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

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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 (RuO$_2$). However, such systems generate H$_2$ and O$_2$ 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.

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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.

$Na_2S_2O_8$ (Riedel De Haën, Germany), NaOH, EtOH (BDH, Germany) and HCl (Fisher, Cambridge, UK) were used in the preparation of sacrificial solutions. $Ni(NO_3)_2\cdot 6H_2O$ was used as a precursor for NiO loading while H_2PtCl_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_2PtCl_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_2O 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-