Application of Highly Ordered TiO_2 Nanotube Arrays in Flexible Dye-Sensitized Solar Cells

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ABSTRACT TiO_2 nanotube arrays prepared by electrochemical anodization of Ti foils show impressive light to electricity conversion efficiency in the dye-sensitized solar cells (DSCs). The length of the TiO_2 nanotube arrays (5−14 μm) was controlled by varying the anodization time from 2 to 20 h. The influence of nanotube lengths on the photovoltaic performance of DSCs was investigated by impedance. A flexible DSC using TiO_2 nanotube arrays on a Ti foil as a working electrode and polyethylene naphthalate (ITO/PEN) as counterelectrode in combination with solvent-free ionic liquid electrolyte achieved 3.6% photovoltaic conversion efficiency under simulated AM 1.5 sunlight.

KEYWORDS: dye-sensitized solar cell · flexible · ionic liquid · nanotube array

Dye-sensitized solar cells (DSCs) have attracted great interest in academic research and industrial applications owing to the potential low cost alternative to the traditional silicon solar cells.[1] DSC typically consists of a nanocrystalline TiO_2 film covered by a monolayer of dye molecules, redox electrolyte, and counterelectrode. Cells based on randomly associated TiO_2 nanoparticles with a size of 10−30 nm have been widely used as photoanode achieving 11% photovoltaic conversion efficiency.[2] Considerable efforts have been devoted to the development of more efficient photoanode materials including ordered meso-structured materials,[3] one-dimension structured materials (nanorod, nanowire, nanotube), *etc.*[4−6] In these materials superior photovoltaic performances may be achieved through the realization of photoanode materials with ordered structure resulting in the improvement of electron transport. Highly ordered TiO_2 nanotube arrays are particularly attractive candidates to achieve this task.[6−8]

Flexible solar cells are of great advantage because of potential low cost roll-to-roll production and have been described previously by a number of groups.[9−11] Metal or transparent conductive copolymers were used as substrate for the working electrode and/or counterelectrode, However photovoltaic performance is hampered by slow electron transport in nanoparticle films that underwent low temperature sintering or/and a large resistance of the ITO polymer current collector. Recently our group has reported a remarkable light to electricity conversion efficiency for the flexible solar cells based on TiO_2 nanoparticles coated on the Ti foil as working electrode and ITO-PEN as counterelectrode.[12] However these flexible DSCs contains volatile organic solvent electrolyte which precludes practical applications due to the organic solvent permeation across the plastic current collector. Hence, the ultimate redox electrolyte for flexible DSC application should be a solvent free electrolyte. Ionic liquids are potential candidates to replace organic solvent because of huge practical advantage over organic solvent electrolytes. Recently, we achieved a new record of 7.6% efficiency for a new binary ionic liquid (1-propyl-3-methylimidazolium iodide and 1-ethyl-3-methylimidazolium tetracyanoborate) electrolyte based DSCs.[13]

Here, we report for the first time on the use of ordered TiO_2 nanotube array as photoanode material for ionic liquid electrolyte-based rigid and flexible dye-sensitized solar cells, that showed impressive photovoltaic performance.

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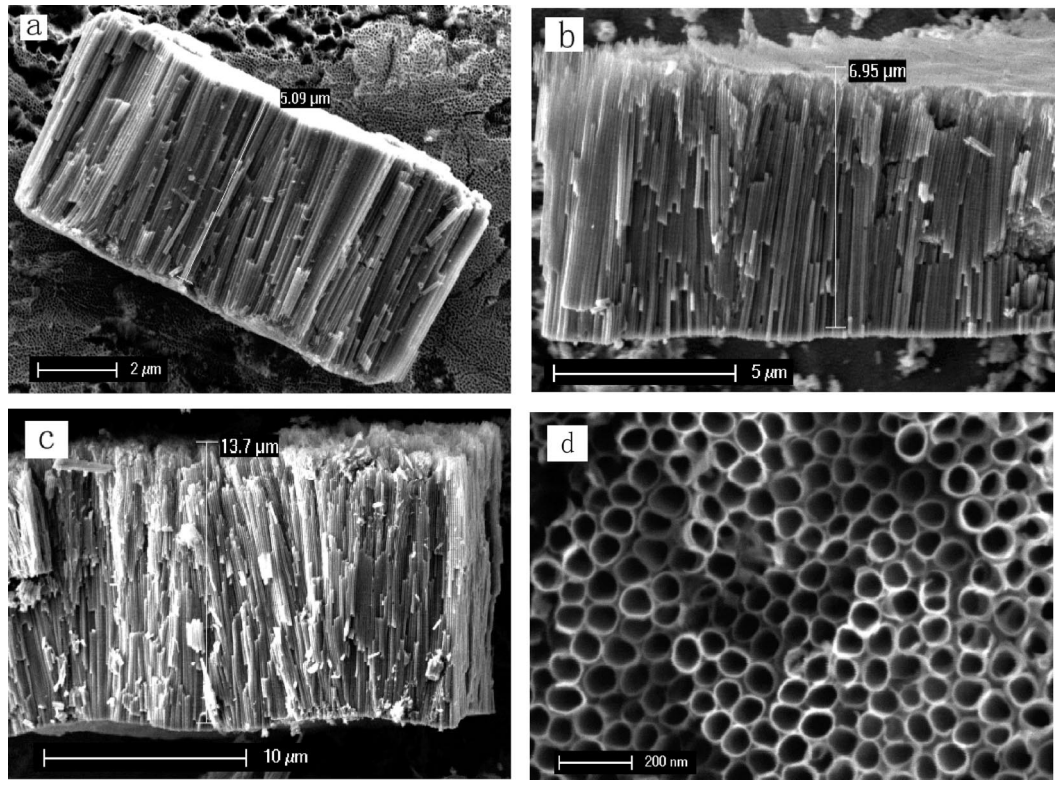

Figure 1. SEM images of TiO_2 nanotube made with different anodization time: (a) 2 h, 5 μm in length; (b) 4 h, 7μm in length; (c) 20 h, 14 μm in length; (d) the enlarged image for 4 h's sample, 70 nm in pore size, and 8 nm in tube wall.

RESULTS AND DISCUSSION

Figure 1 shows the typical SEM images of TiO_2 nanotubes (TNT) obtained by the anodization procedures (see Experimental Section). The average TNT lengths are 5, 7, and 14 μm as the anodization time increased from 2 (a), 4 (b), and 20 h (c), respectively. The closely packed highly ordered TNT were obtained at present anodization conditions independent of the time. Figure 1d is the enlarged image of the sample made with 4 h anodization, which shows ~70 nm in pore size and ~8 nm in the TNT wall. The structures of the sample were characterized by XRD measurements. The XRD patterns (data not shown) of a 7 μm thick TNT film after annealing at 500 °C for 3 h show that the TNT samples have anatase structure in contrast to earlier work where the presence of rutile at the interface between the TNT and Ti substrate was suggested.[14] However, rutile was not witnessed in our present preparations.

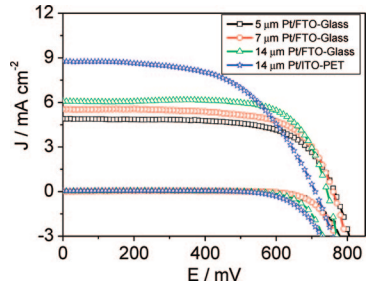

Figure 2. Current−voltage characteristic of solar cells based on different TiO_2 nanotube length using rigid (Pt/FTO-glass) and flexible (Pt/ITO-PEN) substrates. Solid lines were measured under AM 1.5 full sunlight (100 mW/cm^2) illumination. Dot lines were measured in the dark.

Figure 2 shows the current−voltage curves of DSCs based on the organic dyes and the binary ionic liquid electrolyte as a function of TNT length under simulated AM 1.5 light. The short circuit photocurrent densities (J_{sc}) obtained with TNTs of 5, 7, and 14 μm length was 4.95, 5.58, and 6.11 mA cm^{-2}, respectively. The highest photovoltaic performance of 3.3% was achieved with a 14 μm length TNT sample. Detailed photovoltaic performance parameters of the DSCs for films with different nanotube length are presented in Table. 1. The V_{oc} of the DSCs decreases with increasing length of TNT nanotube because of the increase in the dark current

TABLE 1. Photovoltaic Performance Parameters of Solar Cells Based on Different TiO_2 Nanotube Length with Pt/FTO-Glass or Pt/ITO-PEN as Counterelectrode which Measured under AM 1.5 Full Sunlight Illumination (100 mW cm^{-2})[a]

TiO_2 nanotube length (μm)	counterelectrode	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)
5	Pt/FTO-glass	4.95	763	0.666	2.52
7	Pt/FTO-glass	5.58	759	0.675	2.86
14	Pt/FTO-glass	6.11	743	0.725	3.29
14[b]	Pt/ITO-PEN	8.99	709	0.561	3.58
14	Pt/ITO-PEN	7.80	705	0.58	3.19

[a]The spectral distribution of the xenon lamp simulates air mass 1.5 solar light. The active area of the devices with a metal mask is 0.158 cm^{-2}. [b]Open cell.

which scales with the surface area of the titania films, in agreement with previous nanoparticle-based DSCs.[15] The V_{oc} values in table 1 are higher by about 40 mV compared to typical values obtained with nanocrystalline films that show a similar photocurrent of 5−6 mA cm^{-2} and employ the same electrolyte and the same ionic liquid as the TNT cells. This finding is encouraging as it indicates that the recapture of conduction band electrons by the triiodide ions in the ionic liquids is slower for the TNT-based films than for random particular networks.

The dark current curves in Figure 2 confirm that the 14 μm TNT sample has a lower onset potential for the reduction of I_3^- than the other two samples which is in keeping with its higher surface area.

To investigate a lightweight and flexible embodiment of the TNT cell, a ITO-PEN transparent conductive substrate was used to replace the FTO-glass. It is interesting to note that the device made with flexible conductive Pt/ITO-PEN polymer substrate as counterelectrode showed comparable photovoltaic performance to the Pt/FTO/glass devices. The photovoltaic parameters (J_{sc}, V_{oc}, FF and η) of TiO_2 nanotube-based flexible solar cells were 8.99 mA cm^{-2}, 709 mV, 0.561 and 3.58%, respectively (shown in Table 1). The flexible solar cells with Pt/ITO-PEN as counterelectrode shows higher photocurrent compared to rigid solar cells with Pt/FTO-glass as counterelectrode. This probably arises from the fact that the flexible counterelectrode is directly placed on the TNT layer reducing optical losses as the triiodide ions contained in the ionic liquid filter the light that enters through the counterelectrode.

Impedance spectroscopy has been regarded as a powerful technique to characterize the transport and recombination in DSC and suitable physical models have been developed to interpret the results.[16,17] The cells prepared with Pt/FTO-glass and Pt/ITO-PEN as counterelectrode were compared by the electrochemical impedance spectroscopy. Impedance spectra were measured in the dark at an applied potential bias of −0.7 V. The high frequency semicircle in Nyquist plots corresponds to charge transfer at the counterelectrode (Pt/electrolyte interface). The reaction resistance of the counterelectrode was analyzed by software (Z-view) using an equivalent circuit containing a constant phase element (CPE) and resistances (*R*) (Figure 3, inset). The series resistance (R_s) was 8.9 ohm for rigid solar cell (Pt/FTO-glass) and 49.6 ohm for flexible solar cell (Pt/ITO-PEN). Further, the interface resistance of Pt/electrolyte (R_{Pt}) was 4.6 ohm and 62.4 ohm for Pt/FTO-glass and Pt/ITO-PEN, respectively. Therefore, the low FF of flexible DSC based on Pt/ITO-PEN substrate is due to higher R_s value and lower activity of Pt catalyst at the Pt/ITO-PEN.

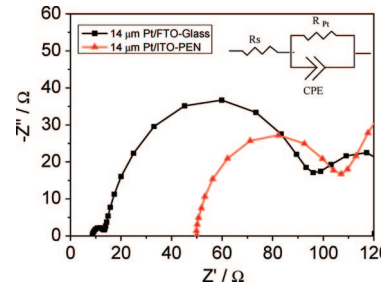

Figure 3. Impedance spectra of DSCs based on 14 μm TiO_2 nanotube and rigid (Pt/FTO-glass) or flexible (Pt/ITO-PEN) counterelectrode, measured in the dark under −0.70 V applied bias. The inset shows the equivalent circuit used to analyze the high frequency semicircle.

In conclusion, this is the first time a flexible DSC prepared with TiO_2 nanotube arrays as photoanode and transparent conductive polymer Pt/ITO-PEN as counterelectrode in combination with ionic liquid electrolyte obtained 3.6% efficiency at AM 1.5 simulated full sunlight. The photovoltaic performance of devices depends on the length of nanotube. Flexible ionic liquid electrolyte solar cells will stimulate considerable interests for academic research and practical applications.

EXPERIMENTAL SECTION

Highly ordered TiO_2 nanotube arrays were prepared by anodization of Ti foils (99.7%, 0.25 mm, Aldrich) in a two-electrode cell containing a Pt counterelectrode.[18–20] The anodization was performed at 35 V at room temperature in a solution of 0.25 wt % NH_4F and 0.75 wt % H_2O in ethylene glycol for different time intervals that resulted in various nanotube lengths. The as-prepared TiO_2 nanotube samples were soaked in 0.04 M aqueous $TiCl_4$ solution for 30 min at 70 °C, which improves the photocurrent and photovoltaic performance. The $TiCl_4$ treated TiO_2 nanotube samples were rinsed with water and ethanol and then annealed in air at 500 °C for 3 h using a heating rate of 2 °C/min to crystallize the initially amorphous anodized films. The sample morphology and crystallinity were characterized using scanning electron microscopy (Philips XL30 FEG) and X-ray diffraction (XRD), respectively. The sintered nanotube samples were immersed into 0.3 mM solution of a novel indoline organic dye coded as D205[21] in acetonitrile and *tert*-butyl alcohol (volume ratio 1:1) for 16 h. The newly developed binary ionic liquid electrolyte contained 0.05 M I_2, 0.5 *N*-butylbenzimidazole (NBB), 0.1 guanidinium thiocyanate (GuNCS) in a mixture of 65 vol % PMII and 35 vol % $EMIB(CN)_4$.[13,22] Pt/FTO-glass or Pt/ITO-polyethylene naphthalate (ITO-PEN, a gift from Konarka Technologies, Inc., MA) were used as counterelectrode for rigid or flexible solar cells, respectively. The detailed fabrication procedures and photovoltaic performance characterizations of dye-sensitized solar cells were explained in our earlier publication.[15] Devices were made with Pt/FTO-glass or Pt/ITO-PEN as a counterelectrodes using Surlyn as a spacer. In addition, in the preparation of an open flexible DSC, first the TiO_2 nanotube array is sensitized with dye. Afterwards, a drop of electrolyte was placed on top of it, and the flexible counterelectrode (Pt/ITO-PEN) was gently placed on top of the electrode. Impedance spectra of DSCs were measured in the dark at −0.7 V forward bias using a potentiostat (EG&G, M273) equipped with a frequency response analyzer (EG&G, M1025).

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