Photocatalytic evolution of hydrogen and oxygen from ceramic wafers of commercial titanias

Sofia Elouali [a], Andrew Mills [b], Ivan P. Parkin [a], Edward Bailey [a], Paul F. McMillan [a], Jawwad A. Darr [a,*]

[a] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom
[b] Department of Pure and Applied Chemistry, University of Strathclyde Glasgow, 16 Richmond Street, Glasgow G1 1XQ, United Kingdom

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ABSTRACT

Several commercial titania photocatalyst powders were formed into thin (ca. 350 μm), 25 mm diameter ceramic wafers, sputter deposited with Pt on one side. The activities of each of the ceramic wafers were tested for hydrogen and oxygen evolution from aqueous sacrificial systems. The commercial sample PC50 (Millennium Chemicals, UK) yielded reproducible ceramic wafers with high activity for water photoreduction. Many of the ceramic wafers displayed low water photo-oxidation activities; however, these were greatly increased with addition of a NiO co-catalyst. In a selected case, hydrogen evolution activity was compared between a PC50 wafer and an identical weight of platinised PC50 powder suspension.

1. Introduction

The conversion of solar to electrical energy using photovoltaic devices such as the silicon solar cell or dye-sensitised solar cells is well-established [1]. However, electrical energy is not easily stored in large amounts and solar energy is diurnal, intermittent and least available when we most need it (i.e. at night in winter). As a consequence, there is a real need for an efficient (>10%), inexpensive (<£5 m^{-2}) solar energy conversion device that generates a readily utilised chemical fuel, e.g. hydrogen, that can be readily transported at minimal energy cost and used when needed [1]. One strategy is to use a photovoltaic device in conjunction with a water electrolysis cell. Such an approach has attracted considerable attention in recent years with many reports appearing on 'hybrid photoelectrodes' [2] and 'tandem' cells [3]. The advantage of a solar-driven, water-splitting system is that it converts the sun's energy into a chemical form, bypassing the need to convert photovoltaic energy into chemical energy by running an electrolytic cell.

Fujishima and Honda were the first to report water-splitting using a semiconductor photoanode in the form of a single crystal of rutile titania coupled directly via an ohmic contact with a platinum dark cathode in a macro-photoelectrochemical cell (PEC cell) [4]. Wrighton et al. were able to improve considerably on the performance of the titania/Pt macro-PEC system for water-splitting using strontium titanate as the photoanode (reported a quantum yield of 20% at 330 nm [5]). However, to be of practical, widespread use, such single crystal semiconductor PECs are too expensive. Attempts

were made to create less-expensive, bifunctional micro-PEC cells in the 1980s, comprising colloidal particles of titania coated with microdots of Pt and an oxygen catalyst (RuO₂). However, such systems generate H₂ and O₂ in the same space as an intimate mixture, making the likelihood of back reaction high and overall solar to chemical energy efficiency low.

In 1977, Nozik [6] demonstrated that a single wafer crystal of cadmium sulphide with a thin foil of Pt stuck onto one face was able to photosensitise the photoreduction of water by sulphide ions, with hydrogen evolution occurring on the Pt face of the wafer (and concomitant oxidation of S^{2-} on the CdS face). This was one of the first examples of a macro-photocatalyst diode (MPCD), which has the advantage of generating the oxidised and reduced products at physically separate locations, not unlike the situation that operates in green plant photosynthesis. This principle has been used recently to create a water-splitting cell using a photochemical diode comprising a titanium metal foil with a thin (1.5 μm) film of titania on one side and Pt on the other [7].

There are several design considerations to take into account in the practical formation of a water-splitting photodiode device such as that envisaged, not least of which is the physical form in which the semiconductor is incorporated into a diode. Single crystal titania diodes [1,6] are of limited application due to the difficulty with which large crystals can be grown, particularly with regard to anatase [8]. Thin films such as those produced through sol–gel techniques have been shown to be relatively high in activity but are dependent on a high degree of contact between the film and a conductive substrate. In contrast, a pressed-powder, ceramic wafer would allow intimate electrical contact between the semiconductor and appropriate co-catalysts which could be applied on either or both sides.

Table 1
Free powder properties of titanias formed into ceramic wafers.

Material	Supplier	Surface area ($m^2\,g^{-1}$)	Anatase crystallite size (nm)	Wafer density after heat-treatment at 300 °C
P25	Evonik Degussa	50	24 (37)[a]	1.97 g cm^{-3} (49.9% dense)
PC10	Millennium	11	60–70	1.70 g cm^{-3} (44.3% dense)
PC50	Inorganic	43	20–30	1.70 g cm^{-3} (44.3% dense)
PC500	Chemicals	>250	5–10	1.57 g cm^{-3} (40.9% dense)

[a] Crystallite size for rutile fraction (30%).

Titania has been extensively studied for photocatalytic and water-splitting applications and it is known to be highly photo-stable under a wide range of conditions. It has been reported to have high water permeability compared with materials tradition-ally used as supports such as alumina [9], which is essential for rapid exchange of reactant species and evolved gases in aqueous systems. It is also abundant and therefore far less-expensive than many other photocatalysts, making it a good choice of material for forming catalyst-only membranes or wafers.

Titania can be prepared as a ceramic wafer through coat-ing onto mesoporous supports [10,11], sol–gel and subsequent sintering [12], wet extrusion [13] or cold powder compaction. Previous studies of compressed titania have mainly focused on pressed films for use in solar cells, such as that of Hagfeldt and co-workers who prepared thin films of titania (ca. 8 μm) from ethanol onto conductive glass and plastic and compressed them after drying [14]. Compaction of greater thicknesses of titania allows the formation of self-supporting photocatalysts which have been unaltered by exposure to solvents, polymerisation agents or other chemicals necessary to facilitate handling which may leave residues on the surface of the titania particles after sinter-ing.

In this work, an initial study was carried out into the pho-tocatalytic behaviours for 350 μm thick, 25 mm diameter porous ceramic wafer photocatalyst discs prepared from several commer-cially available titanias. The wafers were coated on one face with Pt and, in a selected case, a NiO co-catalyst on the reverse side. Via this approach, it was possible to prepare wafers which were capable of both oxygen and hydrogen production using appropriate sacrificial reactions.

2. Experimental

2.1. Materials

The following commercial titania photocatalysts were used in this work – Cristal Global (Stallingborough, UK) PC10, PC50, PC500; Aeroxide P25. Aeroxide P25 is a combination of anatase and rutile in 70:30 mol ratio, whereas the Millennium titanias are pure anatase. The specifications of these titanias according to the manufacturers' data, as well as the bulk densities of the synthesised wafers from these powders, are listed in Table 1.

Na$_2$S$_2$O$_8$ (Riedel De Haën, Germany), NaOH, EtOH (BDH, Germany) and HCl (Fisher, Cambridge, UK) were used in the preparation of sacrificial solutions. Ni(NO$_3$)$_2$·6H$_2$O was used as a precursor for NiO loading while H$_2$PtCl$_6$ and formaldehyde were used in the photodeposition of Pt onto free titania powdered (Sigma Aldrich, Surrey, UK). All gases used in operation of the gas chro-matograph and for purging the oxygen electrode were supplied by BOC. 10 MΩ deionised water was used throughout. Wafer densi-ties were calculated using the theoretical density of pure TiO$_2$ [15] (anatase density = 3.83 g cm^{-3}) except for P25 for which the aver-age theoretical density of anatase and rutile (density = 4.24 g cm^{-3}) in the appropriate ratios.

2.2. Preparation of ceramic wafers from commercial titanias

Each different titania powder (see Table 1) was pressed into 25 mm diameter discs of ca. 350 μm in thickness at a pressure of 1550 kg cm^{-1} in the extraction ram of a non-end-loaded piston cylinder (Depths of the Earth Company, Cave Creek Arizona, USA) of a hand-operated uniaxial hydraulic press, within a stainless steel die (Compacting Tooling, Inc., Philadelphia, USA).

Powder distribution uniformity was the greatest mechanical barrier to obtaining compacts thinner than 300 μm as particle agglomeration became more influential with lower powder depth. In order to avoid pieces fracturing within the die, uniform filling was achieved by using a razor blade to level the surface of the pow-der against the top surface of the die. Mylar sheeting cut to fit the die was used to prevent the titania sticking to the punch surfaces and thereby facilitate removal. After pressing, sample wafers were heat-treated in air at 300 or 500 °C inside a muffle furnace for 1 h holding time at temperature and 5 °C min^{-1} heating and cooling rate. A sputter coater with a platinum target was used to coat one side of each prepared ceramic wafer (coating was carried out at 30 mA for 4 min). For the nickel co-catalysed PC50 sample, NiO was coated onto the ceramic wafer using a method similar to that first reported by Kudo et al. [16]. Briefly, 100 μL of a 1.58 M nickel nitrate solution was dropped onto the green wafer (on the opposite face to that intended to be coated with Pt). The wafer was then calcined in air at 500 °C for 1 h, after which the resulting NiO was reduced in a 500 mL min^{-1} flow of 5% H$_2$ in N$_2$ at 500 °C for 2 h and then partially re-oxidised at 200 °C in air for 1 h. The NiO loaded wafer was then sputtered with Pt on the opposite face. Typical images of a platinised PC50 wafer are given in Fig. 1.

PC50 powder photodeposited with Pt was also prepared, using a previously published method [11]. Briefly, a suspension of the powder in a solution containing H$_2$PtCl$_6$ and formaldehyde was irradiated under the Xe lamp for 4 h under stirring. The powder was then filtered and washed repeatedly with deionised water before being dried in air. 0.275 g of the dried Pt-PC50 was suspended in 40 mL of the sacrificial solution.

2.3. Characterization

The photocatalytic activities of the ceramic wafers were evalu-ated through the separate measurement of water photoreduction and photo-oxidation activities within sacrificial solutions under simulated solar light irradiation (UVA irradiance of 17.5 mW cm^{-2}) using a Xe 75 W light source (Photon Technology International, West Sussex, UK).

Water photoreduction reactions were carried out within a silica glass reactor consisting of a central walled glass chamber sur-rounded by an outer glass water jacket (water was circulated through the jacket by an external chiller maintained at 19 °C). The vessel was filled with 40 mL of a solution comprising of 1:1 EtOH:H$_2$O containing 0.1 M HCl, kept under continuous stirring. The ceramic wafer was suspended from a rubber septum which was also used to seal the reactor to the outside atmosphere. 0.25 cm^3 of gas was removed from the headspace at regular intervals and anal-
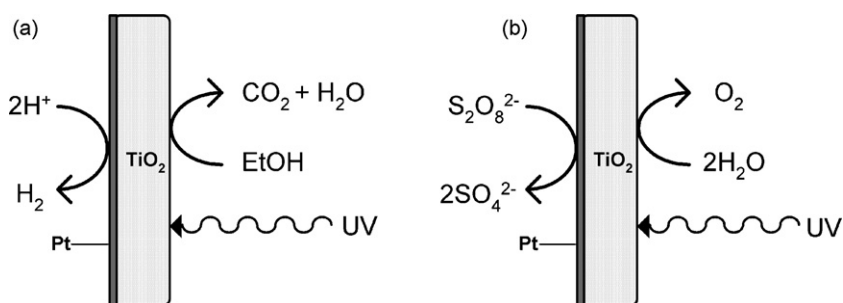
Fig. 1. Schematic diagrams showing sacrificial water photo-oxidation (a) and water photoreduction (b) reactions from the Pt sputtered TiO_2 wafers under UV irradiation.

ysed for hydrogen via gas chromatography by a Varian CP-3800 GC equipped with a 5A molecular sieve column.

Water photo-oxidation reactions were carried out within a Rank Brothers Ltd. Oxygen electrode containing 32 mL of a sacrificial solution comprising of 0.1 M NaOH and 0.01 M $Na_2S_2O_8$ [17]. The solution was purged with argon before addition of the ceramic wafer to obtain a baseline reading on the electrode. Oxygen production was continuously monitored by means of an attached potentiostat and a Picolog ADC-20 high resolution data logger (Pico Technology, Cambridgeshire, UK). During both types of photoreaction the samples were irradiated on the non-Pt coated face, through the vertical wall of the reactor. When wafers were irradiated in pure deionised water, only trace amounts of hydrogen or oxygen were detected. As a control, each sacrificial solution system was chilled to 19 °C and irradiated with the lamp for 1 h without the presence of a wafer sample. No hydrogen or oxygen evolution was measured.

3. Results and discussion

3.1. Synthesis

Overall, it was found that PC50 gave the most reproducible, uniform compacts which were also the most mechanically robust after heat-treatment in air at 300 °C. Conversely, the low bulk powder density and low flowability of P25 made it difficult to press and the compacted green discs shattered upon all attempts to remove the wafer from the die, suggesting a large amount of residual stress was present. In order to obtain an unbroken P25 compact, shattered compacted fragments were re-ground gently by hand in an agate pestle and mortar for 2 min and re-pressed between Mylar sheets (60 μm) at 1550 kg cm^{-2}. The non-heat-treated ceramic wafers were found to swell considerably when placed in any aqueous solutions for testing, therefore it was necessary to heat-treat the green disks in order to provide partial sintering and so render them sufficiently robust mechanically for testing (Fig. 2).
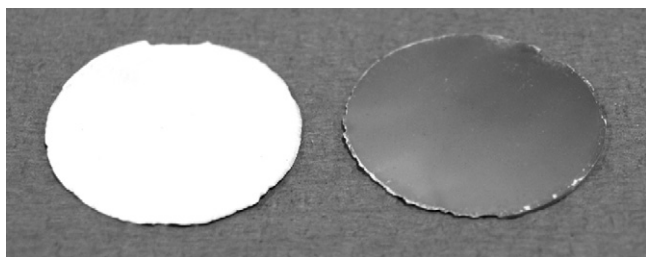

Fig. 2. Images of titania ceramic wafer discs after sintering (L) irradiated (plain) faces, (R) Pt deposited faces.

3.2. Initial photocatalytic activity studies

Ceramic wafers fabricated from P25 powders (heat-treated at 300 °C), having been back coated with Pt only, were found to be the most active of all similar samples for photoreduction (417.4 μmol H_2 h^{-1} g^{-1}): see Fig. 3. Increasing heat-treatment temperature from 300 to 500 °C had a generally negative effect on measured photoreduction activity, 337.2 μmol H_2 h^{-1} g^{-1}. In contrast, there was a significant gain in photo-oxidation activity after 500 °C heat-treatment of the sample, 70.1 μmol O_2 h^{-1} g^{-1} compared to 36.4 μmol O_2 h^{-1} g^{-1} after 300 °C heat-treatment.

Ceramic wafers fabricated from PC50 were found to be slightly more active than P25 for oxygen at both heat-treatment temperatures; 49.8 μmol O_2 h^{-1} g^{-1} (300 °C) and 76.9 μmol O_2 h^{-1} g^{-1} (500 °C). In contrast to P25, relative rates of photoreduction for PC50 were around 10% lower after heat-treatment at 500 °C (373.8 μmol H_2 h^{-1} g^{-1}) and 22% lower after 300 °C (262.5 μmol H_2 h^{-1} g^{-1}). On balance however, PC50 wafers were more physically robust under handling and more easily reproduced than those for P25. On this basis, it was decided to investigate the PC50 discs for NiO co-catalyst loading.

Ceramic wafers made from PC10 and heat-treated at 300 °C were found to be rather fragile under test conditions, whereupon the edges degraded under stirring during the testing. Hence, it was not possible to gain reliable data for this sample during oxygen evolution tests. Wafers produced from PC500 were observed to be inactive for oxygen production, for reasons that remain, as yet, unclear.

All non-platinised titanias showed little or no activity for photoreduction of water.

During the water photoreduction reaction, it was observed that gas bubbles in great number were evolved mainly from the back (non-Pt) edge of the discs, as illustrated in Fig. 3. There were however, a significant number of bubbles from the Pt coated side.
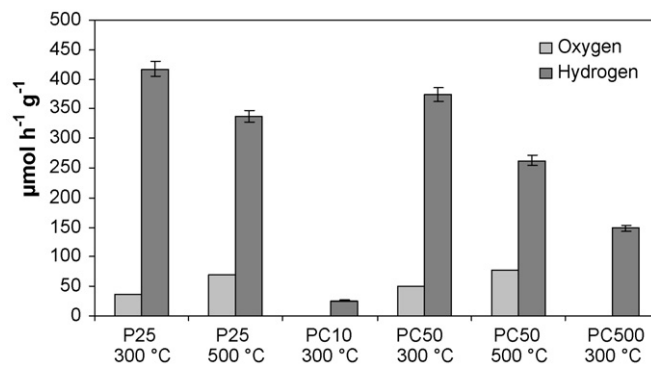

Fig. 3. Oxygen and hydrogen evolution rates from sacrificial solutions for ceramic wafers. All wafers were prepared from commercial TiO_2 materials pressed at 1550 kg cm^{-1} and subsequently heat-treated at 300 or 500 °C before sputtering of Pt onto one face.
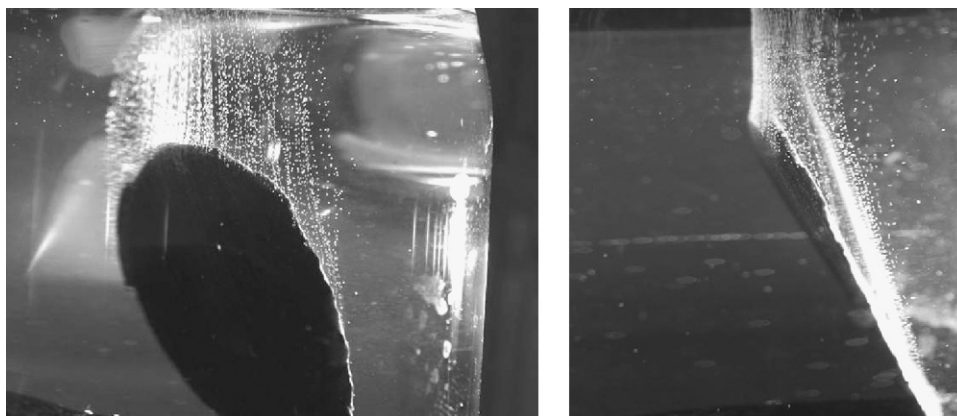
Fig. 4. PC50 ceramic wafer under 75 Xe lamp irradiation showing hydrogen gas production. (L) View directed towards back (Pt) face. (R) Side view of ceramic wafer (images taken with magnetic stirrer switched off).

Within a photodiode device, the photocatalyst side of the diode would need to evolve oxygen separately from hydrogen, which is usually evolved from the exposed face of the platinum. This did not occur exclusively in these particular discs due to the lack of physical barrier between the porous TiO_2 and the platinum. This work does, however, provide a useful baseline study of such wafers, for which the porosity could be further reduced (e.g., through sintering) in order to ensure hydrogen is exclusively evolved from the Pt coated side (Fig. 4).

The photoreduction activity of the PC50 ceramic wafer was directly compared to platinised powder of PC50 in suspension. Photoreduction activity was found to be almost identical ($263.3\,H_2\,h^{-1}\,g^{-1}$) to a PC50 ceramic wafer of identical weight that had been heat-treated at $500\,°C$ ($262.5\,H_2\,h^{-1}\,g^{-1}$). This is surprising given that the latter had been partially sintered by the heat-treatment. Evidently, this effect was more than compensated for by the efficient vectorial charge separation afforded by the compression of PC50 in the thin ceramic wafer.

Apparent quantum efficiencies for the generation of hydrogen can be calculated using the following formula [18–20]: A.Q.E. (%) = (number of reacted electrons or holes)/(number of incident photons) × 100 = (number of H_2 molecules evolved × 2)/(number of incident photons) × 100. For the most active wafer, formed from P25, A.Q.E. across the lamp output ≥300 nm was calculated to be 1.9%. This efficiency is above that reported for unmodified titania film diodes, such as that of Fujishima and Honda's value of 0.4% for TiO_2 films under 500 W Xe irradiation coupled to Pt black electrodes [21], but still far below that which can be achieved by co-catalysed or dye-sensitised systems, which have been reported with efficiencies in the 5–7% range under solar simulated light [19,22]. However, there are future possibilities within this work for modification of the TiO_2 wafer in order to enhance its photoresponse in a similar manner. In a further comparison, work previously carried out by Yasumori et al. [23] into titania spin coatings on sputtered Pt films supported on porous SiO_2 and Al_2O_3 membranes yielded a hydrogen evolution rate from aqueous ethanol of approximately $0.195\,mol\,m^{-2}\,h^{-1}$ under 300 W Xe irradiation. Assuming the area of the wafer is proportional to its activity, $0.256\,mol\,m^{-2}\,h^{-1}$ was achieved for the P25 wafer under 75 W Xe irradiation.

3.3. Effect of NiO co-catalyst upon photocatalytic activity

As the PC50 sample possessed the best balance of ease of manufacture, robustness during handling and photocatalytic activity (second most active of the wafers tested), it was chosen for co-doping with NiO [12] co-catalyst via an incipient wetness method, in order to investigate its effects on gas evolution rate. The NiO
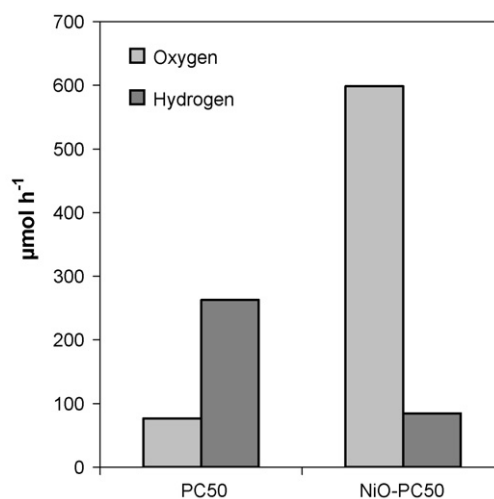

Fig. 5. Bar graph showing effect of 4 wt% NiO loading on oxygen and hydrogen evolution activities for PC50 wafers.

loaded sample was then sputtered with Pt on the reverse side. Oxygen evolution rate from the sacrificial solution was found to be considerably enhanced by NiO loading, an increase of 678% compared to the undoped wafer. In contrast, the introduction of the co-dopant gave a significantly lower hydrogen evolution rate ($85.5\,\mu mol\,H_2\,h^{-1}\,g^{-1}$ vs. $262.5\,\mu mol\,H_2\,h^{-1}\,g^{-1}$, a reduction of 67%) after the addition of NiO. Although the NiO appears to enhance the O_2-generating ability of the wafer, it is also possible that it, instead, is improving the ability of the conductance band electrons to reduce the persulphate sacrificial electron acceptor (Fig. 5).

4. Conclusions

Commercial titanias were compressed, heat-treated and sputtered with Pt to form robust ceramic wafers of c.a. 350 μm thickness and 25 mm in diameter. The commercial sample PC50, prepared by heat-treatment at $300\,°C$ was found to be active for water photoreduction and photo-oxidation using sacrificial systems while also being the most robust sample in testing. Loading with NiO was found to greatly increase photo-oxidation activity by 677% at the expense of a 67% reduction in the hydrogen production rate. This work has shown that photochemical diodes can be formed using efficient photocatalyst-only ceramic membranes through a simple and low cost preparation (pressing) method. Powders can be used to form large monoliths rather than having to prepare or use small single crystals as reported by others. With the ability

to produce self-supporting, photoactive and robust titania ceramic wafers which can produce either hydrogen or oxygen from sacrificial systems, there are now considerable opportunities to further optimise the basic system presented here. For example, significant improvements could be envisaged by optimising the loading of other redox co-catalysts or sensitizers onto such materials, or by reducing significantly, if not eliminating, porosity which should direct hydrogen to be exclusively evolved from the platinum coated side. There is also scope to extend this wafer approach to the photodegradation of water pollutants as a method of water purification, removal of the photocatalyst would be much easier if a wafer-type structure is used.

Acknowledgement

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