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Revision Manuscript for RSC Advances**Ref. No.: RA-ART-07-2014-007162.R1****Fabrication of TiO₂ nanotube arrays and its application in flexible dye-sensitized solar cells**

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ABSTRACT

TiO₂ nanotube arrays have been widely used as the photoelectrode in dye-sensitized solar cells (DSSCs). In this work, free-standing TiO₂ nanotube arrays were prepared by two-step electrochemical anodization of titanium foils, then the TiO₂ nanotube arrays were transferred to a flexible ITO/PEN substrate using titania slurries. SEM images showed that the TiO₂ nanotube arrays with different lengths (10, 14, 20 and 30 μm) were successfully obtained. The photovoltaic properties for incident photon to current efficiency (IPCE) and photovoltaic conversion efficiency were also studied, it showed that the best photovoltaic conversion efficiency of DSSCs based on 20 μm length TiO₂ nanotube arrays was of 3.44%.

Keywords: Flexible dye-sensitized solar cells; TiO₂ nanotube arrays; anodic oxidation process

1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered as one of the most promising power sources because of their relative low cost, easy production and high conversion efficiency.¹⁻⁴ DSSCs with the conversion efficiency over 15% have already been achieved.⁵ Recently, the concept of flexible DSSCs has attracted more attentions due to increasing demand for lightweight, flexible electronic devices and low production cost.⁶⁻⁸ Flexible DSSCs based plastic substrate (PET or PEN) have some unique advantages in their flexibility, lightweight, bend and the possibility of roll to roll production.⁹

However, DSSCs with plastic substrate have a lower efficiency than that of glass substrate, as the plastic substrates need to be treated below 150 °C,¹⁰ and it limits the using of the organic binders, which were always used to achieve a good interface contact between the photoanode film and substrates in preparation of TiO₂ photoanodes.^{11,12}

Till now, many TiO₂ nanomaterials have been used as photoanodes in flexible DSSCs. Compared with TiO₂ nanoparticles,^{13,14} one-dimensional TiO₂ nanomaterials are suggested to be superior in chemical and electrical performance due to its unique channel for carrier transportation.¹⁵⁻¹⁸ Among them, TiO₂ nanotubes are suggested to be superior used in flexible DSSCs due to their high ordered structure with tunable shape and diameter and simple preparation process.¹⁹⁻²² However, it still needs to form the flexible photoanode film with a post-annealing treatment.

Chen et al achieved a power conversion efficiency of 3.6% based TiO₂ nanotubes/Ti photoanodes.²³ However, for the nanotube arrays grown on Ti plate, illuminated sun light is only possible from the opposite side of the cell, and this kind of back-illumination may limit the effective light absorption.²⁴ Recently, it has been reported to prepare free-standing TiO₂ nanotubes and transfer it on a flexible transparent conducting substrate.²⁵⁻²⁷ Most importantly, it may form a whole flexible photoanode film with high crystalline degree, which may avoid the post-annealing treatment. Therefore, it provides a good route to transfer the prepared TiO₂ nanotube arrays on the flexible polyethylene naphthalate (PEN) substrates coated with indium tin oxide (ITO), which may realize the fabrication of the front-illuminated flexible DSSCs to improve the light absorption and the photovoltaic performance.

In this work, free-standing TiO₂ nanotube arrays were prepared on Ti foil in ethylene glycol based electrolyte by two-step anodic oxidation process, which is annealed at 150 °C in advance to form the well-crystallined anatase TiO₂ phase, and then they were transferred onto the flexible ITO/PEN substrate by using titania slurries without any organic binder. It is used as the photoanodes to fabricate the front-illuminated flexible DSSCs.

2. Experimental section

2.1 Materials synthesis

Ti foils with thickness of 100 μm were purchased from Baoji metal Co., Ltd. in China, TiO₂ nanoparticles (P25) with the diameter of 30 nm are purchased from Degussa Co., Ltd. in Germany, N719 dye ((C₄H₉)₄N₂Ru(II)L₂(NCS)₂) is bought from

Solaronix Co., Ltd. in Switzerland, and flexible ITO/PEN substrate and Pt-sputtered ITO/PEN counter electrodes are purchased from Peccell Technologies in Japan with the sheet resistance of $15 \Omega\text{cm}^{-2}$. All of the other chemical reagents used in the experiments are of analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd., and used without further purification.

2.2 Fabrication of free-standing TiO_2 nanotube arrays

TiO_2 nanotube arrays were fabricated by a two-step anodic oxidation process of Ti foil. The Ti foils were firstly subjected to chemical cleaning to remove oil stains and some oxides on the surface using a mixture of deionized water, HNO_3 , H_2O_2 , urea ammonium and fluoride at the same time. Then, they were rinsed with deionized water and ethyl alcohol following dried in air at 60°C . The titanium oxide film was obtained by Ti metal anodization in an the ethylene glycol solution containing 0.08 M NH_4F and 1.5% (volume fraction) H_2O by using graphite plate as the cathode, and the distance between the Ti foil and graphite plate was about 3 cm. Ti foil was accomplished by a direct pre-anodization at room temperature in ethylene glycol solution by applying a DC voltage of 60 V for 1 h. Samples were then subjected to an ultrasonic bath and immersed in 10% H_2O_2 solution to remove the TiO_2 film. The anodization process was continued in the same solution for 2 h, 3 h, 5 h, 8 h respectively. During the two-step anodic oxidation process, we used the anodization voltage of 60 V to obtain the free-standing TiO_2 nanotube arrays with various lengths.

To crystallize amorphous TiO_2 into the anatase phase, the TiO_2 nanotube arrays /Ti foil were calcined at 450°C for 2 h in air. After the annealing treatment, the

free-standing TiO₂ nanotube arrays were obtained by a second anodization process in the same electrolyte solution for 30 min.²⁸ The a new thin film was formed under the nanotube membrane with the reducing of the adhesion strength of the Ti foil and TiO₂ nanotube arrays film in the second anodization process.

The samples were washed and then soaked in 10% H₂O₂ solution for 10 min, and the whole TiO₂ nanotube arrays film might be easily separated from the Ti substrate. The prepared TiO₂ nanotube arrays film was washed with deionized water for 3 times, and then dried naturely at room temperture.

2.3 Transferring of free-standing TiO₂ nanotube arrays on transparent ITO/PEN

The free-standing TiO₂ nanotube arrays were transferred onto the flexible ITO/PEN substrates by using titania slurries without any organic binder. Titania slurries were prepared as following: P25 nanoparticles were mixed with tertiary butanol and deionized water with volume ratio 2:1, and then slurry with TiO₂ content of about 30wt% was obtained by the ball mill with 20 h. Then, the titania slurries were used to make a thin films of about 5 μm on ITO/PEN plastic substrates by using the doctor blading method. The free-standing TiO₂ nanotube arrays were cut into a square thin film with the width of 8 mm and a length of 8 mm, and then put on the top of the layer of the titania slurries quickly. Electrodes were dried in vacuum at 120 °C for 2 h to ensure a good adhesion occurs between film and flexible substrate. It was used as the photoanode to fabricate the front-illuminated flexible DSSCs, as shown in **Scheme 1**.

2.4 Fabrication of DSSCs

The N719 dye of Cis-bis(isothiocyanato) bis (2,2'-bipyridyl-4, 4'-dicarboxylato)-ruthenium(II)bis-terabutyl-ammonium was used as the sensitizer. TiO₂ electrodes were dipped in a 0.5 mM solution of N719 dye in ethanol for 24 h in dark environment, and then the dye molecules may be loaded onto the nanotube array film. The solar cell was fabricated by assembling spinning Pt counter electrode and N719 dye sensitized TiO₂ nanotube arrays film on flexible ITO/PEN substrate. The solar cell was sealed by using a Surlyn thermoplastic frame. A standard redox electrolyte was prepared by dissolving 0.05 M I₂, 0.5 M LiI, 0.3 M DMPII and 0.5 M 4-TBP in acetonitrile solution.

2.5 Characterization

The crystal structures and morphologies of the samples were characterized by X-ray diffraction (XRD, PertPro, PANalytical, Netherlands) and field emission scanning electron microscopy (FESEM, JSM-5610LV, JEOL Tokyo, Japan), respectively. UV-Vis spectra were tested using UV-Vis absorption spectrometer (UV-2550, Shimadzu, Japan). Full sun conversion efficiency was characterized by the Keithley 4200 semiconductor characterization system (Keithley Instruments, USA) under AM 1.5 condition (Newport 91160, 300 W xenon lamp, USA). The light intensity of the illumination under AM 1.5 condition was determined using a reference monocrystalline silicon cell system (Oriel, USA). The incident photon to current conversion efficiency (IPCE) was measured using Newport's IPCE Measurement Kit (CrownTech, Q Test Station Series, USA), where a monochromator

was used to obtain the monochromatic light from a 300 W Xe lamp (Newport). Electrochemical impedance spectroscopy (EIS) was used to investigate electronic and ionic processes in DSSCs, using an Autolab Potentiostat 30 system (Metrohm, Switzerland) at the output frequency of 10^6 Hz-0.01 Hz at an applied bias of V_{oc} with AC amplitude of 10 mV.

3. Results and discussion

XRD patterns of the annealed TiO₂ nanotube arrays on Ti substrates with various anodization time are shown in Fig. 1, which the diffraction peaks are corresponding to anatase TiO₂ phase (JCPDS No. 84-1285), and some diffraction peaks of Ti foil can be also observed.

Fig. 2 shows the FESEM images of TiO₂ nanotube arrays with the anodization time at 2 h, 3 h, 5 h and 8 h at the applied voltage of 60 V, and the corresponding lengths of the TiO₂ nanotube arrays are about of 10 μ m, 14 μ m, 20 μ m and 30 μ m, respectively. Therefore, the lengths of the nanotubes can be controlled by adjusting the anodization time. The cross-sectional views of FESEM images in Fig. 2 show that the TiO₂ nanotubes are highly ordered and packed vertically side by side. It must be noticed that the top views of nanotube with different length are quite smooth and uniform, while some impurities exist in the 30 μ m TiO₂ nanotube arrays in Fig. 2 (d), and this may be caused by anodization process with ultra-long time.

Fig. 3(a) shows the UV-Vis spectra of the dye solutions desorbed from the dye-sensitized TiO₂ nanotube arrays films with the various lengths. On account of the varied thicknesses of the photoanode films, the dye loading content is also

different. Generally, it can be concluded from Fig. 3(a) that the desorbed dye content increases with the increasing of the nanotube arrays length due to the nanotube arrays surface area. Interestingly, the 30 μm TiO_2 nanotube arrays almost have the same optical absorption compared with that of 20 μm nanotube arrays, it may be due to the fact that many impurities block the nanotube arrays to cause a low dye adsorption with the nanotube arrays length over some certain value. The incident photon-to-current conversion efficiency (IPCE) curves in Fig. 3(b) are well fitted with the UV-Vis spectra in Fig. 3(a), and it is believed that most IPCE peaks originate from the dye molecules' absorption. The optical absorption at about 530 nm is assigned to ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ transition of $3d$ electrons of the Ti^{3+} ions,¹² and the excitation of Ti ions has some contributions to the IPCE plots in a certain extent. In general, dye monochromatic incident photon-to-electron conversion efficiency is proportional to the monochromatic light absorbance. Therefore, it is believed that the increasing of maximum IPCE value from 30% to 52% is due to the the dye adsorption amount of photonaode. The IPCE value of the nanotube photoanode with 20 μm length reaches 52%, which is higher than that of the TiO_2 nanotube arrays with 30 μm length.

Fig. 4(a) shows the photocurrent density-voltage (J-V) curves of flexible DSSCs based on TiO_2 nanotube arrays electrode under AM 1.5 conditions, in which the total active cell area is 0.64 cm^2 , and the detailed performance is listed in Table 1. It can be concluded from the Fig. 4 that the photoelectric performance increases with the increasing length of the nanotube arrays, and the corresponding performance is best for the 20 μm nanotube arrays with a J_{sc} of 7.35 mA cm^{-2} , V_{oc} of 688 mV, FF of 0.680

and η (%) of 3.44%. Compared with the performance of photoanode with the 10 μm nanotubes, the short-circuit current density (J_{sc}) and conversion efficiency of the 20 μm nanotube arrays increase by 38% and 58%, respectively, and this is due to the higher dye adsorption. When the length reaches to be 30 μm , the performance decreases with a J_{sc} of 6.83mA cm^{-2} and η (%) of 3.08%, which is in well consistent with the UV-Vis spectra in Fig. 3(a) and IPCE curves in Fig. 3(b). However, the TiO_2 nanotube arrays with the too long length (30 μm) may not favor for the extra loading of the dye molecules. This may be caused by its higher defect densities, as some existed impurities block the nanotube arrays to cause a low dye adsorption with the nanotube arrays length over some certain value. Mostly importantly, the higher defect densities in the TiO_2 nanotube arrays with 30 μm length will act as the recombination center for the transportation of the photo-induced electrons, and it may cause the dark current and decrease the photo-current in the solar cells.

To show the good adhesion between TiO_2 nanoparticles and TiO_2 nanotube with flexible ITO/PEN substrate, the photovoltaic performances with or without bending for the flexible DSSCs of 20 μm nanotube arrays are carried out as shown in Fig. 4(b), which shows a good stability for the photovoltaic performances by the bending of the flexible DSSCs. There are almostly no change for the the J_{sc} and V_{oc} values before and after bending, and this may prove that the TiO_2 nanoparticles and TiO_2 nanotube with ITO/PEN is well adhered.

Electrochemical impedance spectra (EIS) are a widely-used technique to characterize the charge transport and charge recombination processes of the exciting

electrons in the cells.²⁹⁻³¹ It is noticed that there are two main semicircles observed in Fig. 5. Typically, in order to match well with the above EIS data, the equivalent circuit of the DSSCs is also used to explain the transportation and recombination processes of the exciting electrons in the cells (insetted in Fig. 5). The R_s represents the transport resistance of the ITO and the electrolyte, R_1 is charge transfer resistance between the electrolyte and counter electrode, while R_2 is charge recombination resistance between the electrolyte and photoanode. The simulated resistance (R) values in the EIS spectra is calculated by the equivalent circuit, moreover, the relative errors are given by testing the EIS spectra in two cycles, and the detailed values are listed in Table 2. The simulated data of R_s values of various electrodes are almost the same, which means that the resistance of ITO and the electrolyte has no change in spite of the different lengths of nanotubes. Moreover, with the increasing length of the TiO_2 nanotube arrays, the corresponding R_1 value (the semicircle size in the high-frequency) slightly increases, which means that the resistance of counter electrode and the electrolyte is almost the same one. For the recombination resistance, R_2 noticeably increases from 30.3 Ω to 82.4 Ω with the increasing of the TiO_2 nanotube arrays length. The reason of the obviously increased resistance lies in the fact that the transport path of the photo-induced electrons increases along with the increasing of the TiO_2 nanotube arrays length. There is another possible reason for the increasing of the R_2 value, as nanotube arrays of 30 μm possess more impurities and defects preventing the electrons transportation, which increase the electron-hole recombination.

In Table 2, the parameters values with the relative errors show that the R_s , R_1 and R_2 values have exactly the same fitting errors. For the same system and same equivalent circuit, it is well known that the resistance fitting errors in a certain frequency are almost same under a certain scan rate.³²⁻³⁴ Therefore, when we set a fixed scan rates during the measurement, the error range is almost the same in a certain frequency, and then the R_s , R_1 and R_2 values have exactly the same fitting errors, respectively, which is accord with the similar works.³²⁻³⁴

4. Conclusions

In conclusion, the free-standing TiO_2 nanotube arrays have been successfully prepared by two-step electrochemical anodization in titanium foils, and it is transferred onto the flexible ITO/PEN substrate as the photoanodes in flexible DSSCs. The photovoltaic conversion efficiency of DSSCs based on TiO_2 nanotube arrays of 20 μm length on ITO/PEN reaches the maximum value of 3.44%.

Acknowledgment

This work is supported by the International S&T Cooperation Program of China (ISTCP) (No. 2013DFR50710) and Equipment Pre-research Project (No. 625010402).

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Figure captions

Table 1 Typical performance of DSSCs with various photoanodes.

Table 2 Simulated resistance (R) values of of EIS spectra.

Scheme 1 Diagram of the fabrication process of the flexible TiO₂ nanotube arrays and the solar cells.

Fig. 1 XRD patterns of the annealed TiO₂ nanotubes on Ti substrates with various anodization time.

Fig. 2 FESEM images of the TiO₂ nanotubes prepared at various anodization time: (a) 2 h; (b) 3 h; (c) 5 h; (d) 8 h (inset: top views and partial cross-sectional images).

Fig. 3 (a) UV-Vis spectra of the dye solution desorbed from the dye-sensitized TiO₂ nanotubes arrays with various lengths, (b) IPCE measurements of flexible DSSCs of TiO₂ nanotubes with various lengths.

Fig. 4 J-V curves of the flexible DSSCs: (a) TiO₂ nanotube arrays with various lengths, (b) 20 μm TiO₂ nanotube arrays with or without bending.

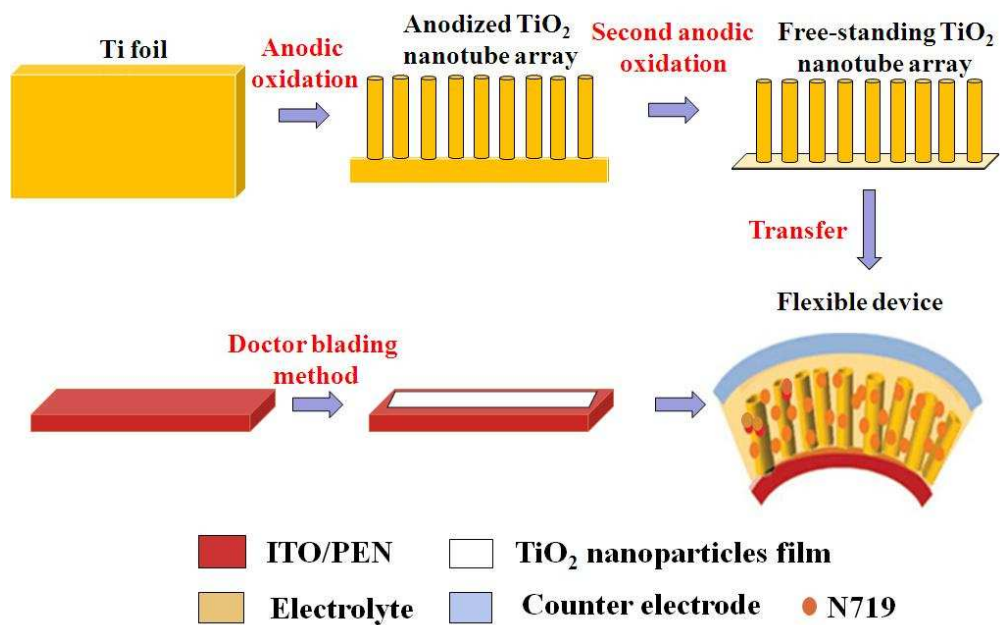
Fig. 5 Electrochemical impedance spectra (EIS) measurement of TiO₂ nanotube electrodes with various lengths (The inset illustrates the simulated equivalent circuit).

Table 1 Typical performance of DSSCs with various photoanodes.

Samples	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η (%)
Nanotube arrays (30 μ m)	6.83	682	0.661	3.08
Nanotube arrays (20 μ m)	7.35	688	0.680	3.44
Nanotube arrays (14 μ m)	6.63	668	0.655	2.90
Nanotube arrays (10 μ m)	5.31	659	0.620	2.17

Table 2 Simulated resistance (R) values of EIS spectra.

Photoelectrode	$R_s (\Omega)$	$R_1 (\Omega)$	$R_2 (\Omega)$
Nanotube arrays (30 μm)	40.2 ± 0.5	15.0 ± 0.4	82.4 ± 1.0
Nanotube arrays (20 μm)	38.4 ± 0.5	14.8 ± 0.4	59.5 ± 1.0
Nanotube arrays (14 μm)	39.2 ± 0.5	14.5 ± 0.4	41.2 ± 1.0
Nanotube arrays (10 μm)	35.6 ± 0.5	14.4 ± 0.4	30.3 ± 1.0



Scheme 1 Diagram of the fabrication process of the flexible TiO₂ nanotube arrays and the solar cells.

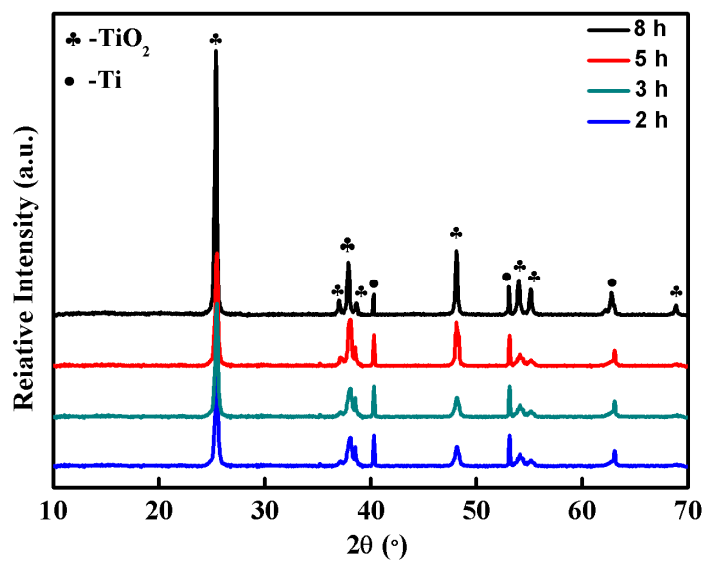


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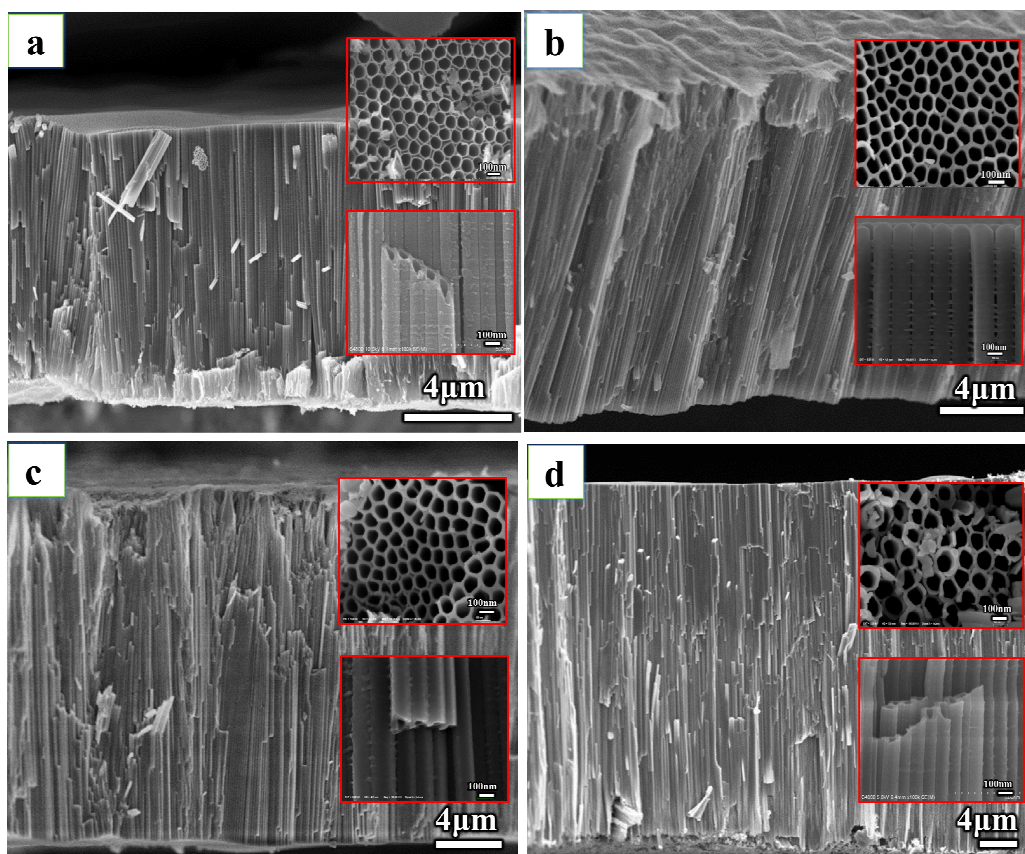


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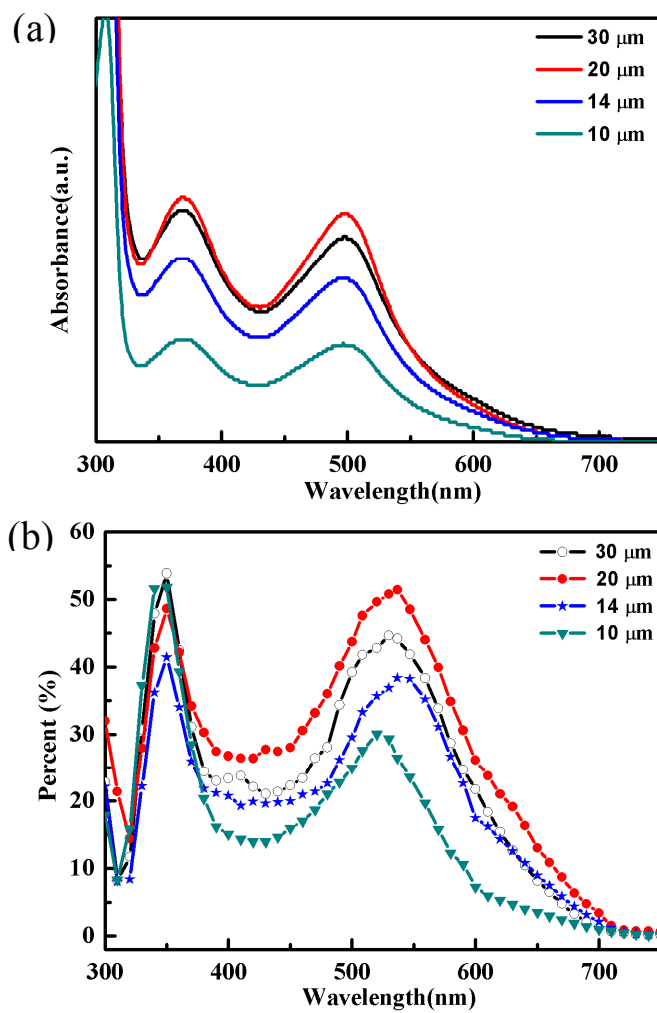


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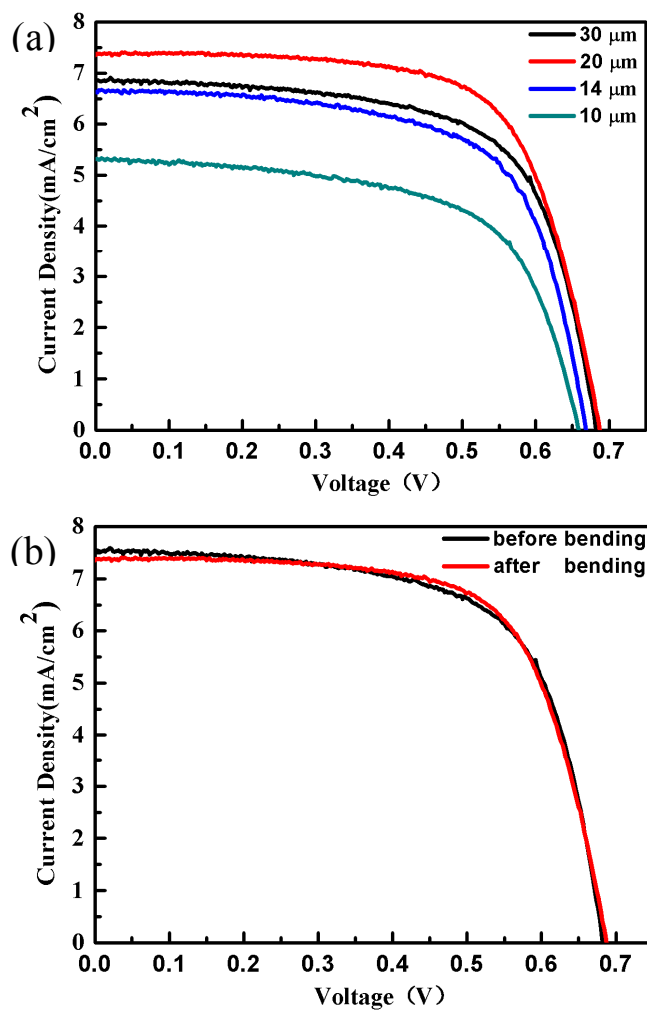


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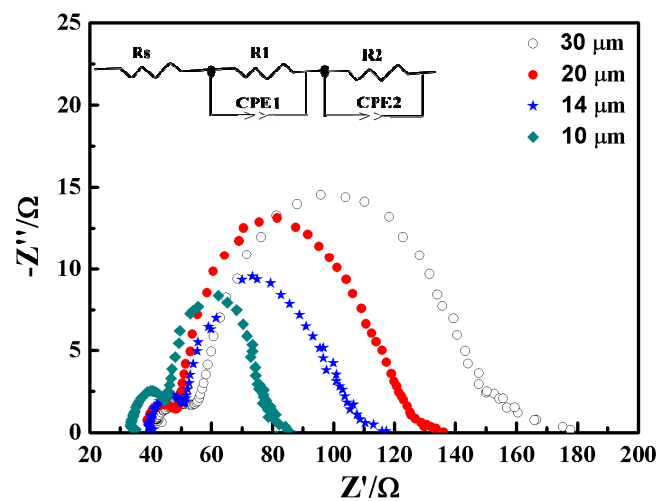
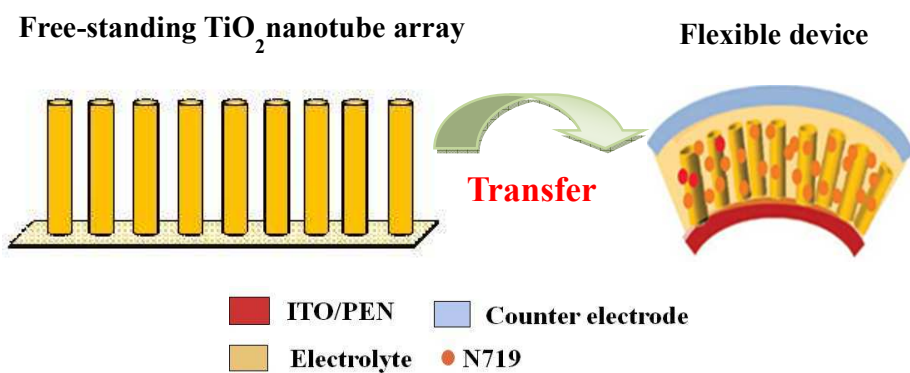


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Transferring and fabrication process of the flexible TiO₂ nanotubes arrays solar cells