The Influence of Electron Donors on the Charge Transfer Dynamics of Carbon Nanodots in Photocatalytic Systems

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Abstract

Carbon nanodots are nanosized light-harvesters emerging as sustainable next-generation photosensitizers in photocatalytic reactions. Despite their ever-increasing potential applications, the intricate details underlying their photoexcited charge carrier dynamics are yet to be well-elucidated – specifically, the interactions of optically excited carbon nanodots with redox-active molecular species such as co-catalysts, mediators, and hole-scavenging additives known as electron donors. In this study, carbon nanodots are selectively excited in the presence of methyl viologen (MV$^{2+}$, redox mediator) and different electron donors applicable to solar fuel synthesis, namely ascorbic acid (AA) and ethylenediaminetetraacetic acid (EDTA). The consequent formation of the methyl viologen radical cation (MV$^+$) is investigated, and the excited charge carrier dynamics of the photocatalytic system are understood on a 0.1 ps to 1 ms time range. AA mediates the fast reduction of MV$^{2+}$, but the radical cation population is short-lived due to the reversibly oxidized AA quenching MV$^+$, explaining the limitation in photocatalytic activity when utilizing AA as an electron donor. EDTA-mediated reduction is at least two orders of magnitude slower due to screening by EDTA-MV$^{2+}$ complexes, but the radical cation population is stable due to the irreversibly oxidized EDTA preventing a back reaction. In general, our methodology provides a distinct solution with which to study charge transfer dynamics in photocatalytic systems on an extended time range spanning 10 orders of magnitude. This approach can generate a mechanistic understanding to select and develop suitable electron donors to promote photocatalytic reactions.
Carbon nanodots (CNDs) have emerged as promising next-generation photosensitizers for use in photocatalysis, in particular solar fuel synthesis, i.e. systems specifically designed to absorb and convert solar energy into various forms of chemical energy. Examples include H₂ solar fuel synthesis via H₂O splitting or solar reforming of biomass waste, alcohol synthesis via CO₂ reduction with H₂, or ammonia synthesis via N₂ reduction with H₂. Such promise is due to their favorable optical properties (broadband light absorption and efficient photoluminescence emission) and environmental friendliness (low toxicity, low-energy synthesis, low cost and high water solubility resulting in good biocompatibility), yielding a sustainable light-harvesting component with potential for large-scale production. CND photocatalyzed systems have displayed excellent activities (13,450 µmol H₂ g⁻¹ CND⁻¹ h⁻¹) in conjunction with a Ni bis(diphosphine) co-catalyst (NiP) under simulated solar light (AM 1.5G, 100 mW cm⁻²), and high turnover frequencies for CO₂ reduction (3.5×10³ h⁻¹) in conjunction with formate dehydrogenase under simulated solar light. CNDs have even been employed as photocatalysts to drive organic transformations, such as fluoroalkylation and epoxide ring-opening. As such, further improvements in performance through mechanistic understanding are desirable for CNDs to reach their full range of applications.

In general, significant activity enhancement is best pursued via “bottom-up” characterization that elucidates mechanisms governing the various reaction rates relevant to processes underlying the photocatalytic cycle. For instance, dynamic studies of CNDs have utilized time-resolved photoluminescence (PL) spectroscopy and transient absorption (TA) spectroscopy to gain insight into the optoelectronic excited state behavior of CNDs; a physicochemical property of CNDs that influences their photocatalytic performance. Another important aspect to consider for their improvement is how other components of photocatalytic systems, such as electron donors (EDs) and molecular co-catalysts, influence the charge-transfer behavior of photoexcited CNDs. These interactions are pivotal to photocatalytic activity and can be tracked via spectroscopic techniques offering sufficient temporal and spectral range, in addition to sensitivity. Despite the information gleaned from previous work in this field, there is still much to be learnt about the physicochemical
properties of CNDs, e.g. the fundamental origin of CND photoluminescence is a still a topic of debate, and how interactions between other components in photocatalytic systems influence their performance in photocatalytic systems. In part, this is due to prior investigations lacking sensitivity to dynamic processes through the 5 ns to 10 μs temporal domain.\textsuperscript{9,20}

To uncover the physical mechanisms governing behavior in CND-based photochemistry, TA spectroscopy has been performed in this study in the sub-picosecond to millisecond range together with steady-state and time-resolved PL spectroscopy to investigate the electron transfer dynamics governing the photocatalytic behavior of different CND-ED combinations in the presence of methyl viologen (MV$^{2+}$). MV$^{2+}$ was chosen owing to its suitability as an indicator for electron transfer processes due to the distinct visible absorption signature it displays upon forming a reversible, singly-charged radical cation upon reduction (MV$^{++}$), in addition to its utilization as an electron relay co-catalyst in classic artificial photosynthesis systems.\textsuperscript{23–25} We examine the distinct CND-based charge transfer processes observed in the presence of different EDs and discuss the repercussions for high-performance applications in light of the potential experimental issues relevant to the study of these systems, including photodegradation and atmospheric effects. Here, we focus on nitrogen-doped graphitic carbon nanodots (NgCNDs) as photosensitizers, as they display superior ultraviolet and visible light absorption compared with amorphous carbon nanodots (aCNDs; see UV-Vis spectra - Figure S1), together with superior photocatalytic activity relative to both aCNDS and graphitic carbon nanodots without nitrogen doping (gCNDs).\textsuperscript{20}

Figure 1a shows the steady-state PL spectrum of NgCNDs in aqueous solution (0.25 g/l). Figure S2 shows the excitation dependence on the PL spectrum together with the emission dependence on the PL decay curves. The addition of hole scavenging molecules of ethylenediaminetetraacetic acid (EDTA; 0.1 M) and ascorbic acid (AA; 0.1 M) has a different influence on the PL; EDTA causes no spectral or intensity changes to the dot PL, while AA causes significant PL quenching. This quenching is concomitant with faster decay of the time-resolved PL signal from the sample with AA (Figure 1b). PL decay curves are fitted with a stretched exponential function reflecting the heterogeneity in transitions
Figure 1: Optoelectronic characteristics of nitrogen-doped graphitic carbon nanodots (NgCNDs) in aqueous solution (0.25 g L⁻¹) with the sacrificial electron donors ethylenediaminetetraacetic acid (EDTA) and ascorbic acid (AA). (a) Photoluminescence spectra for NgCNDs (black), NgCNDs and EDTA (0.1 M; red), and NgCNDs and AA (0.1 M; blue) under continuous wave excitation (400 nm). (b) Normalized time-correlated single photon counting (TCSPC) curves for the same sample configurations under pulsed excitation (404 nm). Solid lines are stretched exponential fits to the normalized kinetic (see Supplementary Note 1). Inset: fitting parameters (τ and β) with associated error bars, for each sample. (c) Long-time (ns – ms) spectrally averaged (530 – 770 nm) transient absorption kinetics for NgCNDs in aqueous solution, and with added EDTA and AA, under 400 nm pulsed excitation (see methods). (d) Long-time spectrally-averaged (530 – 770 nm) TA kinetics under 355 nm pulsed excitation (see methods).
from which luminescence originates (see Supplementary Note 1). EDTA has no appreciable influence on the characteristic decay parameter (τ) or heterogeneity parameter (β) but AA reduces τ by 30% and increases β by 14%. This increased quenching rate and reduction in “disorder” (increasing β) is suggestive of slower radiative transitions being preferably influenced by the introduction of AA.

To complement the picosecond PL study, and before introducing any redox mediators, picosecond TA was used to confirm the ultrafast carrier dynamics and relaxation processes of the NgCNDs. Figures S3a and S3b show the three-dimensional TA data obtained from NgCNDs (0.25 g/l) dispersed in water at two different laser fluences (i.e., Figure S3a – 14 µJ cm⁻²; Figure S3b – 140 µJ cm⁻²), with water-only TA data shown for comparison (Figure S3c). In both cases, a characteristically broad photo-induced absorption feature is exhibited across the full spectral range of our probe (510-775 nm – Figures S3a-e), decaying considerably over tens of picoseconds (Figure S3d). This positive transient is the signature of multiple optically-allowed transitions from newly-populated excited states to higher excited states of the NgCNDs and is consistent with that measured via steady-state UV-Vis absorption spectroscopy. The photo-induced absorbance feature decays within the region 510-775 nm and approximately ca. 7.5% of the initial signal intensity remains after 1 ns (Figure S3g). The decay kinetic of the NgCND absorbance feature within this range is also independent of excitation pulse fluence (Figure S3f), indicating it is governed by some first-order relaxation process within the fluence range investigated. A closer examination of the spectrally-integrated kinetics reveals that the relaxation rate of the absorbance feature deviates slightly at the high energy edge of our probed spectral region (515-520 nm; see Figure S3h and Supplementary Note 1 for fitting function). These distinct kinetics might indicate respective relaxation at bulk and surface states of the carbon dots. Surface states have been identified as facilitating PL decay in carbon dots, but the longer carrier lifetimes from PL measurements (cf. Figure 1) suggest that a proportion of the TA decay may be linked to fast carrier trapping or an alternative nonradiative relaxation process, with both phenomena attributed to CND bulk states.

At timescales of more relevance to charge transfer in photocatalytic applications through diffusion-controlled mass transport (> ns), the TA data shows distinct features, which correlate with different
physicochemical properties of the CNDs than those attributed to ultrafast relaxation processes (<< ns). Figure 1c shows the long-time (pump-probe delay from ns to ms) spectrally averaged TA data for NgCNDs in aqueous solution with and without the presence of EDs (i.e., EDTA and AA) excited by 400 nm pulses. The ultrafast relaxation is contained within the instrument response for this configuration (> 500 ps). In all cases, the rapid relaxation of the NgCND continues for 10 ns before a more gradual relaxation takes over, likely trap mediated. The initial rapid decay in Figure 1c is likely related to the fluorescence decay times observed (cf. Figure 1b), with both displaying faster rates of decay when EDs are present.

The addition of the EDs EDTA (pH 8) and AA (pH 4.5) have distinctly different effects on the relaxation of the CNDs, depending on pump excitation wavelength. With 400 nm excitation, both EDs slightly quench the photoinduced absorption of the dots and reduce the lifetime of the latter decay, but little difference is observed between the EDTA and AA samples (Figures 1c and S4g-h). However, distinct differences are observed upon 355 nm excitation (Figure 1d). For the case of EDTA, a more rapid initial quenching of the CND absorption within 30 ns of excitation is followed by a rise in the photoinduced absorption (PIA) before the decay resumes at >3 μs. Conversely, NgCND relaxation is more delayed in the presence of AA for the first 20 ns, with subsequent faster quenching of the absorption feature. EDTA is a reductive quencher, which will fill the photoexcited hole of the dot before any further charge transfer processes take place. As timescales below 100 ns are short for electron transfer processes to occur from the EDs to the dots, the rise in PIA observed at ca. 30 ns in the presence of EDTA could be due to the formation of a charge transfer complex between the NgCNDs and EDTA. This could be facilitated by the presence of ED molecules (which are in large excess of the dot population) affecting trapping and recombination through electrostatic or van der Waals interactions perturbing the surface state energies - as may also be the case for AA, which appears to screen surface trapping on nanosecond timescales before contributing to quenching at later times. As such, the ns-μs quenching of the dot PIA can be linked to this electron donation, providing evidence that kinetics in this regime are related to photoexcited holes.20
As an indicator of charge transfer in photocatalytic systems owing to its distinctive absorption bands in the visible region, the methyl viologen dication (MV$^{2+}$) was added in a concentration series to consistent concentrations of the dots (0.25 g/l) and AA (0.1 M) at pH 4.5 and the TA spectra subsequently recorded. MV$^{2+}$ has been studied previously in steady-state, in-fiber UV-Vis investigations for electron transfer processes underlying CND-based photocatalytic systems used for hydrogen generation$^{21,22}$ and as such, was deemed suitable for similar purposes for the TA experiments. Figures 2a-c show the ns-ms TA data whereby the MV$^{2+}$ concentration is increased by an order of magnitude for each sample (see Figures S5a-c for intermediate concentrations). A new PIA feature is observed in the range 530-700 nm for all MV$^{2+}$-containing samples (Figure 2d), rising between $\sim$300 ns (high concentration) and $\sim$30 µs (low concentration), and decaying towards the end of the millisecond time range (Figure 2e). The spectral shape of this new absorption feature, which peaks at 600 nm, is characteristic of the methyl viologen radical cation (MV$^+$) and is consistent across the concentration series (slice extract at pump-probe delay of 100 µs - see Figures 2d and S5c).$^{27,28}$ The sub-100 ns relaxation of the NgCNDs appears unaffected by MV$^{2+}$ concentration (see Figures 2e and S5d).

Oxidative quenching is a possible model for this radical cation formation, particularly since viologens are known to support oxidative quenching.$^{9,29}$ Specifically, a photoexcited dot directly transfers an electron to the MV$^{2+}$ molecule before the remaining photoexcited hole is scavenged by the AA molecule. We expect this second process to occur faster than reductive quenching (as is the case for EDTA), which would be temporally limited by the initial ED hole scavenging.

Given the emergence of the MV$^+$ absorption band when AA is used as an ED, the kinetics of the concentration series can be examined, thus allowing for a better characterization of the NgCND-MV$^{2+}$ interaction. In general, from Figure 2e we find both the onset and the peak time of the MV$^+$ PIA to shift to earlier pump-probe delay with increasing concentration of MV$^{2+}$. The maximum signal of the PIA increases by a factor of 5 with a 100x increase in concentration (see Figures 2e and S5d). This will be influenced by the competition of reduction and relaxation, which also appears to increase in rate with concentration. The initial reduction reaction rate for MV$^{2+}$ to MV$^+$ is extracted from the PIA onset, to
Figure 2: Transient absorption of nitrogen-doped graphitic carbon nanodot / ascorbic acid / methyl viologen dication system showing microsecond generation and quenching of methyl viologen radical cation. (a-c) Three-dimensional TA data for NgCNDs (0.25 g L\(^{-1}\)) in aqueous solution with AA (0.1 M) and MV\(^{2+}\) added in a concentration series at the labelled molarities. (d) Normalized TA spectral slices extracted at a pump-probe delay of 100 µs, for varying MV\(^{2+}\) concentration. (e) Spectrally averaged (530 – 700 nm) kinetics for the MV\(^{2+}\) concentration series (normalized). The black dashed arrow indicates the trend of the MV\(^{+}\) radical absorption feature towards earlier time and higher intensity. (f) Growth kinetics of the MV\(^{+}\) radical absorption feature showing an increasing initial reaction rate with MV\(^{2+}\) concentration. Inset: Analysis using Equation 2 reveals a first-order reaction rate dependence on MV\(^{2+}\) concentration.
confirm the reaction order (see Figure 2f). The reaction rate is a power law described as:

\[
\text{Rate} = k[C_{\text{dot}}]^m[C_{\text{MV}}]^n
\]  

(1)

where \( C_i \) is the concentration of the reactant \( i \), \( m \) and \( n \) are the exponents dictating the order of each reactant, and \( k \) is the rate constant. Holding the dot concentration constant and taking natural logarithm of equation 1 we determine the rate order of \( \text{MV}^{2+} \) \( (n) \) with the following linear relationship:

\[
\ln(\text{Rate}) = \ln(A) + n \cdot \ln(C_{\text{MV}})
\]  

(2)

where \( A \) is the constant term \( k[C_{\text{dot}}]^m \). The slope extracted from the Figure 2f fit is \( 1.20 \pm 0.05 \) indicating the dependence of reaction rate on \( \text{MV}^{2+} \) concentration is approximately first order.

The decay of the \( \text{MV}^{+} \) population on sub-ms timescales is inconsistent with the expected lifetime of these cations whose population should build up under an average UV irradiance of \( \sim 240 \, \text{mW} \, \text{cm}^{-2} \). The subsequent decay should span minutes when quenched by oxygen,\(^{27} \) or significantly longer timescales when shielded from air (as in our \( \text{N}_2 \)-purged setup).\(^{28} \) Diffusion of \( \text{MV}^{+} \) out of the probed volume within 1 ms is precluded by the insufficient diffusivity of water.\(^{30} \)

One explanation for the premature quenching could be that back electron transfer occurs from \( \text{MV}^{+} \) to oxidized products of AA,\(^{31-33} \) quenching the PIA rapidly due to the 250-25,000× excess of AA in solution. Dehydroascorbic acid (DHA) is a product of AA oxidation, which is produced via two-electron and two-proton transfer (see Figure 3c).\(^{34} \) DHA formation is energetically more favorable under alkaline conditions where the initial \( \text{H}^+ \) concentration is low.\(^{35,36} \) We find that the evolution of \( \text{MV}^{+} \) radical is modified by the solution pH (see Figure 3a), with the formation of \( \text{MV}^{+} \) confirmed by the identical spectral signatures shown in Figure S6. The onset and initial reaction rate are consistent, suggesting that these are only concentration dependent. However, the quenching decay time of the radical cation population decreases from \( \sim 500 \, \mu\text{s} \) at pH 4.5 to 200 \( \mu\text{s} \) at pH 8.0, suggesting the increased presence of DHA could trigger rapid re-oxidation of the \( \text{MV}^{+} \) radicals (see Figures 3b). The schematic Figure 3c illustrates the formation of DHA as part of the electron donation process to CNDs.
Figure 3: Investigating ascorbic acid degradation as the primary influence on MV⁺* quenching. (a) Spectrally integrated (530 – 700 nm) TA kinetics of the NgCND (0.25 g L⁻¹) / AA (0.1 M) / MV²⁺ (40 µM) system, at varying pH. Kinetics are normalized to the peak of the MV⁺*-related signal. (b) Decay kinetics of the MV⁺*-related signal. Dotted lines are fitted mono-exponential decays. (c) Schematic of DHA formation (denoted ‘A’') during the AA oxidation cycle on sub-millisecond timescales (starting with the singly deprotonated form of AA, i.e. HA⁻). (d) Spectrally integrated (530 – 700 nm) TA kinetics of the same configuration at pH 4.5 with the addition of tris(2-carboxymethyl)phosphine (10 mM and 100 mM).
To explore the role of DHA as an oxidizing agent for MV \(^+\), tris(2-carboxyethyl)phosphine (TCEP) is added to the NgCND-MV-AA solution (10 mM, 100 mM). TCEP is a reducing agent which reduces DHA back to AA, reversing the degradation pathway and preventing the build-up of any significant DHA concentration.\(^{33,37}\) Intriguingly, the addition of TCEP leaves the TA kinetics qualitatively unchanged (see Figure 3d and S6). The appearance and decay of the radical cation signature occur on similar timescales to the systems employing only AA, despite TCEP being added in the same molarity ratio (1:1) that has yielded efficient performance in multiple photocatalytic systems.\(^3,37\) The role of DHA in quenching MV \(^+\) is thus unconfirmed, but the short-lived radical can be rationalized with steady-state absorption measurements which do reveal a difficulty in building up any MV \(^+\) population over illumination periods of minutes when AA is used as the ED.

Having explored the transient kinetics with AA as an ED, the transient kinetics with the same photocatalytic system but with a different ED, \textit{i.e.} EDTA, were also investigated for comparative purposes. Figures 4 and S7 show the TA kinetics of an MV\(^{2+}\) concentration series in the NgCND-EDTA-MV\(^{2+}\) configuration. As with the AA configuration, the NgCND PIA dominates for up to 1 \(\mu\)s after excitation. At later times, the emergence of an MV \(^+\) PIA signature is only weakly observed at high concentrations (see Figure 4a), contrary to the AA case. Figure 4b shows kinetic plots from samples with no MV\(^{2+}\), low concentration (12 \(\mu\)M), and high concentration (120 \(\mu\)M). The combination of EDTA and MV\(^{2+}\) appears to increase the quenching rate of the excited state dot, but only in the high concentration sample is a subsequent MV \(^+\) signal observed (indicated by the black arrow in Figure 4d). Kinetic plots from all concentrations are shown in Figure S7. Low concentrations (MV\(^{2+}\) \(\leq\) 40 \(\mu\)M) show minimal alteration from the sample without any MV\(^{2+}\). High concentrations (MV\(^{2+}\) \(\geq\) 120 \(\mu\)M) see a drop in absorption in the 10 \(\mu\)s range followed by a recovery in absorption at 100 \(\mu\)s. This recovery is assigned to slower MV \(^+\) radical formation than in the configuration with AA.
Figure 4: Slow EDTA-mediated charge transfer is accelerated at high methyl viologen concentration and low pH. (a) 3D TA data for NgCND / EDTA / MV system with 120 µM MV$^{2+}$. White dashed region of interest marks suspected presence of MV·+ radical photoinduced absorption rise at >10 µs. (b) Comparison of spectrally-averaged (530 – 760 nm) kinetics from selected samples from MV$^{2+}$ concentration series. (c,d) TA spectra at several pump-probe delay times for system with (c) 12 µM and (d) 120 µM MV$^{2+}$. Black arrow indicates radical absorption peak in the characteristic wavelength range, at 100 µs.
Overall, these data fit with the picture of reductive quenching. The EDTA has a consistent effect on the TA kinetics at early time across each sample but no transfer or reduction of MV$^{2+}$ is observed because this must occur on longer timescales, as is consistent with the reductive quenching of NgCNDs in the presence of EDTA and the DuBois-type catalyst NiP, i.e. EDTA reduces excited state CNDs on ns – μs timescales, with subsequent reduction of the DuBois-type catalyst by reduced CNDs on μs – ms timescales. Given that hole scavenging by EDTA happens in the ns-μs range (cf. Figure 1), NgCND-MV$^{2+}$ interactions are likely screened by EDTA complexes forming with MV$^{2+}$ and/or on the dot surface. In high MV$^{2+}$ concentration samples, the 100 μs absorption rise at ∼600 nm suggests this screening might be surmountable within the 1 ms time range (see Figures 4b-d and S7). The absorption drop at 10 μs is thus linked to the initialization of the NgCND-MV$^{2+}$ transfer.

A notable difference for the EDTA system is that rapid re-oxidation of any MV$^{+}$ is not expected other than via oxygen infiltration, meaning that the background (time-zero) population of MV$^{+}$ will build up over time, often over several minutes. TA kinetics for the NgCND-MV$^{2+}$-EDTA system does depend on the measurement period in the extreme case of the sample being exposed for 10× the typical period (Figure S8). Long pump laser exposure smooths out the absorption profile relative to that of a fresh sample. As well as establishing a background population of radicals, this level of exposure may trigger photobleaching of the methyl viologen, rendering it inactive within the photocatalytic system. This is less likely since methyl viologen is known to be stable through several photoluminescence and electroluminescence measurement cycles.

To summarize, TA has been used to probe the excited state dynamics of NgCND-based photochemistry. Intriguingly, the choice of ED is determined to be crucial for dictating the reaction kinetics for a particular absorber and acceptor. This influence is not limited to directing a particular quenching mechanism (reductive or oxidative), but also highlights that complexes or degradation products of EDs can support or inhibit the build-up of intermediates, e.g. such as the MV$^{+}$ population. The NgCND-MV$^{2+}$-AA photocatalytic system promotes prompt formation of MV$^{+}$, most likely by oxidative quenching, but cannot maintain this population due to (detrimental) re-oxidation by degradation products such as DHA. Meanwhile, the NgCND- MV$^{2+}$-EDTA system does not see radical formation.
on sub-ms timescales due to an electrostatic screening effect, again attributable to the ED. However, this system is known to support longer term radical formation. Future work will expand this investigation to include other EDs such as triethylamine (TEA) and triethanolamine (TEOA), which are versatile and have been widely applied in configurations for solar fuel chemistry. Beyond solar fuel chemistry, this study highlights the importance of understanding the formation of ED complexes and degradation products in the design of efficient photocatalytic systems.
Experimental Methods

Sample preparation

All chemicals and reagents were purchased from commercial suppliers and used as received unless otherwise noted. Laboratory-grade reagents were used for synthesis, and chemicals for the analytical part were of the highest available purity. Phosphate buffer solutions (0.2 M) and electron donor (ED) stock solutions (0.2 M) were prepared and verified using a pH electrode (Mettler Toledo, FiveEasy Plus) at pH 6 and pH 8. The pH of ED stock solutions was adjusted using sodium hydroxide and hydrochloric acid. A methyl viologen (MV$^{2+}$) stock solution was made up by dissolving methyl viologen dichloride. All stock solutions were made up using Milli-Q purified water.

Nitrogen-doped graphitic carbon nanodots (NgCDs) were synthesized by pyrolysis of aspartic acid at 320 °C. All syntheses and characterization were carried out as previously reported.$^{20}$

For all spectroscopic measurements, NgCNDs (0.25 g/l) were dispersed in aqueous solution. Electron donors ethylenediaminetetraacetic acid (EDTA; 0.10-0.19 M) and ascorbic acid (AA$^-$; 0.1-0.19 M) were added as detailed in the manuscript. For probing photocatalytic activity, the redox indicator methyl viologen (MV$^{2+}$) was added in various molar volumes to alter the NgCND:MV$^{2+}$ ratio in solution. Phosphate buffer was used with EDTA to maintain a constant pH.

Sample solutions were deposited under ambient conditions in a quartz cuvette (1 mm pathlength, Hellma), sealed with a screw cap. During transient absorption measurements, samples were continuously purged with nitrogen to minimize the oxygen content within the cuvette. Samples were prepared directly before measuring unless specified (cf. degradation study).

UV-vis absorption

UV-vis absorption measurements were carried using a Cary 300 UV-Vis spectrophotometer.

Photoluminescence and Time-correlated single photon counting (TCSPC)

Steady-state and time-resolved photoluminescence measurements were carried out using an Edinburgh Instruments FLS 1000 Photoluminescence Spectrometer.
Transient absorption spectroscopy

Short-time (100 fs - 2 ns) transient absorption measurements were carried out using the second harmonic of a Ti:sapphire amplifier (Spectra-Physics Solstice) as the pump beam (90 fs pulse width, 500 Hz repetition rate, 3.1 eV photon energy). The probe spectrum was generated using a home-built noncollinear optical parametric amplifier, pumped by the second harmonic of the same Ti:sapphire amplifier. A motor-driven delay stage was used to mechanically vary the pump-probe delay.

Long-time (ns – ms) transient absorption measurements were carried out in two different configurations:

- Configuration 1: The third harmonic of an electro-optical Q-switched laser (InnoLas picolo AOT) was used as the pump beam (< 800 ps pulse width, 500 Hz repetition rate, 3.49 eV photon energy). The probe spectrum was generated using a home-built noncollinear optical parametric amplifier, pumped by the second harmonic of the aforementioned Ti:sapphire amplifier. A delay generator was used to electronically vary the pump–probe delay.

- Configuration 2: The second harmonic of a Ti:sapphire amplifier (Spectra-Physics Solstice) was used as the pump beam (90 fs pulse width, 500 Hz repetition rate, 3.1 eV photon energy). The probe spectrum was generated by a broadband supercontinuum source (Leukos Disco). A delay generator was used to electronically vary the pump–probe delay.
Supporting Information Available: Supplementary Notes, Figures and Tables are provided in the separate Supporting Information file.

Author Information and Notes

S.D.S. is a co-founder of Swift Solar.

Author contributions

S.M. performed and analyzed transient absorption and photoluminescence measurements, interpreted data, and drafted the manuscript. T.L. fabricated samples, performed UV-Vis absorption measurements, interpreted data and drafted the manuscript. P.A. performed transient absorption measurements. A.A. performed photoluminescence measurements. A.L. fabricated samples. A.G. supervised the project, fabricated samples, interpreted data, and drafted the manuscript. E.R., T.E. and S.D.S. supervised the project, interpreted data, and drafted the manuscript. All authors contributed to finalizing the manuscript and figures.

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