical Ru catalyst supported on γ-Al₂O₃.

The crystallinity of the spherical Ru catalyst is confirmed by XRD analysis, giving reflections for the metallic Ru located at 2θ = 38.39° and 44.01°.

S16. Experimental details for and results from XPS analysis

The XPS-measurements have been carried out in a Quantera SXMtm from ULVAC-PHI (Q1). The measurements have been performed using monochromatic AlKα-radiation and a take-off angle Θ of 45°; at this angle the information depth is approximately 7 nm. A spot size of 100 µm, scanned across an area of 500 x 500 µm was applied for the analyses. By means of wide-scan measurements the elements present at the surface have been identified; accurate narrow-scans have been measured for quantification. Standard sensitivity factors were used to convert peak areas to atomic concentrations. As a result it is possible that the concentrations deviate from reality in the absolute sense (generally not more than 25% relative). When XPS measurements are compared to each other, the relative error is usually within 10%.

The powders were deposited in the holes of a special powder holder, see Figure S17. This was done in an Ar-glove box (O₂ and H₂O < 1 ppm). Subsequently the holder was transported to the XPS machine without contact to ambient air.
Figure S17. XPS holder with powders.
point 44 = RuO$_2$ precatalyst; point 45 = rod-like Ru catalyst after reaction; point 46 = rod-like Ru catalyst.

Table S5. concentrations of the elements present at the surface of the samples.

| Sample                                | Al 2p | O 1s | Ru 3d |
|----------------------------------------|-------|------|-------|
|                                        |       |      | Oxide (280.9 eV) | Metal (279.5 eV) |
| RuO$_2$ precatalyst                    | 31.1% | 66.4%| 2.5%  | -                |
| rod-like Ru catalyst after reaction    | 32.7% | 64.7%| -     | 2.5%             |
| rod-like Ru catalyst                   | 32.9% | 64.5%| -     | 2.5%             |

Figure S18: Al 2p peaks of the samples.
red = RuO$_2$ precatalyst; blue = rod-like Ru catalyst after reaction; green = rod-like Ru catalyst
Figure S19: O 1s peaks of the samples.
red = RuO$_2$ precatalyst; blue = rod-like Ru catalyst after reaction; green = rod-like Ru catalyst

Figure S20: Ru 3d peaks of the samples.
red = RuO$_2$ precatalyst; blue = rod-like Ru catalyst after reaction; green = rod-like Ru catalyst

S17. Determination of the average size of nanospheres and nanorods

In order to determine the average dimensions of the spherical nanoparticles and nanorods present in our RuO$_2$ precatalyst, the rod-like Ru catalyst and the spherical Ru catalyst samples, we first measured the dimensions of > 200 nanoparticles/sample from the corresponding TEM
micrographs, using the image analysis software ImageJ. Thereafter, we performed a Gaussian fit (see size distribution results in Figure S21, S22 and S23).

Figure S21. Histograms depicting: (a) the length ($<\text{length}> = 153 \pm 53 \text{ nm}$) and (b) width ($<\text{width}> = 14 \pm 13 \text{ nm}$) distribution of the nanorods present in a representative RuO$_2$ precatalyst sample; and (c) the diameter distribution ($<\text{diameter}> = 11 \pm 3 \text{ nm}$) of the spherical nanoparticles present in the same sample.
Figure S22. Histograms depicting: (a) the length ($<\text{length}> = 147 \pm 50$ nm) and (b) width ($<\text{width}> = 15 \pm 14$ nm) distribution of the nanorods present in a typical activated rod-like Ru catalyst sample before photomethanation (catalyst activation was performed by reacting the RuO$_2$ precatalyst with H$_2$ at 150 °C and 1 sun light intensity for 2 h). (c) Histogram depicting the diameter distribution ($<\text{diameter}> = 10 \pm 3$ nm) of the spherical nanoparticles present in the same sample.

Figure S23. Histogram depicting the diameter distribution ($<\text{diameter}> = 0.88 \pm 0.11$ nm) of the spherical nanoparticles present in the spherical Ru catalyst.
S18. Experimental details for UV-vis-NIR spectroscopy

The diffuse reflectance spectra of the powders were measured using an Agilent Cary-5000 UV-vis-NIR spectrophotometer equipped with an Internal Diffuse Reflectance Accessory (DRA-2500). For this the catalyst powders were first diluted with spectroscopy grade potassium bromide (KBr, Uvasol), while a blank KBr sample was used as the reference powder for setting the reflectance to 100%.

S19. Characterization of RuO$_2$ precatalyst with UV-vis-NIR spectroscopy

![UV-VIS-NIR spectra of the RuO$_2$ precatalyst (red) and Ru catalyst (blue).](image)

Figure S24. UV-VIS-NIR spectra of the RuO$_2$ precatalyst (red) and Ru catalyst (blue).

The RuO$_2$ precatalyst displays two distinct absorption bands centered at a wavelength of ~350 nm and ~800 nm (Figure S6, red).
Figure S25. UV-VIS-NIR diffuse reflectance spectra of the RuO$_2$ precatalyst (red) and Ru catalyst (blue).

S20. Characterization of the spherical Ru catalyst with UV-vis-NIR spectroscopy

Figure S26. UV-VIS-NIR spectra of the spherical Ru catalyst.

The spectrum clearly shows that the Ru catalyst features a weak broad and asymmetric absorption which spans the UV-vis-NIR range with a maximum at ~320 nm.
S21. Details for the optical modeling based on the boundary element method (BEM).

In order to gain insights into the UV-vis-NIR optical properties of both the RuO$_2$ precatalyst and the Ru catalyst, we performed optical simulations based on the boundary element method (BEM). This numerical method provides a non-analytical solution of Maxwell’s equations for axially-symmetric objects.$^iv$ We used the BEM to determine the UV-vis-NIR extinction, absorption, and scattering cross sections of two representative nanoparticle morphologies present in our precatalyst and catalyst samples, namely a spherical nanoparticle (diameter = 11 nm) and a nanorod (length x width = 153 x 14 nm, aspect ratio = 10.9). Their contour surfaces were defined with 40 points (for the spherical nanoparticle) and with 200 x 100 points (for the nanorod, for its central part and ends, respectively). The tip curvature of the nanorod was fixed at 5 nm. The average dielectric function of RuO$_2$ used for optical modeling was determined from Goel et al.$^v$; while the dielectric function of Ru was taken from Palik et al.$^vi$ and Cox et al.$^vii$ (see Figure S27). All calculations were performed by assuming that both nanoparticle types are embedded in a $\gamma$-Al$_2$O$_3$ medium, which features a refractive index of $\sim$1.766 at 2.059 eV.$^vi$

Figure S27. (a) Average dielectric function of RuO$_2$, determined by fitting and averaging the parallel and perpendicular components of the real and imaginary parts of the dielectric function of single crystal rutile RuO$_2$.$^v$ (b) Dielectric function of Ru, taken from Palik, E. D et al.$^vi$ and Cox et al.$^vii$. 

$^iv$ Phys. Rev. Lett., 1998, 80, 5180; Phys. Rev. B: Condens.Matter Mater. Phys., 2002, 65, 115418.; Chem. Soc. Rev., 2008, 37, 1792–1805
$^v$ Phys. Rev. B, 24, 7342, 1981
$^vi$ Handbook of Optical Constants of Solids I and II; Academic Press: New York, 1995
$^vii$ J. Opt. Soc. Am. 64, 423, 1974
Figure S28. Calculated averaged cross section (comparable to the extinction cross section) of: (a) a single spherical RuO$_2$ and Ru nanoparticle (11 nm diameter) and (b) a single RuO$_2$ and Ru nanorod (length × width = 153 × 14 nm, aspect ratio=10.9) in a γ-Al$_2$O$_3$ medium. The nanorod spectra were determined by averaging over 30 angles of light incidence in order to take into account their (experimentally observed) random orientation on the γ-Al$_2$O$_3$ support.
Figure S29. Calculated extinction, absorption, and scattering cross section of a RuO$_2$ nanorod (a, c, e) and of a Ru nanorod (b, d, f) of dimensions length $\times$ width = 153 $\times$ 14 nm (aspect ratio=10.9) in a $\gamma$-$\text{Al}_2\text{O}_3$ medium at different angles of light incidence with respect to the nanorod’s longitudinal axis, namely: $0^\circ$ (a, b), $45^\circ$ (c, d), and $90^\circ$ (e, f).
S32. Procedure for a typical reaction using a long-pass filter.

A homemade photoreactor equipped with a solar simulator (Newport Sol3A) and reaction cell with quartz window was used for the sunlight fueled methanation reaction (See SI). In between the solar simulator and reaction cell a filter (either a long-pass filter of 395 nm or 495 nm) was placed. N\textsubscript{2} was used as internal standard. The reactor was prepared by filling the reactor with catalyst (typically 300 mg) and N\textsubscript{2} and subsequent evacuation for 3 times. Then, the reactor was filled with the reaction mixture of H\textsubscript{2} (Linde 6.0) and CO\textsubscript{2} (Linde 4.5) and diluted with N\textsubscript{2} (Linde 5.0) with the ratio H\textsubscript{2}:CO\textsubscript{2}:N\textsubscript{2}, (4:1:1) until the total pressure was 3.5 bar (2.5 bar overpressure). Prior to each experiment, the temperature was stabilized to desired reaction temperature in the range from 25 °C to 150 °C using electrical heating. During the experiment, the catalyst was irradiated from the top through the wavelength filter and then through the quartz window. The irradiation source was a solar light simulator provided with a filter of air mass coefficient 1.5 (AM 1.5), conventionally taken to 1 kW m\textsuperscript{-2}. The filters used were Newport 20CGA-395 and Newport 20CGA-495 long-pass filters.

The moment the lamp is switched on is considered the starting time of the reaction, the CH\textsubscript{4} formation before the starting time is subtracted from the light experiments. Gas samples were taken from the reactor using a gas lick tied syringe. 3 mL of gas were taken from the upper part of the reactor at different times and direct measured in the gas chromatograph (compact GC...
Interscience). The GC is equipped with three channels, 2 micro TCD detector and one FID detector. The first channel, used to measure H₂, O₂, N₂ and CO, has a MolSieve 5 Å column and RT-Q bond precolumn and TCD detector. The second channels, used to measure H₂O and CO₂, has a combination of TR-U bond column and RT-Q bond column and TCD detector. The third channel, used to measure methane, ethane and propane, is fitted with a Rtx-1, 2u column and FID detector.

S23. Details of the experiments performed for Figure 8b

| light intensity (sun) | T_reactor (°C) | T_cat rods (°C) | T_cat spheres (°C) | PTM' rods (%) | PTM' spheres (%) | Δ PTM' (PTM'rods− PTM'spheres) |
|----------------------|---------------|----------------|---------------------|---------------|----------------|-------------------------------|
| 1                    | 150           | 164.4          | 159.7               | 11.4          | 8.2            | 3.3                           |
| 5.7                  | 150           | 211.6          | 205.0               | 44.6          | 15.3           | 29.3                          |
| 8.5                  | 150           | 230.6          | 245.3               | 85.2          | 43.7           | 41.5                          |

Table S6. Light intensity, T_cat and reaction rate for the experiments to determine the difference in photon to methane efficiency using spherical and rod-like Ru catalysts.

\[ PTM' = 100\% \frac{k_l-k_d}{\Phi A} \] with \( k_l \) = reaction rate upon illumination, \( k_d \) = reaction rate in dark at T_reactor, \( \Phi \) = photon flux and \( A \) = illuminated area.

S24. Experimental details for inductively coupled plasma optical emission spectroscopy (ICP-OES)

Approximately 10 mg sample was weighed with a precision of 0.01 mg into a platinum crucible. The sample is digested with a mixture of lithium metaborate and sodium carbonate (1:1). Therefore the sample is completely converted with the digestion mixture and heated for 15 minutes at 1100 °C. After the crucible has cooled, the solidified melt is dissolved with hydrochloric acid (1:1) and filled to a volume adapted to the ruthenium content with distilled water. The ruthenium is determined spectrometrically after addition of lanthanum and cesium.