Heteroacoagulation of Lignocellulose Fibers-based biotemplates and functionalized TiO₂ nanoparticles to tailor films microstructures

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Abstract

The heteroacoagulation of lignocellulose nanofibers (LCNF) with functionalized TiO₂ nanoparticles (NP) is presented as an innovative revalorization strategy for the exploitation of lignocellulose wastes. Their use as bio-templates could be considered a promising alternative in a current biorefinery scheme since the massive production of porous materials with numerous nanotechnological applications could be offer new alternative exploitation routes.

The surface modification of TiO₂ NP by adsorption of polyetilenimine (PEI) favors its coupling with LCNF through a peptide bond during heteroacoagulation in aqueous suspension. The functionalization of LCNF with TiO₂ NP allows forming core-shell nanostructures to shape and sinter coatings at low temperature (450°C), where the LCNF used as templates for porous shaping, burn during the nanostructure consolidation. In this work, the inclusion of bioresources (LCNF templates) in the semiconductor microstructure is discussed in terms of dye loading (by UV-Visible Spectroscopy), photovoltaic efficiency and charge transfer (by Electrochemical Impedance Spectroscopy, (EIS) in a Dye Sensitized Solar Cell (DSSC)). Results confirm that the TiO₂/template network yielded better photoefficiency and electron transport properties than mesoporous films assembled only from TiO₂ NP. The preparation of TiO₂-based photoanodes with enhanced performances (with an efficiency value around 6%, for a thickness of 8.7 μm) allows validating the successful colloidal procedure herein employed.

Keywords

lignocellulose exploitation, Heterocoagulation, Bio-template, Semiconductors, TiO₂, films microstructure

1. Introduction

Although in the last years the cellulose market has growth, achieving around \$250 million in 2014 and an increase of 19% in 2019, the most of lignocellulosic biomass is still burnt in the field causing, air pollution, risk of fire and other environmental drawbacks. The development of a bio-based economy requires the exploitation of lignocellulosic residues in a cost-effective way. The economic feasibility of lignocellulosic biomass-based sectors is hindered by our lack of understanding about the biomass structure and industrial processes (Khatri et al. 2018). For these reasons, extensive research efforts are focused on looking for new effective and useful niches of application for the lignocellulose from agricultural wastes. Among them, renewable and biodegradable biomass fibers have been developed to get sustainable and green materials(Arevalo-Gallegos et al. 2017). Under this approach, the development of composites derived from bioresources with lignocellulosic fibers as reinforcement is currently a relevant research area (González et al. 2013; Espinosa et al. 2017a) while the production of cellulosic fibers in nano dimensions has led to promising results as nanotemplates in composites and inorganic materials. In this field, cellulose nanofibers (CNFs) are used for processing 3D nanostructures providing extremely large porosity and specific surface area for high-performance energy harvesting and storage devices (Li et al. 2014a; Wang et al. 2017) or catalyzers to efficiently remove Cr(VI) (Djellabi et al. 2019; Xia et al. 2020a) or pesticide contaminants (Komal et al. 2020). Guo et al. (Guo et al. 2012) employed a hierarchical template made of filter papers with natural cellulose for the preparation, via sol-gel, of hollow SiO_x nanotubes. In 2014, Li et al. (Li et al. 2014b) describes the efficient photoelectrochemical water splitting provided by a hierarchical 3D TiO₂ fiber-nanorod heterostructure synthesized combining atomic layer deposition and vapor deposition techniques using cellulose nanofiber (CNF) as template. Wang et al. (Wang et al. 2012) reported a template growth of TiO₂ nanotubes by adsorbing a precursor solution of Ti(OBu)₄ into filter papers of cellulose. In these works, current procedure to prepare metal oxides-cellulose nanocomposites is based on the wet synthesis of the inorganic phase in a CNF solution(Komal et al. 2020; Xia et al. 2020b). In the field of

renewable energy resources, clean and low cost manufacture of high efficient solar cells, its architectural integration and its high performance under low irradiance conditions and/or indoor environments, continues being a challenge (Bella et al. 2017). The photoelectrochemical responses of these devices depend on the inherent properties of the strategic raw materials (i.e. rare earths or noble metals), but also the efficient capacity of semiconductor materials, mainly doped TiO₂, requires well consolidated porous micro- and nanostructures with large specific surface area and high electron transfer efficiency (Chen and Mao 2007; Hagfeldt et al. 2010)(Gonzalez et al. 2016) . Many attempts to improve the photoresponse of the TiO₂ films aims an enhanced reactant–catalyst contact through the design of complex structures with large surface-to-volume ratio. The TiO₂ structure and photoactivity can be controlled by tuning the semiconductor physical properties (particle size, crystalline phase, preferred orientation) (Maitani et al. 2017) as well as by optimizing the shaping of the TiO₂ hosting material, paying attention to factors that are imperative to the precursors mixture or the slurry preparation, and the films deposition, such as rheological behavior, stability and dispersion of particles, method used, etc. (Sharifi et al. 2014) Among the deposition techniques that can be used to prepare ordered porous films, the endo-templates are commonly used since the pore's dimensions can be determined by the size of the ordered template beads (Asim et al. 2014), offering a high control over the physical features of the shaped films. Complementarily, replica of templates or exo-templates are usually used in combination with another physical or chemical method to improve packing or allow secondary microstructures. Mesoporous thin films, required for an efficient response, are conventionally prepared by surfactant assisted sol–gel techniques such as the evaporation-induced self-assembly (EISA) or the evaporation-induced micelles packing (EIMP) (Sanchez et al. 2008). However, although sol-gel technology allows the molecular design of the films composition, it is associated to complex procedures with numerous steps which should overcome the poor quantity of active material and the limited reactive surface area resulting from a small thickness and/or the low dimension of the substrate or piece (Dewalque et al. 2011). The use of alternative shape-persistent templates is a more advantageous route since they have a defined shape that is maintained throughout the entire process with no any further influence derived from the reaction conditions (Ivanova et al. 2014). The use of

bioresources, coming from agricultural biomass, have raised special attention in the policy context in relation with the concept of circular economy or circular model. The main challenge is aiming to recover, recycle and re-use materials for end applications with more sustainable business models. In this context, the exploitation and revalorization of bioresources as template is an innovative alternative route owing to offer an extensive variety of controllable nanostructures with morphological complexity and generally they can be easily removed (Lu et al. 2013; Thomas et al. 2018).

Concretely, the use of lignocellulosic nanofibers (LCNF) is a very interesting alternative due to their unique features and wide range of applications (Chen et al. 2016; Srisasiwimon et al. 2018)(Satari et al. 2019). Due to their great availability, low cost, biocompatibility and degradability, LCNF are widely used as a large-scale renewable 3D mesoporous structure. They are composed by linear chains of β -1, 4 linked D-glucose units, from of several hundreds to many thousands, which contains multiple hydroxyl and carboxyl groups as well as ether bonds, which support affinities and active sites to the dispersion and growth of inorganic NP (Xiao et al. 2017). Moreover, the large hydrogen bond network of LCNF builds up a hierarchical structure and provides enough space with formation of metallic oxide. The residual OH- groups of cellulose acting as efficient hydrophilic active sites can accelerate the growth of metallic oxide particles (Boury and Plumejeau 2015; Espinosa et al. 2017b). It exhibits high mechanical strength and is also potentially useful for proton conduction (Wang et al. 2019)

In photoanodes, the large surface area offered by the CNF network as a template provide a relevant merit to achieve high photoelectrochemical performance in DSSC design. Ivanova, A. et al. (Ivanova et al. 2014) described the preparation of TiO₂ porous films with a thickness of 1.8 μ m using a direct nanocrystalline cellulose (NCC) templating approach, which was used as photoanode with a efficiency value of 3.12%. Ghadiri et al. (Ghadiri et al. 2010) reported significantly enhanced electron transport properties and an efficiency value of 7.15% for thickness films of 9 μ m. In both cases, the preparation of the TiO₂ templated by cellulose-based materials required of much more complex syntheses routes. Besides, the cellulose used did not come from revalorized wastes. They are nanocrystalline cellulose and 100% pure cotton wool as template sources. Moreover, most of the published works on the performance of photovoltaic devices

fabricated with CNF are mainly focused on the processing parameters of the cellulose or the TiO₂ synthesis. They don't pay especial attention to the description of the dispersion and networking development between both phases in the resulting suspension, key knowledge to obtain homogeneous composites.

A simple way to achieve homogeneous composites materials is mixing well-dispersed systems involving at least two types of particles by concerning aggregation processes (Cao et al. 2020). In this work, we propose a novel and simple strategy to prepare LCNF-TiO₂ hybrids nanomaterials consisting on the intercalation of commercial TiO₂ NP with LCNF, obtained from agricultural biomass, by a colloidal heterocoagulation method. The assembly of both nanostructures, using a polyelectrolyte as surface modifier of the commercial NP, was successfully implemented. Colloidal manipulation and control of the interparticle forces in liquid media is a key issue to break down weak agglomerates, stabilize and facilitate materials mixing (Damasceno and Zarbin 2018). In addition, processes of electrical charge generation favors the particles dispersion, removing heterogeneities and defects that could extensively degrade the properties of the final material (Franks et al. 2017). The composite films were shaped using dip coating method to achieve full covering conductive FTO substrates that were subsequently mild thermally treated to remove the LCNF template and consolidate the TiO₂ microstructure. The effect of the bio template in the tailored TiO₂-LCNF structures were finally evaluated by analyzing their photovoltaic performance as DSSC.

2. Experimental

2.1. Materials characterization

All chemicals were of reagent grade and used without any further purification.

To prepare the TiO₂ colloidal suspensions, the as-received TiO₂ powder (Aeroxide P25, Evonik Degussa GmbH, Germany), with a density of 4.2 g/cm³, specific surface area of 50±15 m²/g and an anatase to rutile ratio of 80:20 was dispersed in deionized water at pH=8 using 6 wt. % (referred to powder) of branched polyethylenimine (PEI, pKa 8.6, Mw 25,000 mol/g, Sigma Aldrich, USA) a stabilizer additive. This polyelectrolyte helps to stabilize the TiO₂ nanoparticles in suspension by providing an electrosteric mechanism of repulsion among them. Although it could be effectively adsorbed at pH 11, where the TiO₂ particles surfaces are more negatives, their amino groups would be partially

deprotonated with the retracted chain over the particle surface (in a train conformation) (Verde et al. 2012). Therefore, the pH 8 was selected in order to have more protonated amine groups favoring the adsorption (with a train configuration) and the later interaction with the surface of nanofibers. More data about the specific procedure has been previously described elsewhere (Gonzalez et al. 2019). The suspension was ball milled during 90 min using Al₂O₃ balls. The resulting suspension of TiO₂ NP modified with PEI was herein labelled as TiO₂-PEI.

Lignocellulosic nanofibers (LCNF) were obtained by cooking wheat straw come from the biomass residues. The pulp used to obtain the LCNF was obtained following the conventional soda-based pulp production method and then the LCNF were isolated by mechanical process and a high pressure homogenization process. The complete description of the obtaining procedure has also been described previously elsewhere (Espinosa et al. 2016).

Two different dispersion methods, ultrasound and mechanical disagregator, were applied on aqueous LCNF suspensions (prepared at pH = 7). The particle size distributions of the LCNF were measured at different ultrasound power (50-100%) and different disagregation speed (190-590 rpm). The application time (1-5 minutes) of both strategies dispersion was additionally considered to achieve the higher dispersion level. The US effect was studied by sonication, using a high intensity ultrasonic horn (24 kHz, titanium T13 tip, Sonopuls HD 2200, Bandelin Electronic, Germany). The LCNF stability was then determined in terms of zeta potential and particle size distribution, optimizing the pH value in which the surface charge is enough to favor the interaction repulsion forces among cellulose fibers.

2.2. Preparation of LCNF-TiO₂ composites

The preparation of the LCNF/TiO₂-PEI structures was carried out by adding the TiO₂-PEI slurries on the LCNF ones inducing heterocoagulation. Both the surface charge of LCNF as well as the exactly amount of TiO₂-PEI NP to completely cover the LCNF surface were also evaluated in terms of zeta potential. The laser Doppler velocimetry was the methodology used to determine the zeta potential values by using the same Zetasizer Nano ZS (Malvern, UK), mentioned previously. Suspensions used for determination were prepared with concentrations of 0.1 g/L using 10⁻² M KCl (Panreac, Spain) as solvent and

inert electrolyte to maintain the ionic strength of the suspension medium. The pH adjustments of the suspensions were carried out by addition of small aliquots of 0.1 M nitric acid (HNO₃, Sigma Aldrich, USA) or Tetramethylammonium hydroxide (TMAH, Sigma Aldrich, USA) and controlled with a pH probe (Metrohm AG, Germany). Additional FTIR and XRD analyses of the LCNF/TiO₂-PEI mixes were also made to study the interaction between both materials and the evolution of the composite fabrication. Fourier-transform infrared (FTIR) spectroscopy of composites materials were performed using ATR mode, with a Perkin-Elmer Spectrum BX spectrometer, in the range of 400–4000 cm⁻¹ with a resolution of 2 cm⁻¹. X-Ray diffractometer (Siemens-Bruker D8 Advance, Germany) using Cu K α radiation (λ =1.540598 Amstrongs) was used to identify the crystalline phases. The diffraction patterns were measured step by step (0.05° in 2 θ). Particle size and morphology of the resulting composites were also examined by field emission scanning electron microscopy (FESEM) in an S-4700 microscope (Hitachi, JAPAN).

After the structure composite assembly, the remaining chemicals were eliminated by removing the supernatant after centrifugation and the resulting wet powder was washed several times with ethanol. The cleaned precipitate, still wet (without drying process to avoid the agglomerates formation), was re-suspended in a desired amount ethanol solution (2% v/v) in order to perform the dip coating studio of the nanocomposite suspensions. 2 wt. % (respect to the LCNF weight) of Pluronic® F-127 (Sigma-Aldrich, USA) was added to the composite suspension to favor its wettability.

Rheology of LCNF/TiO₂-PEI suspensions was first 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±0.5°C. Rheograms were determined to adapt the viscosity of the suspensions to the mentioned shaping technique. A thermogravimetric analysis (TGA) (Perkin Elmer, USA) of the compound suspension was made to determine the decomposition temperature of the organics in air. The test was carried out with constant heating rate of 10°C/min up to temperature of 600°C. According to the results of the thermal characterization,

the LCNF/TiO₂-PEI coatings were further sintered in air at 450°C for 15 min, with heating and cooling rates of 5°C/min.

2.3. Shaping method and films characterization

The withdrawal rate of the dip coating process was optimized in previous work (Gonzalez et al. 2019) to avoid these microstructural defects. All samples were made at withdrawal rate 2.5 mm/s. FTO conducting glass (Dyesol, 15 Ω/sq, Italy) were used as substrates. The coatings thickness was increased by sequential deposition of several layers where a thermal stabilization step between each layer was made by heating the fresh film during 2 minutes on a hot plate at 100°C.

The films microstructure and thickness were characterized by FEG-ESEM XL30 (FEI) with an accelerating voltage of 5 kV under high vacuum.

TiO₂ coatings were sensitized by a Ruthenium complex-based dye, N-719 dye (Solaronix, Switzerland), dissolved in ethanol up to 2.7×10^{-4} M. The coatings were cleaned by UV-O3 for 15min right before the dye adsorption. Electrodes were immersed in the dye solution overnight at room temperature.

The dye loading of the shaped electrodes was measured by UV-VIS spectroscopy with a Perkin Elmer UV-vis Spectrometer Lambda 14 P. The absorbance values of the aqueous solutions (10^{-3} M of potassium hydroxide (KOH, Panreac, Spain)) where dye was previously desorbed were analyzed. A calibration curve was used to calculate the experimental extinction coefficient of N-719 dye, which is $12900 \text{ (mol/L)}^{-1}\text{cm}^{-1}$ at 500 nm. For the dye loading measurements, the area of all the coatings was normalized and determined by image analysis using the GIMP software.

2.4. Assembly and characterization of DSSC

The assembly of the Dye Sensitized Solar Cell (DSSC) was carried out by a conventional procedure at room temperature. Counter electrodes were composed of a FTO conducting glass substrate (Dyesol, 15 Ω/sq) coated with a platinum layer to catalyze electron transfer. The Pt coating was obtained by sputtering performed at 30 mA intensity during 80 s and at a working distance of 3 cm. The electrodes were separated by a polymer spacer SX-1170-60 (60 μm-thick) applied under spring pressure and heating (100°C 30min in an oven). A home-made electrolyte solution composed of 0.6 M 1-butyl-3-methylimidazolium iodide (Sigma Aldrich, USA), 0.03

M iodine (Sigma-Aldrich, USA), 0.1 guanidine thiocyanate (Sigma-Aldrich, USA) and 0.5 M 4-tert-butylpyridine (Aldrich Chemistry) in acetonitrile (ABCR GmbH and Co., Germany)/valeronitrile (Aldrich Chemistry, USA) (85/15, v/v) was prepared and introduced via vacuum backfilling in a hole drilled in the Pt-coated FTO counter-electrode. The hole was sealed with SX-1170-60 polymer and a cover-glass.

Photovoltaic performances were evaluated into a class A solar simulator purchased from Newport Spectra Physics coupled with a Keithley 2400 SourceMeter. Photocurrent-voltage curves were measured under 0.7 SUN simulated illumination (filter AM 1.5). The electrode active area was set to 0.2064 cm² with a mask. Electrochemical impedance spectroscopy (EIS) was performed using a BioLogic SP-200 potentiostat (Science Instrument) and data were analyzed with the EC-Lab software. 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 10⁶ 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

3.1. Colloidal Characterization

Colloidal characterization of the synthesized LCNF (Espinosa et al. 2016) was carried out to understand their behavior in the liquid media. Two different dispersion methods were followed by determining the particle size distribution of the LCNF suspended. When the ultrasound was used, the particle size of the fibers dispersed showed a bimodal volume distribution (Fig. 1a) with peaks centered at 70 and 250 nm. On the other hand the use of a mechanical disagregator shows a particle size distribution with a narrow peak centred on 250 nm (Fig. 1b). The presence of the smaller particle size indicates that US treated LCNF are partially broken or untied to a less homogeneous stage which could impede its effective and homogeneous interaction with the TiO₂ NP. Consequently, dispersion method selected for these materials was the mechanical disagregation.

The stabilization of TiO₂ NP in deionized water was previously described elsewhere (Gonzalez et al. 2019; Sangiorgi et al. 2019). Zeta potential measurements were made to study the surface charge balance of bare NP as well as the adsorption of the branched structure of the polyelectrolyte PEI as dispersant additive (PEI-TiO₂). 6 wt. % of branched PEI was adsorbed on the negative TiO₂ surfaces at pH 8 producing a variation in the zeta potential values from -30 mV to +66 mV. Despite the interaction forces were higher after modification, the particles presented an agglomeration factor of 3, which could affect to the direct contact with the LCNF and therefore to the fabrication of the final composite.

Zeta potential as a function of pH for LCNF and TiO₂-PEI NP (Fig. 1c) was determined to follow their surface behaviour and select the working conditions to produce core-shell nanostructures. Surface charge balance of the TiO₂-PEI NP is positive as a consequence of the adsorption of the cationic polyelectrolyte to the NP surface. On the other side, the surface of the LCNF is negative for the whole pH range as a consequence of the deprotonation of the carboxyl groups (-COOH) as the pH is raised, which increased the anionic charge of the LCNF (Selkälä et al. 2018). At a pH value of 8 (dash square in Fig. 1c), the zeta potential of TiO₂-PEI particles is +66 mV, whereas the value for the LCNF is -40 mV. Then a pH value of 8 was selected as the working pH to achieve the heterocoagulation effect between the negative charged LCNF and the protonated TiO₂-PEI nanostructures

Fig. 1. Dv50 values of the LCNF dispersed by a) 1 min of US and b) 5 min of US at 592 rpm. c) Evolution of Zeta potential of TiO₂-PEI and LCNF as a function of pH

3.2. Preparation and characterization of the LCNF/TiO₂-PEI composites

At the selected colloidal conditions, the individual dispersion of each entity is promoted due to repulsive forces. To fabricate the LCNF/TiO₂-PEI core-shell nanostructure, two stabilized suspensions were separately prepared. The TiO₂-PEI suspension was poured into the LCNF dispersion at different ratios provoking an attractive network development between NP and nanofibers. Positive charged NP approach and neutralize negative sites in nanofibers as outlined in Fig. 2a. Formation of the composite structure was evaluated by monitoring the zeta potential evolution when TiO₂-PEI was added. Fig. 2a shows the neutralization/saturation curve of the LCNF surfaces by the addition of different amounts of TiO₂-PEI NP. Moreover, the inserted pictures also schematize the progressive adsorption of TiO₂-PEI NP onto the

nanofibers. The LCNF capability of adsorption of TiO₂-PEI NP increases until reaching a maximum zeta potential value. A 1000 wt.% of TiO₂-PEI NP adsorbed onto LCNF, calculated on the basis of LFCN weight, leads to positive surfaces (35 mV) indicating that the TiO₂ extensively covers LCNF. No further variation in zeta potential values was observed with higher additions of TiO₂-PEI NP percentages. The picture in Fig. 2b evidences the clear improvement of the suspension stability when 1000 wt.% of TiO₂-PEI is added to the LFCN suspension, while FESEM micrographs illustrate in detail the LCNF/TiO₂-PEI composite formation in Fig. 2c and d.

Fig. 2. a) Evolution of Zeta potential of LCNF vs the amount of TiO₂ NP, b) Picture of the LCNF/TiO₂ suspensions with different organic/inorganic ratios and c, d) FESEM images of a resulting LCNF/TiO₂ nanostructures at different magnifications.

To explore the formation of the TiO₂-PEI-LCNF network, four samples, labelled as LCNF 100%, LCNF-10%TiO₂, LCNF-100%TiO₂, and LCNF-1000%TiO₂, were fabricated by varying the percentage of added TiO₂-PEI (0, 10, 100 and 1000%). Fig. 3a shows the X-ray diffraction patterns for the pure LCNF and the composites TiO₂-PEI-LCNF after heating at 80°C. LCNF 100% diffractogram displayed peaks at 16.2°, and 22.1°, corresponding to

the (110), and (200) crystallographic planes, respectively, which are in agreement with the characteristic diffraction peaks of cellulose I β (Zhang et al. 2019). Although, the intensities of these peaks decreases with the TiO₂-PEI adsorption, the crystalline structure of the cellulose fibers doesn't change, and the position of the peaks keep constant. The appearance of the characteristic peaks of the TiO₂ just indicated the physical coating of the cellulose nanofibers while the ratio 80%/20% of anatase/rutile of the P25 TiO₂ powder keeps constant.

Additionally, IR spectroscopy of the mentioned hybrid composites (LCNF-10%TiO₂, LCNF-100%TiO₂, and LCNF-1000%TiO₂) were additionally carried out, and compared with LCNF spectrum, to explore the interaction between TiO₂-PEI NP and LCNF, Fig. 3b. The development of polyethylenimine cross-linked cellulose-based materials, free of the traditional toxic cross-linkers, has been already reported by others authors in aqueous media. According to the described procedures (Zhao et al. 2017), a peptide coupling could take place via carboxylic groups of the cellulose with the abundant accessible primary amine groups at branch ends of the PEI branched structure we use in our core-shell nanostructure formation.

The characteristic absorption bands corresponding to the vibrations modes of functional groups of the pure LCNF 100% sample can be identified according to the literature (Komal et al. 2020). The most typical cellulosic bands were observed at 3400 cm⁻¹, due to the absorbed water from the atmosphere, at 2893 cm⁻¹, due to –C–H stretching, at 1159 cm⁻¹, induced by the antisymmetric bond deformation of C–O–C, and one wide band between 1010-1050 cm⁻¹ attributed to the C–OH bonds and the pyranose ring ether.

In the case of the polyelectrolyte, PEI, the absence of their associated bands in the spectra, as 3353 and 3277 cm⁻¹ bands, associated with the stretching of the amine NH bonds, 1596 cm⁻¹ band, associated with bending of the amine NH bonds, 2932 and 2807 cm⁻¹ bands, associated with the stretching of the C–H bonds, and 1455 cm⁻¹ band, associate with bending) was already reported by Rodrigues et al. (Rodrigues et al. 2015) due to a covalent modification between the involved compounds in the mixture. Moreover, in our case, although the numerous primary, secondary and tertiary amine groups present in the PEI branched polyelectrolyte we use as TiO₂ surface modifier, PEI

bands are completely masked by both, the anchorage of the PEI to the TiO₂ NP surfaces and the presence of the LCNF bands in the mixtures.

However, after TiO₂-PEI-LCNF peptide coupling, three new bands around 1650, 1558 and 1480 cm⁻¹ were evident in the composites, signifying the characteristic peaks assigned to the bending vibrations of the N-H from amides bonds and amino groups (Zhao et al. 2015; Ling et al. 2016). Fig. 3c proposes the coupling reaction between the carboxylic groups of LCNF and the free amines of PEI, previously adsorbed onto the surface of the TiO₂ NP. The presence of an additional new band at 1480 cm⁻¹, detailed in Fig.3d, provides a clear evidence of the successful introduction of the quaternary ammonium groups on the LCNF surface (Guo et al. 2016). Besides, the band corresponding to the pyranose ring ether seen for the unmodified LCNF at 1010-1050 cm⁻¹ decreases with the addition of TiO₂-PEI, even disappearing in the LCNF-1000%TiO₂-PEI spectra as consequence of their full covering. Therefore, FTIR study confirms zeta potential data (Fig. 2a), allowing us to establish the correspondence between the zeta potential stabilization in a maximum value with the full neutralization of LCNF negative sites. In the maximum covering of LCNF by TiO₂ NP, the branched PEI used as TiO₂ stabilizer plays a relevant role as ligand, by the successful formation of peptide bonds and the introduction of amino groups during the cross-linking.

Fig. 3. a) XRD analysis and b) FTIR spectra of a unmodified LCNF and modified LCNF with TiO₂-PEI. c) Scheme of the peptide coupling, d) detail of the FTIR spectra showing the introduction of the quaternary ammonium groups on the LCNF surface and e) scheme of the interactions between NP and LCNF

378 The heteroaggregation (Fig. 2) and FTIR (Fig. 3b) studies demonstrate the strong
 379 interaction of TiO₂ modified with PEI and LCNF, being a 1000 wt.% of TiO₂-PEI enough to
 380 neutralize and cover LCNF. Suspensions were formulated with this particle/template
 381 ratio, and then centrifuged in order to substitute water by ethanol as solvent, favoring
 382 a quick drying process after dipping. After centrifugation, the suspensions were never
 383 completely dried to avoid as possible the agglomeration of the core-shell

384 nanostructures, being 30 seconds of ultrasound enough to re-disperse them in ethanol.
 385 Both the solid content and the viscosity of the ethanol suspensions were adjusted
 386 according to the shaping method requirements in order to have a better thickness
 387 control as well as well-compacted and uniform coatings. Fig. 4a shows the flux behavior
 388 of 2 vol.% suspensions of TiO₂-PEI, and LCNF-1000wt.%TiO₂-PEI (TiO₂-PEI+LCNF) with
 389 and without Pluronic, added to improve wettability of the suspension with the FTO
 390 substrate.

Fig. 4. a) Rheograms of TiO₂-PEI and LCNF/TiO₂-PEI suspensions with 2 vol.% of solid contents in ethanol, b) TGA of the LCNF, and c) Picture and scheme of the prepared compound coating.

391 A significant rheological change was observed when the LCNF were included in the
 392 suspension formulation. The addition of surfactant did not produce relevant differences
 393 in the resulting flow curves. The TiO₂-PEI+LCNF suspensions exhibited thinning behavior
 394 whereas a dilatant fluid was observed for the TiO₂-PEI suspension. As expected, an
 395 increase of the viscosity values was produced in the whole shear rate range tested. In
 396 fact, the viscosity at rest was high enough to avoid core-shell nanostructures settling
 397 (see picture in Fig. 2b) enhancing the suspension stability. This high viscosity at low shear
 398 rates can be related to the morphology of the LCNF, which present a high aspect ratio
 399 due to their nanometric diameter and long length [16]. Furthermore, the viscosity values

of the TiO₂-PEI+LCNF suspension is 10 mPa·s for shear rates of 100 s⁻¹, increasing for lower rates down to 1-10 mPa·s. Those viscosity values fulfil the mixing and shaping needs, respectively. The addition of Pluronic had not influence in the flux behavior of the TiO₂-PEI+LCNF suspension.

A thermal analysis of the dried composite core-shell nanostructures was additionally carried out to determine the possible effects on the calcining and sintering treatments and their influence on the structure of the final coatings. The TGA of Fig. 4b displays a weight loss of 100% after 425°C, corresponding to organic removal which means that a thermal treatment above this temperature would result in full-inorganic TiO₂ coatings without organic residue after sintering.

3.3. Characterization of the films and the assembled DSSC.

Once the suspensions were optimized, the withdrawal rate was fixed at 2.5 mm/s for shaping. To control the photoelectrode thickness, coatings were growth through the sequential deposition of 3, 6, 9 and 16 layers. Fig. 4c shows an example of the 3 layers coating. The optimization of the heterocoagulated suspension allowed obtaining the homogeneous distribution of both materials, TiO₂ and LCNF, in the microstructure.

To confirm the film homogeneity, top and cross section views of the coatings were analyzed by FESEM after sintering process at 450°C. Fig. 5 and Fig. 6 show the corresponding micrographs.

Fig. 5. SEM top view of the coatings made with a) 3, b) 6, c) 9 and d) 16 layers onto FTO.

As a result of a successful suspension optimization, the top view micrographs of the 3, 6 and 9 layers coatings (5a, 5b and 5c respectively) displayed a good adhesion to the FTO substrate with homogeneous and crack-free surfaces. The coating made with 16 layers, micrograph 5d, showed the presence of surface cracks as consequence of drying a too thick film. Cracks could produce an important decrease of the charge transfer through the semiconductor microstructure and, consequently, a loose of photoanode efficiency. FTO substrates were directly dipped in the TiO₂-PEI+LCNF suspensions to serve as the photoelectrode of the DSSC with designed thickness. Nevertheless, the cross section of these coatings were additionally analyzed to determine their thicknesses. The corresponding micrographs are illustrated in Fig. 6.

Fig. 6 SEM cross section views of the coatings with 3 (a, b), 6 (c, d), 9 (e, f) and 16 (g, h) layers at low (x2500) and high (x10000) magnifications.

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432 The images show that coatings were firmly joined to the FTO substrates and exhibit a
 433 lamellar microstructure without defects at the layer-layer interface. All of them
 434 presented a rough and porous cross-section that is caused by the LCNF removal during

sintering. The thicknesses values increased proportionally as expected with the number of deposited layers resulting in 1.8, 4.8, 8.7 and 25.0 microns for 3, 6, 9 and 16 layers respectively. The absence of cracks for the coatings made with 3, 6 and 9 layers allows determining the critical thickness range. Some cracks were also observed along the cross section for the coating made with 16 layers, resulting from the relaxation of the thermal stresses during the sintering step.

To evaluate the thickness and porosity effects of the prepared photoanode in terms of cell efficiency, dye loading experiments and photoelectrochemical measurements were carried out. Fig. 7a shows the UV-Vis spectrum of the solutions after dye desorption and Fig. 7b displays the photocurrent density-voltage (I-V) characteristics of the DSSC photoanodes of various thicknesses under simulated air mass full sunlight intensity.

Fig. 7 a) UV-Vis spectrum of the desorption solutions of the dye sensitized photoelectrodes, and b) photocurrent vs voltage curves of the assembled DSSC registered in light, made with 3, 6, 9 and 16 layers.

The increase in the intensity of the peaks in Fig. 7a indicates that the impregnation of the dye was higher when the thickness boosted, which could be connected with the photovoltaic performance. Table 1 collects both the dye loading values of the prepared samples and the detailed photovoltaic parameters extracted from the I-V curves (Fig. 7b), namely, the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and the photovoltaic power conversion efficiency (η)

The parameters determined for a 16 layers TiO₂ photoanode, which performance was described elsewhere (Gonzalez et al. 2019) , was also included in the Table 1 with comparative proposes.

Table 1. Dye loading and cell performances of DSSC comprising the photoelectrodes with different thickness. Layer thickness is also shown in the table

Coating	Thickness (μm)	Dye Loading (mol mm^{-2})	$V_{oc}(\text{V})$	$J_{sc}(\text{mAcm}^{-2})$	FF(%)	η (%)
3 L- TiO ₂ -PEI- LCNF	1.8	0.8xE-10	0.74	3.1	52.8	1.9
6 L- TiO ₂ -PEI- LCNF	4.8	1.8xE-10	0.71	5.4	67.2	4.0
9 L- TiO ₂ -PEI- LCNF	8.7	3.2xE-10	0.69	6.4	67.0	5.4
16 L TiO ₂ -PEI- LCNF	25	4.4xE-10	0.67	4.3	65.3	2.9
16L- TiO ₂	12.5	4.5xE-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						

The V_{oc} was observed to be reduced as the thickness of the photoactive layer increases, similar to the effects of others photoanode nanostructures with increasing thicknesses, manufactured by fibers-based modifications. It is due to the enhancement of the dark current, which results from the reduction of the electrolyte by conduction band electrons of TiO₂. An increase of the film thickness increases the solid-electrolyte contact surface area and hence proportionally the dark current. Additionally, the growth of the photoanodes thickness up to 9 layers improved largely the device yield by the increase of the J_{sc} and the FF values and the conversion η . These parameters are comparable to the performance of the photoanodes fabricated from others commercial celluloses fibers (not from bioresources), NP or nanotubes (Ghadiri et al. 2010).

A relevant drop of all parameters was found when the photoanode design overpasses the well-known critical thickness. This is due to the presence of the defects and cracks

previously appreciated in the microstructures corresponding to the coatings made by the sequential deposition of 16 layers, seen in Fig. 5d, 6g and 6h.

On the other hand, compared to the LCNF-free photoanode performances, a relevant improvement was found in terms of photovoltaic parameters. The LCNF-free photoanode with a thickness of 12.6 μm exhibits a η value of 5.7%, while the 9 layers TiO₂-PEI-LCNF photoanode, 8.7 μm thick, delivers a similar efficiency value. Consequently, the incorporation of nanofibers to the suspension formulation and the heterocoagulation of LCNF and PEI modified TiO₂ NP, promotes the adequate organization of the nanofibers within the coating. The LCNF network formed during the film shaping favors the formation of a homogenous open porous nanostructures after sintering. Open porosity produces a large exposed area with a well-connected TiO₂ skeleton, which leads to a higher efficiency in thinner photoanodes also shaped with a lower amount of TiO₂. However, the drop in the Jsc value of the modified photoanodes can be attributable to the roughness factor produced by the LCNF network [22].

Additionally, the charge transfer resistance values were also calculated by EIS. Fig. 8 show the Nyquist plots of the prepared coatings measured in dark conditions.

Fig. 8. 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 Na₂SO₄ as electrolyte. Fig. 10b shows a magnified view in the high frequency range. Experimental data are represented by symbols and solid lines correspond to the fitted curves.

The experimental data were fitted with Z-fit software, EC-Lab v10.4. The following equation shows the used equivalent circuit.

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

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(Phadke et al. 2011), whereas R_2/Q_2 is the response of the TiO₂/electrolyte interface. The straight sloping line in low frequency regions (Q_3) is related to the ions diffusion through the TiO₂ microstructure. The obtained results have been summarized in Table 2.

Table 2 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 (K Ω)	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 L- TiO ₂ - PEI-LCNF	538	786	$1.2 \cdot 10^{-9}$	32.7	$10.3 \cdot 10^{-6}$	$11.9 \cdot 10^{-6}$
6 L- TiO ₂ - PEI-LCNF	502	831	$1.2 \cdot 10^{-9}$	21.5	$8.8 \cdot 10^{-6}$	$13.0 \cdot 10^{-6}$
9 L- TiO ₂ - PEI-LCNF	157	1139	$1.3 \cdot 10^{-9}$	7.5	$7.4 \cdot 10^{-6}$	$13.9 \cdot 10^{-6}$
16 L TiO ₂ - PEI-LCNF	210	1049	$1.5 \cdot 10^{-9}$	5.5	$10.5 \cdot 10^{-6}$	$15.3 \cdot 10^{-6}$

While the increase of R_1 values were directly proportional to the increase of the thickness, it has been found that the charge transport resistance (R_2) decreased as the thickness increases from 3 to 16 layers. This phenomenon was already related to an enhanced electron percolation through the semiconductor microstructure (Gonzalez et al. 2019). Herein again, the application of the colloidal approach to the development of the sequential deposition of robust and homogeneous structures. Furthermore, the increase of the number of layers resulted in steeper slopes at low frequency which signifies better ion-diffusion rate and higher capacitive behavior. Although the TiO₂-PEI-LCNF photoanodes provides higher dye loading and major efficiency values than TiO₂

photoanodes, slow electron transport rate was exhibited due to a slight loss of particles connectivity produced by the rough and wrinkled surfaces after sintering process.

4. Conclusions

LCNF-TiO₂ heterocoagulated structures were successfully prepared, confirming the formation of a peptide bond between the amine group of PEI, the stabilizer used to disperse TiO₂ NP, and the carboxyl groups of the LCNF, respectively. The colloidal strategy allowed stabilize both the TiO₂ NP and the LCNF, individually in aqueous suspension, and favored their dispersion and later coupling between them when mixed resulting in an effective intercalation process between both components. The formation of these LCNF-TiO₂ core-shell nanostructures was monitored by the zeta potential determination, and the complete covering of the nanofibers by the NP was demonstrated with FESEM images.

The use of these LCNF as bio-templates also offered an interesting strategy to revalorize agricultural wastes with relevant applications. An example of this development was the design of porous TiO₂-based photoanodes, carried out in this work. In addition, the manufacturing methodology required less steps since the proposed strategy allowed obtaining major control over the design of the coatings microstructures. LCNF inclusion produced a viscosity boost in comparison with the TiO₂-based suspension resulting in spongier coatings which allowed us to reduce the thickness from 12.6 to 8.7 μm maintaining the photoefficiency around 6%, and therefore saving time and reducing processing costs. The critical thickness value was found for the coatings made with 16 Layers of LCNF-TiO₂ suspensions producing a higher charge transfer resistance and relevant deleterious of the photoactive response.

Finally, it is remarkable the synergistic effect of LCNF and TiO₂ resulting on a superior photoelectrochemical performance. Reported processing strategy could be applied to other semiconductors materials to obtain well-dispersed and homogeneous compound susceptible to be used for different applications.

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