Platinum/Palladium hollow nanofibers as high-efficiency counter electrodes for enhanced charge transfer

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HIGHLIGHTS

● Facile electrospinning method to fabricate Pt/Pd hollow nanofibers.
● Hollow nanofibers were employed as efficient counter-electrode for DSSC.
● Improved electro-catalytic performance of the nanostructured counter-electrode.
● 15% enhancement in power conversion efficiency.

ABSTRACT

Pt/Pd hollow nanofibers were obtained by sputtering a Pt/Pd alloy (80/20 wt%) onto polymer nanofibers (used as sacrificial template) and were used as counter-electrodes (CEs) in dye-sensitized solar cells (DSSCs). We demonstrate that optimization of nanofiber density and Pt/Pd sputtering thickness can increase the short circuit current density and consequently lead to a ~15% enhancement in power conversion efficiency (PCE), when compared to the commonly used flat Pt/Pd CEs with the same thickness. The processes that contribute to such PCE improvement are: (i) increased surface area provided by the high aspect ratio hollow nanofibers and (ii) improved electro-catalytic performance, as validated by electrochemical impedance spectroscopy (EIS) measurements. The latter showed a two-fold decrease in the charge-transfer resistance of the nanostructured-CE, compared to the flat CE. The contribution of the Pt/Pd hollow nanofiber to light scattering was negligible as shown by reflectance measurements. These results suggest a simple and straightforward strategy to increase PCE in DSSCs, to minimize the use of precious metals used in this kind of devices and, more generally, to tailor the CE structure in photoelectrochemical systems to boost their functional properties, thanks to the advantages afforded by this complex morphology.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are photoelectrochemical systems, which are regarded as a potential future alternative to silicon-based solar cells due to their simple and cost-effective fabrication process. However, to compete with the price of electric energy generated by conventional fossil fuels, a significant increase in efficiency and reduction in price per watt generated is required for DSSCs. A typical DSSC device is composed by three
main parts: a transparent conducting oxide (TCO) on glass, a mesoporous metal oxide semiconductor film sensitized by a monolayer of dye molecules, and a counter-electrode (CE) (usually a platinum-coated TCO on glass). The cell is then filled with a suitable redox electrolyte that regenerates the dye [1,2].

Different approaches have been proposed to enhance the performance of DSSCs. Enhanced light-harvesting of the dye by increasing its molar extinction coefficient, or by extending the absorption to the Near-Infra-Red (NIR) region of the solar spectrum [3–5]; improved electrolyte [6,7]; engineered device to increase the charge collection and reduce the recombination [8–11]. The latter can be applied on different elements of the DSSC, in particular at the photoanode or at the CE.

The role of the CE is to transfer electrons arriving from the external circuit back to the redox electrolyte and reduce the redox species used as a mediator in regenerating the dye. Platinum (Pt) remains the preferred material for CEs in this type of cells due to its catalytic properties and its superior chemical and electrochemical stability [12–14]. However, the high cost of Pt can be a detrimental factor for the commercialization of high performance DSSCs and photoelectrochemical systems in general. Therefore, the need to develop a cost-effective CE, without reducing its electrocatalytic activity and durability is a key factor for DSSCs commercial application.

Due to the importance of the CE in DSSC device, a number of studies have been conducted to replace the Pt as the preferred material for CE. Carbon-based and hybrid Pt-free alloys CE showed promising results but still have some unsolved problems: low stability, reduction in DSSC transparency, and long and complicated production processes [15–19]. Rather than completely removing the Pt, another possibility is to reduce its amount in the CE, without sacrificing electrocatalytic activity and stability. Recently, bimetallic platinum alloys, obtained by alloying Pt with transition metals (such as Ni, Pd, Co) have been proposed as alternatives to the traditional Pt CE. These alloys have higher catalytic activity than pure Pt, and have shown improved performance and stability, when applied as CE for DSSCs [20–23].

Recently electrospinning, a facile, low cost and scalable technique was used to produce 1D architectures, including Pt-networks obtained by electrospinning composites from polymer/Pt precursors [13,24]. These studies employed Pt nanofibers to develop transparent CEs for flexible DSSCs, requiring a minimum coating of 80 nm Pt to provide good mechanical flexibility [13,25] and/or electrospinning times longer than 10 min to achieve a performance similar to that of Pt deposited on FTO glass [13,24].

Herein we report an efficient and simple fabrication process for nanostructured CEs for DSSCs with enhanced catalytic activity by using magnetron sputtering to coat electrospun polymer nanofibers, which act as sacrificial templates, with a bimetallic Pt/Pd alloy. Wu et al. used a similar approach to fabricate flexible electrodes deposited using a variety of metals; these 1D structures have been obtained by sputtering metal coating thicknesses of at least 80 nm [25]. It was also shown that the polymer template influences the metal coating homogeneity. Here we demonstrate that the amount of precious metal can be decreased up to a factor of four and we chose a polymer that provides a continuous coating of the deposited alloy, as shown by the CE’s morphological characterization. The nanostructured CEs were tested in DSSCs to provide a complete study of their PEC performance by varying the Pt/Pd sputter coating thickness (20, 40 and 80 nm) and density of the nanofibers on FTO glass substrates (electrospinning time: 40 or 120 s). This allowed us to determine the optimal CE architecture to enhance the PCE and, through a detailed study of the charge-transfer processes occurring in the CEs, we were able to attribute this increase to the improved electro-catalytic performance.

2. Methods

2.1. CE fabrication

Polymer nanofibers were electrospun onto FTO glasses (sheet resistance 8 Ω/sq) from a 23 wt % solution of polyamide-6 (PA6, Sigma Aldrich) in formic acid (FA, Sigma Aldrich) kept under stirring for 4 h. The nanofibers were obtained in a Spraybase, Professor Life Sciences electrosprining unit at 20 kV using a distance of 15 cm and a flow rate of 0.06 ml/h with a 26G needle. CEs were fabricated using two nanofiber deposition times (40 or 120 s). Subsequently, the nanofibers were dried at 70 °C for 15 min followed by sputter coating at the desired thickness using a Pt/Pd alloy (80/20 wt%) target in a Cressington 208HR high resolution sputter coater, equipped with a thickness controller. The process was conducted under a 0.01 mbar Argon atmosphere, at 80 mA using a rotating disk at a determined angle; the desired thickness was achieved by multilayer coating, depositing 20 nm thick layer each time (up to 4 times). Subsequently, the polymer was removed by heating for 15 min at 500 °C using a 10 °C/min heating ramp.

2.2. Solar cell fabrication

We fabricated DSSCs according to standard procedures [1,3,26]. Double layer photoanodes were prepared by tape casting two commercial TiO2 pastes. The first layer consists of anatase nanoparticles with average size of 20 nm (18 NR-T, Dyosol) and it was first tape casted onto transparent FTO glass substrates (sheet resistance 8 Ω/sq). The thickness of the tape during the casting process was 50 μm. The film was dried for 15 min at ambient temperature and then for 6 min at 120 °C. The procedure was subsequently repeated using a commercial scattering layer consisting of a blend of active anatase TiO2 particles (~20 nm) and larger anatase TiO2 scattering particles (diameters up to 450 nm, 18NR-AR, Dyosol). After drying, the bi-layered structure was sintered in ambient atmosphere according to the following steps: 200 °C for 15 min, 400 °C for 15 min and 500 °C for 30 min. Film thickness was measured using a Dektak profilometer and found to be ~18 μm. Subsequently, the photoanodes were sensitized in a 0.5 mM ethanol (Sigma Aldrich) solution of Ru-based complex molecular N719 dye (Dyosol) for 24 h, and then washed with ethanol to remove any unbound dye molecules. DSSCs were fabricated by using a 25 μm thick Surlyn film (Solaronix) between the photoanode and the Pt/Pd CEs, and they were filled using a triiodide/iodide I3-/I− redox couple electrolyte (Solaronix HI-30).

Table 1 shows an example of the labeling system used in this work. The first two digits of the labels are the electrospinning deposition time in seconds, i.e, 40 or 120 s, whereas the second set of digits refers to the coating thickness of the Pt/Pd alloy (20, 40 and 80 nm): a sample labeled 40NF20 nm corresponds to a deposition of nanofibers for 40 s and coated with 20 nm of Pt. The samples labeled as 00NF20 nm, 00NF40 nm and 00NF80 nm correspond to the bare FTO (flat CEs) sputtered at different thickness conditions.

2.3. Characterization

The morphology of the nanofibers was characterized by field emission scanning electron microscopy (FE-SEM) using a JEOL JSM7401F FE-SEM equipped with an energy-dispersive X-ray spectrometer (EDS). The physical properties of the nanostructured CEs were obtained by analyzing different SEM micrographs using ImageJ software with DiameterJ plugin, which automatically segments the images converting the fibers into white pixels and the background (substrate) into black pixels. This plugin provides the amount of pixels in the background and this value was used to
obtain the fiber area coverage ratio. Nanofibers deposited onto the FTO glasses were sonicated for 10 min in ethanol followed by drop casting onto a carbon coated Cu grid and transmission electron microscopy (TEM) images were acquired using a JEOL 2100F TEM. Atomic force microscopy (AFM) was performed in a Veeco Enviroscope AFM. Pt/Pd hollow nano fiber crystallinity was investigated using grazing incidence X-ray diffraction (GIXRD) in a Bruker D8 Advance X-ray diffractometer equipped with Cu Kα radiation. Diffuse reflectance measurements were acquired in a Perkin Elmer, Lambda 750 UV–Vis–NIR spectrophotometer using an integrating sphere setup calibrated with a Spectronan standard.

The current–voltage characteristics of the fabricated cells were measured by using an Agilent Keysight 2901A under simulated sunlight using an ABET2000 solar simulator at AM 1.5G (100 mW cm−2) calibrated with a silicon reference cell and mechanical filters. External Quantum Efficiency (EQE) spectra were acquired in dark using an EQE 200 Oriel integrated system. The measurement step was 10 nm and the photocurrent was recorded using a lock-in amplifier.

Cyclic Voltammetry (CV) was carried out using a SOLARTRON 1255/1287 in a three-electrode electrochemical system. CV curves were recorded at 50 mV s−1 using a Pt plate as a CE, an FTO substrate supported Pt/Pd alloy CE with and without nanofiber as a working electrode, and a saturated calomel electrode (SCE) electrode as a reference electrode in a supporting electrolyte (Solaronix S410, 30%, in acetonitrile).

The electrolyte used triiodide electrolyte were investigated from 0.6 V to 1.2 V at a scan rate of 50 mV s−1 Electrochemical impedance spectroscopy (EIS) was carried out in the dark using a SOLARTRON 1260 A Impedance/Gain-Phase Analyzers, with an AC signal of 10 mV in amplitude, in the frequency range between 100 mHz and 300 kHz. The applied bias during measurements of the dummy-cells in the dark was fixed at 0 V while for the complete DSSCs the bias was between 0 V and 100 mV above the open circuit voltage of the solar cell under illumination. All the samples were measured inside a Faraday cage.

3. Result and discussion

3.1. Morphological and structural characterization

Hollow nanostructures with well-controlled sizes and shapes have shown to exhibit excellent catalytic performance [27–30]. In addition, catalytic activity can be enhanced by templating small grain size nanoparticles of metal catalysts onto 1D structures with large area per unit volume and obtaining an interconnected network with good adhesion to the substrate and mechanical robustness [28,31–34]. These features are desirable for fabrication of highly efficient and stable CE. Accordingly, PA6 nanofibers were randomly assembled onto FTO glasses and after short electrospinning deposition time, the nanofiber networks were used as a sacrificial template to deposit Pt/Pd nanoparticles by magnetron-sputtering. Subsequent polymer removal allowed the production of hollow nanofibers. A scheme of the process is reported in Fig. 1, which also displays SEM images of the Pt/Pd hollow nanofibers with controlled density by tuning the electrospinning deposition time. Using this approach, we obtained a highly uniform and interconnected nanofiber network. We compared two different deposition times to increase the CE surface area. We find that electrospinning deposition time for 120 s results in much higher density of hollow nanofibers, stacked on top of each other.

Fig. 2 displays the morphology of the fibers fabricated at different coating thicknesses. At low Pt/Pd coating thickness the formation of connected fine grains of nanoparticles is clearly visible in the high resolution inset; when increasing coating thickness, the grain size increases. This observation is in agreement with narrowing of the XRD peaks (Fig. S1) ascribed to face-centered cubic (FCC) crystalline Pt (JCPDS card No. 01-087-0646), meaning that the grain size of the sputtered Pt becomes larger at higher Pt/Pd coating. At the smallest coating thickness (Fig. 2 a), the nanofibers were more susceptible to be broken after polymer removal (as shown by the dotted circles), whereas thicker coatings yield to the formation of larger island clusters and subsequently to full coverage of the fibers, forming a continuous and robust surface, which showed few defects at 20 nm Pt/Pd sputter coating (labeled by the arrows in the high magnification SEM image). Consequently, the nanofibers had a better interconnection at their junctions when using a thicker coating.

On the other hand, broken nanofibers could allow easier penetration of the liquid electrolyte within the hollow structure, suggesting a possible improvement in the electrochemical activity of these electrodes.

EDS spectra and semi-quantitative measurements of the chemical composition in the Pt/Pd nanofibers before and after polymer removal are included in Fig. S2 a, b. Carbon was not detected in the EDS after polymer removal. Additionally, the top view of an individual nanofiber (sputtering direction) is displayed in Fig. S2 c whereas Fig. S2 d includes a nanofiber detached from the substrate after breaking the CE. The bottom part of the nanofiber (side facing the FTO) clearly shows the hollow/concave structure of the nanofiber. The fiber diameter increases at higher Pt/Pd thickness as seen in Table S1, with sizes in the range of 120–300 nm. The hollow nanofibers have an average coverage of 16% and 31% of the FTO substrate area for electrospinning deposition times of 40 s and 120 s, respectively. As reported by EDS, the atomic ratio of Pt/Pd to SnO2 (FTO glass) remains similar at different density of the nanofiber deposited and it increases according to the amount of sputtered catalytic metal from 3, to 6 to 15 when the deposition thickness was increased from 20, to 40, to 80 nm, respectively (Table S2).

TEM images included in Fig. 2 d–f display the morphology developed by different thicknesses of the sputtered catalyst. High magnification images show Pt/Pd nanoparticles, 30–60 nm in diameter that are homogeneously assembled on the surface of the nanofibers and hollow nanofibers were obtained after polymer removal (confirmed by the brighter central region of the fiber due to lower mass density caused by the empty space). Small inhomogeneity in Pt/Pd coverage (visible in the higher contrast in one side of the edges of the nanofibers and further confirmed by AFM) is due to sample rotation and sample tilt during sputter deposition (Fig. 3). The fibers are homogenously deposited onto the FTO substrate forming a randomly distributed network (Fig. 3 a), they feature uniform shape and have an average height size of 200 nm.

3.2. Optical and photovoltaic properties

Due to the lateral dimensions of the hollow nanofibers, they could act as scattering medium in the CE, therefore their light-reflecting ability was studied by diffuse reflectance (Fig. 4 a–c). The lower reflectance ability of the hollow nanofiber CEs compared to the analogous flat CE can be attributed to light trapping within
the hollow structures. A systematic decrease of reflectance is recorded at increased spinning time (related to fiber density), suggesting the ability of the fibers to trap light, increasing incoherent scattering and decreasing reflectance. In addition, when the Pt/Pd coating is increased the reflecting behavior becomes similar to that of the flat CE, due to the better coverage of the sacrificial template, as previously shown by SEM images, therefore reducing the amount of light which is trapped within the hollow nanofiber. An increased reflection can be observed in the 700–800 nm region, confirming the incident light-reflecting ability of the Pt CEs. However this enhancement does not contribute significantly to the final increase in PCE of the cell [33]. EQE measurements (Fig. S3) confirm that the light-reflecting properties of the CEs do not contribute to improve the performance of the cells.

Fig. 4 d–f shows the functional properties of DSSCs assembled with different CEs. For 40 s deposition of nanofibers, the PCE increases for all Pt/Pd film thickness, compared to flat CEs. For 120 s deposition, the increase is negligible or even absent. At the optimum nanofiber density (40 s, Fig. 4 d), the main effect for all Pt/Pd thicknesses is to boost the short-circuit current density ($J_{SC}$). Compared to the flat CE, the CE realized with 40 s deposition of the polymer nanofiber template and sputtered with 80 nm of Pt/Pd (40NF80 nm) showed a $J_{SC}$ increase of 13% for maximum PCE equal to 7.50%. Globally, the PCE increased by 15% when compared to the flat CE.

Under the same illumination conditions, the open circuit voltage ($V_{OC}$) and the fill factor (FF) are very similar for all the cells, and do not play a major role in increasing the PCE. The enhancement obtained here (15%), is higher than the one reported in previous work [14] (8%) in which a similar polymer templating/sputtering method was employed.

Our results are comparable to the performance improvement achieved by a similar approach in cells based on a porphyrin sensitizer and Co-based electrolyte. However, in that case hardly scalable processes were used, like atomic layer deposition (ALD) deposition and TiCl₄ photoanode pre- and post-treatment [31], making the fabrication of the photoanode and CE expensive and time-consuming. In our approach, we were able to nanostructure the CE by using simple and straightforward steps to improve the PCE. The hollow nanofibers remain unaffected after testing in the DSSC (Fig. S4).

Table 2 shows the data obtained from current density versus voltage ($J$–$V$) curves, from which we infer that 40 s nanofiber electrospinning deposition is the optimal condition, irrespective of Pt/Pd coating thickness. Increasing the Pt/Pd coating on the CEs has minor influence on the PCE. This “plateau” effect is well known: it
has been previously found that no significant difference in the charge-transfer resistance at the electrolyte/CE interface was observed for flat CEs with Pt film thicknesses ranging from 25 to 415 nm [14,33]. Even with the lowest Pt/Pd coating thickness (20 nm) there is a ~15% improvement in PCE using the nanofiber structured CE, when compared to the flat CE with the same coating thickness. To reduce the amount of required Pt, thereby decreasing the total cost of DSSC, we opted to focus on the electrodes obtained with the thinnest Pt/Pd coating: 20 nm.

The electron lifetime inside the TiO2 photoanode plays a major role in determining the PCE [35,36]. Electron lifetime is affected by many factors, including the photoanode, CE architecture, and materials [36,37]. In this work the photoanode was the same for all the analyzed devices, and we only modified the CE structure. Thus, we can attribute the variation of the functional properties exclusively to the CE. Specifically, electrons at the CE originating from the external load induce the reduction of the I3- species: for this reason, the electron lifetime can be used to evaluate the CE catalytic kinetics.

In a DSSC, there are mainly two possible recombination reactions: electrons transported within the oxide can recombine either with the oxidized dye or with the oxidized state of the redox

![Fig. 3. AFM scan of 40NF20 nm CE. (a) 50 x 50 μm²; (b) 1 x 1 μm²; (c) profile of the line in (b).](image)

![Fig. 4. Diffuse reflectance measurements of the different counter electrodes (a-c). J-V curves of solar cells using different CEs (d-f).](image)
couple \( (I_3) \).

For high \( I_3 \) concentrations (more than 30 mM) it has been shown that the recombination with the oxidized dye is not a significant loss mechanism and therefore does not limit the performance [36,37]. Since the recombination with \( I_3 \) is the main recombination mechanism [38–40], a fast kinetics of its reduction at the CE is critical for reducing recombination losses. In this way, the availability of \( I_3 \) that can recombine with an injected electron in the TiO\(_2\) will be limited, resulting in a slower \( V_{oc} \) decay.

Fig. 5 displays the \( V_{oc} \) decay and the electron lifetime calculated as follows [37]:

\[
\tau_e = \frac{k_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature and \( e \) is the elementary charge. Changing the CE structure affects considerably the \( V_{oc} \) decay and consequently the electron lifetime (Fig. 5). Increased electron lifetime is typically attributed to reduced charge losses. The longest lifetime was achieved in the cell with the highest efficiency, confirming that the optimal condition of fiber density can increase the collection of electrons, therefore reducing the recombination. Indeed, the cell with the longest lifetime confirms that a high reduction kinetics of \( I_3 \) at the CE interface limits the recombination of the photogenerated electrons with the triiodide ions, increasing the regeneration of dye and therefore the charge injection from the dye into the conduction band of TiO\(_2\), decreasing the recombination phenomena. While increased Pt/Pd hollow nanofiber density is expected to provide a higher specific surface for the catalytic process, it is detrimental for the electron lifetime, as inferred from EIS measurements.

### 3.3. Electrochemical performance of CEs

CV was carried out in a three-electrode system. Fig. 6 reports the cyclic voltammograms of the \( I^-/I_3^- \) redox couple on representative CE samples. All the curves exhibit an oxidation and reduction peak in the range –0.5 V to 1.1 V (vs SCE). Comparable shapes can be found in literature for system with Pt or Pt/Pd sputtered nanoparticles [14,38]. The peaks are attributed to the reaction \( 3I_2^- + 2e^- \rightarrow 2I_3^- \) at the CE interface. As visible in Fig. 6a, the cathodic and anodic peak current densities of the samples nanopatterned with the fibers are higher than those of the Pt/Pd electrode without fibers, indicating that the presence of hollow nanofibers increase the catalytic activity.

Another important parameter for comparing catalytic activities of different CEs is the peak to peak separation (\( E_{pp} \)), which is negatively correlated with the standard electrochemical rate constant of a redox reaction [21,38]. The \( E_{pp} \) values decreases in the order 40NF20 nm (\( E_{pp} = 578 \text{ mV} \)) < 120NF20 nm (\( E_{pp} = 670 \text{ mV} \)) < 00NF20 nm (\( E_{pp} = 723 \text{ mV} \)), confirming the higher catalytic activity for the best sample (40NF20 nm). The electrocatalytic stability of the different samples was tested by measuring 20 cycles of CV (shown in SI, Fig. S7). As can be observed in Fig. 6b, the reduction and oxidation peaks remain almost the same suggesting that the nanofiber Pt/Pd CE composite is stable. Moreover, the stability of the best sample with nanofiber is similar to the flat Pt/Pd CE (Fig. S7a) with a variation of only 11.5% in the cathodic current and a 6.5% in the anodic current. These variations are similar to those obtained in recent works on Pt nanofiber network deposited on glass and flexible substrates [13,24].

To gain insights on the catalytic mechanisms of the different CEs, we performed EIS using a symmetric cell configuration, to eliminate the contribution of the TiO\(_2\) cathode. In the symmetric configuration, two identical CEs separated by a 25 \( \mu \)m spacer were filled with the same electrolyte used for all the DSSCs. During the regenerative cycle of DSSCs at the CE, the catalytic reactions are confined to its surface, therefore the charge-transfer resistance in the electrolyte/catalyst is related to the reaction rate on the CEs, which is driven by its surface electro-catalytic activity. The resulting Nyquist plots are displayed in Fig. 7, including the equivalent circuit used for fitting. The extrapolated parameters are reported in Table 3. All the plots display two semicircles: the high frequency arc (leftmost semicircle in Fig. 6) is assigned to the charge transfer process at the electrode/electrolyte interface, while the low frequency arc (rightmost semicircle) is attributed to the Nernst diffusion impedance of the ions in the electrolyte [41–43].

From Fig. 7, it is clearly visible that the best performing cell (40NF20 nm) has the smallest low frequency arc compared to flat CE and to the one with increased density of the nanofiber (120NF20 nm), indicating a faster ion diffusion rate on this sample.

By fitting the data of the high frequency arc we obtain the value of the Nernst diffusion impedance element, \( Z_{W1} \): for the three cells, it increases in the order 40NF20 nm < 00NF20 nm < 120NF20 nm. This means that the diffusion coefficient (\( D \)) of \( I_3^- \) ion for the different cells vary in the inverse order, in fact \( Z_{W1} \) can be calculated as [41,44]:

\[
Z_{W1} = \frac{kT}{n^2e\varepsilon A \sqrt{\pi D}} \tan^{-1}(\frac{\sqrt{\eta D}}{\delta})
\]

where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( n \) is the number of electrons involved in the electrochemical reduction of \( I_3^- \) at the electrode \((n = 2)\), \( \varepsilon \) is the elementary charge, \( c \) is the concentration of \( I_3^- \), \( A \) is the electrode area, \( \omega \) is the angular frequency and \( \delta \) is the thickness of the diffusion layer. This result indicates that \( D \) increases with increasing electrocatalytic activity of the CE, confirming that the 40NF20 nm has the highest catalytic activity.

Additionally, by fitting the arc at higher frequency, the value of the charge transfer resistance (\( R_{ct} \)) can be extrapolated. The series resistance (\( R_s \)) is similar in all the samples because its value is mainly related to the resistance of the FTO substrate and the thickness of the Pt layer, that are kept the same for all the samples [42]. \( R_{ct} \) varies inversely with the \( I_3^- \) reduction activity of the different CEs (therefore, a lower value indicates a higher catalytic activity) [42,44,45]. The values are reported in Table 3, showing that the best CE condition has a \( R_{ct} \) twice lower than the other samples. The chemical capacitance (\( C \)) increases with the insertion of nanofiber, and is maximized for the sample 40NF20 nm. This trend confirms the role of the hollow Pt/Pd nanofibers in increasing the active catalytic surface area of the CE at the optimal condition (40 s nanofibers deposition).

<p>| Table 2 Functional properties of DSSCs under 1 sun irradiation (AM1.5G, 100 mW cm(^{-2})). |</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>( V_{oc} ) (V)</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>00NF20 nm</td>
<td>0.69</td>
<td>12.4</td>
<td>0.72</td>
<td>6.15</td>
</tr>
<tr>
<td>40NF20 nm</td>
<td>0.69</td>
<td>13.9</td>
<td>0.72</td>
<td>7.00</td>
</tr>
<tr>
<td>120NF20 nm</td>
<td>0.69</td>
<td>12.5</td>
<td>0.74</td>
<td>6.45</td>
</tr>
<tr>
<td>00NF40 nm</td>
<td>0.69</td>
<td>13.3</td>
<td>0.72</td>
<td>6.15</td>
</tr>
<tr>
<td>40NF40 nm</td>
<td>0.70</td>
<td>14.2</td>
<td>0.71</td>
<td>7.05</td>
</tr>
<tr>
<td>120NF40 nm</td>
<td>0.69</td>
<td>11.1</td>
<td>0.72</td>
<td>6.00</td>
</tr>
<tr>
<td>00NF80 nm</td>
<td>0.70</td>
<td>12.8</td>
<td>0.72</td>
<td>6.50</td>
</tr>
<tr>
<td>40NF80 nm</td>
<td>0.70</td>
<td>14.4</td>
<td>0.74</td>
<td>7.50</td>
</tr>
<tr>
<td>120NF80 nm</td>
<td>0.69</td>
<td>13.5</td>
<td>0.68</td>
<td>6.35</td>
</tr>
</tbody>
</table>
The sample with the highest amount of nanofibers (120NF20 nm) has lower performance compared to the sample 40NF20 nm, due to the lower electrocatalytic activity confirmed by the higher $R_{ct}$ and the lower diffusion coefficient of the $I_3^-$ compared to the other samples. A possible explanation of this behavior can be attributed to the increased density of nanofiber-nanofiber contact resistance due to sequential nanofiber stacking and formation of inter-fiber gaps during the process of polymer removal [13]. Therefore, most electrons are confined in a region close to the FTO substrate, thus limiting electron availability for $I_3^-$ reduction in this sample, which is similar to that on the flat CE.

From the $R_{ct}$ value obtained from the symmetric cells, it is also possible to calculate the exchange current density ($J_0$), i.e. the current generated at equilibrium (absence of net electrolysis and at zero overpotential) that balances the cathodic and anodic currents, from the following equation [41,45]:

$$J_0 = \frac{RT}{nFR_{ct}}$$

where $R$ is the molar gas constant, $T$ the absolute temperature, $F$ the

![Fig. 5. (a) $V_{oc}$ decay and (b) corresponding electron lifetime of different CEs configurations.](image1)

![Fig. 6. a) CV curves of representative Pt/Pd samples. b) CV stability curve of 40NF20 nm showing the first and the 20th cycle of CV.](image2)

![Fig. 7. Nyquist plot from impedance measurements of symmetrical cells. The Randles circuit used for fitting the data is shown in the inset, it includes a series resistance $R_s$, a charge transfer resistance $R_{ct}$, a constant phase element CPE1 for taking into account the double layer capacitance and a Warburg impedance element W1. The solid lines are the fitted curves.](image3)
Faraday constant and $n$ the number of electrons involved in the electrochemical reduction of $I_3^-$ at the electrode ($n = 2$). The exchange current density calculated for the 40NF20 nm CE is 81.4 mA/cm$^2$ while for the standard flat CE is around 38 mA/cm$^2$. Being $j_0$ proportional to the $I_3^-$ concentration [38] this further confirms that the electrochemical $I_3^-$ reduction reaction on the CE patterned with nanofiber is enhanced.

4. Conclusion and perspectives

Nanostructured CEs were fabricated by coating 1D sacrificial polymer templates with a Pt/Pd thin film, producing hollow nanoﬁbers. We templated a Pt/Pd alloy composed of small grain size nanoparticles onto 1D hollow structures. We optimized the morphology and structure of the CEs for their application in DSSCs. 15% PCE improvement was achieved in hollow nanoﬁbers CE obtained from 40 s electrospinning time and 80 nm thick Pt/Pd film. Additionally, we showed that the amount of sputtered Pt/Pd can be decreased to 20 nm, without a signiﬁcant reduction of the overall efﬁciency. An improved functionality is the result of the enhanced electron lifetime in the assembled DSSCs, attributed to the increased specific surface area of the hollow nanoﬁber architecture and to the improved electro-catalytic performance, as shown by the two-fold decrease in the $R_s$

A higher amount of hollow nanoﬁbers was found to be detrimental for DSSC PCE, due to the decrease in the electro-catalytic activity, possibly caused by increased nanoﬁber junction resistances. At optimal conditions, the interconnected network of Pt/Pd hollow nanoﬁbers can enhance charge transfer, leading to higher efﬁciency DSSCs. This is a viable and cost-effective approach to enhance the catalytic surface area in CEs for photoelectrochemical systems with the purpose of boosting the performances through optimization of the electrochemical processes occurring in the operating devices. Such ﬁndings represent a promising direction to minimize the use of precious metals and to tailor the CE structure. In addition, the application of this approach for obtaining CEs with improved functional properties can be broadened to different electrochemical systems (i.e. fuel cells and catalytic chemical reactors). Moreover, this process can be applied to other metals than platinum.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2016.10.011.

References

[34] F. Navarro Pardo et al. / Journal of Power Sources 335 (2016) 138—145