Electronic supplementary information (ESI)

Understanding the Visible-light Photocatalytic Activity of GaN:ZnO Solid Solution: the Role of Rh_{2-y}Cr_yO₃ Cocatalyst and Charge Carrier Lifetimes Over Tens of Seconds

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Spectroscopic Assignments

As seen in Figures 3C and S2, the shape of the TAS spectra don't change in the presence of the cocatalyst. This indicates that we predominantly monitor charges residing within GaN:ZnO as opposed to those residing in $Rh_{2-y}Cr_yO_3$. In addition, no changes in decay kinetics are seen when the redox-inactive MeCN is used as solvent (Figures S13 and S14), suggesting that TAS solely monitors the recombination of charges within GaN:ZnO as opposed to interfacial charge transfer to the electrolyte. The same behaviour is seen in the PIAS decay kinetics, which were insensitive to the solvent environment (Figure S15).

The initial TAS spectra shows ground state bleaching < 550 nm which disappears at delays times longer than about 1 ms (Figures 3C and S2). We assign this spectral evolution to a change from an electron-dominated spectrum (< 1 ms) to a hole-dominated spectrum (> 1 ms). Electron scavenging experiments were performed to confirm the nature of the signals observed. Addition of electron scavenger (here 10 mM Na₂S₂O₈) is expected to decrease signals associated with photogenerated electrons and promote those of photogenerated holes. PIAS measurements of GaN:ZnO in the presence of Na₂S₂O₈ resulted in the slow growth and decay of signal during the LED irradiation (Figure 4A). After 10 s of irradiation, the PIAS amplitude is significantly higher compared to the same measurement in H₂O, particularly in the 500 – 700 nm spectral region, and no bleach is observed (Figures 4B and S16). The PIAS spectrum of GaN:ZnO in aqueous Na₂S₂O₈ is comparable to that seen for GaN:ZnO/Rh_{2-y}Cr_yO₃ in water (compare Figures S16 and S17), supporting the assignment of the broad long-lived photoinduced absorption to holes following extraction of electrons by Na₂S₂O₈ or Rh_{2-y}Cr_yO₃. In addition, the PIAS spectra in the presence of Na₂S₂O₈ or Rh_{2-y}Cr_yO₃ strongly resembles the TAS spectra at times longer than 1 ms. We attribute the variations in peak wavelength and spectral shape to different ratios of photogenerated holes and electrons.

Timescale of Electron Extraction by Rh_{2-y}Cr_yO₃

Electron scavenging experiments were also useful to infer the timescale of electron transfer from GaN:ZnO to Rh_{2-y}Cr_yO₃. TAS measurements showed that the addition of Na₂S₂O₈ to the aqueous phase reduced the initial signal amplitude seen with bare GaN:ZnO (Figures 5 and S10), supporting the assignment of the sub-millisecond signal to electrons. We note that the kinetics are indistinguishable with and without Na₂S₂O₈ (Figure S14), indicating that the electrons observed on the microsecond and longer timescales are unreactive toward Na₂S₂O₈ reduction, and by extension, the more thermodynamically challenging proton reduction. As such, we conclude that all reactive electrons are transferred from GaN:ZnO to Rh_{2-y}Cr_yO₃ on the fast sub- μ s timescales. Indeed, the lack of electron scavenging by Na₂S₂O₈ for GaN:ZnO/Rh_{2-y}Cr_yO₃ samples (Figures S5B and S18) demonstrates that electron transfer to Rh_{2-y}Cr_yO₃ kinetically outcompetes electron scavenging. In line with these results, PIAS experiments also showed no changes for GaN:ZnO/Rh_{2-y}Cr_yO₃ when Na₂S₂O₈ was added (Figures S15 and S17).



Figure S1. Comparison of the tr-PL decays of GaN:ZnO in argon purged H_2O taken with pulsed excitation (404 nm, ~ 100 pJ/cm²) and continuous wave (CW) excitation (359 nm, 1.4 mW/cm²), monitored at 710 – 715 nm.



Figure S2. TAS spectra of GaN:ZnO samples in H_2O without cocatalyst (left) and with cocatalyst (right) following 355 nm laser pulse excitation (320 μ J/cm²). Delay times are indicated in the legend.



Figure S3. TAS kinetics monitored at 900 nm of GaN:ZnO (black) and GaN:ZnO/Rh_{2-y}Cr_yO₃ (red) in H₂O following 355 nm laser pulse excitation (320 μ J/cm²). Data is plotted on log-log axes to emphasise the power law decay. Linear slopes correspond to the power law exponent: $I \propto t^{-\alpha} \Rightarrow \log(I) \propto -\alpha \log(t)$.



Figure S4. TAS kinetics at 900 nm of GaN:ZnO samples A) without and B) with cocatalyst in H_2O . The samples were photoexcited by 320 μ J/cm² 355 nm laser pulses under no additional background illumiation (black) or with a constant LED irradiation of 10 mW/cm² at 365 nm (red).



Figure S5. TAS kinetics at 900 nm of GaN:ZnO samples A) without and B) with cocatalyst in H_2O (black) and in aqueous $Na_2S_2O_8$ (red). Transients were initiated by 320 μ J/cm² 355 nm laser pulses. The samples were also irradiated by a constant LED irradiation of 10 mW/cm² at 365 nm.



Figure S6. Calibrated Clark electrode response for H_2 (black) and O_2 (red) production under photocatalytic water splitting by GaN:ZnO/Rh_{2-y}Cr_yO₃. Two 45 s irradiation pulses (23 mW/cm²) are highlighted in blue. The average step size before and after the two pulses is used to calculate the gas production rates.



Figure S7. Rate law analysis of overall water splitting. The O_2 production rate is plotted as a function of the optical signal observed at 610 nm after 45 s of LED irradiation at different excitation intensities for GaN:ZnO/Rh_{2-y}Cr_yO₃ in H₂O.



Figure S8. Normalised 610 nm PIAS traces of GaN: $ZnO/Rh_{2-y}Cr_yO_3$ in H₂O under varying 365 nm excitation intensity. Traces were normalised to the amplitude at the end of the 45 s irradiation.



Figure S9. Correlation between the rate of H_2 production and the PIAS optical amplitude at 610 nm. GaN:ZnO/Rh_{2-y}Cr_yO₃ samples were submerged in H₂O (black), 10 mM KI (red), 10 mM Na₂S₂O₈ (green), or 10 mM H₂O₂ (blue). 10 mW/cm² 365 nm excitation was used. Rate of H₂ production is normalised to the value obtained in H₂O.



Figure S10. TAS kinetics at A) 510 nm and B) 900 nm of GaN:ZnO samples without cocatalyst in H_2O (black) and in aqueous $Na_2S_2O_8$ (red). Samples were excited by 320 μ J/cm² 355 nm laser pulses.



Figure S11. Comparison of the decay rates for different charge carrier densities based on the signal at 510 nm. Temporal evolution is indicated by the change in colour from green to red to blue. A dotted line is drawn at a decay rate of 1×10^{-2} % Abs/s.



Figure S12. Comparison of the decay rates monitored at 510 nm over time. The signal amplitude at 1 s is indicated with the legend in the top right corner. A dotted line is drawn at a decay rate of 1×10^{-2} % Abs/s.



Figure S13. TAS kinetics at 900 nm normalised to the amplitude at 5 μ s of GaN:ZnO samples without cocatalyst in H₂O (black), MeCN (red) and in aqueous Na₂S₂O₈ (blue). Samples were excited by 320 μ J/cm² 355 nm laser pulses.



Figure S14. TAS kinetics at 900 nm normalised to the amplitude at 5 μ s of GaN:ZnO/Rh_{2-y}Cr_yO₃ samples in H₂O (black), MeCN (red) and in aqueous Na₂S₂O₈ (blue). Samples were excited by 320 μ J/cm² 355 nm laser pulses.



Figure S15. Normalised 610 nm PIAS traces of GaN:ZnO/Rh_{2-y}Cr_yO₃ in H₂O (black), MeCN (red), and 10 mM aqueous Na₂S₂O₈ (blue) under 10 mW/cm² 365 nm excitation. Traces were normalised to the amplitude at the end of the 10 s irradiation.



Figure S16. Normalised PIAS spectra of GaN:ZnO samples without cocatalyst after 10 s of 365 nm LED irradiation (10 mW/cm²) for H_2O (black), MeCN (red), and aqueous $Na_2S_2O_8$ (blue) solvent conditions. Spectra were normalised to the value at 900 nm for the H_2O condition.



Figure S17. Normalised PIAS spectra of GaN:ZnO/Rh_{2-y}Cr_yO₃ samples after 10 s of 365 nm LED irradiation (10 mW/cm²) for H₂O (black), MeCN (red), and aqueous Na₂S₂O₈ (blue) solvent conditions. Spectra were normalised to the value at 900 nm for the H₂O condition.



Figure S18. TAS kinetics 900 nm of GaN:ZnO/Rh_{2-y}Cr_yO₃ samples in H₂O (black) and in aqueous Na₂S₂O₈ (red). Samples were excited by 320 μ J/cm² 355 nm laser pulses.