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Artificial photosynthesis a brief literature review

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Abstract

Dye Sensitized Photoelectrochemical Cells (DS-PEC) are a promising development for artificial photosynthesis. Currently however photoinduced conversion of water to hydrogen and oxygen remains limited by desorption, alternative processes and charge accumulation. This brief literature review will primarily focus on transition metal complex chromophore catalyst dyads, for water oxidation catalysis (WOC) as well as hydrogen evolution catalysis (HEC). Assessing the dyads individual charge separation, electron transfer and catalytic photoelectrochemical properties. Comparing and contrasting the techniques employed by Dye Sensitized Photoelectrochemical Cells (DS-PEC) dyads in addition to collectively evaluating their current limiting factors and suggesting potential developments for further work.

Keywords: Photosynthesis, photoelectrochemical cells, catalysis, charge

Introduction

Dye-Sensitized Photo electrochemical Cell

Solar panels generate electricity but fuels account for most energy consumption, photo catalytic fuel production should thus expand renewable energies scope ^[1]. In 1972 Fujishima and Honda first verified UV water splitting, eventually evolving into dye-sensitized photoelectrochemical cells a form of artificial photosynthesis ^[2]. Artificial photosynthesis is a promising development for photo conversion of photons into hydrogen a fuel with one of the highest energy densities.

Photosynthesis & Artificial Photosynthesis

Photosynthesis, converts light into chemical-energy. Artificial photosynthesis aims to mimic photosynthesis processes, to convert photons into fuel. During photosynthesis chlorophyll-P680 absorbs photons causing electron photoexcitation, excited electrons transfer to pheophytin then the chloroplast electron transport chain, separating the oxidised chlorophyll-P680 and free electron ^[3]. Oxidised chlorophyll-P680s undergo the Kok Cycle and free electrons produce NADPH.

Artificial photosynthesis encompasses similar processes but typically utilises more broadly absorbing chromophore and Donor-Chromophore-Acceptor(D-C-A) setups comprising versatile functional groups promoting charge separation by pushing and pulling excited electron/hole to acceptor/donor respectively, forming donor⁺-chromophore-acceptor(D⁺-C-A⁻), allowing favourable rates by limiting competing processes ^[4].

Kok Cycle & Water Oxidation Catalysis (WOC)

Oxidised chlorophyll-P680 undergoes the Kok Cycle. Oxidised chlorophyll-P680 remove an electron from a surrounding tyrosine, reforming chlorophyll-P680 and generating a tyrosine radical ^[5]. The radical will oxidise a surrounding Manganese active site, removing an electron from absorbed oxygen atoms. This process repeats 4 times until completion of the Kok cycle, producing O₂/H⁺ plus free-electrons.

Artificial photosynthesis water oxidation catalysis mimics this via various less well understood water oxidation mechanisms. The basic processes are essentially identical the hole will transfer from the oxidised donor to the catalyst where absorbed water is oxidised.^[6] Oxidation is often thermodynamically unfavourable, unpaired valence electron ruthenium catalysts with good energy overlap for faster rates and hole stabilising electron donating substituents mitigate this.

NADPH Production & Hydrogen Evolution Catalysis (WOC)

The free electron produces NADPH ^[5].

Free excited state electrons, transport through the chloroplast electron transport chain and ultimately accumulate at chlorophyll-P700. The chlorophyll-P700 again absorbs light for electron photoexcitation, allowing the excited state electron to reduce NADP^+ to NADPH in Ferredoxin-NADP (+) reductase [3]. The oxidised chlorophyll-P700 are reduced by the accumulated electrons.

Artificial photosynthesis hydrogen evolution catalysis (HEC) mimics this basic processes. WOC excited electron transferring to the counter electrode, where the free electron will reach accumulated donor⁺-chromophore-acceptor(D⁺-C-A⁻) reducing the acceptor hole. First the acceptor-chromophore-donor (A-C-D) setup chromophore undergoes electron photoexcitation causing charge separation, eventually reaching the catalyst to reduce absorbed H^+ .⁷ Similar to water oxidation catalysis the process is often thermodynamically unfavourable so also utilise unpaired valence electron cobalt catalysts and electron withdrawing substituents.

Main Body

Dye-sensitized photo electrochemical dyads (DS-PEC)

Dye-sensitized photoelectrochemical cells are promising developments towards photocatalytic hydrogen production but remain limited by alternative processes, charge accumulation and desorption.¹ Improvements focus on maximising chromophore absorbance, charge separation, catalyst efficiency and driving forces. Typically,

heterogeneous transition metal complexes are studied as they offer greater electronic and structural tunability plus affable analysis but encompass many metal-to-ligand charge transfers potentially increasing non-productive alternative processes. The chromophore and catalyst are typically individual semiconductor surface assemblies but one growing strategy is linking both Chromophore and catalyst into one dyad [8-13]. This mini-review provides recent literature examples illustrating principles and challenges facing artificial photosynthesis, primarily focusing on transition metal complex chromophore-catalyst-dyads.

Water Oxidation Catalysis Dyad (WOC)

The purpose of the WOC is to reduce the chromophore hole by oxidising water into O_2 and H^+ , many catalysts have been proposed for this but most research focuses on Ru^{II} .

The exact mechanism is complex but Brennaman *et al.* investigated the mechanism of Ru^{II} - Ru^{II} -catalysis pH4.6 water oxidation, seen in figure 1.[8] A simplified theorised mechanism:

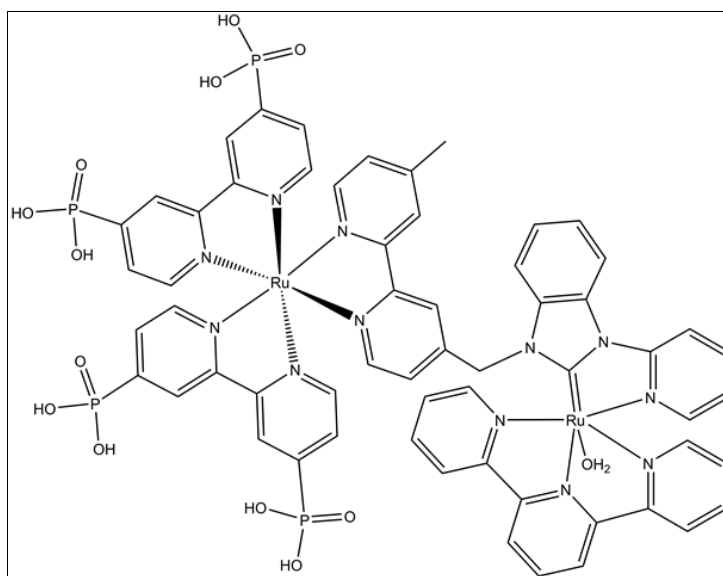
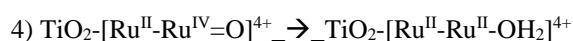
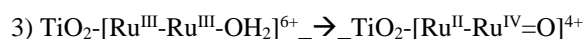
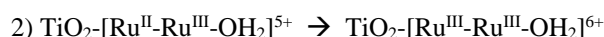
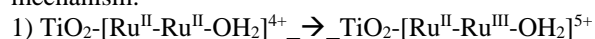


Fig 1: Ru^{II} Chromophore Ru^{II} catalysts alkane linked dyad studied by Brennaman *et al.*

Transient Absorption Spectroscopy and Spectro-electrochemical data indicating each species however dyad metal-to-ligand charge transfer and alternative processes massively increased analytical complexity [9]. Only investigating pH4.6, while catalysis is effected by pH.

Donor-Chromophore-Acceptor (D-C-A)

One of the limiting factors in water oxidation catalysis is alternative processes and unfavourable charge separation, a growing strategy to reduce this is utilising a D-C-A dyad. Wang *et al.* investigated the effects of different D-C-A groups seen in figure 2 on water splitting with a focus on mimicking photosynthesis processes [10].

$\text{RuP}(\text{TPA})(\text{Cat})^{2+}$ dyad transient absorption, showing catalyst to TPA oxidation $\sim 3.6\text{ns}$ and radical TPA to chromophore 827ps or competing catalyst strait to Ru-chromophore $\sim 28\text{ps}$.

Photocurrent comparison of $\text{RuP}(\text{TPA})(\text{Cat})^{2+}$ and $\text{RuP}(\text{Cat})^{2+}$ control show control initial photocurrent was higher before decreasing $\sim 50\%$ over minutes but electron donating (TPA)donor containing photocurrent initially charged slightly before reaching 0.58 mAcm^{-2} maximum also seemingly increasing surface stability $\sim 50\%$ against control over 16h.

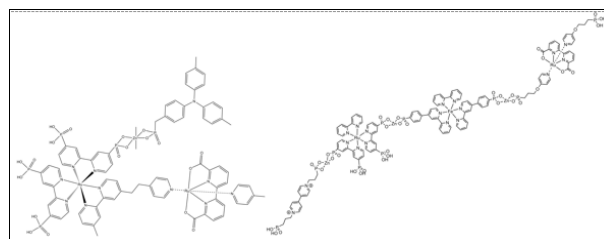


Fig 2: $\text{RuP}(\text{TPA})(\text{Cat})^{2+}$ & $\text{MV}^{2+}\text{-S-Fe}^{\text{II}}\text{-Ru}^{\text{II}}$ dyads respectively Wang *et al.* studied

Also investigating MV^{2+} -S- Fe^{II} - Ru^{II} spectro-electrochemical and transient absorption data at pH4.65 illustrated mechanistic data.¹¹ Notably the electron withdrawing MV^{2+} bridge significantly increased charge separation lifetime and increased oxidation of $-Fe^{II}$, against control. Water oxidation was assessed under 1 sun at pH4.65, $\sim 250 A/cm^2$ maximum photocurrent at $\sim 30s$ but decreasing over 1h to $50 \mu A/cm^2$ and 67% faradaic efficiency.

Interestingly the electron withdrawing MV^{2+} and electron donating TPA, push-pull techniques work well for charge separation against control but the major decrease in photocurrents over time might suggest desorption is occurring however this would ideally require a more detailed study

possibly also investigating the effect to which different substituents effects charge separation rate.

Hydrogen Evolution Catalysis Dyad Dyad Charge Accumulation

The purpose of the HEC is to reduce H^+ to H_2 but its typically slow process relative to light absorption and electron transfer, often leading to a mismatch in dyad rates.

Bold *et al.* investigated the photo-electrochemistry and TON of phosphonate-ruthenium-tris-diimine linked via triazole-bridged to cobalt-diimine-dioxime dyad seen in figure 3^[12].

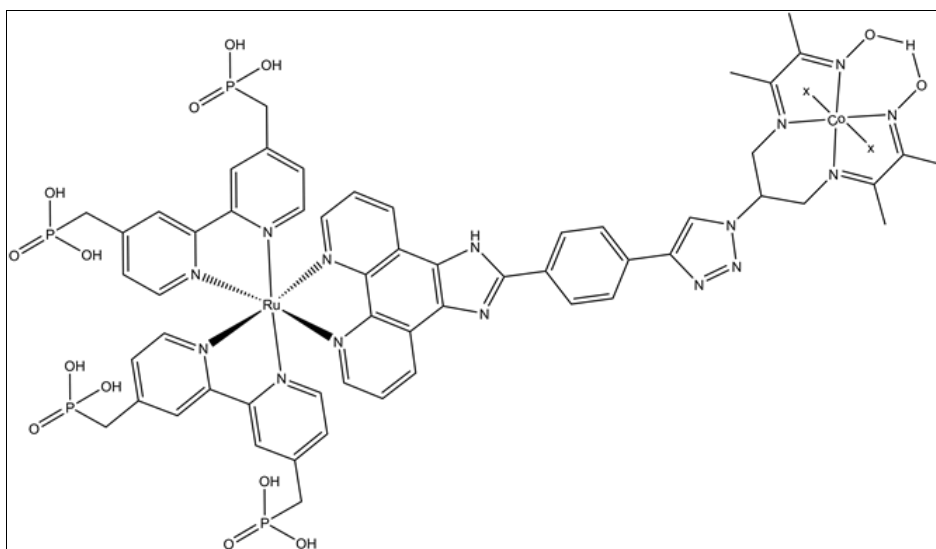


Fig 3: Dyad studied by Bold *et al.* when x characterises a halide

Computational data indicating Co^{II}/Co^I reduction is thermodynamically unfavourable $\sim +0.36eV$, supported via time-resolved spectroscopy reporting 12% active Co^I formation. Rate data illustrated charge separation is favoured at 45ps and recombination is disfavoured at $\sim 4\mu s$, supporting Co^I formation being limiting. Surprisingly, the dyad performed relatively well at AM1.5G, pH5.5, 2h with $84 \mu A \cdot cm^{-2}$ photocurrent, 26% faradaic efficiency and 13 TON however post-operando UV-Vis indicated $\sim 80\%$ absorbance decrease. Time-of-flight secondary ion mass spectrometry illustrated a 1224 peak, theorised to result from charge accumulation leading to hydrolysis of the diimine ligand. Dyad bond cleavage and desorption are undesirable and a more detailed study might fully illuminate if charge accumulation is the cause.

Lyu *et al.* similarly investigated cobaloxime-complex however tried a pyridyl-functionalized axial coordination to ruthenium-diacetylide as illustrated by figure 4.^[13] Cyclic voltammetry and computational data, indicated the system was more energetically favourable. HOMO spanning the entire π -conjugated system with electron density on the anchoring groups, making electron transfer to dyad hole favourable and LUMO electron density localized on pyridine-Co, making excited electron transfer to the catalyst barrierless. However arguably the system is less efficient under 1Sun, pH4.5 with $\sim 5.6 \mu A \cdot cm^{-2}$ photocurrent, 27% faradaic efficiency although different operating conditions are utilised.

The lacklustre performance is again theorised to result from slow cobalt centre kinetics causing charge accumulation illustrated via linear sweep voltammogram traces before reaching equilibrium, cathodic photocurrent spikes when the light is switched on and small anodic spikes when the light is switched off not observed in control. $\sim 60\%$ slow photocurrent decrease is observed attributed to leaching. Against direct bonding, pyridyl coordination substantially reducing photocurrents but decently improving dyad stability although both appear limited by charge accumulation.

Dyad stability and TON are seemingly affected by charge accumulation even when the system is energetically favourable with good orbital overlap and reduced alternative processes, although some of the bond cleavage negatives can seemingly be mitigated utilising coordination systems.

It's not just the catalyst that causes charge accumulation, slow chromophore electron transfer can also cause dyad charge

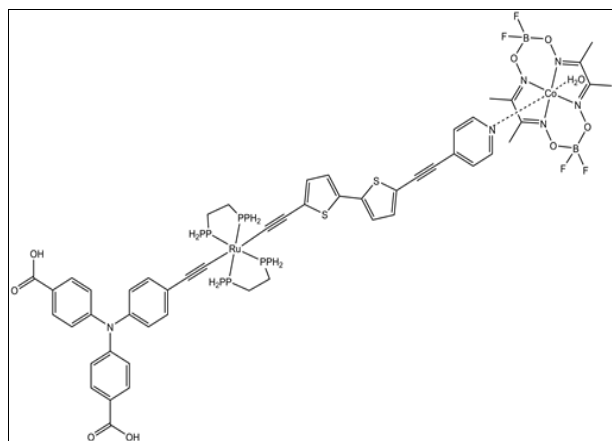


Fig 4: Dyad studied by Lyn *et al.*

accumulation limiting TON and stability. Charalambidis *et al.* investigated porphyrin-cobalt diimine-dioxime dyad photo

physical properties [14].

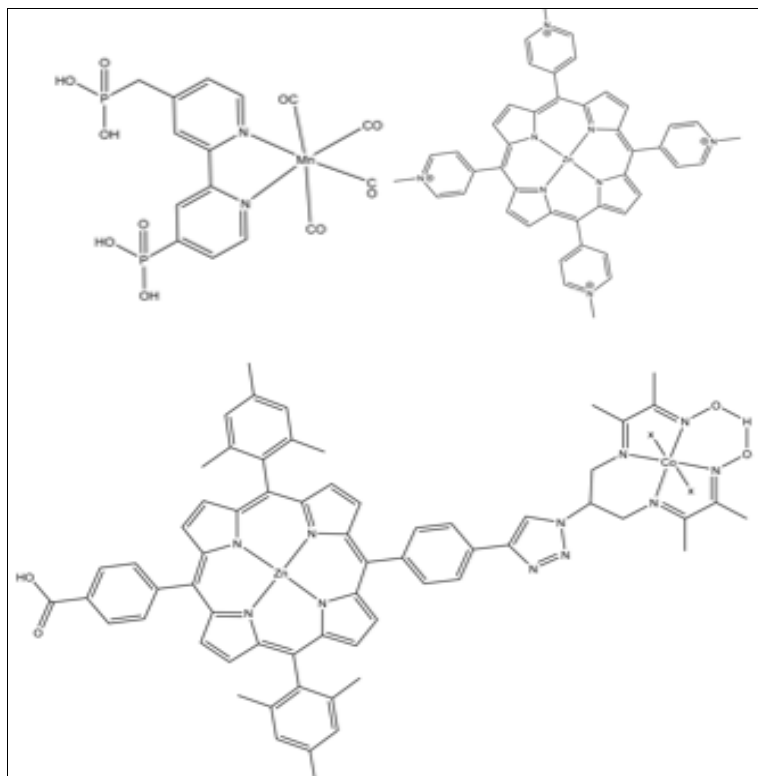


Fig 7: Dyad studied by Shipp and Charalambidis *et al.* when x characterises a halide

Dyad cyclic voltammetry analysis of catalytic couples and porphyrin excitation were used to estimate ΔG° -1.13 high thermodynamic favourability for electron transfer. Dyad linear sweep voltammograms at 2h, pH5.5 showed a 7nmolcm^{-2} hydrogen production and 8% Faradaic Efficiency. Post-operando characterization of the dyad indicated desorption of ~40% and a Q-band indicating possible porphyrin demetallation. Desorption and Q-band are theorised to result from charge accumulation, indicating inefficient electron transfer to the catalyst although thermodynamically

favoured, absorption peaks indicated weak interactions in the dyad ground state.

Shipp *et al.* also investigated Zn-Porphyrin, seen in figure 7, electron transfer but for separately absorbed chromophore catalyst species and CO_2 to CO Mn^{I} Catalysis.[15] Finding first and second reductions of catalyst by the photoexcited porphyrin are thermodynamically unfavorable ΔG_{et} 1.7 and 1.8V, explaining the observed slow rate of CO_2 reduction. Supporting charge accumulation theory and highlighting these issues aren't exclusive to dyads [16].

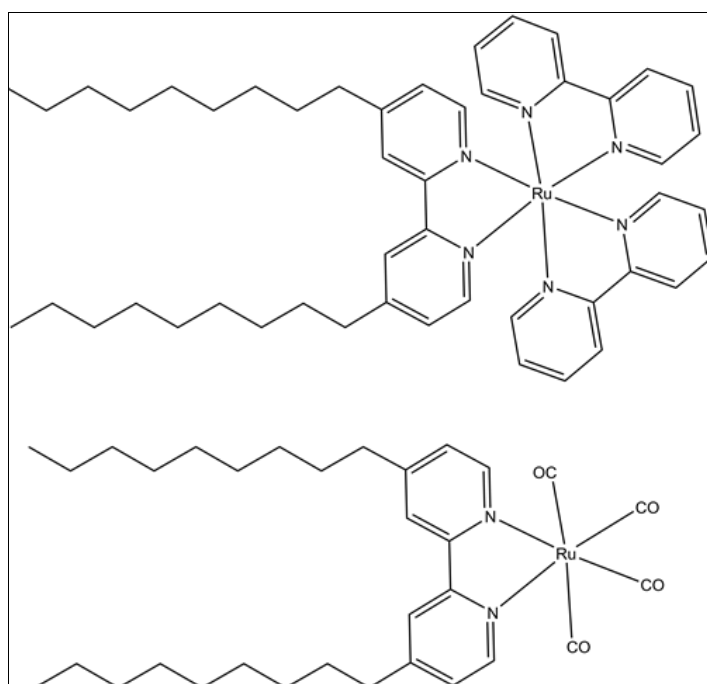


Fig 8: Dyad structure for liposome incorporation

Table 1: Dyad metrics for comparison of TON, FE and Photocurrent

	TON	FE (%)	Photocurrent(μAcm^{-2})
Charisiadis	-	7	-
Lyu	-	27	~5.6
Bold	5	26	84
Shipp	~3.75	-	-
Wang	-	83	-
Wang	-	67	50

Comparing the dyads with the data provided in table 1, its clear Dye-sensitized photoelectrochemical cell dyads are still in early development. Almost all dyads photocurrent decreases after 1h, indicating dyad desorption is a major issue, one possible alternative is to utilise a liposome incorporating structure seen in figure 8 although for dyads this isn't as well studied^[17].

Conclusion

This brief literature review has compared different techniques employed by individual dyads. Although it remains clear dye-sensitized photoelectrochemical cells are still in very early development, it's proving to be a promising development for conversion of photons into fuel.

Dyads generally seem to offer swift analysis of chromophore and catalyst photochemical properties but with added analytical complexity. Push-pull techniques have largely been implemented successfully and offer energetically favourable charge transfer at improved rates. For dye Sensitized Photoelectrochemical Cell dyads however this has been indicated as not being enough for sustained high photoconversion, as if the rate of electron donation and catalysis aren't roughly equal charge accumulation will cause dyad cleave and limit catalysis. Almost all dyads indicated some form of desorption was occurring and with in-depth dyad studies this remains unclear but again charge accumulation and pH dependence are suggested as possible reasons. Further work will hopefully aim to illuminate the causes of desorption and implement strategies to limit charge accumulation such as TPA tyrosine bridge and liposome incorporating structure.

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