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J. Mater. Sci. Technol., 2012, 28(7), 594–598.
JMST
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Effect of MWCNT Inclusion in TiO_2 Nanowire Array Film on the Photoelectrochemical Performance

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[Manuscript received December 30, 2011, in revised form February 14, 2012]

Rutile TiO_2 nanowire array films with multi-walled carbon nanotube (MWCNT) inclusion perpendicularly grown on fluorine-doped tin oxide (FTO) substrate were prepared by a facile hydrothermal method. The absorption edges of the TiO_2 nanowire array films are blue-shifted with increasing MWCNT content. The resistance of the TiO_2 nanowire array film is decreased by MWCNT inclusion. The optimum TiO_2/MWCNT molar ratio in the feedstock is 1:0.1. For the TiO_2 nanowire array film with MWCNT inclusion served as electrode in dye-sensitized solar cell (DSSC), an overall 194% increase of photoelectric conversion efficiency has been achieved.

KEY WORDS: TiO_2 nanowire array; MWCNT inclusion; Hydrothermal synthesis; Photoelectrochemical; Dye-sensitized solar cell

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted extensive interest as a potentially low-cost alternative to conventional solar photoelectric conversion devices[1]. Nanocrystalline TiO_2 has been the main photoanode material for developing high performance DSSCs due to the inhibition of charge recombination to prolong the carrier lifetime[2]. TiO_2 with different morphology such as nanoparticles[3], nanotubes[4], nanorods[5], and nanowires[6] has been investigated in DSSC structures. Among them, the one-dimensional (1D) TiO_2 arrays have been promising as a material due to offering the possibility to improve the charge collection and transport of charge carriers[7]. Many research efforts have devoted to developing TiO_2 nanotube arrays on metal titanium foils by anodic oxidation method. Recently, the rutile TiO_2 nanowire and nanorod arrays have been synthesized by a facile hydrothermal method[8,9]. It is still of interest to modify the rutile TiO_2 nanowire arrays to further improve its performance for application in DSSC.

Owing to their extraordinary electronic and mechanical properties[10], carbon nanotubes (CNTs) have been shown to improve the performance of TiO_2-based materials, such as photocatalytic activity[11], photoelectrocatalytic activity[12] and photovoltaic cells[13]. Kongkanand *et al.*[14] have reported that the photoconversion efficiency of the DSSC increase from 7% to 15% by combining CNTs with TiO_2 nanoparticles. However, the mechanism for the enhanced photoelectrochemical performance of TiO_2 by CNTs remains uncertain. To the best of our knowledge, the photoelectrochemical property of CNT inclusion in TiO_2 nanowire arrays has not been investigated.

Herein, TiO_2 nanowire array films with multi-walled carbon nanotubes (MWCNT) inclusion were prepared by a facile hydrothermal method. For the films employed as electrodes, the photoelectrochemical behaviors in a three-electroded system under UV illumination and photoelectric conversion performances in DSSCs under stimulated sunlight were investigated. The enhanced photoelectrochemical performance of TiO_2 caused by MWCNT inclusion was also discussed.

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2. Experimental

2.1 Materials

All reagents were of analytical grade and used without any further purification. N-719 dye was obtained from Solaronix, Switzerland. Chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, 37.5% as Pt), lithium iodide (LiI), iodide (I_2), anhydrous acetonitrile and tetrabutyl titanate were supplied by Westingarea Corporation, China.

MWCNTs were purchased from Chengdu Organic Chemicals Co., Ltd, China. For the purification, raw MWCNTs were refluxed in 100 mL of concentrated nitric acid (50% HNO_3) for 8 h to get oxygenated functionalities on the nanotube surface. Then, the MWCNTs were filtered, washed with 600 mL distilled water for five times to remove acid, and finally dried at 80 °C in an oven.

MWCNT-TiO_2 nanowire array films were synthesized by a modified literature method[9]. Firstly, acid-treated MWCNTs were dispersed in a 20 mL ethanol solution by the ultrasonic treatment for 4 h. 40 mL of 5 mol/L hydrochloric acid was subsequently added and stirred for 5 min and then 1 mL of titanium butoxide was added under stirring for 10 min. The solution was transferred to a 100-mL Teflon-lined stainless steel autoclave. Subsequently, a piece of the cleaned fluorine-doped tin oxide (FTO) glass was placed against the wall of the Teflon-liner with an inclined angle and the conducting side facing down, and then hydrothermally treated at 150 °C for 18 h. Finally, the FTO glass was taken out, washed thoroughly with deionized water, dried in air at room temperature, and heated in air at 500 °C for 1 h. The MWCNT-TiO_2 nanowire array films, with a different weight ratio of titanium butoxide and MWCNT (1:0.05, 1:0.1, 1:0.2, and 1:0.3, respectively), are named as 0.05-MWCNT-TiO_2, 0.1-MWCNT-TiO_2, 0.2-MWCNT-TiO_2 and 0.3-MWCNT-TiO_2, respectively.

The pure TiO_2 nanowire array film was prepared by the similar procedure without adding MWCNT.

2.2 Characterization

The morphology of the films was inspected by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The crystalline structure of the films was examined by powder X-ray diffraction (XRD, Philip X'pert Pro MPD) with Cu$K\alpha$ radiation from 10 to 80 deg.

2.3 Photoelectrochemical characterization of MWCNT-TiO_2 nanowire array films

2.3.1 Photoelectrochemical behaviors under UV illumination

The photoelectrochemical tests were performed in a three-electroded system consisting of a self-made quartz cell, which was linked with CHI660A electrochemical workstation (Chenhua Instrument Company of Shanghai, China). The TiO_2 nanowire array films were used as the working electrodes and mounted in a special holder with an area of 3 cm^2 exposed to a quartz window for ultraviolet (UV) light illumination. A 300 W Xe arc lamp (PLS-SXE300, Changtuo Ltd., China) with a UV band-pass filter was used as the UV light source. A saturated Ag/AgCl electrode and a platinum mesh were served as the reference and counter electrodes, respectively. A 0.10 mol/L Na_2SO_4 was chosen as supporting electrolyte throughout all the experiments. Electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) were applied to study the photoelectrochemical behaviors of the films.

2.3.2 DSSCs assembly and measurement

The TiO_2 nanowire array film electrodes were soaked in an ethanol solution of N-719 dye (Solaronix, Switzerland) for about 24 h. Then the dye-adsorbed nanowire array film electrodes with the active area of 0.6 cm×0.6 cm were assembled into a sandwich-type cell with a counter electrode (platinum-deposited FTO glass slices) by clamps. A drop of electrolyte solution (0.05 mol KI and 0.01 mol I_2 in 15 ml acetonitrile) was introduced into the clamped electrodes by capillarity.

3. Results and Discussion

3.1 Characterizations of MWCNT-TiO_2 nanowire array films

Morphology of the 0.1-MWCNT-TiO_2 nanowire array film is observed by FE-SEM (Fig. 1). The SEM images (Fig. 1(a) and (b)) display that the TiO_2 nanowires with an average diameter of 40 nm and length of 1.5 μm are piled up to a uniform array on a large area and perpendicularly grown on the FTO substrates. To further investigate the state of MWCNTs in the TiO_2 nanowire arrays, the film scratched off the FTO substrate was also observed. The MWCNTs in the composites are well dispersed and appear as perpendicular inclusions within the TiO_2 nanowires (Fig. 1(c)) or as bridges contacted with the TiO_2 nanowires (Fig. 1(d)). This suggests that, when the TiO_2 nanowires grow in the hydrolysis process of titanium butoxide, the MWCNTs are concomitantly incorporated in the TiO_2 nanowires.

Fig. 2 displays the XRD patterns of TiO_2 nanowire array films with the inclusion of different MWCNT contents. The obvious diffraction peaks of as-prepared nanowire samples at 2θ=36.1 and 62.7 deg., respectively correspond to the characteristic diffraction of the (101) and (002) planes of the tetragonal rutile TiO_2 (JCPDS 21-1276). The enhanced (002) peak of TiO_2 samples indicates that the nanowires are well crystallized and grow highly oriented on the

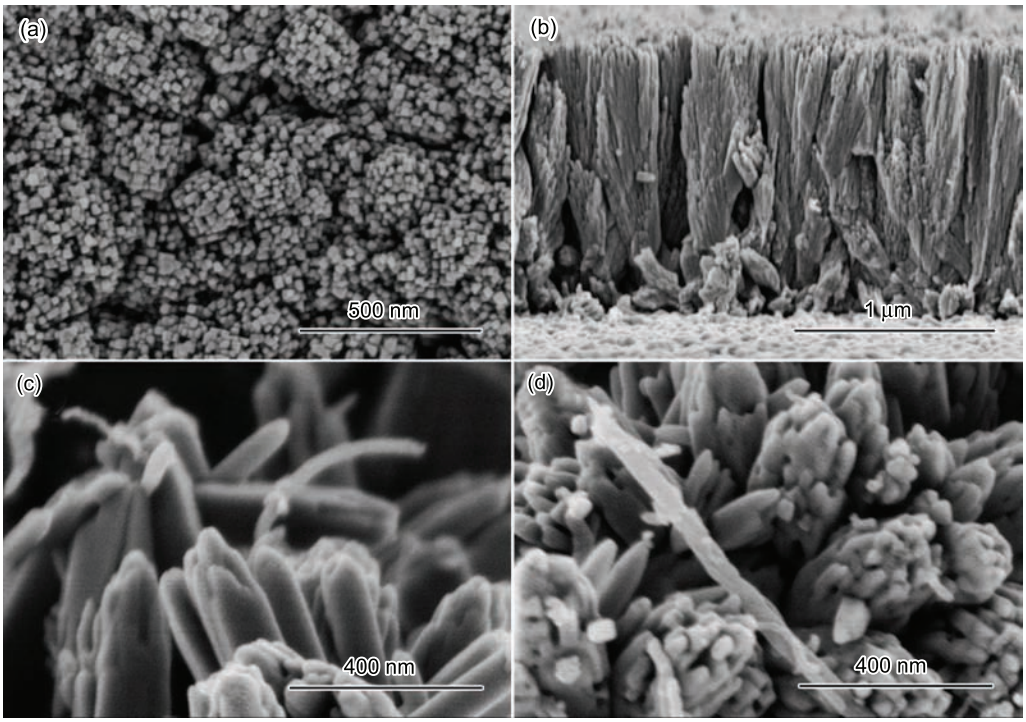

Fig. 1 FE-SEM images of 0.1-MWCNT-TiO_2 nanowire array film for plan-view image (a), cross-sectional image (b), and high magnification SEM image of 0.1-MWCNT-TiO_2 nanowires (c) and (d)

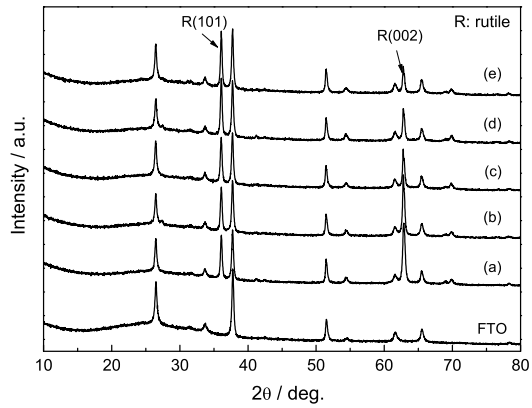

Fig. 2 XRD patterns of pure TiO_2 nanowires (a) and TiO_2 nanowires prepared with 0.05-MWCNT-TiO_2 (b), 0.1-MWCNT-TiO_2 (c), 0.2-MWCNT-TiO_2 (d) and 0.3-MWCNT-TiO_2 (e)

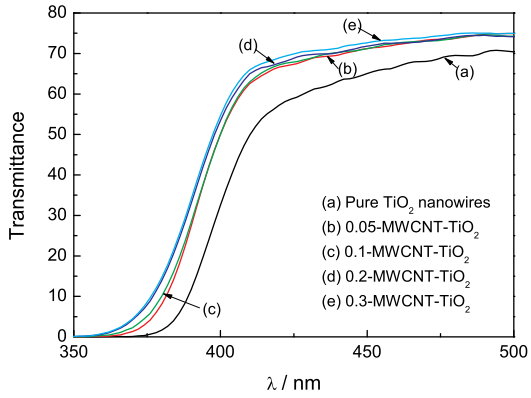

Fig. 3 UV-vis transmittances of the pure and the MWCNT-TiO_2 nanowire array films

substrate surface and the TiO_2 nanowires grow in the [001] direction with the growth axis parallel to the substrate surface normal[9]. The characteristics peaks of MWCNTs are not found in the spectra of the samples in the range investigated. This may be attributed to the overlap of the intense peaks of the MWCNTs and FTO, as the difference in mass between MWCNTs and FTO is relatively large.

Fig. 3 shows the UV-vis transmittance spectra for the TiO_2 films with different MWCNT contents. In comparison with the characteristic spectrum of pure TiO_2 nanowire array film, for the TiO_2 nanowire array films, the absorption edges are blue-shifted and the transmittance is enhanced with increasing MWCNT contents. The blue-shift corresponds to the increase in the band gap energy, that is, similar to carbon-doped rutile TiO_2, substitutional carbon impurities cause a comparable increase of the band gap of rutile TiO_2[15]. It should be implied that MWCNTs not only contacted the surface of TiO_2 but also incorporated into the lattice of TiO_2.

3.2 Photoelectrochemical properties

Electrochemical measurement is a powerful and effective tool for the characterization of TiO_2 film immobilized onto conducting substrates. Herein, EIS and LSV were chosen to evaluate the photoelectrochemical properties of the TiO_2 nanowire array films serving as photoanodes in the three-electroded system under UV illumination.

Table 1 Photovoltaic characteristics of DSSCs with TiO_2 nanowire array electrodes containing various contents of MWCNTs

TiO_2 nanowire array samples	J_{sc}/(mA·cm^{-2})	V_{oc}/V	P_{max}	*FF*	η/%
Pure TiO_2	2.73	0.564	0.674	0.437	0.67%
0.05-MWCNT-TiO_2	3.26	0.572	0.838	0.449	0.83%
0.1-MWCNT-TiO_2	6.62	0.630	1.96	0.471	1.96%
0.2-MWCNT-TiO_2	5.57	0.608	1.23	0.360	1.23%
0.3-MWCNT-TiO_2	4.10	0.615	0.9	0.356	0.9%

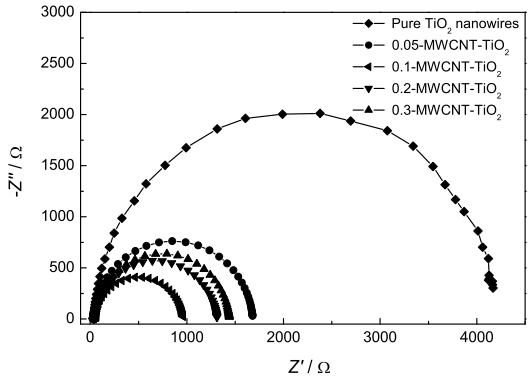

Fig. 4 EIS Nyquist plots of the pure and the MWCNT-TiO_2 nanowire array films under UV illumination in 0.10 mol/L Na_2SO_4 solution

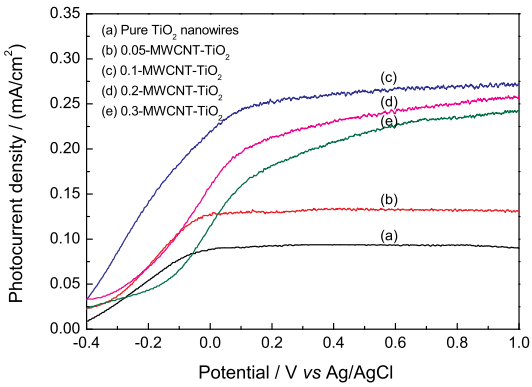

Fig. 5 LSV voltammograms of the pure and the MWCNT-TiO_2 nanowire array films in 0.1 mol/L Na_2SO_4 solution under UV illumination

EIS was used to measure the charge transfer resistance of the electrode materials for characterizing the separation efficiency of the photogenerated electron-hole pairs[16,17]. A larger curvature radius usually represents a larger charge transfer resistance and a lower separation efficiency of the photogenerated electron-hole pairs[18]. Fig. 4 shows the results of EIS Nyquist plots of the pure and the MWCNT-TiO_2 nanowire array films. All the circular radii of MWCNTs incorporating TiO_2 nanowire array film electrodes are remarkably smaller than that of pure TiO_2 nanowire array film electrode. The 0.1-MWCNT-TiO_2 nanowire array film shows the smallest circular radius, indicating that it has the smallest resistance. For the MWCNT-TiO_2 nanowire array film, the small amount of MWCNT would promote the photogenerated electron transfer, thus reducing the charge recombination[19,20]. However, higher MWCNT contents may increase the trap state formation[21], and thus photogenerated electrons would spend more time to reach the FTO substrate due to the increase of residence time in the trap sites.

LSV is always used to investigate the redox performance of semiconductor. The photocurrent increasing linearly with the applied potential could represent the photocatalytic oxidation of semiconductor by photogenerated holes at the interface. It can be seen from Fig. 5 that the photocurrents of the MWCNTs-TiO_2 nanowire array films are much higher than that of the pure TiO_2 nanowire array film under UV illumination and the saturated photocurrent of the 0.1-MWCNT-TiO_2 nanowire array film is the largest, which reveals that there are a larger number of free photogenerated carriers in the 0.1-MWCNT-TiO_2 nanowire array film.

3.3 Performances of DSSCs

The photoelectric conversion performances of DSSCs with the TiO_2 nanowire array films were also investigated under the stimulated sunlight. *I–V* characteristics of the cells are shown in Fig. 6. The photovoltaic parameters derived from the *I–V* curves are listed in Table 1. MWCNT incorporating leads to the increase of the short circuit photocurrent density (J_{sc}), the open circuit voltage (V_{oc}) and the fill factor (*FF*). The value of V_{oc} increases from 0.564 to 0.630 V with increasing MWCNT content from 0 to 0.1 wt%. Due to the fact that the incorporation of a small amount of MWCNTs into the TiO_2 films can reduce the charge recombination rate and resistance[19], an efficient transfer of photoexcited electrons to the collected FTO substrate is resulted. For the 0.1-MWCNT-TiO_2 nanowire array film electrode, the DSSC shows the highest J_{sc} and V_{oc}, and the J_{sc}, V_{oc}, and *FF* have been increased by 142%, 11.7% and 7.8%, respectively. Consequently, an overall 194% increase of the photoelectric conversion efficiency can be obtained for the DSSC with 0.1-MWCNT-TiO_2 nanowire array film electrode.

3.4 Discussion

TiO_2 nanowire array films grown with MWCNT inclusion on FTO substrate are prepared by a facile hydrothermal method. In the composite structure, MWCNTs are well dispersed and incorporated in TiO_2 nanowires. The inclusion of MWCNTs could

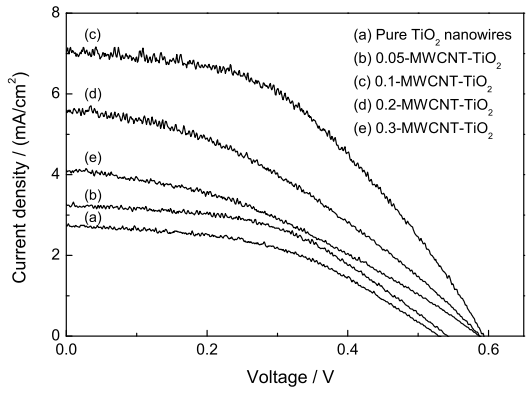

Fig. 6 The *I–V* characteristic curves of DSSCs based on the pure and MWCNT-TiO_2 nanowire array films (AM 1.5, 100% sun illumination)

raise the band gap of TiO_2, which can be identified by the blue shift of the absorption edge (Fig. 3). When the MWCNT-TiO_2 nanowire array films were illuminated under UV light, the increase in band gap could make recombination of the photoinduced hole-electron pairs less likely to occur[22]. On the other hand, in the MWCNT-TiO_2 nanowire array films, electrons excited by TiO_2 nanowires may easily migrate to the MWCNTs due to the electron-drawing ability of MWCNTs[23,24]. The small amount of MWCNTs plays a role in promoting the photogenerated electron-hole pairs separation and the charge collection efficiency. Nevertheless, with further increasing MWCNTs, the excess MWCNTs may increase the formation of larger defect sites, which provides trap states for electrons[21]. Thus, more time should be spent to reach the FTO substrate due to the increase of residence time in the trap sites. Consequently, the optimum content of MWCNTs is crucial for the MWCNT-TiO_2 nanowire array, in which MWCNTs effectively restrain charge recombination and promote the electron-transfer. The results shown above demonstrate that the optimal amount of TiO_2 and MWCNTs in the feedstock is 1:0.1, which are consistent with the TiO_2/CNTs for photocatalytic activity mentioned previously by Yu *et al*[22]. When integrating 0.1-MWCNT-TiO_2 nanowire array film into the DSSC structure, the charge separation performance and the favorable electron-transfer properties in the photoanode should be mainly related to the improvement of photoelectric conversion performance in DSSC. Our results indicate that an overall 194% increase of photoelectric conversion efficiency has been achieved in DSSC with 0.1-MWCNT-TiO_2 nanowire array electrode.

4. Conclusion

The TiO_2 nanowire array films with incorporating carbon nanotube grown directly on FTO substrate were prepared by a facile hydrothermal method. The MWCNT-TiO_2 nanowire array films exhibited improved photoelectrochemical performance under UV illumination. The optimum TiO_2/MWCNT molar ratio in the feedstock is 1:0.1. For the TiO_2 nanowire array film with MWCNT inclusion served as electrode in DSSC, an overall 194% increase of photoelectric conversion efficiency has been achieved.

Acknowledgements

The work was supported by the National Natural Science Foundation of China (Grant No. 51172233) and the National Basic Research Program of China ("973 Program", Grant No. 2009CB220002).

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