A colloidal approach to prepare binder and crack-free TiO₂ multilayer coatings from particulate suspensions: application in DSSCs

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Abstract

Well-compacted and crack-free TiO₂ multilayer coatings have been manufactured from a colloidal approach based on the preparation of particulate suspensions for DSSC. The study of the suspension parameters to optimize dispersion and stabilization of the TiO₂ nanoparticle in the liquid media as well as a thermal stabilization step between the layers have been defined as two key points in the processing method to obtain interconnected microstructures, free of defects and heterogeneities, that prevent the application of an additional scattering layer or any kind of specific or clean conditions during deposition. The sintering process at low temperature, 450°C, has allowed obtaining open microarchitectures avoiding the complete densification and favoring the dye adsorption. A thickness of 12.8 μm resulted in a successful dye loading of 4.52x10⁻¹⁰ mol·mm⁻² and a photoefficiency of 5.7%, both in the range of the others particulate systems. EIS measurements were also made to study the transfer charge phenomena

Keywords

TiO₂ coatings; particulate suspensions, colloidal processing; crack-free; DSSCs

1. Introduction

Dye sensitized solar cells (DSSCs), also known as Grätzel cells by the name of their inventor have received special attention in recent years owing to offer an efficient and easily implementable photovoltaic technology for future energy supply. In comparison with conventional silicon photovoltaic cells, DSSCs exhibit some specific advantages including easy fabrication procedures, low manufacturing cost and compatibility with flexible substrates [1,2].

A typical DSSC is composed of photoanode, counter electrode, electrolyte and photosensitizer (dye). Among them, the photoanode plays an important role to achieve high conversion efficiency as it collects the photo-excited electrons produced from the dye molecules under light exposure. Upon light irradiation, the sensitizer becomes photo-excited and injects electrons into the conduction band (CB) of photoanode. The electrons pass through the external electric circuit until reaching the counter electrode where the oxidized component of the electrolyte (redox couple) is reduced. This reduced component of redox couple in the electrolyte oxidizes the dye regenerating its capacity to the photo-excitation [3,4].

Usually, photoanodes are made of metal oxide semiconductors such as TiO_2 , ZnO , Nb_2O_5 , SnO_2 , etc. which can be prepared through simple and cost effective solution processing route [5]. The transfer of electrons and holes in the semiconductor nanomaterial is primarily governed by the quantum confinement and the transport properties related to phonons, which are largely affected by the size, crystallinity and morphology [6]. The major drawback of these materials arise from the rapid charge recombination of the electron-hole pairs (thereby suppressing the quantum efficiency) and their wide band gap, which limits light absorption to ultraviolet region only (wavelength < 390 nm) and thus limits the practical applications for solar light harvesting. Many strategies have been described in the literature to extend the visible light activity ranges [7] including metal, or even nonmetal doping of the semiconductor.

In addition to the materials composition and characteristic, it is also relevant to design the micro-architecture of the nanocomposite films that would to lower the recombination currents, enhance the light absorption and ensure a good electric

connection. All of these phenomena are often considered to be mutually antagonistic, which makes the attempt of balancing their conflicting requirements a research challenge [8].

Different compositions and deposition methods have been intensely explored for DSSC applications [9]. Highly porous thin films with accessible pores have been developed in comparison to nanocrystalline films prepared by conventional techniques such as doctor blade, screen printing, etc. Mesoporous thin films are usually obtained by surfactant assisted sol-gel techniques known as the evaporation-induced self-assembly (EISA) or the evaporation-induced micelles packing (EIMP)[10]. However, they require complex synthesis procedures with numerous steps to overcome the poor quantity of active material and the limited reactive surface area resulting from a small thickness. In this case, it is necessary to increase the film thickness to obtain better photovoltaic performances [11]. Some authors have already studied the photoresponse of a coating made by a multilayer deposition from a templated sol [12–14], but the methods employed for the preparation of mesoporous films suffered from a large time consuming process to get thick films with crack-free microstructures. Recently, Keshavarzi et al [15] have achieved to reduce the processing time for a wormlike mesoporous TiO_2 film by optimizing the number of calcination steps. However, the thickness was only of 5.7 μm . As alternative to the sol-gel techniques, several groups have studied the photovoltaic behavior of DSSC fabricated directly by deposition of particulate TiO_2 suspensions (prepared from commercial TiO_2 powder) on conducting glasses, which allow obtaining thicker coatings with less consumption time. For these photoanodes, the effectiveness of the coating depends on the physical properties of the respective slurry/paste such as viscosity, nature of binder, solvent type etc. However, not special attention has been paid to the processing variables and any mature protocol has been reported on the preparation of the slurry/paste and the photoanode fabrication [16]. Ito et al. reported a high photoresponse when the thickness of the photoanodes was increased by piling consecutive coating layers of a paste based on commercial TiO_2 powder [17]. However they applied the additional so called TiO_2 scattering layer to reduce the defects and cracks in the microstructure electrode. Fan et al. reported the preparation of coatings at low temperature with a

1 binder-free paste [18]. They mixed the commercial NPs with other additional TiO₂
2 particles synthesized by a hydrothermal method. Other authors have also evaluated
3 the performance of TiO₂ thick films made with modified commercial particles. Liu et
4 al. described the effect of ethyl cellulose content in pastes to prepare 14.5 μm-thick
5 [19]. Pan et al. reported the surface modification of particles with ethylene glycol, citric
6 acid and propylene carbonate for the preparation of 14.3 μm-thick photoanodes [20].
7 Nevertheless, the colloidal stability, the dispersion of particles or the paste viscosities
8 were not determined and no thermal stabilization step or thickness studies were
9 carried out.
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11 Earlier reports suggest the need to address the development of new strategies to
12 control the nanoparticles arrangement during film growth, nanoparticles compaction
13 and/or consolidation structures to achieve higher performance. In the late eighties,
14 advances in colloidal chemistry knowledge have provided the required milestones to
15 successfully apply the colloidal processing methods to the reliable manufacture of
16 nanostructures with specific properties. The colloidal approach of particulate
17 suspensions used herein involves the manipulation and control of the interparticle
18 forces in the liquid media. This is a key step to break down weak agglomerates,
19 stabilize and facilitate powders mixing, removing heterogeneities and defects that
20 degrade relevant properties [21]. Moreover, it is critical to fit processing additives that
21 modify the viscosity, flow, surface tension, wettability, etc., adapting the rheological
22 behavior to the manufacturing technique [22] and controlling the particles assembly
23 [23].
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25 In this work, a colloidal approach of optimized particulate suspensions has been
26 proposed to prepare binder-free TiO₂ coatings based on the improvement of the
27 nanoparticles packing and connectivity through a multilayer system. The suspension
28 and the processing parameters were optimized and short thermal stabilization steps
29 have been applied to promote the crack-free microstructures. The resulting TiO₂
30 coatings were evaluated in terms of homogeneity (SEM), dye loading (UV-VIS
31 spectroscopy) and charge transfer resistance (Electrochemical impedance
32 spectroscopy). Finally their performance in liquid DSSCs was tested.
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2. Experimental

TiO₂ colloidal suspension, TCS, was prepared and optimized to be used as photoactive phase to determine the influence of the colloidal processing in the fabrication of photoelectrodes for DSSC. Besides, a mixture of commercial TiO₂ Paste (Dyesol - DSL 18NR-T, Queanbeyan, Australia) and terpinol was used as reference paste, further reorted as TRP.

The TCS was formulated based on the surface modification of as-received TiO₂ nanopowder (Aeroxide P25, Evonik Degussa GmbH, Germany) in deionized water. As-received commercial nanoparticles (NP) were characterized by He pycnometer (Multipycnometer, Quantachrome Co., USA) to determine their density, and by Physisorption Analyzer (ASAP 2020, Micromeritics, USA) to measure the specific surface area. Polyethilenimine (PEI, Mw 25,000 mol/g, Aldrich, Germany) was used as stabilizer additive. The particle size distribution was determined by Dynamic Light Scattering (DLS) using a ZetasizerNano ZS (Malvern, UK) for TiO₂ concentration ranging between 0.001-0.1 g/L. The conditions for NP dispersion and suspension stability were then determined in terms of zeta potential and viscosity, optimizing the pH and the amount of stabilizer.

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) (Perkin Elmer, USA) were used to study the thermal evolution of NP as well as to determine the calcination temperature to retain the anatase phase. Tests were made in air atmosphere with constant heating rate of 10°C/min up to temperature of 1000°C. A TG analysis was also performed under similar conditions with PEI to determine its temperature of decomposition in air.

Zeta potential was measured by laser Doppler velocimetry in a ZetasizerNano ZS (Malvern, UK). The zeta potential evolution of NP with pH was determined for suspensions with concentrations of 0.1 g/L using 10⁻² M KCl as solvent and inert electrolyte, so as to maintain the ionic strength of the medium. The pH adjustment of the suspensions was carried out by addition of small quantities of 0.1 M HNO₃ or Tetramethylammonium Hydroxide (TMAH) and controlled with a pH probe (Metrohm AG, Germany). The zeta potential saturation curve determined for the addition of PEI was measured without the inert electrolyte at pH 8. Before each measurement, NP

suspensions was dispersed and homogenized by sonication, using a UP400S Ultrasonication probe (Hielscher, Germany) for an optimized period of 30 s.

Rheology of NP suspensions was measured in a Haake Mars rheometer (Thermo Scientific, Germany) with a double-cone plate fix of 60mm of diameter and an angle of 2° (DC60/ 2°). Tests were performed in a control rate mode (CR) shearing up from 0 to 1000s^{-1} in 2 min, dwelling at 1000s^{-1} for 1 min and shearing down to 0s^{-1} in 2min and control stress mode (CS) increasing stress from 0 to 15Pa in 2min and decreasing to 0Pa in the same time. All tests were done at a constant temperature of $23\pm 0.5^\circ\text{C}$. Rheograms were determined to stablish the optimal addition of PEI and adjust the milling time. For that, suspensions with a solid content of 3 vol.% were stabilized with amounts of PEI ranging between 3-9 wt.% (referred to powder) and suspensions with a 7.4 vol.% of solid content were milled in a ball mill during times ranging between 30-120 min (using Al_2O_3 balls of 1 cm in diameter).

NP suspensions were formulated at optimal dispersion conditions, and then centrifuged and re-dispersed in ethanol to achieve the 2 vol.% of solid contents for the TCS.

For comparative purposes regarding to the photoresponse, the TCS shaping into coatings was done by dip-coating technique with a withdrawal rate of 2.5 mm/s, whereas the TRP was processed by a standard spin-coating procedure. In both cases FTO conducting glass (Dyesol, $15\ \Omega/\text{sq}$) was used as substrate. The thickness of the coatings was increased by a sequential deposition of several layers where a thermal stabilization step between each coating was made by heating the fresh film during 10 minutes on a hot plate at 200°C .

The TiO_2 coatings were further sintered in air at 450°C for 15 min, with heating and cooling rates of $5^\circ\text{C}/\text{min}$. The films microstructure and thickness were characterized by FEG-ESEM XL30 (FEI) with an accelerating voltage of 5 kV under high vacuum and by FESEM in an S-4700 microscope (Hitachi, JAPAN). The identification of the crystal phases of the coatings has been carried out by X-ray diffraction (XRD) with a Siemens D5000 diffractometer (Germany) with a Kristalloflex 710 generator ($\text{K}\alpha(\text{Cu})\ \lambda = 1.5405\ \text{\AA}$; 40 kV; 30 mA; $2\theta = 5-70$)

1 TiO₂ coatings were sensitized by a Ruthenium complex-based dye, N-719 dye
2 (Solaronix), dissolved in ethanol up to 2.7×10^{-4} M. The coatings were cleaned by
3 UV-O3 for 15min right before the dye adsorption. Electrodes were immersed in the
4 dye solution overnight at room temperature.
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7 The dye loading of the shaped electrodes was measured by UV-VIS spectroscopy
8 with a Perkin Elmer UV-vis Spectrometer Lambda 14 P. The absorbance values of
9 the aqueous solutions (10^{-3} M of potassium hydroxide (KOH)) where dye was
10 previously desorbed were analyzed. A calibration curve was used to calculate the
11 experimental extinction coefficient of N-719 dye, which is $12900 \text{ (mol/L)}^{-1}\text{cm}^{-1}$ at
12 500 nm. For the dye loading measurements, the area of all the coatings was
13 normalized and determined by image analysis using the GIMP software.
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16 The assembly of the DSSCs was carried out by a conventional procedure at room
17 temperature. Counter electrodes were composed of a FTO conducting glass
18 substrate (Dyesol, $15 \text{ } \Omega/\text{sq}$) coated with a platinum layer to catalyze electron
19 transfer. The Pt coating was obtained by sputtering performed at 30 mA intensity
20 during 80 s and at a working distance of 3 cm. The thickness of the platinum layer
21 was of approximately 29 nm, determined by spectroscopic ellipsometry.
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24 The electrodes were separated by a polymer spacer SX-1170-60 (60 μm -thick)
25 applied under spring pressure and heating (100°C 30min in an oven). A home-made
26 electrolyte solution composed of 0.6 M 1-butyl-3-methylimidazolium iodide
27 (Aldrich Chemistry), 0.03 M iodine (Sigma-Aldrich), 0.1 guanidine thiocyanate
28 (Sigma-Aldrich) and 0.5 M 4-tert-butylpyridine (Aldrich Chemistry) in acetonitrile
29 (ABCR GmbH and Co.)/valeronitrile (Aldrich Chemistry) (85/15, v/v) was prepared
30 and introduced via vacuum backfilling in a hole drilled in the Pt-coated FTO
31 counter-electrode. The hole was sealed with SX-1170-60 polymer and a cover-glass.
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34 Photovoltaic performances were evaluated into a class A solar simulator purchased
35 from Newport Spectra Physics coupled with a Keithley 2400 SourceMeter.
36 Photocurrent-voltage curves were measured under 0.7 SUN simulated illumination
37 (filter AM 1.5). The electrode active area was set to 0.2064 cm^2 with a mask.
38 Electrochemical impedance spectroscopy was performed using a BioLogic SP-200
39 potentiostat (Science Instrument) and data were analyzed with the EC-Lab software.
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A sinusoidal potential perturbation was applied to the cell and the current variation response was recorded. EIS spectra were measured over a frequency range of 10^{-1} to 10^6 Hz, with 10 mV sinusoidal modulation signal. Measurements were performed in the dark, at room temperature by applying a bias equal to the V_{OC} value determined from the I-V curves. Photovoltaic and EIS measurements were repeated several times.

3. Results

TiO₂ nanopowders have been widely studied for shaping photoelectrodes. Examples in the literature describe a high variability of commercially-available powders in terms of particle size and percentage of anatase and rutile phases. Different authors have characterized the same materials obtaining results with slight desviations. The P25 Degussa powders described in [18,19] displayed 70% anatase and 30% rutile with a particle size of 24 nm; on the other hand, the P25 Degussa powder used in [17] presented an average size of 30 nm by BET, 80% anatase (21 nm) and 20% rutile (50 nm). In these cases, the SEM pictures of the same powder showed smaller particles of anatase (20 nm) and rutile (40 nm); in reference [20], the size of the managed P25 nanopowder was of 20–30 nm, with a surface area of 50m²/g. In comparison with these studies, the Aeroxide P25 powder used herein (NPs) has a density of 4.2 g/cm³ and a specific surface area of 50±15 m²/g. Two crystallographic phases corresponding to 95% anatase and 5% rutile were identified by XRD analysis.

In order to fit the optimal conditions for colloidal processing, the evolution of the zeta potential of NPs in deionized water is firstly examined. Figure 1a shows the values of zeta potential for a wide range of pH values (2 < pH < 12). TiO₂ NPs have the isoelectric point at pH 6, exhibiting a positive charge for pH < 6 and a negative surface charge for pH values over the isoelectric point. The zeta potential at pH 8 is negative with an absolute value around 30-35 mV. These are ideal conditions to adsorb on the surface a branched polyethylenimine with a molecular weight of 25.000 g mol⁻¹ (pKa 8.6), widely protonated at this pH [24]. The adsorption of the cationic polyelectrolyte onto the TiO₂ NPs surface and its ionization state can be followed also by zeta potential measurements. Figure 1a additionally shows the evolution of the zeta potential of NPs

1 suspensions with the addition of PEI (wt. %). The strongly negative surface of NPs at pH
2 8 turns to positive with the addition of an amount of PEI as small as 0.5 wt. % related
3 to the solid content of the suspension. The NPs become more positively charged with
4 increasing PEI addition, reaching a maximum of 50 mV for the addition 6 wt. % of the
5 stabilizer.
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9 The particle size distribution of TiO₂ NPs in aqueous suspensions is determined in
10 Figure 1b for different additions of PEI (2.5-7 wt. %). The particle population has a
11 mean particle size (Dv50) ranging between 130-160 nm. These particle size values do
12 not significantly changes with the addition of PEI in the values recorded. Even though
13 the results indicated that primary particle size of those NPs (50nm) cannot be achieved
14 in aqueous suspensions, the level of particle stabilization determined by the absolute
15 zeta potential value (50 mV) was successful. Figure 1b also displays the viscosity values
16 of 3 vol. % TiO₂ NPs suspensions stabilized with increasing amounts of PEI (3-9 wt. %)
17 at pH 8. The values are taken at shear rates of 100 s⁻¹ from the corresponding flux
18 curves (included as supplementary information, figure 2S). All suspensions exhibit a
19 thinning behavior leading to viscosities in the range of 10-100 mPa·s for the mentioned
20 shear rates, except for the suspension with 3 wt. % of PEI, which present a value out of
21 this range. The suspension viscosity decreases with the addition of PEI down to reach a
22 plateau, between 6-8 wt. %, where it stabilizes. Although the dilution effect provoked
23 by the stabilizer incorporation the addition of 9 wt.% made the viscosity increase
24 again, therefore the 6 wt. % of PEI is selected to prepare the suspensions.
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28 Figure 1c shows the rheograms of TiO₂ suspensions modified with 6 wt. % of PEI and
29 milled for 30, 60, 90 and 120 minutes. At low solid content as 3 vol.%, viscosity is too
30 low and the rheograms do not show any significant change. For that reason, a solid
31 content of 7.4 vol.% was choose to clearly evaluate the signal variations. Higher solid
32 content than 7.4 vol.% makes the suspension difficult to handle. The lowest shear
33 stress values are reached when the milling time is 90 min and longer times results in an
34 increase of the stress value.
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38 Suspensions prepared on the better conditions of dispersion (6wt. % of PEI) and milling
39 (90 min.) were centrifuged in order to separate surface modified NPs from water
40 media. Nevertheless, the suspension was never completely dried to avoid the particle
41 flocculation. The water is substituted by ethanol as solvent in order to improve the
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drying process during the shaping. 30 seconds of ultrasounds are applied to favor the particles re-dispersion in ethanol. Processing in ethanol provide the shaping with a better thickness control as well as a uniform and quick drying process of the layers. Both the solid contents of the suspensions and the withdrawal rate of the dip-coating were adjusted to obtain crack-free layers after drying and calcining. 2 vol. % in ethanol and 2.5 mm/s are selected to prepare the coatings.

Figure 1. a) Evolution of the zeta potential of TiO₂ NPs in aqueous suspensions varying the pH (2 < pH < 12) and the addition of PEI (ranging from 0.5 to 8 wt.%) (a), evolution of the mean particle size (Dv50) and viscosity (at a shear rate of 100s⁻¹) of the TiO₂ NPs in 3 vol.% aqueous suspensions with the addition of PEI at pH 8 (b) and rheograms of aqueous suspensions of TiO₂ NPs modified with 6wt.% of PEI with 3 and 7.4 vol.% of solid contents dispersed by ultrasounds and ball milling respectively (c).

The dispersant (PEI) and the as-received TiO₂ powder are thermally analyzed to study the possible effects on the calcining and sintering treatments and their possible influence on the structure of the final coatings. Figure 2 shows the TGA and DTA-TGA analysis of the PEI and TiO₂ NPs respectively.

Figure 2. TGA of PEI a) and DTA-TGA of the as- received TiO₂ NPs b)

The TGA of the PEI (without TiO₂ particles) in figure 2a displays a weight loss of 100% between 250 and 400°C, corresponding to organic stabilizer removal which means that a thermal treatment above this temperature would result in binder-free coatings. The polyelectrolyte is completely removed and any remainder would be found at the coating after sintering over 400°C. Consequently, the photoresponse or the transport electron charge between particles will not be affected by any possible interference caused by significant residues of the dispersant.

On the other hand, the thermal analysis of TiO₂ powder is showed in Figure 2b. In this case, the weight loss is extremely low, (< 2%) and there are no appreciable differences with similar reported studies in the literature. For example Di Paola, A. et al. [25] has identified discrete steps in weight loss in relation to the different OH groups: one, in the 30–120°C range, due to the physically adsorbed water and others, in the 120–

300°C and 300–600°C ranges, related to weakly bonded OH groups and strongly bonded OH groups, respectively. In addition, a wide peak was identified between 600–900°C in the DTA curve, and attributed to the phase transformation from anatase to rutile. In order to assure debinding and simultaneously avoid the phase transformation of TiO₂, a temperature within the range 400–600°C could be selected. In this sense 450°C was selected as sintering temperature for the final multilayer systems in a muffle, while a thermal treatment of calcination of 200°C in a heating plate was applied to dry and densify the NPs arrangement after each dip-coating.

To analyze the suitability and the photovoltaic performance of the TCS suspensions, a multilayer strategy is followed to prepare the coatings. A dip coating procedure followed by a thermal stabilization step were repeated for several times (3, 6, 9 and 16 layers) to shape the mentioned coatings. Figure 3 shows the cross section and top views micrographs of a 3 layers TCS sample after a final thermal treatment at 450°C.

Figure 3) Low and high magnification SEM images of the cross section (a) and (b) and top view (c) and (d) of the TiO₂ coatings obtained by depositing 3 layers of TCS onto FTO.

As a result of successful suspension optimization, the cross section micrographs 3a and 3b indicate a homogeneous thickness while in top view micrographs 3c and 3d it can be observed a crack-free coating on the glass surface. The details at high magnification seen in figures 3b and 3d displayed that the adjustments on particles stabilization, solid content, viscosity and the subsequent thermal stabilization steps at 200°C and the sintering treatment at 450°C resulted in crack-free microstructures and a high level of consolidation.

XRD analysis of the sintered coatings (figure 1S) was also carried out to determine the ratio of the crystallographic phases (anatase:rutile). Slight variations, from 95.0% to 93.7% for anatase and from 5.0% to 6.3% for rutile, were determined before and after the applied thermal treatment. In spite of the DTA-TGA analysis showed that the full phase transformation occurs above of the selected temperature of sintering, 450°C, the percentage of photoactive phase was partially reduced due to the heating and cooling rates, remaining the TiO₂ coatings under relatively high temperature a considerable time. According to the literature this fact can limit the process.

In addition, the microstructure of this sample is also compared with a coating made of TRP in order to evaluate the influence of the film morphology in the final photoresponse, figure 4a. Both samples were prepared with the same thickness onto FTO substrates and thermally treated under the same conditions. The micrograph of the TRP sintered sample showed some microstructural differences in respect to the TCS coating. The film made with the reference paste presented more homogeneity and continuity than the coating made with the TCS (figure 4a). While the first displayed a high uniformity, the second one presented a wrinkled appearance with higher exposed surface area.

Both TCS and TRP based TiO₂ photoanodes were used to fabricate DSSCs and their performance was evaluated. The IV curves registered for the corresponding cells are shown in figure 4b.

Figure 4. SEM cross section of the microstructure of the coating made with TRP (a) and photocurrent vs voltage curves of the assembled DSSCs made with TCS and TRP (b).

Table 1 collects the photovoltaic parameters obtained from the I-V curves (figure 4b) for the TCR and TRP samples.

Table1 DSSCs parameters for the cells based on TCS and TRP coatings. Film thickness is also mentioned in the table

Sample	Thickness (μm)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	η (%)
TCS	1.88	0.57	2.52	67.8	1.95
TRP	1.85	0.51	2.29	64.8	1.18

V_{oc}: open circuit voltage; J_{sc}: short-circuit current density; FF: Fill Factor; η: Efficiency

The open circuit voltage (V_{oc}), the short-circuit current density (J_{sc}) and the fill factor (FF) values of the TCS sample were higher than those of the TRP sample leading to higher conversion efficiency. This is mainly attributed to the higher accessible surface area in mesostructured films, along with a better control on the pore diameter and connectivity, favoring a better dye loading and electrolyte impregnation.

After proving that considerable conversion efficiency is achieved with 3 layers, the cells efficiency was further improved with thicker coatings made from several layers of TCS. Figure 5 shows the cross section micrographs of those coatings made with 6, 9 and 16 layers of TCS onto FTO and sintered at 450°C.

Figure 5 SEM cross section views of the TCS coatings (6, 9 and 16 layers) at different magnifications.

Although all samples were sintered under the same thermal treatment, the visual consolidation level of the microstructures was significantly different with the increase of thickness. The micrographs, at higher magnification, corresponding to the sample

made with 16 layers showed the details of the consolidated microstructures after the thermal treatment.

It is reported that the application of successive thermal steps during the deposition process leads to excessive grain growth and sintering, with a subsequent decrease in the roughness factor [26,27]. However, the packing density of our coatings made with 3 layers, (figure3) was significant higher than the coatings made with 6, 9 and 16 layers, which present more opened porosity, which is directly related to the dye adsorption. The open porosity favors the impregnation of the dye and the electrolyte and eventually could improve the photovoltaic performance of the assembled DSSCs. Nevertheless, the decrease of consolidation level could affect the charge transfer along the microstructure and therefore an intermediate compromise between porosity and packing density should be reached.

In addition, top view micrographs of these coating were also analyzed at very low magnification to probe that the increase of thickness did not affect the surface homogeneity. The obtained crack-free microstructures (figure 6) with a uniformly distributed porosity confirmed the benefits of the colloidal approach, either by the suspension optimization and/or the application of the thermal stabilization steps at 200°C carried out between each layer during the dip coating process. The obtained microstructures confirmed that the adjustment of the TCS avoid cracking for overpass the critical thickness for both the drying and sintering processes. A little rippling was observed above 9 layers caused by the withdrawal in the dip coating process.

Figure 6. SEM top view of the coatings made with 6, 9 and 16 layers TCS onto FTO.

The influence of the microstructural features, such as the thickness and porosity, and hence the exposed surface area, on the dye loading and therefore on the photovoltaic performance of the assembled cells was also evaluated. Figure 7 shows a picture of the TCS coatings on the FTO conducting glass after the dye absorption (figure 7a) as well as the UV-Visible spectrum corresponding to the desorption solutions for the 3, 6, 9 and 16 layer TCS samples (figure 7b) and the thickness and the dye loading per area unit (figure 7c).

Figure 7 Picture of the dye sensitized photoelectrodes made with 3, 6, 9 and 16 Layers of TCS (a), UV-Vis spectrum of the desorption solutions of the samples (b) and evolution of thickness and dye loading with the number of layers (c).

The increase in the color intensity of the coatings means that the impregnation of the dye was higher when the thickness increased as confirmed by the absorption spectra. The slope of the thickness curve was more pronounced than the slope of the dye curve (figure 7c), which means the multilayer system is more densified with the increase of the number of layers and the dye impregnation is not completely proportional

Table 2 collects the dye loading values of the prepared samples and the photovoltaic parameters extracted from the I-V curves (figure 8).

Figure 8. I-V curves registered in light of the DSSCs made with 3, 6, 9 and 16 layers of TCS.

Table 2. Dye loading and cell performances of DSSCs comprising the TCS electrodes with different thickness. Layer thickness is also shown in the table

TCS	Thickness (μm)	Dye Loading (mol mm^{-2})	$V_{oc}(\text{V})$	$J_{sc}(\text{mAcm}^{-2})$	FF(%)	η (%)
3 Layers	2.2	1.26×10^{-10}	0.75	2.4	67.2	1.9
6 Layers	4.3	1.48×10^{-10}	0.72	3.6	54.3	2.3
9 Layers	7.9	2.54×10^{-10}	0.70	5.2	64.5	3.6
16 Layers	12.8	4.52×10^{-10}	0.71	8.7	62.0	5.7

V_{oc} : open circuit voltage; J_{sc} : short-circuit current density; FF: Fill Factor; η : Efficiency

It can be seen that, as the film thickness increases, the solar cells exhibit a continuous improvement of the J_{sc} and the η values, when the film thickness increase from 3 to 16 layers, while the V_{oc} and the FF slightly decrease. The J_{sc} parameter is known to be largely determined by the dye loading and thus the surface area and the pores connectivity. It has to be noted that from 3 to 16 layers the increment of J_{sc} in a factor of 3.6 is a similar increment that in the dye loading per area, meaning that, in addition to the dye loading increment with the film thickness reported for the materials here processed (figure 7.c), That confirms that the dye impregnation within the

microarchitecture of the coatings was successful and thus presented an excellent pore accessibility. In the case V_{oc} values there is a slightly decrease of 5% when the thickness increases due to the longer path of photogenerated electrons to reach the collecting electrode. This slightly decrement confirms the microscopic observations that there are no appreciable interface between layers as a consequence of the high homogeneity of the suspension and the adequate calcining treatment that promotes firstly the adhesion between layers during the sequential dipping process, and later the full consolidation of the multilayer structure after sintering. Additionally, figure 9 shows a linear progress of the dye loading and the efficiencies values with the film thickness. This performance means that our coatings are far from reaching the typical solar conversion plateau (non-proportional behavior) described in the literature and therefore they still have improvement capability with a photovoltaic yield above 5.7%.

Figure 9. Dye loading expressed in moles of N-719 dye per mm² of projected electrode area (left) and efficiency evolution (right) with the film thickness

Efficiency is in the range of similar coatings processed from nanoparticles in suspension using commercial powder. Table 3 compares the results showed in the most recent publications to compare them with the results of coatings fully shaped from commercial TiO₂ by the described simple method. Important coating details, such as thickness, processing method, photoactive nanostructures and the intercalation of the so called scattering layer, were considered. In these manuscripts any specific description dealing with the nanoparticles stabilization and/or suspension

optimization was reported. Furthermore, in some cases the heterogeneity of the resulting coatings produces cracking and connectivity lacks in their microarchitectures, which difficult the achievement of an available, controllable and effective range of thicknesses built on commercial nanopowders, and consequently many times the mixture of the commercial nanopowder with synthesized TiO₂-nanostructures, the application of a sol-gel healing coating or the application of a dense scattering layer is necessary to increase the photoefficiency

Table 3. Comparative of the efficiency values obtained in other similar works based on particulate suspensions

Efficiency (%)	Thickness (μm)	Processing Method	Additional Info	Ref.
9.2	17.0	Screen-printing	Scattering layer of 5.7 μm	[17]
4.6	9.0	Doctor Blade	Commercial powder mixed with synthesized particles	[18]
7.5	14.5	Multilayer Screen-printing	Ethyl Cellulose as Pore former	[19]
5.5	14.3	Doctor Blade	High surface area anatase TiO ₂ or TiO ₂ sol are added into pure commercial paste	[20]
5.7	12.8	Multilayer sequential dip coating + thermal stabilization step	----	Our work

Furthermore, the internal resistances and the charge transport properties were also studied by electrochemical impedance spectroscopy (EIS). Figure 10 show the Nyquist plots of the TCS coatings with different thicknesses measured in dark conditions. The equivalent circuit used to fit the data is described as follows:

$$R_s + \frac{R_1}{Q_1} + \frac{R_2}{Q_2} + Q_3$$

where + is used for series connection and / for parallel connection. Here R_s is the resistance of the contacts and electrolyte, R_1/Q_1 is attributed to the FTO/ electrolyte interface, with an extra contribution expected from the FTO/TiO₂ interface [28], whereas R_2/Q_2 is the response of the TiO₂/electrolyte interface.

The straight sloping line in the low frequency region is associated to Q_3 and it is related to the ions diffusion in the microstructure. The EIS curves were fitted by the Z-fit software (EC-Lab v10.4) and the results are shown in table 4.

Figure 10. Nyquist plots of the TCS coatings for different thickness, measured in dark in the 10^{-1} to 10^6 Hz frequency range, using 0.5 mol/L Na_2SO_4 as electrolyte. Figure 10b shows a magnified view in the high frequency range. Experimental data are represented by symbols and solid lines correspond to the fitted curves.

Table 4 Results of the fitting of the EIS spectra of the TCS coatings with different thickness.

Sample	R_s (Ω)	R_1 (Ω)	Q_1 ($\Omega \cdot \text{cm}^2 \cdot \text{s}^{-(1-a)}$)	R_2 ($\text{K}\Omega$)	Q_2 ($\Omega \cdot \text{cm}^2 \cdot \text{s}^{-(1-a)}$)	Q_3 ($\Omega \cdot \text{cm}^2 \cdot \text{s}^{-(1-a)}$)
3 Layers	598	994	$0.8 \cdot 10^{-9}$	28.5	$6.2 \cdot 10^{-6}$	$10.5 \cdot 10^{-6}$
6 Layers	550	774	$0.8 \cdot 10^{-9}$	16.2	$7.5 \cdot 10^{-6}$	$11.6 \cdot 10^{-6}$
9 Layers	619	800	$0.5 \cdot 10^{-9}$	9.2	$6.4 \cdot 10^{-6}$	$13.2 \cdot 10^{-6}$
16 Layers	582	790	$0.8 \cdot 10^{-9}$	6.3	$7.0 \cdot 10^{-6}$	$13.9 \cdot 10^{-6}$

The R_s and R_1 were almost the same among samples, showing slight resistance variations, which are associated to the slight different contacts/FTO and TiO_2 /FTO resistances. Contrarily to the literature [29], it has been found that the charge transport resistance (R_2) decreased as the thickness increases from 3 to 16 layers. This increment in the conductance is the result of a better electron percolation through the TiO_2 as a consequence of the developed colloidal approach as well as the sequential thermal steps applied during the shaping and the well-defined sintering process which provide better particle connectivity. On the other hand, a steeper slope at low frequency signifies higher ion-diffusion rate and an capacitive behavior which means

1 lower resistance values [30]. This is explained by the fact that after the sintering
2 process, the microstructure of the thinnest coating, (figure 3 a, b) was closer than the
3 thickest film (figure 5 e, f). The increase of the number of layers facilitated the
4 transport and intercalation of ions through the TiO₂ microstructure.
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10 **4. Conclusions**

11 Well connected and crack-free TiO₂ multilayer coatings were successfully prepared by
12 a colloidal approach consisting in depositing a particulate suspension by sequential
13 dip-coating. The optimization of the suspension combined with the use of the
14 sequential multilayer dipping system with thermal stabilization steps between layers
15 allow obtaining interconnected microstructures without appreciable defects and
16 heterogeneities in the shaped material nor between the interfaces. The Titania
17 Colloidal Suspension (TCS) was formulated using a surface modified powder with 6.5 %
18 wt. of PEI as dispersant and a 2 % vol. of solid content in ethanol. The described
19 sequential stabilization allows larger drying and sintering critical thicknesses than in
20 the one step layer.
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32 The multilayer strategy allows for obtaining coatings with high thickness values (above
33 12.8 µm). The increase of the thickness from 3 to 16 layers did not produce the
34 complete densification of the microstructures, thus open and uniformly distributed
35 porosities have been obtained along the thicknesses of the coatings. This has allowed
36 the homogeneous and proportional dye adsorption (4.52×10^{-10} mol·mm⁻²) improving
37 the photoefficiency (up to 5.7%) and decreasing the electron charge transfer
38 resistance. Although the photovoltaic parameters of our thicker coatings are in the
39 range of others particulate systems previously reported, our alternative proposed
40 route still have improvement capability because it avoid the microstructure cracking
41 and did not require of the additional scattering layer to achieve a good charge transfer
42 along the coating. The previous optimization of the TiO₂ colloidal suspension and the
43 application of the thermal stabilization steps between layers could be also considered
44 in the case of applying other processing methodology and they would be compatible
45 with other scalable colloidal techniques, such as the screen printing.
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Table1 DSSCs parameters for the cells based on TCS and TRP coatings. Film thickness is also mentioned in the table

Sample	Thickness (μm)	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	η (%)
TCS	1.88	0.57	2.52	67.8	1.95
TRP	1.85	0.51	2.29	64.8	1.18
V _{oc} : open circuit voltage; J _{sc} : short-circuit current density; FF: Fill Factor; η: Efficiency					

Table 2. Dye loading and cell performances of DSSCs comprising the TCS electrodes with different thickness. Layer thickness is also shown in the table

V_{oc}: open circuit voltage; J_{sc}: short-circuit current density; FF: Fill Factor; η: Efficiency

Table 3. Comparative of the efficiency values obtained in other similar works based on particulate suspensions

Efficiency (%)	Thickness (μm)	Processing Method	Additional Info	Ref.
9.2	17.0	Screen-printing	Scattering layer of 5.7 μm	[17]
4.6	9.0	Doctor Blade	Commercial powder mixed with synthetized particles	[18]
7.5	14.5	Multilayer Screen-printing	Ethyl Cellulose as Pore former	[19]
5.5	14.3	Doctor Blade	High surface area anatase TiO ₂ or TiO ₂ sol are added into pure commercial paste	[20]
5.7	12.8	Multilayer sequential dip coating + thermal stabilization step	----	Our work

Table 4 Results of the fitting of the EIS spectra of the TCS coatings with different thickness.

Sample	Rs (Ω)	R ₁ (Ω)	Q ₁ (Ω.cm ² .s ^{-(1-a)})	R ₂ (KΩ)	Q ₂ (Ω.cm ² .s ^{-(1-a)})	Q ₃ (Ω.cm ² .s ^{-(1-a)})
3 Layers	598	994	0.8 • 10 ⁻⁹	28.5	6.2 • 10 ⁻⁶	10.5 • 10 ⁻⁶
6 Layers	550	774	0.8 • 10 ⁻⁹	16.2	7.5 • 10 ⁻⁶	11.6 • 10 ⁻⁶
9 Layers	619	800	0.5 • 10 ⁻⁹	9.2	6.4 • 10 ⁻⁶	13.2 • 10 ⁻⁶
16 Layers	582	790	0.8 • 10 ⁻⁹	6.3	7.0 • 10 ⁻⁶	13.9 • 10 ⁻⁶

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Figure captions

-Figure 1. a) Evolution of the zeta potential of TiO_2 NPs in aqueous suspensions varying the pH ($2 < \text{pH} < 12$) and the addition of PEI (ranging from 0.5 to 8 wt.%) (a), evolution of the mean particle size (Dv50) and viscosity (at a shear rate of 100s^{-1}) of the TiO_2 NPs in 3 vol.% aqueous suspensions with the addition of PEI at pH 8 (b) and rheograms of aqueous suspensions of TiO_2 NPs modified with 6wt.% of PEI with 3 and 7.4 vol.% of solid contents dispersed by ultrasounds and ball milling respectively (c).

-Figure 2. TGA of PEI a) and DTA-TGA of the as- received TiO_2 NPs b)

- Figure 3) Low and high magnification SEM images of the cross section (a) and (b) and top view (c) and (d) of the TiO_2 coatings obtained by depositing 3 layers of TCS onto FTO.

- Figure 4. SEM cross section of the microstructure of the coating made with TRP (a) and photocurrent vs voltage curves of the assembled DSSCs made with TCS and TRP (b).

- Figure 5 SEM cross section views of the TCS coatings (6, 9 and 16 layers) at different magnifications.

-Figure 6. SEM top view of the coatings made with 6, 9 and 16 layers TCS onto FTO.

-Figure 7 Picture of the dye sensitized photoelectrodes made with 3, 6, 9 and 16 Layers of TCS (a), UV-Vis spectrum of the desorption solutions of the samples (b) and evolution of thickness and dye loading with the number of layers (c).

- Figure 8. I-V curves registered in light of the DSSCs made with 3, 6, 9 and 16 layers of TCS.

- Figure 9. Dye loading expressed in moles of N-719 dye per mm^2 of projected electrode area (left) and efficiency evolution (right) with the film thickness

- Figure 10. Nyquist plots of the TCS coatings for different thickness, measured in dark in the 10^{-1} to 10^6 Hz frequency range, using 0.5 mol/L Na_2SO_4 as electrolyte. Figure 10b shows a magnified view in the high frequency range. Experimental data are represented by symbols and solid lines correspond to the fitted curves.

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