Easily manufactured TiO\textsubscript{2} hollow fibers for quantum dot sensitized solar cells†

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TiO\textsubscript{2} hollow fibers with high surface area were manufactured by a simple synthesis method, using natural cellulose fibers as template. The effective light scattering properties of the hollow fibers, originating from their micron size, were observed by diffuse reflectance spectroscopy. In spite of the micrometric length of the TiO\textsubscript{2} hollow fibers, the walls were highly porous and high surface area (78.2 m\textsuperscript{2} g\textsuperscript{-1}) was obtained by the BET method. TiO\textsubscript{2} hollow fibers alone and mixed with other TiO\textsubscript{2} pastes were sensitized with CdSe quantum dots (QDs) by Successive Ionic Layer Adsorption and Reaction (SILAR) and integrated as a photoanode in quantum dot sensitized solar cells (QDSCs). High power conversion efficiency was obtained, 3.24\% (\textit{V}_{oc} = 503 \text{mV}, \textit{J}_{sc} = 11.92 \text{mA cm}^{-2}, \text{FF} = 0.54), and a clear correspondence of the cell performance with the photoanode structure was observed. The unique properties of these fibers: high surface area, effective light scattering, hollow structure to facile electrolyte diffusion and the rather high efficiencies obtained here suggest that hollow fibers can be introduced as promising nanostructures to make highly efficient quantum dot sensitized solar cells.

1. Introduction

Recently inorganic semiconductors have received considerable interest as alternative sensitizers to dye molecules in the so-called quantum dot sensitized solar cells (QDSCs).\textsuperscript{1–7} In dye sensitized solar cells, DSCs, molecular dyes are used as light absorbing materials to produce photogenerated electrons, which are injected into a porous matrix of a wide band gap semiconductor (e.g. TiO\textsubscript{2}). This wide bandgap semiconductor transfers the photogenerated electrons to the external circuit. The dye molecules are regenerated by a redox electrolyte, which acts as hole transporting media.\textsuperscript{8}

The quantum dots exhibit unique properties as easy fabrication, tunable absorption spectrum by controlling their size, shape, and composition and high molar extinction coefficients.\textsuperscript{9,10} Consequently, these materials are extremely interesting for photovoltaic applications. The experimental confirmation of the theoretical predictions of Multiple Exciton Generation (MEG) in colloidal QDs has boosted the interest in semiconductor QD as a light absorbing material in solar cells.\textsuperscript{11–13} At this point it is worth mentioning that the MEG effect on colloidal QDs has generated certain controversy regarding its efficiency.\textsuperscript{14–16} In spite of the mentioned advantages of QDs, the efficiency of QDSCs is much lower compared to conventional DSCs and the optimal QDSCs configuration has not been obtained yet.\textsuperscript{4,7} Improving the poor performance of QDSCs requires the improvement of some issues like: homogeneous assembly of QDs onto the TiO\textsubscript{2} surface, charge injection and recombination, efficient electrolyte and suitable TiO\textsubscript{2} film structure.\textsuperscript{1,4,17}

Recently, it was shown that the structure of the TiO\textsubscript{2} films has a crucial role for high efficiency QDSCs; nearly 5\% efficiency for CdS/CdSe quantum dot sensitized cells was obtained by controlling the structural properties of TiO\textsubscript{2} photoelectrodes, using a polysulfide liquid electrolyte.\textsuperscript{17} To the best of our knowledge this is the highest efficiency reported for QDSCs in the polysulfide liquid electrolyte. A potentially suitable TiO\textsubscript{2} photoanode should satisfy properties as: moderate-high surface area for optimizing the QDs loading, wide and interconnected pores for facile diffusion of the hole transport electrolyte and preventing blockage by QD sensitizers, efficient transport of photoinjected electrons, efficient light harvesting and easy fabrication. At present, different TiO\textsubscript{2} structures have been tested to prepare efficient QDSCs. High surface area TiO\textsubscript{2} nanoparticles have been used in QDSCs for high QDs loading.\textsuperscript{17,18} Inverse opals were sensitized with CdSe, encompassing the beneficial effects of ordered interconnected pores in inverse opals together with their light scattering properties.\textsuperscript{19,20} One dimensional TiO\textsubscript{2}
or ZnO nanorods/wires and tubes were used for efficient electron transport in QDSCs.\textsuperscript{21–23} In spite of the mentioned advantages of these structures, none of them simultaneously satisfy all the potentially required properties. For example, high surface area nanoparticles lead to high QD loading but also to pore blockage by QDs and intense trapping of electrons can occur at the particle surface and at grain boundaries.\textsuperscript{24} Inverse opals exhibit a too low surface area for QD loading, although moderate electron transport could be expected. On the other hand, the synthesis is complicated and the structures are mechanically fragile. One dimensional nanorods/wires and tubes usually suffer from low surface area and manufacturing is not so easy compared to conventional nanocrystalline films for DSCs and QDSCs. In this context, we propose here the use of hollow fibers as interesting nanostructured materials for QDSCs possessing the mentioned advantages altogether. Hollow fibers are synthesized using natural cheap cellulose cotton fibers as template. Simply synthesized hollow fibers have several microns length while their walls are highly porous. The surface area of hollow fibers (78.2 m\textsuperscript{2} g\textsuperscript{-1}) is larger compared to conventional nanoparticulate paste (72.9 m\textsuperscript{2} g\textsuperscript{-1}) for DSCs and QDSCs. The micrometric size of the fibers shows interesting light scattering properties as characterized by diffuse reflectance spectroscopy. On the other hand, the electronic transport can be potentially improved in these one dimensional hollow fibers. Enhanced electron collection efficiency in hollow fibers compared to mesoscopic films made of spherical nanoparticles has been observed.\textsuperscript{25} In addition, effective light scattering and light trapping properties of the hollow fibers for DSCs were also reported recently by some of us.\textsuperscript{26} Besides the mentioned properties, “hollow” fibers with wide pores, as confirmed by SEM and BET, prevent pore blockage by QDs and favor the homogeneous electrolyte diffusion into the photoanode. Efficient CdSe QDSCs with efficiencies of 3.24\% were obtained using hollow fibers. We show that the synthesized hollow fibers can be used as an efficient nanostructure to make highly efficient QDSCs. Scheme 1 illustrates the architecture of some of the different morphologies employed for QDSCs to compare with the hollow fibers.

2. Experimental section

2.1. Synthesis of the hollow fibers

Hollow fibers were synthesized as previously described.\textsuperscript{27} Briefly, HCl was added to 1 litre of Milli-Q water until pH was adjusted to 1.8. Then, tetraisopropylorthotitanate (TiPT) was added drop-wise to the acidified water while stirring, to make a 0.05 M solution. Adding TiPT leads to a white precipitate which changed to a semi transparent solution after stirring for a few days. The temperature of the solution was adjusted to 60 °C and then about 10 g cotton fiber was dipped into the solution for 5 h. The impregnated fibers were squeezed to remove the extra solution and dried overnight at room temperature. The as-dried fibers were heat treated at 450 °C for 60 min in air. The obtained residue is a white fibrous substance of TiO\textsubscript{2} composition.\textsuperscript{26,27}

2.2. Electrode preparation

Three different TiO\textsubscript{2} pastes were used to prepare the electrodes. The first paste is “18NR-T Dyesol” containing 20 nm TiO\textsubscript{2} nanoparticles. This paste is used to make transparent TiO\textsubscript{2} layers, termed below “T”. The second paste was based on hollow fibers and is named “F”. For this purpose, 1 g of ethyl cellulose was dissolved in 12.5 ml ethanol assisted by ultrasonication.
The paste was prepared by milling 0.2 g TiO$_2$ hollow fibers and 1 ml of prepared ethyl cellulose in ethanol in mortar for 30 minutes while 1 ml of terpineol was added dropwise during the milling process. The third paste is prepared by mixing the 60% wt of paste T with 40% wt of paste F, we name this paste as "X". Nine different electrode configurations were prepared as photoanode in QDSCs by using these three TiO$_2$ pastes.

The photoanodes were doctor-bladed on transparent conducting fluorine doped tin oxide (FTO) glass substrates (sheet resistance $\approx 10$ $\Omega$ $\square^{-1}$). The resulting photoelectrodes were sintered at 450 °C, to obtain good mechanical and electrical contact at the interfaces nanoparticle/nanoparticle and nanoparticle/substrate. Before doctor-blading, the FTO substrates were coated by a compact layer of TiO$_2$ deposited by spray pyrolysis ($\sim$100 nm thick). These electrodes were calcinated at 450 °C for 30 min.

### 2.3. Electrode sensitization

TiO$_2$ electrodes were in situ sensitized by CdSe QDs grown by SILAR. The SILAR process was carried out following the method developed before.$^{28}$ Briefly, 0.03 M Cd(NO$_3$)$_2$ in ethanol was used as the Cd$^{2+}$ source and the in situ prepared 0.03 M Se$^{2-}$ in ethanol was used as Se$^{2-}$ precursor (see ref. 28 for more details). For sensitization, the electrodes were successively dipped into these solutions inside a glove box under a N$_2$ atmosphere. One SILAR cycle for CdSe consisted of 30-second dipping of the TiO$_2$ working electrode into the Cd$^{2+}$ precursor and subsequently into the selenide solution, during 30 seconds. After each bath, the photoanode was rinsed by immersion in pure ethanol to remove the chemical residuals from the surface and subsequently dried with a N$_2$ gun.$^{18}$ In order to improve the stability and performance of cells, all the samples were deposited with a ZnS protective coating,$^{18,29–31}$ by twice dipping alternatively into 0.1 M Zn(CH$_3$COO)$_2$ and 0.1 M Na$_2$S solutions for 1 min/dip, rinsing with Milli-Q ultrapure water between dips.$^{31}$

### 2.4. QDSC preparation

The cells were prepared by sandwiching a Cu$_2$S counter electrode and a QD-sensitized photoelectrode using a scotch tape spacer (thickness 50 $\mu$m) and permeating with the polysulfide electrolyte. The polysulfide electrolyte was 1 M Na$_2$S, 1 M S, and 0.1 M NaOH solution in Milli-Q ultrapure water.$^{32,33}$ The Cu$_2$S counter electrodes were prepared by immersing brass in HCl solution at 70 °C for 5 min and subsequently dipping it into polysulfide solution for 10 min, resulting in a porous Cu$_2$S electrode. The geometric area of the cells was 0.28 cm$^2$.

### 2.5. Photoanode and solar cell characterization

Gas adsorption measurements were performed on a Micromeritics ASAP 2020 surface area and porosity analyzer with ASAP 2020 V3.04 E software. Three tests were carried out for each specimen in order to assess the reproducibility of the measurement. The optical absorption spectra of the photoanodes were recorded at 300–800 nm by a Cary 500 UV-VIS Varian spectrometer. $J$–$V$ curves, Impedance Spectroscopy (IS) measurement, Applied Bias Voltage Decay (ABVD)$^{34}$ were carried out with a FRA equipped PGSTAT-30 potentiostat from Autolab. $J$–$V$ measurements were carried out using mask (0.24 cm$^2$) and no antireflective layer was used. Cells were illuminated using a solar simulator at AM1.5 G, where the light intensity was adjusted with an NREL calibrated Si solar cell with a KG-5 filter to one sun intensity (100 mW cm$^{-2}$). Incident photon to electron conversion efficiency (IPCE) measurements have been performed employing a 150 W Xe lamp coupled with a computer-controlled monochromator, the photocurrent was measured using nanoamperimeter 70310 from Oriel Instruments. Impedance spectroscopy measurements were carried out under dark conditions applying a 20 mV AC signal with the frequency ranging between 400 kHz and 0.1 Hz at different forward biases.

### 3. Results and discussion

A representative SEM micrograph of the hollow fibers is shown in Fig. 1(a). The walls of the fibers are highly porous. Consequently, in spite of their micron size, Fig. 1(b), high surface area of the hollow fibers is expected. The surface area of the hollow fibers was measured and compared to that of the TiO$_2$ nanoparticles which are commonly used in transparent layers for DSSCs and QDSCs. TiO$_2$ paste with 20 nm nanoparticles (18NR-T, Dyesol) was deposited on the FTO substrate by Dr Blade and after annealing at 450 °C for 30 min was scratched from the FTO for BET analysis. The surface area of 72.9 m$^2$ g$^{-1}$ was obtained for this paste, with a pore size distribution around 23 nm, Fig. 2(a). On the other hand, the surface area obtained for the fibers was 78.2 m$^2$ g$^{-1}$. The scattering of the BET

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Fig. 1  SEM micrograph from hollow fibers, (a) general view of TiO$_2$ fibers (scale bar 10 μm), (b) zoom of a fiber porous wall (scale bar 10 nm).
The intrinsic properties of each paste are also important for the final solar cell performance. The low efficiency of F, FF

**Table 1** Photovoltaic parameters of the QDSCs prepared and analyzed: photocurrent $j_{sc}$, open circuit voltage $V_{oc}$, fill factor FF, and efficiency $\eta$, as a function of the different cell structures sensitized by SILAR, tested under standard light illumination conditions (100 mW cm$^{-2}$ AM 1.5G). The results for the only transparent paste (TT) and the conventional configuration transparent + scattering pastes (TS)$^{18}$ are also included for comparison. In addition to light scattering, increasing the number of TiO$_2$ layers has two opposing effects. On one hand, light harvesting is increased as the thickness of the photoanode is increased due to higher amount of light absorbing sensitizers. On the other hand, as the thickness of the photoanode is higher, the effective surface of the electrode concomitantly increases, causing an enhancement of recombination. In this sense, a balance among light scattering, QD loading and recombination is mandatory to optimize the QDSC performance as we have recently showed.23 Note, for example that the highest efficiencies have been obtained for XX and TF samples with an intermediate diffuse reflectance, see Fig. 2(b).

![Fig. 2](image)

**Fig. 2** (a) Pore size distributions derived from BET measurements of T and F structures, (b) diffuse reflectance spectrum of the different TiO$_2$ structures analyzed containing fibers with T structure.
and FFF cells, see Table 1, can be mainly ascribed to the low deposition of hollow fibers on the FTO substrate by doctor blade, see Fig. 3(a). In this case there are some fibers randomly deposited on the FTO substrate and there is no good mechanical connection between the individual fibers and between fibers and the FTO substrate. This morphology leads to low quantum dot sensitization and poor transport of charge carriers to the external circuit. It is very interesting to compare the F structure with X structures. While the efficiency of the F structure is just 0.66%, Table 1, the efficiency of cells with X structures increased to 2.73% which constitutes a 4-fold enhancement. In this structure, the 20 nm nanoparticles act as a glue crosslinking the fibers and also improving the adhesion with the FTO substrate, Fig. 3(b)–(d). This morphology allows a significantly higher loading of QDS on the photoelectrode, leading to better solar cell performance. Mixing both fibers and nanoparticles (X structures) has the additional beneficial effect of light scattering and facile electron transport provided by the one dimensional hollow fiber structure. The best efficiencies have been obtained with the TX (2.89%), TF (3.04%) and XX (3.24%) structures, although still slightly lower than the conventional configuration transparent + scattering nanoparticles, see Table 1. Taking into account that the fiber paste studied in this work has not been further optimized, the results, in comparison with the commercial pastes TS, are promising.

Representative diffuse reflectance, IPCE and current–voltage (J–V) curves obtained for SILAR sensitized cells are plotted in Fig. 4(a), (b) and (c), respectively. We only show the results for the best configurations (TF, TX, XX) and also for TFF structures since the good efficiency of the TF structure (3.04%) has dramatically decreased to 1.44% after depositing one more layer of hollow fibers on the top of TF structure (TFF structure), see Table 1. The same information for F, FF, FFF, X and TXX can be found in Fig. S3 (ESI†). The measured IPCE for the TF, TX and XX structures sensitized by SILAR is very similar and the IPCE for the TFF structure is clearly decreased compared to these structures, in good agreement with the final obtained photocurrents, Fig. 4(c). Note that TF, TX and XX structures present the same layer thickness.

To better understand the physical characteristics of these solar cells, impedance spectroscopy measurements and ABVD were carried out on QDSCs. Chemical capacitance, $C_m$, Fig. 5(a), and recombination resistance, $R_{rec}$, Fig. 5(b), have been obtained from IS measurements using the previously developed model. The chemical capacitance, $C_m$, is plotted against the voltage drop in the sensitized electrode, $V_F$. $V_F$ was obtained by subtracting the voltage drop of the series resistance, $V_{series}$ (contacts, counter electrode, electrolyte diffusion), by $V_F = V_{app} - V_{series}$, where $V_{app}$ is the applied potential in the IS measurements. $R_{rec}$ is plotted against the voltage drop in a common equivalent conduction band (CB), $V_{ecb}$, where the effect of different TiO$_2$ CB between samples is removed. Plotting $R_{rec}$ against $V_{ecb}$ allows an analysis of the recombination resistance on the basis of an equal density of electrons $n$ (i.e. the same distance between the electron Fermi level and the TiO$_2$ CB). This procedure is carried out by shifting $V_F$ until the chemical capacitance overlaps; see also Fig. S6 and Table S3 (ESI†). The methods to obtain the dependences against $V_F$ and $V_{ecb}$ from IS measurements have been previously reported. Considering the chemical capacitance, Fig. 5(a), all the samples show very similar slopes for $C_m$, indicating a similar density of states. On the other hand, $C_m$ is shifted, indicating
a displacement of the TiO$_2$ CB. Taking the XX sample as a reference, an upward shift of the TiO$_2$ CB band is observed in the case of TF, TX and especially for TFF samples, Fig. 5(a). After correcting this shift, the TFF samples show the lowest recombination resistance (the highest recombination) observed, see Fig. 5(b). This higher recombination arises from the larger thickness of TFF (15 ± 1 μm) structures (and consequently larger effective surface) compared to the TF, TX and XX samples (11 ± 1 μm), in good agreement with the highest dark current obtained for this cell, see Fig. S5 and Table S1 (ESI†).

In addition, the lower recombination resistance of the TFF cells has been confirmed by comparing the electron lifetime, $\tau_n$, of the samples, Fig. 5(c). $\tau_n$ has been obtained from IS and ABVD measurements, under dark conditions. Conversely, the highest efficient cell with XX structure (3.24%), Table 1, has the highest recombination resistance, Fig. 4b, confirmed by $\tau_n$, Fig. 5(c). This fact points out the dramatic role of recombination in the QDSC performance. The valleys observed in $R_{\text{rec}}$, see Fig. 5(b), can be related with recombination through surface states as discussed elsewhere. 5

4. Conclusions

We have synthesized highly porous TiO$_2$ hollow fibers using natural cellulose fibers as template with a simple method. The unique properties of hollow fibers: high surface area (78.2 m$^2$ g$^{-1}$), effective light scattering, highly porous structure and hollow structure to facile electrolyte diffusion clearly pushed the efficiency of QDSCs up. We sensitized TiO$_2$ hollow fibers and fibers mixed with other TiO$_2$ pastes, with CdSe QDs grown by SILAR, integrating these electrodes as photoanodes in QDSCs. High power conversion efficiency ($\eta = 3.24\%$, $V_{oc} = 503$ mV, $J_{sc} = 11.92$ mA cm$^{-2}$, FF = 0.54) was obtained using a mixed paste of fibers and small nanoparticles. The unique properties of these fibers and the rather high efficiencies obtained here suggest that, hollow fibers are promising

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**Fig. 4** Diffuse reflectance (a), IPCE (b) and $J$–$V$ curves (c): for SILAR sensitized cells.

**Fig. 5** Chemical capacitance (a), recombination resistance (b) and electron lifetime (c) for QDSCs. Chemical capacitance and recombination resistance have been obtained from IS measurements while electron lifetime from ABVD measurements. 34
materials to develop highly efficient QDSCs. It is also highlighted
the key role of the photoanode structure in the final cell performance.
A rational balance among QD loading, light scattering
and recombination is mandatory in order to optimize the perfor-
mance of the photoanodes for QDSCs.

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