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Photocatalytic reforming of glycerol to H₂ in a thin film Pt-TiO₂ recirculating photoreactor

Nathan Skillen,* Kathryn Ralphs, David Craig, Sam McCalmont, Aline F. V. Muzio, Christopher O'Rourke, Haresh Manyar and Peter K. J. Robertson

Abstract

BACKGROUND: With an increase in global bioenergy production, the ‘biorefinery concept’ has now become a significant focus of research. The desire to achieve efficient conversion of biomass material into both energy and value-added products requires a combination of technologies and processes. As such, the photocatalytic reforming of feedstocks such as glycerol to hydrogen (H₂) has a lot of potential.

RESULTS: Reported here is the first example of a thin film-based photocatalytic system capable of achieving H₂ evolution using a glycerol feedstock. Using a titania (TiO₂) sol–gel, glass columns were coated with a thin TiO₂ layer before using photodeposition to add platinum (Pt) as a co-catalyst. The coated columns were assembled into a simple yet effective recirculating system which used low power UV irradiation. Under optimum conditions (two coated columns and a 40 mL min⁻¹ flow rate), a steady state of 0.9—1.0 mol min⁻¹ H₂ with a photonic efficiency [η photon (%)] of 10.22 % was achieved. Furthermore, only one column showed flaking and loss of coating whereas the remaining columns were stable for the duration of the study, which equated to > 100 h of experimental testing including replicates and determining optimal parameters.

CONCLUSION: H₂ evolution via photocatalytic glycerol reforming in a Pt-TiO₂ thin film catalyst recirculating system has been demonstrated under UV irradiation and ambient conditions. The system developed highlights that it is both catalyst development and reactor engineering that are required to continue to advance the field of photocatalysis.

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Keywords: glycerol reforming; immobilized thin film catalyst; photocatalytic reactor design; H₂ evolution; reactor engineering

INTRODUCTION

The reforming of waste compounds and biomass for the generation of hydrogen (H₂) has been shown to be a viable and potentially cost-effective method for alternative energy.¹⁻⁵ In recent years, photocatalytic applications have turned their attention towards bioenergy and reforming processes with a view towards both energy production and value-added products.⁶⁻⁸ Photocatalytic formation of H₂ has been an area of intense research since the initial publication from Fujishima and Honda⁹ in 1972; however, with the stringent requirements of pure water splitting, a number of alternative sources have been investigated. Sacrificial electron donors (SEDs) such as methanol, oxalic acid and trimethylamine are among the most commonly reported in the literature,¹⁰⁻¹² however, the cost-effectiveness of such a system is low. A more viable approach is biomass feedstocks which are both readily available and of relatively low commercial value. Cellulose-derived substances have been reported for reforming to H₂ by Zhang et al.,¹³ Caravaca et al.,¹⁴ and more recently by Wakerley et al.⁶ Although cellulose conversion can be limited due to its stable structure, glycerol as a feedstock for reforming to H₂ presents a number of advantages including: high potential stoichiometric yield of H₂, low commercial value due to overproduction and good solubility in water.

The process of photocatalytic reforming of biomass-based substances over a single photocatalyst can be considered a combination of both water splitting and biomass oxidation. Upon electron–hole generation, two electrons in the conduction band are involved with the reduction of H⁺ to H₂ via a co-catalyst such as platinum (Pt), whereas C₅H₁₀O₂ based compounds are oxidized to H₂O and CO₂ at the valence band. This process can occur...
directly through photogenerated holes or indirectly via hydroxyl radicals, to irreversibly oxidize the substrate. Such a process has the advantage over traditional water splitting of supressing recombination to increase efficiency and avoiding the back reaction of H₂ with O₂. Furthermore, the reforming of glycerol is a favourable reaction in regard to thermodynamics as the heat content of H₂ is theoretically higher than that of glycerol. H₂ has a lower heat content of ΔH₂H₂ = 285.8 kJ mol⁻¹ which corresponds to 2000 kJ mol⁻¹ (7 × ΔH₂H₂) based on the stoichiometry of the reaction, whereas glycerol is less at 1660 kJ mol⁻¹.

The photocatalytic valorization of glycerol to potential green fuels has been reported in the literature, with the focus primarily on H₂ evolution. The initial research into photocatalytic glycerol reforming was first described in the work by both Bowker et al. and Kondarides et al. in 2008 and 2009, respectively. The work by Bowker et al. identified that H₂ evolution from glycerol was four times greater over palladium-titania (Pd-TiO₂) than gold (Au)-TiO₂, whereas Kondarides and colleagues investigated Pt loading, photocatalyst content, glycerol concentration, pH and temperature for optimal H₂ evolution under ambient conditions. Subsequent papers by Kondarides et al. also investigated the kinetics and mechanism of glycerol reforming focusing on both reduction and oxidation to a range of liquid-phase products along with the activity of copper oxide (CuO)/TiO₂ for the photo reforming of glycerol. To achieve a high photocatalytic activity in H₂ evolution, a co-catalyst is often used in conjunction with TiO₂. Although to date a number of metals have been reported including Pt, Pd, Cu, Au and tungsten (W), Pt and Pd are frequently favoured. In 2008, Fu et al. showed Pt to be the most active co-catalyst for H₂ evolution from glycerol with the activity decreasing in the order of Pt > Au > Pd > Rh > Ag > Ru. Recently, Estahbanati et al. reported on the impact of operating parameters such as glycerol concentration, catalyst loading, Pt % and pH for H₂ evolution over Pt-TiO₂. Their work identified 50 % glycerol (v/v), 3.9 g L⁻¹ catalyst, 3.1% Pt and pH 4.5 to be optimum conditions. Previously, Jiang et al. investigated the role of the co-catalyst Pt and its deposition route on the formation of H₂, finding that the nature of the light harvesting of P2S and the chemical state and size of Pt along with its interaction with P2S are fundamental for glycerol reforming. Slamet et al. focused on the activity of Pt-NiO nanotube materials, reporting a maximum quantum efficiency of 37.36 % for Pt (1%)–NiO nanotubes.

Despite the increasing number of publications on glycerol reforming, there are currently none that utilize a thin film catalytic system. Within the field of photocatalysis, there has always been a strong research focus on the synthesis of new materials; however, the deployment of such materials is also paramount. The advantages of thin film-based systems including reduced downstream processing and increased viability for scale-up, have been documented previously, yet there are a number of limitations which must be overcome. The primary obstacle is eliminating mass transfer to ensure increased interaction between the catalyst and substrate. Moreover, promoting sufficient light penetration and distribution coupled with complete catalyst surface irradiation is equally important. Previously this has been achieved by coating the catalyst onto a range of supports including glass rods and spheres, optical fibres, rotating discs and stainless steel. A drawback to a number of thin film-based systems is the reduced catalyst surface area which often equates to reduced activity. Therefore, it is essential that reactor design maximizes the catalyst coating and irradiation characteristics with a view towards future scale-up.

This paper reports on the development of a simple yet effective, small-scale thin film-based system capable of glycerol reforming to H₂. A Pt-TiO₂ film was coated onto the inner wall of thin borosilicate glass columns before being irradiated by low power UV sources. To date there have been no examples in the literature of such a unit being deployed for glycerol reforming. The unit was operated as a closed recirculating batch system with samples taken from the feed-tank headspace for H₂ detection. The development of such a system reported here demonstrates that immobilized reactor designs are not just suitable for glycerol reforming to H₂ but present a potential method for feasible scale-up.

MATERIALS AND METHODS

Thin film Pt-TiO₂ coated onto glass column

Thin film Pt-TiO₂ catalyst coated on to a glass column was prepared in two steps. At first the titania films were coated onto glass columns using a modified titania paste method shown by Mills et al., followed by subsequent photodeposition of Pt nanoparticles on titania films. Twenty millilitres of titanium (IV) isopropoxide were added in a round-bottomed flask containing 4.65 g glacial acetic acid under an inert N₂ atmosphere. To this, 120 mL of 0.1 mol L⁻¹ nitric acid was added and, after mixing the reaction solution, was heated rapidly to 80 °C and maintained for 8 h. The reaction solution was allowed to cool to room temperature and any remaining aggregate particles were removed using a 0.45 μm syringe filter. The resulting colloidal solution was hydrothermally treated in a teflon pot with lid in an autoclave at 220 °C for 12 h. This hydrothermal step was used to grow the particles from 5 to 10–15 nm. Upon removal of the solution from the autoclave the separated out colloidal particles were re-dispersed using ultrasound. The reaction solution was then concentrated to ~9 μL L⁻¹ by a rotary evaporator, followed by the addition of polyethylene glycol (50 wt% Carbowax 20 mol L⁻¹) as a binder to help prevent the formation of small surface cracks when the paste is cast and allowed to dry. The titania paste was cast on the glass column using the doctor-blade technique, which allows a homogeneous spread of the paste. After drying at ambient conditions, the titania thin films were annealed at 450 °C, for 2 h.

The coated tubes were weighed obtaining the value for the weight of TiO₂ on one tube (c. 0.03417 g), this value was necessary for determining how much of the platinum precursor solution is required. The amount of precursor was determined from the weight of TiO₂ present to obtain a 1 wt% loading of Pt. Titania thin film-coated glass columns were then filled with the required amount of dihydrogenhexachloroplatinate (IV) hydrate in methanolic solution (75:25 v/v MeOH:H₂O). Subsequently, the films were irradiated with a UVA lamp for ~20 min. As a result, the ~1 wt% Pt-TiO₂ films had a dark brown-black appearance. The thin film-coated glass columns were washed with distilled water and dried in air.

Catalyst characterisation

X-ray diffraction (XRD) measurements were conducted on unused samples (i.e. not irradiated or used in any photocatalytic experiments) along with samples that had been used extensively under experimental conditions. In addition, scanning electron microscopy (SEM) analysis was conducted only using the latter sample. Samples for both XRD and SEM were prepared by cutting a
section of the quartz tube and further breaking it into smaller pieces suitable for analysis. For XRD, a Pt-TiO₂ coated tube that remained stable and active throughout the experiments was used along with an unused coated sample and a sample that had the lost the catalyst coating as a result of flaking. For SEM, a small piece of the Pt-TiO₂ coated sample was mounted onto a specimen stub equipped with a screw to secure the sample in place. The XRD measurements in this work were carried out on a PANanalytical X’Pert Pro X-ray diffractometer. The X-ray source was Cu with a wavelength of 1.5405 Å. All measurements were carried out ex situ using a spinning stage. The diffractograms were recorded from 4° to 75° with a step size of 0.017°. The SEM analysis in this work was carried out on a Quanta FEG 250 Scanning Electron Microscope. SEM was then carried out under high vacuum and images of the sample recorded in the magnification range of x100–7000.

Immobilized reactor design concept
The immobilized recirculating reactor comprised a reactor feed tank and an illumination unit, which is detailed in Fig. 1. The feed tank utilized the Propeller Fluidised Photo Reactor (PFPR) as a controllable air-tight environment in which the glycerol feedstock was mixed and gas samples were removed. The full details of the PFPR can be found in our previous publication. The illumination unit comprised coated tubes with a bespoke half-moon structured design which held up to six 8 W black lamps (Koninklijke Philips, Netherlands. Supplied by RS Components, UK). The 8 W black lamps emitted light in the UV-A region and was measured to have a peak wavelength at 370 nm using a StellaNet Black Comet spectrometer (StellaNet INC, Tampa, Florida, USA). To accurately monitor the spectral output of the lamp, the photon flux was determined using the potassium ferrioxalate actinometrical method and Eqn (1). To calculate the flux in the reactor, an uncoated glass column was filled with actinometry solution and irradiated for a dedicated period of time before analysis by UV-visible spectroscopy.

\[
\text{Photon flux} = \frac{\text{Fe}^{2+}}{\sigma \text{Fe}^{2+} \times t}
\]

where \( \text{Fe}^{2+} \) (mol) were determined based on the potassium ferrioxalate method \((7.68 \times 10^{-6})\), \( \sigma \text{Fe}^{2+} \) was set at 0.97 and \( t \) was the time (min) the actinometry solution was irradiated for. The photonic efficiency was then determined based on the calculated photon flux \((1.75 \times 10^{-5} \text{ mol min}^{-1})\) and Eqn (2).

\[
\eta_{\text{photon}}(\%) = \frac{2r_{\text{H}_2}}{\text{photon flux}} \times 100
\]

where \( \eta_{\text{photon}}(\%) \) is the photonic efficiency, \( r_{\text{H}_2} \) is the \( \text{H}_2 \) formation rate (mol min⁻¹) and photon flux is the rate of photons entering the reactor (mol min⁻¹), as determined by actinometry. As \( \text{H}_2 \) formation is a 2-electron step, the \( r_{\text{H}_2} \) was multiplied by 2.

Photocatalytic procedure
In a typical experiment, 100 mL of a predetermined concentration of glycerol feedstock was added to the reactor (unless otherwise stated, the initial concentration was 1 mol L⁻¹) and stirred at 400 rpm (2.5 dcV). The entire reactor system was purged with \( \text{N}_2 \) at 150 mL min⁻¹ for 20 min before any illumination. Upon completing purging, the pump was started and recirculated the solution through the reactor system for approx 30 min before illumination was started.

Figure 1 (i) Schematic representation of the thin film recirculating photoreactor: (a) PFPR; (b) sample point for GC syringe and analysis; (c) needle bonnet valves; (d) catalyst-coated glass column; and (e) irradiation source. (ii) Images of the reactor set-up: (a) irradiation housing; (b) PFPR under operation; (c) 8 W UV black lamp; (d) catalyst-coated column under irradiation; and (e) catalyst column filled with quinine under irradiation (for illustration purposes only).
During the photocatalytic procedure, gas samples were taken periodically from the headspace of the PFPR and analyzed by gas chromatography-thermal conductivity detection (GC-TCD) for the formation of H₂. The first sample was taken after purging to ensure that no H₂ or O₂ was present. An Agilent Technologies 7280 A GC system was used coupled with a packed column (RESTEK, 2 mm inner diameter) and a TCD. The injector was operated at temperature 150 °C, pressure 26.1 psi and flow rate 22.9 mL min⁻¹. The flow rate in the column was 20 mL min⁻¹ with an oven temperature of 50 °C, whereas the detector was maintained at 200 °C with a flow rate of 5 mL min⁻¹. Argon was used as the carrier gas. The detection of H₂ was determined by comparison to a standard injection of pure H₂, whereas quantification was determined from a calibration of known concentrations.

RESULTS AND DISCUSSION

Catalyst characterization

The XRD pattern of the synthesized Pt-TiO₂ films coated onto glass columns is shown in Fig. 2. Fig. 2(a) and (b) show the XRD diffractograms of Pt-TiO₂ films on glass columns before and after experimental use, respectively. The latter was a sample that remained stable and active throughout the experimental investigation, which also showed no signs of catalyst loss through flaking. The crystal structures of these fully coated samples were confirmed to be anatase TiO₂ based on the 2θ peaks that correspond to standard peaks for the compound. This also is in agreement with data published previously in the literature, which confirmed the sol–gel synthesis route produced a pure anatase thin film.³¹ The samples show minimal difference before and after use, with anatase peaks identified in both, confirming the stability of the coating. By contrast, the XRD diffractogram shown in Fig. 2 (c) was for a sample that had lost the catalyst coating as a result of flaking during experimental testing. Visually, the sample appeared clear and showed no activity for H₂ formation from glycerol reforming when under irradiation. The sample showed only a single broad peak around 23° corresponding to quartz with no other peaks detected, which confirmed that anatase TiO₂ was not present.

Fig. 3 shows SEM images of the Pt-TiO₂ film coated onto the glass column supports, which corresponds to the sample analyzed by XRD in Fig. 2(b). Although this sample had been used under experimental conditions, the XRD and H₂ evolution data confirmed that it remained active and stable. Fig. 3(a) is a low magnification image showing the glass column sample coated with the thin film secured by a screw on the specimen stub. Fig. 3 (b) and (c) shows the surface of the glass column at a higher magnification. The Pt-TiO₂ thin film was seen as a roughened surface with thickness ≈5 μm.

Photocatalytic H₂ production

The production of H₂ was monitored in the immobilized recirculating unit to assess the overall efficiency of the system with a view towards stability, reusability and the effect of feedstock flow rate. The stability and reusability of the Pt-TiO₂ catalyst coating was a key consideration in determining the efficiency of the reactor. Although an immobilized system is often mass transport limited, it has the advantage of being easily recycled with fewer downstream processing requirements than traditional suspended units. The reusability of the current unit is demonstrated in Fig. 4, showing the evolution of H₂ over six reaction cycles under light and dark conditions along with N₂ purging and the addition of fresh glycerol. Before the final cycle, fresh glycerol was added to the system to further confirm the stability of the catalyst coating.

A linear profile of H₂ can be seen under irradiation, whereas production plateaued under dark conditions. Under dark conditions the photocatalytic formation of H₂ stopped with only a small increase observed as a result of the pump continuing to recirculate, thereby transporting H₂ formed in the irradiation chamber to the feed tank gas headspace. These results indicate that the reaction was induced by the adsorption of photons onto the catalyst surface. Furthermore, all blank experiments conducted in the absence of light and/or catalyst showed no H₂ evolution (see Fig. S1). In the absence of glycerol and/or Pt, and therefore under pure water splitting conditions, no significant H₂ (or O₂) was

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**Figure 2** XRD diffractograms for (a) an unused Pt-TiO₂-coated glass column, (b) a Pt-TiO₂-coated glass column used under experimental conditions, and (c) a Pt-TiO₂-coated glass column after the catalyst had been lost due to flaking.
recorded showing that the H2 evolution detected was a result of glycerol photoreforming coupled with electron trapping at Pt (see Fig. S1).

Upon purging the system with N2 in later cycles, the evolution of H2 can be seen to be reproducible indicating the coated columns were stable. An average reaction rate ($r_{H2}$) of 1.03 μmol H2 min$^{-1}$ was recorded with a standard deviation of only 0.02. The slight variation that can be observed between individual time points could be a result of the appearance of partial oxidation products contributing towards H2 formation. The photocatalytic reforming of glycerol, via oxidation and reduction reactions, can lead to both H2 and a range of liquid phase products with the initial compounds expected to be dihydroxyacetone and glyceraldehyde. From these parent intermediates, compounds such as glyceric acid, glycolaldehyde, glyoxylic and oxalic acid were expected to be formed. These products are likely to be generated directly or indirectly from both OH radical attack and direct hole interaction at the valence band which also was discussed by Minero et al. 33,34 They showed that the formation of dihydroxyacetone and glyceraldehyde were formed via H-abstraction as a result of OH- attack, whereas glycolaldehyde was thought to occur via direct hole interaction and β-fragmentation. Based on the products likely to be formed, however, it can be assumed that they can subsequently undergo further oxidation rapidly, leading to proton reduction to H2. The identification and quantification of such products is currently the focus of future work with a view to better understanding the mechanism and attempting to capture these high value compounds.

Reduced activity through the loss of catalyst thin films is currently a limitation with immobilized photocatalytic designs. Parameters such as mechanical stress, sheering, heat and viscosity can all significantly impact the strength and adhesion of the thin film to the support material. In the current system, the viscosity of glycerol and flow rate were two key parameters which impacted the activity of the catalyst film. After completing a series of stability experiments (as shown in Fig. 4), it was observed that the coating on one of the columns was beginning to ‘flake’ with particles becoming suspended in the system. The initial flaking of the catalyst coating was found to be minimal, with no significant impact on activity detected. Upon prolonged

Figure 3  SEM images of the Pt-TiO2-coated glass columns: (a) large piece of coated glass column with the inner surface coated with Pt-TiO2; (b) and (c) magnified images of the thin film coating.

Figure 4  The evolution of H2 as a function of time in the photoreactor under light and dark conditions and continuous cycles with the 1st cycle (orange -), 2nd cycle in the dark (grey -), 3rd cycle (yellow -), 4th cycle after purging (blue -), 5th cycle after purging (green -) and 6th cycle after purging and addition of fresh glycerol (navy -). Experimental conditions: 1 mol L$^{-1}$ glycerol feedstock, 560 min of UV irradiation (1.75 × 10$^{-5}$ mol min$^{-1}$) under a N2 atmosphere with samples (100 μL) taken every 20 min.
use and washing with distilled H₂O, however, more substantial flaking was observed along with a corresponding drop in photocatalytic activity. After a series of washing stages, it was found that the column became transparent. The inactivity was confirmed by results shown in Fig. S1 (supported by Fig. S2), which showed that recirculating the glycerol feed through one coated and uncoated column (Fig. S1) generated a \( \Delta \text{H}_2 \) equal to a single coated column (Fig. S1(b)). Using two Pt-TiO₂ coated columns, which showed no catalyst loss, produced a \( \Delta \text{H}_2 = 0.62 \text{μmol min}^{-1} \), which was almost double that of a single column (\( \Delta \text{H}_2 = 0.35 \text{μmol min}^{-1} \)). Interestingly, the remaining columns were stable throughout the duration of the study with only minor flaking observed, which showed no impact on photocatalytic activity. To ensure that no suspended particles were present, thorough washing steps were carried out between runs.

### The Effect of Flow Rate

The primary challenge in any immobilized film-based photocatalytic reactor is overcoming the mass transfer limitations which can significantly restrict the efficiency of a system. Moreover, as the mechanical stability of catalyst films can often be an additional issue, the method of eliminating mass transfer limitations should ensure the coating is not removed in the process. This is particularly challenging given the viscosity of glycerol solutions.

In an immobilized system, it is ideal to have a thin film of solution passing over a fully irradiated catalyst surface. In the literature, this has often been achieved by creating a thin falling film by using coated plates positioned at different angles and by using a pump to create a ‘fountain-like’ effect. In the unit investigated here, a peristaltic pump was used to recirculate the glycerol solution through narrow coated columns. As the columns had an internal diameter of 5 mm, which was fully coated with catalyst, the equivalent of a thin film of solution was created which had increased residual contact with the activated surface.

The effect of flow rate was found to impact \( \text{H}_2 \) evolution in relation to both mass transfer between glycerol and the catalyst surface and movement of the photogenerated \( \text{H}_2 \) [Fig. 6(a); and see Fig. S3]. It was found that an optimum recirculating flow rate of 40 mL min\(^{-1} \) was achieved, in which the residual contact time (\( R_t = 0.06 \text{ min} \)) between the catalyst and substrate was sufficient to allow for \( \text{H}_2 \) evolution (89 μmol after 100 mins irradiation), while ensuring transport of \( \text{H}_2 \) from the catalyst surface to the reactor gas headspace. Interestingly, the order of efficiency of glycerol flow rates was 40 > 30 > 50 > 20 > 10 > 0 mL min\(^{-1} \) [Fig. 6(a)]. At 0 mL min\(^{-1} \), the data confirms that the system was entirely mass transfer limited as no evolution of \( \text{H}_2 \) was recorded in the time frame, however upon starting the pump and recirculating the feedstock, \( \text{H}_2 \) was detected in the headspace. Alternatively, increasing the flow rate to 50 mL min\(^{-1} \) showed a drop in \( \text{H}_2 \) production, which suggested that mass transfer limitation no longer predominated at flow rates > 40 mL min\(^{-1} \). At flow rates ≥10 and ≤40 mL min\(^{-1} \), Fig. 6(c) shows a linear relationship existed when \( \ln (\text{H}_2) \) versus \( R_t \) was plotted, suggesting first-order kinetics and a rate order of 0.35.

Fig. 6(b) also shows \( R_t \) for the system at increasing flow rates. Although significantly increased at lower flow rates (\( R_t = 0.23 \text{ min} \) at 10 mL min\(^{-1} \)), it is interesting to note that this did not equate to higher levels of \( \text{H}_2 \); \( R_t \) decreased at higher flow rates and the data showed that \( \text{H}_2 \) evolution increased until 40 mL min\(^{-1} \) (\( R_t = 0.06 \text{ min} \)). Furthermore, Reynolds number calculations (Table 1) showed that at flow rates >30 mL min\(^{-1} \), the flow regime was in the transition region and approaching turbulent flow, which is favourable for overcoming mass transfer limitations.

In relation to the reaction rates, a steady-state of \( \text{H}_2 \) evolution (c. 0.9 μmol min\(^{-1} \)) was achieved after 40 min of irradiation (see SI-Fig. S3). Although this value can be compared to that reported previously in the literature, it is important to note that comparison of photocatalytic systems is challenging. There are a number of parameters which influence the activity of heterogenous photocatalysis such as irradiation positioning and intensity, substrate concentration, reactor geometry including catalyst deployment (i.e., suspended or immobilized) and the physical and chemical properties of the catalyst. Therefore, to allow for a more direct comparison with previous studies, the steady-state reaction rate achieved in this study has been calculated as a function of irradiation time (h\(^{-1} \)) and quantity of catalyst present (g\( \text{TiO}_2 \)\(^{-1} \)) for a single column.

A \( \text{H}_2 \) formation rate of 1580 μmol \( \text{H}_2 \) g\( \text{cat} \)\(^{-1} \) h\(^{-1} \) per \( \text{TiO}_2 \)-coated column (based on 3.4 × 10\(^{-2} \) g catalyst coated onto each tube) was determined for this study. This rate is within values reported in previous publications, which typically have a range of 1500–4300 μmol g\( \text{TiO}_2 \)\(^{-1} \) h\(^{-1} \) for Pt-loaded \( \text{TiO}_2 \) photocatalysts\(^{16,17,19} \). Furthermore, the use of NiO (NiOx-TiO₂) in the place of Pt as a co-catalyst shows slightly lower rates of formation at 1230 and 900 μmol g-\( \text{TiO}_2 \)\(^{-1} \) h\(^{-1} \)^{37,38} The value reported here is higher than that observed when using NiO as a co-catalyst and, although lower than previous Pt-TiO₂ systems in the literature, remains comparable despite being an immobilized system.

A reaction rate as a function of \( g_{\text{cat}} \) is often used as an equivalent unit in the literature and is a useful metric for comparison, yet the implications of using such a high loading are rarely considered. In the majority of suspended systems, without sufficient reactor design optimization, a loading of 1 \( g_{\text{cat}} \) could result in significant light scattering and attenuation coupled with decreased light penetration which subsequently would impact photon-induced excitation and activity. Furthermore, this could have significant impact with a view towards any attempts at reactor scale-up. In 1998 Ray and Beenackers developed Eqn (3) to express how photocatalytic reactor volume can be determined\(^{39} \) although the equation was directed primarily towards environmental remediation.
Figure 6  (a) The formation of H$_2$ as a function of irradiation time and increasing feed flow rate over 0 (■), 10 (●), 20 (♦), 30 (–), 40 (▲) and 50 (■) mL min$^{-1}$. (b) The relationship between flow rate, rH$_2$ (●) and R$_t$ (▲). (c) a plot of Ln(rH$_2$) versus Ln(R$_t$). Experimental conditions: 1 mol L$^{-1}$ glycerol feedstock, 100 min of UV irradiation ($1.75 \times 10^{-5}$ mol min$^{-1}$) under a N$_2$ atmosphere with samples (100 μL) taken every 20 min.

Table 1  Calculated flow rates, R$_t$, Reynolds number and flow regime of the recirculating thin film column reactor in relation to rH$_2$

| Flow rate (mL min$^{-1}$) | R$_t$ (min) | Reynolds number | Flow regime | rH$_2$ (μmol min$^{-1}$) |
|---------------------------|-------------|-----------------|-------------|------------------------|
| 0                         | 0           | 0               | Laminar     | 0                      |
| 10                        | 0.23        | 682             | Laminar     | 0.54                   |
| 20                        | 0.12        | 1364            | Laminar     | 0.68                   |
| 30                        | 0.08        | 2046            | Laminar     | 0.78                   |
| 40                        | 0.06        | 2728            | Transition  | 0.89                   |
| 50                        | 0.05        | 3410            | Transition  | 0.76                   |

Figure 7  Schematic representation of glycerol reforming in the thin film recirculating photoreactor.
applications, it highlights the complexity and importance of irradiated catalyst surface.

\[ V_R = \frac{QC_iX}{ICDAMP} \]  

(3)

Where \( Q \) is the volumetric flow rate (\( m^3 \) s\(^{-1} \)), \( C_i \) is the inlet pollutant concentration (mol m\(^{-3} \)), \( X \) is the desired fractional conversion, \( ICD \) is the illumination catalyst density and \( AMP \) is the average mass conversion rate.

Therefore, increasing the loading of catalyst while maintaining a desirable reaction rate is dictated by the ability of the irradiation source to deliver sufficient photons to the surface of the catalyst. In the system presented here, to obtain a catalyst loading equal to 1 g would simply require either an increase in the length or number of glass rods used, which importantly could be achieved without impacting the irradiation pathway.

With light and reactor design clearly impacting overall photocatalytic activity, it is important to consider further measurements of efficiency that take these parameters into account. Moreover, although light penetration and distribution are key factors in any photocatalytic system, their role is crucial in an immobilized design due to limitations that the catalyst platform presents. In the current investigation the coating on the inside of the glass rods ensured that maximum light penetration could be achieved more readily than in a traditional slurry system. If the coating is considered in its most basic form, which is a thin layer of catalyst particles, then the ideal method of activation is to irradiate from one side, thus allowing the generation and movement of electrons which react with glyceral molecules as it passes through the inside of the column (Fig. 7). This reduces the number of ‘objects’ between the source of irradiation and the target which subsequently improves the efficiency. A similar approach was adopted by Peill and Hoffmann in their optical Program (PRP) at Queen’s University for funding his research.

Supporting information may be found in the online version of this article.

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**SUPPORTING INFORMATION**

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Table 2  Calculated H₂ evolution rates \((rH₂ max)\), photon flux and \(\eta_{photon} (%)\) for the thin film system with 24 W black lamps

| Irradiation source | \(rH₂ max\) \((mol \text{ min}^{-1})\) | Photon flux \((mol \text{ min}^{-1})\) | \(\eta_{photon} (%)\) |
|-------------------|-----------------|-----------------|--------------|
| Thin film system with 24 W black lamps | \(1.8 \times 10^{-6}\) | \(1.75 \times 10^{-5}\) | 10.22 |

\(rH₂ max\) was calculated as \(2 \times rH₂\) based on a two-electron step for \(H^+\) to \(H₂\).
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