

Supplementary information

Enhanced photoelectrochemical water splitting at hematite photoanodes by effect of a NiFe-oxide co-catalyst

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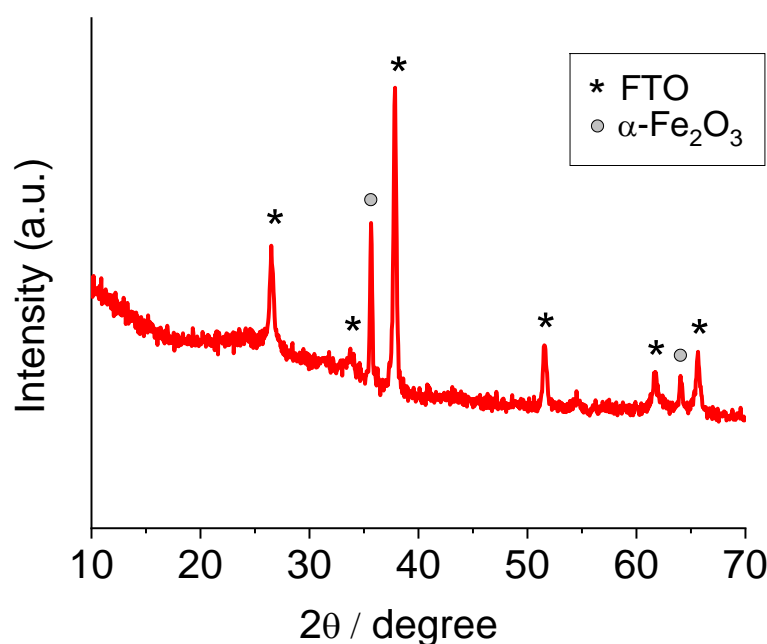


Fig. S1. XRD pattern for a hematite/FTO electrode calcined at 650 °C for 1 h.

The reference pattern corresponds to the 01-073-0603 card in the ICDD database.

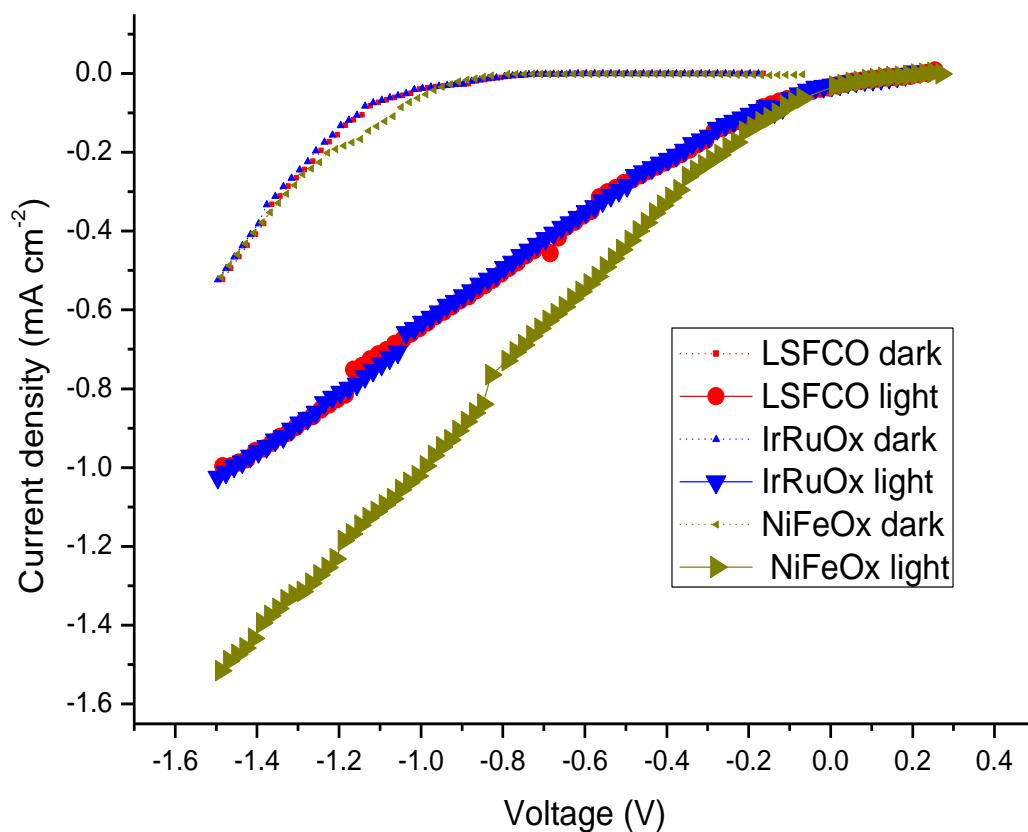


Fig. S2. Polarisation curves in an extended window under illumination and in the dark for the co-catalyst-based cells reported in Fig 3.

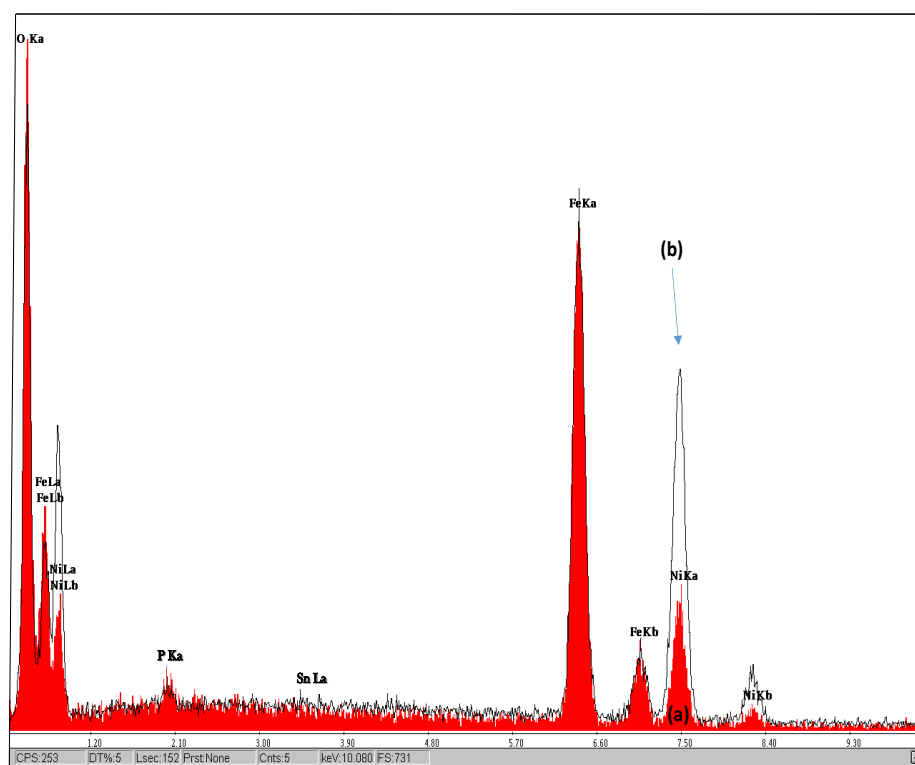


Fig. S3. EDX analysis of the outer NiFeOx-coated hematite photoanode surface. (a) The red area refers to the analysis of the overall surface; (b) the black curve is obtained with the beam mainly focused on a NiFeOx agglomerate and surrounding area.

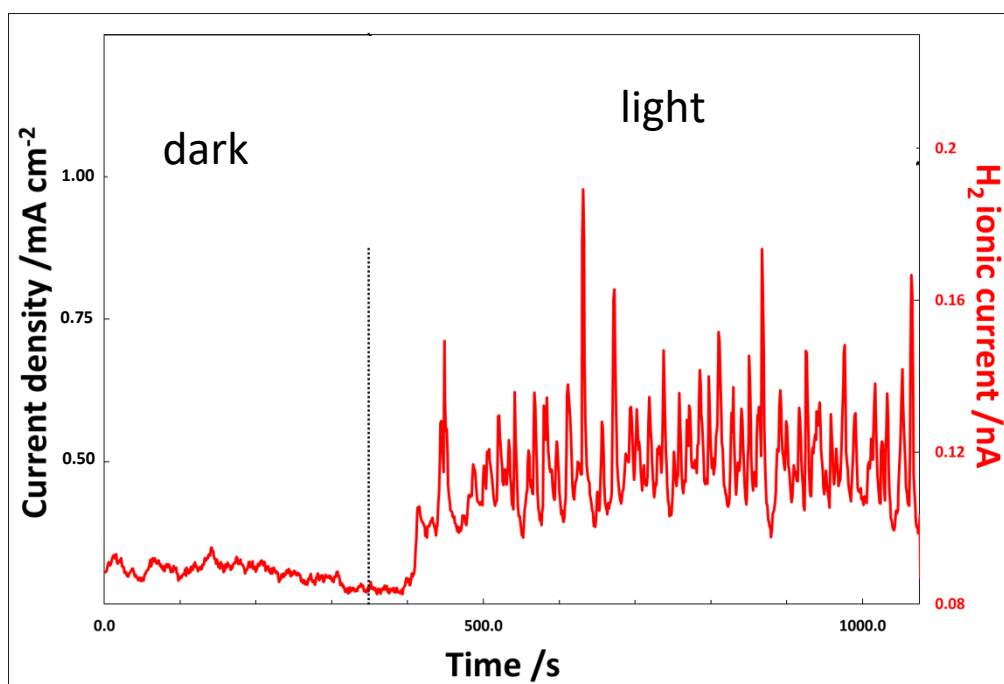


Fig. S4. Registration of H₂ ionic current at the cathode outlet of a specifically designed 4 cm² tandem photoelectrolysis cell using a mass spectrometer (ThermoStar™ GSD320, Pfeiffer Vacuum, Ablar, Germany), under dark and light conditions.

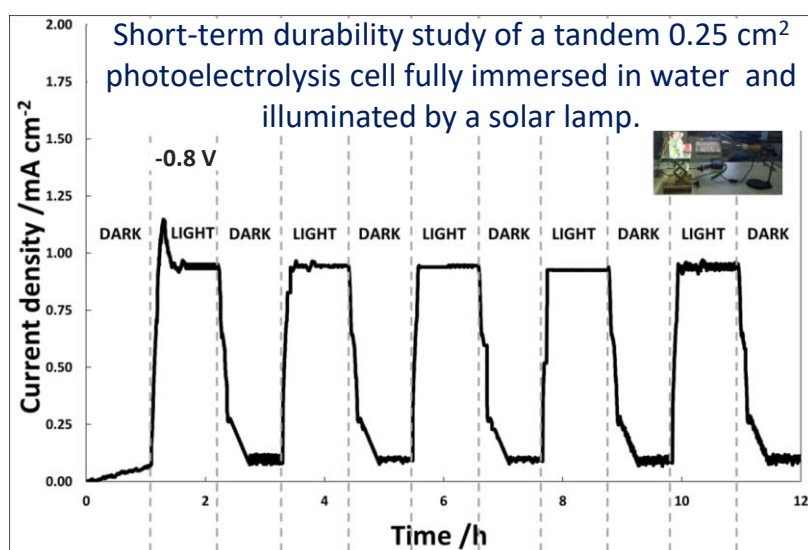


Fig. S5. Short-term durability study of a tandem 0.25 cm² photoelectrolysis cell fully immersed in water and illuminated by a solar lamp.

The cell was fully immersed in pure water and continuously flushed with nitrogen. This allowed proper hydration of the cell for the experiment duration without the need to refill water. A solar lamp was used in this experiment instead of a solar simulator with an irradiation power of about 100 mW cm⁻². In this experiment, under dark conditions, the lamp was off but the cell was still exposed to the diffusive light of the laboratory.

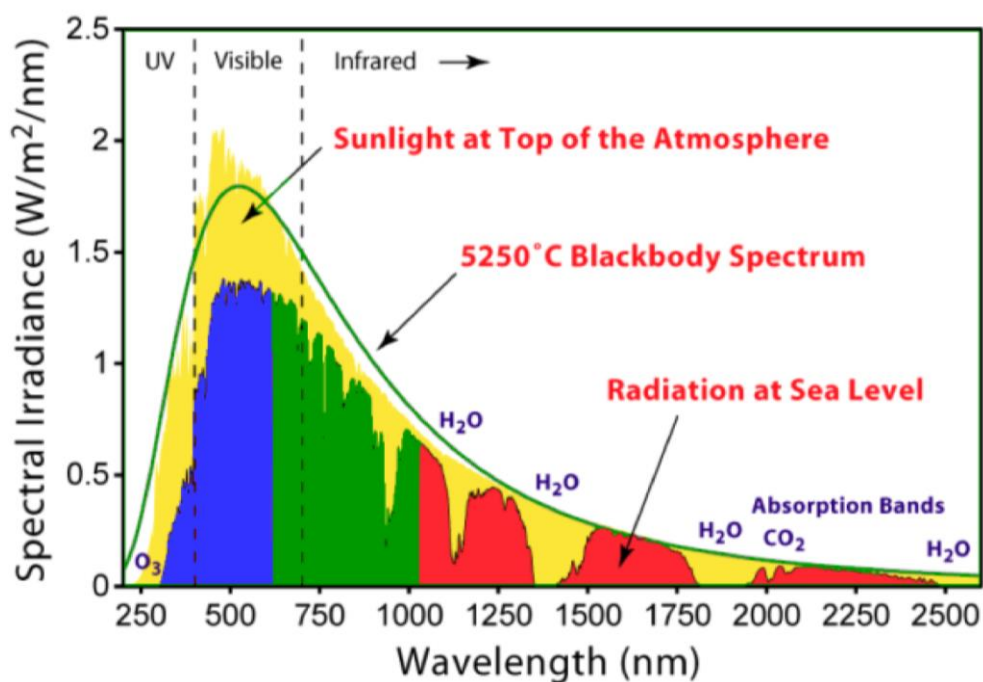


Fig. S6. AM1.5 spectrum utilisation by 2.1 eV bandgap of doped Fe₂O₃ (blue shading) and by 1.2 eV bandgap CuO underneath (green shading)

The solar simulator used in this work that closely matches the solar radiation spectrum under AM1.5 conditions (figure S6). The higher wavelength range of the total irradiation is not absorbed either by high energy gap hematite photoanode or by the transparent membrane and it can thus reach the photocathode. Thus, in principle, wavelengths smaller than 620 nm are mostly absorbed by the hematite semiconductor, wavelengths between 1033 nm and 620 nm (lower wavelengths have been already absorbed by Fe_2O_3) are absorbed by CuO and the remaining wavelengths larger than 1033 nm are not absorbed.

About 77% of the incoming light energy consists of utilisable over-bandgap photons. Hematite in principle should absorb 35 % of the total irradiation power, CuO should absorb 42% of the incident power in this specific tandem cell configuration and the remaining fraction (23 %) corresponding to the higher wavelengths of the solar spectrum in the near infrared regions is not absorbed. This is just a simple theoretical analysis that does not take into account reflection losses, light scattering effects, light absorption caused by the co-catalyst etc.