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Visible-Light Driven Photocatalytic Water Oxidation by a n-Conjugated Donor-Acceptor-Donor Chromophore/Catalyst Assembly

Journal:	ACS Energy Letters
Manuscript ID	nz-2018-01020x.R1
Manuscript Type:	Letter
Date Submitted by the Author:	03-Aug-2018
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Visible-Light Driven Photocatalytic Water Oxidation by a π-Conjugated Donor-Acceptor-Donor Chromophore/Catalyst Assembly

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chromophore,

18 19 **ABSTRACT:** The organic

(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(thiophene-3carboxylic acid), T2-BTD was prepared and investigated along with metal complex $[Ru(bda)(pyP)_2]$ (bda = 2,2'bipyridine-6,6'-dicarboxylate; руР 3-(pyridine-4-= yloxy)propyl)phosphonic acid), **RuC**, for light-driven water splitting in dye-sensitized photoelectrochemical cells. The resulting co-loaded organic chromophore plus catalyst surface assembly was evaluated by photocurrent transient measurement and direct O₂ detection using a collector-generator cell. The complete SnO₂/TiO₂ core-shell based photoanode exhibited an enhanced photocurrent (~38 μ A cm⁻²) compared to that with only the chromophore ($\sim 24 \ \mu A \ cm^{-2}$). A modest Faradaic efficiency of 12% was recorded for O₂ generation under 1 sun illumination in pH 3.9, 0.1 M acetate buffer solutions.

Table of Contents (Graphic Abstract)



Artificial photosynthesis is a green technology that can convert solar energy to chemical fuels by driving high-energy chemical reactions. An artificial photosynthetic system must integrate multiple processes to achieve solar-to-fuel conversion: 1) solar light harvesting, 2) conversion of excited state energy to transiently stable redox equivalents, and 3) water oxidation or CO₂ reduction for production of carbon-based fuels.¹ In this regard, the dye-sensitized photoelectrochemical cell (DSPEC) represents a combined system to drive water splitting and CO₂ reduction at n- or p-type semiconductor based electrodes with light absorption and catalysis by molecular chromophore-catalyst assemblies.²⁻⁴ At each electrode, the respective chromophore-catalyst assembly absorbs light and carries out the solar fuel forming half-reaction.

Solar-driven water oxidation occurs at the photoanode. A molecular chromophore bound to the surface of an n-type semiconductor oxide such as TiO_2 absorbs light, injects an electron into the conduction band (CB) of the semiconductor, and transfers a redox equivalent to the catalyst. The catalytic cycle for water oxidation occurs after the absorption of four photons leading to the conversion of two water molecules into four protons and one oxygen molecule (eqn. 1).

$$2H_20 + 4hv \to 0_2 + 4H^+ + 4e^- \qquad (1)$$

Most photoanodes used in DSPECs utilize covalently linked chromophore-catalyst assemblies,⁵ layer-by-layer polychromophore/water oxidation catalyst multilayer assemblies,6-7 or surface co-adsorbed chromophores/water oxidation catalyst species⁸ bound to semiconductor oxide films (co-loading).¹ Preformed covalently linked assemblies have been investigated in photoanodes and have demonstrated advantages from the chemically stable connection between chromophore and catalyst, high surface loading9 and by minimizing the back electron transfer from the semiconductor oxide surface to the catalyst. This approach has some drawback, however, including the need for multistep syntheses.^{2, 10} As an alternative strategy that uses Zr(IV)-phosphonate coordination linkages has been used to bond chromophores and catalysts on the surface of a semiconductor.¹¹⁻¹² This approach provides a modular and stepwise method for self-assembly of bilayer structures on semiconductor oxide surfaces, but it relies on hydrolytically unstable bonds. In contrast to these strategies, co-loading is the simplest approach to assemble the chromophore and catalyst together on the oxide surface.^{10, 13} Although co-loading can suffer from rapid back electron transfer from the semiconductor oxide to the oxidized catalyst, it is a straightforward approach allowing adjustment of the conditions as a function of chromophore and catalyst loading, and in principle allowing researchers to rapidly screen different chromophore and catalyst structures.

Organic chromophores are desirable sensitizers for DSPEC photoanodes because they are relatively inexpensive, absorb strongly in the visible region, and their frontier orbital energies (e.g., bandgap, redox potentials) are readily tunable by systematic synthetic modifications.14 A notable class of organic dyes are donor-acceptor-donor (D-A-D) molecules which can be introduced easily for the chromophore in the photoanode.¹⁵ For example, 2,1,3-benzothiadiazole (BTD) has a simple molecular structure and is a unit that is commonly used for synthesizing many low-band-gap conjugated polymers with intramolecular charge transfer interactions.16-17 Interestingly, BTD flanked with thiophene units is a simple D-A-D type organic chromophore and an worthy candidate for photovoltaic application.¹⁸ Thiophene is a common electron donating group, which leads to relatively high hole mobility and intermolecular ordering.19

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This work explores the use of a BTD-based D-A-D chromophore and a Ru-based catalyst for light driven water oxidation at a DSPEC anode. Previously, we reported a similar BTDbased D-A-D polymer in a dye sensitized solar cell.¹⁸ The simple molecular D-A-D structure, **T2-BTD** in Figure 1a, leads to charge separation in the excited state, which we proposed would facilitate charge injection into TiO₂. The carboxylic acid anchoring groups allow coupling of the chromophore to the TiO₂ surface for charge injection. Here, we report the characteristics of a photoanode using an organic chromophorecatalyst assembly made by the co-loading method. The results reveal a remarkable dependence of DSPEC photoanode efficiency on the co-loading method used to fabricate the photoanode, guiding future work in the field.



Figure 1. (a) Structures of **T2-BTD** and **RuC**. (b) Absorption (red solid) and fluorescence (red dash) spectra of **T2-BTD** in tetrahydrofuran solution. (c) Energy diagram comparing the TiO₂ conduction band, reduced and oxidized **T2-BTD** and onset potential for water oxidation by **RuC**.

The structures of the molecular catalyst and chromophore used here, [Ru(bda)(pyP)₂] (**RuC**) and **T2-BTD**,¹⁸ are shown in Figure 1a. The UV-visible absorption and fluorescence spectra of **T2-BTD** in THF solution feature a single absorption band and a strong green fluorescence at λ_{max} ~377 nm and ~527 nm, respectively. This Stokes shift (*ca*. 150 nm) indicates intramolecular charge transfer character in the singlet excited state of **T2-BTD**.¹⁸

The electrochemistry of T2-BTD was studied in acetonitrile containing 0.5 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆) as the electrolyte (Table S1). The cyclic voltammogram (CV) of **T2-BTD** shows two reversible reduction peaks. The onset of the first reduction is at -1.06 V vs. NHE. Next, the oxidation potential of T2-BTD was also investigated electrochemically. The anodic branch of the CV reveals a pronounced irreversible wave that has an onset of 1.70 V vs NHE. The irreversible behavior arises because the alpha positions on the thiophene units are not substituted and thus electropolymerization occurs during the oxidation. The electrochemistry allows us to estimate the approximate HOMO and LUMO levels for **T2-BTD**, and these are shown in Figure 1c.²⁰ It can be seen that the energy levels of the chromophore are positioned to allow charge injection into TiO₂ while also having a sufficiently positive oxidation potential to allow hole transfer to the catalyst **RuC** catalyst.²¹⁻²²

The utility of the **T2-BTD** chromophore as a sensitizer for the DSPEC photoanode application was evaluated. Electrodes were prepared by immersing an FTO|SnO₂/TiO₂ film in THF/ethanol (v/v = 7/3) solution²³ of **T2-BTD** (0.2 mM) for 30 min (see Supporting Information²⁴). (It has been previously shown that SnO₂/TiO₂ core-shell electrodes show enhanced performance in DSPEC applications compared to TiO₂, motivating this approach.)^{6, 25} The photocurrent transient response of the FT0|Sn0₂/Ti0₂|-[T2-BTD] electrode in an aqueous electrolyte during light on/off cycles was examined. Figure 2 shows the response of the electrode in the presence and absence of hydroquinone (H₂Q) as the sacrificial electron donor. H₂Q was used to gauge the upper limit for the photocurrent response of the interface under water oxidation conditions. H₂Q has an irreversible oxidation potential of 1.37 V vs NHE, which is well below the first oxidation potential of T2-BTD.²⁶ The photocurrent transients were measured by on/off modulation of the incident light under AM 1.5G illumination (100 mW cm⁻²), with an applied bias of 0.4 V vs NHE.



Figure 2. Photocurrent-time traces with (black) and without (red) 20 mM H_2Q in 0.1 M acetate/acetic acid buffer (pH 3.9) and 1 M NaClO₄ under illumination (100 mW cm⁻², 400 nm cut-off filter) with applied bias of 0.4 V vs. NHE.

Several points are of interest when considering the results in Figure 2. First, there is considerable photocurrent in the absence of H_2Q . The origin of the photocurrent was puzzling until further experiments were conducted to demonstrate that dye oxidation occurs at the photoanode (*vide infra*). Second,

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the photocurrent is enhanced in the presence of H_2Q , which is expected given that this species can serve as a source of electrons, regenerating the oxidized dye following charge injection. Finally, close inspection of the photocurrent transients with and without H_2Q reveals that there is a marked current decay when the donor is not present. The photocurrent decay is also associated with the irreversible dye oxidation at the illuminated electrode. In the presence of H_2Q the photocurrent does not decay because the dye is stabilized, since it is quickly regenerated after charge injection, and the dye reduction must be kinetically competitive with the irreversible reaction the dye undergoes.²⁷

In order to investigate the irreversible dye reaction more directly, the UV-visible absorption of an FTO[TiO₂]-[**T2-BTD**] electrode was monitored as a function of irradiation time. The photocurrent at the electrode was monitored concurrently. These results are summarized in Figure 3. First, as shown in Figure 3a, the absorption of **T2-BTD** changed significantly during the illumination, featuring a decrease in absorption at $\lambda \sim 380$ nm combined with the appearance of a new redshifted absorption band at $\lambda \sim 450$ nm. This behavior can be explained by the formation of an irreversibly oxidized dye species.²⁸ Second, as shown in Figure 3b, it can be seen that there is a (qualitative) correlation between the kinetics of the dye absorption change (λ = 450 nm) and the decrease of the photocurrent at the electrode. This confirms that 1) the photocurrent is likely due to dye oxidation, and 2) the decrease in photocurrent seen in Figure 2 (absence of H₂Q) is due to irreversible dye oxidation. Point 1 is confirmed by incident photon to current efficiency (IPCE) measurements (Figure S2) which show that the IPCE for the FTO|TiO2|-[T2-BTD] electrode correlates with the absorption of the **T2-BTD** dye.



Figure 3. (a) Absorption-difference spectra for FTO|TiO₂|-[**T2-BTD**] electrode as a function of illumination time. Spectrum was obtained every 1 min over a total irradiation period of 17 min. (b) Current density and change in optical density as a function of illumination time. Broad band illumination (100 mW-cm⁻², $\lambda > 400$ nm) with electrode in 0.1 M acetate buffer solution (pH 3.9) with 1 M NaClO₄.

Next we turned to investigate the photoresponse of electrodes that contain both the T2-BTD chromophore and the water oxidation catalyst, RuC. In these experiments, the aim was to use $FTO|SnO_2/TiO_2$ substrates given that previous work demonstrates that recombination is suppressed and the efficiency of catalytic turnover is enhanced.²⁹⁻³¹ However, in order to provide comparison, studies were also carried out on FT0|TiO₂ as well. Initially, we examined the rate of adsorption of the two components on the mesoporous substrates. As shown in Figure S3a chromophore T2-BTD is rapidly adsorbed from solution, and in less than 20 min surface saturation is achieved on both SnO_2/TiO_2 and TiO_2 substrates ($\Gamma \sim$ 2.5 x 10⁻⁸ mol-cm⁻²). By contrast, the adsorption of catalyst RuC is slower. Figure S3b compares the adsorption of T2-BTD and **RuC** on the core-shell SnO₂/TiO₂ substrates and it is apparent that saturation coverage of RuC is not even achieved in 80 mins.

In contrast to previous reports,³¹ we found that the conditions necessary to accomplish reproducible enhancement in the photocurrent for the chromophore-catalyst electrode were difficult to establish. This is apparently due to the need for the two molecular elements to be in close proximity on the surface, and for the configuration of the T2-BTD chromophores to be optimal for hole transport to the catalyst. As shown in Tables S2 and S3, three different sets of conditions were used to fabricate the chromophore-catalyst modified electrodes on both FTO|SnO₂/TiO₂ and FTO|TiO₂ substrates. We first decided to use sequential deposition, as this approach was reported to give highly active TiO₂ photoanodes coloaded with a subporphyrin chromophore and a Ru water oxidation catalyst.³¹ Specifically, electrodes A and B (Tables S2 and S3) were fabricated by stepwise deposition of T2-BTD (2 hr or 40 min) followed by **RuC** (1 min), by analogy to the published method.³¹ Surprisingly, on both FTO|SnO₂/TiO₂ and FTO|TiO₂, this method lead to a significant decrease in photocurrent after treatment with the catalyst (Figures S3 and S4). By contrast, when the chromophore and catalyst are deposited concurrently (co-deposition) from solution containing a mixture (electrodes C, T2-BTD:RuC 3:1 molar ratio, 30 mins deposition, see Table S2), an obvious enhancement in photocurrent is observed for the mixed film on the FTO|SnO2/TiO2 core-shell substrate, Figure 4a. From the absorption spectrum of the co-deposited electrode (Figure S6), the surface coverage (Γ) values were calculated to be 1.75 x 10⁻⁸ mol-cm⁻² for **T2**-**BTD** and 7.21 x 10^{-9} mol cm⁻² for **RuC**. Thus, the molar ratio between **T2-BTD** and **RuC** was *ca.* 2.4 : 1, which is slightly less than anticipated based on the ratio in solution.^{32,33} We suspect the poor photoresponse of the films constructed by the stepwise method arises because the **T2-BTD** has effectively saturated the surface, and the RuC is unable to directly adsorb on the surface, perhaps depositing in an aggregated state on top of the chromophore layer. Even though **T2-BTD** absorbs faster than RuC, when the two species are co-deposited the catalyst can effectively compete with the chromophore for surface binding, giving rise to a homogeneous distribution of the two species on the surface, a condition which is needed for effective cross surface hole-transport.

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Using the co-loaded photoanode FT0|SnO2/TiO2|-[T2-**BTD**]/[**RuC**] the photocurrent density was $\sim 38 \, \mu\text{A}\text{-cm}^{-2}$, while that of the photoanode with only chromophore FT0[Sn02/TiO2]-[T2-BTD] gave a photocurrent density of ~24 μ A cm⁻² (Figure 4a). This >50% photocurrent increase in the presence of RuC is consistent with effective hole transfer from T2-BTD to RuC, leading to the formation of catalytically active RuC. Importantly, using the same co-loading deposition conditions on the TiO2 substrate a ~60% decrease in the photocurrent is observed for FT0|TiO2|-[T2-BTD]/[RuC] electrode compared to the chromophore only modified electrode, FT0|TiO₂|-[T2-BTD] (Figures S4c and d). The poor response on the TiO₂ electrode is consistent with considerable previous data showing that charge recombination is suppressed on the SnO₂/TiO₂, allowing more time for turnover of the water oxidation catalyst.²⁹⁻³¹



Figure 4. (a) Photocurrent-time traces with light on/off cycles for FTO|SnO₂/TiO₂|-**[T2-BTD]** (red) and for FTO|SnO₂/TiO₂|-**[T2-BTD]**//**RuC** (blue). (b) Top: Photocurrent-time traces (60-300s) for FTO|SnO₂/TiO₂|-**[T2-BTD]**/**RuC** (2.4:1 ratio) in 0.1M acetate buffer (pH 3.9) and 1M NaClO₄ aqueous solution

with an applied bias of 0.4 V vs NHE. Bottom: Photocurrenttime traces at FTO collector electrode, ~ 1 mm from the generator with an applied bias of -0.7 V vs NHE measured concurrently with generator measurement. Inset shows schematic diagram of collector-generator cell.

In order to investigate O_2 production at the co-loaded FT0|Sn02/Ti02|-[T2-BTD]/[RuC] photoanode, we used the collector-generator (C-G) dual electrode method.34-36 The C-G combines an O_2 "collector" electrode which is biased at -0.7 V (vs NHE) in a sandwich configuration with the photoanode (Figure 4b, inset). By using a bipotentiostat, the photocurrent at the anode and at the collector electrode are monitored concurrently; the current at the collector is due to reduction of O_2 generated by the photoanode. As shown in Figure 4b, the cathodic current observed at the O2 collector electrode gradually increased during the illumination of the photoanode and then it decays to the background level after the light source is blocked. This behavior is consistent with generation of O_2 at the photoanode during illumination, diffusion of the generated O₂ to the collector electrode, and then reduction of the O₂ at the collector. Integration of the total currents passed at both electrodes and taking the

ratio of the charge at the O_2 collector relative to the photoanode allows determination of the Faradaic efficiency for O_2 production which was ~12%. A photoanode with the configuration FTO|SnO₂/TiO₂(4.5 nm)|-[**T2-BTD**] (**T2-BTD** only) revealed no measurable cathodic current at the collector, indicating negligible production of O_2 in the absence of **RuC** (Figure S7).

Several important conclusions can be drawn from the results presented here. It was discovered that 1) the method of depositing the chromophore and catalyst onto the electrode and 2) the nature of the semiconductor $(SnO_2/TiO_2 \text{ vs } TiO_2)$ are both key factors in obtaining an active DSPEC photoanode. Both of these factors are clearly related to determining the competition between hole transfer from the chromophore to the catalyst, along with recombination of the injected electron and the hole that is located on the chromophore or catalyst. When the **T2-BTD** and **RuC** are deposited sequentially, either on SnO_2/TiO_2 or TiO_2 substrates, recombination dominates, as the photocurrent is suppressed in the assembly modified interface. By contrast, when the two components are concurrently deposited onto SnO₂/TiO₂ substrates, the photocurrent is enhanced, and we are able to detect the production of O_2 , confirming that hole transfer from T2-BTD to RuC is occurring. From this we conclude that recombination is sufficiently suppressed to allow some catalytic turnover to occur. These findings establish that the detailed nanostructure at the interface, although not clearly defined, is key in enabling DSPEC activity.

Furthermore, while O₂ production is confirmed, the Faradaic efficiency is comparatively low. This means that recombination (or irreversible **T2-BTD** oxidation) is still competing quite effectively with hole transfer to **RuC**. It is likely that the **T2-BTD** structure is the basis for the low hole transfer efficiency. In particular, it is known for π -conjugated chromophores such as **T2-BTD** that hole transfer is most effective when the structures are in a π -stacked configuration.³⁷⁻³⁸ It is possible that the **T2-BTD** units are arranged in such a way on the surface (e.g. disordered or face down) so that hole transfer between the units and to **RuC** is slow and cannot compete effectively with recombination. This might explain the appar1

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ent discrepancy when comparing the much higher Faradaic efficiency observed when different organic chromophores are co-loaded onto metal oxides with similar water oxidation catalysts.^{21, 31, 39} The results here point to the importance of hole transfer from the chromophore to the catalyst in determining the efficiency of DSPEC photoanodes comprised of co-loaded chromophore/catalyst assemblies.

In conclusion, a facile method to assemble an organic D-A-D type chromophore and water oxidation catalyst onto semiconductors by the co-loading has been evaluated. The organic chromophore-catalyst assembly successfully demonstrated light-driven water oxidation. This result indicates that the approach of using organic chromophore-catalyst is promising for water oxidation applications. Further work with the organic chromophore-catalyst assemblies will explore strategies to promote hole transfer from the oxidized dye to the water oxidation catalyst and inhibit back electron transfer at the surface.

ASSOCIATED CONTENT

Supporting Information

Materials and methods, experimental description, additional data analysis. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This material is based on work supported solely as part of the UNC EFRC: Center for Solar Fuels, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001011. Soojin Kim and Jinheung Kim acknowledge the KSF for travel support (Grant No. 2017M1A2A2042517).

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