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ARTICLE TYPE

Highly Efficient Photoanodes for Dye Solar Cells With a Hierarchical Meso-ordered Structure

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An engineered bi-layered photoelectrode for dye solar cells has been developed which profitably employs two synergistic meso-ordered components, namely a thin meso-ordered TiO₂ film and a main microparticles-based photoelectrode. The former has been deposited as an interfacial layer at the FTO-coated substrate and suppresses the back-transport reaction by blocking direct contact between the electrolyte and conductive oxide. The latter is made of hierarchical micro- and nano-structured building blocks prepared by template synthesis which permits efficient light scattering without sacrificing the internal surface area. The optimization of light harvesting and charge recombination dynamics allowed to achieve an as high energy conversion efficiency as 9.7%.

Introduction

Mesoporous materials with crystalline framework, high surface area and tunable pore size have received extensive research attention because of their potential applications in many fields such as photocatalysis, electrochromism, energy storage and conversion.¹

For a variety of above-mentioned practical applications, the preparation of desired morphologies is important as well as the control in crystallinity and composition.

The synthesis of mesoporous oxides with high surface area and ordered porous structure is commonly carried out by sol-gel procedure using triblock copolymers as structure directing agents.²⁻⁴ These synthetic routes offer many advantages, as low temperature, high scalability, low cost equipments and have been recently used to prepare ordered mesoporous TiO₂ thin films with hexagonal, cubic and lamellar mesostructures.^{5,6} The latter are promising candidates as photoelectrodes for dye-sensitized solar cells (DSSCs) due to their huge surface area, few grain boundaries and uniform pore structure with excellent connectivity of mesopores.

In fact, it is well-accepted that a superior photoanode for DSSCs requires high surface area for a large amount of dye molecule loading and an optimal morphological engineering for light harvesting and fast electron transport.⁷⁻¹⁰

The application of highly ordered mesoporous TiO₂ in DSSC was reported for the first time by Grätzel and co-workers:¹¹ 1 μm thick nanochannels-based TiO₂ photoanode with a pore size of about 6 nm was fabricated using an amphiphilic triblock copolymer of ethylene oxide and propylene oxide as a template.

The obtained power conversion efficiency was up to 4.0%, which

was about 50% higher than the outcome achieved using standard mesoporous TiO₂ photoanodes (2.7%) with comparable thickness.¹¹ Nonetheless the implementation of mesostructured TiO₂ films as self-consistent photoelectrodes for DSSCs is impracticable since their typical thickness cannot be extended above a few hundred nanometers; consequently, further improvement in cell performance is limited by the thinness of the mesoporous TiO₂ film, resulting in less dye up-take. So, in order to obtain thicker ordered films, dip-coating, self-assembly and precalcination processes had to be done many times;¹² however, the repeated procedures result in an opaque film with degraded mesostructure. As an example Arakawa et al. prepared a 20 μm-thick TiO₂ photoanode through the deposition of mesoporous TiO₂ powders made with a Pluronic P123 template,¹³ but a short-range ordered-framework structure was reported in this case.

Furthermore, together with the improvement in materials quality, the interfacial engineering may be studied in order to decrease the recombination rate of photogenerated carriers in dye-sensitized photoanode, that is still one of the most critical factors limiting the solar-to-electricity conversion capabilities of these devices.¹⁴⁻¹⁵

There are basically two routes for the loss of photoinjected electrons by back reaction to redox ions in the electrolyte: via the dye-sensitized nanocrystalline TiO₂ and via the F:SnO₂ substrate (FTO);¹⁶ in particular, when the nanocrystalline TiO₂ does not completely cover the SnO₂ substrate there are numerous spaces between the colloidal particles where the transparent conductive oxide (TCO) comes into direct contact with the electrolyte solution originating electron transfer to redox ions which strongly affects the performances of the cell.

Starting from these remarks, our strategy to improve the

Figure 1. SEM (a and b) and TEM (c) images at different magnification of mesoporous powder; SEM (d and e) images at different magnification of ordered thin buffer layer; (f) representative sketch highlighting the nano-/microstructure of the bifunctional photoanode.

performance of DSSCs aims to exploit the versatility of novel meso-ordered TiO_2 building-blocks in both the compact under layer (henceforth referred as 'buffer layer' or BL) and the mesoporous main layer, thus introducing a novel bifunctional photoanode.

At the bottom level, an highly ordered thin TiO_2 film, was applied as an interfacial layer between the nanocrystalline main photoanode and the FTO electrode. It suppressed the back-transport reaction by blocking direct contact between the electrolyte and TCO and provided excellent adhesion to the FTO of the upper TiO_2 layer. The latter consists of hierarchical structures prepared by template synthesis and composed of nanocrystallinities that cluster in well-organized larger secondary particles, thereby functioning as light scatterers without sacrificing the internal surface area which is indispensable for a good dye-uptake.

The introduction of meso-ordered TiO_2 BL has been demonstrated to be responsible of a tremendous increment of the photovoltaic performances; an as high PCE as 9.7% was recorded under the illumination of simulated AM 1.5 solar light (100 mW/cm^2). A scrupulous electrochemical analysis has been also carried out to investigate the relationship between the photovoltaic performances and the charge transfer and recombination processes within the meso-ordered structures and at the interface with TCO.

Results and discussion

Meso-ordered titania powder was prepared using the P123 triblock copolymer as soft template.¹⁷ Titanium(IV) ethoxide, the TiO_2 precursor, was added to P123 previously dissolved in 1-butanol and stirred for 3 hours; the use of 1-butanol as solvent, instead of ethanol, allows to improve the thermal stability and to produce well-ordered mesostructured titania.¹⁷ Samples were then stored at 25°C for 2 days and finally sintered at 350°C for 2 hours; concomitantly the mesoporous powders were obtained by aging of the solution at 25°C for 5 days and sintering the resulting suspension at 350°C for 4 hours.

The morphology of these nanomaterials was examined through an FE-SEM microscope with high spatial resolution. A preliminary study of mesoporous titania powder (Fig. 1a) reveals the presence of grains with heterogeneous size up to one micron (0.5 - 1 μm). However, images at high magnifications allowed to observe that the surface of these grains is mainly composed of particles with a main diameter of about 20 nm (Fig. 1b, c). In addition the SEM images of the buffer layer in Fig. 1d and 1e show the presence of domains with an highly ordered structure. Mesopores with a cavity diameter of about 10 nm were aligned periodically, suggesting the formation of an uniformly organized structure.

Evidence of the presence of an ordered mesoporous structure have been obtained by using small angle X-ray diffraction measurements; the diffraction peaks at low angles, displayed in Fig. 2a, suggest the presence of mesoporous structures with a long range order.¹⁷ The X-ray diffraction patterns of titania powder, reported in Fig. 2b, reveals that all the peaks can be attributed to anatase titania. The main crystallite diameter was 15.4 nm and was calculated from the line broadening of the most intense reflection using the Scherrer equation.¹⁸ Insights on the structure of titania were also obtained by means of Raman spectroscopy, which was used to investigate the presence of crystalline phases. The Raman spectra of mesoporous titania thin film and powder in fig. S1 show the typical modes of anatase at 144, 197, 398, 514, and 640 cm^{-1} , which are assigned to Eg, B1g, A1g or B2g, and Eg modes, respectively, according to the literature¹⁹. We observed the formation of anatase for titania thin films and powder at the relative low calcination temperature of 350 °C; this is very attractive in order to optimize the thermal balance for the preparation of the photoanode.

The surface area and the pore specific volume of the powder were determined by the BET method and resulted 165 m^2/g and 0.23 cm^3/g , respectively. In particular, the surface area of the mesoporous powder is 3.3 times that of the value, 50 m^2/g , reported for the most popular TiO_2 reference (Degussa P25).

Figure 2. a) small angle X-ray diffraction patterns of mesoporous titania thin films (black line) and powder (red line); b) X-ray diffraction pattern of mesoporous titania powder; the pattern of pure anatase titania is shown as reference.

Mesoporous ordered TiO₂ clearly benefits from the high surface-to-volume ratio of the fine nanostructure which appears suitable to upload abundant amount of dye molecules.

The dye-loading capabilities of the photoelectrodes were assessed by spectrophotometric determination of the corresponding amounts of dye molecules desorbed in an alkaline medium (see Table 1). 18 μm thick films assembled from ordered mesoporous TiO₂ were found to accommodate a number of N719 molecules per projected unit area as high as 3.07*10⁻⁷ mol/cm² which was appreciably larger than the dye amount loaded on the corresponding photoanode made from TiO₂ P25 Degussa (1.88*10⁻⁷ mol/cm²). This result was in good agreement with the BET measurement and indicated that the ordered mesoporous TiO₂, in spite of their noticeable bulkiness, present more availability of sites for N719 anchoring with respect to P25, thus leading to superior light harvesting properties.

The performances of the meso-ordered TiO₂-based electrodes with and without BL were examined under standard illumination test conditions (AM1.5G) and compared with benchmark devices based on commercial TiO₂ P25 Degussa. Figure 3a displays the relevant photocurrent density-voltage (IV) curves of DSCs while the characteristic parameters such as open-circuit voltage (V_{oc}), short-circuit photocurrent density (J_{sc}), fill factor (FF), and efficiency (η), extracted from the analysis of IV curves are summarized in Table 1.

The devices based on a hierarchical double-scale roughness noticeably exhibited superior performances with respect to the P25-based reference: a 18.1 μm thick electrodes generated a short-circuit current density of 14.88 mA/cm² and an energy conversion efficiency of 7.49%, whereas film made from P25 nanocrystals showed a current density of 10.02 mA/cm² and a conversion efficiency of 6.17%, this being mainly ascribable to the larger amount of N719 molecules adsorbed on the meso-ordered electrode. Furthermore an important contribution to the photocurrent density is related to the light recycling properties of the photoanode. Figure 3b shows incident photon to current efficiency (IPCE) spectra of the devices; the DSSCs based on ordered mesoporous nanomaterials showed the highest IPCE values over the whole spectral range. In particular, the quantum

Table 1. Photovoltaic parameters of DSCs based on ordered mesoporous photoanodes with and without the buffer layer measured under 1 sun illumination (AM 1.5, 100 mW cm⁻²).

DEVICE	main layer thickness	Buffer layer	η %	V _{oc} [V]	J _{sc} [mA/cm ²]	FF	Dye loading capability [mol/cm ²]
ordered mesoporous TiO ₂	18.1 μm	no	7.49	0.73	14.88	0.69	3.07*10 ⁻⁷
P25	18.5 μm	no	6.17	0.81	10.02	0.76	1.88*10 ⁻⁷
ordered mesoporous TiO ₂ BL1	18.0 μm	300 nm	8.28	0.75	15.78	0.70	3.18*10 ⁻⁷
ordered mesoporous TiO ₂ BL2	18.2 μm	450 nm	9.67	0.78	17.22	0.72	3.25*10 ⁻⁷
ordered mesoporous TiO ₂ BL3	17.8 μm	770 nm	9.27	0.76	16.94	0.72	3.30*10 ⁻⁷
BL	0 μm	800 nm	0.69	0.79	1.22	0.72	0.28*10 ⁻⁷

Figure 3. Figure 3. a) IV curves of DSCs based on ordered mesoporous photoanodes with and without the buffer layer and b) IPCE spectra of ordered mesoporous- and P25-based DSSC

efficiency in the longer wavelength region (600–700 nm) of the films containing large aggregates of nanocrystallinities is much more prominent than that of the P25 film as a consequence of the stronger light scattering effect of our materials, which led to an improvement of the light harvesting in this region.

Nevertheless, in order to obtain higher conversion efficiencies, interfacial recombination of the photogenerated electrons needs to be prevented or greatly reduced. The so far referred photoelectrode is in fact formed by colloidal TiO₂ particles larger than 500 nm which don't uniformly cover the FTO surface and don't guarantee a good adhesion. Direct contact of FTO and electrolyte induces, as well known,²⁰ preferential channels for back reaction, thereby detrimentally affecting the open circuit voltage of the cell.

Keeping this in mind, we implemented an engineered bifunctional photoanode by introducing a thin buffer layer, which was properly designed to improve the interfacial charge transfer resistance at the electrolyte/FTO interface.

We thus realized a thin meso-ordered buffer layer by spin coating the Titanium(IV) ethoxide/P123 solution at 2400 rpm for 20" prior to the deposition of the main TiO₂ crystallites-based paste. A remarkable increment of the PV performances was so detected: J_{sc} was increased from 14.88 mA/cm² of the bare photoelectrode to 15.78, 17.22 and 16.94 mA/cm² achieved with the introduction of 300 nm, 450 nm and 770 nm thick mesoporous buffer layers, respectively; the photocurrent density raised up as the BL grew up to 450 nm, but no appreciable enhancement resulted at higher thickness. V_{oc} also increased, as expected, from 0.73 V of the basic device to 0.75, 0.78 and 0.76 for 300 nm, 450 nm and 770

Figure 4. Dependence of dark current density on the blocking layers thickness.

nm thick underlayers, respectively, due to the attenuated back reactions. As a result, the overall efficiency was improved by ~30.0% from 7.49% to 9.67%, due to the ordered TiO₂ thin underlayer.

Such improvement is scarcely correlated to the increment of the photoanode thickness, that is just in the order of few hundreds of nanometers. As reported in Table I in fact a single 800nm-thick BL, thanks to the high surface area of the meso-ordered network, is able to produce a photocurrent density of 1.22 mA/cm². This is not enough to explain the overall 30% enhancement of the efficiency brought by the implementation of the buffer layer.

The question therefore remains regarding the role of the interfacial ordered TiO₂ in increasing the photovoltaic conversion efficiency. Several factors might be involved in the observed increase of J_{SC} and V_{OC}.

As first, we found that the ordered buffer layer demonstrated excellent adhesion to FTO glass: stripping off the TiO₂ thin film without damaging the FTO layer was revealed to be almost impossible. Beside this, the upper mesoporous TiO₂ exhibited better adhesion to the underlayer than to the TCO. Thus it is deduced that the contact between the FTO layer and TiO₂ was greatly improved by introducing thin interfacial TiO₂. The tight contact between these two layers suggests that the charge transfer resistance at this interface can be considerably reduced.

In the second instance, the back-transport of electrons in the interface of FTO electrode should be suppressed by introducing the buffer layer, since it blocks the direct encounter between the electrolyte and FTO effectively preventing the electron transfer back from the conductive oxide to the I₃⁻ ions, and thus increasing both J_{SC} and V_{OC}.²¹⁻²²

Fig. 4 compares the dark current characteristics of nanocrystalline TiO₂ electrodes with and without blocking layer. It's possible to observe that the onset of the dark currents moves from around 0.3 V in the case of no blocking layer to around 0.55 V upon the insertion of the meso-ordered layer. A decrease of the dark current was revealed in all the BL-based PEs with a maximum reduction for a 450 nm-thick film. This phenomenon is correlated to the more efficient blocking of the leakage current at the FTO substrate which lead to an increase of the shunt resistance, as detectable from the slope of the IV curves near the short-circuit current point. On the other hand, a slight increment of the dark current was revealed for the 770 nm-thick BL with respect to 450

Figure 5. Nyquist plots of the electrochemical impedance spectra for the cells assembled with and without the BLs under 1 sun illumination at an applied voltage of 0.75 V.

nm thin film, along with a decrement in the open circuit voltage, reasonably associated to a less favourable balancing between charge collection and recombination in thicker buffer films.

A further elucidative insight into the beneficial features of these electrodes was provided by an Electrochemical Impedance Spectroscopy (EIS) analysis. Figure 5 shows the Nyquist plots of the EIS for the cells assembled with and without the BLs under 1 sun illumination at an applied voltage of 0.75 V (close to V_{OC}). Nyquist plots have been fitted by means of the well-established equivalent-circuit model proposed by Wang et al.,²³ whereby constant-phase elements, instead of pure capacitors, are used to account for the uneven and porous structure of the photoelectrodes.

The arcs observable in the Nyquist diagram reveal the existence of defined electrochemical interfaces with different time constants.²⁴ The highest-frequency arc is due to the coupling between the capacities of the counter electrode and the TCO/electrolyte interface at the bottom of the TiO₂ film and the resistance given by the sum of the counter electrode/electrolyte and TCO/TiO₂ interface. The largest medium-frequency arc is related to the recombination resistance (R_{rec}) associated to electron recombination at the interface between TiO₂ and the electrolyte combined with the chemical capacitance (C_μ) of electrons in TiO₂. A minor lowest-frequency arc (in the rightmost region of the diagram) is attributed to the impedance of diffusion of redox species in the electrolyte. Finally, the displacement of the arc is attributed to the contribution of the total series resistance (R_{series}) of wiring, FTO, BLs (R_S), resistance of the electrolyte and the resistance within the TiO₂ film.²⁵

As observable in figure 5, the displacement in R_{series} due to R_S is proportional to the thickness of the BL, as well as to the enlargement of the first arc. This issue didn't turn into a lowering of the fill factor as it should be expectable.²⁶ Such anomalous behaviour is related to the suppression of the back reaction with I₃⁻ ions species at the interface with FTO, which lead to a beneficial rise of the charge recombination resistance (R_{ct}) as has been highlighted in Figure 6a.

Figure 6b shows the measured capacitance C_{meas} versus corrected potential. At intermediate and high potentials, we can observe the characteristic exponential growth of C_μ, indicating the charging of the semiconductor nanocrystalline matrix. A considerable increment of the charge accumulated where the devices are equipped with the 450 nm and 770 nm thick buffer layer is

Figure 6. a) recombination resistance and b) electrode capacitance obtained by electrochemical impedance spectroscopy for the DSSCs assembled with and without the BLs under 1 sun illumination; the capacitance and recombination resistance are plotted versus potential drop at the sensitized electrode.⁸

detectable at relatively low bias voltages which is unambiguously attributed to the relevant contribution of the Helmholtz capacitance as a consequence the larger surface area of the ordered mesoporous thin film.

- 5 Finally, from the correlation of the electrochemical and photovoltaic parameters it can be assumed that the optimum thickness of the here referred engineered meso-ordered blocking layer is around 450 nm while 770 nm is probably a too much high thickness and the detrimental effect associated to higher series resistance prevails on the benefits proven from the reduction of the charge recombination.

Conclusions

- In conclusion, we have proposed a novel bifunctional photoanode with a double-scale morphology which comprises a meso-ordered thin TiO_2 buffer layer and a main layer consisting of well-organized clusters of nanocrystallinities. A such engineered architecture enabled control over the light harvesting and the recombination dynamics and allowed to achieve an energy conversion efficiency of 9.7% which is a direct result of its excellent and synergistic peculiarities, namely large surface area, uniform distribution of pores size, effective light-scattering and negligible recombination at the FTO/ TiO_2 interface.

Experimental section

Synthesis of mesoporous TiO_2

- 25 Mesoporous titania was prepared according to a procedure reported in the literature.¹⁷ A triblock copolymer (P123) was used as template in order to obtain a porous structure with a tailored geometry. In a typical synthesis, 1.4 ml of concentrated HCl were slowly added to 2.1 g of titanium(IV) ethoxide at room temperature. In another flask, 0.65 g of triblock copolymer (P123) were dissolved in 6 g of 1-butanol and subsequently added to the titanium solution. The system was kept under stirring at room temperature for 3 hours. The as-prepared solution of titania precursor was aged at 25°C for 5 days and the obtained sample was then calcined at 350°C for 4 hours using a ramp rate of 1°C/min to remove the template and the residual organic precursors.

TiO_2 paste preparation and DSSC fabrication.

- 40 Dried powder was dispersed in ethanol (EtOH), treated with ultrasonic bath for 30 min, then stirred at 50 °C for 1 h. This procedure was repeated three times in order to obtain a homogeneous and opalescent colloidal suspension. The latter was mixed with ethylcellulose (5-15 mPa*s) previously dissolved in ethanol (10% w/w) and stirred again at 50 °C overnight. Terpineol was added and the resulting mixture was further stirred for 6 h. Finally ethanol was removed by a rotary evaporator to obtain pastes suitable for doctor-blade deposition. The paste had the following weight percentage composition: TiO_2 : 12%; ethylcellulose: 6%; terpineol: 82%.
- 50 Fluorine-doped tin oxide (FTO, 10 Ω/sq ., provided by Solaronix S.A.) glass plates were first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. TiO_2 buffer layers with a mesoporous structure were prepared by using a solution of titania precursor and P123 polymer that was prepared as reported above. The solution was stirred for 3 hours and then deposited on FTO conducting glass substrates (Dyesol, 15 Ω/sq .) by spin-coating at 2400 rpm for 20 seconds. After aging at 25°C for 2 days, optically uniform and transparent films were obtained. These films were calcined at 350°C for 2 hours using a ramp rate of 1°C/min to remove the block copolymer and the residual precursors.
- 60 For the fabrication of photoelectrodes, the TiO_2 paste was deposited onto FTO glass (by doctor blading and dried at 160 °C for 15 minutes. This procedure was repeated several times in order to obtain the desired film thickness. The film thickness and the dimensions of the active area (0.16 cm^2) were measured using a profilometer. For comparison a Degussa P25-based TiO_2 photoelectrodes was prepared according the reported literature.²⁷
- 70 The electrodes coated with the TiO_2 pastes were gradually heated under an air flow and sintered at 480 °C for 30 min. After cooling to 80 °C, the TiO_2 electrodes were immersed into a solution of 0.3 mM (bis (tetrabutylammonium)-cis-di(thiocyanato)-N,N 0-bis-(4-carboxylato-40-carboxylic acid-2,2-bipyridine) ruthenium(II) (N719, provided by Solaronix S.A.) in a mixture of acetonitrile and tertbutyl alcohol (v/v, 1 : 1) and kept at room temperature for 14 h. The counter electrodes were prepared by sputtering a 50 nm Pt layer on a hole drilled cleaned FTO plate. The two plates were faced and assembled by means of a gasket of 50 μm -thick Surlyn® foil interposed between them. The redox electrolyte (0.1 M LiI, 0.05 M I_2 , 0.6 M 1-methyl-3-propylimidazolium iodide, and 0.5 M tert-butylpyridine in dry acetonitrile) was vacuum-injected into the space between the electrodes.
- 85 **Characterization.**
- Low-magnification transmission electron microscopy (TEM) images were recorded with a Jeol Jem 1011 microscope operating at an accelerating voltage of 100 kV. FE-SEM characterizations were carried out with a high-brilliance LEO 1530 field emission scanning electron microscope apparatus equipped with an INCA 450 energy-dispersive X-ray spectrometer (EDS) and a four-sector backscattered electron detector (BSD). Before the analysis, the surfaces were coated with a thin layer of carbon in order to avoid charging effects. The carbon coating was deposited by using an Emitech sputter coater K550 unit, a K 250 carbon-

coating attachment, and a carbon cord at a pressure of 1×10^{-2} mbar in order to produce a carbon film with a thickness of a few nanometers.

X-ray diffraction measurements of TiO_2 powder were recorded with a Siemens D5000 using $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Small angle X-ray diffraction patterns were registered in the angular range $2\theta = 0.7\text{--}5^\circ$ with a Bruker D5000 vertical goniometer. A 0.03° step size in 2θ with a counting time of 12 seconds per step were used.

The microstructural properties of titania powder were determined from N_2 adsorption–desorption isotherms at -196°C using a Sorptomatic 1900 (Carlo Erba) instrument. Before the measurements, samples were heated in vacuum at 250°C for 3 h and the specific surface area was obtained using the Brunauer–Emmett–Teller (BET) method.

The Raman measurements were performed with a Renishaw spectrometer equipped with a cooled CCD detector in conjunction with a Leica microscope. A $100\times$ objective was used to focus the laser light on the samples and to collect the Raman signal. The excitation light was the 514 nm line of an argon ion laser.

Photocurrent–voltage I–V measurements were performed using a Keithley unit (Model 2400 Source Meter). A Newport AM 1.5 Solar Simulator (Model 91160A equipped with a 300W Xenon Arc Lamp) serving as a light source. The light intensity (or radiant power) was calibrated to 100 mW/cm^2 using as reference a Si solar cell. An aperture 0.25 cm^2 mask was applied to the devices before measurements. The incident photon-to-current conversion efficiency (IPCE) was measured by a DC method.

IPCE measurements were carried out with a computerized setup consisting of a xenon arc lamp (140 W, Newport, 67005) coupled to a monochromator (Cornerstone 260 Oriel 74125). Light intensity was measured by a calibrated UV silicon photodetector (Oriel 71675) and the short circuit currents of the DSSCs were measured by using an optical power/energy meter, dual channel (Newport 2936-C).

To evaluate the dye loading the stained photoelectrodes were placed in a NaOH solution in water/ethanol (0.1 M) for 14 h in order to achieve a complete desorption, as testified by substrate discoloration. The evaluation of the dye concentration in the solvent, obtained by UV-Vis measurements, allowed the calculation of the amount of the adsorbed molecules, expressed in terms of moles of dye anchored per projected unit area of the photoelectrode.

Electrochemical impedance spectroscopy (EIS) spectra were recorded using an AUTOLAB PGSTAT302N potentiostat operating in a two-electrode mode. Measurements were carried out both in the dark and under illumination at various forward bias voltages in the 300 kHz to 10 mHz frequency range and applying an AC voltage of 10 mV. Bias potentials ranged between 0.5 and 0.80V depending on the open-circuit photopotential of the cell under illumination at 1 sun. The frequency-dependent impedance was fitted by using the Z-view software.

Notes

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GRAPHICAL ABSTRACT