

# Preparation of titanium dioxide-double-walled carbon nanotubes and its application in flexible dye-sensitized solar cells

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**Abstract** Titanium dioxide-double-walled carbon nanotubes ( $\text{TiO}_2$ -DWCNTs) with DWCNTs/ $\text{TiO}_2$  of 20 wt.% is prepared by a conventional sol-gel method. Doping the  $\text{TiO}_2$ -DWCNTs in  $\text{TiO}_2$  photoanode, a flexible dye-sensitized solar cell (DSSC) is fabricated. The sample is characterized by scanning electron microscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) absorption, ultraviolet-visible spectroscopy (UV-vis) absorption spectra, electrochemical impedance spectroscopy (EIS) technique and photovoltaic measurement. It is found that adding a certain amount of  $\text{TiO}_2$ -DWCNTs can efficiently decrease the resistance of charge transport, improve dye adsorption. Under an optimal condition, a flexible DSSC contained with 0.50 wt.%  $\text{TiO}_2$ -DWCNTs achieves a light-to-electric energy conversion efficiency of 3.89% under a simulate solar light irradiation of  $100 \text{ mW} \cdot \text{cm}^{-2}$ .

**Keywords** flexible dye-sensitized solar cell (DSSC), titanium dioxide ( $\text{TiO}_2$ ), double-walled carbon nanotube (DWCNT), sol-gel method

## 1 Introduction

Since the prototype of a dye-sensitized solar cell (DSSC) was reported in 1991 by O'Regan and Grätzel, it has aroused intensive attentions over the past decades due to its low cost and simple preparation procedure, and a DSSC with light-to-electric energy conversion efficiency of 12% has been achieved [1,2]. However, the potential problems caused by the transparent conductive glass substrates, such

as the weight and frangibility, are considered as some critical factors limiting DSSC's practical applications. Recently [3,4], the flexible DSSC has attracted wide interests and researches because of its merits, such as light weight, good flexibility, impact proof, lower cost. And the shape or surface can be devised and constructed. Large-scale continuous production and rapid coating can be used, which further decreases its production cost. For general DSSC, a sintering over  $450^\circ\text{C}$  is needed to solidify titanium dioxide ( $\text{TiO}_2$ ) on conductive glass substrate. However, when treated over  $150^\circ\text{C}$ , the flexible polymer substrate will be distorted and loss transparency. Thus, low-temperature preparation of a  $\text{TiO}_2$  film photoanode has become a key issue for the flexible DSSC [5].

Recently, some efforts have been made to use carbon nanotubes (CNTs) in DSSCs. Lee et al. [6] synthesized titanium dioxide-multi-wall carbon nanotubes (MWCNTs/ $\text{TiO}_2$ ) via a sol-gel method, the DSSCs obtained a conversion efficiency of 4.97%. Muduli et al. [7] synthesized MWCNTs/ $\text{TiO}_2$  nanocomposites by hydrothermal method and realized an efficiency of 7.37%. Double-walled carbon nanotubes (DWCNTs) possess excellent electronic, mechanical and thermal conductivity due to their coaxial structure compared with single-walled nanotubes (SWCNTs) and MWCNTs [8,9]. However, little significant study on DWCNTs using in DSSCs was reported.

In this work,  $\text{TiO}_2$ -DWCNTs are prepared by a conventional sol-gel method (shown in Fig. 1(a)), using the  $\text{TiO}_2$ -DWCNTs and titania particles (P25), a highly stable and uniform titania colloid is prepared by hydrothermal treatment [10]. Based on the titania colloid, a flexible DSSC is fabricated (shown in Fig. 1(b)) at low temperature. It is expected that the photovoltaic performance of flexible DSSC can be enhanced.

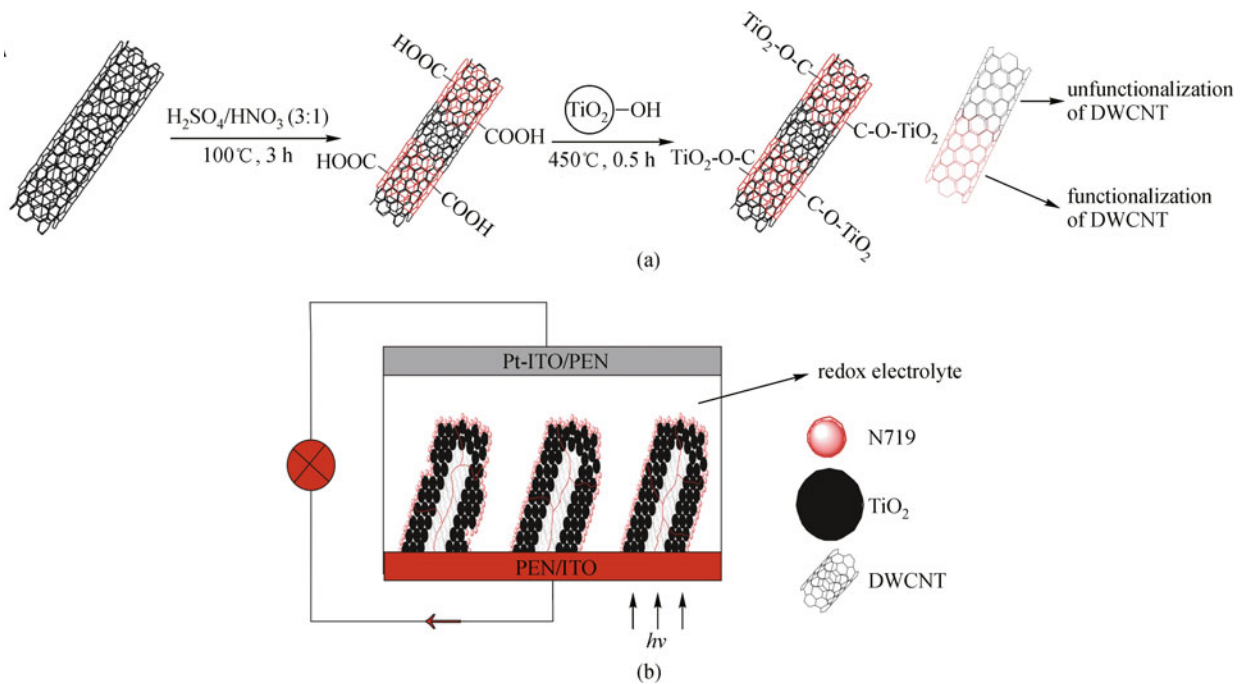


Fig. 1 Schematic view of (a) synthetic process of TiO<sub>2</sub>-DWCNTs nanocomposites; (b) flexible DSSC

## 2 Experimental methods

### 2.1 Materials

Polyvinyl pyrrolidone (PVP K-27), anhydrous ethanol, iodine, lithium iodide, tetrabutyl ammonium iodide, acetonitrile (AN), and 4-*tert*-butyl-pyridine (TBP), titanium (IV) isopropoxide (TTIP) were all A. R. grade and purchased from Sinopharm Chemical Reagent Co., Ltd, China. Sensitized-dye N719 [cis-di(thiocyanato)-*N*, *N*-bis(2,2-bipyridyl-4- carboxylic acid-4-tetrabutylammonium carboxylate) ruthenium (II)] was purchased from Solaronix SA, Switzerland. Titania nanopowder (P25) was purchased from Degussa, Germany. The above agents were used without further purification. The DWCNTs were purchased from Nanotech Port Co. Ltd (NTL), Shenzhen. The polymer substrate of ITO/PEN ( $12 \Omega \cdot \text{cm}^{-2}$ ) and Pt-ITO/PEN ( $5 \Omega \cdot \text{cm}^{-2}$ ) were purchased from PECCELL Technologies, Inc, Yokohama, Japan.

### 2.2 Preparation of the TiO<sub>2</sub>-DWCNTs nanocomposites

TiO<sub>2</sub>-DWCNTs nanocomposites were prepared by a sol-gel method [11]. Firstly, DWCNTs were oxidized as follows: DWCNTs were mixed with the mixture acid of concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> with a volume ratio of 3:1. The mixture was refluxed at 100°C for 2 h and cooled naturally to room temperature. The oxidized DWCNTs were washed with mixture of absolute ether and ethanol

twice and then washed with deionized water until the pH value reached neutrality. The product was then dried at 80°C in an oven and kept in a desiccator for further use. Secondly, the 0.1 g DWCNTs was dispersed into a 30 mL solution containing 5 mL water and 25 mL isopropanol, under sonication for 1 h. The titanium precursor solution, 1.86 mL titanium isopropoxide in 18 mL isopropanol, was added dropwise into the DWCNTs suspension under vigorous stirring for 2 h to complete the hydrolysis reaction. The suspension solution was then filtered and washed with ethanol and water for twice and dried at 100°C for 1 h. The resultant solids were ground and sintered at 450°C for 30 min, thus TiO<sub>2</sub>-DWCNTs was obtained.

### 2.3 Preparation of TiO<sub>2</sub> film electrode

TiO<sub>2</sub> precursor was prepared according to the procedures described in the literature [10]. PVP and P25 were mixed at a molar ratio of 1/10 in the mixed solution of distilled water and anhydrous ethanol (volume ratio of 1:5) by stirring adequately. 0.50 wt.% TiO<sub>2</sub>-DWCNTs were mixed with the P25 and added to the mixture solution to disperse by ultrasonic vibration for 30 min. The system was stirred for 6 h to form a homogeneous suspension, then the suspension was put into an autoclave (packing volume < 80%) and hydrothermally treated at 185°C for 12 h to form a TiO<sub>2</sub> colloid.

TiO<sub>2</sub> colloid was coated on a clean ITO/PEN substrate

by using “doctor blade” technique. The thickness of the TiO<sub>2</sub> film was controlled at 8 μm by adhering a plastic tape around the edge of the ITO/PEN substrate. The resultant flexible TiO<sub>2</sub> film was heated at 90°C for 30 min in air and treated by UV illumination for 60 min to decompose residual organic compounds. Finally, the film was immersed in a 2.5 × 10<sup>-4</sup> mmol·L<sup>-1</sup> N719 absolute ethanol solution for 24 h to absorb the dye adequately. Thus a flexible TiO<sub>2</sub> film electrode was obtained [10].

#### 2.4 Fabrication of flexible DSSCs

Flexible DSSC was assembled by injecting a redox electrolyte into the aperture between the dye-sensitized flexible TiO<sub>2</sub> film electrode (anode electrode) and a Pt-ITO/PEN counter electrode. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte from leaking. Epoxy resin was used for further sealing the cell. The redox electrolyte was consisted of 0.60 mmol·L<sup>-1</sup> tetrabutyl ammonium iodide, 0.10 mmol·L<sup>-1</sup> LiI, 0.10 mmol·L<sup>-1</sup> I<sub>2</sub>, and 0.50 mmol·L<sup>-1</sup> 4-tert-butyl-pyridine in acetonitrile.

#### 2.5 Characterization and measurements

Morphologies of samples were observed with a scanning electron microscope (SEM) (S-3500N, Hitachi, Japan). The X-ray diffraction (XRD) (D8-advance, Bruker, Germany) and FT-IR spectroscopy were used to character the samples. The amount of dye adsorbed on the electrode was determined by measuring the dye amount released in the solution of 5 mL 0.05 mmol·L<sup>-1</sup> NaOH. The measurement was carried out with an UV-vis spectrometer (UV-2401PC, Shimadzu, Japan). Photovoltaic performance of the DSSCs were determined by measuring the current-voltage (*J-V*) characteristic curves using an Electrochemical Workstation (CHI660C, Shanghai Chenhua Device Company, China) under irradiation with a simulated solar light from a 100 W xenon arc lamp (XQ-500W, Shanghai Photoelectricity Device Company, China) in ambient atmosphere. The photovoltaic parameters fill factor (*FF*) and light-to-electric energy conversion efficiency (*η*) of the flexible DSSC were calculated according to the following equations [12]:

$$FF = \frac{P_{\max}}{J_{\text{sc}} \times V_{\text{oc}}} = \frac{J_{\max} \times V_{\max}}{J_{\text{sc}} \times V_{\text{oc}}}, \quad (1)$$

$$\eta(\%) = \frac{P_{\max}}{P_{\text{in}}} \times 100\% = \frac{J_{\text{sc}} \times V_{\text{oc}} \times FF}{P_{\text{in}}} \times 100\%, \quad (2)$$

where *J*<sub>SC</sub> is the short-circuit current density (mA·cm<sup>-2</sup>), *V*<sub>OC</sub> is the open-circuit voltage (V), *P*<sub>in</sub> is the incident light power, *P*<sub>max</sub> is the maximum power output, *J*<sub>max</sub> (mA·cm<sup>-2</sup>) and *V*<sub>max</sub> (V) are the current density and voltage at the point of maximum power output in the *J-V* curves, respectively.

## 3 Results and discussion

### 3.1 Morphology of TiO<sub>2</sub>-DWCNTs nanocomposites

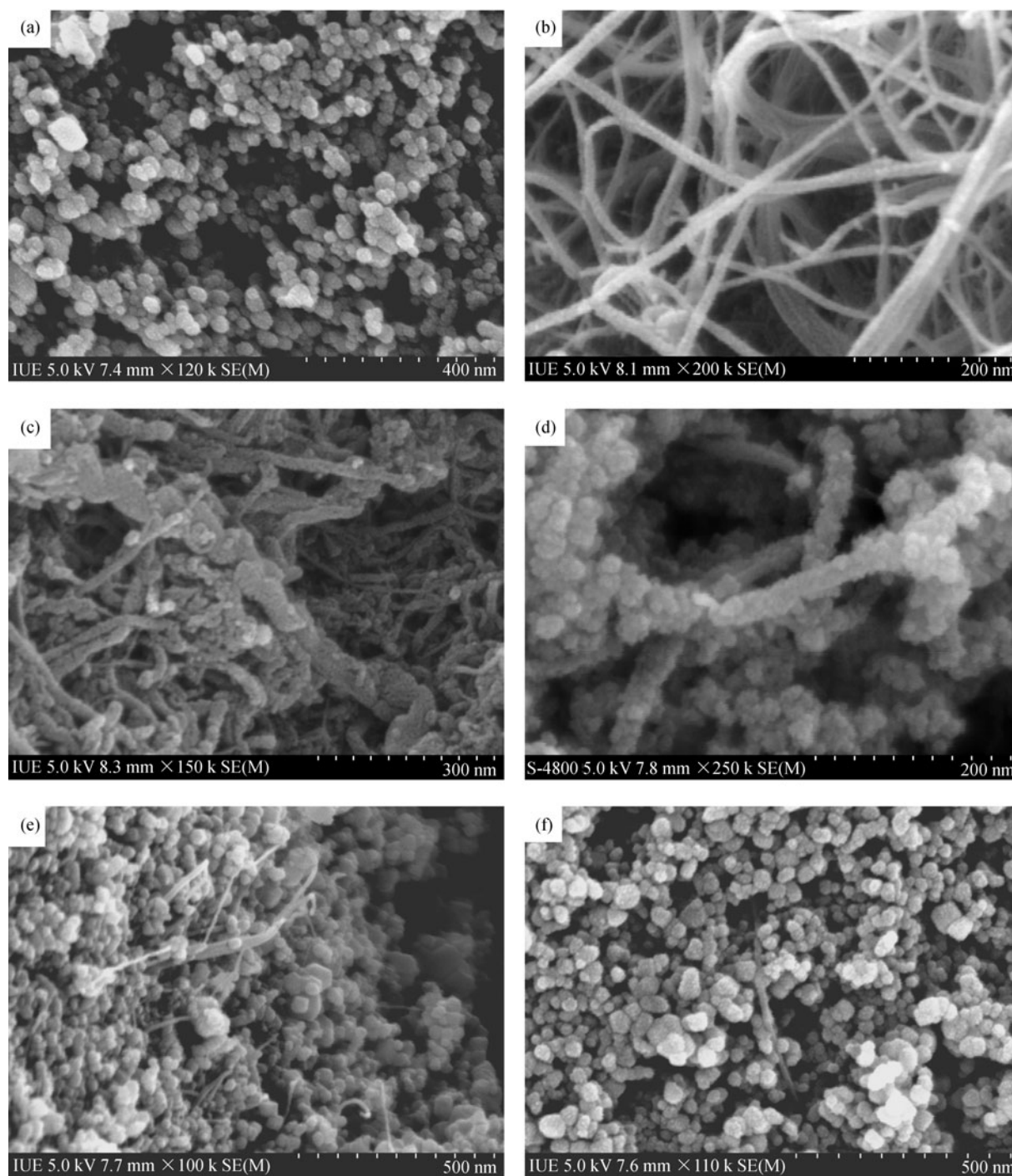
Figure 2 shows SEM images of mesoporous TiO<sub>2</sub> alone (Fig. 2(a)), oxidized DWCNTs (Fig. 2(b)) and of TiO<sub>2</sub>-DWCNTs nanocomposites (Figs. 2(c) and 2(d)) prepared from DWCNTs and titanium sources under optimized conditions. As shown in Fig. 2(d), it can be seen that the DWCNTs were homogenously covered by well-hydrolyzing TiO<sub>2</sub> particles with only a few of TiO<sub>2</sub> aggregates. According to Brozena et al. [13], the DWCNTs can be achieved high water solubility while preserving the electrical properties of the inner tube chemistry through carboxylic acid functional groups introduced to the outer wall using a combination of concentrated H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>. It was well explained that a good dispersion of DWCNTs into the mix solution of water and isopropanol provided the more reactive sites for the titanium sources. Figures 2(e) and 2(f) show images of TiO<sub>2</sub> film covered with 0.50 wt.% TiO<sub>2</sub>-DWCNTs. The TiO<sub>2</sub>-DWCNTs are well-dispersed in TiO<sub>2</sub> nanoparticles, and the TiO<sub>2</sub>-DWCNTs particles and TiO<sub>2</sub> nanoparticles have a good contact.

Figure 3 compares the XRD patterns for TiO<sub>2</sub> powder and resultant TiO<sub>2</sub>-DWCNTs powder. It can be seen that the formation of pure anatase crystallites in both cases. No characteristics peaks for CNTs are found in the XRD. This may be attributed to that small amount of DWCNTs is added in larger amount of TiO<sub>2</sub> [11], anatase (001) peak overlap with the DWCNTs (002) peak, and the TiO<sub>2</sub> crystallinity is much stronger than DWCNTs, which shield the DWCNTs diffraction peaks [14].

FTIR spectra of (a) pristine DWCNTs, (b) TiO<sub>2</sub>, (c) oxidized DWCNTs, and (d) TiO<sub>2</sub>-DWCNTs are shown in Fig. 4. The band from 500 to 800 cm<sup>-1</sup> is due to the Ti-O bond. The peaks at 1707 and 3114 cm<sup>-1</sup> are attributed to the -OH stretch vibration, and indicate the presence of a -COOH group in the oxidative process of DWCNT. Besides, it can be noted that in the TiO<sub>2</sub>-DWCNT nanocomposites the same signature appears a bit shifted to 1730 cm<sup>-1</sup>, suggesting an effect of conjugation of TiO<sub>2</sub> on the modified DWCNT surface [7].

### 3.2 Influence of TiO<sub>2</sub>-DWCNTs contents on dye adsorption

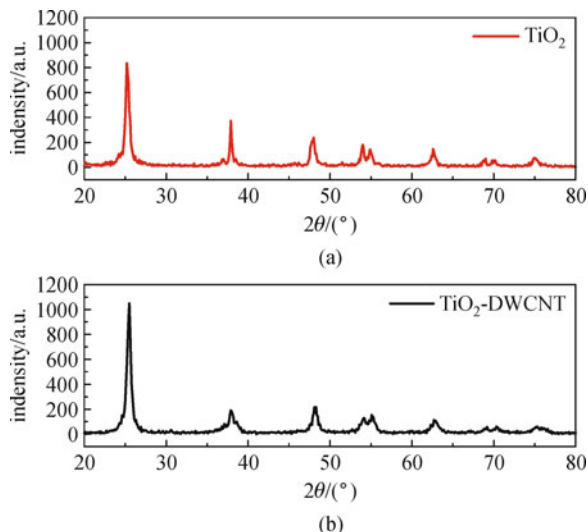
TiO<sub>2</sub>-DWCNT content affects dye adsorption amount on the flexible TiO<sub>2</sub> film. Figure 5 shows the absorption spectra of dye N719 desorbed from the flexible TiO<sub>2</sub> films with the same thickness and with different TiO<sub>2</sub>-DWCNTs percentages. According to the Lambert-Beer's law, higher absorbance means the more dye N719 absorbed on the TiO<sub>2</sub> film, which is in favor of enhancing the photocurrent of the flexible DSSC [15]. It is obvious that the absorbance for the sample with 0.50 wt.% TiO<sub>2</sub>-DWCNTs is the highest, the samples with 0.25 wt.% and 0 wt.% TiO<sub>2</sub>-



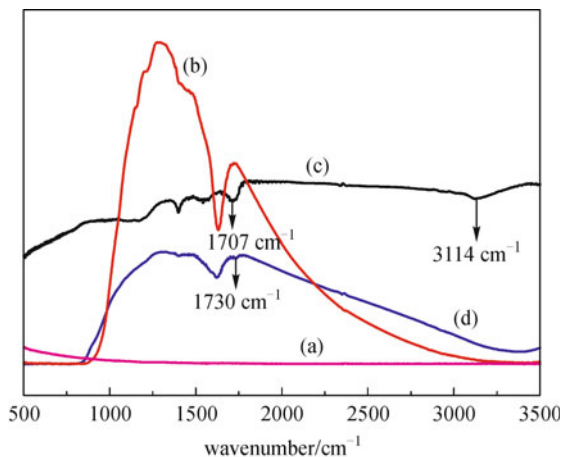
**Fig. 2** SEM images of (a) TiO<sub>2</sub> nanoparticles; (b) oxidized DWCNTs; (c) and (d) DWCNTs covered with TiO<sub>2</sub> nanoparticles ; (e) and (f) TiO<sub>2</sub> film covered with 0.5 wt.% TiO<sub>2</sub>-DWCNTs

DWCNTs are lower, and the sample with 0.75 wt.% TiO<sub>2</sub>-DWCNTs is the smallest. As reported in Refs. [16,17], incorporating CNTs in a TiO<sub>2</sub> matrix will decrease the TiO<sub>2</sub> crystallinity or the reduce TiO<sub>2</sub>-CNTs size due to the interaction between CNTs and TiO<sub>2</sub>. Moreover, smaller particles or crystallinity result in larger surface area of the materials, which will provide more surface active sites for

adsorbing dye molecules. Besides, the roughness factor of the TiO<sub>2</sub> film was enhanced by adding DWCNTs, which increase dye adsorption. However, higher loaded TiO<sub>2</sub>-DWCNTs (0.50 wt.%) may cause the formation of DWCNT aggregation and decrease the adsorption of TiO<sub>2</sub> film to the dye. In our experimental conditions, the TiO<sub>2</sub> film contained 0.50 wt.% TiO<sub>2</sub>-DWCNTs can absorb most dye N719 [16–18].



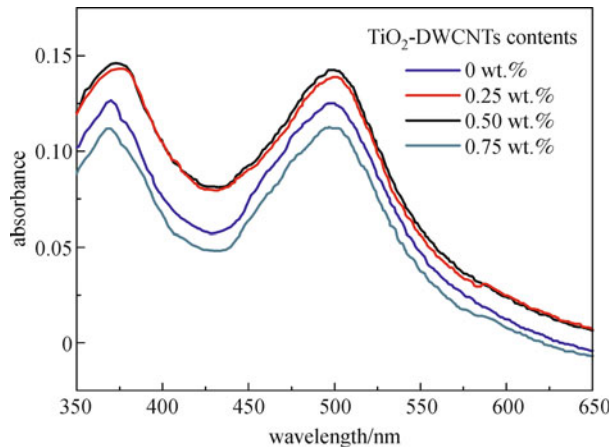
**Fig. 3** XRD patterns of  $\text{TiO}_2$  (a) and  $\text{TiO}_2$ -DWCNT (b) nanopowder



**Fig. 4** FTIR spectra of (a) pristine DWCNTs; (b)  $\text{TiO}_2$  nanoparticles; (c)  $\text{TiO}_2$ -DWCNTs nanocomposites and (d) oxidized DWCNTs

### 3.3 Photovoltaic properties of flexible DSSCs with different amounts of $\text{TiO}_2$ -DWCNTs

Photovoltaic parameters of the flexible DSSCs with different percentages of  $\text{TiO}_2$ -DWCNTs in the  $\text{TiO}_2$  film were measured and the results are summarized in Table 1. It can be seen that the open-circuit voltage ( $V_{OC}$ ) of the flexible DSSC are not changed with different percentage  $\text{TiO}_2$ -DWCNTs in the  $\text{TiO}_2$  films. However, the short-circuit current density ( $J_{SC}$ ), fill factor ( $FF$ ) and the light-to-electric energy conversion efficiency ( $\eta$ ) of the flexible DSSC increase with the increase of  $\text{TiO}_2$ -DWCNTs from 0 to 0.50 wt.%, then decrease with the further increase of  $\text{TiO}_2$ -DWCNTs, and 0.50 wt.%  $\text{TiO}_2$ -DWCNTs is an optimal percentage. It is due to enhancement of the



**Fig. 5** Absorption spectra of dye desorbed from  $\text{TiO}_2$  films contained different amount of  $\text{TiO}_2$ -DWCNTs

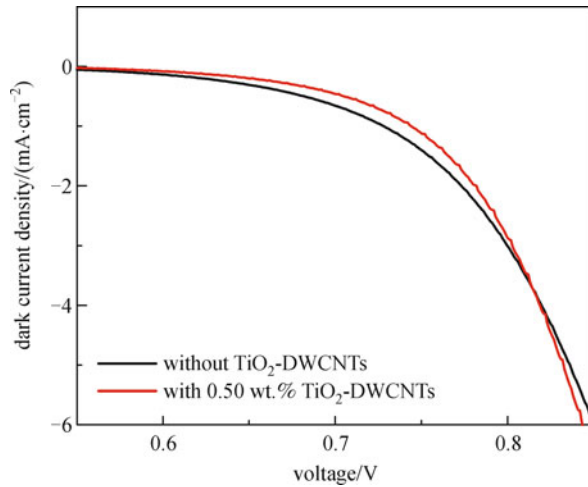
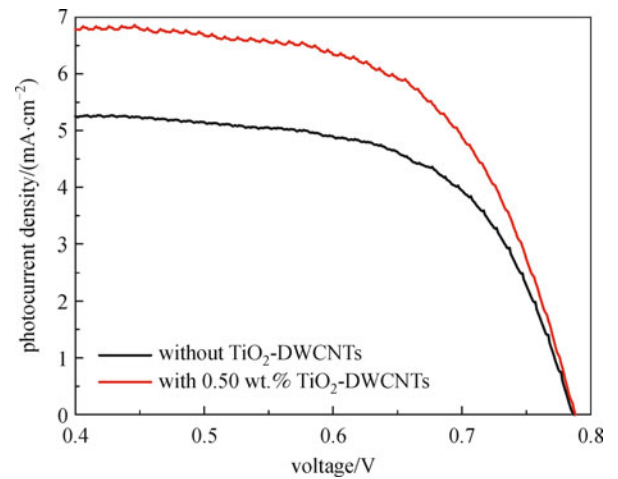
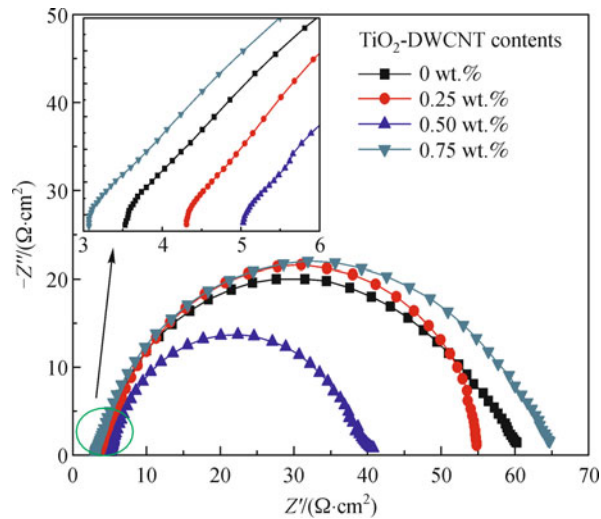
collection and transport of electrons by adding DWCNTs [17–19]. Nevertheless, when the content of  $\text{TiO}_2$ -DWCNTs exceeded 0.50 wt.%, the DWCNTs aggregation might be the main reason to decrease the quantity of dye-sensitizer adsorption, resulting in a lower current density. In addition, if the  $\text{TiO}_2$  film contained too many DWCNTs, the bare surfaces of the DWCNTs which are not covered by dyes would increase the electron recombination process on the working electrode surface, resulting in a lower  $V_{OC}$  [20].

Dark current curves for the flexible DSSCs were measured and the results are shown in Fig. 6. It can be seen that the slopes of the steep part of the current voltage curves reveal changes in series resistance of the different films [10,21]. For the same applied voltage, the dark current is greater for the film without  $\text{TiO}_2$ -DWCNTs than with 0.50 wt.%  $\text{TiO}_2$ -DWCNTs, suggesting that the main effect of adding  $\text{TiO}_2$ -DWCNTs is to decrease the back electron-transfer rate. The overall steeper slope of the  $\text{TiO}_2$  film with  $\text{TiO}_2$ -DWCNTs has a lower series resistance than that of the  $\text{TiO}_2$  film without  $\text{TiO}_2$ -DWCNTs.

Furthermore, the internal resistances of the  $\text{TiO}_2$  films with different percentages of  $\text{TiO}_2$ -DWCNTs in DSSCs were also studied by using electrochemical impedance spectroscopy (EIS). Figure 7 shows the Nyquist plots of the electrochemical impedance spectra of the DSSCs with different  $\text{TiO}_2$ -DWCNTs contents measured under  $100 \text{ mW} \cdot \text{cm}^{-2}$ . Generally, all the spectra of DSSCs exhibit three semicircles, which are assigned to electrochemical reaction at the Pt counter electrode, charge transfer at the  $\text{TiO}_2$ /dye/electrolyte and Warburg diffusion process of  $\text{I}^-/\text{I}_3^-$  [22]. In our case, it was found that the charge transport resistance at the  $\text{TiO}_2$ /dye/electrolyte interface decreased with the increase of  $\text{TiO}_2$ -DWCNTs from 0 to 0.50 wt.% and increased in a percentage of 0.75 wt.%. This phenomenon may be due to decrease the dye adsorption. This result was consistent with the previous results obtained from cell performance.

**Table 1** Photovoltaic performance of flexible DSSCs with different TiO<sub>2</sub>-DWCNTs contents

TiO <sub>2</sub> -DWCNTs: TiO <sub>2</sub> /(wt.%)	$V_{OC}/V$	$J_{SC}/(\text{mA} \cdot \text{cm}^{-2})$	$FF$	$\eta/\%$
0	0.787	5.44	0.706	3.02
0.25	0.786	6.13	0.717	3.45
0.50	0.788	6.69	0.738	3.89
0.75	0.771	5.34	0.674	2.86

**Fig. 6** Dark current curves for the flexible DSSCs**Fig. 8** Current-voltage curves for the flexible DSSCs**Fig. 7** Electrochemical impedance spectra of the DSSCs with different TiO<sub>2</sub>-DWCNTs contents

### 3.4 Photovoltaic characterization of flexible DSSCs

Based on the optimal conditions for flexible TiO<sub>2</sub> film preparation, flexible DSSCs were assembled by using the TiO<sub>2</sub> film contained 0.50 wt.% TiO<sub>2</sub>-DWCNTs and TiO<sub>2</sub> film without TiO<sub>2</sub>-DWCNTs as photoanodes, respectively. The photocurrent-voltage curves (Fig. 8) of the flexible DSSCs were measured under a simulated solar light

irradiation of 100 mW·cm<sup>-2</sup>. It is obvious that the photovoltaic performance of the DSSC with TiO<sub>2</sub>-DWCNTs is higher than the DSSC without TiO<sub>2</sub>-DWCNTs. The DSSC without TiO<sub>2</sub>-DWCNTs obtains  $J_{SC}$  of 5.44 mA·cm<sup>-2</sup>,  $V_{OC}$  of 0.787 V,  $FF$  of 0.706 and  $\eta$  of 3.02%; while the DSSC with TiO<sub>2</sub>-DWCNTs nanocomposites achieves  $J_{SC}$  of 6.69 mA·cm<sup>-2</sup>,  $V_{OC}$  of 0.788 V,  $FF$  of 0.738 and  $\eta$  of 3.89%, respectively. The results indicate that adding suitable amount of TiO<sub>2</sub>-DWCNTs is an effective method to improve the photovoltaic performance of the flexible DSSC, especially for increasing the photocurrent.

## 4 Conclusions

In conclusion, TiO<sub>2</sub>-DWCNTs are prepared by a convenient sol-gel method with the DWCNTs and TTIP as titanium source. Then TiO<sub>2</sub>-DWCNTs prepared are introduced to low temperature preparation a good quality TiO<sub>2</sub> film used in flexible DSSCs. By characteristics and measurements, it is found that the proper TiO<sub>2</sub>-DWCNTs can efficiently increase the adsorption of dye and enhance the collection and transport of electrons for flexible DSSC. Under an optimal condition, a flexible DSSC using TiO<sub>2</sub> film with 0.50 wt.% TiO<sub>2</sub>-DWCNTs composites achieves a light-to-electric energy conversion efficiency of 3.89% under irradiation with a simulate solar light intensity of 100 mW·cm<sup>-2</sup>.

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