

# Solar Light Complete Photocatalytic CO<sub>2</sub> Reduction to Methane by H<sub>2</sub> at near Ambient Temperature

Francesc Sastre, Alberto V. Puga, Lichen Liu, Avelino Corma,\* and Hermenegildo García\*

Instituto Universitario de Tecnología Química CSIC-UPV, Univ. Politécnica de Valencia, Av. De los Naranjos s/n, 46022 Valencia, Spain.

## SUPPORTING INFORMATION

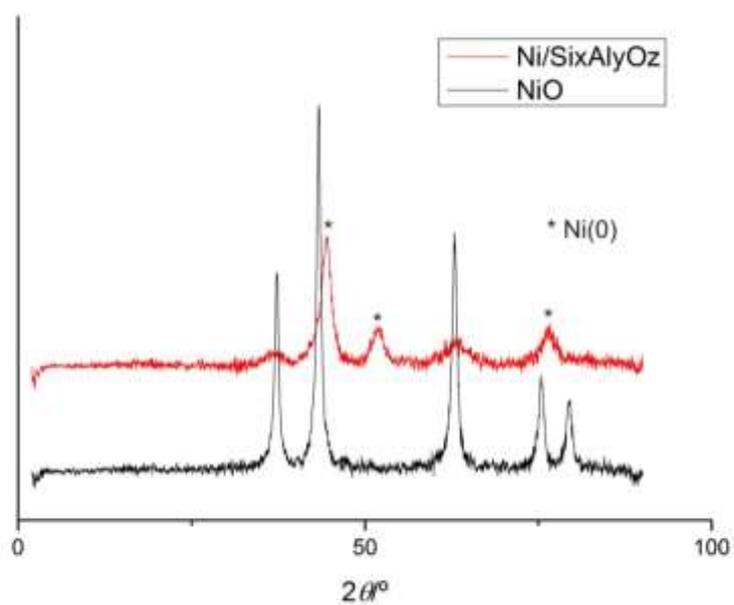
**Table S1:** Photocatalysts. All the metal oxides used in this study were commercial samples used as received. The main textural data are the following:

	Reference	BET (m <sup>2</sup> /g)	Particle size
TiO <sub>2</sub>	P25 Aeroxide 236-675-5	50	25
NiO	Aldrich-637130	17	<50 7–30 (TEM)
CuO	Aldrich-203130	15	<50
CoO	Aldrich-637025	40	<50
Ni/SiO <sub>2</sub> .Al <sub>2</sub> O <sub>3</sub>	Alfa Aesar-31276	100	<50 7–16 (TEM)
Fe <sub>3</sub> O <sub>4</sub>	Aldrich-637106	>60	<50
Fe <sub>2</sub> O <sub>3</sub>	Aldrich-544884	50-245	<50

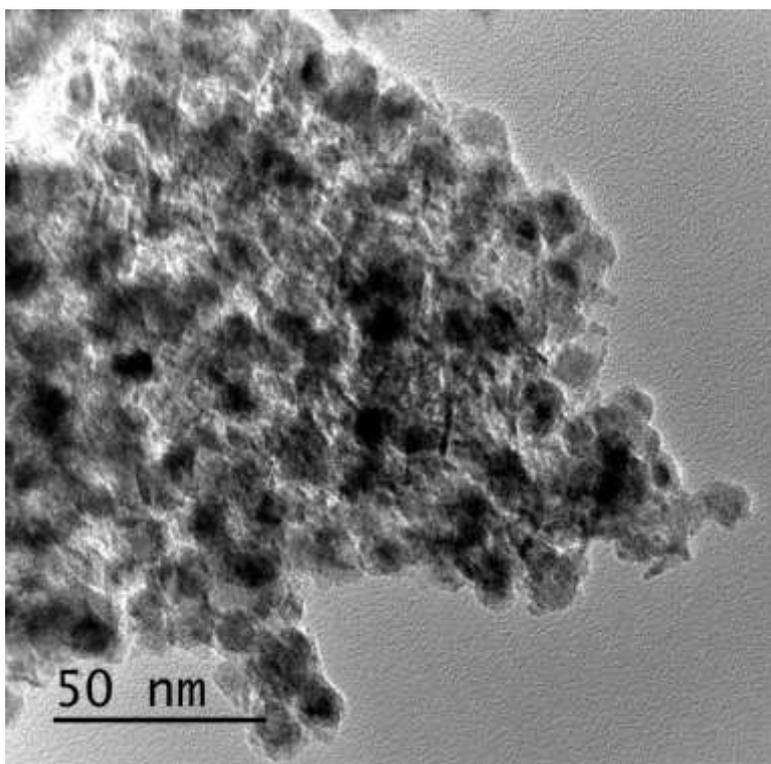
**Table S2:** Composition of the commercial Ni/SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub> photocatalyst, based on inductively coupled plasma (ICP) analyses.

	% (wt.)		% (wt.)
Ni	70.8	Ni <sup>0</sup>	33.7
		NiO	47.2
Al	6.2	Al <sub>2</sub> O <sub>3</sub>	11.7
Si	3.5	SiO <sub>2</sub>	7.4

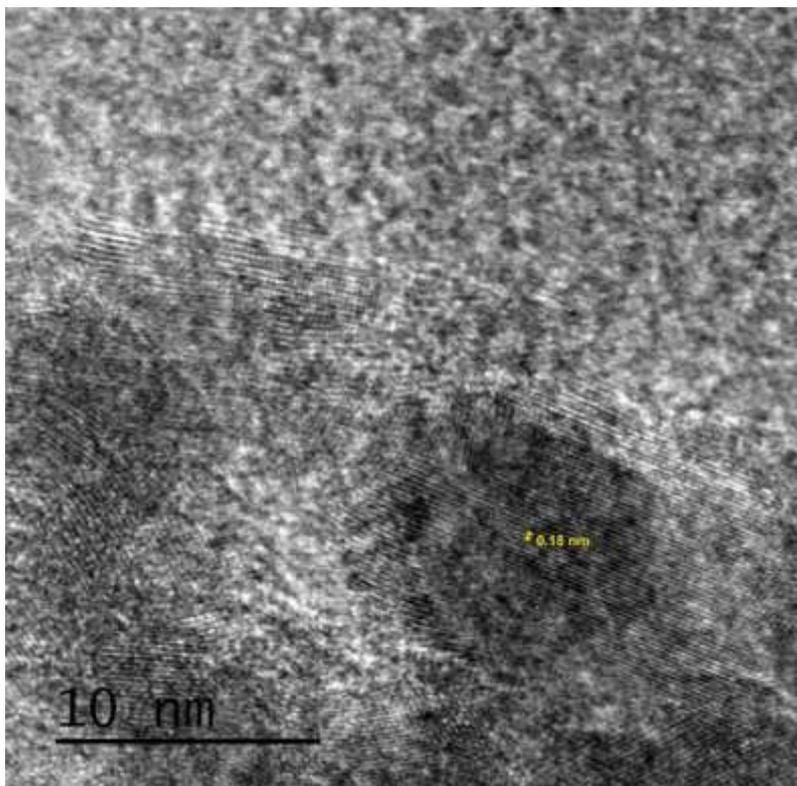
**Figure S1:** XRD diffractograms of the commercial Ni/Si<sub>x</sub>Al<sub>y</sub>O<sub>z</sub> and NiO photocatalysts.



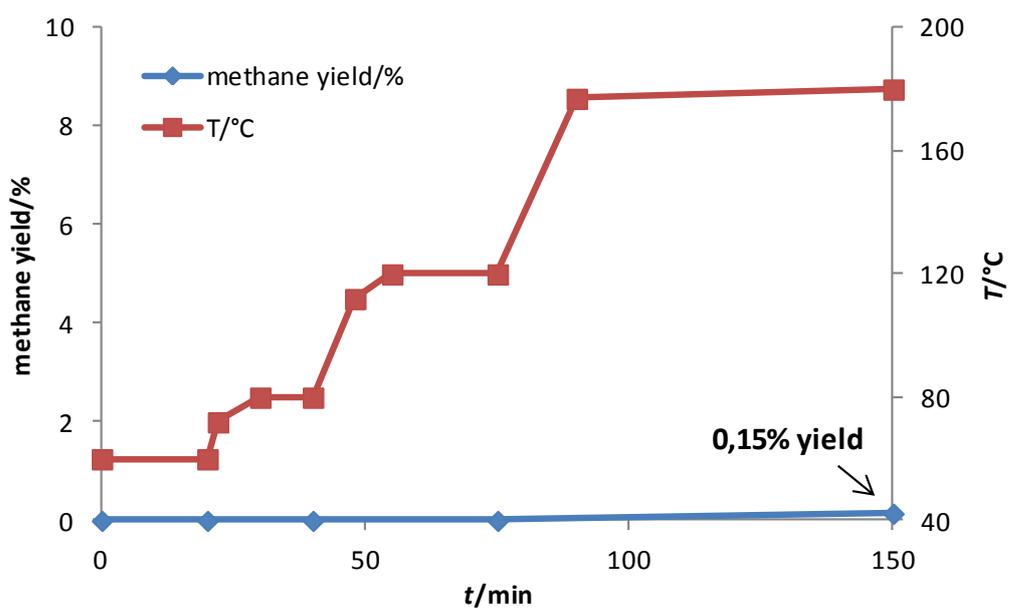
**Figure S2:** TEM micrographs of the commercial Ni/SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub> photocatalyst (diameter: 7–16 nm).



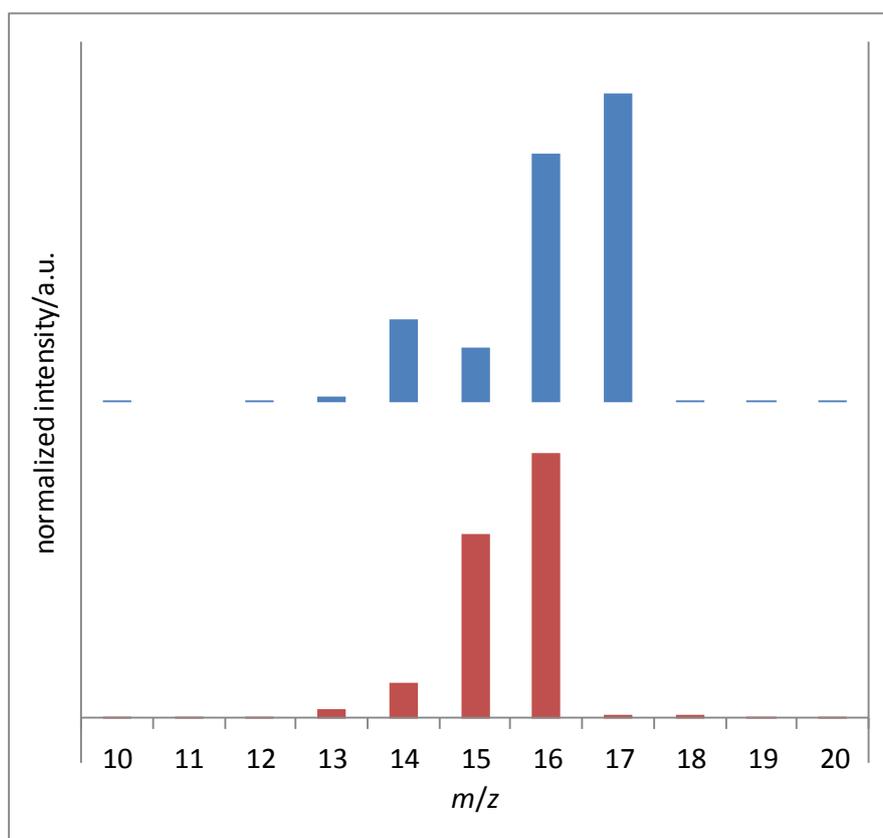
**Figure S3:** HRTEM micrograph of the commercial Ni/SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub> photocatalyst showing the lattice fringes.



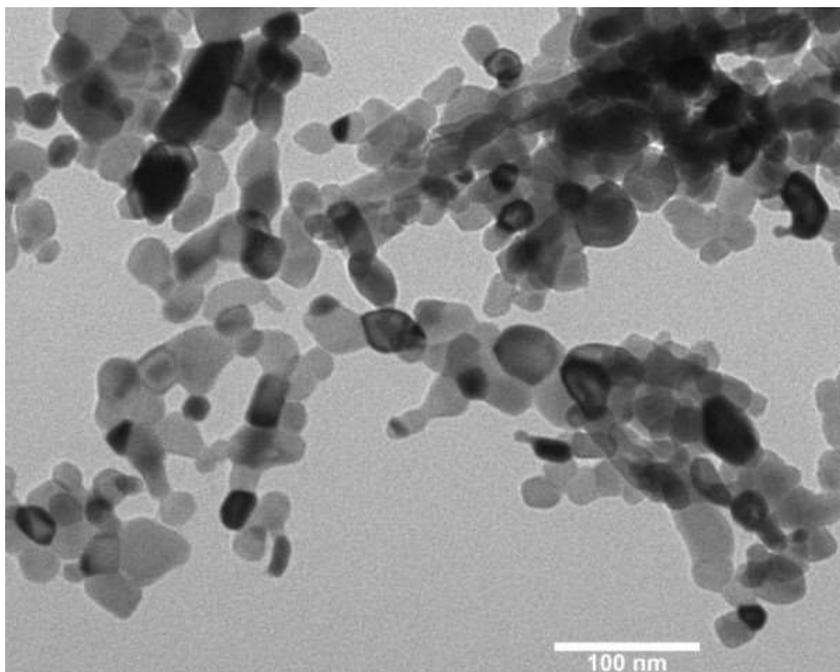
**Figure S4:** Profile for the reaction between CO<sub>2</sub> and H<sub>2</sub> in the dark (autoclave) on Ni/SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub> at increasing temperatures.



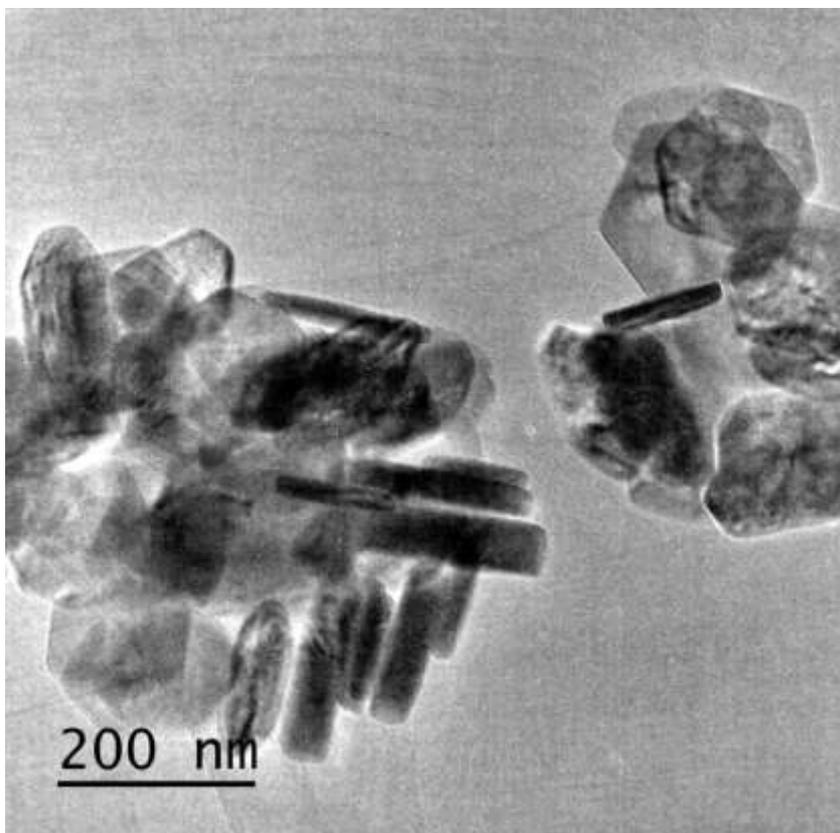
**Figure S5.** Top, blue: Mass spectra of the reaction product from  $^{13}\text{CO}_2$  and  $\text{H}_2$  on  $\text{Ni/Si}_x\text{Al}_y\text{O}_z$  clearly showing that  $^{13}\text{CH}_4$  was the main product of the reaction, as revealed by the peak at  $m/z = 17$  (further fragmentation results in peaks at  $m/z - 1$ ,  $m/z - 2$  and so on). Bottom, red: Mass spectra of a sample of commercial  $\text{CH}_4$  (methane 4.5, Abelló Linde), where the peak at  $m/z = 17$  is insignificant and the main peak is shifted down one  $m/z$  unit, that is  $m/z = 16$  as compared to the  $^{13}\text{CO}_2$  reaction product. The relatively intense peak at  $m/z = 14$  on the top spectrum is due to  $\text{N}^+$  ion fragments from  $\text{N}_2$ , used as internal standard in the reaction; otherwise, the fragmentation patterns are similar and as expected for  $^{13}\text{CH}_4$  and  $^{12}\text{CH}_4$  for top and bottom spectra, respectively. Instrument: Agilent 5973, electronic ionization, positive mode.



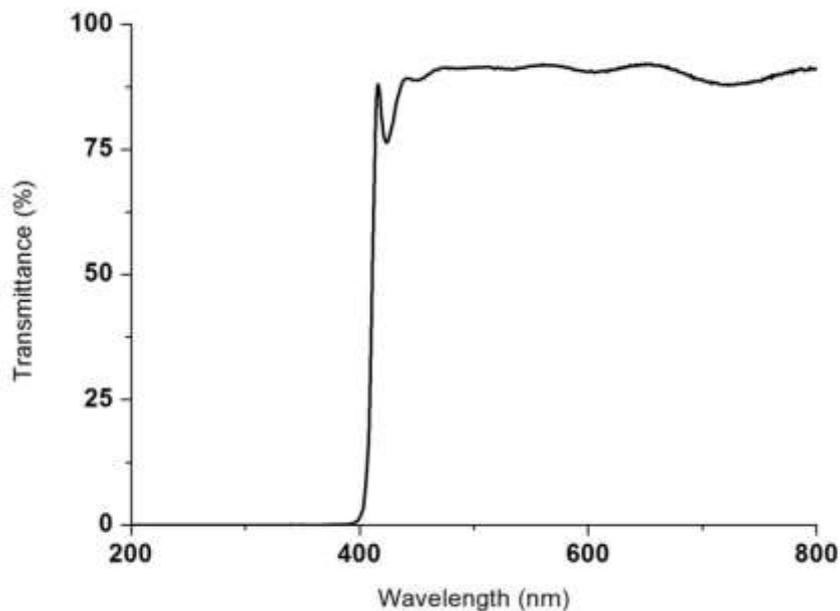
**Figure S6:** TEM micrograph of the synthesized NiO nanoparticles (diameter: 12–50 nm).



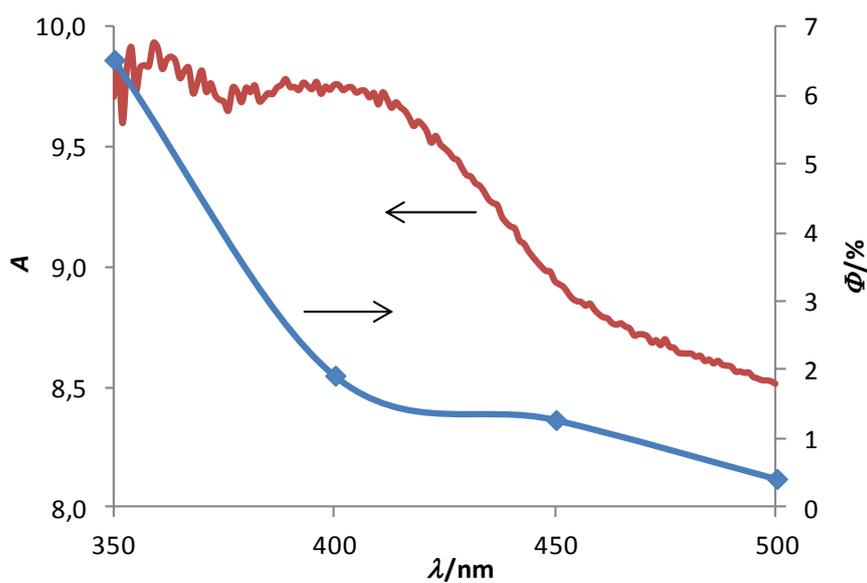
**Figure S7** TEM micrograph of the synthesized NiO nanoplates (diameter: 120–200 nm, thickness: 20–50 nm).



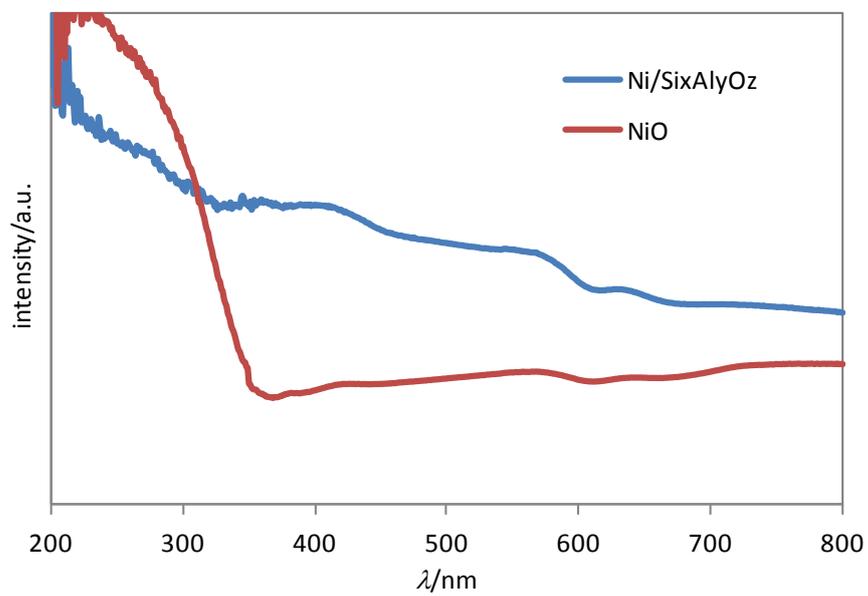
**Figure S8:** Spectra of the cut-off filter added to the solar simulator for irradiated only with visible light.



**Figure S9:** Apparent quantum yield for the reduction of  $\text{CO}_2$  by  $\text{H}_2$  on  $\text{Ni/SiO}_2\cdot\text{Al}_2\text{O}_3$ . Note that the product formed in this experiments was ethylene. The measurements were carried out using a 150 W Xe lamp adapted to a Czerny-Turner monochromator. The intensity of the light to determine the quantum yield was measured with a calibrated diode.

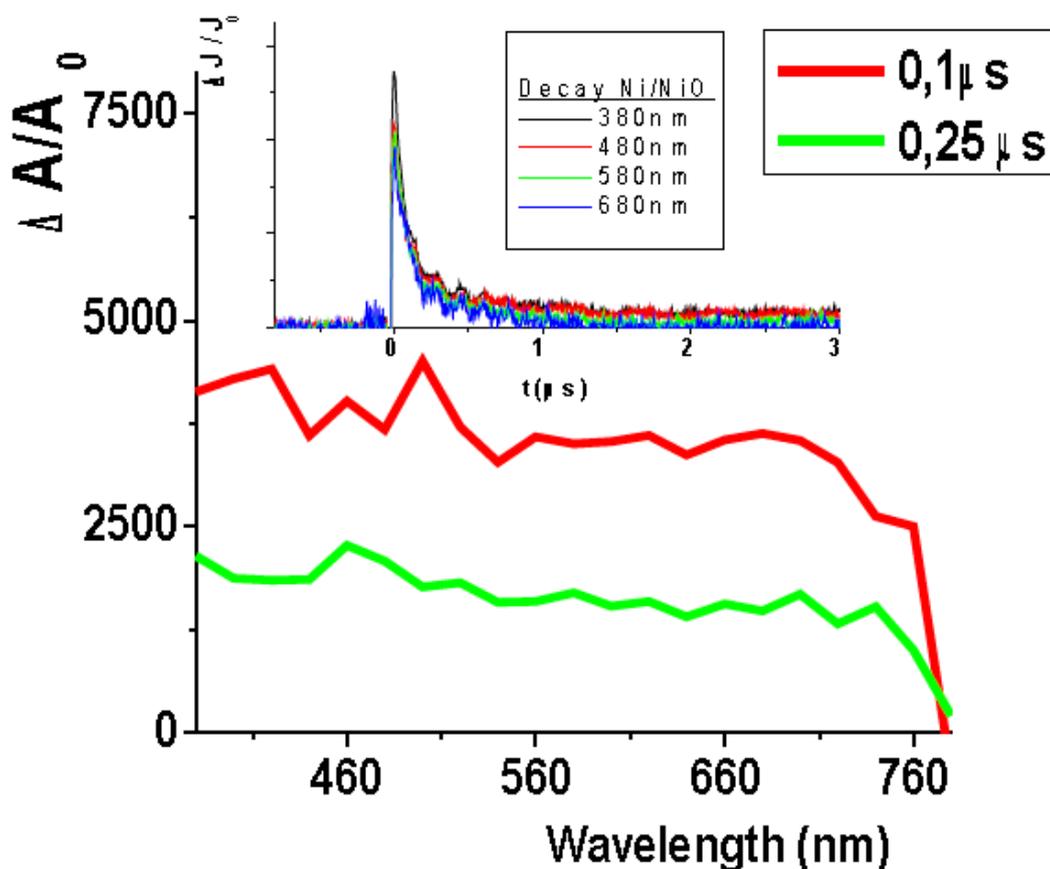


**Figure S10:** DRUV-vis spectrum of the commercial Ni/SiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub> and NiO photocatalysts.

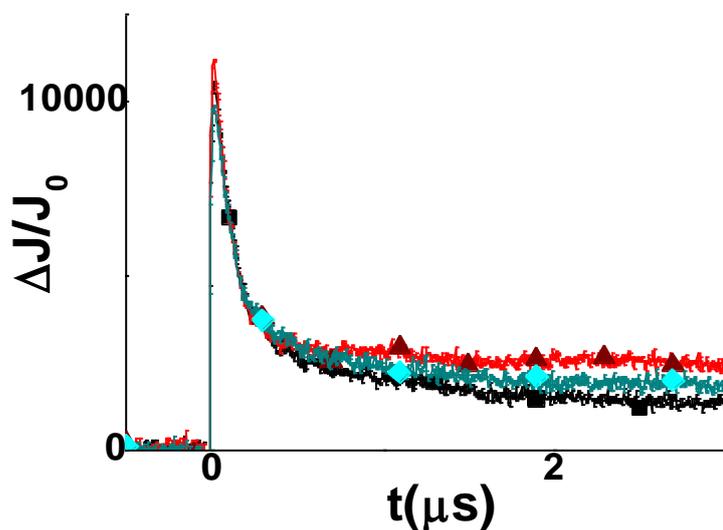


**Transient spectroscopy study.** Ni/SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub> (1.5 mg) was suspended in acetonitrile (5 ml) by sonication (250 W/30 min) and the resulting transparent suspension was separated from any solid sediment. Laser flash photolysis (LFP) experiments of the suspensions in transmission mode were carried out using the third (355 nm) or the second (532 nm) harmonic of a Surelite Nd:YAG laser for excitation (20 mJ, pulse  $\leq$  10 ns). The signal from the monochromator/photomultiplier detection system was captured by a Tektronix 2440 digitizer and transferred to a PC computer that controlled the experiment and provided suitable processing and data storage capabilities. The rise time of the detector/digitizer is  $\sim$ 3 ns up to 300 MHz (2.5 GHz sampling). The monitoring beam is provided by a ceramic xenon lamp and delivered through fiber optic cables. The laser pulse is probed by a fiber that synchronizes the LFP system with the digitizer operating in the pretrigger mode. Transient spectra of suspension were recorded using 10 mm  $\times$  10 mm quartz cells of 4 mL capacity and were bubbled for 30 min with argon or the corresponding gas quencher (O<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub> or CO<sub>2</sub>) before data acquisition. The absorbance of the samples was 0.3 O.D. at the laser excitation wavelength (355 nm).

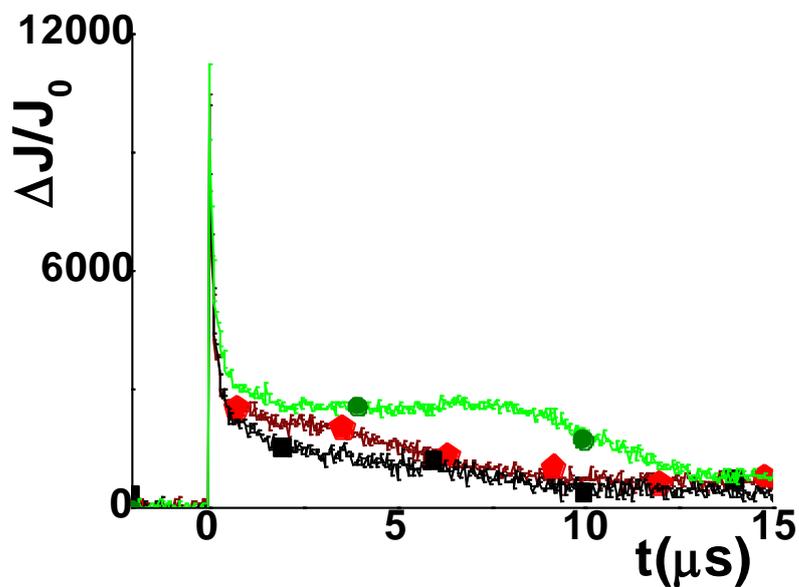
**Fig. S11.** Transient absorption spectra recorded 0.1 and 0.25 ms after 532 nm laser flash from an acetonitrile suspension (0.2 mg/ml) of Ni/SiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub> photocatalys purged under Ar. The inset shows the temporal profile for the signal monitored at various wavelengths.



**Figure S12.** Temporal profile of the signal monitored at 400 nm recorded by transmission mode from an acetonitrile suspension of Ni/SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub> after 355 nm laser pulse. The curves correspond to the signals monitored after Ar (black) or O<sub>2</sub> purging (blue) or after Ar purging and injection of methanol (25 ml) (red).



**Figure S13.** Temporal profile of the signal monitored at 400 nm recorded by transmission mode from an acetonitrile suspension of Ni/SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub> after 355 nm laser pulse. The curves correspond to the signals monitored after Ar (black), H<sub>2</sub> (red) or CO<sub>2</sub> (green) purging.



**Fig. S14.** Photographs of the irradiation system (top) and the photoreactor (bottom).

