TiO₂ nanoparticles optimized for photoanodes tested in large area Dye-sensitized solar cells (DSSC)

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Abstract

Dye-sensitized solar cells (DSSCs) are still attracting great attention as a potential alternative to conventional silicon solar cells, and a lot of current research is focusing on enhancing their efficiency through the individual improvement of the DSSCs components, as well as their integration. Among all components, mesoporous TiO₂ plays a major role, because it is the charge collector for the dye molecules or perovskite in liquid and solid DSSCs, respectively. Specifics of TiO₂ are now well-known: an anatase crystalline structure for an optimized bandgap, small particle size to shorten the charge diffusion path, reduced grain boundaries to limit current resistivity, significant porosity to enhance integration and interaction between the photon absorbers and the charge-collecting anode. We reported previously how well-crystallized small nanoparticles were successfully synthesized via a room temperature synthesis by Hegazy and Prouzet (2012) [10], leading to very small crystallites (4–10 nm) of pure TiO₂ anatase. Since as-synthesized materials still contain hydration water, a major drawback in DSSCs, we report here how dehydration and crystallinity can be improved by annealing at a moderate temperature, without any sintering or significant particle coarsening. The resulting impact on properties is confirmed by testing the resulting annealed TiO₂ nanopowder in photovoltaic liquid DSSCs. In addition, we describe a comprehensive study of the preparation and test of TiO₂ based photoanodes, including UV exposure and HCl treatment. Photovoltaic tests were conducted on a large active surfaces (5 cm²) cells to give a more realistic picture of the influence of each parameter involved in the cell performance, characterized under AM 1.5 illumination with 100 mWcm⁻² light intensity. The specific contribution of each parameter on the cell performance is discussed. We demonstrate why the TiO₂ nanopowder developed in our previous synthesis, in connection with the suitable treatments during the photoanode preparation, can replace commercial powders, with a greater success in cell photoefficiency.

1. Introduction

Since their initial discovery [1,2], liquid-based dye-sensitized solar cells (DSSCs) are known as alternatives to conventional silicon-based photovoltaic devices. The first generation of liquid electrolyte-containing DSSCs displayed significant Power Conversion Efficiencies (PCE > 13%) at lab scale and 10% in module [3–5], but the use of a liquid electrolyte prohibits any significant large-scale developments. Therefore, research on solid-state DSSCs (ss-DSSCs) has significantly increased over the last years, with the recent breakthrough of perovskites, especially organic–inorganic perovskites, which act as light harvester in place of organic dyes, and Hole Transporting Material (HTM) [3,5,7]. Nevertheless, TiO₂ anatase remains an important component in both types of DSSCs, as an electron collector. The reduction of interface transport resistance between all components is also a major requirement, which requires a high interfacial intimacy between components.

The electronic conduction in the protonated TiO₂ film, usually made of 20 nm TiO₂ particles, is the result of a complex mechanism in liquid DSSCs. First, the presence of both dye cations and iodine species, with the resulting formation of a positive layer on the surface of titania, create a Helmholtz double layer screening shell around the particles, which contributes to the reduction of the electron–hole recombination in TiO₂ [8]. It is also stated that the electrons are diffusing along the surface of the particles, as a...
result of a short screening Debye length (1.5 nm) [8]. If this limits the electron diffusion to a surface process for particles larger than 10 nm, we could wonder what would be the effect of using smaller (sub-10 nm) nanoparticles, resulting in almost the whole particle volume being used for conduction.

Two major contributing factors to the efficiency of titania-based photoanodes are the crystalline structure and size of TiO2 crystals. Although the reduction in crystal size influences positively the amount of dye adsorbed onto the surface and the dye-to-TiO2 charge transfer, it affects negatively the total internal resistance of the cell as more grain boundaries are created per unit volume, reducing the light internal reflection. For example, it was demonstrated that mesoporous TiO2 single crystals can deliver both an enhanced mobility, good optoelectronic performances, and high material intimacy [9]. Reducing the crystal size can lead to crystallinity loss, which is also a drawback as crystal structure governs the electronic band structure.

We have prepared anatase nanocrystals at room temperature, as a result of synthesis parameters being finely optimized via a mixture design method [10]. This material, successfully tested for in photocatalysis [11], could become the raw material for future roll-to-roll manufacturing of large-scale DSSCs, if the nanosstructure can be dehydrated with thermal annealing without particle sintering or coarsening. As we showed that the initial particle size can be preserved up to \( \approx 400 \) °C [10], We decided to verify the efficiency of a dehydration treatment, which would not modify drastically the crystal structure and particle size. We validated the process parameters by testing photovoltaic cells assembled with this material. Different parameters in the photoanode treatment were tested and compared in order to improve the final performance of the TiO2 photoanode. The influence of these parameters is reported, along with a comparison of our material with commercially available compounds assembled with the same method.

2. Experimental

2.1. Materials

Chloroplatinic acid hexahydrate (H3PtCl6·6H2O, ACS reagent, 37.50% Pt basis) was purchased from Sigma-Aldrich. FTO (Fluorine-doped Titane Oxide) glass, 2.2 mm thickness with a sheet resistance of 15 \( \Omega \) cm \(^{-2}\), Indolodye Z-50, 50 mM of tri-iodide in methoxyl alcohol, and PlateTai™ (transparent platinum catalyst paint), and Meltonix™ 1170-60, a 60 microns thick thermoplast hot-melt sealing foil, were purchased from Solaronix. Different organic additives were tested as adhesives and plasticizers of the TiO2 photoanode film: (i) a mixture of Span™ 80 (sorbitan monooleate, \( d=1.08, \text{Mw}=428.6 \text{~g} \)) and Tween™ 20 (polyoxyethylene (20) sorbitan monooleate, \( d=0.994, \text{Mw}=1310 \text{~g} \)) and Sigma), (ii) polyethylene glycol 12000 (PEG 12,000, Alfa Caesar), (iii) Pluronic™ P123 (PEO20POP70PEO20, Aldrich), The photoactive molecule was a cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2,2'-bipyridyl) ruthenium(iii) (2907 dye, Sigma). All were used without further purification.

2.2. Synthesis of TiO2 nanoparticles

We reported the detailed study of this synthesis previously [10]. This study allowed us to extrapolate the best composition, which would give both small nanocrystallites, and a pure anatase phase. This specific composition was chosen inside the composition mixture diagram giving the pure TiO2 anatase phase. It corresponds to a composition between the (A) and (J) data points in the mixture phase diagram of our previous study [10].

The material was prepared as follows: 2.9 mL of HCl was added drop-by-drop within 5 min under vigorous stirring (200 rpm) to 5 mL of Ti(O-n-Pr)4 left in an ice bath. Then, 2.86 mL formamide (FA) and 2.17 mL deionized water were mixed before being added drop-by-drop to the previous solution within 15 min. After full addition, the sample was left for aging in a thermostated bath at 30 °C for 24 h. The solution experienced a phase separation during this aging phase, with a physical gel formed at the bottom and supernatant liquor on the top. The gel container was covered and left at 60 °C for one week before drying. Ammonium chloride, a byproduct of the reaction, was removed by washing the sample three times with 100 mL of deionized water, the powder being recovered by filtration afterward. At this stage, the gel could easily be dispersed in water by sonication. After different tests (see hereinafter), the nanopowder was finally annealed at 350 °C (4 h, 100 °C h\(^{-1}\) ramp). This temperature was chosen to optimize both the bandgap and crystal size, and allow for the most efficient energy absorption [10].

2.3. Synthesis of the TiO2 paste

The paste was prepared by mixing the TiO2 nanopowder with different organic additives used as plasticizers. Depending on their nature, we proceeded differently for their addition. In method 10.35 g Pluronic™ P123, was dissolved into 5 mL EtOH, and then mixed with a suspension of 1.0 g of TiO2 dispersed into 10 mL of EtOH. The resulting mixture was left at 100 °C for 24 h, in a sealed vial. The vial was further cooled down before using the paste. The same method was used for the addition of a similar mass of PEG 12,000. In method 2, a mixture of Span™80/Tween™80 was prepared with the aim to obtain a final Hydrophilic Lipophilic Balance (HLB) of 13.6 [12], and 0.035 g of this mixture (equiv. one to two drops) was directly added into a suspension of 1 g TiO2 in 10 mL acetic acid (N). The resulting paste was ground in a mortar to ensure good dispersion of the organics among the solid phase before being pasted.

2.4. Preparation of the TiO2 film

The film was coated onto a FTO glass substrate, with doctor-blade method. The film thickness was controlled by the thickness of a 17 μm 3M adhesive tape, and the paste was spread with a glass rod over the space between the tape strips. The electrode was left to dry at 80 °C for 3 h. We cured organics used as plasticizers by either a thermal, or UV treatment. With the thermal treatment, the electrode was heated at 450 °C for 30 min, cooled down, and immersed into a 0.1 M HCl aqueous solution for 2 h. With UV treatment, the electrodes were exposed to an intense curing (300 W in.\(^2\)) UV radiation for 20 min, before being immersed in the HCl solution. After analysis, we decided to combine both methods, and all electrodes used for the cell assembly, were made out of the TiO2 nanopowder, first annealed at 350 °C for 4 h, then cured at 450 °C for 30 min, and exposed to UV. All electrodes were further sprayed with the 2907 dye molecule. Adsorption of the dye was undertaken by immersing the TiO2 electrode overnight in a 0.4 mM dye in 50:50 vol. t-butanol:acetonitrile solution. The sprayed electrodes were finally washed with acetone to remove the excess of dye.

2.5. Counter electrode preparation

The presence of Pt nanoparticles at the surface of the counter-electrode is mandatory to achieve the reduction of the iodide/triiodide couple [13]. A commercial platinum paste (Platisol-T,
Solaronix) was used as received and fired at 450 °C for 30 min in order to remove organic binders. The electrode was immersed in DI water, before being sonicated for 20 min in ethanol, without any noticeable wicking of the Pt layer from the substrate. The thickness of the Pt layer is around 20 nm (see Fig. S1 in ESI), a good compromise between conductivity and catalytic activity [14].

2.6. Cell assembly

The Pt electrode and the dye-adsorbed TiO₂ electrode were assembled as a sandwich-type, leading to a 5 cm² photoactive surface (Fig. S2). The redox electrolyte was introduced to the cell by capillary action.

2.7. Instruments

X-ray diffraction (XRD) was recorded on a Bruker D8-Advance powder diffractometer using Cu Kα radiation (λ = 1.5405 Å) operating from 2θ = 10–90°. The N₂ adsorption isotherms were measured with a Quantachrome AUTOSORB-B-1. The samples were outgassed at 200 °C under vacuum for 12 h before measurement. Surface area was determined by the BET method in a relative pressure range of 0.05–0.25. The pore size distribution (PSD) was calculated with the Broekhoff & deBoer Model applied to the desorption branch [15–17]. Porosity was calculated by using the following equation [18,19]:

\[
P = \frac{V_p}{\rho \cdot \pi \cdot r^2 \cdot h}
\]

where \( V_p \) is the specific cumulative pore volume calculated from desorption branch observed in the N₂ isotherm adsorption/desorption, cm³ g⁻¹; \( \rho \) is the inverse of the density of TiO₂ (anatase), g cm⁻³. 3.89. UV–vis absorption spectra were collected with a Varian Cary 5000 UV–vis–NIR spectrophotometer. Quartz cuvettes (Spectrosil, Starna Cells Inc.; transparency 170–2700 nm) and the 1 cm optical path length were used to measure the electronic absorption spectra. The UV–vis spectra were corrected from nonspecific absorption before analysis. TGA was carried out using a Q600 TA Instrument, with a heating rate of 10 °C min⁻¹, from 25 to 800 °C in air. The presence of the Z 907 dye chemisorbed on TiO₂ was detected by attenuated-total-reflection Fourier Transform Infrared spectroscopy (ATR-FTIR, Pike Technologies) [20,21], using a ZnSe crystal (n=2.42). When required, the TiO₂ films were exposed to UV light irradiation with a F300S from Fusion UV Systems Inc. (300 W/in. microwave-powered electrodeless lamp with power supply model P300MT). TEM imaging was performed with FEI Titan 80–300 microscope (FEI company, Eindhoven, The Netherlands), operated at 300 kV. The specimens were prepared by dropping dilute suspensions of colloidal TiO₂ in methanol on a standard copper TEM grid containing lacy carbon.

The I–V measurements of these DSSCs were obtained under AM1.5 illumination (100 mW m⁻²). The power of the simulated light was calibrated by using a Si photodiode reference. For every tested sample, three cells were assembled and measured to assess result reproducibility. We measured the photovoltaic characteristics of the DSSC by applying an external potential bias to the cell and measuring the generated photocurrent (Keithley source meter).

The J–V equation of a solar cell is:

\[
J = \frac{nq}{q} \ln(\frac{J_{sc}}{J_0} - 1) - \frac{V + J_R}{J_{sh} + 1} - J_R
\]

With V the voltage, \( J \) the current density, \( J_{sc} \) the injected electron current density, \( R_s \) the series resistance, \( R_{sh} \) the shunt resistance, \( J_0 \) corresponds to the resistance in parallel with an ideal solar cell, and describes the current leakage losses within the actual cell), \( J_r \) the saturation current density, and \( J_f \) the surface recombination current [22].

The fill factor and the overall energy efficiency were calculated according to the following equations:

\[
\text{Fill Factor } FF = \frac{I_{max} \cdot V_{max}}{I_{oc} \cdot V_{oc}}
\]

Overall energy efficiency : \( \eta = \frac{FF \cdot V_{oc} \cdot I_{sc}}{E_{in} \cdot A} \)

With \( I_{max} \) and \( V_{max} \) the current and the voltage at maximum power point, respectively; \( V_{oc} \) is the open circuit voltage and \( I_{sc} \) the short circuit current. It is considered that the \( I_{oc} \) and \( V_{oc} \) are the highest current and voltage obtained from the cell. \( E_{in} \) is the incident irradiation power (100 mW cm⁻²). The active surface area \( A \) of our cells was 5 cm².

The impedance measurements were performed using SI-1287 electrochemical, and SI-1260 impedance analyzer interfaces, with a Solartron FRA, working in the potentialstate/galvanostate mode with a 0.01–10⁵ Hz frequency range and 0.2 V ac amplitude under dark and 100 W light conditions. The measurements were carried out after the open circuit voltage had been stabilized. The obtained spectra were fitted with Z-View software (v2.8d, Scribner Associates, Inc.) in terms of the proposed equivalent circuit. The parameters for the circuit were optimized to ensure the best fit of experimental data.

2.8. Measurement of dye adsorption

We measured the amount of dye molecules being initially adsorbed onto dyed TiO₂ films, after desorption in a (50% 0.1 M NaOH:50% EtOH) solution, and measurement of the solution UV–vis absorbance. The TiO₂ films used for this test were prepared by mixing the TiO₂ nanoparticles, initially annealed at 350 °C and then mixed with different organic additives (Pluronic or Span/ Tween). All TiO₂ films were thermally cured at 450 °C for 30 min followed by UV for 15 min, then immersed in a 0.1 M HCl aqueous solution, before dye anchoring. Different concentrations of the dye were prepared beforehand to determine the dye extinction coefficient (\( e \)). Every dyed TiO₂ film was immersed in a definite solution volume. Each solution was finally equally diluted to concentrations where the Lambert–Beer’s law applies, i.e. when absorbance is proportional to the dye concentration:

\[
A = \log \left( \frac{1}{T} \right) = e \cdot c \cdot l
\]

where \( A \) is the absorbance, \( T \) the transmittance, \( c \) the concentration of the dye, \( l \) is the thickness of the solution which is considered the thickness of the cuvette (1 cm²), and \( e \) is the extinction coefficient which can be calculated through the slope of the calibration curve. The calculated value of the extinction coefficient was 14 mM⁻¹ cm⁻¹.

3. Results and discussion

3.1. Influence of pretreatment on the structure of TiO₂

3.1.1. Thermal annealing

A fully dehydrated material is a compulsory requirement for use in DSSCs. We have demonstrated that the crystallinity of an synthesized TiO₂ anatase can be improved without any dramatic change in crystal size, if the maximum temperature remained below 450 °C [10]. Thermogravimetric analyses (Fig. 1) show that a maximum temperature at 450 °C is sufficient to remove both
physi- and chemisorbed water, upon continuous temperature ramp.

We analyzed by TEM the influence of annealing on the crystalline and particle structure for nanopowders annealed for 4 h at 350 °C (Fig. 2a), 450 °C (Fig. 2b), and 500 °C (Fig. 2c). TEM diffraction reveals an improved crystallinity from 350 °C to 450 °C (see figures inset), without any significant change in crystal size. HR-TEM investigation of the sample annealed at 450 °C (Fig. 2d) confirms the formation of 10 nm average single crystal particles with high crystallinity. The inter-recticular distances of 3.62 Å and 2.1 Å correspond to the (101), and (200) planes, respectively. They are in the usual value range reported in literature for nanocrystalline TiO2. The crystal size increases at 500 °C (Fig. 2c), leading to well-defined diffraction patterns, as a result of this larger crystal size.

In the following of the study, we decided to adopt a moderate annealing temperature of 350 °C (4 h) for the nanopowder, below the 450 °C temperature limit where complete dehydration is observed by TGA (with a continuous temperature ramp).

3.1.2. Organic curing

A TiO2 paste was prepared with the addition of various organic additives used as binders: (i) Pluronic P123, (ii) PEG 12,000, or (iii) Span80/Tween20/acyetic acid. These organics were chosen as binders and plasticizers to facilitate the film formation. They were added to the anatase nanoparticles previously annealed at 350 °C for 4 h. As these organics must be removed after the film formation, we tested two types of curing: (i) a short thermal treatment (450 °C, 30 min), and (ii) a high intensity UV (300 W in.−2, 15 min). Compared to the initial structure (Fig. 2b), an observation by TEM (Figs. S3 and S4) did not reveal any drastic change in the structure of titania particles, after either thermal or UV curing, irrespective of the type of additive: Pluronic™ P123 (Fig. S3a and b, Fig. S4-I), PEG 12,000 (Fig. S3c and d, Fig. S4-II), and Tween/Span mixture with acetic acid (Fig. S3e and f, Fig. S4-III). We conclude from this TEM analysis, that neither the thermal nor UV curing do modify significantly the structure of TiO2 nanocrystals. This stability was confirmed by XRD performed on the TiO2 film coated onto the FTO substrate, after thermal curing. The diffraction patterns reveal relatively broad diffraction peaks, characteristic of small anatase nanocrystals (Fig. S5).

Both surface area and porosity of the film are two important parameters, and porosity should be typically in the 50–65% range to allow high cell performance [23]. Previous analyses showed that the small size of these nanoparticles create a significant textural
Nitrogen adsorption isotherms for the nanopowder after thermal annealing (350 °C, 4 h), and the same material after addition of the Span/Tween mixture additive, and either thermal (450 °C, 30 min) or UV (15 min) curing: (a) adsorption/desorption isotherms; (b) Pore size distribution deduced from the desorption isotherms. (Materials prepared with Span/Tween additives). 

Fig. 3. Nitrogen adsorption isotherms for the nanopowder after thermal annealing (350 °C, 4 h), and the same material after addition of the Span/Tween mixture additive, and either thermal (450 °C, 30 min) or UV (15 min) curing: (a) adsorption/desorption isotherms; (b) Pore size distribution deduced from the desorption isotherms. (Materials prepared with Span/Tween additives).

Porosity in the mesoporous range, with both specific surface area and porous volume changing with the thermal treatment [10]. We display in Fig. 3, the N₂ adsorption/desorption isotherms for the powder annealed at 350 °C, and the same powder prepared with the Span/Tween mixture plasticizing additive and cured either at 450 °C, or under UV. Fig. 3a shows that all isotherms are rather similar (Type IV isotherms), with a steep adsorption between 0.6 and 0.9 of partial pressure, characteristics of a well-defined mesopore size. The specific surface area calculated via the multipoint BET model, gives values of 130, 160 and 200 m² g⁻¹ for the annealed, thermally cured, and UV cured samples, respectively. Their respective porous volume is 58% for the annealed powder, and 63% for both cured samples. The modeling of the pore size distribution (PSD), using the desorption isotherm, (Fig. 3b) allowed us to assess the possible influence of curing on the material porous structure. The initial PSD lies between 8 and 13 nm. After either thermal or UV curing, a slight broadening of PSD toward larger pores (8–18 nm range) is observed. We assign this PSD shift toward larger values, as a result of the organic additive that acts as a pore promoter and contributes to create some larger pores in addition to the initial PSD. Since the PSD is only broadened toward larger values, not fully shifted, we conclude that the average particle size, and its related textural porosity remain unchanged.

The particle network morphology and their degree of percolation is another important parameter controlling the electron diffusion, which can be quantified by a single factor, the material surface roughness [24]. It can be determined by calculating the surface fractal dimension (Ds) from the N₂ adsorption isotherms curves [25,26]. A value close to Ds=2 means a rather smooth surface, whereas values close to Ds=3 indicates a very rough surface. We compare in Fig. 56 the results obtained for the samples displayed in Fig. 3. The powder after thermal annealing displays a rather high surface roughness (Ds=2.4) (Fig. 56a), and rather similar values are observed after thermal or UV curing with Ds (2.44 and 2.36, respectively). All these values are significantly higher than values of 2.28, previously reported for similar titania thin films prepared for DSSC [24]. This means that our initial nanopowder, beyond its single crystal anatase structure obtained at room temperature, leads to films with an optimized film morphology. Moreover, the film preparation does not alter the material open structure. This was confirmed by a second calculation of the roughness factor by using the following formula [24]:

\[ R = \rho (1 - P) S \]

with R the roughness factor, ∊ the volumic mass of TiO₂ (anatase) (g cm⁻³), P the porosity (%), and S the specific surface area (cm² g⁻¹). The roughness factor was calculated for the three samples displayed in Fig. 3, in μm⁻¹. Values of 218, 236 and 296 μm⁻¹, were obtained for the nanopowder after thermal annealing, and after addition of the Span/Tween mixture additive, and either thermal or UV curing, respectively. Still, this model gives higher values than previously reported in literature (between 88 and 136), which confirms that our nanopowder leads to a film nanostructure favorable for use as a photoanode in DSSCs [24].

SEM analyses confirm that the film obtained by the doctor blade method, with the TiO₂ paste, after thermal curing and UV irradiation, is homogenous and has a good adhesion to the FTO substrate with no cracks or mechanical defects (Fig. 57).

### 3.2. Optimization of the TiO₂ film for dye adsorption and photo-electronic properties

The cell performance is strongly affected by the efficiency of injected electrons from the dye to the conduction band of the TiO₂, which reflects the importance of the way the dye anchored to TiO₂ surface. As it was demonstrated that both UV exposure and HCl treatment improve the photoanode properties [20,27,28], the thermally cured TiO₂ film was additionally activated under UV (10 min) and immersed into a 0.1 M hydrochloric aqueous solution for two hours, then rinsed with DI water until no acid trace could be found in washing water. The major effect of UV exposure is to reversibly create a high concentration of photoactive surface states, which were described as being continuously distributed below the conduction-band edge as shallow electron traps that would be beneficial for electron injection from the dye and transport by thermally activated detrapping [20]. The major effect of acid treatment is to increase the density of protonated sites, which favors multidentate dye adsorption. Another effect of HCl treatment is illustrated by comparing the UV–vis spectra for both films prepared according to the procedure (thermally annealed and cured), and exposed to UV: adding an HCl treatment before dye adsorption increases the absorbance at higher energy (Fig. S8). In addition, a small blue-shift is observed for the bandgap values, from 3.24 down to 3.3 eV, without and with HCl treatment, respectively (Fig. S8, Inset). A similar blue-shift was observed for all samples, which reveals a change in the electronic structure of the thin films surface, probably due to surface hydroxylation.

Many studies have shown that the dye anchors to the TiO₂ surface through different carboxylate anchoring modes, like physically absorbed through hydrogen bonding, or chemisorbed via various
types of chemical bonds (unidentate, bidentate, and bridging), with bridging and bidentate being the most stable ones [20,29,31].

The adsorption of Z907 Dye on the TiO2 surface was characterized by ATR-FTIR spectroscopy. Fig. 4 shows the ATR-FTIR absorption spectra of the Z907 dye adsorbed onto the TiO2 surface. Strong peaks were observed at 1380 cm$^{-1}$ and 1613 cm$^{-1}$ characteristics of the $\nu_{\text{asym}}$(COO$^-$) and $\nu_{\text{sym}}$(COO$^-$), respectively [31,32]. There is no indication of the presence of carboxylic bond at 1716 cm$^{-1}$. There is no indication of the presence of carboxylic bond at 1716 cm$^{-1}$. This indicates that the dye is anchored to the TiO2 surface via bidentate or bridging, not unidentate mode. The saturated hydrocarbon chains are identified by the C–H stretch modes in the 2800–3000 cm$^{-1}$ region with vibration modes of 2852 cm$^{-1}$ and 2924 cm$^{-1}$ for symmetric and asymmetric –CH$_2$–, respectively. The corresponding CH$_2$– peak is observed at 2956 cm$^{-1}$. A broad absorption peak is observed between 3200 and 3400 cm$^{-1}$ (not displayed), corresponding to the –OH stretching modes of hydroxio and aquo ligands.

### 3.3. Photovoltaic properties

Several DSSC devices were fabricated based on the TiO2 films treated under different conditions. Unlike usual testing cells with an active surface area close to 1 cm$^2$, our cells were assembled with an active surface area of 5 cm$^2$. Surface roughness measurements (Fig. S9) show that the whole photoanode is homogeneous, despite the rather basic technology used for its preparation. Using significantly larger surfaces may increase the probability of defects, hence reduce the properties overall, but it gives a more realistic comparison between different options. However, parallel tests conducted on smaller (0.56 cm$^2$) surfaces gave the same results (Fig. S10) as with 5 cm$^2$ cells (Fig. 5a), which demonstrates that the limited performances of our cells, compared with the best reports in the literature, are more relevant on the lack of an optimized simple assembling process than the cell surface itself, which is not a major drawback for the aim of our comparative study on the photoanode material characterization. As specified, all samples were tested three times, and all results were in good agreement, within a 5% variation (see Fig. S11).

Fig. 5a shows the best result obtained with one cell prepared with our nanopowder. The powder was annealed at 350 °C, and the film prepared with the Span/Tween mixture, cured at 450 °C for 30 min, then UV activated for 10 min, and treated with HCl before dye adsorption. The $J$–$V$ characteristics gave an open circuit voltage of 0.764 V and short circuit current density of 9.61 mA cm$^{-2}$ for an incident light intensity of 100 mW cm$^{-2}$. Overall, a power conversion efficiency of 4.93% was achieved. This result demonstrates the potential improvement that the TiO2 nanopowder synthesized by our method could give to DSSC, if one bears in mind that these tests are run on a very large surface (5 cm$^2$) with a non-optimized cell preparation. Fig. 5b illustrates the positive effect of using the HCl immersion before dye adsorption.

Table 1 compares the photovoltaic parameters of devices made with the TiO2 nanopowder, initially annealed either at 350 °C, or 450 °C (all other steps being similar), and with or without HCl treatment. Whatever the annealing temperature, the short-circuit photocurrent density ($J_{sc}$) and the photoconversion efficiency of both HCl-treated TiO2 films are higher than those of the untreated counterparts. After HCl treatment, both $J_{sc}$ and photoefficiency of the sample annealed at 350 °C were increased by 28.4% and 4.5%, respectively; $V_{oc}$ was slightly changed and FF decreased. For the sample annealed at 450 °C, $J_{sc}$ increased by 36.3%, the efficiency by 37.2%, and $V_{oc}$ by 8.6%, after HCl treatment. Proportionally, the improvement is higher with the sample annealed at 450 °C, because the initial dehydroxylation was higher, due to the higher annealing temperature. Nevertheless, the HCl treatment cannot manage to fully overcome the surface dehydroxylation resulting from the 450 °C thermal treatment.

Comparison of photovoltaic parameters of devices made with the TiO2 nanopowder initially annealed at 350 °C (Fig. S12a) or 450 °C (Fig. S12b), and either thermally or UV cured, shows that thermal curing significantly improves the cell properties (the samples were purposely not HCl treated to highlight the curing
parameter influence). A positive contribution is also observed for samples exposed to HCl treatment (Fig. S13; dark current curves are displayed).

Finally, we compared the photovoltaic parameters of devices made with our nanopowder with cells made with a commercial (Degussa) powder (Fig. 6, Table 2). No HCl treatment was applied. Thin films were prepared with the help of either Span/Tween, or Pluronic P123. In both cases, the photovoltaic efficiency of cells prepared with our nanopowder is higher (Span/Tween: 4.67 vs 2.77) [Pluronic P123: 4.21 vs 2.47], compared to the commercial powder.

Another significant difference between our nanopowder and the commercial one is the difference in dye adsorption (Fig. 7; for sample ref, see Table S2 in ESI). UV–vis analyses reveal that the amount of dye molecules initially adsorbed onto samples prepared with Span/Tween is seven times higher than for samples prepared using the commercial TiO2 powder, which we ascribe to our high surface and surface hydroxylation density that result from our specific room temperature synthesis and moderate annealing process.

We carried out an EIS analysis on different configurations to get more insights into the effect of resistances on the cell performance. We display the results obtained with TiO2 films prepared with Span/Tween (Fig. 8a) or Pluronic P123 (Fig. 8b). A large semicircle can be observed in the Nyquist plot, which corresponds to the TiO2/dye/electrolyte triple interface. The interface between the high-frequency semicircle and the intermediate-frequency semicircle is difficult to distinguish due to the strong overlap of the charge transfer resistance on the TiO2 surface and that on the Pt surface. A sub-circle in the low-frequency response is observed, which accounts for the contribution of the diffusion of the electroactive species in the liquid electrolyte [33]. In the dark, the solar cells showed high impedance and the time constants are not well defined. For all devices tested (see Table S2), almost all the impedance parameters show a difference between illuminated and non-illuminated cells. The response at the intermediate interface under dark condition is much higher than the one under illumination, which corresponds to a high capacitance because of the expected accumulation of electrons and redox species at this interface [34]. The lifetimes of the electron were calculated, according to the methodology proposed by Pauporte et al. [35,36], from the low frequency loop parameters of the spectra and the dispersion of the capacitance was obtained according to the

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency %</th>
<th>$R_s$ ($\Omega$)</th>
<th>$R_{sh}$ ($\Omega$)</th>
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</thead>
<tbody>
<tr>
<td>TiO$_2$ 350 °C, HCl</td>
<td>0.738</td>
<td>12.69</td>
<td>42.2</td>
<td>3.95</td>
<td>5.6</td>
<td>125</td>
</tr>
<tr>
<td>TiO$_2$ 350 °C, no HCl</td>
<td>0.727</td>
<td>9.88</td>
<td>52.7</td>
<td>3.78</td>
<td>5.3</td>
<td>120</td>
</tr>
<tr>
<td>TiO$_2$ 450 °C, HCl</td>
<td>0.719</td>
<td>7.99</td>
<td>51.3</td>
<td>2.95</td>
<td>6.7</td>
<td>226</td>
</tr>
<tr>
<td>TiO$_2$ 450 °C, no HCl</td>
<td>0.662</td>
<td>5.86</td>
<td>55.5</td>
<td>2.15</td>
<td>6.7</td>
<td>176</td>
</tr>
</tbody>
</table>

**Fig. 6.** $J$–$V$ curves of dye-sensitized TiO2 films prepared on FTO/glass prepared with the commercial nanopowder (das;) and our sample (line); each was prepared with either Span/Tween (squares) or Pluronic P123 (circles). b: $J$–$V$ characteristics of the solar cells fabricated using our synthesized TiO2 nanoparticles and commercial nanoparticles. The active area of the device is 5 cm$^2$.

**Table 1** Photovoltaic parameters of DSSCs prepared with TiO2 either annealed at 350 °C, or 450 °C, and with or without HCl treatment (all other parameters being equal).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>Efficiency %</th>
<th>$R_s$ ($\Omega$)</th>
<th>$R_{sh}$ ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ 350 °C_Span/Tween</td>
<td>0.72</td>
<td>7.99</td>
<td>51.3</td>
<td>2.95</td>
<td>6.7</td>
<td>226</td>
</tr>
<tr>
<td>TiO$_2$ Degussa_Span/Tween</td>
<td>0.734</td>
<td>5.47</td>
<td>68.9</td>
<td>2.77</td>
<td>4.12</td>
<td>606</td>
</tr>
</tbody>
</table>

**Fig. 7.** UV–vis absorption spectra of the Z907 dye initially desorbed from TiO2 films prepared with different organic additives compared to those desorbed from TiO2 commercial. ‘A’ refers to the synthesized TiO2 nanoparticles prepared with S (Span/ Tween) or P (Pluronic) additives, ‘R’ refers to reference electrodes prepared by TiO2 Degussa with S or P additives. (the numbers beside each electrode refers to its order ).
following equations [35]:

$$C^2 = \frac{R_1}{P_2 P_2^2 T}$$

(7)

$$\tau_c = 2 \pi R_2 C_2$$

(8)

From our results (Table S2), it appears that the cells prepared with our material have a longer electron lifetime than the reference cells (commercial TiO2 powder) [34]. This observation seems in contradiction with the I–V measurements, but it must be compared under the light of differences in film thickness, hence resistance, as checked by profilometry (Fig. S9) [37]. The cells made with the reference commercial TiO2 powder, showed an electron lifetime six times shorter for recombination under illumination compared to the cells made with our nanocrystalline TiO2 material. Higher electron lifetime leads to significant electron transfer, and thus, an improved $J_{sc}$. Therefore, EIS analysis confirms the promising results obtained with cells assembled with our synthesized nanocrystalline material.

4. Conclusion

Thanks to the successful synthesis of small crystalline TiO2 anatase nanoparticles by a novel soft chemistry method, we managed to demonstrate in the present study that precocrystalline nanoparticles can be successfully prepared, i.e. fully dehydrated, by a moderate thermal annealing, without involving a nanoparticle growth that could hamper photoactive properties. This method allowed us to fully decouple the crystallinity, achieved at room temperature, and the crystal size, which remained restricted because of the lack of high temperature treatment.

It results from the specific structure of this material that the photoanodes prepared for DSSC application, present excellent textural features, like high porosity and surface roughness, which make them excellent candidates for this application, especially for dye adsorption. Indeed, after some additional improving operations such as UV exposure and HCl treatment, all cells present a much larger photoefficiency than similar cells made with commercial TiO2 powder usually used in these devices.

We assembled deliberately large area DSSCs, with a 5 cm$^2$ active surface – to compare with the usual 1 cm$^2$ active surface used in most of the literature – in order to provide a realistic comparison between the different optimization parameters. Our best result gave a photoefficiency of 4.9%, and a preparation method based on the following steps: (i) annealing the nanopowder at 350 °C for 4 h, (ii) mix with either Pluronic P123 or a Span80/Tween20/acetic acid mixture used as film plasticizers, (iii) cure the organics by a short thermal treatment at 450 °C (30 min), (iv) expose to high UV irradiation for surface activation, and (v) immersed in HCl aqueous solution for improved surface hydroxylation before dye anchoring.

In addition to the optimized film nanostructure, we showed that the amount of adsorbed dye for our TiO2 films was seven times higher, compared to the amount actually absorbed on a commercial powder after the same treatment. The internal resistance of the cells were checked with EIS analysis, which shows higher electron lifetime, smaller charge transfer resistance for
counter electrode and high recombination resistance compared to the commercial cells.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.solmat.2016.04.004.

References
