

A photocatalytic water splitting device for separate hydrogen and oxygen evolution

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A two-compartment Plexiglas cell has been set up and tested for separate hydrogen and oxygen production from photocatalytic water splitting on a thin TiO₂ layer deposited by magnetron sputtering on a flat Ti electrode inserted between the two cell compartments.

The production of renewable and non-polluting fuels by the direct conversion of solar energy into chemical energy is one of the main issues of this 21st century. Hydrogen, the fuel with the highest energy capacity per unit mass, has the potential to supplement and possibly replace fossil fuels in the next decades. Since the discovery of photocatalytic splitting of water in a cell consisting of a Pt and a TiO₂ electrode under a small electric bias,¹ the photoassisted production of hydrogen and oxygen from water offers an extremely promising way for clean, low-cost and environmentally friendly conversion of solar into chemical energy.

Many efforts have been directed in recent years to the development and characterisation of new types of powdered photocatalysts for water splitting,^{2–4} possibly able to absorb a consistent part of visible light. However, only a mixture of H₂ and O₂ can be obtained from photocatalysts in powder form, while pure H₂ gas is needed to be used as a fuel on a large scale. Thus, there is an urgent need to develop devices, based on the use of photocatalysts in the form of thin layers with different arrays, able to separately produce H₂ and O₂ from water photosplitting.^{5,6}

We present here the first results of photocatalytic water splitting obtained employing a newly set up two-compartment Plexiglas cell, which allows the decomposition of H₂O separately into H₂ and O₂ on the opposite sides of an illuminated photoactive Ti electrode. A sketch of the cell is shown in Fig. 1.

The photoactive electrode was obtained through deposition of thin TiO₂ films on pure titanium disks (TI000420/8, Goodfellow), starting from TiO₂ powder (Puratronics[®] Alfa Aesar, 99.995%), employing a high vacuum (10⁻³ Pa) radio frequency (RF) magnetron sputtering system, consisting of three confocal RF sputtering guns at 50 mm from the substrate centre. Titanium disks were previously treated for *ca.* 1 min with a pickling aqueous solution (DeTitan 90, Kemar), containing HF and H₂SO₄ mixed with H₂O₂, and kept at 450 or 600 °C during the 3 h-long depositions. Pure argon (99%) was used as the working gas, at

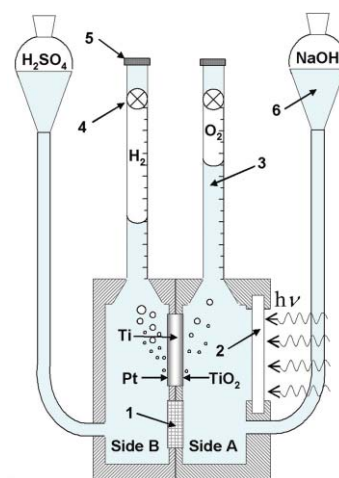


Fig. 1 Sketch of the Plexiglas cell for photocatalytic water splitting, with separate H₂ and O₂ evolution. 1 cation exchange membrane; 2 glass filter window; 3 burette; 4 stopcock; 5 rubber septum; 6 reservoir.

2.3 Pa. The sputtering power was kept constant at 200 W. Platinum was deposited on the opposite side of the disks, either by RF magnetron sputtering at room temperature, employing a 70 W RF power, argon at 1.7 Pa as process gas and a 200 μm-thick Pt foil (99.95%, Goodfellow) as source material (Pt-1), or in a vacuum evaporator (Pt-2), up to *ca.* 20 μg cm⁻² loading in both cases.

Fig. 2 shows the 3D-AFM image of the TiO₂ film deposited at 600 °C, which was obtained with an Autoprobe CP microscope (ThermoMicroscope-VEECO), operating in intermittent contact mode (IC-AFM), by means of a high resolution golden silicon cantilever with silicon conical tip (resonance frequency: 150 kHz;

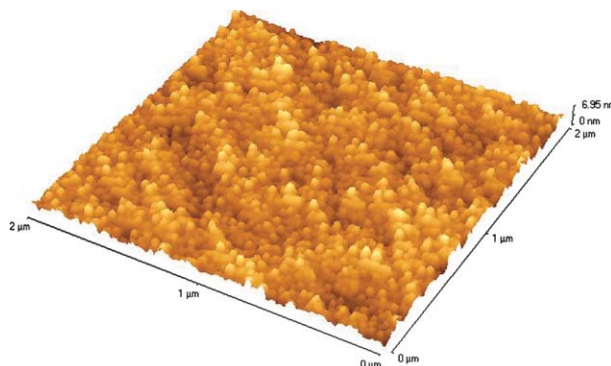


Fig. 2 AFM image of the TiO₂ film deposited at 600 °C.

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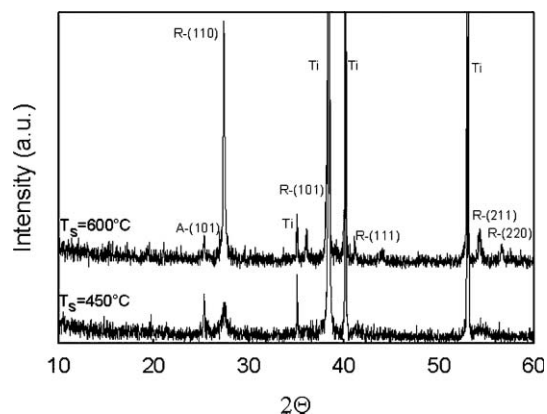


Fig. 3 XRPD patterns of the TiO_2 films deposited at $T_s = 450$ and 600 °C.

force constant: 5.5 N m^{-1}) and a scan rate of 1.5 Hz . The surface has a very low roughness ($1.15 \pm 0.04 \text{ nm}$) and is formed by nanocrystalline grains with an average size of 50 nm ($\pm 15 \text{ nm}$), characterised by a relatively narrow grain size distribution.

X-ray powder diffraction (XRPD) patterns, collected using a Bruker-D8 Advance Diffractometer and Cu anticathode radiation, are reported in Fig. 3. From the intensity ratios between the reflexes appearing at $2\theta = 25.4^\circ$ (anatase 101) and 27.5° (rutile 110) one may conclude that the TiO_2 film deposited at 600 °C consists almost completely of the rutile phase and that deposited at 450 °C contains almost equal amounts of anatase and rutile.

Reflectance measurements, performed with a Perkin Elmer Lambda 35 spectrometer equipped with integrating sphere, evidence the presence of interference fringes in the visible light region (Fig. 4) and confirm that the thin (*ca.* $0.5 \mu\text{m}$) TiO_2 layer deposited on titanium at 600 °C absorbs light up to longer wavelengths compared to that deposited at 450 °C, in line with its higher content of rutile.

Side A of the cell (Fig. 1) was irradiated through a 4-cm side square window, in which different cut off glass filters could be inserted. Either an iron halogenide mercury arc medium pressure 250 W lamp (Jelosil HG 200), emitting mainly in the $320\text{--}400 \text{ nm}$ range (UV), or an Osram Powerstar HCL[®]-T Neutral White 150 W lamp (VIS), mounted on a Twin Beam support, emitting at $\lambda > 350 \text{ nm}$ with maximum emission in the $450\text{--}600 \text{ nm}$ range, was employed as an irradiation source. Their full emission

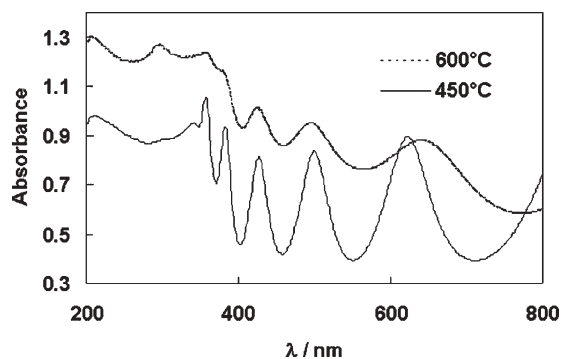


Fig. 4 Reflectance properties of the TiO_2 films deposited at 450 and 650 °C.

intensities on the TiO_2 film were 1.3×10^{-7} and 2.0×10^{-7} Einstein $\text{s}^{-1} \text{ cm}^{-2}$, respectively, according to ferrioxalate actinometry.⁷ The modified titanium disk (surface area: 10 cm^2) was mounted between the two compartments of the cell, with the TiO_2 layer facing the irradiation source, *i.e.* side A. A cation exchange membrane was mounted below the photoactive titanium disk, in the frame separating the two compartments of the cell. In order to provide a small chemical bias assisting the electron transfer from the TiO_2 surface layer to the Pt-modified face of the titanium disk during irradiation, side A of the cell was filled with an aqueous NaOH solution and side B with an aqueous H_2SO_4 solution of the same normality. No sacrificial reagents were ever employed.

At the beginning of the experiment, the two compartments, surmounted by two upside down burettes, were totally filled with the two solutions, which had been previously kept close to their boiling point for several minutes, in order to minimise the amount of dissolved air. After the beginning of irradiation, gas bubbles evolved at an almost constant rate from both compartments and accumulated in the upper part of the burettes, which were outgassed every hour. The composition of the evolved gas was determined both qualitatively, by injecting small samples ($250 \mu\text{L}$) in a mass spectrometer with quadrupolar detector (Q-MS), and quantitatively, by injecting the same volume in a gas chromatograph (GC), previously calibrated for H_2 and O_2 percent analysis, employing nitrogen as carrier gas. Q-MS analysis evidenced that oxygen was the main gas evolving from the illuminated TiO_2 layer in side A, thus acting as a photoanode, and hydrogen was the main gas evolving from the opposite, Pt-modified face of the titanium electrode, where water was reduced by the photoelectrons transferred through the Ti disk. Almost constant amounts of nitrogen (around $15\text{--}18\%$) were detected in both burettes. Very small CO_2 traces also evolved from side B, probably originating from residual air, while some hydrogen (between 1 and 3.5%) was also found in the gas evolving in side A, resulting from the direct reduction of water by the electrons photopromoted in the conduction band of TiO_2 . Typical trends of the H_2 and O_2 amounts evolved under irradiation are shown in Fig. 5, while Table 1 reports the rates of H_2 and O_2 evolution under irradiation with differently filtered light, evaluated by taking into account the effective composition of the gas mixtures in the two compartments of the cell, as determined by GC analysis.

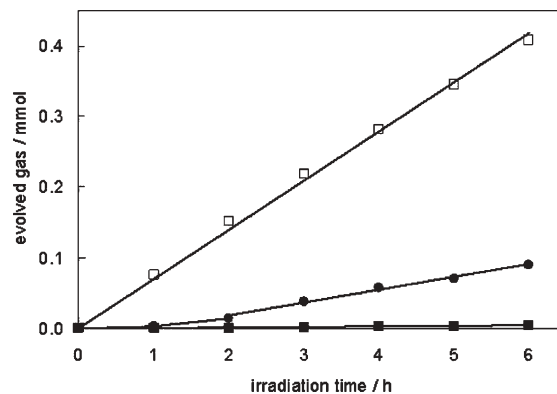


Fig. 5 Typical example of H_2 (squares) and O_2 (circles) evolution in side A (full symbols) and side B (open symbols) of the cell under irradiation.

Table 1 Rates of H₂ and O₂ evolution from sides B and A, respectively, employing different TiO₂/Ti/Pt electrodes, lamps and cut off filters

Photoelectrode ^a	Lamp ^b	Cut off	Evolution rate/ $\mu\text{mol h}^{-1}$	
			H ₂	O ₂
600 °C/Pt-1	UV	300 nm	100 ± 6	26 ± 3
600 °C/Pt-2	UV	300 nm	99 ± 1	40 ± 2
600 °C/Pt-1	VIS	350 nm	26	15
600 °C/Pt-1	VIS	400 nm	8	4
450 °C/Pt-1	UV	300 nm	49	13
450 °C/Pt-1	UV	350 nm	36	8

^a Pt-1 = Pt deposited by magnetron sputtering; Pt-2 = Pt deposited in evaporator. ^b UV = iron halogenide mercury arc lamp; VIS = Neutral White lamp.

Several runs were carried out employing each Ti electrode, with a good reproducibility between the runs carried out under identical conditions. In particular, we verified that the activity in water photosplitting of the electrode prepared by TiO₂ deposition at 600 °C with Pt also deposited by magnetron sputtering remained almost unchanged after more than 30 runs, *i.e.* after having been working for more than 180 h.

The rate of gas evolution was found to increase with increasing normality of the NaOH and H₂SO₄ solutions, up to 1.0 N, while the amount of gas evolved when the two compartments were filled with pure water was practically undetectable. As shown by the values of gas evolution rate from 1.0 N solutions, reported in Table 1, photocatalytic hydrogen production was not affected markedly by the method employed for depositing Pt on the Ti disk face opposite to that covered by the TiO₂ thin layer. The higher rate of O₂ evolution from the illuminated side of the 600 °C/Pt-2 photoelectrode might be a consequence of the beneficial effect of some Pt deposited on the TiO₂ thin layer, which occurred in the Pt evaporator.

Furthermore, the rutile phase, predominant when TiO₂ was deposited at 600 °C, appears to be more active in the photocatalytic production of hydrogen with respect to the anatase phase, present in a higher amount when the TiO₂ layer was deposited at 450 °C. This is compatible with the superior ability of the rutile phase to absorb longer wavelength light. Indeed, the 600 °C/Pt-1 photoelectrode showed activity also under irradiation at wavelengths above 400 nm (Table 1). In general, the amount of oxygen evolved in side A of the cell was lower than expected on the

basis of H₂ evolution, probably because of the often encountered difficulties in oxygen evolution in water photocatalytic splitting,⁸ and also because photocatalytically produced O₂ was in part retained in the initially de-aerated NaOH solution.

The first results obtained with our photocatalytic cell thus appear very promising: by verifying the actual composition of the evolved gases, we demonstrate that hydrogen, and no oxygen, is photocatalytically produced from water splitting in side B of the cell. The device is rather simple, much simpler and more efficient than the previously proposed two-compartment cell described in ref. 5, it works efficiently in the absence of any sacrificial reagent and the rates of hydrogen evolution under such conditions appear to be higher than those recently reported for a similar system.⁶

With both the best performing 600 °C/Pt-1 and /Pt-2 electrodes, in the absence of any sacrificial reagent, the photon efficiency in hydrogen production under irradiation with the UV lamp at wavelength above 300 nm is 2.1%; under irradiation with the VIS lamp ($\lambda > 350$ nm) it decreases to 0.36%. Such values were calculated on the basis of photon fluxes, obtained by ferrioxalate actinometry, extending to the whole emission spectra of the lamps and thus should be regarded as underestimated values of the photon efficiencies in the effective range of light absorption by the TiO₂ film. They indicate that the efficiency of the photocatalytic device can be improved by making the TiO₂ thin layer deposited on the Ti electrode more sensitive to visible light.

Notes and references

- 1 A. Fujishima and K. Honda, *Nature*, 1972, **238**, 37.
- 2 K. Maeda and K. Domen, *J. Phys. Chem. C*, 2007, **111**, 7851.
- 3 X. Chen and S. Mao, *Chem. Rev.*, 2007, **35**, 3523.
- 4 R. Abe, K. Sayama, K. Domen and H. Arakawa, *Chem. Phys. Lett.*, 2001, **344**, 339; R. Abe, K. Sayama and H. Sugihara, *J. Phys. Chem. B*, 2005, **109**, 16052.
- 5 K. Fujihara, T. Ohno and M. Matsumura, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 3705.
- 6 M. Kitano, M. Takeuchi, M. Matsuoka, J. M. Thomas and M. Anpo, *Catal. Today*, 2007, **120**, 133; M. Matsuoka, M. Kitano, M. Takeuchi, K. Tsujimaru, M. Anpo and J. M. Thomas, *Catal. Today*, 2007, **122**, 51; M. Kitano, M. Matsuoka, M. Ueshima and M. Anpo, *Appl. Catal., A*, 2007, **325**, 1.
- 7 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, 1956, **235**, 1351; M. Mrowetz and E. Selli, *New J. Chem.*, 2006, **30**, 108.
- 8 K. Sayama and H. Arakawa, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 1647.