Vol. **123** (2013) *ACTA PHYSICA POLONICA A* No. 2

Proceedings of the 2nd International Congress APMAS2012, April 26–29, 2012, Antalya, Turkey

TiO_2 Nanotube Array as Efficient Transparent Photoanode in Dye-Sensitized Solar Cell with High Electron Lifetime

A. Lamberti[a,*], A. Sacco[a], D. Hidalgo[a], S. Bianco[a], D. Manfredi[a], M. Quaglio[a], E. Tresso[a,b] and C.F. Pirri[a,b]

[a]Center for Space Human Robotics @ PoliTo, Istituto Italiano di Tecnologia, C.so Trento 21, 10129 Torino, Italy
[b]Applied Science and Technology Department, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy

In the present work, the fabrication and characterization of non-curling, free-standing TiO_2 nanotube membranes and their integration in front-side illuminated dye-sensitized solar cells are reported. Vertically oriented TiO_2 nanotube arrays were fabricated by anodic oxidation of a titanium foil. Nanotube membranes were detached from the metallic foil, transferred and bonded on transparent fluorine-doped tin oxide/glass substrates employing a TiO_2 sol as a binder. Crystalline phase and morphology of the film were investigated, evidencing the formation of a highly ordered 1D nanotubes carpet, with a pure anatase crystalline structure. TiO_2 nanotube-based DSCs were fabricated using reversible microfluidic architecture. The cell performances were studied by I–V electrical characterization, incident-photon-to-electron conversion efficiency, electrochemical impedance spectroscopy and open circuit voltage decay measurements, showing an increase in electron lifetime compared to nanoparticle-based dye-sensitized solar cells.

DOI: 10.12693/APhysPolA.123.376

PACS: 73.63.Bd, 72.20.Jv, 72.40.+w, 73.40.Mr, 88.40.H−, 81.07.De

1. Introduction

Dye-sensitized solar cells (DSCs) are a promising alternative to silicon based solar cells, with relatively high light-to-energy conversion efficiency and low production costs [1]. The energy harvesting mechanism is based on the absorption of the light by means of dye molecules anchored on the surface of a porous wide band gap semiconductor. Electrons are injected into the conduction band of the semiconductor and collected at the transparent conductive oxide (TCO) electrode. The cell is completed by a cathode covered by a thin layer of platinum (that acts as catalyst) and it is filled with an electrolytic solution that closes the circuit regenerating the dye molecules. The state-of-the-art efficiency is around 11% for small-area experimental cells based on TiO_2 nanoparticles (nps) covered by ruthenium based dye molecules [2].

With the aim of improving the charge transport and minimizing the recombination mechanisms at the various interfaces [3], different dimensionally confined materials such as nanowires [4], nanorods [5], nanotubes [6] and others [7] have been proposed for photoelectrodes fabrication. In particular anodized titanium oxide nanotube (nt) array stands out for a faster and more efficient electron transport with respect to traditional np-based photoanodes [8]. These nts can be simply grown by the electrochemical oxidation of a Ti foil. The huge inconvenience is that the best working configuration of DSCs is based on a front-side illumination (to avoid light reflection at the cathode and absorption by the electrolyte) and so transparent electrodes are needed [8]. To overcome this problem TiO_2 nts can be grown on a Ti film deposited on a TCO substrate but in that case the length of the tubes, that strictly affects DSCs efficiency, is limited by the starting Ti film thickness. A possible alternative is based on the growth of a thick TiO_2 nts array on Ti foil and its detachment and subsequent bonding onto a common transparent conductive oxide electrode [9, 10].

Following a procedure similar to the last proposed, in this paper the fabrication and characterization of free-standing TiO_2 nt membranes and their integration in front-side illuminated DSCs are reported. The detached TiO_2 nt arrays have been bonded on transparent fluorine-doped tin oxide (FTO)/glass electrode employing a TiO_2 sol. Material characterization demonstrates the formation of a highly ordered 1D nt arrays with a pure anatase crystalline structure. TiO_2 nts-based DSCs have been fabricated using a reversible microfluidic architecture [11] and the effect of a $TiCl_4$ treatment has been studied measuring the cell performances by I–V electrical characterization under AM 1.5 illumination, incident photon-to-electron conversion efficiency (IPCE), electrochemical impedance spectroscopy (EIS), and open circuit voltage decay (OCVD).

2. Experimental details

2.1. Materials and method

Titanium foil (250 μm thick, 99.6% purity, Goodfellow) was used as working electrode for the anodic growth of TiO_2 nt array in a homemade two-electrode configuration electrochemical cell made of Teflon. It was cleaned by sonication in acetone, rinsed in ethanol and then dried under N_2 flow. Anodic oxidation was carried out in an

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*corresponding author

ethylene glycol electrolyte containing 0.5 wt% NH_4F and 2.5 vol.% deionized water under a constant voltage of 60 V for 2 h, using a dc power supply (GW Instek SPD--3606). Free-standing nt membranes were then easily separated by the metallic substrate without any crack, following a self-detaching procedure consisting in repeated rinsing in DI-water and ethanol. FTO covered glasses (7 Ω/sq, Solaronix) were cleaned in acetone in an ultrasonic bath and then rinsed with ethanol. Afterwards the glasses were immersed for 10 min in a 3:1 (sulfuric acid : hydrogen peroxide) "piranha" solution to remove organic residues. In order to obtain a good interface between the FTO and the nts bottom a TiO_2 sol was used as a binder. This sol was prepared by sol–gel technique using titanium(IV) isopropoxide as precursor according to the procedure described by Venkatachalam et al. [12], modified with the non-ionic surfactant Tween 20 and optimized for the preparation of TiO_2 films.

The TiO_2 nt membranes, with a 0.8 cm^2 area, were then transferred and bonded on FTO/glass substrates employing a drop of the TiO_2 sol before annealing at 450 °C for 1 h for crystallization. The as prepared photoanodes were treated with 50 mM $TiCl_4$ aqueous solution for 30 min at 70 °C to obtain a uniform coverage of nts with a thin layer TiO_2 nps. After rinsing in deionized water and drying, the electrodes were annealed again at 450 °C for 30 min. Photoanodes were soaked into a 0.3 mM N719 (Ruthenizer535bis-TBA, Solaronix) dye solution in ethanol for 18 h at room temperature. The fabrication of FTO/Pt counter electrodes and PDMS spacers, the assembling of DSCs with a microfluidic architecture, and the electrolyte (Iodolyte AN 50, Solaronix) filling procedure were previously described [13].

2.2. Characterizations

Morphological analysis on TiO_2 nts array was carried out using a ZEISS Supra 40 field emission scanning electron microscope (FESEM).

X-ray diffraction technique was used to investigate the crystalline structure of the membranes (Panalytical PW1140-PW3020, Cu K_α X-ray source).

The cell performances were characterized through I–V measurements under AM1.5G illumination (1000 W/m^2) using a class A solar simulator (91195A, Newport) and a Keithley 2440 source measure unit. IPCE spectra were acquired in DC mode using a 150 W xenon halogen lamp and a dual grating Czerny Turner monochromator. Electrochemical impedance spectra were collected under the same illumination and in dark condition using an electrochemical workstation (760D, CH Instruments) in the frequency range 10^{-1}–10^5 Hz, at different applied bias voltages; the amplitude of the AC signal was 10 mV. Experimental data of EIS were fitted using an equivalent circuit in order to obtain information about transport and recombination of charges [14]. OCVD measurements were performed using the same electrochemical workstation. All the cells were measured using a 0.22 cm^2 black mask.

3. Results and discussion

The growth mechanism of TiO_2 nts arrays in fluoride--based electrolyte can be described as the occurrence of three competitive reactions [15]. The field-assisted oxidation of Ti and dissolution of Ti ions in the electrolyte are the first two processes, while the third is the chemical dissolution of Ti and TiO_2 through the etching due to fluoride ions. The final appearance of the TiO_2 nt array, before and after detachment, is shown in Fig. 1a and b. For an anodization time of 2 h, a 12 μm thick TiO_2 nts membrane was obtained (Fig. 1c).

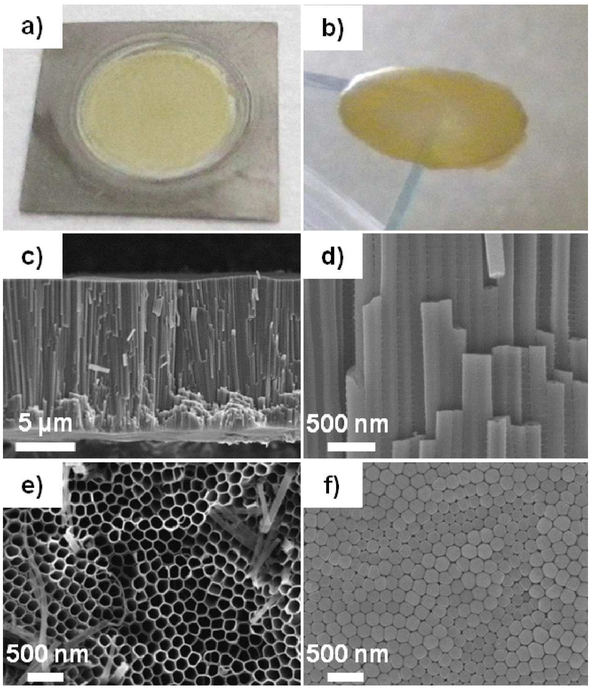


Fig. 1. Photograph of as anodized Ti foil (a) and self--standing membrane of TiO_2 nts (b); FESEM micrographs showing the cross-section of TiO_2 nts array at different magnifications (c, d) and the top (e) and bottom (f) views of TiO_2 nts.

The walls of the tubes are quite smooth (Fig. 1d) thanks to the polar organic nature of the electrolytic solution [16]. The average external diameter of the tubes was 120 nm. Figure 1e and f shows the top and the bottom of the nt membrane, revealing the hexagonally-packed assembly typical of the anodized titanium oxide. The wall thickness was not constant from the top to the bottom (results not shown) but increases resulting in an inner conical shape of the tube, as discussed elsewhere [15].

Figure 2 shows the XRD spectra of the as grown and annealed TiO_2 nt array. It is possible to see that the former is completely amorphous while the latter presents peaks in perfect agreement with the reference patterns for titania anatase (JCPDS 89-4921), both in peak positions and relative intensities.

The process flow for the fabrication of a transparent photoanode is described in Fig. 3: after anodization (a),

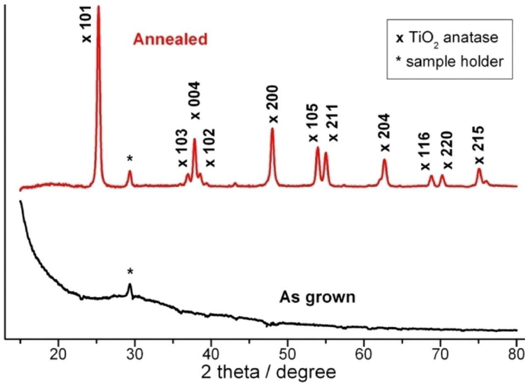


Fig. 2. X-ray diffraction pattern of as grown and annealed TiO_2 nt array. The experimental data are in perfect agreement with JCPDS reference pattern (JCPDS 89-4921), both in peak positions and relative intensities.

free-standing nt membranes (also shown in Fig. 1b) were easily separated by the metallic substrate without any crack following a self-detaching procedure consisting in repeated rinsing in DI-water and ethanol (b). The membranes were then transferred (c) and bonded (d) on FTO/glass substrates employing a 4 μl drop of TiO_2 sol as a binder and applying a slight pressure with a N_2 flow (d). At the end, annealing treatment was made to sinter the TiO_2 nps of the sol and crystallize the nanotubes array (e).

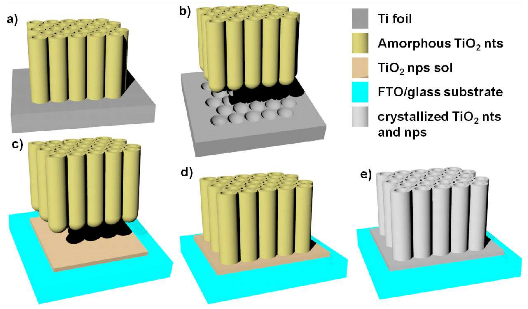
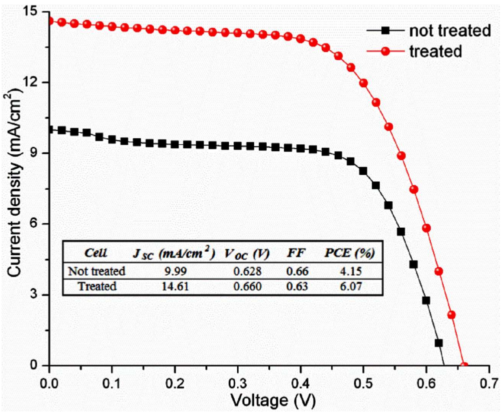


Fig. 3. Schematic of fabrication process flow of transparent photoanode employing TiO_2 nts array.

This approach for membrane detachment and bonding is easier than other previously reported in the literature [10, 15] since it does not involve any chemical etching or mechanical splitting for membrane separation and only one thermal step is required both for membrane crystallization and attachment.



Cell	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
Not treated	9.99	0.628	0.66	4.15
Treated	14.61	0.660	0.63	6.07

Fig. 4. Current density–voltage curves of TiO_2 nts based DSC with and without $TiCl_4$ treatment; photovoltaic parameters are summarized in the table reported in the inset.

The results of I–V measurements performed on the cells fabricated with the transparent TiO_2 nts array photoanode employing the microfluidic architecture are shown in Fig. 4 and photovoltaic parameters are summarized in the inset. As expected, the effect of the $TiCl_4$ treatment led to an improvement of the photovoltaic performances. The main effect of the treatment is a downward shift of the TiO_2 conduction band [17] that enhances the electron injection efficiency thus resulting in an increase of the total $J_{\rm sc}$ value: the overall power conversion efficiency raised from 4.15% up to 6.07%, also thanks to a little increase in $V_{\rm oc}$. The increase of the short circuit current density was evidenced also through IPCE measurement (not shown here): the height of the N719 IPCE-peak centered at around 540 nm is 40% higher for the treated cell with respect to the not-treated one.

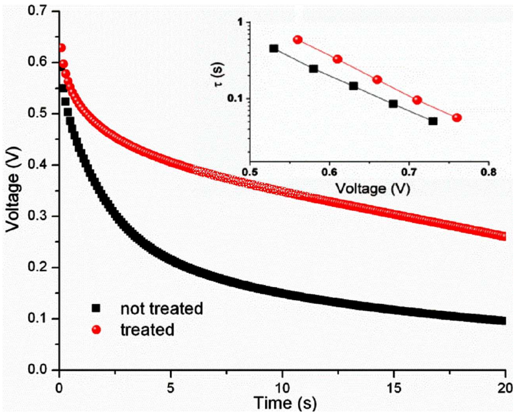


Fig. 5. Open circuit voltage decay curves of TiO_2 nts based with and without $TiCl_4$ treatment. In the inset the dependence of the electron lifetime as function of voltage is reported.

In order to evaluate the carrier lifetimes into the nanotubes array, open circuit voltage decay and electrochemical impedance spectroscopy measurements were performed. Figure 5 shows the exponential decay of the photovoltage after turning off the illumination [18]. For the $TiCl_4$-treated cell, the effect of reduced recombination losses due to the nps coverage of nts led to a slower decay of the open circuit voltage. From the fitting of the EIS spectra, the electron lifetime for different bias voltages has been calculated using the formula $\tau = (R_{\rm CT}Q_{\rm D})^{1/\beta}$, where the resistance R_{CT} is the charge transfer resistance related to the recombination of electrons at the nts–electrolyte interface, Q_{D} is the constant phase element (CPE) associated with the chemical capacitance at the same interface and β is the exponent of the CPE Q_{D} [19]. The calculated lifetimes as function of the applied voltage are reported in the inset of Fig. 5: the typical exponential dependence of τ from V_{oc} is evident in the semilogarithmic plot, and the values are higher for the treated cell. In particular, for this cell the electron lifetime value obtained at V_{oc} (177 ms) is very high compared to the one previously reported in similar transparent nts-based DSC [10]. This result can be related to the bonding procedure: employing TiO_2 sol instead of nps paste it is possible to reduce the thickness of the adhesion layer, obtaining a lower electron recombination at the nts/nps/FTO interfaces.

4. Conclusions

Front-side illuminated DSCs based on TiO_2 nt array were fabricated and fully characterized. Vertically oriented TiO_2 nts were obtained by anodic oxidation of a titanium foil and free-standing nt membranes were easily separated by the metal substrate following a self--detaching procedure. The approach presented for photoanode fabrication is innovative if judged against others previously reported in the literature: no chemical dissolution or mechanical splitting are involved for membrane separation and membrane crystallization and attachment steps are joined in the same thermal treatment. Employing a TiO_2 sol as a binder and using a $TiCl_4$ treatment, a conversion efficiency of 6.07% and an electron lifetime at V_{oc} of 177 ms have been achieved.

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