Clean Donor Oxidation Enhances H_2 Evolution Activity of a Carbon Quantum Dot-Molecular Catalyst Photosystem

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Abstract: Carbon quantum dots (CQDs) are new-generation light absorbers for photocatalytic H_2 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_{H2} $(mol_{Ni})^{-1}$ 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 H_2-evolution catalyst **NiP** (Figure 1).[13] 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 TON_{Ni} 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), triethylamine (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, H_2O is often considered the ideal donor molecule. However, its oxidation produces intermediates such as the reactive oxygen species $OH^{\cdot}$ and H_2O_2 and even the final product O_2 can prove damaging to the components of the reductive half reaction.[16] **NiP** was shown to be irreversibly inhibited by O_2 due to the oxidation of the phosphine ligands.[16–18] Further, even in cases where O_2 is not malevolent to the system, it would rarely be considered a commercially useful product and requires separation from mixtures of gaseous products.

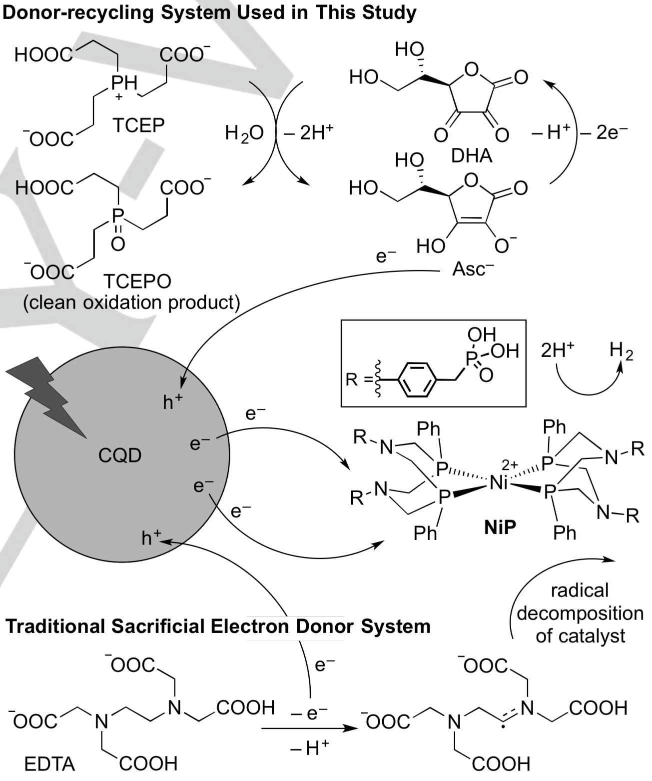

Figure 1. Schematic representation of solar H_2 production using CQD-**NiP.** The electron donor systems, TCEP/NaAsc or EDTA, quench the photoinduced vacancies in the CQDs, but EDTA forms radicals upon its oxidation and causes decomposition of the catalyst and cessation of H_2 evolution. DHA recycling 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 H_2 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

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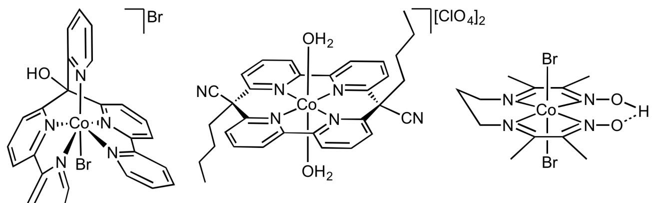
destructive to the molecular catalyst component and report a record performance of the CQD–**NiP** photosystem.

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.[13,20–24] The water-soluble DuBois-type catalyst **NiP** is active in aqueous electrocatalytic and photocatalytic schemes,[22,25,26] whereas the majority of Ni-P_2N_2 complexes are active only in acidic organic solutions.[27] **NiP** has a low overpotential ($\eta \approx 200$ mV) for H_2 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 H_2 evolution rate (TOF_{Ni} of 460 h^{-1}) but low stability (final TON_{Ni} of 723) is observed.[22]



1 **2** **3**

Figure 2. 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).[28] The maximum catalytic rates (expressed in a TOF_{Ni} 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 TON_{Ni} of 64 ± 4, whereas the system in TCEP/AA continues almost linearly for around 24 h giving rise to a TON_{Ni} of 1094 ± 61, a 17-fold increase. This is a record TON for **NiP**,[13,22,25] and indeed any water-soluble DuBois-type catalyst,[29] achieved by replacing the most expensive component of the previous benchmark system, the ruthenium dye,[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.[30–34] Although an impressive TON_{Ni} 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.[35]

Control experiments using either TCEP (0.1 M, pH 5) or AA/NaAsc (0.1 M, pH 5) alone showed much lower photoactivty (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 (TOF_{Ni} 20 h^{-1}, TON_{Ni} 50). When only TCEP was used the stability was longer (> 12 h) but the initial rate of activity was slower (TOF_{Ni} 10 h^{-1}, TON_{Ni} 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).[19]

Proof that TCEP is the ultimate source of electrons in the photocatalytic system comes from quantitative analysis of the product TCEPO using ^{31}P NMR spectroscopy. Time-resolved

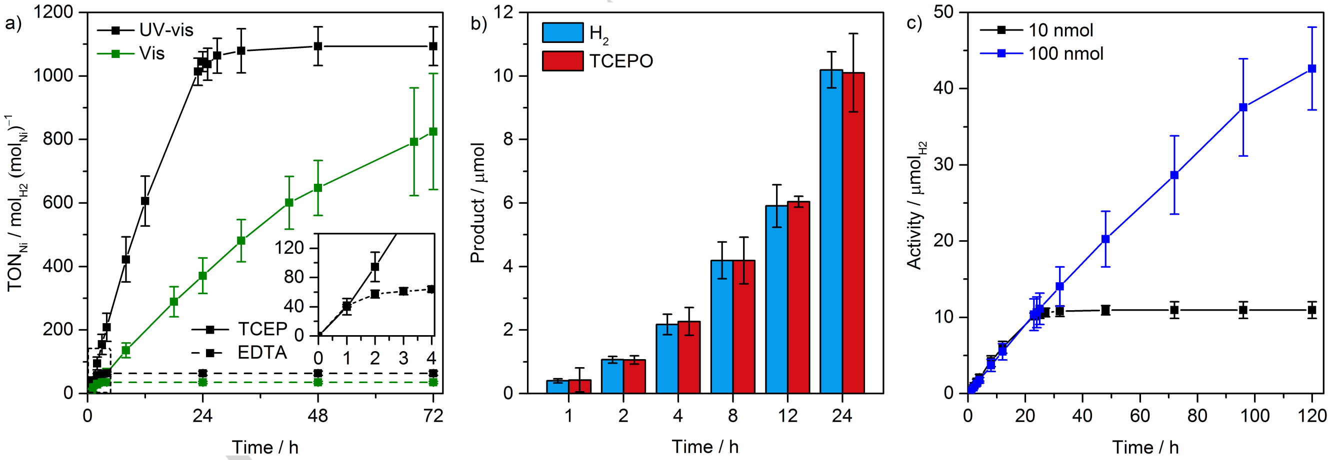


Figure 3. (a) H_2 generation using CQD (10 mg) and **NiP** (10 nmol) in aqueous solution containing TCEP/NaAsc (0.1 M each, pH 5, 3 mL, solid lines) under 1 sun UV-visible (λ > 300 nm, black lines) and visible-only (λ > 400 nm, green lines) irradiation as compared to the analogous systems in EDTA (0.1 M, pH 6, 3 mL, dashed lines). Inset: Zoom-in of first 4 hours. (b) Time-resolved H_2 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) H_2 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 H_2: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 (H_2) 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 O_2 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.[36,37] Monitoring the peak at 499 nm reveals negligible loss of **NiP** in the dark or with visible-light irradiation ($\lambda > 400$ nm), but under UV-visible solar irradiation ($\lambda > 300$ 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 Ni^{2+} in TCEP/NaAsc solution is not an active catalyst as demonstrated by control experiments using $NiCl_2$ under these conditions (Figure S6). As a result of the higher **NiP** stability under visible-only irradiation the H_2-photosystem was also more stable, with linear performance for the first 2 d (TON_{Ni} 825 after 3 d). The decreased H_2 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 O_2 in solution and shown to be inactive as H_2 evolution catalyst.[16–18] 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 H_2 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 H_2 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.[22,38]

Complexes **1**, **2** and **3** are established cobalt H_2 evolution catalysts with polydentate sp^2-nitrogen, pentapyridyl, pyrphyrinoid and diimine-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 polypyridyl complexes ($\eta \geq 800$ mV),[39] but the increased stability of these ligand frameworks lead to long-term activity over a period of days with a final TON_{Co} of 33,300 and 21,900, respectively.[19,24] Catalyst **3** has a lower overpotential ($\eta \approx 400$ mV) than **1** and **2**,[40] but display a lower catalytic rate.[41] Photocatalytic systems involving catalyst **3** hence showed a low maximum TON_{Co} of 90.[15,21] 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.

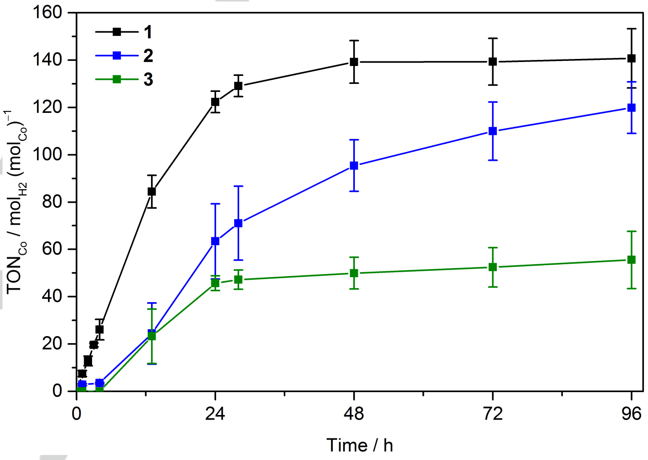


Figure 4. H_2 generation using CQD (10 mg) and various Co containing molecular catalysts (10 nmol) in aqueous solution containing TCEP/NaAsc (0.1 M each, pH 5, 3 mL) under 1 sun UV-visible irradiation at 25 °C. The structures of the catalysts **1**, **2** and **3** are shown in Figure 2.

Analogous photocatalytic systems comprising of CQDs as photosensitizer with this series of Co catalysts were tested for solar H_2 production in the TCEP/AA donor system (Figure 4). All the systems performed with a significantly slower rate of H_2 production than those using the **NiP** catalyst, with the fastest rate observed using **1** (TOF_{Co} of 8 h^{-1}). Complex **2**, whilst slower, has greater stability and some activity persists even after 4 d irradiation, leading to similar final TON_{Co} 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 (TON_{Co} 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 $CoCl_2$ and no catalyst where negligible H_2 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 CQD/CQD$^-$ couple (Figure S8).[42] 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 reductive quenching of the charge separated excited state by the electron donor.[19] An excited CQD (estimated average $\eta \approx 550$ mV for proton reduction) gives ample driving force for **NiP** ($\eta \approx 200$ mV) and **3** ($\eta \approx 400$ mV) to produce H_2, but limited driving force for the stable Co-based catalysts **1** and **2** ($\eta > 800$ 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 TON_{Ni} for photo-H_2 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 H_2 evolution and likely other fuel forming reactions. This study also revealed that the presented CQDs are ideally suited to sensitize low overpotential ($\eta < 500$ mV) catalysts, where comparable or greater TONs can be achieved, eliminating the need for high-excited 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-to-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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Keywords: carbon • quantum dots • photocatalysis • hydrogen • molecular catalysis

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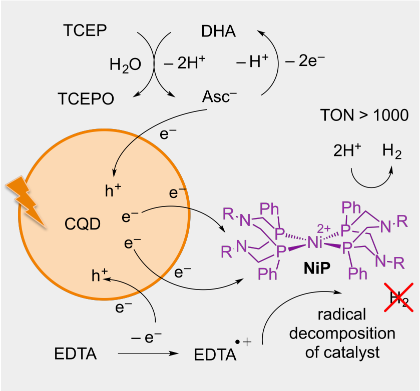

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Page No. – Page No.

Title