Clean Donor Oxidation Enhances H₂ Evolution Activity of a Carbon Quantum Dot-Molecular Catalyst Photosystem

Benjamin C. M. Martindale,[a] Evelyne Joliat,[b] Cyril Bachmann,[b] Roger Alberto,[b] and Erwin Reisner*[a]

Abstract: Carbon quantum dots (CQDs) are new-generation light absorbers for photocatalytic H₂ evolution in aqueous solution, but the performance of CQD-molecular catalyst systems is currently limited by the decomposition of the molecular component. Here, we demonstrate that clean oxidation of the electron donor via donor recycling prevents the formation of destructive radical species and non-innocent oxidation products. This approach allowed a CQD-molecular Ni bis(diphosphine) photocatalyst system to reach a benchmark lifetime of more than five days and a record turnover number (TON) of 1094 ± 61 mol/(mol) for a defined synthetic molecular Ni catalyst in purely aqueous solution under AM1.5G solar irradiation and 825 ± 183 under visible-only light.

Carbon quantum dots (CQDs) have recently emerged as an exciting new allotrope of carbon due to their optical properties of UV-visible light absorption and fluorescence. Their fluorescent properties have found use in a variety of applications from biosensing and fluorescence probes to chemical sensing and light-emitting devices.[1–5] More recently, their light absorption properties have also been utilized for photocatalytic applications such as the co-sensitization of metal oxides in solar cells, photodegradation of organic dyes and as a photosensitizer in solar fuel synthesis.[6–13]

A recent study showed that carboxylate-terminated amorphous CQDs produced from a bottom-up synthetic method could photosensitize the water-soluble molecular Ni H₂ evolution catalyst NiP (Figure 1).[15] This unique example of a CQD–molecular catalyst hybrid system made use of a sacrificial electron donor (ethylenediaminetetraacetic acid, EDTA) to quench the holes formed on formation of the photoexcited state, but only achieved a final TON₄ of 64 with a lifetime of 4 h due to degradation of NiP during catalytic turnover and/or decomposition by the unwanted products of the overall reaction scheme, in this case the oxidation products of EDTA.

Sacrificial electron donors (and acceptors) have been used extensively to isolate a half-reaction in photocatalytic reactions due to the difficulty of coupling catalysts and conditions required for a full redox cycle.[14] Triethanolamine (TEOA), triethyamine (TEA) and EDTA are commonly used sacrificial electron donors, but they undergo one-electron oxidations resulting in potentially destructive radical species. Ascorbic acid (AA) is a known proton and electron donor, but its oxidation product, dehydroascorbic acid (DHA), is known to self-inhibit the electron donor ability of AA.[15] As an effectively unlimited resource, H₂O is often considered the ideal donor molecule. However, its oxidation produces intermediates such as the reactive oxygen species OH⁻ and H₂O₂ and even the final product O₂ can prove damaging to the components of the reductive half reaction.[15] NiP was shown to be irreversibly inhibited by O₂ due to the oxidation of the phosphine ligands.[16–18] Further, even in cases where O₂ is not malevolent to the system, it would rarely be considered a commercially useful product and requires separation from mixtures of gaseous products.

Donor-recycling System Used in This Study

Figure 1. Schematic representation of solar H₂ production using CQD-NiP. The electron donor systems, TCEP/NaAsc or EDTA, quench the photoinduced vacancies in the CQDs, but EDTA forms radicals upon its oxidation and causes decomposition of the catalyst and cessation of H₂ evolution. DHA recycling by TCEP prevents the formation of large quantities of reactive oxidation products. Two bromide anions in NiP are omitted for clarity.

A suitable electron donor for a photocatalytic scheme should generate an oxidized product that is stable and innocent, causing no adverse effects on the components of the system. A donor system consisting of AA (proton/electron relay) and tris(carboxyethyl)phosphine (TCEP) has been previously shown to extend the lifetime of a solar H₂ production system using molecular Ru and Re dyes improving performance by 2–3 times by preventing electron back-transfer from the photosensitizer to DHA.[19] Here, we employ this donor system to avoid the formation of intermediates/products, which are...
destructive to the molecular catalyst component and report a record performance of the CQD–NiP photocatalyst system.

Carboxylate-terminated amorphous CQDs (7 nm diameter), NiP (Figure 1), and the Co catalysts 1 to 3 (Figure 2) were synthesized according to established procedures.\cite{13,20,24} The water-soluble DuBois-type catalyst NiP is active in aqueous electrocatalytic and photocatalytic schemes,\cite{22,25,26} whereas the majority of Ni-P-P complexes are active only in acidic organic solutions.\cite{27} NiP has a low overpotential (η = 200 mV) for H₂ evolution, which is a significant advantage when using photosensitizers with an excited state potential closely matched to the thermodynamic potential for proton reduction. When NiP is used in conjunction with a molecular ruthenium dye (E(RuP/RuP) = −1.08 V vs. NHE), a high initial H₂ evolution rate (TOFₜ₀ of 460 h⁻¹) but low stability (final TONₜ₀ of 723) is observed.\cite{22}

![Figure 2](image-url) Chemical structures of the molecular Co catalysts used in this work.

Photocatalytic systems comprising of CQDs as the photosensitizer with the catalyst NiP and the regenerating donor system TCEP/AA were assembled and placed under simulated solar light irradiation (100 mW cm⁻², AM 1.5G; Figure 3). The results support indeed that the CQD-NiP photocatalyst system is remarkably more stable in this donor than in EDTA, which can be attributed to the clean formation of the stable product TCEPO, which does not act to degrade NiP in contrast to the destructive radicals formed during EDTA oxidation (see Figure S1).\cite{28} The maximum catalytic rates (expressed in a TOFₜ₀ of 41 and 53 h⁻¹ for EDTA and TCEP/AA, respectively) are similar for both systems, but the activity decreases after the first hour in EDTA leading to a final TONₜ₀ of 64 ± 4, whereas the system in TCEP/AA continues almost linearly for around 24 h giving rise to a TONₜ₀ of 1094 ± 61, a 17-fold increase. This is a record TON for NiP,\cite{13,22,25} and indeed any water-soluble DuBois-type catalyst,\cite{29} achieved by replacing the most expensive component of the previous benchmark system, the ruthenium dye,\cite{22} with the low-cost, scalable and photo-stable CQDs. This CQD-NiP photosystem also achieves the highest turnover with a defined synthetic molecular nickel catalyst in purely aqueous solution and is competitive with the best-performing systems in molecular photocatalysis, which make use of toxic, expensive and fragile photosensitizers as well as organic co-solvents.\cite{30,31,32}

Although an impressive TONₜ₀ was previously reported in a photocatalytic scheme using thiol-capped CdSe QDs and Ni ions, this system suffers from toxicity, does not make use of a well-defined molecular catalyst and it uses a sacrificial ligand (displaced capping ligand) and electron donor.\cite{33}

Control experiments using either TCEP (0.1 M, pH 5) or AA/NaAsc (0.1 M, pH 5) alone showed much lower photoactivity (Figure S2). With AA/NaAsc the system stability was low (4 h) in agreement with the previous reports of DHA being re-reduced to AA by the photosensitizer creating a short circuit in the system (TOFₜ₀ 20 h⁻¹, TONₜ₀ 50). When only TCEP was used the stability was longer (> 12 h) but the initial rate of activity was slower (TOFₜ₀ 10 h⁻¹, TONₜ₀ 143). This suggests that although direct photo-oxidation of TCEP by CQD is possible, it is kinetically slower than AA oxidation and the primary quenching of photo-induced holes occurs by AA, followed by subsequent irreversible reduction of DHA back to AA by TCEP (Figure 1).\cite{34}

Proof that TCEP is the ultimate source of electrons in the photocatalytic system comes from quantitative analysis of the product TCEPO using ³ⁱP NMR spectroscopy. Time-resolved

![Figure 3](image-url) (a) H₂ generation using CQD (10 mg) and NiP (10 nmol) in aqueous solution containing TCEP/NaAsc (0.1 M each, pH 5, 3 mL, solid lines) under 1 sun UV-visible (λ > 300 nm, black lines) and visible-only (λ > 400 nm, green lines) irradiation as compared to the analogous systems in EDTA (0.1 M, pH 6, 3 mL, dashed lines). Inset: Zoom-in of first 4 hours. (b) Time-resolved H₂ and TCEPO formation using CQD (10 mg) and NiP (10 nmol) in aqueous solution containing TCEP/NaAsc (0.1 M each, pH 5, 3 mL) under 1 sun UV-visible (λ > 300 nm). (c) H₂ generation using CQD (10 mg) and NiP (10 and 100 nmol) in aqueous solution containing TCEP/NaAsc (0.1 M each, pH 5, 3 mL) under 1 sun UV-visible (λ > 300 nm). All experiments thermoregulated at 25 °C.
measurements confirmed a 1:1 ratio of H₂/TCEPO throughout the reaction (Figure 3b). These results also confirmed the presence of TCEPO as the only detectable product of TCEP oxidation in agreement with the quantitative and irreversible formation of TCEPO and no radical breakdown products (Figure S3). Thus, the products of reduction (H₂) and oxidation (TCEPO) can accumulate over prolonged periods of time in this closed photosystem in the gas and solution phase, respectively. The absence of apparent quenching of compensating half-reactions and clean product separation is remarkable and emphasizes the benefit of organic substrate oxidation rather than water oxidation in a single compartment. Classical water splitting would result in O₂ generation, which induces issues of product separation and interference with the reductive half-reaction.

A long lifetime of approximately 1 d is observed for this system with low catalyst loading (10 nmol). We subsequently studied the stability of NiP in TCEP/AA solution in the dark, under visible-light and under UV-visible solar irradiation by UV-vis spectroscopy (Figure S4). The absorption spectrum of NiP shows two bands: a weak band at 499 nm, characteristic of square-planar complexes and a stronger charge transfer band below 350 nm. Monitoring the peak at 499 nm reveals negligible loss of NiP in the dark or with visible-light irradiation (λ > 400 nm), but under UV-visible solar irradiation (λ > 300 nm) there is a 17% reduction in the NiP signal after 24 h (Figure S5), which is presumably due to ligand displacement from the metal center. The ligand substituted Ni²⁺ in TCEP/NaAsc solution is not an active catalyst as demonstrated by control experiments using NiCl₂ under these conditions (Figure S6). As a result of the higher NiP stability under visible-only irradiation the H₂-photosystem was also more stable, with linear performance for the first 2 d (TON₆₈ 825 after 3 d). The decreased H₂ evolution rate (TOF) with visible-only irradiation compared to under UV-Vis irradiation is due to decreased light absorption (Figure S7).

Other possible degradation pathways for NiP are degradation of the ligand framework during catalytic turnover or quenching of holes in the CQD excited state by NiP. The latter pathway is proved viable by the aforementioned capability of CQDs to oxidize the phosphine TCEP under irradiation (Figure S2). Hence, we infer that the phosphine ligands of NiP can also, albeit slowly, be oxidized in a similar way by holes in the presence of water (Figure S5). Oxidized NiP has also previously been formed by O₂ in solution and shown to be inactive as H₂ evolution catalyst. Nevertheless, decomposition of NiP by radical oxidation products in EDTA is the dominant pathway and hence when using the TCEP/AA donor system with stable oxidation product, TCEPO, the overall system lifetime of the CQD–NiP photosystem is vastly increased.

When using a 10 times higher loading of NiP the amount of H₂ produced during the first 24 h is the same as at lower loading, indicating that the optimal loading has been reached for the concentration of CQD and light intensity used (Figure 3c). However, the increased amount of NiP resulted in almost linear H₂ evolution over days and the system was still active when the experiment was halted after 5 d. This demonstrates clearly the long-lived stability of CQDs as light absorbing component in such photosystems; a significant advantage over organic and some precious-metal based molecular dyes which have poor photostability under solar irradiation.

Complexes 1, 2 and 3 are established cobalt H₂ evolution catalysts with polydentate sp²-nitrogen, pentapyridyl, pyrpyrinoid and dimine-dioxime ligands, respectively (Figure 2). Compounds 1 and 2 have been previously photosensitized only by high excited state potential molecular Re- and Ru-dyes due to the large overpotential of cobalt poly(pyridyl) complexes (η ≥ 800 mV) but the increased stability of these ligand frameworks lead to long-term activity over a period of days with a final TON₆₈ of 33,300 and 21,900, respectively. Catalyst 3 has a lower overpotential (η = 400 mV) than 1 and 2 but display a lower catalytic rate. Photocatalytic systems involving catalyst 3 hence showed a low maximum TON₆₈ of 90. These catalysts were employed to establish CQDs more widely as a general photosensitizer for molecular catalysts other than NiP and to examine the relationship between CQD and catalyst overpotential.

Analogous photocatalytic systems comprising of CQDs as photosensitizer with this series of Co catalysts were tested for solar H₂ production in the TCEP/AA donor system (Figure 4). All the systems performed with a significantly slower rate of H₂ production than those using the NiP catalyst, with the fastest rate observed using 1 (TON₆₈ of 8 h⁻¹). Complex 2, whilst slower, has greater stability and some activity persists even after 4 d irradiation, leading to similar final TON₆₈ in both cases (141 ± 13 and 120 ± 11 for 1 and 2, respectively). These systems also have lower performance compared to the same catalysts using precious-metal based molecular dyes, indicating that high driving force photosensitizers are required to gain best performance out of these high overpotential molecular Co catalysts. Complex 3 is shown to be an inferior catalyst with both a low initial rate and stability that only lasts about 24 h (TON₆₈ 56 ± 12). This overall performance is, however, broadly similar to that observed using high driving force Re-dyes due to the lower overpotential requirement of this catalyst type. The molecular mechanism of catalysis with the Co-based catalysts was
confirmed by control experiments with CoCl₂ and no catalyst where negligible H₂ was evolved (Figure S6).

Cyclic voltammetry of the soluble CQDs in aqueous solution showed a wave centered at around -550 mV vs. RHE, which corresponds to the potential of the CO/D/CO²⁻ couple (Figure S6).²² There is likely a heterogeneity of surface chromophores on the CQD, but this half-wave gives a rough estimate of the average redox potential and the thermodynamic driving force of a photoexcited electron in the CQD following the expected redox quenching of the charge separated excited state by the electron donor.¹⁹ An excited CQD (estimated average η ~ 550 mV for proton reduction) gives ample driving force for NiP (η ~ 200 mV) and 3 (η ~ 400 mV) to produce H₂, but limited driving force for the stable Co-based catalysts 1 and 2 (η > 800 mV). Hence, catalysts with an overpotential lower than that determined for the excited CQD (such as NiP and catalyst 3) display excellent performance, which matches or even succeeds that of Ru/Re dyes. The Co catalysts 1 and 2 on the other hand require a higher overpotential for catalysis and the catalytic rates are therefore slow. We have therefore unraveled an important selection criterion for catalysts to function with low-cost and scalable CQDs.

In summary, we report herein a hybrid photosystem, CQD–NiP, using the donor system TCEP/NaAsc with a benchmark photostability of over 5 d and a record TONₘ for photo-H₂ evolution of 1094 ± 61 with a defined synthetic molecular nickel catalyst in purely aqueous solution. Several cobalt catalysts were also successfully photosensitized using CQDs, demonstrating that CQDs can be widely used in conjunction with molecular catalysts for H₂ evolution and likely other fuel forming reactions. This study also revealed that the presented CQDs are ideally suited to sensitize low overpotential (η < 500 mV) catalysts, where comparable or greater TONs can be achieved, eliminating the need for high-exited state potential Ru/Re dyes.

The use of the TCEP/NaAsc donor system was key to unlocking this great potential as the clean two-electron oxidation of TCEP to TCEPO resulted in no inhibition of the system and prevented rapid radical decomposition of the catalyst observed with conventional sacrificial electron donors. This concept can be extended to incorporate valuable clean synthetic transformations in place of phosphine-phosphine oxide conversion, which will enable coupling of solar fuel with solar chemical synthesis. Future adaptation of the photosystem into a flow system through integration of the CQDs in a flow reactor will lead to efficient separation of gaseous and solution products.

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