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TiO₂-coated window for facilitated gas evolution in PEC solar water splitting†

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Photoelectrochemical (PEC) cells for water splitting generally have a transparent front window for the sunlight to reach the surface of the photoelectrode or tandem photoelectrode. The overall efficiency of a PEC system for solar hydrogen production is strongly affected by the evolved gases that get trapped in the front window. This negative effect is clearly observed when the PEC cells are placed in tilted positions to maximize light harvesting. Titanium dioxide coatings become superhydrophilic when exposed to UV light, facilitating the gas bubbles to slip up. The present study focuses on the development of a thin TiO₂ coating to minimize the adhesion of the evolved bubbles in the front window of PEC cells, thereby maximizing its transparency. Highly transparent, crack-free, and stable thin films of TiO₂ were prepared by spin coating followed by sintering at 465 °C for 45 min. A water contact angle (WCA) of 0° was obtained after irradiating the surface of the sample for 30 min with UV-light (365 nm, 2 W m⁻²), confirming the superhydrophilic behaviour. The irradiance loss during the evolution of H₂/O₂ was assessed using a silicon PV cell; the cell, tilted at 45° and equipped with a TiO₂-coated glass window, showed ca. 10% higher irradiance as compared to the uncoated glass window cell for both hydrogen and oxygen evolutions, whereas no significant differences were observed when the cells were vertically placed.

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1. Introduction

Sunlight continuously strikes the earth's surface with approximately 89 PW of solar energy. This renewable energy source is capable of overcoming the energy needs of human beings.¹ Nowadays, photovoltaic (PV) cells remain the best technology to convert solar energy into electrical energy; however, they are strongly dependent on the intermittency of solar irradiance. Therefore, converting solar energy into chemical energy in the form of a fuel is a promising alternative to overcome this limitation.² The photoelectrochemical cells (PECs) comprising two processes in a single device, namely solar energy harvesting and water electrolysis, convert solar radiation and water into hydrogen and oxygen *via* light-induced electrochemical processes.^{3,4} Currently, one of the main challenges concerning the PEC cells lies in improving the solar to hydrogen conversion efficiency to make the PEC solution commercially attractive.⁵ For an efficient solar conversion, a PEC cell has to comply with several requirements. Among these, the electrolyte container should have optically transparent windows such that light can reach the photoelectrode surface, triggering the correspondent electrochemical reactions responsible for water splitting. However, during operation, the evolved gases can easily get

trapped in the cell window, especially when the cell is tilted to maximize the sunlight harvesting. The evolved bubbles reduce the light intensity that reaches the photoactive electrode and consequently decrease the overall efficiency. Recent reports suggested that simultaneously using the front- and back-illumination could increase the photoelectrode light absorption.³ However, the accumulation of the evolved gases inside the cell remains a limiting factor. The use of coated windows that facilitate the evolved gas bubbles to slip on their surface, together with the upward movement of the circulating electrolytes, should substantially improve the transparency of the PEC device windows. To date, studies that describe the use of coatings to facilitate the evolved gas bubbles to slip over the glass windows of PEC cells for solar hydrogen production have not been reported.

Titanium dioxide has been widely studied as a photocatalyst in environmental and energy-related fields.⁶ In fact, the first study on the photoelectrochemical water splitting was reported in 1972 by Fujishima–Honda, in which titanium dioxide semiconductor material was used as a photoanode.⁷ At the end of twentieth century, Fujishima also found that titanium dioxide exhibited photoinduced superhydrophilicity (PSH) state when exposed to UV light; this allowed water to completely spread on a TiO₂-coated surface, as depicted in Fig. 1.⁸

Titanium dioxide-photoinduced superhydrophilicity (PSH) is not yet completely understood and different mechanisms have been proposed in literature.⁹ Miyauchi and co-workers¹⁰ have attributed the PSH to structural changes at the surface. Photo-generated excitations (e⁻/h⁺) participate in the surface reduction

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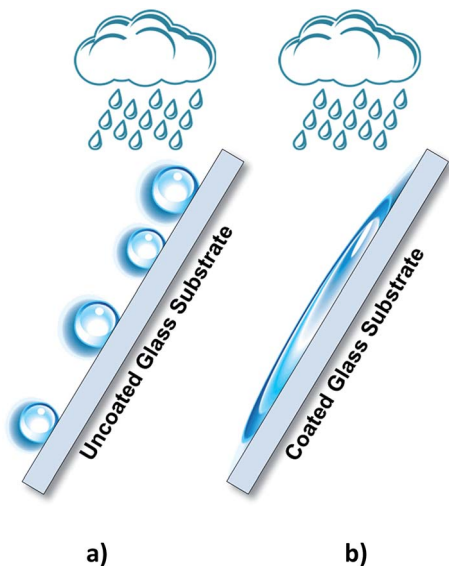
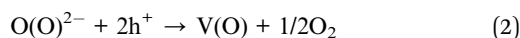
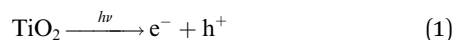


Fig. 1 Schematic representation of water droplets behaviour over (a) uncoated glass substrates and (b) TiO_2 -coated glass substrates exhibiting the photoinduced superhydrophilicity state.

and oxidation of the TiO_2 sites. Ti^{4+} sites are reduced to Ti^{3+} and oxygen vacancies are created at the two-coordinated bridging oxygen bonds as follows:¹⁰



The highly hydrophilic surface of TiO_2 can be ascribed to the Ti^{3+} sites, which are favorable to dissociative water adsorption and thereby create hydrophilic domains, with water contact angles close to zero.¹¹ Wang *et al.*¹¹ observed a gradual reversion of these domain structures, *i.e.* the weakly bound hydroxyl groups ($-\text{OH}$) reactively desorbed from the surface after some days under dark conditions.^{12,13}

Titanium dioxide is highly resistant to corrosion; moreover, it is cheap, environmentally friendly, and a widely available semiconductor.¹⁴ Different deposition techniques can be used to prepare the transparent thin films of TiO_2 : doctor blade,¹⁵ spray pyrolysis,¹⁶ chemical vapour deposition (CVD),¹⁷ sol-gel,¹⁸ sputtering,¹⁹ and spin coating.²⁰ In this study, pristine TiO_2 thin films were deposited over soda-lime glass substrates *via* spin coating to obtain a superhydrophilic, transparent and adherent coating to improve the overall efficiency of the PEC devices for solar hydrogen production.¹

2. Experimental

2.1 Preparation of the thin TiO_2 films

Soda-lime glass substrates, $10 \times 5 \text{ cm}^2$, were cleaned to remove contaminants and greasy impurities: first, the glass substrates were washed under ultrasonic conditions in an alconox/water

solution, then washed with pure ethanol, and finally treated in a UVO-cleaner for 20 min. A two-step method was used to deposit the TiO_2 films over soda-lime glass substrates. In the first step, the cleaned substrates were immersed in a 40 mM aqueous solution of titanium(IV) chloride tetrahydrofuran complex ($[\text{TiCl}_4 \cdot 2\text{THF}]$, reagent grade 97 wt%, Sigma-Aldrich) for 30 minutes at 70°C . The prepared films were then annealed at 200°C for 30 minutes using a blow dryer. In the second step, titanium dioxide paste (Dyesol Industries Pty, 18 NRT) was diluted in ethanol (reagent grade 99.5 vol%, Aga) at 1 : 4 wt% and stirred for 20 minutes at room temperature to achieve good homogenization. The prepared dispersion was then deposited on glass substrates *via* spin coating (5 mL of solution, spin speed of 2000 rpm for 20 s). Finally, the as-deposited film was heat-treated in air for 45 minutes at 465°C in a blow dryer.

2.2 Characterization techniques

The TiO_2 film thickness was determined *via* SEM (FEI Quanta 400FEG) analysis, and the transmittance spectra were obtained using a UV-vis spectrometer (UV 3600, Shimadzu) in the wavelength range from 200 to 800 nm. Surface hydrophilicity was examined *via* water contact angle measurements (OCA 20, DataPhysics) before and after 30 minutes exposure to UV light irradiation. The chemical composition of the TiO_2 film was analysed by Fourier transform infrared (FTIR) spectroscopy using Vertex 70 from Bruker equipped with an ATR cell. The films were measured in the $400\text{--}4000 \text{ cm}^{-1}$ spectral range with the resolution of 4 cm^{-1} and spectra of 64 scans were obtained.

3. Results and discussion

The replacement of the front window in a PEC device for solar hydrogen production (normally made of quartz) by a TiO_2 -coated window enhances the light harvesting of the photo-electrode and implies the development of a transparent TiO_2 thin film, crack-free and with a good adhesion to the glass substrate. Several deposition techniques were considered: spin coating, doctor blade, spray pyrolysis, and sputtering. The films deposited *via* doctor blade, spray pyrolysis, and sputtering significantly reduced the transparency of the glass window and were then abandoned.^{16,21–23} Moreover, the film deposited *via* doctor blade also showed weak adhesion to the glass substrate. Spin coating technique showed the best results in terms of both transparency and adherence. The spin coating deposition was then optimized in terms of mass ratio of the TiO_2 paste and ethanol solvent, spin time, spin velocity, and spin acceleration. A pre-treatment with $\text{TiCl}_4 \cdot 2\text{THF}$ was also performed since it was reported that a chemical bath of $\text{TiCl}_4 \cdot 2\text{THF}$ favored the bonding strength with the subsequent TiO_2 layer.²⁴ The pre-treated glass windows were then spin-coated with the prepared TiO_2 dispersion. After solvent evaporation, they were annealed at 465°C for 45 min, as described in the experimental section.



3.1 Optical and morphological properties of the applied coatings

High film transparency is a critical requirement for the final application of the developed coatings. Fig. 2 compares the transmittance of the uncoated and TiO₂-coated glass window samples for the wavelength range between 200 nm and 800 nm. In the spectral range between 350 nm and 800 nm, the transmittance of both samples was *ca.* 90%. However, an earlier drop was observed in the transmittance of the coated sample for wavelengths smaller than *ca.* 390 nm due to the presence of the anatase phase. Between 400 nm and 600 nm, the coated sample showed slightly lower transmittance; this was assigned to a larger light scattering on the coated sample due to its surface roughness and higher refractive index, $n = 2.52$, of the anatase phase, whereas the refractive index of the soda-lime glass was about $n \approx 1.52$.²⁵

Fig. 3 shows the top and cross-section SEM images of the obtained TiO₂ films. These films were homogeneous, densely packed, and crack-free with very small grains. This favorable morphology can be ascribed to the TiCl₄·2THF pre-treatment,

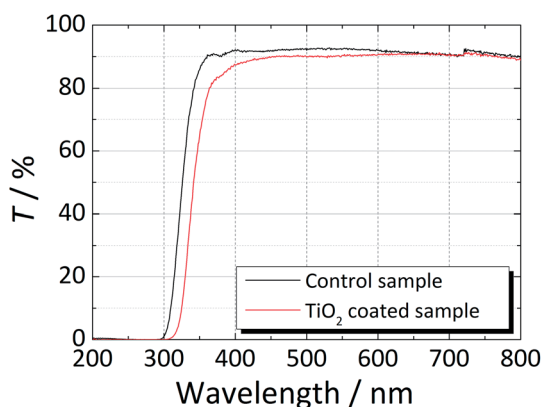


Fig. 2 Transmittance spectra of a regular soda-lime glass (control glass) and a soda-lime glass coated with TiO₂ in the wavelength range from 200 nm to 800 nm.

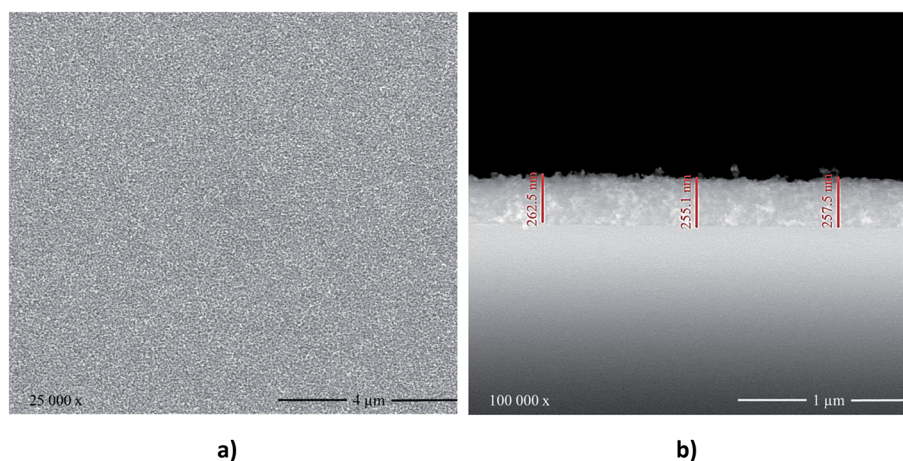


Fig. 3 (a) Top-view and (b) cross-section SEM images of the TiO₂ films deposited on soda-lime glass *via* spin coating.

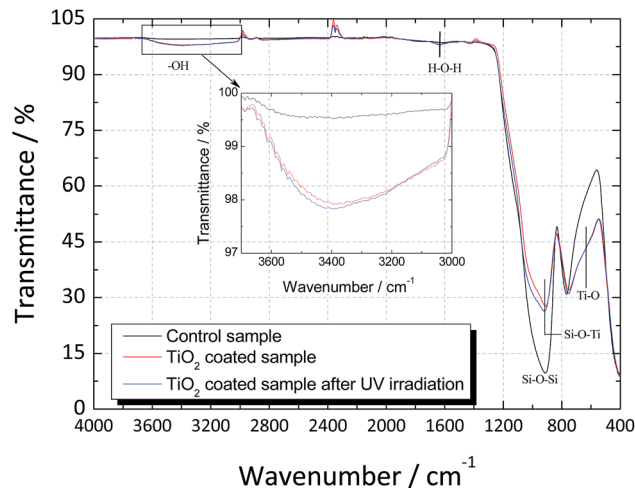


Fig. 4 FTIR Spectrum of the regular soda-lime glass and TiO₂-coated glass before and after UV light activation.

which improved the bonding of the glass substrate to the TiO₂ nanoparticles layer. The film thickness was estimated to be *ca.* 260 nm based on the cross-sectional SEM images.

FTIR spectra of the uncoated and coated glass substrates before and after the UV light activation are shown in Fig. 4. In the control glass sample, a strong band at 1000–800 cm⁻¹ associated to the symmetric stretching of pure SiO₂ (Si–O–Si bonds) was observed. When TiO₂ was deposited over the glass substrate, the intensity of the Si–O–Si bonds was found to decrease and a shift towards lower frequencies was observed. This shift can be associated to the presence of Si–O–Ti bonds, confirming the good adhesion between the glass substrate and the TiO₂ film.

In the TiO₂-coated sample, a broad transmittance peak was observed at 3400 cm⁻¹ that was assigned to the stretching modes of O–H bond due to the surface absorbed water.²⁶ The peak at 1625 cm⁻¹ corresponded to the bending vibration of H–O–H bond was related to the chemisorbed water.²⁷ After UV light activation, a slight increase in both peaks was observed,



confirming that TiO_2 had higher capacity to adsorb water from moist environments when irradiated with UV light.²⁶

Finally, the band observed at 550 cm^{-1} in the spectrum of the TiO_2 -coated sample can be attributed to the vibrations of the Ti–O bonds, and the appearance of a shoulder in this band confirms that pure TiO_2 has been deposited.

3.2 Photoinduced superhydrophilicity of the TiO_2 coating

The wettability transition of the TiO_2 coating was studied by measuring the water contact angle (WCA) before and after UV illumination (365 nm , 2 W m^{-2}). Fig. 5 shows the plots of the WCA for uncoated (control) and TiO_2 -coated samples before and after 30 min of UV irradiation. The non-irradiated coated surface presented a water droplet contact angle of *ca.* 3° , which was considerably lower than that of the uncoated sample (*ca.* 40°). After UV illumination for 30 minutes, the coated sample exhibited a WCA of *ca.* 0° , thereby indicating that the photoinduced superhydrophilicity state was achieved.²⁸

As explained earlier, hydrophilicity is related to the density of the hydroxyl groups present in the surface of the TiO_2 film. They are able to combine with water molecules to form hydrogen

bonds, thereby promoting the surface wettability.²⁸ Accordingly, higher surface areas lead to a more hydrophilic film. In fact, the SEM top-view image, as shown in Fig. 3a, indicates a porous coating made of small TiO_2 particles, which promotes natural impregnation of atmospheric water; the latter improved the surface wettability, and consequently, lower WCA values were obtained.²⁹

3.3 Experimental setup to simulate H_2 and O_2 evolution in a PEC cell

The uncoated and TiO_2 -coated glass windows were tested in the experimental setup depicted in Fig. 6. The assembled setup comprised a quartz vessel filled with 1 M NaOH aqueous solution, and two platinum meshes (Alfa Aesar, Germany) were used as a counter- and working-electrode connected to a DC power supply to promote the electrolysis of water (*ca.* 10 mA cm^{-2} of current density). A Plasma-I AS1300 solar simulator (Plasma International, Germany) equipped with a standard sulphur lamp was used as a light source, and a cSi-PV cell with an active area of 25 cm^2 (ETM 750 – 0.5 V, Everstep, China) was placed in the opposite side and connected to a potentiostat workstation (Metrohm Autolab, Netherlands). Each glass window was then immersed in the electrolyte between the light source and the cSi-PV cell, as displayed in Fig. 6. The measurement of the photocurrent produced by the cSi-PV cell was used to evaluate the overall transparency of the glass windows with the evolving bubble curtain. One of the platinum meshes was adequately positioned for producing gas bubbles towards the window surface, as depicted in Fig. 6b. Depending on the polarity applied to the platinum mesh, oxygen (positive) or hydrogen (negative) was formed.

The photocurrent produced by the cSi-PV cell was measured in two configurations: vertical and tilted, as shown in Fig. 7. The vertical configuration, 90° (Fig. 7a), was also studied since this is the common configuration used during lab characterizations. On the other hand, the tilted configuration, 45° (Fig. 7b), allowed the simulation of a PEC cell operating under real outdoor conditions for maximizing the amount of light reaching the photoactive material. The cSi-PV cell current density was

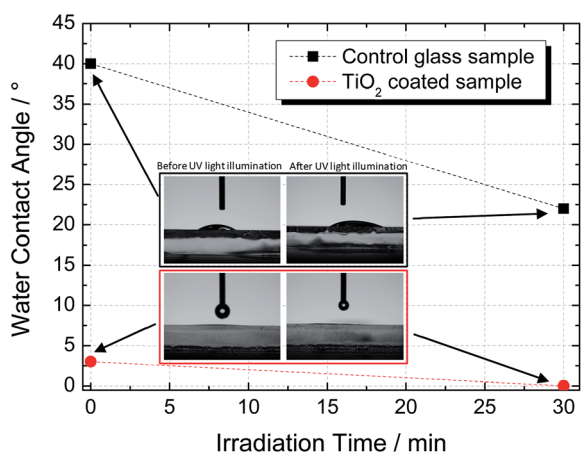


Fig. 5 Wetting properties of the coatings.

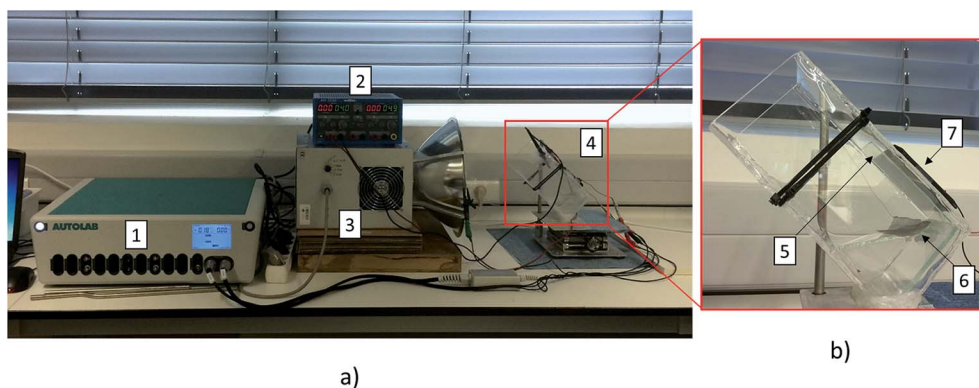


Fig. 6 (a) Experimental setup to assess the role of the TiO_2 -coated window to reduce the shading effect of the gas bubbles evolution: (1) Autolab/PGSTAT302N workstation; (2) DC power supply; (3) solar simulator; (4) quartz vessel. (b) Detailed image of the tilted quartz vessel: (5) glass window sample; (6) platinum mesh, and (7) photovoltaic (cSi-PV) cell.



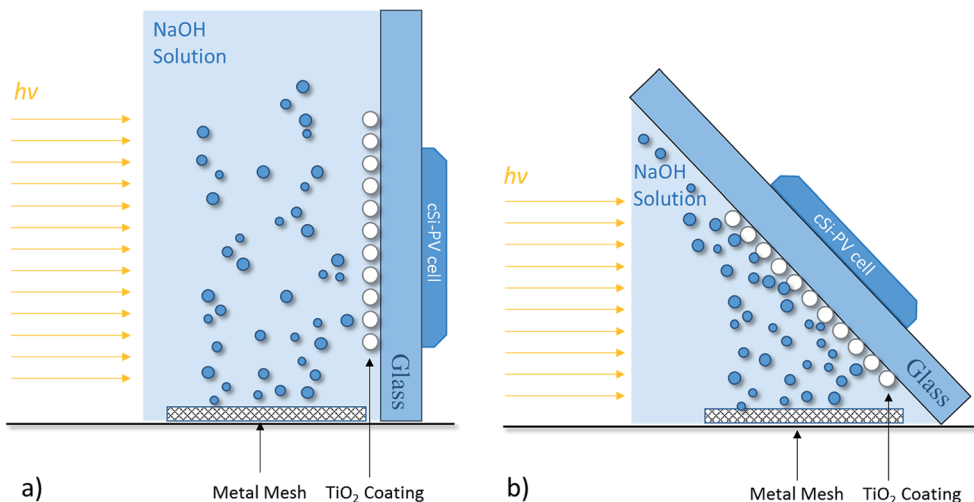


Fig. 7 Schematic representation of different configurations for assessing the photocurrent density under (a) vertical position, 90° , and (b) tilted position, 45° .

measured in the following cases: (i) no gas evolution (blank measurement); (ii) when hydrogen bubbles strike the glass window; and (iii) when oxygen gas reaches the glass window. In the blank experiment (with no gas evolution), the photocurrent signals from the cSi-PV cell with and without coating were approximately the same.

Fig. 8 shows the photocurrent signal from the cSi-PV cell for the vertical position at 90° (J_{90°) normalized by the photocurrent signal obtained for the blank determination, ($J_{\text{blank}@90^\circ}$). No difference was observed when coated or uncoated glass windows were used since the gas bubbles (H_2/O_2) followed a natural vertical upward movement, not directly hitting on the glass surface (see Fig. 7a). Moreover, when O_2 was evolving, the photocurrent signal read by the cSi-PV cell was lower than that when H_2 was produced. This can be related to the larger size of the oxygen bubbles. Moreover, in both case-scenarios, the presence of bubbles affected the transmittance within the reactor.

A different response was obtained when the glass windows were positioned at 45° , as shown in Fig. 9. Again, a blank measurement, without gas evolution ($J_{\text{blank}@45^\circ}$), was performed, and the obtained values were used to normalize the photocurrent density obtained when H_2 or O_2 was being produced (J_{45°). In the 45° tilted configuration, the photocurrent signal was higher for the coated glass than that for the uncoated glass window, both for evolution of H_2 and O_2 as shown in Fig. 9a and b, with ca. 9% and 10%, respectively. The overall improvement of the TiO_2 -coated glass was assigned to the thin homogenous water film formed on the hydrophilic surface, which prevented the adhesion of the evolved gas bubbles. On the other hand, the evolved gas bubbles tend to slow-down over the untreated glass surface. The results obtained with the TiO_2 -coated glass windows showed the effectiveness of this layer in reducing the drag against the natural upward movement of the evolved gases nearby the window. Moreover, it is expected that

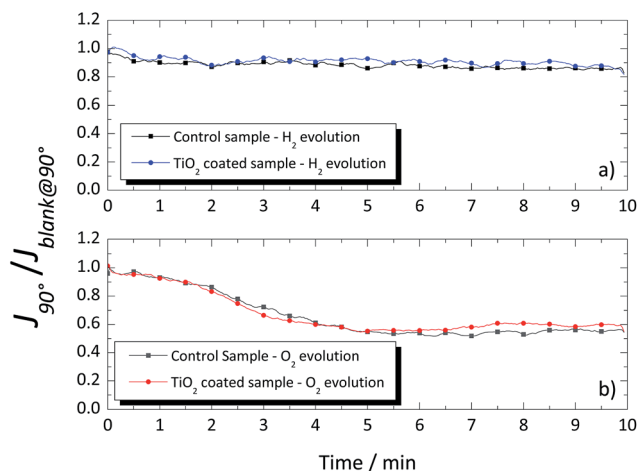


Fig. 8 Normalized photocurrent signal of the cSi-PV cell vs. time for the coated and uncoated glass windows when placed vertical for (a) hydrogen and (b) oxygen evolutions.

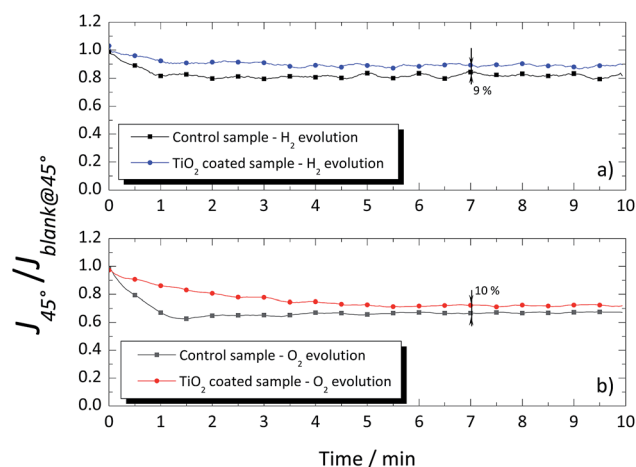


Fig. 9 Normalized photocurrent signal of the cSi-PV cell vs. time for the coated and uncoated glass windows when placed at 45° for (a) hydrogen and (b) oxygen evolutions.



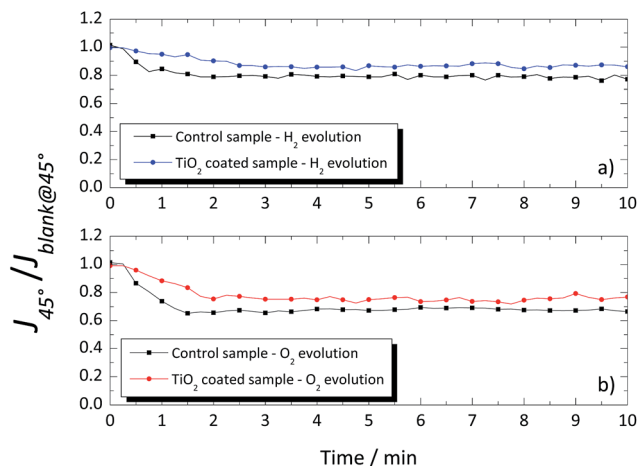


Fig. 10 Normalized photocurrent signal of the cSi-PV cell vs. time for the coated and uncoated glass windows when at 45°, recorded during 10 min after 10 h of aging for (a) hydrogen and (b) oxygen evolutions.

in larger cells, the differences between the coated and uncoated windows would be greater due to the larger amount of the evolving bubbles.

In the PEC cells used for solar hydrogen production, the use of the developed coated window can improve their overall efficiency, especially when there is no upward circulation of the electrolyte. It can also decrease the needed electrolyte flow rate when considered, saving the pump energy. Additionally, the use of a superhydrophilic, photoactive layer may also be of interest for photobioreactors where biofilm formation can be delayed or even avoided.^{30,31}

3.3.1 Stability tests. An experimental setup was assembled to assess the performance stability of the TiO₂-coated window under operating conditions, similar to those used in a PEC cell for water splitting: *i.e.* when gas bubbles were continuously striking the window surface immersed in an alkaline electrolyte. Both coated and uncoated glass windows were then left in contact with the electrolyte for 10 hours at 45° with H₂ or O₂ forced to strike the window surface. Fig. 10 shows the normalized photocurrent obtained for the last 10 min operation. On comparing Fig. 9 and 10, it was observed that after 10 hours of continuous operation, the developed TiO₂ coating maintained its performance when O₂ and H₂ were produced. Additionally, the stability test shows that the coated soda-lime glass is resistant to 10 h of continuous operation under 1000 W m⁻² in 1 M NaOH. It is known that bare soda-lime glass starts to corrode when exposed to a strong alkaline media. Thus, the TiO₂ coating can delay or prevent this corrosion effect.

4. Conclusion

An optically transparent, superhydrophilic, and stable TiO₂ coating was developed to improve the overall efficiency of tilted PEC cells for solar H₂ production. The thin-TiO₂ film (*ca.* 260 nm) was deposited *via* spin coating on soda-lime glass windows. A homogeneous, crack-free, and strongly bonded coating was obtained. The superhydrophilic state of the coating was

assessed from the water contact angle. The optimized TiO₂ film presented a water contact angle of *ca.* 0° when irradiated with UV light.

An experimental test bench was assembled to assess the use of TiO₂-coated glass windows in PEC cells for water splitting. As expected, the accumulation of evolved gas bubbles at a tilted window surface reduced the light reaching the photoelectrode. When the uncoated glass window was replaced by a TiO₂-coated glass window in a 45° tilted configuration, the relative photocurrent signal obtained by the cSi-PV cell increased *ca.* 9% and 10% for the oxygen and hydrogen evolutions, respectively. Moreover, the performance of the coated glass window was proven to be stable for more than 10 h. The obtained results were relevant for the envisioned use of PEC panels for solar hydrogen production.

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References

- 1 R. V. D. Krol, Y. Liang and J. Schoonman, Solar hydrogen production with nanostructured metal oxides, *J. Mater. Chem.*, 2008, **18**(20), 2311–2320.
- 2 T. Lopes, L. Andrade and A. Mendes, *Photoelectrochemical cells for hydrogen production from solar energy in Solar Energy Sciences and Engineering Applications*, ed. N. E. A. Akbarzadeh, CRC Press, 2013.
- 3 T. Lopes, *et al.*, An innovative photoelectrochemical lab device for solar water splitting, *Sol. Energy Mater. Sol. Cells*, 2014, **128**, 399–410.
- 4 F. Trieb, *Concentrating solar power for the mediterranean region*, German Aerospace Center (DLR), Germany, 2004.
- 5 L. J. Minggu, W. R. W. Daud and M. B. Kassim, An overview of photocells and photoreactors for photoelectrochemical water splitting, *Int. J. Hydrogen Energy*, 2010, **35**(11), 5233–5244.



- 6 K. Nakata and A. Fujishima, TiO₂ photocatalysis: design and applications, *J. Photochem. Photobiol., C*, 2012, **13**(3), 169–189.
- 7 A. Fujishima and K. Honda, Electrochemical photolysis of water at a Semiconductor Electrode, *Nature*, 1972, **238**(5358), 37–38.
- 8 R. Wang, K. Hashimoto and A. Fujishima, Light-induced amphiphilic surfaces, *Nature*, 1997, **388**, 431–432.
- 9 A. V. Emeline, *et al.*, Factors affecting UV-induced superhydrophilic conversion of a TiO₂ surface, *J. Phys. Chem. C*, 2013, **117**(23), 12086–12092.
- 10 M. Miyauchi, *et al.*, Photoinduced surface reactions on TiO₂ and SrTiO₃ films: photocatalytic oxidation and photoinduced hydrophilicity, *Chem. Mater.*, 2000, **12**(1), 3–5.
- 11 R. Wang, *et al.*, Photogeneration of highly amphiphilic TiO₂ surfaces, *Adv. Mater.*, 1998, **10**(2), 135–138.
- 12 A. Fujishima, T. N. Rao and D. A. Tryk, Titanium dioxide photocatalysis, *J. Photochem. Photobiol., C*, 2000, **1**, 1–21.
- 13 O. Carp, C. L. Huisman and A. Reller, Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.*, 2004, **32**(1), 33–177.
- 14 R. Dholam, *et al.*, Hydrogen production by photocatalytic water-splitting using Cr-or Fe-doped TiO₂ composite thin films photocatalyst, *Int. J. Hydrogen Energy*, 2009, **34**(13), 5337–5346.
- 15 J. Akilavasan, M. Al-Jassim and J. Bandara, Designing nanostructured one-dimensional TiO₂ nanotube and TiO₂ nanoparticle multilayer composite film as photoanode in dye-sensitized solar cells to increase the charge collection efficiency, *J. Nanophotonics*, 2015, **9**(1), 093091.
- 16 A. Nakaruk, D. Ragazzon and C. C. Sorrell, Anatase thin films by ultrasonic spray pyrolysis, *J. Anal. Appl. Pyrolysis*, 2010, **88**(1), 98–101.
- 17 H.-Y. Lee and H.-G. Kim, The role of gas-phase nucleation in the preparation of TiO₂ films by chemical vapor deposition, *Thin Solid Films*, 1993, **229**(2), 187–191.
- 18 M. A. M. L. de Jesus, *et al.*, Superhydrophilic self-cleaning surfaces based on TiO₂ and TiO₂/SiO₂ composite films for photovoltaic module cover glass, *Appl. Adhes. Sci.*, 2015, **3**(1), 5.
- 19 K.-S. Lee and S. H. Lee, Influence of SiO₂ interlayer on the hydrophilicity of TiO₂/SiO₂/glass produced by RF-magnetron sputtering, *Mater. Lett.*, 2007, **61**(16), 3516–3518.
- 20 A. Mills, *et al.*, Thick titanium dioxide films for semiconductor photocatalysis, *J. Photochem. Photobiol., A*, 2003, **160**, 185–194.
- 21 B. A. Nejand, S. Sanjabi and V. Ahmadi, The effect of sputtering gas pressure on structure and photocatalytic properties of nanostructured titanium oxide self-cleaning thin film, *Vacuum*, 2010, **85**(3), 400–405.
- 22 Y. Wang, *et al.*, Development of high dispersed TiO₂ paste for transparent screen-printable self-cleaning coatings on glass, *J. Nanopart. Res.*, 2013, **15**(1), 1384.
- 23 A. I. Martinez, D. R. Acosta and A. A. Lopez, Effect of deposition methods on the properties of photocatalytic TiO₂ thin films prepared by spray pyrolysis and magnetron sputtering, *J. Phys.: Condens. Matter*, 2004, **16**(22), S2335.
- 24 S. Ito, *et al.*, Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%, *Thin Solid Films*, 2008, **516**(14), 4613–4619.
- 25 D.-J. Won, *et al.*, Effects of thermally induced anatase-to-rutile phase transition in MOCVD-grown TiO₂ films on structural and optical properties, *Appl. Phys. A: Mater. Sci. Process.*, 2001, **73**(5), 595–600.
- 26 K. Hashimoto, H. Irie and A. Fujishima, TiO₂ photocatalysis: a historical overview and future prospects, *Jpn. J. Appl. Phys.*, 2005, **44**(12R), 8269.
- 27 J. M. H. Enriquez, *et al.*, Synthesis of Solid Acid Catalysts Based on TiO₂-SO₄²⁻ and Pt/TiO₂-SO₄²⁻ Applied in *n*-Hexane Isomerization, *Open J. Met.*, 2013, **3**, 34–44.
- 28 C. Euvananont, *et al.*, TiO₂ optical coating layers for self-cleaning applications, *Ceram. Int.*, 2008, **34**(4), 1067–1071.
- 29 M. Houmard, *et al.*, Morphology and natural wettability properties of sol-gel derived TiO₂-SiO₂ composite thin films, *Appl. Surf. Sci.*, 2007, **254**(5), 1405–1414.
- 30 J. Wang, J. Liu and T. Liu, The difference in effective light penetration may explain the superiority in photosynthetic efficiency of attached cultivation over the conventional open pond for microalgae, *Biotechnol. Biofuels*, 2015, **8**, 49.
- 31 O. Zerriouh, *et al.*, Biofouling in photobioreactors for marine microalgae, *Crit. Rev. Biotechnol.*, 2017, 1–18.

