



## Solution processable titanium dioxide precursor and nanoparticulated ink: Application in Dye Sensitized Solar Cells



Pau Bosch-Jimenez<sup>a</sup>, Youhai Yu<sup>b</sup>, Mónica Lira-Cantu<sup>b</sup>, Concepción Domingo<sup>c</sup>, José A. Ayllón<sup>a,\*</sup>

<sup>a</sup> *Departament de Química, Universitat Autònoma de Barcelona, Campus UAB, 08193 Bellaterra, Spain*

<sup>b</sup> *Centre d'Investigació en Nanociència i Nanotecnologia (CIN2, CSIC-ICN), Campus UAB, 08193 Bellaterra, Spain*

<sup>c</sup> *Institut de Ciència dels Materials de Barcelona (CSIC), Campus UAB, 08193 Bellaterra, Spain*

### ARTICLE INFO

#### Article history:

Received 6 September 2013

Accepted 3 November 2013

Available online 19 November 2013

#### Keywords:

Titanium dioxide

Dye Sensitized Solar Cells (DSSCs)

Proton Nuclear Magnetic Resonance

(<sup>1</sup>H NMR)

Nanoparticles

Ink

Low-temperature

### ABSTRACT

Colloidal TiO<sub>2</sub> anatase nanoparticles of 4–8 nm diameter capped with 3,6,9-trioxadecanoic acid (TODA) were synthesized at low temperature using water and ethanol as the solvents. ATR-FTIR and <sup>1</sup>H NMR characterization showed the capping acid capability of stabilizing the TiO<sub>2</sub> nanoparticles through labile hydrogen bonds. The presence of the capping ligand permitted the further preparation of homogeneous and stable colloidal dispersions of the TiO<sub>2</sub> powder in aqueous media. Moreover, after solvent evaporation, the ligand could be easily eliminated by soft treatments, such as UV irradiation or low-temperature thermal annealing. These properties have been used in this work to fabricate mesoporous TiO<sub>2</sub> electrodes, which can be applied as photoanodes in Dye Sensitized Solar Cells (DSSCs). For the preparation of the electrodes, the as-synthesized mesoporous TiO<sub>2</sub> nanoparticles were mixed with commercial TiO<sub>2</sub> (Degussa P25) and deposited on FTO substrates by using the doctor blade technique. A mixture of water and ethanol was used as the solvent. A soft thermal treatment at 140 °C for 2 h eliminated the organic compound and produced a sintered mesoporous layer of 6 μm thickness. The photovoltaic performance of the DSSCs applying these electrodes sensitized with the N3 dye resulted in 5.6% power conversion efficiency.

© 2013 Elsevier Inc. All rights reserved.

### 1. Introduction

The increasing world energy demand and the problems associated with fossil fuels highlight the need to develop clean, sustainable and economically viable alternatives, such as solar cells. A key issue in this scenario is to have a technology capable of producing a large number of solar cells in a short time and with a low energy payback time (EPT) [1]. Dye Sensitized Solar Cell (DSSC) is a prospective solution to convert solar power into useful electrical energy. The great interest in this type of solar cells is justified by the important potential advantages over other photovoltaic technologies: low production cost, low EPT, use of materials of standard purity, good efficiency under diffuse light and at high temperatures, and adaptability to a large diversity of designs (transparency, colorful, flexible, lightweight, bifacial cells, etc.) that would facilitate their integration into buildings or appliances [2,3]. However, in order to be competitive with current inorganic solar cells, DSSC technology must increase power conversion efficiency, reduce fabrication cost and increase lifetime. The reduction of fabrication costs requires a cutback in the environmental and economic costs [4].

Low temperature procedures, involving the elimination of the sintering steps of the TiO<sub>2</sub> electrode at high temperature (~450 °C), could be advantageous to achieve this objective. Currently, TiO<sub>2</sub> DSSCs showing record efficiencies in the order of 12% require two annealing steps at high temperature, the second one after treatment of the TiO<sub>2</sub> mesoporous layer with a TiCl<sub>4</sub> solution [5,6]. Low temperature processed electrodes results in DSSCs with lower power conversion efficiency [7–12] and mechanical stability than electrodes sintered at high temperature [13]. Some of the main drawbacks observed in TiO<sub>2</sub> electrodes fabricated at low-temperature are variable quality of the film due to irregular distribution of the nanomaterial in the film and appearance of cracks, voids or pinholes that are mainly originated by an inadequate or inhomogeneous texture of the TiO<sub>2</sub> precursor paste [13]. To design low-temperature fabrication efficient methods of TiO<sub>2</sub> electrodes, the use of high boiling temperature organic compounds should be avoided. Hence, the use of water and/or ethanol user-friendly solvents to the formulation of TiO<sub>2</sub> inks is desirable. Other volatile additives applied in low quantity, such as HCl or NH<sub>3</sub>, can also be added; but organic compounds with high boiling points, frequently used as additives to control the viscosity of the paste and the porosity of the resulting film, must be avoided [14,15]. On the other hand, the intimate contact between nanoparticles is mandatory to reach a good electron transport, but it is hard to achieve in

\* Corresponding author. Fax: +34 93 581 2176.

E-mail address: joseantonio.ayllon@uab.es (J.A. Ayllón).

processes performed at low temperature. An attractive alternative to increase nanoparticles contact introduced by Hagfeld et al. [16] was the application of high pressure on the film, resulting in increased DSSCs efficiencies up to 7.6% [17,18].

A different explored strategy consists in the fabrication of colloidal TiO<sub>2</sub> pastes involving a mixture of preformed anatase nanoparticles and a molecular TiO<sub>2</sub> precursor [19,20]. After a thermal or UV treatment, the molecular TiO<sub>2</sub> precursor is transformed into nanocrystallites of TiO<sub>2</sub> that act as cement between the different nanoparticles. In this route, the thermal sintering is replaced by a chemical process, in which the connection between nanoparticles is done by deposition of additional TiO<sub>2</sub> [21]. The easiest developed methodology consists in the use of a mixture of a titanium(IV) alcoxide precursor and preformed TiO<sub>2</sub> nanoparticles [8,9,22]. However, this route has the shortcoming of the difficulty of controlling the degree of alcoxide hydrolysis during the manipulation and/or storage of the paste. In a similar approach, the titanium molecular precursor is replaced by small size titania nanoparticles (<10 nm) that act as a glue due to its great tendency to aggregate and to get anchored to the larger titania nanoparticles [23,24].

Without surface ligands, colloidal nanoparticles have a strong tendency to aggregate, which is accentuated as the particle size is reduced. Surface modification of inorganic colloids with organic ligands is a common method applied to facilitate further processing as inks. The coating allows thin film deposition from colloidal dispersions by different processes, such as spray-coating, ink-jet printing [25–27]. Particularly, TiO<sub>2</sub> thin films have a wide range of applications as optical coatings, gas sensors, protective layers of transparent conductive coatings and in optoelectronic devices, catalytic processes, etc. Therefore, easily processable colloidal TiO<sub>2</sub> ink is a focal material to develop. The stability of colloidal dispersions in different solvents is determined by the nature of the ligands anchored to their surface. On the other hand, the presence of capping ligands could be a drawback for many applications that require a close contact between deposited nanoparticles. Frequently, a thermal processing at high temperature is necessary to remove the organic coating and to allow for the direct contact between nanoparticles, which limits both the materials and the processes that can be used [28,29].

In this work, the use of 3,6,9-trioxadecanoic acid (TODA) as a capping ligand for TiO<sub>2</sub> is described. This ligand has sufficient affinity to the titania surface to stabilize the nanoparticles as a colloidal dispersion in aqueous solvents. Moreover, the capping agent can be easily removed with a simple and smooth post-treatment. This precursor is further applied in the formulation of colloidal inks, which permit the preparation of TiO<sub>2</sub> mesoporous layers at low temperature to be employed as photoanodes in DSSCs.

## 2. Experimental methods

### 2.1. Reagents

All chemicals used in this work were commercially available and were used without further purification: titanium(IV) isopropoxide (TTIP, 97%, Aldrich), 3,6,9-trioxadecanoic acid (TODA, 98.4%, Aldrich), hydrochloric acid (HCl, 37%, Panreac) and ethanol (EtOH, 99.5%, Panreac). TiO<sub>2</sub> Degussa P-25 (80% anatase–20% rutile) was kindly gifted by Degussa (Spanish delegation). Ultra pure water (Milli-Q system, conductivity lower than 0.05 μS cm<sup>-1</sup>) was used.

### 2.2. TODA@TiO<sub>2</sub> nanoparticles synthesis

TODA (0.301 g, 1.66 mmols) was dissolved in ethanol (40 mL) and 1.0 mL of hydrochloric acid (37%) was added. Then, titanium

isopropoxide (5 mL, 16.9 mmols) was added and a clear solution was obtained after moderate agitation. This solution was slowly added over a reactor containing boiling water (250 mL). The volume of the clear suspension so obtained was reduced to 40 mL by solvent evaporation at boiling temperature. The recovered white suspension was then ultrasonicated during 25 min to obtain a slightly yellow translucent suspension. The white solid material was isolated from the suspension by slow water evaporation at 50 °C. The recovered solid residue was crushed in a mortar and treated as a water redispersible powder. The TiO<sub>2</sub> percentage by weight was estimated as 78% by measuring the weight reduction after annealing (30 min at 450 °C). The concentrated translucent colloidal solution obtained after sonication was used either as obtained or diluted with ethanol (3 mL ethanol for each 1 mL of colloidal suspension) to deposit thin films by spin-coating.

### 2.3. TiO<sub>2</sub> ink formulation

The optimized composition includes a mixture of 0.750 g of solid TODA@TiO<sub>2</sub> powder and 1.750 g of TiO<sub>2</sub> Degussa P25. The combined solids were suspended in a mixture of 3 mL of H<sub>2</sub>O and 2 mL of EtOH.

### 2.4. Solar cell fabrication

The FTO glass (Solems SnO<sub>2</sub>:F, 7–10 ohm/sq) was first cleaned for 20 min in a detergent aqueous solution (Empigem BB, Aldrich) using an ultrasonic bath, then rinsed with ultra pure water and ethanol and dried under N<sub>2</sub> flux. Finally, it was cleaned for 20 min in a UV-O<sub>3</sub> surface decontamination system (Novascan, PSD-UV, Novascan, IA, USA) connected to an oxygen gas source. TiO<sub>2</sub> porous layers were deposited by doctor blade technique. After drying at room temperature, different treatments were studied to promote the sinterization of the pre-formed TiO<sub>2</sub> layer: thermal treatment and/or UV light irradiation. The heating was performed in a conventional oven with forced ventilation at temperatures in the 90–140 °C range. For ultraviolet irradiation treatment, films were located at 8 cm from a medium-pressure Hg lamp (125 W, HPK Cathodeon) and no filter was placed between the lamp and the sample. The electrodes were immersed into a 0.5 mM solution of N3 dye (Greatcell Solar S.A.) in ethanol and kept at room temperature for 24 h to assure complete sensitizer uptake. The dye-sensitized TiO<sub>2</sub> films were rinsed with acetone and dried under nitrogen before being used. A Pt back electrode (made by e-beam deposition) was attached by the Surlyn hot-press film. The final active area was 0.2 cm<sup>2</sup>. The electrolyte Iodolyte AN-50 and the N-719 dye, were all purchased from Solaronix.

### 2.5. Characterization

XRD spectra were recorded on a Rigaku Rotaflex RU-200B diffractometer with Cu Kα radiation (λ = 1.5418 Å). Ultraviolet–visible (UV–vis) spectroscopy was performed using a UV Helios γ Thermo Electron Corporation spectrophotometer. Aqueous suspensions were used to register the UV–Vis absorption spectra of the nanoparticles. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded in a Perkin Elmer apparatus (Spectrum One, model equipped with a Universal ATR Sampling Accessory). <sup>1</sup>H NMR spectra were recorded on an NMR-FT Bruker AC-250 MHz spectrometer in D<sub>2</sub>O; chemical shifts are referenced to the residual proton signal of the deuterated solvent and are given in ppm. SEM images were recorded with a Zeiss Merlin FE-SEM microscope operating at 1 kV. EDX Electron-diffraction patterns and high-resolution transmission electron microscopy (HR-TEM) images were recorded in a JEOL 2011 microscope operated at 200 kV. Textural properties of the porous TiO<sub>2</sub> layer were

Download English Version:

<https://daneshyari.com/en/article/607430>

Download Persian Version:

<https://daneshyari.com/article/607430>

[Daneshyari.com](https://daneshyari.com)