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An Investigation into the Optimum Thickness of Titanium Dioxide Thin Films Synthesized by Using Atmospheric Pressure Chemical Vapour Deposition for Use in Photocatalytic Water Oxidation

Geoffrey Hyett,[a] Jawwad A. Darr,[a] Andrew Mills,[b] and Ivan P. Parkin*[a]

Abstract: Twenty eight films of titanium dioxide of varying thickness were synthesised by using atmospheric pressure chemical vapour deposition (CVD) of titanium(IV) chloride and ethyl acetate onto glass and titanium substrates. Fixed reaction conditions at a substrate temperature of 660 °C were used for all depositions, with varying deposition times of 5–60 seconds used to control the thickness of the samples. A sacrificial electron acceptor system composed of alkaline sodium persulfate was used to determine the rate at which these films could photo-oxidise water in the presence of 365 nm light. The results of this work showed that the optimum thickness for CVD films on titanium substrates for the purposes of water oxidation was ≈200 nm, and that a platinum coating on the reverse of such samples leads to a five-fold increase in the observed rate of water oxidation.

Keywords: photocatalysis · thin films · titanium · water splitting

Introduction

The rising cost of energy in both environmental and economic terms is of increasing concern to society, and a motivation for scientists to investigate and develop alternative, renewable energy sources.[1] One such source is solar energy, and one method of capturing this energy is a photodiode, which through the use of a photocatalyst monolith supported on an inert or catalytically active metal, promotes the vectorial separation of photogenerated oxidising and reducing species, that is, holes and electrons. The key feature of such photodiodes is the production of oxidised and reduced products at physically well-separated, different sites, thus, minimising the likelihood of their recombination. The investigation of photocatalysts for use in water splitting has a long history,[2] starting with TiO_2, but now encompassing a range of materials.[3,4] In most of this prior work the photocatalyst has been in powder form, leading to an inherent problem of hydrogen and oxygen being synthesised at the same catalytic surface, allowing significant back reaction—these problems can be averted by the use of a photodiode where the gases are generated at different sides of the device.

$$2\,H_2O + 4\,h^+ \rightarrow O_2 + 4\,H^+ \tag{1}$$

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^- \tag{2}$$

A generic water-splitting photodiode consists of a metallic substrate with a photocatalyst and oxygen catalyst deposited on the obverse, and a hydrogen catalyst deposited on the reverse. The device is sandwiched between two water sources, which are connected electrically through a proton-conducting membrane. Figure 1 shows a schematic layout of the system. The photocatalyst is used to trap light, generating electron–hole pairs in the semiconductor. The holes are used to oxidise water to oxygen [Eq. (1)], and the electrons are transferred through the substrate to the hydrogen catalyst where they reduce water [Eq. (2)]. The separation of the reduction and oxidation steps in different locations prevents back reaction of the hydrogen and oxygen gases, increasing yield and removing the necessity for a gas separation step.

Working water-splitting photodiodes have been demonstrated by using TiO_2 as a combined photocatalyst and

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[a] Dr. G. Hyett, Dr. J. A. Darr, Prof. I. P. Parkin
Christopher Ingold Laboratory, University College London
20 Gordon Street, London, WC1H 0AJ (UK)

[b] Prof. A. Mills
Department of Pure and Applied Chemistry
University of Strathclyde
Thomas Graham Building, 295 Cathedral Street
Glasgow, G1 1XL (UK)
Fax: (+44) 207679 7463

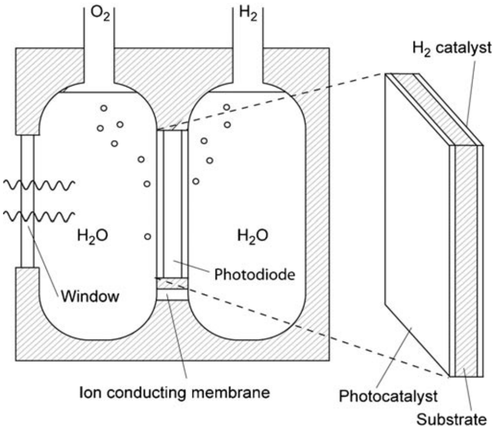

Figure 1. Schematic illustration of a generic photodiode, consisting of a substrate with a photocatalyst on one side and an H_2 catalyst on the other, sandwiched between two water sources. An ion-conducting membrane connects the two water sources to allow transfer of H^+ to maintain charge neutrality.

oxygen catalyst, and with platinum as the hydrogen catalyst, on titanium substrates.[5,6] TiO_2 can be used to generate oxygen without an additional oxygen catalyst because it has a sufficient over potential of 1.8 eV to efficiently effect the reaction.[3] In the previous literature examples of photodiodes, UV light was used to activate the devices by using separated acid and alkaline solutions for the oxidation and reduction reactions respectively, and TiO_2 films synthesised by using RF sputtering.

Such pioneering work demonstrated the feasibility of the TiO_2/Pt photodiode for water splitting, but is far from optimised. In this work, we address this problem with a thorough investigation of one half of the water-splitting system: the photo-oxidation of water [Eq. (1)]. As a $4e^-$ process it is the more difficult reaction to conduct and it is carried out on the titania film,[7] which is also the photon capture part of the device. The photo-oxidation of water can be studied in isolation to the reduction by the use of a sacrificial electron acceptor, $Na_2S_2O_8$ as described in Equation (3).[8]

$$2\,S_2O_8^{2-} + 2\,H_2O \xrightarrow[h\nu \geq E_{bg}]{TiO_2} 4\,SO_4^{2-} + 4\,H^+ + O_2 \qquad (3)$$

In our study to optimise this half of the device we used atmospheric pressure chemical vapour deposition (APCVD) to produce the TiO_2 coatings, rather than RF sputtering, as APCVD is an inexpensive coating technique, that is readily applicable to industrial scale up, and is already used in the mass market production of TiO_2 thin film coatings.[9] To our knowledge this is the first study of CVD TiO_2 for use in water oxidation, and by investigating a range of film thicknesses we demonstrate the ability of titania films made by using APCVD to generate O_2 in a sacrificial electron-acceptor solution and determine the optimum film thickness for maximum O_2 production.

Experimental Section

Synthesis: Thin films of titania were synthesised by using atmospheric pressure chemical vapour deposition onto glass and titanium substrates of area 25×25 mm^2. Titanium(IV) chloride (Aldrich, 99.9%) and ethyl acetate (Fisher, Reagent Grade) were used as precursors. In order to generate the necessary vapour pressure, both precursors were placed in heated bubblers to generate a precursor vapour that was then transported to the main reaction chamber with carrier gas flows of oxygen free N_2 (BOC). The metal source, $TiCl_4$, was heated to 75°C and transported with 1 L min^{-1} of N_2. The oxygen source, ethyl acetate, was heated to 40°C and transported with a nitrogen flow of 0.5 L min^{-1}. The precursors were combined in a mixing chamber with an additional plain flow of 10 L min^{-1} of nitrogen, before passing through the reactor across the substrate. All gas lines were heated to 200°C and the mixing chamber to 250°C to prevent condensation of the precursors.

The cold-walled reaction chamber consisted of a 330 mm long silica tube of 105 mm diameter, containing a half-cylinder of graphite, itself containing three Whatman heater cartridges that provided the thermal energy to the substrate. A steel top plate was suspended 20 mm above the graphite, providing the gas flow channel through which the precursor-laden nitrogen stream passed. For deposition on both glass and titanium the substrates were heated to 660°C with the only experimental variable being the deposition time, used to control the thickness of the film deposited. Figure 2 shows a schematic diagram of the reactor setup.

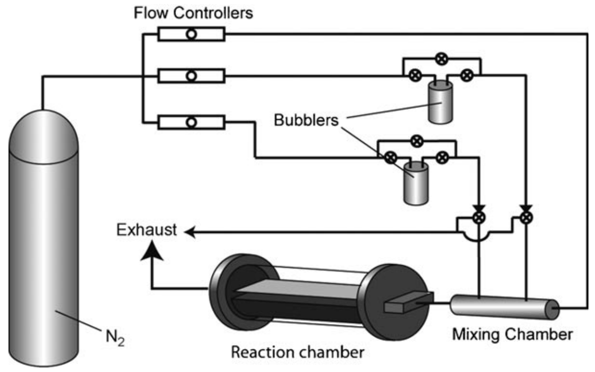

Figure 2. Schematic representation of the atmospheric pressure chemical vapour deposition apparatus.

A number of the TiO_2-coated samples on titanium substrates were also coated with platinum on their reverse sides. This was carried out by using a sputter coater, with an argon pressure of 0.1 Torr, and a current of 25 mA for 4 min.

Analysis: Powder X-ray diffraction was conducted by using a Bruker D8 Discover fitted with a GADDS area detector and a $Cu_{K\alpha1+2}$ source. Diffraction patterns were recorded in the range $10° < 2\theta < 66°$ with a collection time of 30 min per sample, by using a fixed incident angle of 10°.

Spectroscopic measurements were conducted by using a Helios spectrometer in the range 300–2500 nm. The titania films on glass were recorded in transmission, the films on titanium substrates in reflection.

The ability of the films to photo-oxidise water was determined and quantified by using a Rank Brothers oxygen electrode. This device consists of 50 mm diameter glass chamber with a water cooling jacket, at the base of which is a Clark cell consisting of a platinum working electrode, and a silver–silver chloride reference counter electrode separated from the reaction solution by a gas permeable, ion impermeable membrane, so as to allow only O_2 through to the electrode. The Pt electrode of the cell was polarised by using an in-house built potentiostat to −0.8 V relative to the Ag reference electrode. In such a device the current is proportional to the concentration of dissolved oxygen in the reaction solution. The analogue output of the potentiostat was converted to a digital signal by a Pico Technology Picoscope 2200 and associated software (PicoLog), allowing the dissolved oxygen content of the solution in the electrode chamber to be recorded as a function of time by a PC. Experiments were conducted by suspending sample films inside the oxygen electrode chamber in aqueous solutions of KOH (0.1 M) and $Na_2S_2O_8$ (0.01 M), which had first been purged by bubbling oxygen-free nitrogen through the solution for 10 min. The sample and solution were then sealed in the chamber and irradiated with a 16 W, 365 nm UV lamp, at a distance of 50 mm, for a test time of 1800 seconds. A schematic diagram of this equipment is shown in Figure 3. Plots of the generated dissolved oxygen against time were then made, and the rate of oxygen generation reported from the gradient of these plots. Reference standards were carried out without a sample, with an uncoated titanium substrate and with 10 mg of stirred Degussa P25 powder.

SEM imaging was carried out by using a JEOL 6301 field emission instrument with secondary electron imaging.

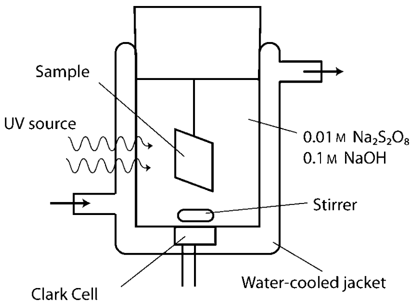

Figure 3. Schematic illustration of the apparatus used to determine the rate of water oxidation under UV-light irradiation.

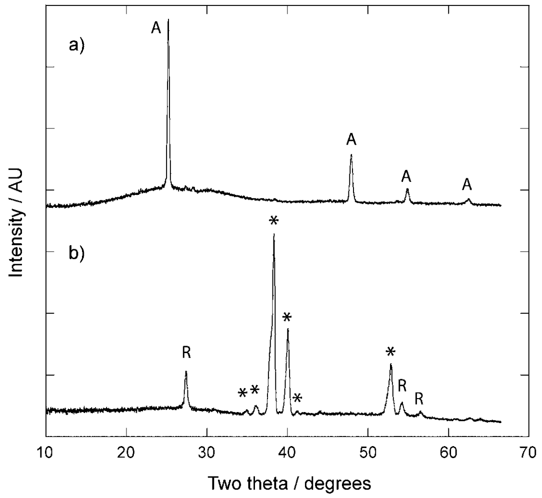

Figure 4. Example diffraction patterns of the TiO_2 films, recorded by using $Cu_{K\alpha 1}$ radiation. a) On glass substrate. Peaks corresponding to the anatase polymorph (A). b) On titanium substrate. Peaks marked with asterisk (*) are due to the titanium substrate, remaining peaks correspond to rutile (R).

Results

Atmospheric pressure chemical vapour deposition was used to deposit fourteen films of titania onto glass substrates, and fourteen films onto titanium-metal substrates from $TiCl_4$ and ethyl acetate. These films were all deposited onto substrates at 660 °C by using identical conditions as detailed in the Experimental Section, except for the deposition time, which was varied to modulate the thickness. The films were characterised by powder X-ray diffraction and VIS/IR spectroscopy. The ability of the films to photocatalyse the oxidation of H_2O to O_2 in the presence of persulfate by using a monochromatic 365 nm light was then determined.

Characterisation: Powder X-ray diffraction showed that all of the films grown on glass substrates were crystalline titania, with the anatase structure. In contrast, the films formed on titanium-metal substrates all had diffraction patterns, which could be matched to the rutile polymorph of titania (Figure 4). The crystallinity of the films, as determined by the peak broadening in the patterns, was the same for all the samples. The strong difference in the phase of TiO_2 deposited on the different materials, despite apparently otherwise identical conditions, shows a surprising substrate directing affect, due either to an epitaxial match between rutile and the titanium metal, or other surface energy effect. It is also significant in terms of the aims of this work, as anatase is widely reported as being the more photocatalytically active polymorph in the previous work carried out on glass substrates.[10–12]

The spectroscopic measurements conducted on all the titania samples in the range $\lambda = 300–2500$ nm showed characteristic interference patterns, from which the thickness of the film could be determined.[13] Figure 5 shows an example spectra and the resulting analysis of the data. Conducting this analysis revealed the expected strong positive correlation between deposition time and thickness. The TiO_2 de-

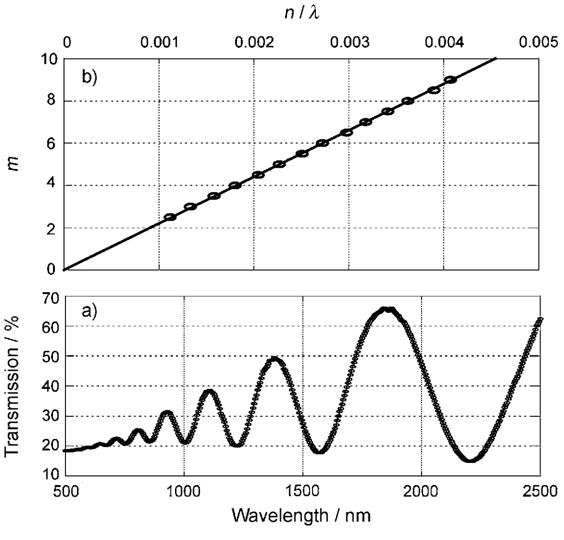

Figure 5. a) Raw spectroscopic data of a TiO_2 film on glass in transmission, showing interference effect ($y = 2201.2x$). b) Plot of the refractive index (n) to wavelength (λ) ratio against m (whole or half integer) for the successive maxima and minima observed in the spectra. As $m = 2d \times (n/\lambda)$ the gradient of this plot is equal to twice the thickness d of the TiO_2 film.

posited onto glass substrates was found to be in the range 84(3)–1560(50) nm, whereas the fourteen samples on titanium metal had thicknesses of 90(20)–1323(13) nm, with an average growth rate on both substrates of 20 nm s^{-1}.

Photo-oxidation test: All twenty eight thin-film TiO_2 samples were tested for their ability to photo-oxidise water; in addition an uncoated titanium coupon, a 10 mg sample of Degussa P25 and an experiment with no sample loaded were used for reference. All TiO_2-coated samples were found to be photocatalytically active to some extent, and produced a linear increase in dissolved oxygen as a function of time, over the 1800 s test time. This rate of oxygen production for all samples was plotted as a function of film thickness as illustrated in Figure 6. In the test of the uncoated titanium control coupon the dissolved oxygen increased at a rate of 2×10^{-6} mol min^{-1} m^{-2}, (approximately 150 times less than that of the most effective TiO_2/Ti film tested) presumably due to the presence of a very thin layer of titania on the titanium substrate, whereas the standards run without any sample present and with uncoated glass showed no measurable oxygen production.

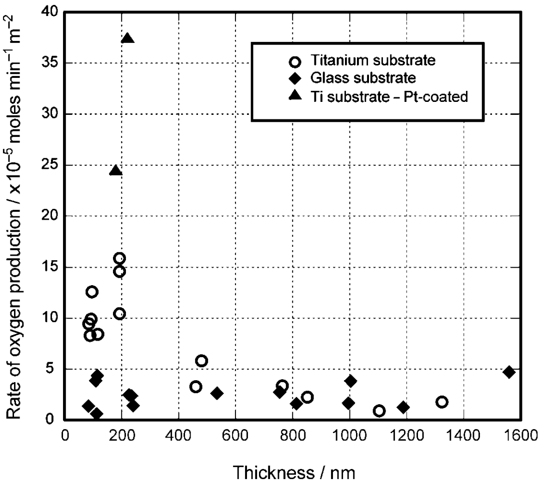

Figure 6. Plot of the observed oxygen production rates for the titania films in conjunction with a sacrificial aqueous electron acceptor solution of KOH (0.1 M) and $Na_2S_2O_8$ (0.01 M), against the film thickness. Samples on glass substrates are shown by filled diamonds, those on titanium substrates by empty circles, and the two samples represented by empty triangles are on titanium substrates, which have been coated on the reverse with platinum.

The results of the photo-oxidation test on the TiO_2 film on glass substrates showed that there was no correlation between the thickness of the film on glass and the rate. The mean rate of oxygen generation observed over the fourteen samples is 2.5×10^{-5} mol min^{-1} m^{-2}, and although there is considerable variation about this mean between the samples, $\pm2\times10^{-5}$ mol min^{-1} m^{-2}, this cannot be described as a function of the TiO_2 film thickness. Some of the fastest and slowest rates were observed in both the thickest and thinnest films. In contrast, the titania films deposited onto titanium substrates showed oxygen production rates that were strongly dependent on the thickness of the deposited film. The six films with a thickness of greater than 400 nm had a mean oxygen generation rate of 2.9×10^{-5} mol min^{-1} m^{-2}, similar to that observed in the glass substrate samples. Further, the eight samples with a thickness of less than 200 nm were found to have a mean rate of $1.1\times10^{-}$ mol min^{-1} m^{-2}, some 3.8 times greater. The two best-performing samples were both found to have a thickness of 190 nm, and had recorded rates of 1.46×10^{-4} and 1.59×10^{-4} mol min^{-1} m^{-2}. Significantly, this pair of samples produced oxygen at least three times faster than even the best titania films formed on glass substrates tested in this work.

The morphology of the film surfaces were investigated by using SEM imaging. This showed that all of the films have a similar morphology, being composed of densely-packed isotropic crystals of approximately 50–200 nm in diameter. Figure 7a shows a representative image of a glass substrate film, Figure 7b shows that of a titanium substrate film, both at the same level of magnification. These images show that there is some difference in the morphology between the two types of sample dependant on the substrate, with an apparently slightly smaller crystallite size and greater degree of fusion between the particles for the film on the titanium substrate.

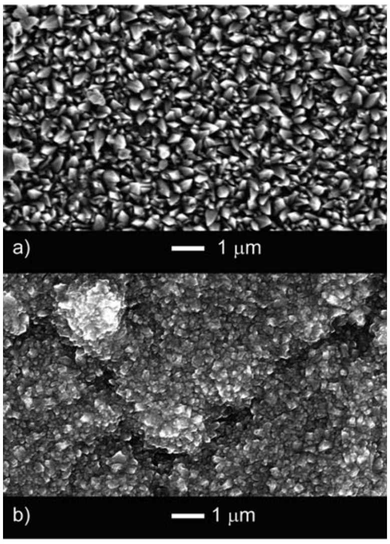

Figure 7. SEM images of the titania film: a) TiO_2 on glass substrate and b) TiO_2 on titanium metal substrate.

Effect of platinum coating: In a further experiment, three TiO_2 films were synthesised on titanium coupons by using deposition times of 10 and 60 seconds, yielding films with thicknesses of 220(5), 179(3) and 1501(10) nm, respectively. These films, along with an uncoated titanium coupon were sputter-coated with platinum metal on the reverse, uncoated side. This is a necessary step for the conversion into a water-splitting photodiode, as although the TiO_2 band energies have sufficient over-potential to rapidly drive the production of O_2, a catalyst (Pt) is required to produce H_2.[14] The platinum-coated samples were tested to determine the effect of the Pt coating on oxygen production by using the sacrificial electron acceptor system.

Each of the samples (three TiO_2-coated and one uncoated titanium substrate) were tested three times before platinum coating, and three times after being platinum-coated, by using the photo-oxidation test with $Na_2S_2O_8$ as an electron acceptor, as described in the previous section. As before, linear oxygen production was observed as a function of irradiation time, and the resulting rates were averaged over the three tests. As expected from the results of the previous sections, the analysis of the titania films before the platinum coating showed that the thinner titania films of 220 and 179 nm thickness had the highest rates of $8(1)\times10^{-5}$ and $5(2)\times10^{-5}\,\text{mol}\,\text{min}^{-1}\,\text{m}^{-2}$ compared to the 1501 nm thick titania with $1.0(6)\times10^{-5}\,\text{mol}\,\text{min}^{-1}\,\text{m}^{-2}$; the uncoated slide had a marginal rate of $2(4)\times10^{-6}\,\text{mol}\,\text{min}^{-1}\,\text{m}^{-2}$. After platinum coating on the reverse of the coupons the rate of thin titania films increased dramatically to $4(1)\times10^{-4}$ and $2.4(6)\times10^{-4}\,\text{mol}\,\text{min}^{-1}\,\text{m}^{-2}$ for the 220 and 179 nm thick samples, respectively. In both cases this is an effective five-fold increase in the rate observed after reverse platinum coating. The 1501 nm thick titania film and uncoated sample showed no such large increase after platinum coating with the observed oxygen production rates being, within experimental error, the same as the uncoated rates. The average values obtained were $1.1(6)\times10^{-5}$ and $4.9(8)\times10^{-7}\,\text{mol}\,\text{min}^{-1}\,\text{m}^{-2}$ for the 1501 nm thick titania and the coupon without TiO_2, respectively—indicating that the increase in rate observed for the 150–250 nm TiO_2 films was not an artefact of the platinum coating alone, but of an interaction between the film and the platinum.

Similar experiments conducted with TiO_2 films on glass substrate samples showed that platinum coating on the back of the glass substrate had no effect on the observed rate of oxygen production.

Discussion

The results presented here, describe the effect of thickness on the ability of titania films to produce oxygen in a sacrificial system.[8] The use of TiO_2 in a water-splitting photodiode has been investigated previously[5,6,15] but this is the first example of APCVD being used to form the titania photocatalyst. Previous investigations of titania-based water-splitting photodiodes have used RF sputtering to generate the TiO_2 films—the use of APCVD is an improvement upon this, as it allows the formation of films from inexpensive reagents and with the potential for industrial scale up[9,16] Indeed, APCVD is already the synthetic method of choice for the large-scale use of photocatalytic TiO_2 in self-cleaning windows. This is also the first time that the effect of thickness of the TiO_2 film upon oxygen production has been investigated and optimised (Table 1).

Table 1. Summary of the thickness, composition and rate of oxygen production of all samples discussed.

Thickness [nm]	Composition	Substrate	Rate of O_2 production $[10^{-5}\,\text{mol}\,\text{min}^{-1}\,\text{m}^{-2}]$
234(10)	anatase	glass	2.4(1)
535(18)	anatase	glass	2.6(2)
115(1)	anatase	glass	4.4(3)
226(8)	anatase	glass	2.5(1)
754(30)	anatase	glass	2.7(2)
1003(27)	anatase	glass	3.8(2)
813(22)	anatase	glass	1.6(1)
996(20)	anatase	glass	1.7(1)
240(12)	anatase	glass	1.4(1)
113(25)	anatase	glass	0.6(1)
84(9)	anatase	glass	1.4(1)
1559(50)	anatase	glass	4.7(3)
1188(28)	anatase	glass	1.2(1)
109(1)	anatase	glass	3.9(2)
480(22)	Rutile	Ti	5.8(3)
460(7)	rutile	Ti	3.3(2)
764(19)	rutile	Ti	3.4(2)
851(23)	rutile	Ti	2.3(1)
85(20)	Rutile	Ti	9.5(6)
192(5)	rutile	Ti	16(1)
96(16)	rutile	Ti	12.6(8)
1323(13)	rutile	Ti	1.8(1)
1104(10)	rutile	Ti	0.9(1)
92(20)	rutile	Ti	9.9(6)
193(17)	rutile	Ti	10.4(6)
192(11)	rutile	Ti	14.6(9)
89(12)	rutile	Ti	8.3(5)
116(13)	rutile	Ti	8.4(5)
220(5)	rutile	Ti	8(1)
179(3)	rutile	Ti	5(2)
220(5)	rutile	Ti and Pt	38(2)
179(3)	rutile	Ti and Pt	24(6)

The oxygen production rate observed on the TiO_2 films grown on glass substrates showed no correlation with thickness. As the SEM imaging shows that the films are composed of a densely-packed array of titania crystallites, with no apparent porosity then, per unit area of substrate, each of the films has comparable surface areas exposed to the solution, regardless of the thickness. This active, surface layer covers and effectively inactivates the titania underneath it by preventing contact with the solution. This active layer is identical in each of the films explaining why increasing the thickness had no obvious effect on the rate of water oxidation in the glass substrate samples.

The results of the experiments on the titanium substrate samples show that the oxygen production rate depends strongly upon the TiO_2 film thickness. This is in contrast to the glass substrate samples and suggests that a different mechanism applies. However, the morphology of the titanium substrate films is of the same dense, non-porous type, and the same limited surface area of the film will be in contact with the solution. The results also indicate that the best titanium substrate film is three times more active than any of the films on glass. In the photo-oxidation of water by persulfate, sensitised by titania on glass, clearly the photogenerated electron–hole pairs must diffuse to a common surface, that of the titania film, in order to effect the two halves of the overall photoreaction [Eqs. (4) and (5)]:

$$S_2O_8^{2-} + 2\,e^- \rightarrow 2\,SO_4^{2-} \qquad (4)$$

$$2\,H_2O + 4\,h^+ \rightarrow 4\,H^+ + O_2 \qquad (5)$$

The overall rate of water oxidation by titania on glass will be low, given the need for the above component half reactions of Equation (3) to occur on the same surface, as illustrated in Figure 8a. In such circumstances there is no obvious barrier to the efficiency-lowering process of electron–hole recombination, which can, of course, occur on the surface, as well as in the bulk. At first it might appear curious that for the titania on glass samples the rate of the photocatalysed reaction (3) seems largely indifferent to titania film thickness, as it would seem likely that the thicker the film the greater the fraction of incident light absorbed. However, previous work carried out by this group[17] on CVD anatase films revealed a large absorption coefficient ($\alpha = 5\times10^6\,m^{-1}$ at 365 nm) for such films, which indicates that whereas a 200 nm film would absorb ≈ 63 % of the 365 nm incident light, a 1 micron film would absorb over 99 %. The difference between these two figures is not great (a factor of 1.6) and a close examination of the data illustrated in Figure 6 does seem to suggest, if anything, that there is a gradual increase in rate as the film thickness is increased from 100–1000 nm. Indeed, the ratio of the rates of O_2 production for 200 and 1000 nm titania/glass films is 1.6.

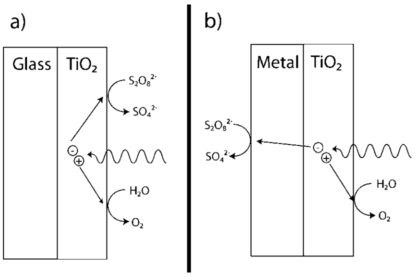

Figure 8. Diagram of the mechanism of photocatalysis of a) TiO_2 on glass substrate and b) TiO_2 on titanium-metal substrate.

In contrast, the use of a metal substrate in conjunction with a titania film, (albeit rutile) allows the semiconductor to form an ohmic contact with the metal, and a depletion layer in the semiconductor. Electron–hole pairs photogenerated in the depletion layer will separate under the associated electric field, with the electrons migrating towards the metal and the holes to the solution-exposed surface of the semiconductor, as illustrated in Figure 8b. In contrast, photogenerated electron–hole pairs generated outside this region are only able to move by diffusion and so are much less likely to be photocatalytically active. As a consequence, when the thickness of this quasi-neutral region exceeds $1/\alpha$, electron–hole pair recombination becomes increasingly the dominant process[18–20] and the kinetics of photocatalysis become more like those of a metal-free (titania on glass) system. It also follows that for such semiconductor/metal systems the optimum thickness in terms of photocatalytic activity is usually when the depletion layer width is approximately equal to the reciprocal of the absorption coefficient,[18] $1/\alpha$, which, interestingly, for CVD anatase films is ≈200 nm. The results in Figure 6 suggest that the rutile APCVD titania/Ti diodes exhibit an optimum photocatalyst performance for the 200 nm titania films because the depletion layer width and $1/\alpha_{365}$ (for rutile APCVD films) are approximately 200 nm. The addition of Pt (on the reverse of the Ti metal coupon) simply improves the ability of the metal for mediating reaction (4) and so increases the overall rate of photocatalysis, without affecting the semiconductor-film-thickness-dependence of the system.

Further evidence of improved electron transfer between the substrate and the reaction surface of the thinner TiO_2 coatings comes from the platinum coating experiment. Platinum was sputter-coated onto the reverse of three titania samples on titanium. The two thinnest samples (220 and 179 nm) showed a significant (five times) enhancement in the rate observed after platinum coating compared to pre-platinum—the first time to our knowledge that this has been observed and strongly indicating transfer of electrons between the two faces of the coupon. However, for the thick titania film no such enhancement was observed, indicating an insufficient electron transfer between the surface of the TiO_2 and the Pt-coated side. The high rates observed in the thinner films are not simply an artefact of platinum sputtering alone, but require ohmic contact between the titania surface and the platinum coating of the photodiode. This is confirmed by the results of oxygen-production testing on titanium diode films on glass substrates. When these samples were coated on the reverse with platinum no increase in the oxygen production rate was observed.

Overall, the highest oxygen production rate observed in this work by using the sacrificial electron acceptor (alkaline $Na_2S_2O_8$) with a 16 W, 365 nm light was the 220 nm thick TiO_2, rutile, on a titanium substrate, with platinum-sputter-coated on the reverse. This sample gave an oxygen production rate of $4(1)\times10^{-4}\,mol\,min^{-1}\,m^{-2}$, or in units by mass of $6.68\,mol\,g^{-1}\,s^{-1}$. By using the same experimental setup 10 mg samples of stirred Degussa P25 were found to have a considerably lower per mass oxygen production rate of $0.40\,mol\,g^{-1}\,s^{-1}$. This is a somewhat surprising result, as Degussa P25 is a commonly used and highly active standard, which in other tests, such as the stearic acid decomposition test,[21] has often been shown to have much higher activity.[9] Additionally, the far greater surface area of Degussa P25 of $50\,m^2\,g^{-1}$ compared to that of approximately $0.1\,m^2\,g^{-1}$ for titania films grown by CVD would lead to an expectation of greater rate to be observed in P25 powder TiO_2.[22,23] However, the greater oxygen production seen in the best sample presented here seems to be related to the electronic interaction between the TiO_2 coating and the substrate and platinum coating. In the glass substrate samples, which are a fairer comparison to P25, an average rate of 0.3 $mol\,g^{-1}\,s^{-1}$ was observed. This is still slightly greater than might be expected based upon the comparison of surface area. We can conclude that the method of synthesis of APCVD leads to a high activity per unit surface area for water oxidation in the films, (i.e., similar to that of P25, despite the three orders greater magnitude surface area of the powder), which can then be enhanced further again by almost an order of magnitude if the film is sufficiently thin to communicate with a platinum coating on the other side of the substrate.

The comparison of the films synthesised here, indicate that far higher rates can be observed than in powder slurries. Limited work has been conducted elsewhere on titania thin films for water splitting,[5,6] although comparison with the work of other authors and that presented here is difficult due to variations in measurement conditions, the illumination intensity in the experiment and the use of sacrificial reagents. Kitano et al.[6] investigated titania deposited by RF sputtering, and reported a maximum rate of 0.2 $mol\,g^{-1}\,s^{-1}$, by using a 0.05 M $AgNO_3$ sacrificial solution. The films deposited were 3 μm thick, and this rate is similar to the rates observed in the thicker films reported in this study.

Conclusion

We have demonstrated for the first time that atmospheric pressure chemical vapour deposition can be used to make titania films that can photo-oxidise water in conjunction with a sacrificial electron acceptor, and that the rate of this oxidation is strongly dependant on the thickness of the film. The results show an apparent optimum thickness of 200 nm. We have further demonstrated for the first time that platinum coating of the reverse side of TiO_2-coated titanium substrate can lead to an enhancement of up to five times in the rate of photo-oxidation over non-coated samples. We interpret these faster rates of water splitting as due to vectoral charge separation and the ease of electron and hole separation facilitated by platinum metal.

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