Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Continuous Flow Photoassisted CO_2 Methanation

Experimental methods:

Commercial Ni-Al_2O_3/SiO_2 was purchased from Aldrich and used as received, without further purification. Prior utilization, the photocatalyst was reduced under H_2 atmosphere at 500 ^{0}C for 2 h, but essentially identical results can be achieved without this pretreatment. In typical reaction, 200 mg of the reduced photocatalyst were compressed at 1 Ton×cm^{-2} for 2 min, and the resulting wafer, crushed and sieved at 0.2 – 0.4 μm, then, loaded on the top of a fritted glass filter inside a cylindrical quartz reactor. The photoreactor was heated using a heating mantle equipped with thermocouple to monitor the reaction temperature. After temperature stabilization illumination was switched on using a UV-Vis 300 W Xe lamp as light source through an optical guide that irradiates the catalyst bed from the top.

The gas mixtures were introduced from the upper part of the reactor, flowing down through the photocatalyst bed and after leaving the reactor the reaction products were analysed by a micro-GC equipped with two Agilent columns (PPQ and MS5A) and a TCD, using Ar as carrier gas.. Quantification was performed by calibrating the response with mixtures of known compositions.

XRD patterns were acquired with a Philips Xpert Pro diffractometer in the 2Θ range from 5 to 70 ^{0} using the Cu K_α radiation (λ=1.415 nm) at a rate of 0.5 ^{0}/min. UV-visible absorption spectra were recorded with a Jasco V-650 spectrophotometer. The Si/Al ratio present in the samples was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) by immersing a known catalyst amount into aqua regia at room temperature for 3 h and analyzing the Al and Si content of the resulting solution. HRTEM images were recorded in a JEOL JEM 2100F under accelerating voltage of 200kV. Samples were prepared by applying one drop of the suspended material in ethanol onto a carbon-coated copper TEM grid, and allowing them to dry at room temperature. XPS spectra were measured on a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a non-monochromatic X-ray source (Al and Mg) operating at 200 W. The samples were evacuated in the prechamber of the spectrometer at 1·10^{-9} mbar. The measured intensity ratios of the components were obtained from the area of the corresponding peaks after nonlinear Shirley-type background subtraction and corrected by the transition function of the spectrometer.

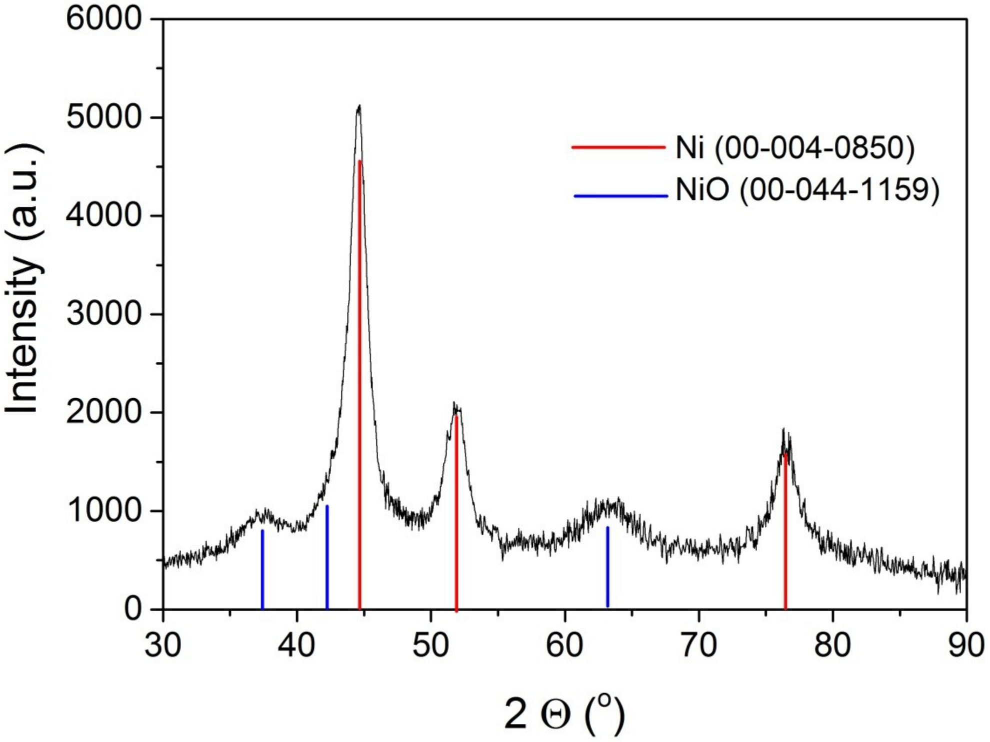

Fig. SI1. XRD spectrum of a Ni-Al_2O_3/SiO_2 sample after H_2 reduction treatment at 500 ^oC.

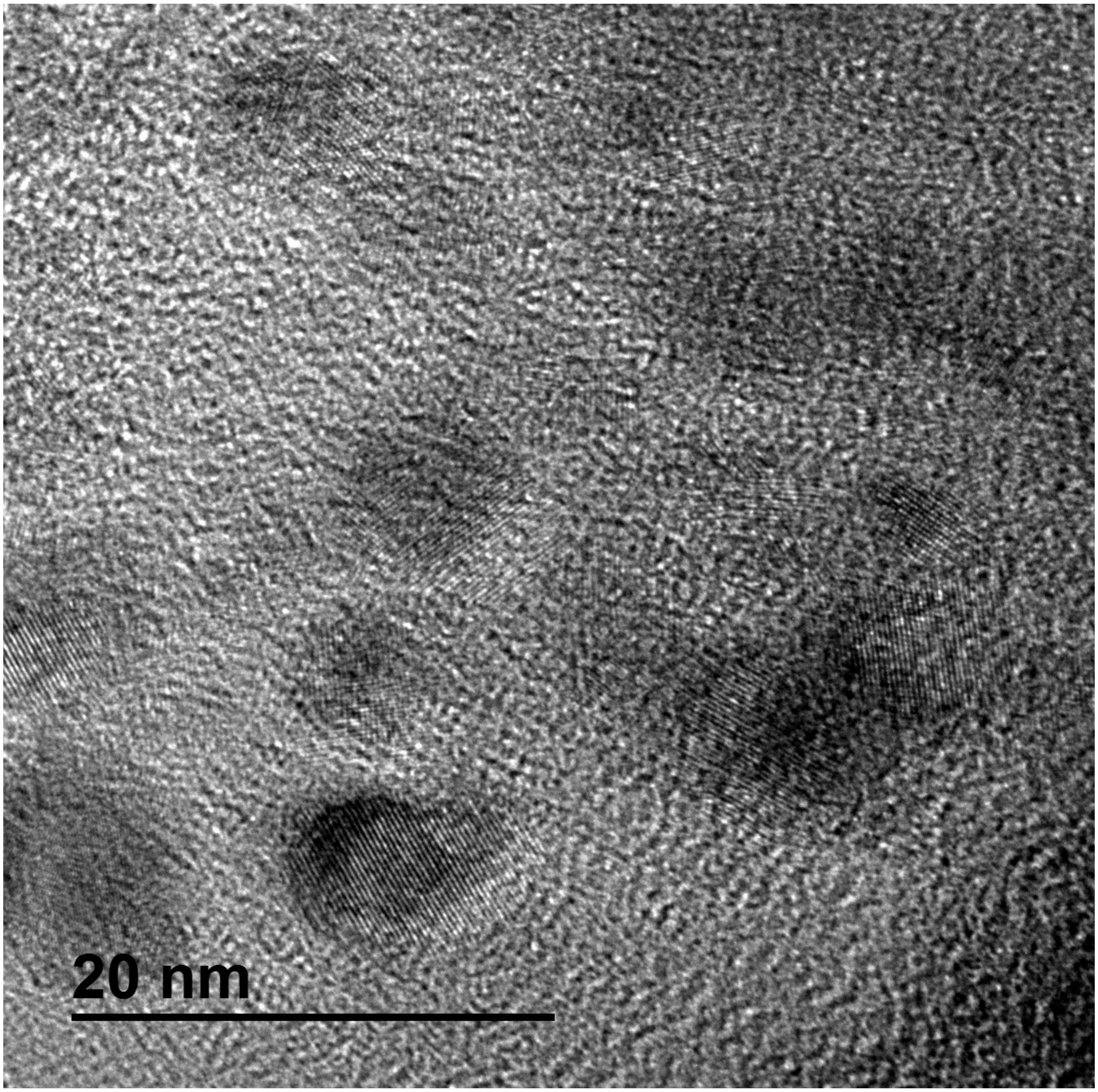

Figure SI2. HRTEM image of the Ni-Al_2O_3/SiO_2 photocatalyst.

Figure SI3. Digital images of the cylindrical reactor coated with the heating mantle and the optic fibre (left) and the photocatalyst loaded in the reactor with the lamp on (right).

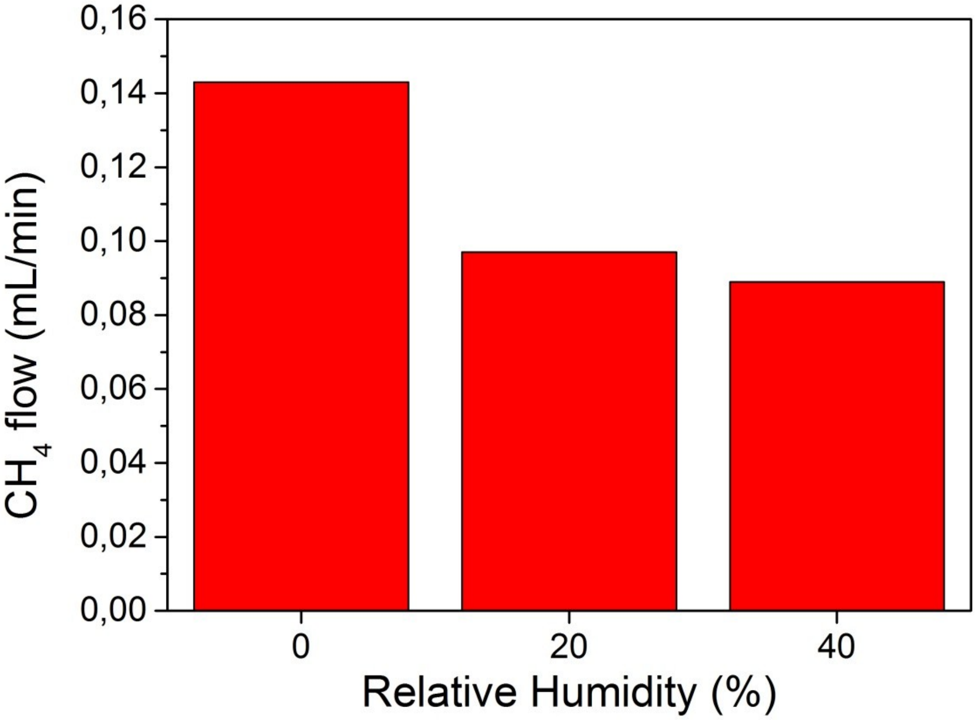

Figure SI4. Flow of CH_4 as function of the relative humidity of the steam. Reaction conditions: photocatalyst 200 mg, temperature 225 ^oC, total gas flow 13.9 mL/min with a composition of 81.7% N2, 3.1 % of CO2 and 15.2 % of H2. Light from a 300 w Xe lamp.

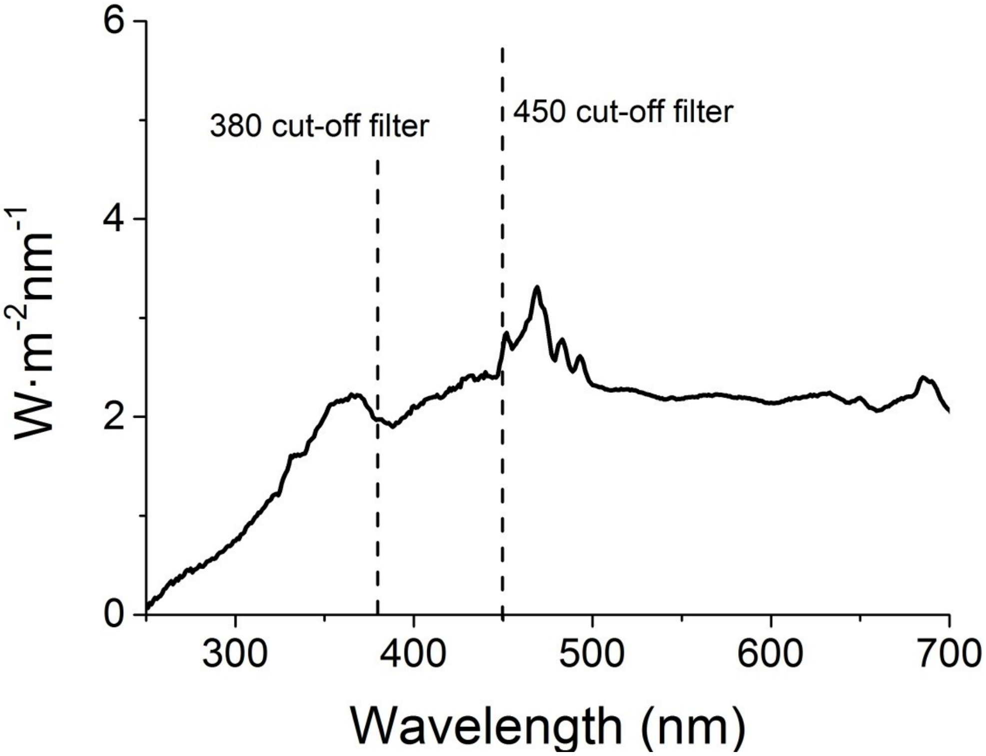

Figure SI5. Spectral response of the Xe lmap employed in the photocatalytic experiments. The dotted straight lines indicate the cut-off lamp spectrum.

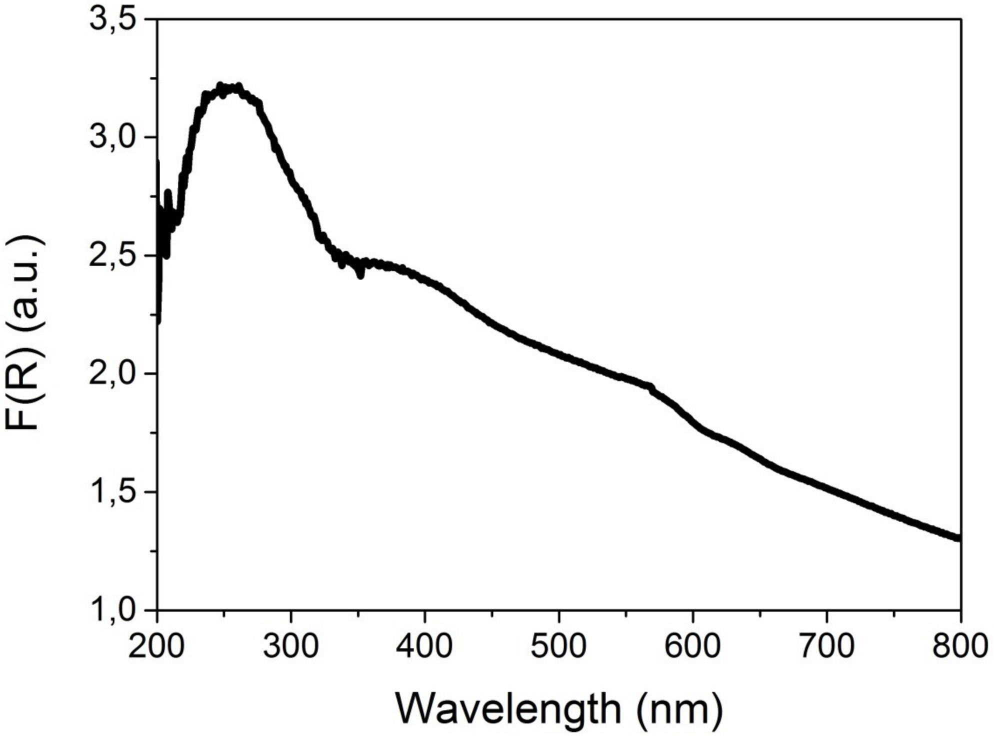

Figure SI6. Diffuse-reflectance UV-Vis spectrum of the Ni-Al_2O_3/SiO_2 photocatalyst.