Fabrication of transparent TiO_2 nanotube-based photoanodes for CdS/CdTe quantum co-sensitized solar cells

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Abstract. In order to fabricate a solar cell, ordered TiO_2 nanotube (TNT) arrays were prepared by double anodization. TNT arrays with variable lengths were obtained by changing the duration of the anodizing process of up to 3h. TNT membranes were transferred to indium tin oxide substrates and attached with a B-TiO_2 sol. TNT photoanode with the best photoelectrochemical performance was sensitized with CdS by SILAR method. On other hand, CdTe quantum dots prepared via colloidal synthesis were deposited on TNT photoanodes for 2h, 4h and 6h. In addition, TNT/CdS was loaded with CdTe quantum dots for 4 h. Morphology and chemical modification of TiO_2 were characterized by FESEM and XPS, while their photoelectrochemical performance was measured by open-circuit photopotential and photovoltammetry under visible light. TiO_2 nanotubes grown during 2.5h showed the highest photocurrent due to presence of Ti^{3+} donor states by N and F co-doping, increasing the number of photogenerated electrons transported to back collector. TNT/CdS/CdTe photoanode reach the highest conversion efficiency under AM 1.5G simulated solar illumination.

1. Introduction

In recent years, sunlight harvesting has been considered the most attractive green alternative to decrease the use of non-renewable energy sources and diminish the environmental contamination. In order to collect high amounts of photons from solar energy, fourth-generation photovoltaic devices such as quantum dots sensitized solar cells (QDSSC) have been used. Cadmium chalcogenides (CdS, CdSe and CdTe) based quantum dots (QDs) have been studied due to their narrow band gaps, high extinction coefficient and multiple electron-hole pair generation [1], which extends the light harvesting of the device to visible or IR regions and improves its energy conversion efficiency. To fabricate QDSSC, QDs are deposited on wide-band gap semiconductors as TiO_2, promoting the injection of photogenerated electrons from QDs to TiO_2 and their transport through the solar cell [1-3]. Transport of electrons is hindered by the presence of grain boundaries in photoanodes prepared for photovoltaic applications from TiO_2 nanoparticulated films [4]. To overcome this disadvantage, oriented TiO_2 nanotube photoanodes are used to address the electron mobility through their tubular structure. TiO_2 nanotube membranes can be easily transferred to conductive glass substrate allowing the front-side illumination of solar cell to enhance its photovoltaic performance [4]. Nevertheless, the preparation of TiO_2 nanotubes with adequate characteristics is still a huge challenge in order to deposit a sufficient QDs content to improve the light harvesting, the electron transport through the photoanode and the energy conversion efficiency of solar cell.

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2. Experimental

2.1. Preparation of transparent TiO_2 nanotubes photoanodes

Ti foils (99.5% of purity, 2.5×2.0cm^2) were polished with different SiC emery papers. These foils were sonicated in ethanol, acetone, and rinsed with deionized (DI) water each one for 5min. Samples were anodized in an electrolyte solution containing 0.45wt% NH_4F and 2wt% DI water in ethylene glycol. A bias potential of 60V was supplied in a two-electrode cell, using a cathode of Cu. Anodization time was variated at 2h, 2.5h and 3h. Anodized samples were again rinsed with DI water, dried at 100°C, and calcined at 400°C for 2h with a heating rate of 3°Cmin^{-1}. In order to obtain transparent TiO_2 nanotubes (TNT) in a membrane form, a second anodization for 15min was carried out to the samples under the same experimental conditions to the first anodization. Materials were immersed in a 30wt% H_2O_2 solution during 2min. TNT membranes were removed from Ti and deposited on ITO substrate to prepare photoanodes using a boron doped TiO_2 sol as adhesive, whose preparation has been described elsewhere [5]. Photoanodes were again dried at 100°C and calcined at 400°C at a heating rate of 3°Cmin^{-1}.

2.2. Physicochemical and photoelectrochemical characterization of TNT photoanodes

The morphology of TNT was analyzed with a JOEL Quanta 650 FEG, and XPS spectra of materials were acquired by a SPECS PHOIBOS 100 spectrometer with a hemispheric analyzer operating at X-ray energy of 1486.6eV from Al Kα radiation. The peak fitting of high-resolution XPS spectra of C 1s, O 1s, N 1s, F 1s and Ti 2p was carried out with the CASA-XPS software. C 1s (284.6eV) signal was used as reference energy. The photoelectrochemical performance of TNT photoanodes was measured in a conventional three-electrode cell using an Autolab PGSTAT 302N potentiostat. A graphite rod (AGKSP grade) and Ag/AgCl(3.0M KCl) electrode were used as counter and reference electrode, respectively. The electrolyte solution was 1.0M Na_2S, which was deaerated for 20min by N_2 bubbling. A metal halide lamp (MHN-TD Phillips, 60mWcm^{-2}) was used as illumination source. Photopotential measurements were carried out at open circuit. Photovoltammetry measurements were performed at 10mVs^{-1} in positive direction from open circuit potential to 1.6V. The exposed geometric area of photoanodes was 1cm^2.

2.3. Preparation of TNT/CdS/CdTe photoanodes

CdTe QDs were synthesized by mixing 4mmol of $CdCl_2$, 3.2mmol of tioglycolic acid and 200mL of DI water in a 250mL three-neck flask under vigorous stirring and inert atmosphere. A 2.0 N NaOH solution was used to adjust the pH of the mixture to 10. The chalcogenide precursor was prepared mixing 0.6mmol $NaBH_4$ and 0.2mmol Te in 5mL of DI water under vigorous stirring and Ar inert atmosphere. The freshly prepared NaHTe solution was quickly injected into the Cd precursor solution and the final mixture was refluxed for 4h. The obtained QDs were purified by centrifugation at 5000rpm for 15min. CdTe QDs showed an average particle size of 4.2nm obtained by DLS. TNT photoanodes were immersed in 50mM dispersion of CdTe QDs during 2h, 4h and 6h. TNT photoanodes were also sensitized with CdS quantum dots by SILAR method. Thereby, photoanodes were dipped into methanol solutions of 0.1M $3CdSO_4{\cdot}8H_2O$ and 0.1M Na_2S each one during 1min. Eight SILAR cycles were performed according to literature [6]. Finally, photoanodes were immersed in 0.1M $Zn(CH_3COO)_2{\cdot}2H_2O$ and 0.1M Na_2S aqueous solutions (two SILAR cycles) to deposit a ZnS layer.

2.4. Photovoltaic measurements of assembled solar cells

In order to investigate the photovoltaic performance of TNT/CdS/CdTe photoanodes, solar cells were elaborated assembling the photoanodes with CoS based cathodes, which were prepared by mixing methanol solutions 0.5M $Co(NO_3)_2.6H_2O$ and 0.5M Na_2S, forming a black paste. The CoS paste was deposited on ITO and dried at 100°C during 15min. Solar cells were filled with polysulfide solution consisting of 1.0M Na_2S and 1.0M S. Typical current-voltage curves were acquired by using an

Autolab PGSTAT 204 potentiostat under solar illumination (AM 1.5G, 75mWcm^{-2}) simulated with a Suntest CPS+ solar simulator (ATLAS, GmBH). The exposed geometric area of photoanodes was 0.15cm^2.

3. Results and discussion

3.1. Morphology and chemical environment of TNT photoanodes

Figure 1 shows the typical top view and the cross section FESEM images of transparent TNT membranes obtained varying the anodization time. TNT average pore diameter was 85.8nm, 95.6nm and 116.0nm and an average length of 16.7μm, 20.1μm and 35.9μm was obtained at 2h, 2.5h and 3h of anodization time, respectively. This indicates to increase the anodization time keeping constant the NH_4F concentration and the applied potential, the compact oxide can be dissolved more deeply by fluoride ions, thereby enlarging the pores and the length of TNT. In addition, a well-oriented tubular structure is observed in the prepared materials.

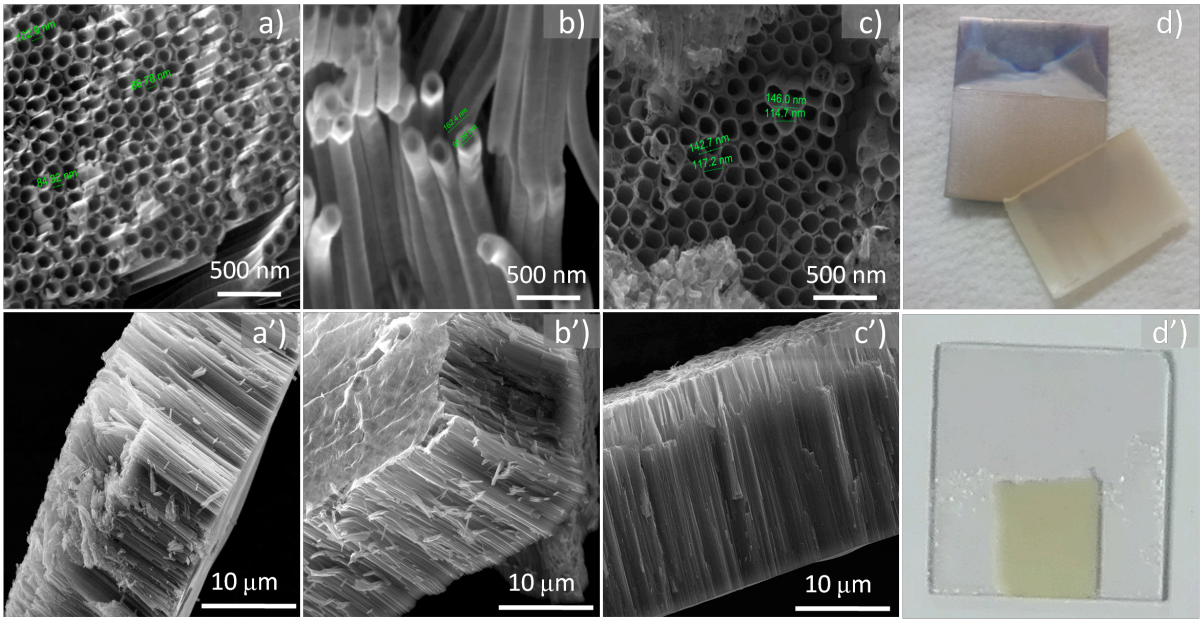


Figure 1. FESEM images of TNT grown at 2h (a), (a'), 2.5h (b), (b') and 3h (c), (c'), respectively. Photograph of a TNT membrane (d) before and after detachment from Ti (d) and (d') after deposition on ITO.

The chemical environment of typical TNT grown at 2.5h was determined by XPS analysis. Ti, O, C, N and F elements were identified in the general spectrum (Figure 2(a)). High resolution XPS N 1s spectrum (Figure 2(b)) exhibits two signals at binding energies of 399.4eV and 401.1eV, associated to the presence of N-O-Ti and N-Ti-O type bond into TiO_2, which indicates nitrogen was incorporated in interstitial and substitutional positions into TiO_2 lattice [7]. XPS peak at 684.2eV (Figure 2(c)) is ascribed to incorporation of fluorine in substitutional positions into TiO_2. It is well known that fluorine atoms are introduced into TiO_2 as fluoride ions, which induces the formation of Ti^{3+} donor states in semiconductor allowing its photoactivation under visible light [8]. This is confirmed by Ti $2p_{3/2}$ and Ti $2p_{1/2}$ photoelectron signals at 457.0eV and 461.1eV (Figure 2(d)), respectively, besides to Ti^{4+} signals from TiO_2 lattice (458.5eV) and the N-O-Ti bond (459.9eV). The coexistence of N and F species into semiconductor indicates the TiO_2 modification by co-doping, which would contribute to its photoactivity in the visible region.

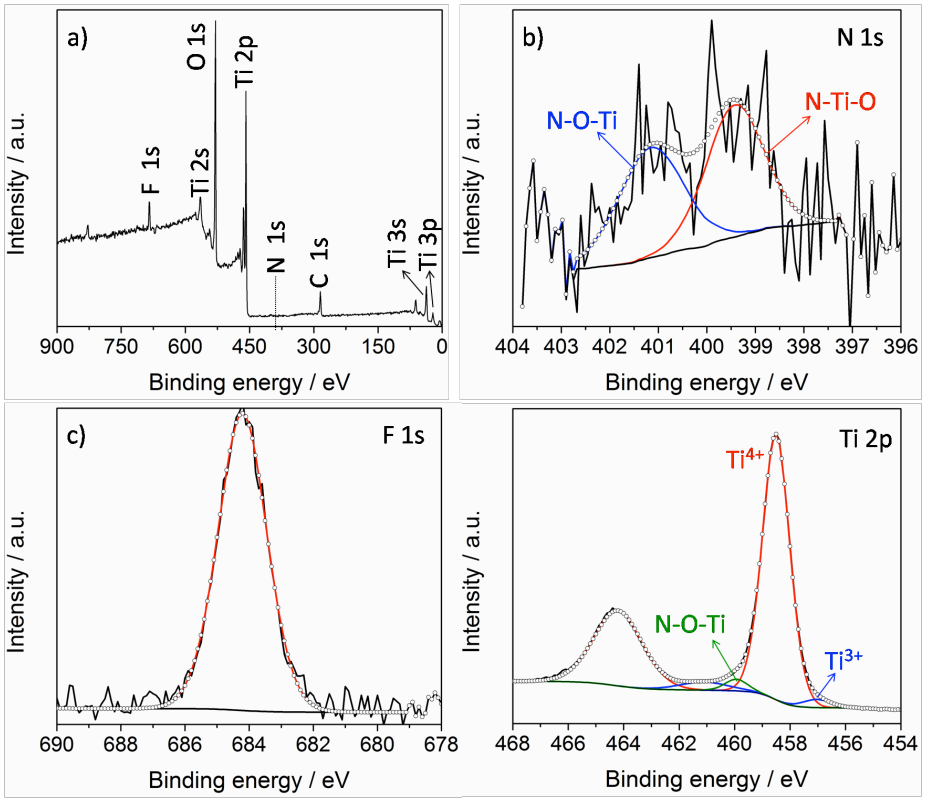


Figure 2. XPS general (a) and high-resolution XPS spectra of (b) N 1s, (c) F 1s, and (f) Ti 2p spectra of TNT photoanode grown at 2.5h.

3.2. Photopotential and photoelectrochemical measurements

Open-circuit potential measurements for the TNT based photoanodes are showed in Figure 3(a). To illuminate the photoanodes, a displacement of photopotential to more negative potentials is observed, indicating, first, the accumulation of photogenerated electrons in each material and second, a n-type semiconductivity. Increasing anodizing time leads to an increase in the photopotential, due to TNT enlargement, forming more lattice defects [9]. According to high resolution XPS Ti 2p spectrum, presence of fluoride ions induces the formation of Ti^{3+} donor states which are located below the bottom of conduction band of TiO_2 [8], allowing the photoactivation of semiconductor in visible region. Thus, to grow TNT to 35.9µm, more fluoride ions could be incorporated into TiO_2 lattice after anodization to form a high Ti^{3+} species content, promoting the accumulation of more electrons photogenerated under illumination.

In order to choose the electrode material with best photoactivity, TNT photoanodes were characterized by photovoltammetry (Figure 3(b)). To increase TNT length from 16.7µm to 20.1µm, an increment in photocurrent was observed. It is ascribed to formation of more Ti^{3+} donor species by fluoride ion modification. This lead to an increase of photogenerated electrons transported through the photoanode to reach the back collector, which enhances the conducting properties of material. For TNT of 35.9µm, the photoresponse decreased implying the formation of an excessive Ti^{3+} species content, which can act as recombination centers, hindering the electron mobility into the photoanode and thereby its photoelectrochemical performance. This is confirmed by the slow return to rest potential (in the dark) when light is turned off (Figure 3(a-iii)), indicating an increase of charge carrier trapping and recombination which adversely affect the electron transfer rate [10].

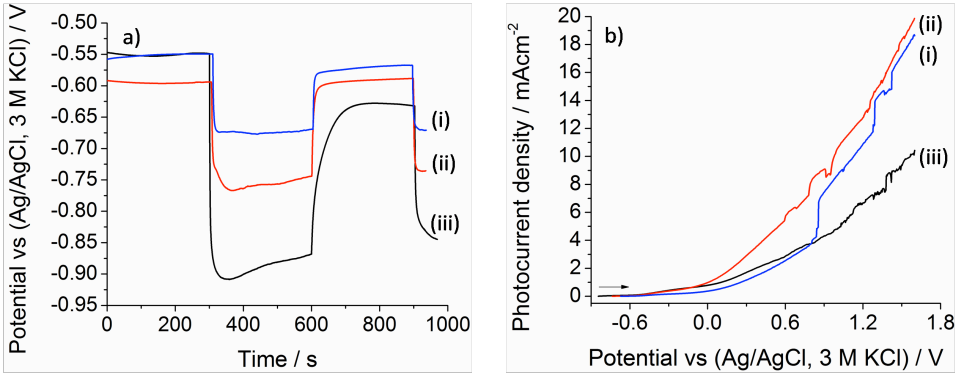


Figure 3. (a) Open-circuit photopotential and (b) photovoltammetry measurements performed in 1.0M Na_2S at $10mVs^{-1}$ for TNT photoanodes obtained for (i) 2h, (ii) 2.5h and (iii) 3h, respectively.

3.3. Photovoltaic performance of assembled CdTe sensitized solar cells

In order to prepare the photoanode for solar cell, CdTe QDs were deposited on TNT membrane supported on ITO with the best photoelectrochemical performance (Figure 3(b)). To improve the solar cell performance a ZnS layer was coated on the photoanodes to avoid the charge carrier recombination with the polysulfide solution [1,11]. Solar cells performance was evaluated for different load of CdTe QDs deposited on TNT membrane. Figure 4 shows the behaviour of the short-circuit current density (J_{sc}), the open circuit voltage (V_{oc}) and fill factor (FF). To increase the deposition time from 2h (2-CdTe) to 4h (4-CdTe), an increment of both J_{sc} and V_{oc} was observed. This indicates that at 4h, a sufficient CdTe QDs content can enhance the light harvesting of TNT photoanode, thereby increasing the number of electrons transported to back collector. Nevertheless, to raise the deposition time at 6h (6-CdTe), a decrease of J_{sc} and V_{oc} was evidenced, which could be associated to the presence of an excessive CdTe QDs content acting as recombination sites and/or an obstruction for the polysulfide solution to reach the TNT. Thus, although the FF was increased to increment the CdTe QDs load as response of improvement of light harvesting, electron transport through the device is inhibited, obtaining low J_{sc} and V_{oc} values.

The abovementioned can restrain the charge carrier separation and diminish the number of electrons injected to TNT. With the purpose of photogenerate more electrons under artificial solar illumination, CdS QDs were deposited on TNT photoanodes prior to 4-CdTe QDs sensitization. An increase of photocurrent was obtained due to light harvesting from CdS besides to transport the photogenerated electrons injected from CdTe QDs. A high J_{sc} is directly related to an increase of energy conversion efficiency of cell (η) which reached a value of 0.16% for TNT/CdS/CdTe photoanode. It is noteworthy that conversion efficiency for TNT/CdS is lower than TNT/CdS/CdTe, hence sensitization with both CdS and CdTe shows a synergistic effect. The photovoltaic parameters of solar cells are given in Table 1. In spite of the V_{oc} shift to ~-0.30V, a low short circuit-current was registered; this may possibly be attributed to a deficient contact between TNT membrane and ITO substrate or to some internal resistance of the cell.

Table 1. Solar cell parameters obtained from J-V curves for different photoanodes here prepared.

Photoanode	$J_{sc}/mAcm^{-2}$	V_{oc}/V	FF	$\eta/\%$
TNT	0.33	-0.18	0.13	0.01
TNT/2-CdTe	0.21	-0.18	0.13	0.01
TNT/4-CdTe	1.04	-0.24	0.24	0.08
TNT/6-CdTe	0.31	-0.22	0.33	0.03
TNT/CdS	1.15	-0.27	0.29	0.12
TNT/CdS/4-CdTe	1.39	-0.29	0.30	0.16

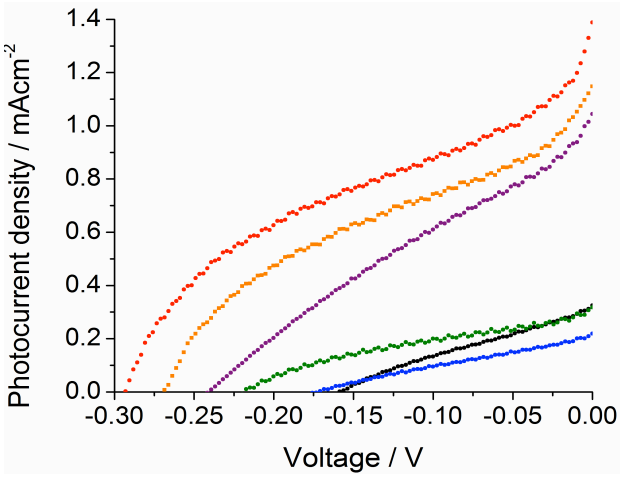


Figure 4. J-V characteristics of solar cells based on (a) TNT, (b) TNT/2-CdTe, (c) TNT/4-CdTe, (d) TNT/6-CdTe, (e) TNT/CdS and (f) TNT/CdS/4-CdTe photoanodes.

4. Conclusions

Highly oriented transparent TiO_2 nanotube photoanodes with different average pore diameter and length were prepared by double anodization by varying the TNT growth time. The materials were photoactive to visible region due to the presence of N and F into the TiO_2, causing the co-doping of semiconductor. The TNT photoanode obtained at 2.5h showed the best photoelectrochemical performance, due to the enhancement of electron flow to back collector by the presence of an adequate Ti^{3+} species content formed by N, F co-doping. A solar cell was fabricated modifying TNT with both CdS and CdTe QDs, achieving a maximum of conversion efficiency of 0.16% under ¾ sun illumination for 4h of CdTe deposition and using a CoS cathode. Synergistic effect was obtained by TNT sensitization with CdS/CdTe QDs assembly improving the light harvesting of solar cell. Current efforts are conducted to enhance the synergy of cadmium chalcogenides by band-gap engineering and to obtain a best cathode material.

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