Solvent-controlled O₂ diffusion enables air-tolerant solar hydrogen generation

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Solar water splitting into H₂ and O₂ is a promising approach to provide renewable fuels. However, the presence of O₂ hampers H₂ generation and most photocatalysts show a major drop in activity in air without synthetic modification. Here, we demonstrate efficient H₂ evolution in air, simply enabled by controlling O₂ diffusion in the solvent. We show that in deep eutectic solvents (DESs), photocatalysts retain up to 97% of their H₂ evolution activity and quantum efficiency under aerobic conditions whereas in water, the same catalysts are almost entirely quenched. Solvent-induced O₂ tolerance is achieved by H₂ generation outcompeting O₂-induced quenching due to low O₂ diffusivities in DESs combined with low O₂ solubilities. Using this mechanism, we derive design rules and demonstrate that applying these rules to H₂ generation in water can enhance O₂ tolerance to >34%. The simplicity and generality of this approach paves the way for enhancing water splitting without adding complexity.

Broader context

Green hydrogen production is a key process for the transition to a carbon-neutral economy, but oxygen, ubiquitous in air and generated during water splitting, interferes with hydrogen generation. Not only does the presence of O₂ lower the hydrogen evolution efficiency, it can also degrade hydrogen evolution catalysts; in addition, O₂ causes problems in other key energy technologies, such as Li–O₂ batteries, fuel cells and in many other redox processes. The current approaches to improving O₂ tolerance add complexity and often come at the expense of consuming redox equivalents for O₂ removal, which lowers the overall efficiency. Here we show that by simply choosing solvents with a low O₂ diffusivity and solubility, photocatalysts normally inefficient for H₂ generation in air become highly O₂ tolerant, with minimal loss in activity and efficiency in air, even for extended periods of time. By unravelling the mechanism of the solvent-induced O₂ tolerance, we can translate it to achieve oxygen tolerance even in water, making it an important new concept with general applicability independent of the catalyst, solvent or process – a key step in making green H₂ production simpler and more efficient on a global scale.

Introduction

Solar hydrogen production from water is viewed as a viable method for generating clean renewable fuel to aid in combatting global energy challenges.1–3 Materials employed for solar-driven H₂ production should be considered based on their cost, stability, toxicity and most importantly their practical applicability on a large scale. Real-world photocatalytic H₂ production systems must be active in the presence of O₂ generated in situ by water splitting and by exposure to air.3

However, H₂ evolution in an aerobic environment is usually suppressed because of the more favourable oxygen reduction reaction.4 In addition, molecular O₂ can inhibit H₂ evolution co-catalysts via interaction with the active site or by forming reactive oxygen species (ROSs).5, 6 Proton reduction in the presence of O₂ has been achieved by developing electrocatalysts with selectivity for H₂ evolution over O₂ reduction7 or by creating a local anaerobic environment around the catalyst. Methods of lowering the effective O₂ concentration at the catalyst include O₂ reduction at catalysts capable of performing both O₂ reduction and H⁺ evolution8–10 and at organic dyes,11 constructing layered architectures in which O₂ is reduced before it reaches the active site,12–14 introducing antioxidant additives,15, 16 and modifying catalytic sites with O₂-blocking layers.17–19 However, these approaches require a costly re-design of the catalyst to enhance O₂ tolerance and in many cases photons and charges are used to reduce O₂, leading to a decrease in quantum and Faradaic yield, respectively. Recent work has demonstrated O₂-tolerant CO₂ reduction enabled by controlling O₂ diffusion to the electrode using selective membranes and coatings.20, 21 Related approaches have been used in lithium-oxygen batteries.22 To date, research in hydrogen evolution has not exploited solvent effects for promoting O₂ tolerance, even though O₂ solubility and diffusivity in the reaction medium are the primary factors controlling the availability of O₂ to the catalytically active site.
In this work we demonstrate that using deep eutectic solvents (DESs) as a reaction medium enables O₂-tolerant photocatalytic H₂ production with O₂-intolerant photocatalysts without making any catalyst modifications and without affecting the quantum efficiency. DESs are an alternative class of low-cost, highly tuneable ionic liquids that can be prepared from readily available precursors and possess lower toxicities than conventional ionic liquids. DESs have been employed for air-tolerant organic reactions involving highly reactive organolithium compounds and it has recently been shown they can stabilise O₂-sensitive radicals in air. Using a carbon nitride photocatalyst, we now show that DESs create a near-anerobic environment in which up to 97% of the photocatalytic H₂ evolution activity is retained under air (Fig. 1). Mechanistic studies reveal a close interplay between O₂ solubility and diffusivity and allow us to develop a quantitative model of the O₂ tolerance. Based on this model we derive key design criteria for tailored reaction media that promote efficient and cost-effective O₂ tolerance with established H₂ generation photocatalysts without synthetic modification.

Results and Discussion

Deep eutectic solvents as a medium for solar H₂ generation

To investigate solvent effects on the photocatalytic H₂ evolution performance, we chose cyanamide functionalised carbon nitride (NCCN) as a model photocatalyst (Fig. S1-S4) and studied its activity in three well-known type-III DESs: choline chloride:urea 1:2, choline chloride:glycerol 1:2, and choline chloride:ethylene glycol 1:2, termed reline, glyceline and ethaline, respectively. These solvents were chosen due to their facile preparation, low cost, low toxicity and infinite miscibility with water. Pt was used as a co-catalyst, in situ photodeposited from H₂PtCl₆ (Pt/NCCN). In reline, Pt/NCCN generated 138±5.2 μmolH₂ after 14 h irradiation with simulated solar light (AM 1.5G, 1 sun) at an activity of 8.9±0.9 μmolH₂ g⁻¹CN, h⁻¹ using triethanolamine (TEOA) as a sacrificial electron donor (Fig. 2). Addition of water (12.5% by volume) was essential as in neat DESs, H₂ evolution activity was negligible (Fig. S5). The same conditions yielded an activity of 8.0±0.6 and 4.1±0.1 μmolH₂ g⁻¹CN, h⁻¹ for ethaline and glyceline, respectively with cumulative values of 105.1±8.6 and 58.7±3.5 μmolH₂ after 14 hours (Table S1). Depending on the solvent, a decay in activity was observed after 5-9 h which we attribute to the well-known decomposition of the redox mediator methyl viologen (MV²⁺) as with a further addition of MV²⁺, the rate increased again (Fig. S6). In the absence of MV²⁺, H₂ evolution was slower but no decay in activity was observed (Fig. S7) proving that the DESs do not compromise the stability of the NCCN, photocatalyst. In water, NCCN, displayed a maximum activity of 6.5±0.7 μmolH₂ g⁻¹CN, h⁻¹ and a cumulative production of 86.1±5.4 μmolH₂ after 14 h irradiation under optimised conditions (0.38 M TEOA, pH 7.0, no MV²⁺) which is on par with recent literature values. This was lower in comparison to reline and ethaline and higher than the activity in glyceline (see Figures S8-9 for optimisation and controls). The external quantum efficiency for H₂ evolution in reline was determined at 3.7±1.5% and was stable even after 20 h of irradiation (Table S2). We can therefore state that under the given conditions, DESs are a competitive solvent with water for solar H₂ generation.

A notable difference between water and DES is the effect of added MV²⁺ on the H₂ evolution: While adding MV increases H₂ generation in DES, a decrease in activity is observed in water (Figure S10). A suppression of H₂ evolution has been previously observed in cases where there is good electron transfer between the photocatalyst and the HER co-catalyst. In this case, adding MV²⁺ does not enhance HER but instead causes a visible accumulation of reduced MV⁺ in the solution which blocks light penetration to the photocatalyst due to its deep blue colour. The beneficial effects of adding MV in DESs, in turn, suggest poor electron transfer between NCCN and Pt in DESs. To prove this, we performed recycling experiments in which we separated the photocatalyst after 4 h irradiation in the presence of H₂PtCl₆ from its supernatant and re-suspended it in a fresh solution without added Pt, before continuing irradiation. In water, the photocatalytic H₂ evolution activity was not affected by this procedure, suggesting Pt is deposited on the NCCN, photocatalyst (Fig S11), in line with previous literature. In DES, however, the photocatalytic activity was almost completely quenched, corroborating poor immobilisation of Pt on NCCN in DES, possibly due to differences in solvation in DESs.

Figure 1. Schematic representation of solvent-mediated oxygen-tolerant photocatalytic hydrogen production in deep eutectic solvents demonstrated in this work.

Figure 2. Photocatalytic H₂ generation in DESs at Pt/NCCN: (a) H₂ production in different DESs and water; (b) max. H₂ production rate in DESs vs. H₂O. Conditions: NCCN, (2.0 mg), H₂PtCl₆ (0.05 mg Pt), in 2 mL DES (12.5% v/v H₂O, 0.38 M TEOA, 2 mM MV²⁺) or water (0.38 M TEOA, pH 7, no MV²⁺); AM 1.5G, 1 sun, 40°C, constant N₂ purge.

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O₂-tolerant H₂ generation in DESs

Inspired by their application as solvents to perform air-sensitive syntheses under an aerobic atmosphere, we set out to achieve air-tolerant H₂ evolution in DESs. It is well known that photocatalytic H₂ evolution is suppressed in air even for highly active materials arising from the thermodynamically favourable O₂ reduction and quenching of the photosensitiser. Figure 3a indicates that Pt/NCCN generates only 0.8±0.2 mmolH₂ g⁻¹CNx h⁻¹ upon irradiation in aerated water corresponding to a retention of only 8.8±1.5% of its photocatalytic activity seen under inert conditions. When the redox mediator MV was added the reduction dropped to 1.7±0.7%. However, in the DES reline, the same catalyst without any modification achieved an activity of up to 8.7±0.9 mmolH₂ g⁻¹CNx h⁻¹ in air, corresponding to a remarkable activity retention of up to 97.3±17.5% compared to anaerobic conditions (Fig. 3b, Table S3). While the O₂ tolerance in water decreases further over time with almost complete deactivation after 10 hours, DESs maintain a high level of O₂ tolerance over prolonged periods of time (Fig. S12). After 14 h, 123.5±8.1 μmolH₂ were produced in air (Fig. 3c) corresponding to 89.3±6.1% of the amount produced under N₂ and the system remained active (Fig. 3d). Similarly, an activity of 5.7±1.3 mmolH₂ g⁻¹CNx h⁻¹ was seen in aerobic ethylene (73.5±9.0% retention) and 3.6±0.3 mmolH₂ g⁻¹CNx h⁻¹ in aerobic glycerine (90.4±7.9% retention). The external quantum efficiency for H₂ evolution in aerobic reline was determined at 3.9±0.3% after 20 h of irradiation (Table S4) which is within error identical to the EQE observed in anaerobic conditions. The optimum O₂ tolerance was observed at 12.5% water content. Increasing the water content led to a lower O₂ tolerance (Fig. S13), whereas without added water, H₂ evolution activity was much lower, presumably for lack of available protons (Fig. S5).

The O₂ tolerance induced by DESs compares favourably with examples of O₂-tolerant H₂ evolution from the literature (Table S5). A range of CdS-based photocatalysts achieve O₂ tolerances between 40-80%; air can even increase the activity of CdS by suppressing photocorrosion. These studies typically operate at high H₂ production rates due to high electron donor concentrations, closed photoreactors and often high light intensities, where O₂ in the solution and the reactor headspace is rapidly depleted by reduction to H₂O, effectively generating anaerobic conditions in situ; often indicated by an observed lag period before H₂ evolution occurs. In contrast, H₂ production in DESs shows no detectable lag period and a high O₂ tolerance despite a continuous air purge maintaining a constant O₂ concentration. The latter is particularly important to exploit O₂ tolerance to enhance overall water splitting, where O₂ is continuously generated and H₂ production rates are much lower than in sacrificial systems. Photocatalysts operating at lower rates where O₂ depletion is less effective have shown lower O₂ tolerances, e.g. Ru/P/OH-QDD (64%) and PF BT polymer dots (37%). To the best of our knowledge, there is no literature on O₂-tolerant H₂ generation using carbon nitride-based photocatalysts. The advantage of solvent-induced O₂ tolerance lies in its applicability independent of the photocatalyst. When Pt/TiO₂ was used as the photocatalyst instead of Pt/NCCN, the O₂ tolerance similarly increased from 29.6±6.5% in water to 86.1±12.8% in reline after 12 h irradiation (Figure S14), proving this effect is not limited to a single photocatalyst. To further demonstrate the generality of this approach, we also studied H₂ evolution at the homogeneous photocatalyst Pt/Eosin Y (Pt/EY). Even though the H₂ evolution in ethylene and reline (17.5±1.7 μmolH₂ mmol⁻¹EY and 11.4±1.7 mmolH₂ mol⁻¹EY after 5.5 h, respectively, non-optimised conditions, Fig. S15) was slower than in water (81.1±6.8 μmolH₂ mmol⁻¹EY), the DESs promote excellent retention of activity in air. Pt/EY in aerobic H₂O produced 0.7 mmolH₂ mol⁻¹EY after 5.5 h (<1% activity retained), whereas 14.9 mmolH₂ mol⁻¹EY was generated in ethylene corresponding to 85.5% O₂ tolerance. This, again, compares well with literature examples of aerobic H₂ evolution at homogeneous photocatalysts e.g. Co/P/EY retained 70±4% activity in air, however activity was limited to 2 h.

The mechanism of solvent-induced O₂ tolerance

Having demonstrated that DESs promote O₂ tolerance of photocatalytic H₂ evolution independent of the photocatalyst, we sought to gain understanding of the underlying mechanism. Previous work on DESs enabling air-tolerant alkylation with organolithium and Grignard reagents suggested that the high halide concentration in DESs increases the reagents’ reactivity to levels where they can outcompete hydrolysis. However, no explanation for the observed insensitivity to O₂ was given. To elucidate the mechanism by which DESs promote O₂-tolerant H₂ evolution, we first studied the formation and stability of reduced NCCN in both H₂O and DESs in air. NCCN is known to form a turquoise-blue photoreduced state NCCN* originating from charge accumulation in the material when irradiated in the presence of an electron donor and absence of a hydrogen
evolution co-catalyst.\textsuperscript{29} \(\text{NCN}_x^*\) persists in an anaerobic environment but is quenched rapidly by reaction with \(\text{O}_2\). In water, \(\text{NCN}_x^*\) is therefore only formed under \(\text{N}_2\) and immediately quenched upon exposure to air as indicated by the blue material regaining its original yellow colour. However, when \(\text{NCN}_x\) is irradiated in DESs, \(\text{NCN}_x^*\) is quickly formed even in an aerated solution. Moreover, the blue colour is stable in air for several days, with a noticeable absorbance at \(\approx 680\) nm in the DR-UV spectrum, ascribed to the reduced photocatalyst (Fig. 4). This absorbance is not observed in an aerated aqueous solution, highlighting the solvent effect on limiting the quenching of the photosorber from \(\text{O}_2\). To further corroborate the absence of \(\text{O}_2\) quenching in aerated DESs, we investigated photocatalytic degradation of the organic dye methylene blue in aerated DESs using \(\text{NCN}_x\) as a photocatalyst. Dye degradation relies on reactive oxygen species (ROSs) such as \(\text{O}_2^-\) to act as oxidants, generated by the quenching of the excited state of a photocatalyst by \(\text{O}_2\); it is therefore strongly dependent on dissolved \(\text{O}_2\).\textsuperscript{44} Consistently, we observed that the degradation of methylene blue was much slower in DESs than in water, which lends further evidence to a suppression of \(\text{O}_2\) quenching depending on the solvent (Fig. S16).

Further quantitative insight was sought from determining the saturation concentration and diffusion coefficient of \(\text{O}_2\) in DESs by studying the electrochemical \(\text{O}_2\) reduction at a Pt microwire electrode.\textsuperscript{45} Potential step chronoamperometry was performed in each solvent and the observed current transients for the electrocatalytic \(\text{O}_2\) reduction were fitted according to the Shoup-Szabo equation\textsuperscript{46} to simultaneously derive the \(\text{O}_2\) concentrations and the \(\text{O}_2\) diffusion coefficients in aerated DESs and water, under the conditions tested for photocatalytic \(\text{H}_2\) evolution (Table 1, Fig. S17-S20).\textsuperscript{47} All the DES-based solutions exhibited lower \(\text{O}_2\) solubility values than conventional organic solvents,\textsuperscript{48, 49} presumably due to their high ionic strengths causing a salting-out effect.\textsuperscript{50, 51} In addition, \(\text{O}_2\) diffusion coefficients were found to be lower than in most other solvents,\textsuperscript{48, 49} including water\textsuperscript{52} but varied strongly between the different DESs. This behaviour is likely a result of their high viscosities combined with their complex liquid structure,\textsuperscript{53} in which hydrogen bond donor dependent cluster formation presumably influences molecular diffusion in the liquid as well as causing large variations in viscosity.\textsuperscript{54}

### Table 1. \(\text{O}_2\) solubility and diffusivity in different solvents determined by microwire chronoamperometry and observed \(\text{O}_2\) tolerance during photocatalytic \(\text{H}_2\) generation in these solvents. Conditions: DESs (12.5\% H\textsubscript{2}O, 0.38 M TEOA, 2 mM MV\textsubscript{2+}) or water (0.38 M TEOA, pH 7), 40°C; photocatalysis: \(\text{Ni/CN}_x\) (2.0 mg), \(\text{Pt/PCl}_x\) (0.05 mg Pt) in 2 mL solvent, AM 1.5G, 1 sun, constant air purge.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(c(\text{O}_2)) ([\text{M}])</th>
<th>(D(\text{O}_2)) ([m\textsuperscript{2}\text{ s}^{-1}])</th>
<th>(\text{O}_2) tolerance Total H\textsubscript{2}[\text{H}]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reline</td>
<td>167.8±9.1</td>
<td>2.93±0.02×10\textsuperscript{-10}</td>
<td>89.3±6.1%</td>
<td></td>
</tr>
<tr>
<td>Ethaline</td>
<td>250.7±0.4</td>
<td>3.32±0.01×10\textsuperscript{-10}</td>
<td>73.5±9.0%</td>
<td></td>
</tr>
<tr>
<td>Glycline</td>
<td>218.8±2</td>
<td>9.52±0.01×10\textsuperscript{-11}</td>
<td>90.4±7.9%</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>223.5±0.4</td>
<td>2.94±0.01×10\textsuperscript{-9}</td>
<td>8.8±1.5%[\text{H}]</td>
<td></td>
</tr>
</tbody>
</table>

[a] \(\text{O}_2\) tolerance = \(n(\text{H}_2)\) produced under air relative to \(n(\text{H}_2)\) produced under \(\text{N}_2\) at Pt/\(\text{Ni/CN}_x\), after 14 h irradiation under otherwise identical conditions; [b] without added MV\textsuperscript{2+}.

We expect \(\text{O}_2\) tolerance to be a function of the effective \(\text{O}_2\) concentration at the photocatalyst surface, which depends on both solubility and diffusivity of \(\text{O}_2\) in the reaction medium.

Comparing the trends in these parameters for the different DES-based solutions to the trend in \(\text{O}_2\) tolerance shows a clear correlation between the observed retention of photocatalytic activity in air (glyceline > reline > ethaline > water) and the \(\text{O}_2\) diffusivities (glyceline < reline < ethaline < water). As \(\text{O}_2\) in solution is being consumed due to \(\text{O}_2\) reduction at the photocatalyst, the steady-state \(\text{O}_2\) concentration at the catalyst surface depends on how rapidly more \(\text{O}_2\) is supplied to the photocatalyst, therefore \(\text{O}_2\) tolerance is primarily dominated by the \(\text{O}_2\) diffusivity. The \(\text{O}_2\) solubility of the solutions (reline < glyceline < ethaline < water) is of secondary importance: glyceline and reline solutions show comparable \(\text{O}_2\) tolerances despite them showing varying \(\text{O}_2\) solubilities and diffusivities – this is likely because the lower diffusivity in glyceline is compensated by a higher \(\text{O}_2\) solubility, and vice versa. Water shows poor \(\text{O}_2\) tolerance because it exhibits the highest \(\text{O}_2\) diffusion coefficient among the solvents studied here and a relatively high \(\text{O}_2\) solubility. Due to a combination of low \(\text{O}_2\) diffusivities and low \(\text{O}_2\) solubilities, DESs thus create pseudo-inert conditions by limiting \(\text{O}_2\) mass transport, which is outcompeted by \(\text{H}_2\) diffusion.

### Table 2. \(\text{O}_2\) solubility and diffusivity in brines of different concentration and observed \(\text{O}_2\) tolerance during photocatalytic \(\text{H}_2\) generation. Conditions: \(\text{Ni/CN}_x\) (2.0 mg), \(\text{Pt/PCl}_x\) (0.05 mg Pt) in 2 mL water (0.38 M TEOA, pH 7, 2 mM MV\textsuperscript{2+}); AM 1.5G, 1 sun, 40°C, constant air purge.

<table>
<thead>
<tr>
<th>Solvent\textsuperscript{49}</th>
<th>(c(\text{O}_2)) ([\text{M}])</th>
<th>(D(\text{O}_2)) ([m\textsuperscript{2}\text{ s}^{-1}])</th>
<th>(\text{O}_2) tolerance Total H\textsubscript{2}[\text{H}]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0 M NaCl</td>
<td>223±0.4</td>
<td>2.94±0.01×10\textsuperscript{-9}</td>
<td>3.11±7.7%</td>
<td></td>
</tr>
<tr>
<td>1 M NaCl</td>
<td>265±0.6</td>
<td>2.30±0.01×10\textsuperscript{-9}</td>
<td>13.9±3.3%</td>
<td></td>
</tr>
<tr>
<td>2 M NaCl</td>
<td>165±0.2</td>
<td>1.55±0.01×10\textsuperscript{-9}</td>
<td>19.0±11.4%</td>
<td></td>
</tr>
<tr>
<td>4 M NaCl</td>
<td>128±0.3</td>
<td>1.13±0.01×10\textsuperscript{-9}</td>
<td>34.2±24.4%</td>
<td></td>
</tr>
</tbody>
</table>

[a] Solubilities were determined under the same conditions as the photocatalysis experiments were performed. [b] \(\text{O}_2\) tolerance = \(n(\text{H}_2)\) produced under air relative to \(n(\text{H}_2)\) produced under \(\text{N}_2\) at Pt/\(\text{Ni/CN}_x\), after 14 h irradiation under otherwise identical conditions.

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Figure 4. (a) Absorption spectra of \(\text{Ni/CN}_x\) in DES – 0.38 M TEOA solution (green trace) and aqueous 0.38 M TEOA (black trace) prior to irradiation with simulated solar light. \(\text{Ni/CN}_x^*\) absorption spectra in DES-0.38 M TEOA solution (blue) recorded in ambient air. (b) Photo of \(\text{Ni/CN}_x^*\) in DES solutions exposed to air (left) and in inert atmosphere (right).
Having identified the combination of low O$_2$ solubility and O$_2$ diffusivity as key factors to O$_2$ tolerance, we use these design criteria to promote O$_2$ tolerance in other solvents. Saline water is an attractive feedstock for renewable H$_2$ production since seawater is much more abundant than freshwater and its use avoids competition with drinking water supplies. While using seawater can be challenging, we show here that it can enable highly O$_2$-tolerant H$_2$ evolution. It is well known that high salt concentrations lower the O$_2$ solubility in water as well as the O$_2$ diffusion coefficients. We therefore determined the O$_2$ solubility and diffusivity in brines under photocatalysis conditions (40°C, 0.38 M TEOA, pH 7) by microwire electrochemistry. Table 2 shows that the O$_2$ solubility and diffusivity both decrease by approx. 50% upon increasing the NaCl concentration from 0 to 4 M. Consistently, figure 5 demonstrates that in line with our identified design criteria, the O$_2$ tolerance in water increases with increasing NaCl concentrations. In 4 M aqueous NaCl a cumulative O$_2$ tolerance of 34.2±4.4% is observed after 14 h (Fig. S21, Table S6), more than 10 times higher than without added NaCl (Table 2). However, despite lower O$_2$ solubilities, the O$_2$ tolerance never reaches the levels observed in DESs consistent with the higher O$_2$ diffusion coefficient in water. This demonstrates that the O$_2$ diffusivity is decisive for the overall O$_2$ tolerance, ideally when paired with a low O$_2$ solubility. Furthermore, we studied the direct use of seawater collected from Swansea Beach as a solvent for H$_2$ evolution (Fig. S22). While the H$_2$ generation activity was lower than in pure brines, presumably due to its brownish colour, the observed O$_2$ tolerance of 7.2±4.4% was higher than in pure DI water. Considering the local salinity of 0.41-0.53 M, this data is in good agreement with Table 2 and demonstrates the usefulness of using non-potable water for solar H$_2$ generation.

**Figure 5.** Enhanced oxygen tolerance by control of O$_2$ diffusion. Effect of aerobic conditions on H$_2$ production in (a) H$_2$O (a) and (b) 4 M aqueous NaCl; (c) total H$_2$ evolved after 15.5 h depending on the NaCl concentration and atmosphere; (d) O$_2$ tolerance of H$_2$ evolution depending on the NaCl concentration. Conditions: $^{185}$HCl (2.0 mg) H$_2$PtCl$_4$ (0.05 mg Pt) in 2 ml saline water (0.38 M TEOA, pH 7, 2 mM MUV$^+$); AM 1.5G, 1 sun, 40°C, constant N$_2$ or air purge.

Design rules from a quantitative model for O$_2$ tolerance

To explain the effect of O$_2$ diffusivity and solubility on the O$_2$ tolerance quantitatively, we have developed a mechanistic model based on fluxes to and from the photocatalyst particles (Figure 6a). The rate of charge carrier generation, $R_{(hv)}$, depends on light intensity and quantum efficiency and is assumed largely independent of the solvent. O$_2$ is expected to quench charge carriers with consuming O$_2$ expressed as the rate $R(O_2)$. Approximating the O$_2$-dependent quenching as O$_2$ reduction at a spherical particle at the limit of diffusional control gives eqn. 1:

$$R(O_2) = 4\pi \times r \times n \times D(O_2) \times c(O_2)$$  \hspace{1cm} (1)

with $r$ the particle radius and $n$ the number of electrons quenched per O$_2$ molecule.\(^{47}\) The flux of H$_2$ from the particle, $R(H_2)$, is assumed not impeded. The O$_2$ tolerance can then be expressed as the efficiency of H$_2$ production in competition with O$_2$-dependent quenching (eqn. 2), which upon expressing $R(O_2)$ according to eqn. 1 shows a linear dependence of the O$_2$ tolerance on the product of $D(O_2)$ and $c(O_2)$ (eqn. 3).

$$O_2 \text{tolerance} = 100\% \times \frac{R(H_2)}{R(hv)} = 100\% \times \frac{R(H_2) - R(O_2)}{R(hv)}$$ \hspace{1cm} (2)

$$O_2 \text{tolerance} = \left(1 - \frac{4\pi n r}{R(hv)} \times D(O_2) \times c(O_2)\right)$$ \hspace{1cm} (3)

Figure 6 shows that the experimentally observed O$_2$ tolerances fit well to this model (see supplementary information for details). At high O$_2$ tolerances, the slope represents the consumption of photo-generated charge carriers by O$_2$ in diffusion-limited quenching. When the O$_2$ flux increases with higher O$_2$ solubility and diffusivity, the quenching process is no longer diffusion limited but instead kinetically limited by the rate of O$_2$ reduction, resulting in O$_2$ tolerance gradually tailing towards zero at a much lower slope. From this model, we can infer a set of design rules for improving O$_2$ tolerance through further solvent design:

1. Minimise the cxD parameter (low O$_2$ solubility and diffusivity, high viscosity)
2. Increase particle size (small particles increase O$_2$ flux)
3. Increase light intensity (outcompete O$_2$ flux which is independent of light)
4. Increase photon-to-charge carrier conversion
Future work should focus on exploring all variables of the model to further verify and refine its predictive ability and achieve sustained, fully O₂-tolerant H₂ generation.

Conclusions
We have shown that O₂-tolerant H₂ evolution can be achieved by controlling O₂ diffusion and solubility in the reaction medium. We introduced DESs as a versatile medium for solar H₂ generation with both heterogenous and homogeneous light absorbers and showed that DESs induce a high O₂ tolerance to otherwise O₂-intolerant photocatalysts without compromising the quantum efficiency. We demonstrated this effect results from their low O₂ solubilities and diffusivities. Exploiting these properties as design criteria enables a 20-fold increase in O₂ tolerance in water by controlling O₂ diffusion and solubility. Through developing a quantitative model for oxygen tolerance, we believe this investigation paves the way for further solvent-enhanced solar fuel production and, owing to the tuneable nature of DESs, allows for a wide scope of solvents to be examined. The fact that a relatively small change in the solvent constituents (replacing ethylene glycol with glycerol) causes a considerable change in the O₂ diffusivity and thus in the O₂ tolerance demonstrates the enormous potential of solvent design for solar water splitting, yet it highlights the need for establishing structure-function relationships to allow a rational solvent design. Future studies will expand the concept of O₂ diffusion control to fully explore all parameters of our model with the potential to massively enhance solar water splitting without adding complexity.

Author Contributions
The corresponding author for this work is M.F.K. (m.f.kuehnel@swansea.ac.uk). M.F.K. conceived, supervised and led the project. M.G.A. conducted most of the experimental work and analysed the data. M.J.M. performed dye degradation experiments. F.M. conceived and supervised electrochemical measurements. M.F.K., M.G.A. and F.M. wrote the manuscript. There are no conflicts to declare.

Acknowledgements
This work was supported by EPSRC through a DTA studentship to M.G.A. (EP/R517925/1), and a capital investment grant to M.F.K. (EP/S017925/1). We thank Swansea University for providing start-up funds to M.F.K. We thank Prof. Alex Cowan and Dr. Gaia Neri (University of Liverpool) for recording DR-UV spectra. We wish to thank Julian Kivell and Phil Hopkins in the Swansea University mechanical workshop for their assistance with the experimental setup. M.F.K. is grateful to the Ernst Schering Foundation for support.

Conflict of interest
The authors declare no conflict of interest.

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