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Water oxidation by P25 TiO₂ photoanodes in acidic solution

Christopher O'Rourke and Andrew Mills*

Queens University Belfast, School of Chemistry and Chemical Engineering, David

Keir Building, Stranmillis Road, Belfast, UK, BT9 5AG

*: e-mail: andrew.mills@qub.ac.uk

Abstract

P25 TiO₂ photoanodes are used to photo-oxidise water in two different acids, 0.5 M H₂SO₄ and 1 M HClO₄. In the former acid, the linear sweep voltammogram, LSV, appears to exhibit two photocurrent waves, whilst only one in the latter. In 0.5 M H₂SO₄, the recorded LSV coupled with a low faradaic efficiency (0.58) for the photooxidation of water to O₂, f_{O_2} , and a significant level of persulfate, $f_{S_2O_8} = 0.12$, shows that the electrochemical kinetics are not simply those for water oxidation. In 1 M HClO₄, the LSV coupled with a high f_{O_2} value (0.91) suggest that the photocurrent is due to water oxidation. Photo-induced absorption spectroscopy, PIAS, measurements made using the P25 TiO₂ photoanode reveal a steady state absorbance change, ΔAbs_{ss} , associated with the steady-state concentration of surface accumulated holes, $[h^+]_{ss}$, which varies with: (i) monitoring wavelength, with a peak at ca. 500 nm, and (ii) applied potential, flattening off at ca. 0.7 V vs Ag/AgCl. PIAS measurements, coupled with concomitant transient photocurrent (TC) measurements, on the P25 TiO₂ photoanode polarised at 1.3 V vs Ag/AgCl, in 1 M HClO₄, show that the oxidation of water is second order with respect to the concentration of the surface-accumulated, photogenerated holes, $[h^+]_{ss}$, which have a calculated turnover frequency of 19 s⁻¹, under 1 sun irradiation. This is the first reported example of the use of PIAS/TC to probe the photoelectrochemical kinetics exhibited by mesoporous semiconductor photoanode derived from a powder, for water oxidation and the significance of such is discussed briefly.

Key words: photoanode; titanium dioxide; P25, perchloric acid; oxygen; persulfate

Introduction

No semiconductor photocatalyst has been studied more than TiO_2 , due in part to its high activity, low cost and biological and chemical inert nature (Mills et al., 2015). Not surprisingly, given these features, all the current, major commercial photocatalytic products, such as self-cleaning glass, paint, concrete and plastics, employ TiO_2 as the semiconductor photocatalyst. Thus, despite its ability to absorb only UV irradiation, TiO_2 continues to play a very important role in the field of photocatalysis and any new insights into how it functions remain highly relevant both to researchers in the field and the photocatalyst industry.

One of the most commonly used powder forms of photocatalytic TiO_2 , is P25 TiO_2 , a 80:20 mix of anatase and rutile crystalline forms; indeed, it is now often referred to as 'benchmark photocatalyst' (Kafizas et al., 2016). When any new photocatalyst is used it is often initially in powdered form and its activity compared with that of P25 TiO_2 . In this work such materials are usually employed as powdered dispersions, and the kinetics of photocatalysis probed by measuring the initial rate of reaction under steady-state irradiation conditions as a function of different values of key reaction parameters such as the incident irradiance, ρ , and the bulk concentrations of the reactants. Although, effective for making quick comparisons of activity, such studies provide little mechanistic information. In particular, the direct measure of the steady state levels of photogenerated holes and/or electrons is usually not possible, due to their low concentration and the significant degree of light scattering often exhibited by such powder-dispersion systems. As a consequence, most photocatalytic mechanisms proposed for powdered photocatalysts need to make an assumption with regard to nature of the rate determining step, rds, and the order of reaction, n , of the photogenerated holes or electrons therein (Mills et al., 2015).

Recently, photoinduced absorption spectroscopy, PIAS, coupled with transient photocurrent (TC) measurements, i.e. PIAS/TC, have been used to probe the kinetics of water oxidation exhibited by a number of different semiconductor oxide

photoanodes, including TiO₂ (Kafizas et al., 2017a; Le Formal et al., 2015; Ma et al., 2016; Mesa et al., 2020). In these PIAS/TC studies the optical absorption, $\Delta\text{Abs}_{\text{ss}}$, exhibited by photogenerated holes accumulated at the surface of the semiconductor photoanode and the photocurrent, J_{ss} , are monitored under *ultra* bandgap, steady-state irradiation conditions, under a large anodic bias. The bias ensures that the steady-state level of photogenerated electrons is so low that the reaction of the surface-accumulated photogenerated holes is in the oxidation of water, i.e.

In a typical PIAS/TC study of reaction (1), the values of $\Delta\text{Abs}_{\text{ss}}$ (monitored at a wavelength, λ_{m} , where it is proportional to $[\text{h}^+]_{\text{ss}}$) and photocurrent, J_{ss} , are measured as a function of incident irradiance. It follows that a plot of $\log(J_{\text{ss}})$ vs $\log(\Delta\text{Abs}_{\text{ss}})$, for a photoanode tested in this way, yields the order of reaction, with respect to h^+ , i.e. n , for water oxidation, since,

$$J_{\text{ss}} = k_{\text{PIAS}}[\text{h}^+]^n \quad (2)$$

where k_{PIAS} is the rate constant for the reaction of the steady-state photogenerated, long-lived, surface-accumulated holes, h^+_{ss} , with water.

To date, the semiconductor photocatalyst photoanodes studied using PIAS/TC have been in the form of dense, flat films, and not the mesoporous films derived from powdered photocatalysts. This is perhaps not surprising given that transient absorption spectroscopic studies, carried out using sol-gel based mesoporous TiO₂ photoanodes, shows that most (ca. 80%) of the pulsed laser-induced change in optical signal, ΔAbs , is lost within 10 μs , which suggests that under steady state irradiation conditions the value of the steady-state change in absorbance, $\Delta\text{Abs}_{\text{ss}}$, would be negligible in these and probably all mesoporous films (Cowan et al., 2010; Kafizas et al., 2017a).

As noted above, most kinetic studies of powdered photocatalysts have employed them as dispersions in aqueous solution. However, over the years, a number of research

groups have, deposited photocatalyst powders, including P25 TiO₂, on a conducting surface, such as conducting glass, or a metal foil, and use them as photo-electrodes (Byrne et al., 1998; Whal et al., 1994; Zhang et al., 2011). But, rather like the traditional steady-state irradiation studies carried out using powder dispersions noted above, such studies provide only a limited amount of *indirect* mechanistic information with regard to the rds and the value of *n* (Mills et al., 2015). In this paper, we report for the first time the use of PIAS/TC to probe the kinetics of water oxidation by a P25 TiO₂ photoanode and provide direct information with regard to the rds and *n* for that reaction.

Experimental

Materials

Unless stated otherwise all chemicals were purchased from Sigma-Aldrich and used as received. The water used to make up the solutions was doubly distilled and deionised. All gases were purchased from BOC, UK.

Methods

Preparation of the P25 TiO₂ photoanodes

Briefly, the supporting substrate, FTO (TEC-15, Pilkington Glass plc) was first coated with a 100 nm dense TiO₂ blocking layer using the spin-coating method reported by (Oku et al., 2015), in order to prevent direct contact of the background electrolyte with the FTO. Copper adhesive tape was used to provide an electrical connection between the FTO and the potentiostat. This allowed for a better grip for the crocodile clip. For linear sweep voltammetry (LSV) and O₂ yield measurements, 25 mm x 75 mm x 4 mm slides of FTO were used. For Photo-induced Absorption Spectroscopy (PIAS) measurements, smaller, 20 mm x 15 mm x 4 mm, slides were used. A small 5 mm deep track at the top of the FTO slide was masked with Scotch® Magic™ tape prior to spin-coating to preserve an area of bare FTO to allow electrical contact to be made with the potentiostat, when used. Each substrate was then spin-coated with a titanium

diisopropoxide bis(acetylacetonate) in butanol (0.3 M) solution and the barrier film-coated product annealed at 500 °C for 30 min. This was followed by doctor-blade deposition of a ca. 1.7 μm thick layer of P25 TiO_2 from a paste of TiO_2 (76 mg of P25 TiO_2 in: 20 μL acetic acid, 20 μL water, 3.98 mL ethanol, 0.43 g terpineol, and 0.74 g of 10% w/w ethyl cellulose in methanol) which was cast as a 60 μm thick wet layer and then annealed at 500°C for 30 min. Scanning electron microscopy revealed the film to be 1.7 μm thick, mesoporous, and comprised of a network of loosely packed interconnected particles ca. 30-40 nm in diameter, and similar in appearance to the P25 TiO_2 photoanodes reported by others (Wahl et al., 1994). Example SEM images are illustrated in Fig. S0(a), section S0, in the Electronic Supplementary Information (ESI) file.

Electro- and photo-electrochemical measurements: potentiostat and cell

All electrochemical measurements were performed using an Autolab potentiostat (Metrohm, PGSTAT128N) with a FRA32M module installed for electrochemical impedance spectroscopy (EIS) measurements. Electrical connection between the photoanode and the potentiostat was made using a copper foil and crocodile clip.

The PTFE electrochemical reaction cell used for all linear sweep voltammetry (LSV) measurements and oxygen yield experiments is described in detail elsewhere (Tang-Kong et al, 2018) and a schematic of which is illustrated as Fig. S1, in the ESI of this paper. The PTFE cell holds 10 mL of electrolyte. All measurements were performed using a Ag/AgCl reference electrode and a Pt-coil counter electrode and so all applied voltages, E_{ap} , are with respect to Ag/AgCl.

All Linear sweep voltammetry (LSV) plots were acquired at a scan rate of 5 mV s^{-1} , typically from -0.5 V – 2.5 V). The electrolyte was purged with argon at a flow rate of 12 $\text{cm}^3 \text{min}^{-1}$ for 10 min before acquiring the LSVs, which were carried out either in the dark or with UV irradiation, ca. 40 mW cm^{-2} , using a 365 nm light (2.7 W, LED ENGIN, LZ1-10UV00-0000)), through the FTO.

Measurement of faradaic efficiency for O₂ production, f_{O_2}

The faradaic efficiency for O₂ production, f_{O_2} , was measured for the P25 TiO₂ photoanode' biased at a voltage sufficient to provide a photocurrent of 0.4 mA cm⁻², in 0.5 M H₂SO₄ or 1 M HClO₄ and irradiated with ca. 40 mW cm⁻² of 365 nm light from a UV LED. The %O₂ generated by the photoanode was measured as a function of time before, during and after the potential bias was applied. In the %O₂ measuring system, a mass flow controller (Aalborg, GFC17, 0-20 cm³ min⁻¹) was used to provide a constant stream (12 cm³ min⁻¹) of argon to the PTFE electrochemical reactor described previously and illustrated in Fig. S1 in the ESI. The gas outlet for this cell was connected to a custom-made, 3D printed O₂ detector cell which allowed the carrier gas to pass over a thermostatted, fluorescence-based oxygen sensor, O2xyDot™, (OxySense Inc.). A schematic illustration of the whole system is illustrated in Fig. S2(a) of the ESI, along with Fig. S2(b), an expanded view of the 3D printed O₂ detector cell. The change in the lifetime of the OxyDot™ sensor due to the presence of O₂ was measured using a NeoFox-GT probe (OceanOptics) and converted into %O₂, using a Stern-Volmer equation. The measured %O₂ was related to the value of f_{O_2} via the following eqn.

$$f_{O_2} = \frac{\%O_2 \text{ (measured)} \times F \times n \times f_r}{J_{ss} \times (10^{-5}) \times A \times 60 \times V_m} \quad (3)$$

where, J_{ss} = steady state photocurrent in mA cm⁻² (0.4 mA cm⁻²) **A** is P25 TiO₂ photoanode area (= 1 cm²), **F** is Faraday's constant, f_r is the carrier gas flow rate (12 cm³ min⁻¹), n (=4) is the number of electrons involved for water oxidation, and V_m is the molar volume of gas at 20°C (2400 cm³).

The O₂-detecting system was first calibrated using a variety of different photocurrents, which spanned the value of 0.25 – 2.00 mA cm⁻², using a RuO₂/TiO₂ DSA on Ti foil anode prepared using a well-established procedure (O'Brien et al, 2005). A typical set of %O₂ vs time plots generated when using this calibration RuO₂/TiO₂ DSA anode, in 0.5 M H₂SO₄, before, during and after the potential bias was applied (but with no

concomitant UV illumination) is illustrated in Fig. S2(c) in the ESI, along with the resulting plot of f_{O_2} vs J_{ss} , Fig. S2(d), from which an average value of $f_{O_2} = \text{ca. } 1.0$ was calculated. Finally, the % O_2 vs time profiles generated by the P25 TiO_2 photoanode biased at a voltage sufficient to provide a photocurrent of 0.4 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$ and 1 M HClO_4 , during and after UV illumination are illustrated in Fig. S2(e) in the ESI, from which f_{O_2} values for these two acids were determined to be 0.58 and 0.91 respectively.

PIAS/TC measurements

A schematic illustration of the photoinduced absorption spectroscopy (PIAS) and transient photocurrent (TC) system is illustrated in Fig. S3(a) in the ESI. In this work the P25 photoanode was excited using a 10 W , 365 nm LED (LedEngin Inc., LZ4-44UV00-0000) focused onto a photoanode irradiation area of 0.64 cm^2 . The incidence irradiance, ρ , was varied from $\text{ca. } 112 \text{ mW cm}^{-2}$ down to 1.9 mW cm^{-2} by varying the applied current to the LED using a variable power supply unit (PSU) (Aim and Thurlby Thandar Instruments, QL355P). The timing of the irradiations was controlled using a diaphragm shutter (ThorLabs, SHB1T) connected to a data acquisition (DAQ) card (National Instruments, USB-6361). The custom 3D printed photoelectrochemical cell, with 25 mm diameter quartz windows, illustrated in Fig. S3(b) in the ESI, was used to house the P25 TiO_2 photoanode, along with an Ag/AgCl reference electrode and Pt-coil counter electrode. The potential was applied (typically, $E_{ap} = 1.3 \text{ V}$ vs Ag/AgCl) using an Autolab potentiostat (Metrohm, PGSTAT128N). A 150 W tungsten-halogen lamp (ThorLabs, SLS301) with a stabilized power supply was used as the transient absorbance monitoring light source. In order to reduce stray and scattered light, two monochromators, and appropriate optical cut-off filters, were placed before and after the sample. The irradiance of the monitoring light source after passing through the photoanode under test was measured using a Si photodiode (ThorLabs, DET100A2), the signal from which was passed through an amplifier (ThorLabs, PDA200C) and then

measured using the DAQ card. Both photo-induced absorbance and currents were monitored simultaneously, and the transient absorbance traces presented in this work are the average of between 10 – 50 acquisitions.

IPCE measurements

IPCE measurements were performed using the PIAS cell illustrated in Fig. S3(b) in the ESI, with an illumination area of 0.64 cm². The cell contained the P25 TiO₂ working electrode, Ag/AgC reference electrode and a Pt-coil counter electrode; the electrolyte was always 1 M HClO₄. A potential of 1.3 V vs Ag/AgCl was applied using an Autolab potentiostat (Metrohm, PGSTAT128N). The TiO₂ photoanode was irradiated using irradiation provided by a 1 kW Xe-arc lamp (OBB KiloArc™) coupled with a monochromator and IR filter (Optical Building Blocks). The irradiance of the incident light was measured using a calibrated spectroradiometer (Gooch and Housego, OL 756). In this work, the wavelength range assessed was from 300 nm – 450 nm at 10 nm intervals. At each selected wavelength, the difference in the average steady light on and light off currents was obtained by periodically chopping the light using a mechanical shutter (10 s intervals) and was then to calculate the photocurrent.

Measurement of roughness factor

The real surface area of the P25 TiO₂ films on FTO, as compared to their geometric surface area, was determined by adsorption of the azo-dye Orange II, which has been shown to form a monolayer on nanocrystalline TiO₂ at a concentration of 1.5 mM in water of pH 3.5, and to occupy an area of 0.40 nm² per adsorbed dye molecule (Bandara et al., 1999; Kay et al., 2006). Thus, a P25 TiO₂ electrode of 4.3 cm² geometric surface area was exposed for 15 min to a 100 cm³ of the dye solution, and then the adsorbed dye desorbed with 10 mL of 1 M NaOH solution. The concentration of the dye in the desorbed dye solution was then determined from the measured absorbance of the solution at 450 nm measured in a 1 cm cuvette. From the results

of this work, the ratio of the real surface area to geometric surface area, i.e. the roughness factor, was determined to be 33. Note: Note, Kiwi and his co-workers (Bandera et al, 1999) have shown that this method of dye adsorption can be used to determine accurately the specific surface areas of a variety of different metal oxides, including, Fe_2O_3 , TiO_2 and Al_2O_3 .

Other methods

All UV/Vis absorption spectra were measured using a Cary 60 UV/Vis spectrophotometer and the emission spectrum of the UV LED was measured using a Gooch and Housego, OL 756 spectroradiometer. All scanning electron micrographs were measured using a FEI Quanta FEG - Environmental SEM, Oxford Ex-ACT.

Results and discussion

P25 TiO₂ film Characterisation

A picture of the typical 1.7 μm thick P25 TiO₂ film on FTO used in this work is illustrated in Fig. 1(a) and shows that although the film scatters light to some extent, and so appears slightly opalescent, it is largely transparent to visible light. Fig. 1(b) illustrates the UV/Vis absorption spectrum of the P25 TiO₂ film which overlaps strongly with the emission spectrum of the 365 nm LED used as the excitation source in all this work. There is little difference between the UV/Vis diffuse reflectance and absorption spectrum of the P25, as illustrated by Fig. S0(b) in the ESI.

Fig. 1. (a) Photograph of the P25 TiO₂ film on FTO and (b) its UV/Vis absorption spectrum (broken line) along with that of the FTO/100 nm TiO₂ blocking layer support substrate (solid black line) and the emission spectrum of the 365 nm UV LED (red line). Scanning electron microscopy of the P25 TiO₂ film revealed it to be mesoporous and comprised of a network of loosely packed interconnected particles ca. 30-40 nm in diameter, and very similar in appearance to the P25 TiO₂ photoanodes reported by others (Ito et al., 2007; Zhang et al., 2011).

The n-type nature of the P25 TiO₂ photoanode, due to 'non-stoichiometry or impurities in the lattice' (Boschloo et al., 1997), and its flat-band potential, E_{fb} , were determined by measuring the open-circuit potential, OCP, exhibited by the P25 TiO₂ photoanode

in air-saturated 1 M HClO₄, as a function of UV irradiance, ρ (Chen et al. 2010; Chen et al., 2013). The resulting plot of OCP vs ρ is illustrated in Fig. 2, from which it appears, (i) the OCP decreases with increasing irradiance, thereby indicating the semiconductor is n-type, and (ii) the value of E_{fb} , i.e. the photovoltage at which the OCP vs ρ plot flattens out is ca. -0.25 V vs Ag/AgCl, which compares well with the reported flat-band potentials of rutile and anatase TiO₂ (i.e. -0.201 and -0.4 V vs Ag/AgCl (Fujishima et al., 2008)). The difference in the OCP measured in the dark and under intense UV illumination, indicates that the maximum photovoltage exhibited by the system under OCP conditions is ca. 0.45 V. Individual nanoparticles of TiO₂, which are only 30-40 nm in diameter, would not be expected to behave like a bulk semiconductor photoelectrode and exhibit an OCP effect. However, the above results suggest that when these nanoparticles are aggregated and form a mesoporous network, as in the P25 film electrode, the latter shows many of the characteristics expected of a bulk semiconductor photoelectrode. This finding is consistent with the work of other on mesoporous sol-gel films (Cowan et al. 2013).

Fig 2. Open Circuit Potential, OCP, exhibited by the P25 TiO₂ photoanode, as a function of irradiance, ρ .

274 Different acids: Linear Sweep Voltammetry (LSV) and O_2 yields

275 From the LSVs illustrated in Fig. 3, it appears that the voltages at which the onset of a
 276 photocurrent occurs in the two acids are similar (i.e. $E_{on} = -0.17$ and -0.18 V vs
 277 Ag/AgCl for 1 M $HClO_4$ and 0.5 M H_2SO_4 and respectively), but not identical. In
 278 addition, whereas the LSV for the P25 TiO_2 electrode in $HClO_4$ appears to be very
 279 much what would be expected for a single electrochemical process, presumably the
 280 oxidation of water by photogenerated holes, h^+ , i.e. reaction (1), there is a clear
 281 inflection in the LSV, at ca. 0.7 V vs Ag/AgCl, for the same photoanode when in H_2SO_4 .
 282 The lower photocurrent onset and inflection in the LSV suggests that in 0.5 M H_2SO_4
 283 the P25 TiO_2 photoanode promotes at least one other photoelectrochemical oxidation
 284 process in addition to reaction (1). This feature was confirmed by measuring the
 285 faradaic efficiencies for O_2 production, i.e. f_{O_2} , exhibited by the P25 TiO_2 in the two
 286 acids, when biased at 1.3 V vs Ag/AgCl. Thus, in 1 M $HClO_4$ the faradaic efficiency
 287 was near unity (i.e. 0.91) but was significantly lower (0.58) in 0.5 M H_2SO_4 .

Fig. 3. Linear sweep voltammograms recorded for a P25 TiO_2 photoanode with (solid line) and without UVA illumination (40 mW cm^{-2}), in (a) 1 M $HClO_4$ and (b) 0.5 M H_2SO_4 ; sweep rate 5 mV s^{-1} .

Low f_{O_2} values, i.e. 0.05-0.42, have been reported previously by others (Kung et al., 1997) for TiO_2 (single crystal rutile) photoanodes in (0.2 M) H_2SO_4 and have been ascribed to the formation of H_2O_2 . In the latter work the lowest f_{O_2} values were

produced at the lowest photocurrents, produced using either a low UV irradiance or low polarising voltage (Kung et al., 1997). A similar study carried out by Wrighton and his co-workers (Wrighton et al., 1975) revealed a f_{O_2} value of 0.53 in 0.5 M H_2SO_4 for a single crystal rutile photoanode, although no H_2O_2 could be detected using the Ti(IV) test, i.e. < 0.1 ppm (Mi et al., 2012). In addition, other workers have reported that persulfate, $S_2O_8^{2-}$, is generated, albeit with a low faradaic efficiency, ca. 0.05, when a single crystal TiO_2 photoanode is used in 0.5 M H_2SO_4 (Kohayakawa et al., 1978). Support for the photoelectrochemical generation of $S_2O_8^{2-}$ by photoanodes in H_2SO_4 comes from the work of Lewis and his co-workers (Mi et al., 2012) who recently reported that WO_3 photoanodes mediate almost exclusively its production the *via* the following photoelectrochemical reaction,

Thus, using a WO_3 photoanode, Lewis et al (Mi et al., 2012), reported a faradaic efficiency of 0.85 for reaction (4) and $f_{O_2} = 0$ in 1 M H_2SO_4 , and no $S_2O_8^{2-}$ production and $f_{O_2} = 0.9$ for reaction (1) in 1 M $HClO_4$. As in the work reported here (see Fig. 3), these workers found the value of E_{on} was more cathodic (by ca. 200 mV) in 1 M H_2SO_4 compared to 1M $HClO_4$ and noted that ‘the value of E_{on} is affected by the semiconductor properties of WO_3 as well as the redox potential of the electrolyte’ (Mi et al., 2012). Thus, it appears likely that in this work on P25 TiO_2 the slight negative shift in the value of E_{on} observed when the P25 TiO_2 photoanode was in 0.5 M H_2SO_4 , compared to 1 M $HClO_4$, is due to the mixed redox potential of the former electrolyte, due to reactions (1) and (4), compared to the latter, which is only due to reaction (1). The production of persulfate by the P25 TiO_2 photoanode used in this work in 0.5 M H_2SO_4 was confirmed by sampling the electrolyte after a set electrolysis time (2 h, applied voltage = 1.3 V vs Ag/AgCl) and analysing it for persulfate production using a test based on the oxidation of potassium iodide (Mi et al., 2012). This work revealed a faradaic efficiency for persulfate production of ca. 0.12, which, when added to the value of $f_{O_2} = 0.58$ reported above for the same electrode under the same conditions,

suggests that reaction (1) and (4) are the primary photoelectrochemical oxidation reactions that occur on the P25 TiO₂ electrode in 0.5 M H₂SO₄. Note: other work showed that persulfate is readily reduced at the Pt counter electrode in the electrochemical cell illustrated in Fig. S3(b) in the ESI, typically by 50% over the time used in this work (2 h), which would help explain the lower-than-expected faradaic efficiency of 0.12 for persulfate production reported here. The results of this work and that of others (Kung et al., 1997; Wrighton et al., 1975) suggest that most photoelectrochemical studies carried out using TiO₂ in H₂SO₄, e.g. (Haisch et al. 2017), are likely to be mistaken in their assumption that the measured photocurrent is due to water oxidation alone, as significant persulfate production *via* reaction (4) is also likely. This concern with regard to significant persulfate production by all photoanodes in H₂SO₄ has been highlighted recently (Reinhard et al., 2016). It follows that in studies in which photoinduced absorption spectroscopy, PIAS, is used to determine the order of reaction with respect to the steady state photogenerated holes, n , it is vital that the photocurrent is due to just one oxidation reaction only, such as the oxidation of water, i.e. reaction (1). Thus, in this work, all subsequent work on the P25 TiO₂ photoanode was carried out in 1 M HClO₄, so that the photoelectrochemical oxidation reaction under study was limited to that of water, i.e. reaction (1).

Incident photon-to-current efficiency, IPCE

The incident photon-to-current efficiency, IPCE, spectrum of the P25 TiO₂ photoanode in 1 M HClO₄ was recorded and the results are illustrated in Fig. 4, alongside those previously recorded by others (Haisch et al. 2017), but for a screen printed P25 photoanode in 0.5 M H₂SO₄. A brief inspection of the data in Fig. 4 shows that both spectra exhibit very similar absorption features, including a photocurrent onset at ca. 400 nm which is in good agreement with the observed absorption edge of P25 TiO₂ (Haisch et al. 2017). The higher IPCE values found for the screen printed P25 photoanode in 0.5 M H₂SO₄, compared to the P25 photoanodes in 1 M HClO₄ used in

this work may well be simply due to a higher surface area. However, others (Reinhard et al., 2016) working on WO_3 photoanodes have noted that ‘the electrolyte producing the highest photocurrent was the electrolyte with the lowest oxygen evolution’, which is also what is found here using a P25 photoanode (compare the LSVs illustrated in Fig. 3). Thus, the greater IPCE values reported for the screen-printed P25 photoanode (in 0.5 M H_2SO_4) compared to a P25 TiO_2 photoanode (in 1 M HClO_4), see Fig. 4, may be because in the latter case both water and sulfate oxidation occurs, resulting in increased photocurrents and so higher IPCE values, but accompanied by a significantly lower value of f_{O_2} , compared to that measured in 1 M HClO_4 .

Fig. 4 IPCE spectra for water oxidation measured for the P25 TiO_2 on FTO (black) photoanode in 1 M HClO_4 at a bias of 1.3 V vs Ag/AgCl. The broken red line illustrates a previously reported IPCE spectrum for a screen printed P25 TiO_2 photoanode in an aqueous 0.5 M H_2SO_4 solution at a bias of 1 V vs. NHE.

The IPCE values reported here for the P25 TiO_2 photoanode in 1 M HClO_4 are similar to those reported for mesoporous TiO_2 film prepared by a sol-gel method which are often used for transient absorption studies (Cowan et al. 2013; Ma et al., 2016). For example, here, at 365 nm, the IPCE for the P25 TiO_2 photoanode in 1 M HClO_4 is ca.

0.08, whereas Cowan et al., (Cowan et al. 2013) report a value of ca. 0.05 for a TiO₂ sol-gel mesoporous film at pH 2 in 0.5 M NaClO₄.

PIAS/TC

In order to use the PIAS system to probe the kinetics of water oxidation exhibited by the P25 TiO₂ photoanode it was necessary to determine if the system is able to produce a steady-state concentration of photogenerated holes that is high enough that it can be detected optically using the PIAS system. The optical signal measured by the PIAS system and generated by the P25 TiO₂ film under steady state irradiation is the change in absorbance, i.e. $\Delta\text{Abs}_{\text{ss}}$, exhibited by the film. The latter parameter depends upon, (i) the applied polarising voltage used, E_{ap} , (ii) the UV irradiance, ρ , and (iii) the molar absorptivity, ϵ_{λ_m} , at the monitoring wavelength, λ_m , selected to measure the absorbance of the photogenerated holes. In order to determine an appropriate value for λ_m for a P25 TiO₂ photoanode in 1 M HClO₄, the photoanode was biased at 1.3 V vs Ag/AgCl, i.e. in the middle of the plateau region of its LSV, see Fig. 3(a), irradiated with a high UV irradiance (76 mW cm⁻²) and the value of $\Delta\text{Abs}_{\text{ss}}$ determined using the PIAS system, as a function of λ_m . The resulting plot of $\Delta\text{Abs}_{\text{ss}}$ vs λ_m is illustrated in Fig. 5(a) and compares well with that reported by Kafizas et al. (Kafizas et al., 2017a) in their transient absorbance study of an anatase TiO₂ flat, dense film photoanode biased at 1.5 V vs RHE in 1 M NaOH, and subjected to a 6 ns pulse of 355 nm radiation, $\rho = 1.98 \text{ mJ cm}^{-2}$. As in the latter study, a value of 500 nm was selected for λ_m in all subsequent PIAS work and all subsequent values of $\Delta\text{Abs}_{\text{ss}}$ reported here are for that monitoring wavelength.

Fig. 5 Plots of the PIAS measured change in absorbance, ΔAbs_{ss} exhibited by the P25 TiO_2 photoanode as a function of (a) monitoring wavelength, λ_m , with $E_{ap} = 1.3 \text{ V}$ vs Ag/AgCl and (b) E_{ap} , using a monitoring wavelength of 500 nm. The open circles in (a) show the same plot reported by Kafizas et al (Kafizas et al., 2017a) for a dense, flat TiO_2 film biased at 1.5 V vs RHE in 1 M NaOH and measured using transient absorbance spectroscopy.

In order to demonstrate that the photoinduced change in absorbance, ΔAbs_{ss} , exhibited by the P25 TiO_2 photoanode, was related to the steady state concentration of photogenerated holes, i.e. $[h^+]_{ss}$, and not say a system artifact (Kafizas et al., 2017a), this parameter, ΔAbs_{ss} , was measured as a function of the applied voltage, E_{ap} , and the results are illustrated in Fig. 5(b). The results show that ΔAbs_{ss} increases with increasing E_{ap} , as expected, given that the greater the value of E_{ap} , the greater the rate of removal of photogenerated electrons from the photoanode and so the greater the concentration of surface accumulated photogenerated holes, $[h^+]_{ss}$ and the value of ΔAbs_{ss} . As might be expected from the LSV illustrated in Fig. 3(a) for the P25 TiO_2 photoanode, increasing the value of E_{ap} above 0.7 V vs Ag/AgCl produces no significant improvement in the value of ΔAbs_{ss} , presumably because the steady-state concentration of photogenerated electrons at the surface of the TiO_2 blocking layer is

zero at $E_{ap} \geq 0.7$ V vs Ag/AgCl and thus the rate of extraction of photogenerated electrons in the P25 TiO₂ film is then wholly diffusion-controlled.

The above work shows that, in the study of the photo-oxidation of water by a P25 TiO₂ photoanode in 1M HClO₄, the combination of an applied potential 1.3 V vs Ag/AgCl, a monitoring wavelength of 500 nm and a high UV irradiance (76 mW cm⁻²) is sufficient to produce a readily measured value of ΔAbs_{ss} . In order to determine the order of reaction, n , for the oxidation of water by the photogenerated holes in this system, it is necessary to measure the rate of water oxidation as a function of $[h^+]_{ss}$, and this can be achieved by measuring the steady state photocurrent, J_{ss} , and ΔAbs_{ss} , exhibited by the a P25 TiO₂ photoanode system outlined above as a function of the incident UV irradiance. The results arising from this work, in the form of the observed variation in photocurrent, i.e. J , and absorbance at 500 nm, Abs , exhibited by the P25 TiO₂ photoanode, as a function of time – before, during and after steady state irradiation - are illustrated in Fig. 6(a) and (b) respectively.

Fig 6 Plots of the measured (a) photocurrent, J , and (b) change in absorbance at 500 nm, ΔAbs , as a function of time, exhibited by a P25 TiO₂ photoanode poised at 1.3 V vs Ag/AgCl and in 1 M HClO₄, before during and after steady state irradiation, using different 365 nm UV irradiances. In both plots the UV irradiances used were (from bottom to top): 112, 56, 22, 7.5 and 1.9 mW cm⁻², respectively.

Using the light-on – i.e. steady-state irradiation - data illustrated in Fig. 6(a) and (b) values for the steady state photocurrent, J_{ss} , and ΔAbs_{ss} , exhibited by the P25 TiO₂ photoanode poised at 1.3 V vs Ag/AgCl and in 1 M HClO₄ system, were extracted as a function of the UV irradiance, ρ , and the results of this work are illustrated in Fig. 7(a).

Fig 7 (a) Plots of the steady state changes in absorbance, ΔAbs_{ss} , and photocurrents, J_{ss} , due to the photocatalysed oxidation of water by a P25 TiO₂ polarised at photoanode 1.3 V vs Ag/AgCl in 1 M HClO₄, as a function of UV irradiance, ρ ; and (b) plot of J_{ss} vs $(\Delta Abs_{ss})^2$, revealing a good straight line with zero intercept and a gradient of 11.1 mA cm⁻²/(mOD²).

Kafizas et al (Kafizas et al., 2017a), in their study of the oxidation of water by dense, flat TiO₂ photoanodes in neutral solution (0.05 M K₂HPO₄ plus 0.05 M KH₂PO₄, pH 6.7), reported J_{ss} and ΔAbs_{ss} values as a function of ρ that indicated that J_{ss} was proportional to $(\Delta Abs_{ss})^2$, and so the value for the order of reaction for water oxidation by surface accumulated photogenerated holes, i.e. n , is 2. This also appears to be the case in this work, using a P25 TiO₂ photoanode, as indicated by the plot of J_{ss} vs $(\Delta Abs_{ss})^2$, illustrated in Fig. 7(b), which reveals an excellent straight line of best fit with zero intercept. The latter plot work shows that the rate of water oxidation, i.e. reaction

(1), is proportional to $([h^+]_{ss})^n$, where $n = 2$, since the rate and $[h^+]_{ss}$ are directly proportional to J_{ss} and ΔAbs_{ss} , respectively. Further evidence that the rate determining step in reaction (1) has a rate which is proportional to $([h^+]_{ss})^2$, is the fact that all the light off, ΔAbs vs t decays illustrated in Fig. 6(b) give a good fit to second order kinetics, a typical illustration of which is illustrated in Fig. S4 in the ESI.

It can be shown that if the IPCE curve exhibited by the P25 TiO₂ photoanode, which is illustrated in Fig. 4, is combined with the emission spectrum associated with 1 sun (i.e. AM 1.5) (National Renewable Energy Laboratory), then the value for the solar predicted photocurrent, SPP, (Kafizas et al., 2017b) of ca. 0.074 mA cm⁻² can be calculated for the P25 TiO₂ photoanode; see section S5 in ESI. For comparison purposes, it can be shown that an ideal (IPCE = 1, from 280 to 400 nm) UV absorbing photoanode would generate a photocurrent of 1.37 mA cm² under 1 sun irradiation, i.e. a photocurrent that is 18.5 times greater than that predicted for the P25 TiO₂ photoanode used here.

In this work, it follows from fig. 7(a) a UV irradiance of ca. 37 mW cm⁻² would be necessary to generate the same value as the SPP, i.e. a photocurrent of 0.074 mA cm⁻², using the P25 TiO₂ photoanode in 1 M HClO₄, when polarised at 1.3 V vs Ag/AgCl, and, from the results illustrated in Fig. 7(b) that such a photocurrent would be associated with a ΔAbs_{ss} value of 0.082 mOD. If we assume the value for the molar absorptivity, ϵ_{500} , for the photogenerated holes at 500 nm is 2000 M⁻¹ cm⁻¹, (Kafizas et al., 2017a) then it follows from the above data that the turnover frequency at 1 sun irradiation, TOF, where $TOF = (\text{steady state rate of holes removed cm}^{-2} \text{ s}^{-1})/(\text{steady state level of holes cm}^{-2})$ would be ca. 19 s⁻¹ which compares very well with the value of 22 s⁻¹ reported by Kafizas et al (Kafizas et al., 2017a) for flat, dense film of TiO₂ photoanodes in neutral solution (0.05 M K₂HPO₄ plus 0.05 M KH₂PO₄, pH 6.7), for which it was also found $n = 2$ for reaction (1).

As noted above, at 1 sun, the predicted value of $\Delta\text{Abs}_{\text{ss}}$ is estimated to be ca. 0.082 mOD, which, assuming ϵ_{500} is 2000 M^{-1} , approximates to a $[\text{h}^+]_{\text{ss}}$ value of 0.25 holes per nm^2 , based on geometric surface area and ca. 7.6×10^{-3} holes per nm^2 , based on real surface area, given the P25 TiO_2 photoanode has a roughness factor of ca. 33. This very low hole density (ca. 131 times lower than that reported for flat, dense TiO_2 films (Kafizas et al., 2017a) is probably due to the light scattering exhibited by the photocatalyst film.

In electrochemistry, the measured current vs voltage curves for the oxidation of water for many oxide anodes have been interpreted using various different mechanisms (Trasatti et al., 1981), one of the most popular of which is the 'Electrochemical oxide path' mechanism reported by Bockris (Bockris et al., 1956), i.e.

where S is a surface site and S-OH and S-O are surface adsorbed hydroxyl radicals and oxygen atoms, respectively. Note, in this work, the usual 'electron', i.e. e^- , that is employed in such electrochemical reaction mechanisms, and which would appear on the right hand side of the equation, has been replaced by a hole, h^+ , on the left hand side to facilitate comparison with the commonly employed reaction equations for water oxidation by semiconductor photoanodes, such as reaction (1). A typical example of an anode which exhibits current-voltage characteristics that are described by the above mechanism is rutile RuO_2 anode in acid; for which a Tafel plot of the current-voltage data reveals a slope of 40 mV per decade that is consistent with reaction 5(b) as the rate-determining step (Iwakura et al., 1977). Not surprisingly, there are strong similarities between the electrochemical reactions, such as reactions 5(a-c), often used to underpin electrochemical models for water oxidation by oxide *anodes*, and those used in mechanisms of water oxidation by oxide *photo-anodes*. For example, electron

transfer steps similar to reactions 5(a and b), have been used recently to explain the observed 1st and 3rd order hole dependence for water oxidation on haematite photoanodes (Mesa et al., 2020).

In the case of TiO₂ photoanodes, the generation of adsorbed hydroxyl radicals by TiO₂ photocatalysts has been demonstrated using numerous analytical techniques, including, diffuse reflectance FT-IT (Szczepankiewicz et al., 2000), scanning tunnelling microscopy (Tan et al., 2012) and spin trapping (Grela et al., 1996, Jaeger et al., 1979).

If, as in the electrochemical model for rutile RuO₂ anodes, it is assumed that reaction 5(a) is a fast, equilibrium reaction and reaction 5(b) is the rds, then it follows that the overall rate of water oxidation will be proportional to the square of the steady-state concentration of holes, i.e. $\propto ([h^+]_{ss})^2$. This electrochemical model prediction appears consistent with the results found in the PIAS/TC study of the P25 TiO₂ electrode, in which, as we have seen, the photocurrent/rate is found to be proportional to the square of the steady state absorbance at 500 nm, see Fig. 7(b), ΔAbs_{ss} , which in turn is assumed here and elsewhere (Mesa et al., 2020, Kafizas et al., 2017a) to be proportional to $[h^+]_{ss}$.

Conclusions

P25 TiO₂ can be used to fabricate photoanodes to photo-oxidise water, although in 0.5 M H₂SO₄ the photoelectrochemical reaction appears to be a combination of water and sulfate oxidation, whereas in 1 M HClO₄ it is just the water oxidation. In 1 M HClO₄, open circuit potential measurements reveal a flat band potential for P25 TiO₂ of ca. -0.25 V vs Ag/AgCl, which is consistent with its mixed anatase/rutile composition. From IPCE measurements the P25 TiO₂ photoanode appears far from ideal as a solar UV light photoanode, as its solar predicted photocurrent is 0.074 mA cm², whereas that for an ideal (i.e. IPCE = 1 from 300 to 400 nm) photoanode is ca. 1.37 mA cm². PIAS measurements show the P25 TiO₂ photoanode exhibits a steady state absorbance

change, $\Delta\text{Abs}_{\text{ss}}$, associated with the steady-state concentration of surface accumulated holes, $[\text{h}^+]_{\text{ss}}$, which varies with: (i) monitoring wavelength, with a peak at ca. 500 nm, and (ii) applied potential, flattening off at ca. 0.7 V vs Ag/AgCl. PIAS/TC measurements, carried out under steady state irradiation conditions using a P25 TiO_2 photoanode polarised at 1.3 v vs Ag/AgCl, in 1 M HClO_4 , show the oxidation of water to be second order with respect to $[\text{h}^+]_{\text{ss}}$, which is consistent with an 'Electrochemical oxide path' mechanism that is used to interpret the electrochemical kinetics exhibited by metal oxide anodes. All of the electrochemical features exhibited by the P25 TiO_2 photoanode are consistent with those reported previously for flat, dense TiO_2 films (Kafizas et al., 2017a) and suggest that PIAS/TC can be used to probe the photoelectrochemical kinetics exhibited by mesoporous semiconductor photoanodes derived from P25 TiO_2 and so, most likely, a wide range of different photocatalyst powders, and in so doing provide previously unavailable valuable mechanistic insights into the role of surface-accumulated photogenerated holes in the oxidation of water and other reactants. This work show how PIAS/TC can be used to probe a classic photoelectrochemical reaction, i.e. the oxidation of water, and provide direct information regarding the role of the photogenerated holes in the rate determining step. Its success opens up the way to using this same technique to probe other photocatalysed oxidation reactions such as that of organic and inorganic environmental contaminants, which are an important feature of all industrial photocatalysts.

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