Supporting Information

Band alignment investigations of heterostructure NiO/TiO$_2$
nanomaterials used as efficient heterojunction earth-abundant
metal oxide photocatalysts for hydrogen production

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Fourier Transform Infrared Spectroscopy

The FITR spectra (KBr pellets) of the various photocatalysts prepared after drying and calcination in air are shown in Fig. S1.

![FTIR spectra of dried nanomaterials](image)

**Fig. S1:** FTIR spectra of dried nanomaterials **A:** TiO$_2$ (a, black) and 1wt% NiO/TiO$_2$ (b, red); calcined nanomaterials **B:** TiO$_2$ (a, black), 0.25wt% NiO/TiO$_2$ (b, magenta), 0.5wt% NiO/TiO$_2$ (c, blue) and 1wt% NiO/TiO$_2$ (d, red).

XRD characterization of photocatalysts before calcination

The XRD patterns of TiO$_2$ and 1wt% NiO/TiO$_2$ after drying are shown in Fig. S2. In both cases the diffraction lines expected for anatase TiO$_2$ crystallites were observed showing that this polymorph was formed at low temperature.

![XRD patterns of dried TiO$_2$ and 1wt% NiO/TiO$_2$](image)

**Fig. S2:** XRD patterns of dried TiO$_2$ (a, black) and 1wt% NiO/TiO$_2$ (b, red) photocatalysts.
Raman characterization of the photocatalysts

The 170-800 cm⁻¹ region of the Raman spectra of the different samples studied is shown in Fig. S3. Each spectrum shows symmetric bands around 197, 399, 513, 519 and 639 cm⁻¹ which can be clearly attributed to anatase TiO₂. No band typical of the brookite (323, 416, 636 cm⁻¹) or of rutile (435, 613 cm⁻¹) TiO₂ phase was detected.¹

**Fig. S3:** Expansion of the 170-800 cm⁻¹ region of the Raman spectra of pure TiO₂ (a, black), 0.25wt% NiO/TiO₂ (b, magenta), 0.5wt% NiO/TiO₂ (c, blue), 1wt% NiO/TiO₂ (d, red) and 4wt% NiO/TiO₂ (e, olive) nanomaterials.

**Fig. S4:** The peak position and Full Width at Half Maximum (FWHM) of Raman peak as a function of the NiO loading.
TEM-EDX characterization of the 1wt% NiO/TiO₂ photocatalyst

TEM image and elemental analysis mapping using energy dispersive X-ray (EDX) analysis of 1wt% NiO/TiO₂ after calcination are shown in Fig. S5.

**Fig. S5**: (A) TEM-SEI image and (B, C, D) EDX maps of Ti K, Ni K and Ti K + Ni K of 1wt% NiO/TiO₂ photocatalyst.

**Optical properties of pure NiO prepared by the sol-gel route**

The diffuse reflectance absorption spectra of pure NiO synthesized in this study is shown in Fig. S6. Assuming that NiO is a direct band gap semiconductor, the band gap energy of the NiO was determined from a plot of \((F(R) \times h\nu)^2\) versus \(h\nu\) (Figure S6, inset) and was estimated to be 3.4 eV.

**Fig. S6**: UV-visible diffuse reflectance spectrum and Tauc plot (inset) for pure NiO materials.
Fig. S7. (A) XPS survey spectra of pure anatase TiO$_2$ (a, black) and 1wt% NiO/anatase TiO$_2$ nanomaterials (b, red). High resolution XPS spectra of 1wt% NiO/anatase TiO$_2$ nanomaterials: (B) Ti 2p spectrum, (C) Ni 2p spectrum and (D) O 1s spectrum.

Quantum efficiency and light-to-hydrogen conversion

There are several possibilities to obtain the quantum efficiency. The most elegant is the conduct of chemical actinometer experiments,
\textsuperscript{iii} which we have done for comparable systems in the same setup.\textsuperscript{iv,v} Comparison of these values with those obtained from measurements of the light intensity proved that only about 60% of the light irradiation entered the used reactor at exemplarily wavelengths of 415 and 440 nm.

A more technical way to determine the quantum efficiency is comprised by the quotient of the enthalpy of combustion and the energy input. In the case of 1wt% NiO/TiO$_2$ 808µmol of H$_2$ give an energy of about 231J (based on upper heating value). The power of the irradiated light was 1.6W giving an energy of 9.6Wh or 34560J in the period of 6 hours yielding a light-to-hydrogen conversion efficiency of 0.67%. Considering only the 60% of light, which enter the reactor, this value will be 1.11%.

The more proper way of calculation of q. y. would be the division of generated H atoms per incident photon: However, as there is no integration of the photon output spectrum of the mercury lamp available, we can either rely on literature of the number of photons, which are emitted by the sun in the range between 280 and 680 nm (1.185 x 10\textsuperscript{17} per s and cm\textsuperscript{2}),\textsuperscript{vi} or on our own measurements with that emitted by the mercury lamp at a medium wavelength of 440 nm and an output power of 1.0W (1.1 x 10\textsuperscript{18} per s and cm\textsuperscript{2}; these photons enter the reactor). After correction to 1.6 W lamp output both result in 4.0% and 2.6%, respectively. Although
those are only rough estimations, they are in the same order of magnitude as the calculation based on the energy contents.

As it is shown, there is a significant input of photons. Thus, the system is oversaturated with respect to the photon number. Those are worst conditions for optimizing the quantum yield resulting in such low values. However, the focus laid on the optimization of the catalytic activity

![Graph](image)

**Fig. S8.** Effect of NiO loading on the H$_2$ production normalized with respect to BET surface area.

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