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Exploring the photocatalytic hydrogen production potential of titania doped with alumina derived from foil waste

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ABSTRACT

The multifunctional potential of a catalyst previously synthesised for thermal processes is explored by investigating its activity for photocatalytic production of H₂ from glycerol, a by-product from the manufacture of bio-diesel. The studied catalyst contains TiO₂ doped with Al₂O₃ that was derived from aluminum foil waste. This catalyst showed higher photocatalytic activity than the analogous catalyst prepared with a commercial Al₂O₃. Pt and Pd act as electron traps while the Al₂O₃ demonstrated a promotional effect, partially through proton donation. Under optimum conditions, a steady-state of 4.2 millimole H₂ gTiO₂⁻¹ hr⁻¹ was produced, which is comparable to the 4.7 millimole H₂ gTiO₂⁻¹ hr⁻¹ obtained with Pt-TiO₂, which is a standard photocatalytic material. It should be noted that the reported Pt/Pd/TiO₂-ANFL catalyst has not yet been optimised and so this result is encouraging. It is hoped that these findings can inspire more sustainable and less expensive hydrogen production, including from biomass feedstocks such as glycerol.

KEYWORDS: Hydrogen production; glycerol; aluminium foil waste; photocatalysis

Introduction

The deployment of cost-effective catalyst supports with low power technologies such as photocatalysis presents the potential to develop more favourable systems. Photocatalysis is a light-induced chemical reaction during which electron-hole charge carriers are generated that are capable of undergoing redox reactions on the surface of an active material. Since the initial publication by Fujishima and Honda in 1972 [1], photocatalytic technology has been deployed over a diverse range of fields including water splitting [2] and reduction [3], CO₂ reduction[4], water disinfection [5] and air purification [6]. Moreover, a number of novel photocatalytic materials have now been reported in the literature for each of these applications [7–13].

As an application, H₂ production remains one of the most challenging yet promising domains of photocatalysis. Pure water splitting, however, is both thermodynamically unfavourable and limited by a number of stringent requirements. As such, the use of sacrificial electron donors (SEDs) which are irreversibly oxidised and thus improve recombination and suppress back reactions, present a more viable option. Previously reported SEDs include alcohols [14], oxalic acid [3] and acetic acid [15]. An issue with the majority of these compounds is their use in current industrial processes and commercial value, both of which cannot be offset with the potential H₂ produced. As a result, focus has shifted to utilising alternative products such as cellulose [16,17] and glycerol [18]. As a feedstock, glycerol is an excellent choice as stoichiometrically it can generate a high yield of hydrogen and glycerol is a by-product (10% by volume) of biodiesel production and is generated in high volume with relatively low commercial value[19]. With the USA and Europe both producing 1.8 billion gallons of bio-diesel each year, this means there is a significant sustainable feedstock of glycerol available [19]. A number of publications have shown the potential of glycerol including Bowker *et al.* [18] who stated that H₂ evolution from glycerol was four times greater over Pd-TiO₂ than Au-TiO₂. Estahbanati *et al.* [20] also reported on the optimum conditions they established for H₂ to glycerol conversion: 50 % glycerol (v/v), 3.9 gL⁻¹ catalyst, 3.1 % Pt and a pH of 4.5. Furthermore, Jiang *et al.* [21] identified the role of the co-catalyst Pt and its deposition route to be crucial for glycerol reforming.

Usually alumina supports are produced from bauxite ore, which is mined in countries such as West Africa, the West Indies and Australia. It causes massive environmental damage by generating considerable levels of waste such as tailings, red mud, emissions of perfluorocarbon and CO₂ gases during the production process [22].

The conversion of aluminium foil waste (AFW) into mesoporous γ -Al₂O₃ (catalyst/support) using a cost-effective green synthetic route is highly desirable. Recently, we reported an eco-

friendly and less expensive synthesis of mesoporous γ -Al₂O₃ from AFW where the produced mesoporous alumina catalyst (γ -Al₂O₃) had surface and bulk characteristics better than commercial alumina in relation to the surface structure [22,23]. A further additional benefit is that our alumina is generated from AFW, therefore reducing the need for landfill.

Presented here is the use of our previously reported AFW catalyst support [22,24] for the application of photocatalytic reforming of glycerol to H₂. TiO₂, Pd and Pt were loaded onto the AFW derived Al₂O₃ and used in conjunction with a propeller fluidised photo reactor (PFPR) [3] under low power UV irradiation. As a proof of concept study, the photocatalytic activity and stability of the material are reported.

Experimental

The AFW was collected from the laboratories in the David Keir building at Queen's University Belfast. The chemicals used in the present study were all analytical grade and most were supplied by Aldrich, UK. These included glycerol, Al(NO₃)₃·9H₂O, Pd(NO₃)₂·2H₂O, ~40% Pd basis, Nano-powder TiO₂, 99.7%, anhydrous aluminium chloride (AlCl₃), nitric acid (≥65%), hydrochloric acid (≥37%), Hg(NO₃)₂ · H₂O (≥99.99% trace metals basis), pyridine anhydrous (99.8%), AgNO₃ (≥99.0%) and ammonia solution (35%). Pt(NH₃)₄(OH)₂, assay 9.09% was obtained from Alfa Aesar. TiO₂ P25 was supplied by Evonik Degussa. All gases (H₂, He, Ar and N₂) were obtained at 100% purity from BOC gases, UK.

The preparation of AlCl₃·6H₂O and Al(NO₃)₃·9H₂O single crystal

The preparation method is described elsewhere¹. While the AFW was collected from our laboratory, any variance as a result of previous use can be negated through hydrothermal treatments. The AFW, in this case, was previously used for insulation of heat traced gas lines. The AFW was dissolved in acidic solutions, and then the solution was kept under a desiccator until different single crystallites formed. After the re-crystallisation, a novel facile preparation route was followed to prepare the γ -Al₂O₃ via ammonia precipitation. The alumina support prepared from the AFW designated as ANFL.

Preparation of modified ANFL

The preparation of a bimetallic Pd-Pt loaded on a dual component support ($\text{TiO}_2/\text{ZSM-5(80)}$) has been described in previous work¹⁵. This previous preparation was for alkane oxidation applications, and the same metal loadings were utilised in the current work. The catalysts were prepared using a wet impregnation method with the aid of sonication using a catalyst composition of 5% Pd+ 2% Pt + 17.5% TiO_2 + 75.5% Al_2O_3 (ANFL). Pure ANFL support was placed in a vial and the mass of metal precursor solution or slurry, required to give 5 wt% palladium and 2 wt% platinum loading was added followed by TiO_2 to give 17.5 wt% in deionised water. The mixture was sonicated at 80 °C, under a 45 kHz frequency for 3 hrs. All mixtures were dried at 120 °C overnight in an oven before being calcined in air at 500 °C for 4 hrs with a heating ramp of 2 °C min⁻¹. Finally, the produced catalysts were further washed with hot deionised water until no chlorine was detected using AgNO_3 . A benchmark catalyst was prepared using the same procedure mentioned above with a composition of 5% Pd+ 2% Pt + 17.5% TiO_2 + 75.5% commercial alumina and was designated as commercial.

Determination of Chlorine Content

The chlorine content was measured using Oxygen Flask analysis by subjecting the sample to combustion in an oxygenated flask containing water, followed by shaking; in which chlorine dissolved in water forming HCl solution, the latter solution was titrated with 0.02 M Hg_2NO_3 to obtain the percentage of chlorine. There was no chlorine detected in the samples after preparation.

Catalyst Characterisation

Brunauer-Emmett-Teller (BET) analysis was performed using a Micromeritics ASAP 2020 system. BET surface area and pore volume were measured by N_2 adsorption and desorption isotherms at liquid nitrogen temperature (77.15 K).

The acidity populations over the surface of catalysts were measured thermogravimetrically using the adsorption of pyridine as a probe molecule. Small portions (50 mg) of each sample were pre-heated at 250 °C for 2 h in the air before the exposure to the probe molecule. 15-20 mg of pyridine-covered samples were subjected to TG analysis on heating up to 600 °C (at 20 °C min⁻¹ heating rate) in dry N₂ (flow rate = 40 mL min⁻¹). The mass loss due to desorption of pyridine from the acidic sites was determined as a function of total surface acidity as sites.g⁻¹_{cat}. Determination of the concentration of Lewis and Brönsted acid sites on the pyridine-covered samples was performed using a Perkin Elmer-Spectrum 100 FT-IR spectrometer.

Transmission electron microscope (TEM) characterisation was performed using a Philips Tecnai F20 ST with a high tension of 200 kV and point resolution of 0.24 nm.

Photocatalysis Testing

All photocatalytic experiments were conducted in the PFPR, the full details of which can be found elsewhere⁴. In a typical experiment, 100 mL of a predetermined concentration of glycerol feedstock (typically 1 M) was added to the reactor along with 0.75 g L⁻¹ of catalyst and stirred at 250 rpm (2.5 dcV). The entire reactor system was sealed and purged with N₂ at 150 mL min⁻¹ for 20 min prior to any illumination. Upon completing purging, a sample was taken to confirm no O₂ or H₂ was present. The reactor propeller speed was then increased to 1200 rpm (5.5 dcV) and the illumination started.

Illumination was provided by two compact fluorescent non-integrated lamps (Phillips), powered by a dual ballast (Tridonic). Each lamp had an electrical power of 36 W and peak wavelength of 355 nm. The lamps were positioned on either side of the PFPR at a distance of 5 mm from the annular glass body. The intensity of light at the quartz glass body of the PFPR was measured using a radiometer (UV-X) and was found to be 4.7 mW cm^{-2} . An image of the PFPR under irradiation can be seen in Figure 1.

Figure 1: *Image of the PFPR under irradiation from two 36 W compact fluorescent lamps*

During the photocatalytic procedure, gas samples were taken periodically from the headspace of the PFPR and analysed by GC-TCD for the formation of H_2 . An Agilent Technologies 7280 A GC system was used coupled with a packed column (RESTEK, 2 mm ID) and a Thermal Conductivity Detector (TCD). The injector was operated at a temperature of 150°C , pressure of 26.1 psi and a flow rate of 22.9 mL min^{-1} . The flow rate in the column was 20 mL min^{-1} with an oven temperature of 50°C , while the detector was maintained at 200°C with a flow rate of 5 mL min^{-1} . Ar was used as the carrier gas. The detection of H_2 was determined by comparison to a standard injection of pure H_2 , while quantification was determined from a calibration of known concentrations.

Results and Discussion

The photoactivity of the various materials tested for H_2 evolution are shown in Figure 2. With a loading of TiO_2 onto the surface of the Al_2O_3 support structures, it was expected all the materials would exhibit photoactivity under UV irradiation. In contrast, when TiO_2 was not present, no photoactivity was observed for the support material on its own. In the absence of both Pt and Pd, a small amount of H_2 was recorded with the rate increased significantly upon the addition of both co-catalysts. This confirmed that Pt and Pd were likely acting as reaction centres and electron traps to facilitate the reduction of protons to H_2 . Additionally, in the absence of irradiation and glycerol, no H_2 was detected which confirmed the process was photo-induced and H_2 was evolving from the irreversible conversion of glycerol.

Figure 2: photocatalytic reforming of glycerol to H_2 over various catalysts as a function of irradiation time. H_2 evolution over Pt/Pd/ TiO_2 -ANFL (*), Pt/Pd/ TiO_2 -commercial (•) and TiO_2 -ANFL (•)

Figure 2 also highlights the impact of the support materials (ANFL and commercial alumina) on photocatalytic H₂ evolution. As already shown, the support on its own was not photoactive, yet was evidently capable of affecting the photocatalytic activity. The characterisation of the catalysts (Table 1) revealed the catalysts derived from commercial alumina and ANFL have similar surface areas: 278 and 264 m² g⁻¹, respectively. Furthermore, the pore volumes were 0.35 and 0.5 cm³ g⁻¹ for commercial Al₂O₃ and ANFL catalysts, respectively. Despite having a lower surface area however, the ANFL catalyst interestingly showed up to 22 % higher photocatalytic activity than the catalyst prepared using commercial alumina (Figure 2). This may be in part due to the ANFL catalyst having lower mass transfer limitations due to the larger pore volume. In general, however, an increase in photocatalytic activity is primarily achieved through improving charge separation and the availability of acceptor and donor species on the catalyst surface. Typically, this involves the presence of OH⁻ for the generation of the OH• at the valence band and a suitable electron scavenger (e.g. O₂ or protons) at the conduction band.

Table 1: Surface area (S_{BET} (m² g⁻¹)) and pore volume (cm³ g⁻¹) for acidic support derived from foil waste

Catalyst	S _{BET}	Pore volume	Total acidity ^a ,	Total acidity ^b ,
	(m ² g ⁻¹)	(cm ³ g ⁻¹)	A(sites g ⁻¹)	B(sites m ⁻²)
ANFL	264	0.5	8.13	3.1
commercial	278	0.35	6.91	2.5

^a Total acidity = A x 10²⁰.

^b Acid density = B x 10¹⁸.

Interestingly, the characterisation of the support materials revealed the Pt/Pd/TiO₂-ANFL catalyst to have significantly higher total acidity (sites g⁻¹) than the commercial Al₂O₃ equivalent. The total acidity of the commercial Al₂O₃ catalyst in sites/g was 6.91×10^{20} , which was significantly increased to 8.13×10^{20} in case of ANFL catalyst. The acid density of the ANFL was also higher than that of the commercial catalyst of 3.1×10^{18} and 2.5×10^{18} , respectively, as shown in Table 1.

This higher level of acidity was likely due to increase the availability of protons at the surface of the ANFL support. Subsequently, the higher number of available protons may result in accelerated electron transfer to adsorbed protons at the conductance band of TiO₂, which would increase H₂ formation. Based on this, it can be shown that while the addition of the ANFL support did not alter the catalytic activity through changes to the parent photoactive material (TiO₂), it did provide an increased number of electron acceptor species (protons) and hence enhanced H₂ formation. The impact of Al on the photocatalytic activity of TiO₂ has previously been reported by Murashkina *et al.* [25]. Their report found that, as expected, the addition of Al resulted in an increase in the anatase fraction of mixed-phase TiO₂ along with a decrease in particle size and subsequently an increase in the surface area of the material. Interestingly, the paper found that while the addition of Al to TiO₂ did not alter the reaction sites, it did increase the concentration of them available and thus accelerated the rate of phenol degradation [25].

Figure 3: TEM images of Pd, Pt and TiO₂ loaded onto Al₂O₃ supports (ANFL).

While it was the presence of TiO₂, Pt and Pd (see Figure 3) which primarily drove the photocatalytic reduction reaction in the current work, the increase in proton availability and affinity at the ANFL support was crucial for improved H₂ generation. Equations 1-4 detail the typical process occurring during the photo-reforming of glycerol to H₂. In order for photocatalytic H₂ evolution to occur, a photon was adsorbed by TiO₂ leading to photo-excitation (Equation 1) and subsequently, electron trapping by either Pd or Pt. Simultaneously however, OH⁻ from the glycerol-water solution will lead to OH• formation (Equation 2), which facilitates glycerol oxidation to a range of liquid phase products and protons (Equation 3). The liquid phase products include dihydroxyacetone, glycolaldehyde and glyceraldehyde which can occur *via* either direct hole or OH• interaction. The key step in the formation of H₂ from glycerol is this initial oxidation, which also releases protons. The release and increased availability of protons through the use of ANFL, resulted in the accelerated two-electron reduction of protons to H₂ (Equation 4). Based on Equations

1-4, the illustration in Figure 4 represents the proposed mechanism for photocatalytic glycerol reforming to H₂ over Pt/Pd/TiO₂-ANFL.

Figure 4: Illustration of the proposed mechanism of photocatalytic glycerol reforming over Pt/Pd/TiO₂-ANFL

The Pt/Pd/TiO₂-ANFL catalyst also showed stable activity over a prolonged irradiation time frame of 6 h. This confirmed linear H₂ formation and zero order kinetics with a rate constant of 0.95 μmol min⁻¹. In addition, steady-state H₂ production was also achieved after 180 min at a rate of ~4.2 millimole H₂ gTiO₂⁻¹ hr⁻¹ (Figure 5).

Figure 5: photocatalytic reforming of glycerol to H₂ over Pt/Pd/TiO₂-ANFL over prolonged irradiation (•) and the corresponding reaction rate (•)

As Pt/Pd/TiO₂-ANFL was evidently active, comparison to a standard catalyst used in this field (0.5 % Pt-TiO₂ P25) was valuable. Under the same experimental conditions 0.5 % Pt-TiO₂ was shown to be the optimum loading for H₂ formation, achieving a rate constant of 5.9 μmol min⁻¹ (see Figure S1 and S2 in the Supplementary Information), which was significantly higher than that of Pt/Pd/TiO₂-ANFL. In order for an accurate comparison, however, the amount of photo-active material present should be taken into consideration. While a loading of 0.75 g L⁻¹ was used in both experiments, in the case of ANFL this was not entirely photo-active material, as only 17.5 % was TiO₂. Therefore, recalculating the yields under these conditions as a function of 1 gram of active TiO₂ material then it was found 0.5 % Pt-TiO₂ produced 4.7 millimole H₂ gTiO₂⁻¹ hr⁻¹ while

Pt/Pd/TiO₂-ANFL produced 4.2 millimole H₂ gTiO₂⁻¹ hr⁻¹. These numbers are clearly far more comparable than just the individual rates. Furthermore, this number is also within typical values previously reported in the literature for glycerol conversion to H₂ using Pt-TiO₂ catalysts. The comparison between heterogeneous photocatalytic systems can often be challenging due to the number of parameters which can influence the activity such as irradiation intensity and time of exposure, catalyst and substrate concentration, reactor design and physical catalyst morphology. Therefore, comparison in this study has been based only on reaction rate as a function of irradiation time (hr⁻¹) and quantity of catalyst used (gTiO₂⁻¹). A number of papers have used Pt-TiO₂ for glycerol reforming to H₂ with a typical reported range of 1.5 to 4.3 millimole gTiO₂⁻¹ hr⁻¹ which included the use of fluorinated Pt-TiO₂ and Pt on TiO₂ nanotubes [21,26,27]. In addition, a rate of 1.23 and 0.9 gTiO₂⁻¹ hr⁻¹ was reported by Fujita *et al.* [28] and Liu *et al.* [29] respectively, who both utilised NiO (NiO_x-TiO₂) in replace of Pt as a co-catalyst. While the reaction rate reported here is clearly within that achieved in previous papers, this paper is the first to achieve it using a catalyst support synthesised from AFW. It should also be noted that 0.5 % Pt on TiO₂ has often been reported as the optimum co-catalyst loading [3], however, the co-catalysts present on ANFL are yet to be optimised for peak production. It has already been shown in multiple publications that Pt [15,30], with its high work function (5.5 eV), is typically the most active co-catalyst for H₂ evolution. Therefore, it is feasible to assume that the 4.2 mmole H₂ gTiO₂⁻¹ hr⁻¹ could be an underestimation and can be improved with modification to the co-catalyst ratio. This is the current focus of on-going work with a view towards optimising the catalyst.

The development of an eco-friendly and cost-effective catalyst material is largely dictated by first its initial activity and second, its stability over time. Figure 6 demonstrates the stability of the Pt/Pd/TiO₂-ANFL catalyst for the evolution of H₂ from glycerol over repeated runs. The catalyst and glycerol mass remained constant throughout the run with N₂ being used to purge the system in-between irradiation cycles to remove H₂ from the gas headspace. Over a run of five cycles,

Pt/Pd/TiO₂-ANFL showed steady photoactivity and interestingly appeared to reach a stable state after two cycles. At cycle 5, a zero-order rate constant of 1.1 $\mu\text{mol min}^{-1}$ was achieved, which was a $\sim 14\%$ increase from cycle 1. The data also confirmed the presence of an induction period, which was evident in Figure 2 and the first cycle of Figure 6. In a number of H₂ evolving photocatalytic systems, an initial period of inactivity or an induction period is often observed [16]. The cause of this varies depending on the parameters which are being tested, however, it can often be due to the initial reduction of the co-catalyst or the adsorption of the target to the catalyst site.

Figure 6: Photocatalytic reforming of glycerol to H₂ over Pt/Pd/TiO₂-ANFL and 5 experimental cycles as a function of irradiation time. The reactor was purged with N₂ for 20 mins between each cycle while the reaction suspension (glycerol + catalyst) remained constant throughout.

In the case reported here, despite a polynomial trend in the first cycle, a linear trend is observed from cycle two onwards. While the induction period in H₂ evolving catalysts has been documented [16], it does not necessarily explain the increase in activity in the later cycles. One explanation could be the presence of partial oxidation products (Equation 3) which will remain in the liquid phase between cycles. Moreover, the formation of partial oxidation products would increase the concentration of protons at the surface of ANFL. With a high number of protons available upon stating irradiation in cycle 2, linear and increased H₂ production would be expected.

In addition to the gas evolution rate, the η_{photon} of the system was also determined based on the calculated photon flux and the maximum rate of H₂ formation ($r_{\text{max}}\text{H}_2^{\text{a}}$). The determination of efficiencies in photocatalysis is a useful metric, especially for allowing for more accurate comparison between studies. The calculation of quantum efficiency and quantum yield is typically determined based on the absorbed light flux. In heterogeneous photocatalytic systems, however, accurately determining this value can be extremely challenging. Therefore, photonic efficiency (or apparent quantum efficiency) is often reported and as such is reported here to be in keeping with common practice. The photon flux was calculated to be 1.12×10^{-4} moles min^{-1} based on Equation 5, while the $r_{\text{max}}\text{H}_2^{\text{a}}$ was calculated as r_{H_2} multiplied by two as H₂ formation is a two-electron step.

$$\text{Equation 5} \quad \text{Photon flux} = \frac{I \times A_I}{\left(\frac{c \times h \times N_a}{\lambda} \right)}$$

Where, ' I ' is the intensity of light (47 W m^{-2}) at the surface of the PFPR quartz body ' A_I ' is the surface area of the reactor illuminated (0.014 m^2), ' c ' is the speed of light, ' h ' is plank's constant, ' N_a ' is Avogadro's number and λ is the peak wavelength emitted from the lamps (measured to be 355 nm , $3.55 \times 10^{-7} \text{ m}$). The η_{photon} was then determined as the ratio between $r_{\text{max}}\text{H}_2^{\text{a}}$ and the photon flux, Equation 6.

$$\text{Equation 6} \quad \eta_{photo} (\%) = \frac{r_{max}H_2^a}{\text{phot flux}} \times 100$$

Where ' η_{photon} ' is photonic efficiency, ' $r_{max}H_2^a$ ' is the maximum rate of H_2 production based on the number of electrons involved (moles min^{-1}) and ' photon flux ' is as described above.

Table 2 shows Pt/Pd/TiO₂-ANFL achieved the highest η_{photon} at 1.4 %, with Pt/Pd/TiO₂-commercial achieving slightly lower at 1.1 %. In comparison, TiO₂-ANFL achieved a significantly lower η_{photon} of 0.09 %, confirming the presence of co-catalysts on the support were crucial to H_2 evolution. While a relatively low efficiency, it highlights the potential of using a cost-effective catalyst support synthesised from AFW over that of commercially available alternatives.

Table 2: Calculated efficiencies of Pt/Pd/TiO₂-ANFL, Pt/Pd/TiO₂-commercial and TiO₂-ANFL where $r_{max}H_2^a$ is the max moles of H_2 produced per min, $r_{max}H_2^b$ is the max rate of H_2 as a function of 1 gram of active photocatalyst material present (TiO₂) and 1 h of irradiation and η_{photon} was the photonic efficiency of the materials based on the PFPR photon flux of $1.21 \times 10^{-4} \text{ moles min}^{-1}$ and the $r_{max}H_2^a$.

Catalyst	$r_{max}H_2^a$ (mol min^{-1})	$r_{max}H_2^b$ ($\text{mol gTiO}_2^{-1} \text{ hr}^{-1}$)	η_{photon} (%)
Pt/Pd/TiO ₂ -ANFL	1.72×10^{-6}	7.9×10^{-3}	1.4
Pt/Pd/TiO ₂ -commercial	1.31×10^{-6}	6.0×10^{-3}	1.1
TiO ₂ -ANFL	1.1×10^{-7}	5.1×10^{-4}	0.09

Conclusion

Glycerol is known to be a significant waste stream from the production of bio-diesel. In the current work a photoactive catalyst derived from aluminium foil waste (AFW) with high activity (per g of photoactive material) for the production of H_2 from glycerol has been reported. This AFW derived catalyst was found to be more active than the analogous catalyst made from commercially

available Al_2O_3 . Under optimum conditions, a steady-state of $4.2 \text{ mmol H}_2 \text{ gTiO}_2^{-1} \text{ hr}^{-1}$ was achieved after 180 min of irradiation. Despite TiO_2 being the only photoactive material present in the catalyst, it was evident that the ANFL and commercial alumina supports were both capable of impacting activity through the increase in proton availability.

In summary, the current work has utilised a catalyst that is synthesised using waste aluminium foil as a resource, limiting the single-use of aluminium foil. In a two-fold approach to improving the eco-friendliness and the circular economy, we have applied this catalyst to the production of H_2 from a significant waste stream, i.e. glycerol.

Our approach opens doors for designing an environmentally sustainable catalyst from waste materials which could be of great interest for many industrial applications in the future, including hydrogen production from glycerol (and other biomass feedstocks). It is anticipated that such an approach will make hydrogen production more sustainable, more eco-friendly and less expensive. Furthermore, it is anticipated that the catalyst can be further optimised via the investigation of varying the co-catalyst loadings. Additional future work will investigate such optimised catalysts for other common photocatalytic activities such as dye removal and water remediation applications.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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- [1] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 1972;238:37–8.

- [2] Skillen N, McCullagh C, Adams M. Photocatalytic Splitting of Water. vol. 35. 2015.
https://doi.org/10.1007/698_2014_261.
- [3] Skillen N, Adams M, McCullagh C, Ryu SY, Fina F, Hoffmann MR, et al. The application of a novel fluidised photo reactor under UV-Visible and natural solar irradiation in the photocatalytic generation of hydrogen. *Chem Eng J* 2016;286. <https://doi.org/10.1016/j.cej.2015.10.101>.
- [4] Li K., An X Park K H, Khraisheh M, Tang J. A critical review of CO₂ photoconversion: Catalysts and reactors. *Catal Today* 2014;224:3–12.
- [5] Robertson PKJ. Semiconductor photocatalysis: an environmentally acceptable alternative production technique and effluent treatment process. *J Clean Prod* 1996;4:203–12.
[https://doi.org/http://dx.doi.org/10.1016/S0959-6526\(96\)00044-3](https://doi.org/http://dx.doi.org/10.1016/S0959-6526(96)00044-3).
- [6] Boyjoo Y, Sun H, Liu J, Pareek VK, Wang S. A review on photocatalysis for air treatment: From catalyst development to reactor design. *Chem Eng J* 2017;310, Part:537–59.
<https://doi.org/http://dx.doi.org/10.1016/j.cej.2016.06.090>.
- [7] Hu Z, Mi Y, Ji Y, Wang R, Zhou W, Qiu X, et al. Multiplasmon modes for enhancing the photocatalytic activity of Au/Ag/Cu₂O core–shell nanorods. *Nanoscale* 2019;11:16445–54.
<https://doi.org/10.1039/C9NR03943K>.
- [8] Navakoteswara Rao V, Lakshmana Reddy N, Mamatha Kumari M, Ravi P, Sathish M, Kuruvilla KM, et al. Photocatalytic recovery of H₂ from H₂S containing wastewater: Surface and interface control of photo-excitons in Cu₂S@TiO₂ core-shell nanostructures. *Appl Catal B Environ* 2019;254:174–85. <https://doi.org/10.1016/J.APCATB.2019.04.090>.
- [9] Reddy CV, Reddy IN, Reddy KR, Jaesool S, Yoo K. Template-free synthesis of tetragonal Co-doped ZrO₂ nanoparticles for applications in electrochemical energy storage and water treatment. *Electrochim Acta* 2019;317:416–26. <https://doi.org/10.1016/J.ELECTACTA.2019.06.010>.
- [10] Reddy KR, Reddy CV, Nadagouda MN, Shetti NP, Jaesool S, Aminabhavi TM. Polymeric graphitic carbon nitride (g-C₃N₄)-based semiconducting nanostructured materials: Synthesis

methods, properties and photocatalytic applications. *J Environ Manage* 2019;238:25–40.

<https://doi.org/10.1016/J.JENVMAN.2019.02.075>.

- [11] Reddy CV, Reddy IN, Akkinapally B, Harish VVN, Reddy KR, Jaesool S. Mn-doped ZrO₂ nanoparticles prepared by a template-free method for electrochemical energy storage and abatement of dye degradation. *Ceram Int* 2019;45:15298–306.
<https://doi.org/10.1016/J.CERAMINT.2019.05.020>.
- [12] Mehta A, Mishra A, Basu S, Shetti NP, Reddy KR, Saleh TA, et al. Band gap tuning and surface modification of carbon dots for sustainable environmental remediation and photocatalytic hydrogen production – A review. *J Environ Manage* 2019;250:109486.
<https://doi.org/10.1016/J.JENVMAN.2019.109486>.
- [13] Venkata Reddy C, Reddy IN, Akkinapally B, Reddy KR, Shim J. Synthesis and photoelectrochemical water oxidation of (Y, Cu) codoped α -Fe₂O₃ nanostructure photoanode. *J Alloys Compd* 2020;814:152349. <https://doi.org/10.1016/J.JALLCOM.2019.152349>.
- [14] Chen W-T, Chan A, Sun-Waterhouse D, Llorca J, Idriss H, Waterhouse GIN. Performance comparison of Ni/TiO₂ and Au/TiO₂ photocatalysts for H₂ production in different alcohol-water mixtures. *J Catal* 2018;367:27–42. <https://doi.org/https://doi.org/10.1016/j.jcat.2018.08.015>.
- [15] Zheng X-J, Wei L-F, Zhang Z-H, Jiang Q-J, Wei Y-J, Xie B, et al. Research on photocatalytic H₂ production from acetic acid solution by Pt/TiO₂ nanoparticles under UV irradiation. *Int J Hydrogen Energy* 2009;34:9033–41.
<https://doi.org/http://dx.doi.org/10.1016/j.ijhydene.2009.09.019>.
- [16] Caravaca A, Jones W, Hardacre C, Bowker M. H₂ production by the photocatalytic reforming of cellulose and raw biomass using Ni, Pd, Pt and Au on titania. *Proc R Soc A Math Phys Eng Sci* 2016;472.
- [17] Zhang G, Ni C, Huang X, Welgamage A, Lawton LA, Robertson PKJ, et al. Simultaneous cellulose conversion and hydrogen production assisted by cellulose decomposition under UV-light

photocatalysis. *Chem Commun* 2016;52:1673–6. <https://doi.org/10.1039/C5CC09075J>.

- [18] Bowker M, Davies PR, Al-Mazroai L. Photocatalytic Reforming of Glycerol over Gold and Palladium as an Alternative Fuel Source. *Catal Letters* 2008;128:253. <https://doi.org/10.1007/s10562-008-9781-1>.
- [19] Bewley BR, Berkaliev A, Henriksen H, Ball DB, Ott LS. Waste glycerol from biodiesel synthesis as a component in deep eutectic solvents. *Fuel Process Technol* 2015;138:419–23. <https://doi.org/10.1016/J.FUPROC.2015.05.025>.
- [20] Estahbanati MRK, Feilizadeh M, Iliuta MC. Photocatalytic valorization of glycerol to hydrogen: Optimization of operating parameters by artificial neural network. *Appl Catal B Environ* 2017;209:483–92. <https://doi.org/https://doi.org/10.1016/j.apcatb.2017.03.016>.
- [21] Jiang X, Fu X, Zhang L, Meng S, Chen S. Photocatalytic reforming of glycerol for H₂ evolution on Pt/TiO₂: fundamental understanding the effect of co-catalyst Pt and the Pt deposition route. *J Mater Chem A* 2015;3:2271–82. <https://doi.org/10.1039/C4TA06052K>.
- [22] I. AO, Abu-Dahrieh JK, McLaren M, Laffir F, Nockemann P, Rooney D. A Facile Green Synthetic Route for the Preparation of Highly Active γ -Al₂O₃ from Aluminum Foil Waste. *Nat Sci Reports* 2017.
- [23] Osman AI, Abu-Dahrieh J, McLaren M, Laffir F, Rooney DW. Characterisation of Robust Combustion Catalyst from Aluminium Foil Waste. *ChemistrySelect* 2018;3:1545–50. <https://doi.org/10.1002/slct.201702660>.
- [24] Osman AI, Abu-Dahrieh JK, Laffir F, Curtin T, Thompson JM, Rooney DW. A bimetallic catalyst on a dual component support for low temperature total methane oxidation. *Appl Catal B Environ* 2016;187:408–18. <https://doi.org/https://doi.org/10.1016/j.apcatb.2016.01.017>.
- [25] Murashkina AA, Murzin PD, Rudakova A V, Ryabchuk VK, Emeline A V, Bahnemann DW. Influence of the Dopant Concentration on the Photocatalytic Activity: Al-Doped TiO₂. *J Phys Chem C* 2015;119:24695–703. <https://doi.org/10.1021/acs.jpcc.5b06252>.

- [26] Slamet, Ratnawati, Gunlazuardi J, Dewi EL. Enhanced photocatalytic activity of Pt deposited on titania nanotube arrays for the hydrogen production with glycerol as a sacrificial agent. *Int J Hydrogen Energy* 2017;42:24014–25.
<https://doi.org/https://doi.org/10.1016/j.ijhydene.2017.07.208>.
- [27] Vaiano V, Lara MA, Iervolino G, Matarangolo M, Navio JA, Hidalgo MC. Photocatalytic H₂ production from glycerol aqueous solutions over fluorinated Pt-TiO₂ with high {001} facet exposure. *J Photochem Photobiol A Chem* 2018;365:52–9.
<https://doi.org/10.1016/J.JPHOTOCHEM.2018.07.032>.
- [28] Fujita S, Kawamori H, Honda D, Yoshida H, Arai M. Photocatalytic hydrogen production from aqueous glycerol solution using NiO/TiO₂ catalysts: Effects of preparation and reaction conditions. *Appl Catal B Environ* 2016;181:818–24. <https://doi.org/10.1016/J.APCATB.2015.08.048>.
- [29] Liu R, Yoshida H, Fujita S, Arai M. Photocatalytic hydrogen production from glycerol and water with NiO_x/TiO₂ catalysts. *Appl Catal B Environ* 2014;144:41–5.
<https://doi.org/10.1016/J.APCATB.2013.06.024>.
- [30] Yang J, Yan H, Wang X, Wen F, Wang Z, Fan D, et al. Roles of cocatalysts in Pt–PdS/CdS with exceptionally high quantum efficiency for photocatalytic hydrogen production. *J Catal* 2012;290:151–7. <https://doi.org/http://dx.doi.org/10.1016/j.jcat.2012.03.008>.