Using two-step anodized TiO2 nanotubes to increase the collection efficiency of DSSCs at low illumination angles

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Received: 2015/10/06 Accepted 2016/1/06

Abstract

Photonic crystals (PCs) with extraordinary optical properties, can be used to enhance light absorption and improve solar cell's conversion efficiency. Prohibition of propagation for some particular wavelengths of light in PCs result in increasing the path length of light in working electrode of solar cell that enhance the probability of photon absorption. In our work, we present a two-step anodization method for manufacturing the dye-sensitized solar cells (DSSCs), having a three-dimensional roughness material as working electrode that looks like a semi-photonic crystal mesoporous structure. This approach is a facile one to produce a PC-like structure and it plays a great role in improvement of output power of DSSC. Measurements show that solar cell's photovoltaic conversion efficiency based on this 3D roughness structure is higher than the conventional DSSC.

Keywords: Photonic crystal; Light absorption; Dye-sensitized solar cell (DSSC); Optimized structure.

Introduction

The pioneering work of O'Regan and Grätzel introduce dye-sensitized solar cells (DSSCs) as a promising technology for future sustainable energy generation. Due to their great potential for cost-effective photovoltaic devices, TiO_2 was widely used as photo-electrode semiconductor in DSSCs [1]. Improving the light-to-current conversion efficiency is one of the biggest challenges of DSSCs and researchers have many efforts to overcome this challenge by modifying the cell's structure and using new materials [2-5].

DSSCs are typically consist of a mseoporous semiconductor nanostructures like TiO_2 nanoprticles on a conducting substrate (working electrode), a sensitizer such as N719 dye molecules which is anchored to the surface of mesoporous layer of semiconductor, an electrolyte and a platinum coated substrate as counter electrode. Under sunlight irradiation, electrons excited from HOMO band of dye to LUMO band and can then be injected from the LUMO into the conduction band of semiconductor electrode. These carriers path through the mesoporous layer to the external circuit and finally collect by counter electrode [6]. The oxidized dye is reduced to its original state by electron donation from the redox couple in the electrolyte. Usually electrolyte is an organic solvent or ionic I_3^-/I^- redox (fig. 1a).

In DSSCs, mesoporous film thickness is a major factor in light absorption limitation [7]. Optical adjustments such as using highly scattering layers are one way to enhance the light absorption. Highly scattering layers have large particles that lead to increase the photon path length in DSSCs. Using photonic crystal as photo-electrode is another choice to manage photon transport in the DSSCs. Some structures such as 3D inversed TiO_2 opal and porous brag stacks have been previously used in DSSCs [8-12].

Today various materials and photoanode structures with different processes like 1D or 3D mesoporous by hydrothermal/solvothermal, electrochemical anodization, electrospinning and spray pyrolysis or atomic layer deposition methods are used to improve the efficiency of DSSCs. Also doping of different ions, decoration of noble metals and metal oxides and coating with up/down conversion materials are the other fields of research. As the sensitizers of the device there is some new fields like the perovskite-based

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sensitizers, quantum-dots, porphyrin dyes and metal-free organic materials are under investigation [13].

Fabrication of working electrodes of DSSCs with an inversed opal TiO_2 PC structures improve photovoltaic conversion efficiency by enhancing light harvesting in the working electrodes [10]. In some previous reports, two main mechanisms for effect of periodic working electrode structure on the light absorption of DSSCs have been proposed; slow photon effect and back scattering effect. The slow photons in PCs have a group velocity very close to zero at the edges of PC's band gap. Little group velocity of slow photons leads to increase the path length of light and then increase the apparent thickness of the light absorbent material [14]. Back scattering effects is enhancement of light absorption resulted from the prevention of passing light at the photonic band gaps [8].

Photonic band gap leads to prohibition of propagation for some wavelengths of light in PCs. The band gap of photonic crystal is similar to the band gap of semiconductors, in which the electrons with particular energies cannot find in the semiconductors. In PCs, photons with particular frequencies cannot propagate in photonic crystals [15,16]. Photonic band gaps that prevent photon propagation in all directions are named as three dimensional band gaps.

Mallouk et al. in their report showed an enhancement of light harvesting by coupling a TiO_2 PC layer into a TiO_2 working electrode, due to increase in the path length of light in photo-electrode [8,10]. Some other theoretical and experimental studies have been done to investigate the effect of PC structures in improving the photo-conversion efficiency of DSSCs [11,12,17]. However, fabrication of a PC with a band gap in the visible light range and also one with a large active area is so difficult [18,19]. Here, we offer a facile approach to fabricate a DSSC with a PC working electrode and show improvement of the photo-conversion efficiency.

In this research, we produce photonic crystal structure using a new and facile method based on the TiO_2 nanotubes. TiO_2 nanotubes array have been widely used as photo-electrode of DSSCs [20-26]. Electrochemical anodization is an efficient approach to prepare TiO_2 nanotube membranes due to its simplicity, low cost, self-ordering process, ease to controlling nanotube morphology and large area production [27]. By using a two-step anodization with different angle between the electrodes in two steps, we could prepare a PC structure in TiO_2 nanotubes array. This structure is almost like a woodpile structure. Woodpile photonic crystals have some classes such as diamond like symmetry [28].

Fabrication of such structure was started by anodization of TiO2 foil by setting two electrodes in parallel positions. In the next anodization step, holes in second direction were drilled by taking an angle between the two electrodes (as see in fig.1b). The final structure includes two cylindrical arrays which their axis is in different directions and their crossing points produce a 3D periodic structure that look like a photonic crystal material. This structure acts like a photonic crystal and prepare an optical band gap. Transmittance spectrum of the obtained structure proves this matter. Finally we fabricate DSSCs using this structure and compare them with conventional photo-electrode.

Experimental Section

Titanium foils with a thickness of 1 mm were cleaned by sonication in ethanol for 5 minutes, rinsed with deionized water (DI), and finally dried in an oven at 100 °C for 5 minutes. A solution containing 0.1M HF and ethylene glycol/DI water with 98/2 ratio was used as the electrolyte of anodization. All anodization processes were carried out at the room temperature. In the electrochemical cell, the titanium foil as anode electrode and Cu as counter electrode were placed in the parallel position with a distance of 5cm. The

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anodized samples were then placed in ethylene glycol and aceton for 15 and 20 minutes respectively to remove the undesirable residues.

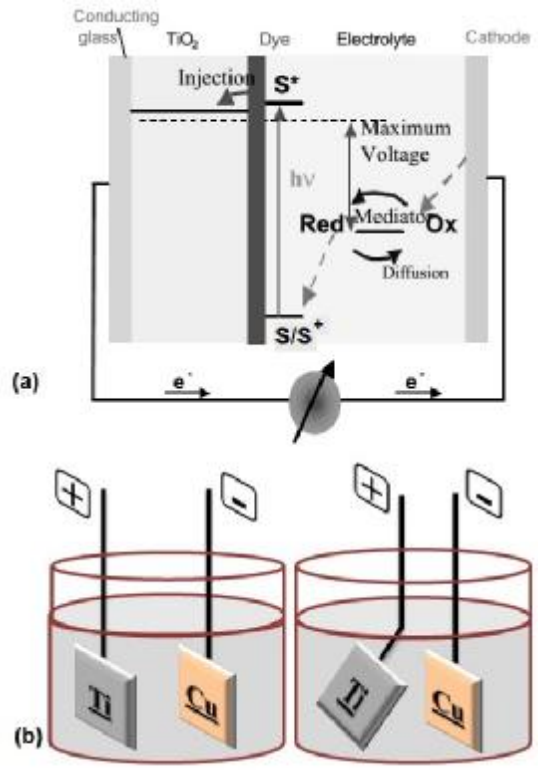

Fig. 1: (a) Schematic of a DSSC work condition [7], (b) Two-step anodization process; Anodization by two parallel electrodes as the first step (left) and anodization by electrodes with an angle between them (right).

To fabricate the solar cell, prepared TiO_2 nanotubes photo-electrodes were immersed overnight (18 hours) in a 0.1 mM solution of N719 dye, then immersed in ethanol for 1 minute for establishment the dye-loading of the TiO_2 nanotubes layers. The dye loaded layers were used as working electrode in DSSC. A platin coated TCO glass as counter electrode was placed on the TiO_2 nanotubes photo-electrodes. Sealing the cell was carried out using a hot melt polymer with 25μm thickness. An iodine based electrolyte was introduced into the space between the sealed electrodes.

Results and discussions

Electrochemical anodization includes several processes [28]: (1) Interaction of the metal with O^{2-} or OH^- ions leads to oxide growth at the surface of the metal. Migration of anions through the oxide layer establishes the oxide growth in the metal/oxide interface. The anodic oxidation reactions can be represented as:

$$2H_2O \rightarrow O_2 + 4H^+ \quad (1)$$

$$Ti + O_2 \rightarrow TiO_2 \quad (2)$$

(2) Applying an electric voltage leads to movement of Ti^{4+} cations (metal cations) toward the oxide/electrolyte interface. (3) Due to the applied electric field the Ti-O bond undergoes polarization and is weakend promoting dissolution of the metal cations that leads to abandon Ti^{4+} cations into the electrolyte. Movement of the O^{2-} anions toward the metal/oxide interface makes the oxidation process feasible. (4) Formation of nanotubes rather than nanoporous structure is due to the chemical dissolution of titania in the HF electrolyte (by the following reaction).

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \quad (3)$$

This dissolution process reduces the thickness of the oxide layer, keeping the electrochemical etching (field-assisted oxidation and dissolution) process active. By setting an angle between two electrodes in the second anodization step, holes in new direction will be drilled as a consequence of the above mentioned processes (field-assisted oxidation and dissolution). These holes in the sidewall of TiO_2 nanotubes array can be seen in the SEM images of figure 2.

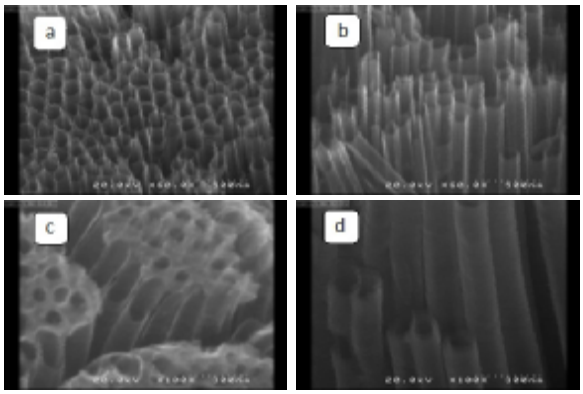

Fig.2: SEM images of one dimension TiO_2 nanotubes array with perfect walls (a and b) and three dimension TiO_2 nanotubes array with holes in walls of first nanotubes array (c and d)

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The reflection spectra of 1D and 3D TiO_2 nanotubes array are shown in figure 3. The 1D TiO_2 array was produced using electrochemical anodization method by applying 60V voltage for 180 minutes. To produce 3D TiO_2 nanotubes array, we used two-step anodization by applying 60V voltage for 60 and 150 minutes, respectively. In the second step, angle between two electrodes was 45˚ relative to vertical direction. According to the Lambert's cosine law, intensity of reflection from the surface changes as a function of angle from the vertical axis [30]. The law explains that the reflection intensity decreases with increasing the angle relative to the vertical axis. Such a manner can be seen in the 1D TiO_2 nanotubes array. Reflection measurements of the 3D structure show an abnormal behavior. As can be seen from figure 3, intensity of the reflection decreases by increasing the incident angle up to about 20˚ and after that increases by increasing the incident angle. Such variation can be assigned to 3D roughness of the sample obtained by two step anodization.

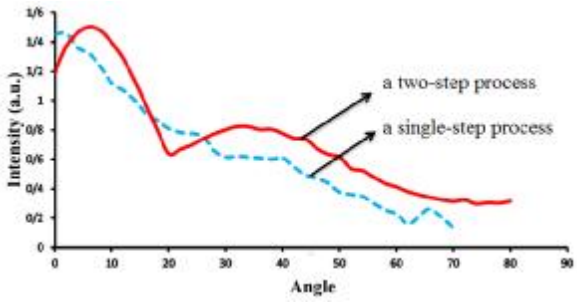

Fig. 3: Reflection intensity as a function of angle. Red continuous curve shows reflection spectrum of three dimensional nanotubes array and blue dashed curve shows reflection spectrum of one dimensional nanotubes array. The irradiation wavelength is 330.090 nm

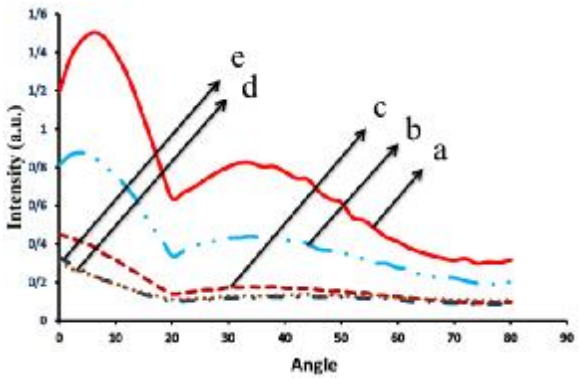

Fig. 4: Reflection intensity as a function of angle in different irradiance wavelength. (a) 330 nm, (b) 450 nm, (c) 550 nm, (d) 660 nm, (e) 720 nm

3D structure has also a different response to the various wavelengths which is illustrated in figure 4. It is obvious from this figure that maximum ratio of the second pick to the first pick occurs in a wavelength of 330.090 nm which can be explained by the radius of nanotubes.

At the end of the anodization process, electric voltage was decreased to zero over 1 minute. Then the fabricated TiO_2 nanotube layer was detached by sonication in a methanol bath for 45 seconds and dried in air stream. In this step, the stress in metal/oxide interface lead to monolith separation of TiO_2 nanotube layer from the Ti substrate.

Comparison between the transmittance spectra of 1D and 3D TiO_2 nanotubes array, shows that the 3D structure acts like a photonic crystal and prohibit propagation of special photons through the material, fig. 5. There is a decrease in transmission intensity specially, the spectra is flattened in the range of 580 – 700 nm, evidencing the photonic band gap of the fabricated 3D structure.

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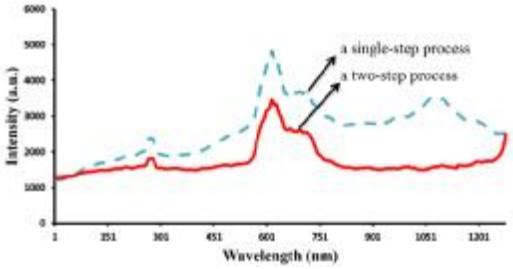


Fig. 5: Transmittance spectrum of three dimensional nanotubes array (red continuous curve) and one dimensional nanotubes array (blue dashed curve).

As mention before, reduction in the transmittance and therefore enhancement in the light harvesting of 3D structure leads to increase the path length of light and accordingly leads to enhance the light absorption and increasing the photo-current of DSSC. To investigate the influence of 3D TiO_2 nanotubes array on the efficiency of DSSC, we fabricated solar cells from the obtained 1D and 3D photo-electrodes. Figure 6 shows the current density versus voltage for as prepared solar cells. Table 1 includes the electrical parameters of these two solar cells.

As expected, using the 3D TiO_2 nanotubes array in DSSC causes an increase in photo-current of the cell. I-V tests show that the photovoltaic conversion efficiency of the cell based on the PC structure is higher than the traditional DSSC.

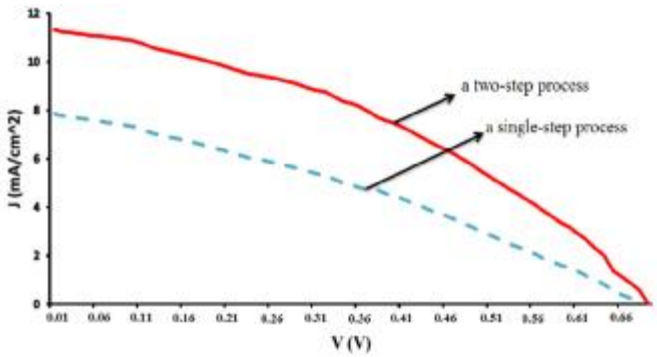


Fig. 6: Current density versus voltage of DSSC. Red continuous curve shows behavior of DSSC with a three dimensional TiO_2 nanotubes array as working electrode and blue dashed curve shows same solar cell with a one dimensional nanotubes array as working electrode

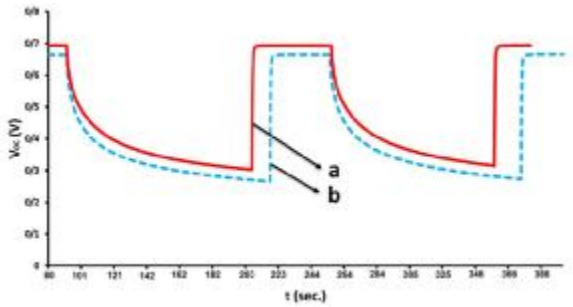
Table 1: Electrical Parameters of DSSCs with three dimensional structures as working electrode

	Open-circuit voltage V_{OC} (V)	Short-circuit current density J_{SC} ($mAcm^{-2}$)	Fill-Factor (FF)	Efficiency (%)
Solar cell with **1D** TNT working electrode	0.66	7.86	0.34	1.69
Solar cell with **3D** TNT working electrode	0.68	11.33	0.37	2.91

The value of V_{oc} was recorded versus the measuring time when the illumination was changed from 1 sun to dark. The electron lifetime τ_n can be related to the Voc decay as,

$$\tau_n = -(k_BT/e).(dVoc/dt)^{-1}$$

Here, k_BT is the thermal energy, e is the positive elementary charge, and dV_{oc}/dt is the time derivative of Voc [30]. The V_{oc} decay and lifetimes curves of these two solar cells are shown in figure 7. Solar cell based on the 3D TiO_2 nanotubes array has a higher lifetime than solar cell fabricated by 1D TiO_2 nanotubes array photo-electrode. It means that PC structure leads to decrease the electron recombination rate.



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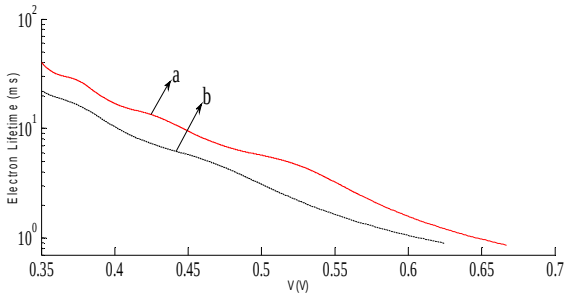

Fig. 7: V_{oc} decay curve (top) and lifetimes curve (bottom) of solar cells with three (a) and one (b) dimensional structures as working electrode.

As the final test, we measured photo-current of these two solar cells as a function of illumination angle, fig. 8. As shown in this figure, the photo-current of traditional DSSC decreases by increasing the illumination angle and at the 70˚ the current has a so little value. But, in the case of DSSC based on the PC structure, before the 55˚, behavior of cell is similar to the traditional cell but after this point there is an increase in photo-current of the cell due to presence of nanotubes array in second direction. Also, the main decrease occurs at 85˚ rather than 70˚. It can be said that presence of nanotubes array in second direction in DSSCs based on the PC photo-electrode leads to more light absorption in higher angles. Therefore, using such a 3D structure as working electrode of DSSC have the advantage of better solar cell's performance in the higher illumination angle conditions.

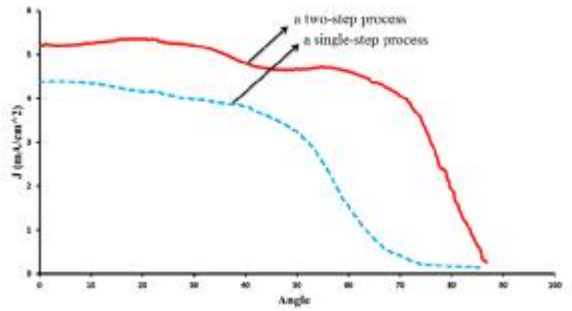

Fig. 8: Photo-current as a function of illumination angle for solar cells with three (red continuous line) and one (blue dashed line) dimensional structures as working electrode.

Conclusion

Application of a PC structure as working electrode of DSSCs leads to an improvement in light harvesting of the solar cells. Results show that such improvement was occurred mainly in a special wavelengths corresponding to the photonic band gap of the PC. 3D TiO_2 nanotubes array (PC structure) was fabricated by using two-step electrochemical anodization process. Existence of photonic band gap can be perceived by transmittance and reflection spectrum of the structure. To investigate effect of this structure on performance of solar cells, two DSSC fabricated with 1D and 3D TiO_2 nanotubes array separately. Results showed that photo-current and power conversion efficiency of the DSSC based on the PC structure as working electrode has 57% enhanced compared with the cell without a PC layer (under similar total thickness). Also using 3D structure leads to a better operation of DSSC under higher illumination angles.

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