

Incorporating carbon nanotube in a low-temperature fabrication process for dye-sensitized TiO₂ solar cells[☆]

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ABSTRACT

Dye-sensitized solar cells (DSSCs) incorporating TiO₂ porous films, prepared at a low temperature (150 °C), along with multi-wall carbon nanotubes (MWCNTs) were studied using two different electrolytes, namely LiI and THI. Electrochemical impedance spectroscopy (EIS) was employed to quantify the charge transport resistance and electron lifetime (τ_e) under different levels (wt%) of MWCNTs and electrolytes. The charge transport resistance at the TiO₂/dye/electrolyte interface (R_{ct2}) increased as a function of the MWCNT concentration, which ranged 0.1–0.5 wt%, due to a decrease in the surface area and decreased dye adsorption. The characteristic peak shifted to a lower frequency at 0.1 wt% of MWCNT, indicating a longer electron lifetime. The DSSC with the TiO₂ electrode containing 0.1 wt% of MWCNT resulted in a higher short-circuited current density (J_{sc}) of 9.08 mA/cm², an open-circuit voltage (V_{oc}) of 0.781 V, and a cell conversion efficiency of 5.02%. EIS was also conducted under dark conditions. The large value at a middle frequency represented electron transport at the TiO₂/dye/electrolyte interface (R_{rec}). The R_{rec} for 0.1 wt% MWCNT/TiO₂ was found to be 114 Ω, and for those with 0.3 and 0.5 wt% were 35 and 30 Ω, respectively. The significantly higher value of R_{rec} suggested that the charge recombination between injected electrons and electron acceptors in the redox electrolyte, I₃⁻, was remarkably retarded. Finally, electrolytes with LiI and THI were used to compare the cell conversion performance under the same conditions. It was found that more electrons were injected in the TiO₂ electrode and the electron recombination reaction was faster in the DSSC with THI than that with LiI.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention as the next-generation solar cells with low production costs and good efficiency for energy conversion, reaching 11% and a module efficiency of 7% in some cases [1]. Their energy conversion working principle is based on injection of electrons from a photoexcited state of the sensitizer into the conduction band of the semiconductor. A charge mediator, i.e., a suitable redox couple, must be added to the electrolyte to reduce the oxidized dye. The mediator also needs to be renewed in the counter-electrode, meaning that the photoelectrochemical cell can be regenerated.

At present, research work has focused on developing inexpensive solar cells based on flexible plastic substrates such as

nanocrystalline TiO₂ electrodes and counter-electrodes [2]. However, the conventional method for preparing TiO₂ electrodes for DSSCs using colloidal suspensions of TiO₂ nanoparticles includes high-temperature sintering at 450–500 °C, in order to remove organic additives such as the precursor or polymer for the interconnection between TiO₂ particles and the substrate. This is also necessary to establish a good interconnection among TiO₂ particles; however, it cannot be applied to prepare films on plastic substrates because they crack at such high temperatures.

The development of low-temperature fabrication methods should overcome two main problems of incomplete necking of the particles and the presence of residual organics in the film [3]. These problems cause lower electron diffusion coefficients and electron lifetimes. Therefore, enhancing the electron transport rate and electron lifetime is compulsory for low-temperature fabrication processes. Recently, some efforts have been made to develop methods compatible with plastic substrates [4–9], and the conversion efficiency level reached 5.8% under irradiation of 100 mW/cm² [9].

Carbon nanotubes (CNTs) are remarkable materials, which are being widely studied because of their extraordinary electronic

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and mechanical properties. Some reports have shown that incorporation of CNTs in a poly(3-octylthiophene) polymer film enhanced the electrical conductivity of the composite film [10,11]. A composite of poly(*p*-phenylene vinylene) with CNTs in a photovoltaic device showed good quantum efficiency, owing to the formation of a complex interpenetrating network with the polymer chains [12]. The CNTs also conferred electrical conductivity to metal oxide nanocomposites [13]. However, only a few reports have been found in the literature where CNTs are used along with TiO₂ films in DSSCs [14–16], despite the expected potential to enhance the solar energy conversion efficiency due to favorable electrical conductivity. To the best of our knowledge, those reports which are associated with the addition of CNTs to TiO₂ films focused on high-temperature fabrication of TiO₂ electrodes, while no report was found which deals with the application of TiO₂ electrodes containing CNTs fabricated at low temperature in DSSCs. Herein, we investigated these aspects in order to improve the electrical conductivity of TiO₂ films.

In addition, electrochemical impedance spectroscopy (EIS) is a useful tool for analyzing the charge transport process. EIS is a steady-state technique which measures the current response to the application of an AC voltage as a function of the frequency [17]. EIS has been widely employed to study the kinetics of electrochemical and photoelectrochemical processes, including elucidation of the salient electronic and ionic processes occurring in DSSCs [18–20]. In this study, we utilized EIS to analyze the charge transport resistances in DSSCs. By fitting and calculating the exact resistance, capacitance, and time constants of DSSCs in Nyquist plots, the effects of MWCNTs on the TiO₂ electrodes fabricated with a low-temperature process in DSSCs were investigated.

2. Experimental

2.1. Materials

Anhydrous I₂, ethanol (99.5%), tertiary butanol, and 4-tertiary butyl pyridine (TBP) were obtained from Merck, and titanium (IV) tetraisopropoxide (TTIP) (>98%) was purchased from Acros; all were used as received. Cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) (N3 dye) is a commercial product of Solaronix (Aubonne, Switzerland). MWCNTs were purchased from Nanotech Port (Taiwan). These MWCNTs were produced via a chemical vapor deposition (CVD, sometimes called catalytic pyrolysis) method [21]. The MWCNTs were oxidized in a concentrated 3:1 v/v acid mixture of H₂SO₄/HNO₃ under ultrasonication for 24 h at 50–60 °C to produce MWCNTs with terminal –COOH groups [22]. We expected that after the acid treatment the MWCNTs with terminal –COOH groups would have good contact around the TiO₂ nanoparticles.

2.2. Preparation of TiO₂ electrodes

The TiO₂ precursor and electrodes were prepared according to the procedures described in the literature [8]. TTIP and P25 TiO₂ were mixed at a molar ratio of 0.08/1 in an ethanol solution, and various amounts of acid-treated MWCNTs were added to the TiO₂ paste and dispersed using an ultrasonic horn for 30 min. After stirring for 2 h, the paste was coated onto fluorine-doped SnO₂-coated conductive glass (15 Ω/sq. FTO glass) using a glass rod, followed by evaporation of the ethanol in air at room temperature after a few minutes. Then the films that had formed were sintered at 150 °C for 4 h.

2.3. Cell assembly of DSSCs

An active area of 0.25 cm² was selected from the sintered electrode, and the electrodes were immersed in a 3 × 10^{−4} M solution of N3 dye containing acetonitrile and tertiary butanol (in a volume ratio of 1:1) overnight. Pt (100 nm thick) sputtered onto the FTO was used here as the counter-electrode.

Cells were fabricated by applying an ionomer resin (Surlyn 1702, Dupont, USA), at a thickness of 50 μm, between the two electrodes, and then two holes were made on the resin. The whole setup was heated to 100 °C on a hotplate until all of the resin had been melted, and the electrolyte was injected into the space between the electrodes through these two holes. Finally, these two holes were completely sealed using Torr Seal[®] cement (Varian, MA, USA). The electrolyte was composed of 0.5 M LiI/0.05 M I₂/0.5 M TBP in CH₃CN.

2.4. Instruments and measurements

Photoelectrochemical characterizations of the DSSCs were carried out using AM 1.5 simulated light irradiation. The light source was a 450 W Xe lamp (#6266, Oriel, USA) equipped with a water-based infrared (IR) filter and an AM 1.5 filter (#81075, Oriel). UV–visible absorption data were measured by a UV–visible spectrophotometer (V-570, Jasco, Japan). Photoelectrochemical characteristics and EIS measurements of the DSSCs were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, The Netherlands). The frequency range explored was from 10 mHz to 65 kHz. The applied bias voltage and AC amplitude were set at the open-circuit voltage of the DSSCs and 10 mV between the FTO/Pt counter electrode and the FTO/TiO₂/dye working electrode, respectively, starting from a short-circuit condition [23]. The impedance spectra were analyzed by an equivalent circuit model which interpreted the characteristics of the DSSCs [24]. The photovoltage transients of the assembled devices were recorded with a digital oscilloscope (model LT322, LeCroy, USA). Pulsed laser excitation was applied by a frequency-doubled Q-switched Nd:YAG laser (model Quanta-Ray GCR-3-10, Spectra-Physics laser) with a 2 Hz repetition rate at 532 nm, and a 7 ns pulse width at half-height. The beam size was slightly larger than 0.25 cm² to cover the area of the device with an incident energy of 1 mJ/cm². The average electron lifetime can approximately be estimated by fitting a decay of the open-circuit voltage transient with $\exp(-t/\tau_e)$, where t is the time and τ_e is an average time constant before recombination.

3. Results and discussion

Acid-treated MWCNT and P25 TiO₂ nanoparticles were used to fabricate the TiO₂ photoelectrodes in this study. Due to the favorable electrical conductivity of the CNTs on metal oxide nanocomposites [13], we expected that the presence of the CNTs should enhance the electron transport rate and extend the electron lifetime in the TiO₂ electrode, so as to improve the solar energy conversion efficiency. In addition, from the literature [22], it was noted that the oxidation of CNTs in a concentrated acid treatment could produce CNTs with terminal –COOH groups, which have better contact around TiO₂ nanoparticles to improve the collection of electrons. The TEM images of MWCNTs and P25 TiO₂ particles, and the SEM images of the TiO₂ electrode containing 0.1 wt% MWCNT in the TiO₂ are shown in Fig. 1. From the SEM images, we found that the MWCNTs were well-dispersed among the TiO₂ nanoparticles, and there was good contact between the MWCNTs and TiO₂ nanoparticles. To optimize the ratio of

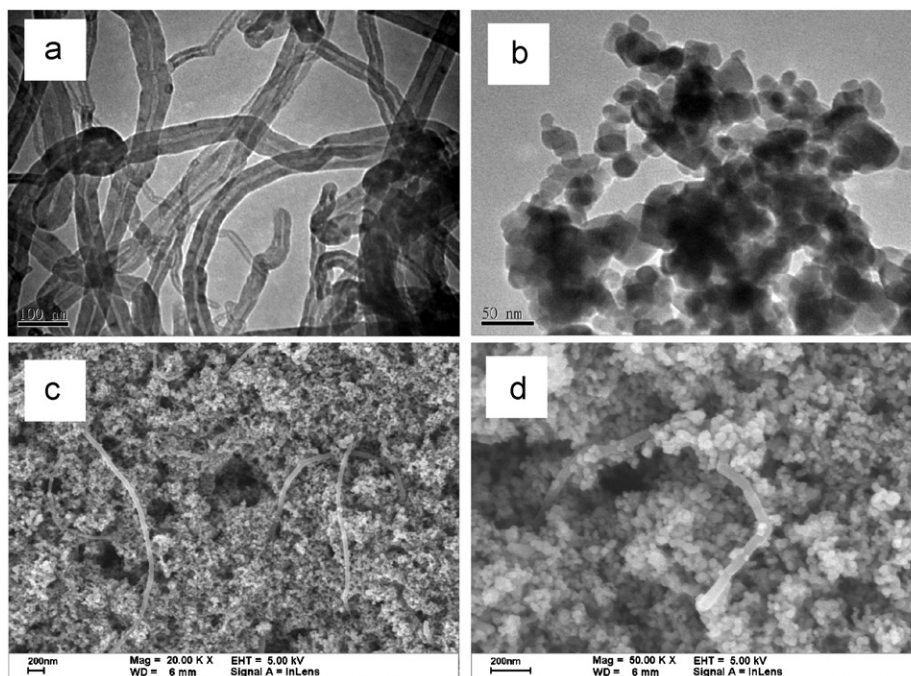


Fig. 1. TEM images of (a) MWCNT and (b) P25 TiO₂. (c) and (d) are the SEM images of the side view of 0.1 wt% MWCNT/TiO₂ film.

MWCNTs with respect to TiO₂ powder for film preparation, films composed of pastes with various weight percentages of MWCNTs were investigated. The EIS analysis of the DSSCs based on the TiO₂ films with different ratios of MWCNTs/TiO₂ from 0 to 0.5 wt% are shown in Fig. 2. Generally speaking, the impedance spectra of the DSSCs exhibited three semicircles, which were assigned to the electrochemical reaction at the Pt counter electrode (R_{ct1}) in the high-frequency region, to charge transfer at the TiO₂/dye/electrode interface (R_{ct2}) in the middle-frequency region, and to the Warburg diffusion process of I⁻/I₃⁻ in the electrolyte (R_{diff}) in the low-frequency region. The overall series resistance of the cell (R_s) is the resistance measured when electrons are transported through the device in the high-frequency range exceeding 10⁶ Hz. The Nyquist plot (Fig. 2a) showed that the R_s decreased from 40 to ~26 Ω, as TiO₂ particles were incorporated in the MWCNTs, which increased the conductivity of the TiO₂ film, resulting in a decrease in the R_s of the solar cells. The reduction in the R_s can improve the fill factor (FF) of the DSSCs to achieve a higher cell performance. Meanwhile, with the addition of 0.1 wt% of MWCNT to the TiO₂ films, the value of the charge transport resistance at the TiO₂/dye/electrolyte interface (R_{ct2}) was almost the same as that using only the pure TiO₂ electrode. However, with further increases in the amount of MWCNTs (from 0.3 to 0.5 wt%), the R_{ct2} increased (Fig. 2a). This phenomenon may have been due to a decrease in dye adsorption on the TiO₂ electrode when the TiO₂ film contained more MWCNTs, resulting in fewer electrons injected from the dye to the TiO₂ electrode. Correspondingly, the characteristic frequency peaks (1–10³ Hz) in the Bode phase plots (Fig. 2b) showed that the characteristic frequency peak shifted to a lower frequency when the MWCNT was at 0.1 wt% and then shifted back again to a higher frequency when the MWCNTs exceeded 0.3 wt%. The characteristic frequency peak can be related to the inverse of the recombination lifetime (τ_r), or electron lifetime (τ_e) in TiO₂ films [25–27]. This implies that the collection and transport of electrons in the TiO₂ film were faster with 0.1 wt% of MWCNT than in its absence, thereby reducing the electron recombination and extending the electron lifetime in the TiO₂ film. Nevertheless, when the content of MWCNTs exceeded

0.3 wt%, the surface area of the TiO₂ with adsorbent dyes significantly decreased and the number of cracks on the surface of the porous TiO₂ electrode increased, resulting in a lower current density. In addition, the surface of MWCNTs only had a few –COOH groups for dye adsorption even after the acid treatment. If the TiO₂ film contained too many MWCNTs, the bare surfaces of the MWCNTs which are not covered by dyes would increase the electron recombination process on the working electrode surface, resulting in a lower V_{OC} . The J – V characteristics and EIS data of the DSSCs of TiO₂ containing various amounts of MWCNTs measured under 100 mW/cm² are listed in Table 1. Based on the bare TiO₂ film, the cell conversion efficiency was about 4.15%. In the cell with the TiO₂ electrode containing 0.1 wt% of MWCNT, the J_{SC} was 9.08 mA/cm², V_{OC} was 0.781 V, η was 5.02% and FF was 0.708. The value of V_{OC} increased from 0.761 to 0.781 V with a subsequent increase in MWCNTs of 0.0–0.1 wt%. It has been observed that surface treatment usually increases the value of V_{OC} regardless of the nature and characteristics of the materials coated onto the electrode [28,29]. Furthermore, for the TiO₂ electrode containing 0.1 wt% of MWCNT, the value of J_{SC} increased by about 14% from 7.96 to 9.08 mA/cm² compared to the as-prepared TiO₂ electrode, due to enhancement of the collection and transport of electrons. The existence of MWCNTs in the TiO₂ film increased the FF from 0.68 to ~0.71, which showed a better performance due to the increase in the conductivity of the TiO₂ electrode. These results were also supported by the EIS analysis, as described above.

For comparison, the effect of MWCNT in the TiO₂ electrode on the average electron lifetime (τ_e) was also studied by a laser-induced photovoltage transient technique, and the results are shown in Fig. 3. The average electron lifetime can approximately be estimated by fitting a decay of the open-circuit voltage transient with $\exp(-t/\tau_e)$, where t is the time and τ_e is an average time constant before recombination. It was found that values of τ_e of TiO₂ films were 2.75 and 2.00 ms for TiO₂ electrode with and without 0.1 wt% of MWCNT, respectively. The study of τ_e further proved the rationale that the TiO₂ electrode containing 0.1 wt% of MWCNT possesses a reduced electron recombination and longer electron lifetime.

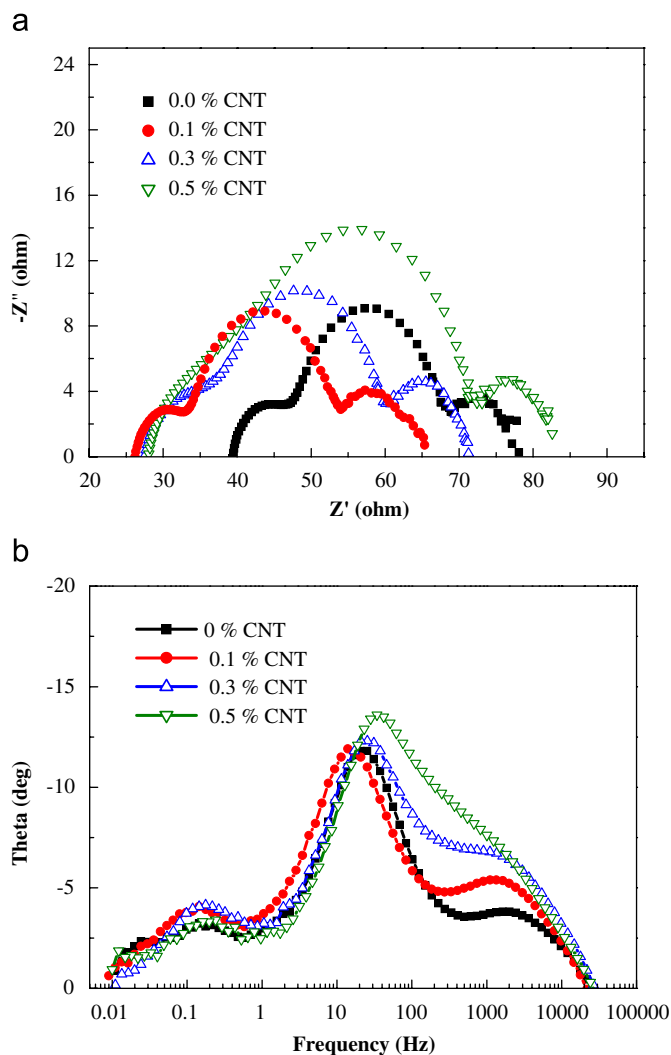


Fig. 2. Electrochemical impedance spectra of the DSSCs based on TiO_2 electrode with different weight percents of MWCNTs measured at -0.8 V , 100 mW/cm^2 . (a) Nyquist plot and (b) Bode phase plot.

Table 1

The photovoltaic performances and impedance data of the DSSCs with low-temperature fabricated TiO_2 electrode containing various amounts of MWCNTs measured under 100 mW/cm^2

Sample (% CNT)	R_s (Ω)	R_{ct2} (Ω)	CF (Hz) ^a	J_{sc} (mA/cm^2)	V_{oc} (V)	η (%)	FF
0.0	40.0	21.4	20.5	7.96	0.761	4.15	0.685
0.1	26.0	22.0	10.2	9.08	0.781	5.02	0.708
0.3	27.5	28.7	25.3	6.52	0.740	3.43	0.710
0.5	27.6	37.3	39.6	5.64	0.716	2.85	0.707

^a CF: the peak frequency of the semicircle in the Nyquist plot.

The EIS of the DSSCs was also measured in the dark to elucidate the correlation of electron transport with different molar ratios. In these cells, electrons were transported through the mesoscopic TiO_2 network and reacted with I_3^- . At the same time, I^- was oxidized to I_3^- at the counter electrode. To further study the enhancement of V_{oc} , EIS was measured at an applied bias voltage of -0.8 V in the dark. Three semicircles were observed in the Nyquist plot. The large one in the middle frequency represents electron transport at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface (R_{rec}). The larger the R_{rec} is, the smaller the charge recombination rate will be. In Fig. 4, values of R_{rec} for 0.0, 0.1, 0.3, and 0.5 wt% of MWCNT

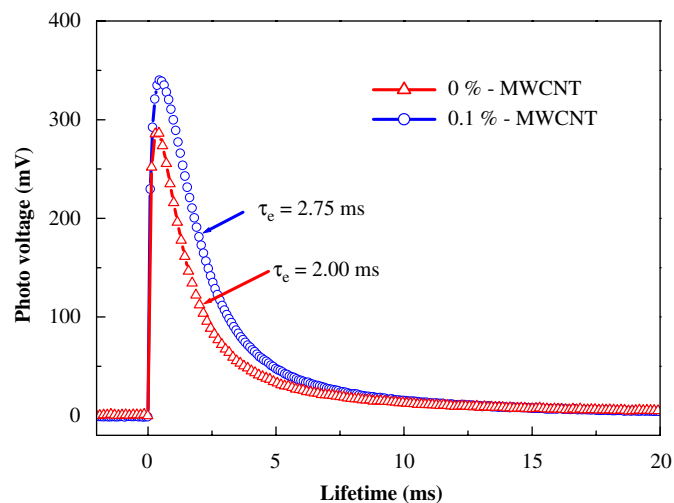


Fig. 3. Transient photovoltage measurements of the DSSCs with various TiO_2 electrodes prepared with or without 0.1 wt% MWCNT.

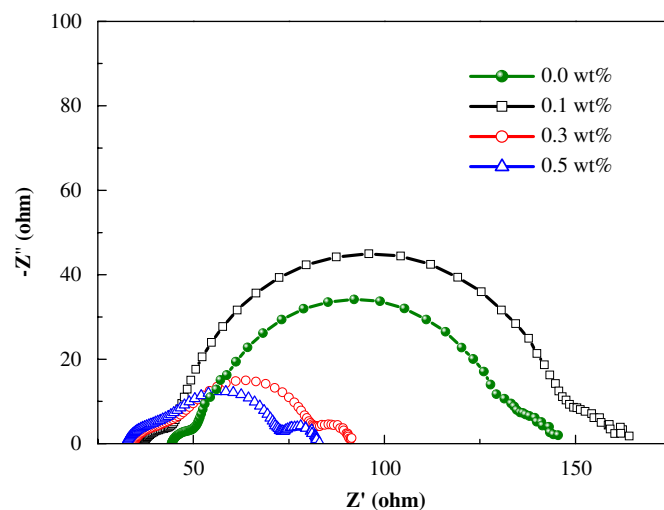


Fig. 4. The EIS measurement of the DSSCs with various TiO_2 electrodes having various ratios of MWCNTs in the dark and applied -0.8 V .

in the TiO_2 film were determined to be 89, 114, 35, and 30Ω , respectively. The significantly high R_{rec} values suggest that charge recombination between injected electrons and electron acceptors in the redox electrolyte, I_3^- , was remarkably retarded.

Herein, the net current was largely dependent on the applied bias. The fitted data of the electron transport resistances and capacitances obtained from the Nyquist plots measured under different biases were obtained (data not shown), and the time constant can be calculated by Eq. (1)

$$\tau_n = R_{ct2} \times C_{\mu 2} \quad (1)$$

where R_{ct2} and $C_{\mu 2}$ are the charge transport resistance and the chemical capacitance at $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface, respectively.

It was found that at the ratio of 0.1 wt% had higher resistances than the pure one, indicating that DSSCs based on the TiO_2 electrode with 0.1 wt% MWCNT had less recombination and a higher open-circuit voltage (V_{oc}). The chemical capacitances for DSSCs with and without MWCNT increased with an increase in the bias. The time constants of electrons in the TiO_2 electrode increased with the forward bias, and it was also found to be higher at a ratio of 0.1 wt% as shown in Fig. 5, which revealed that devices containing the TiO_2

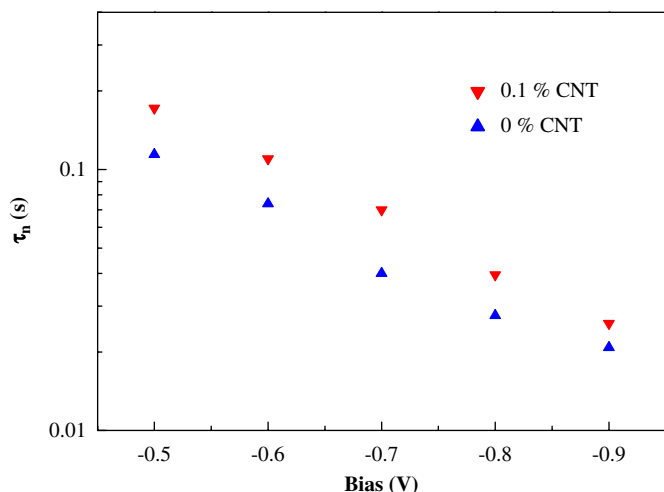


Fig. 5. The time constant of electron in TiO_2 electrode of the DSSCs based on different wt% of MWCNTs. The impedance measurement and the calculation are recorded in the dark and various applied biases.

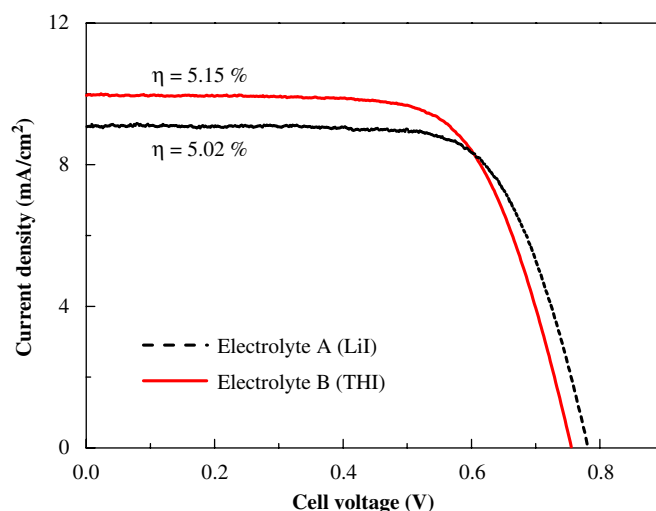


Fig. 7. The J - V characteristic curves of DSSCs based on 0.1 wt% MWCNT/ TiO_2 film with different electrolytes.

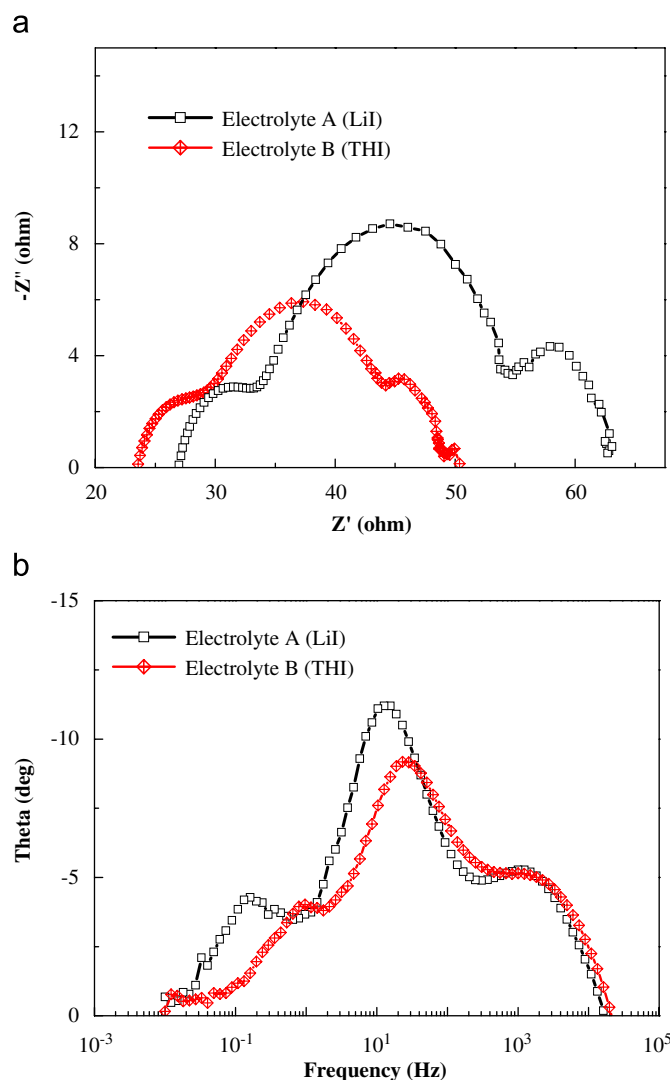


Fig. 6. EIS of the DSSCs based on 0.1 wt% MWCNT/ TiO_2 film with different electrolytes measured at -0.8 V, 100 mW/cm^2 . (a) Nyquist plot and (b) Bode phase plot.

electrode with 0.1 wt% MWCNT had a larger time constant due to the slower recapture of conduction-band electrons by I_3^- . This result is consistent with the previous argument.

Finally, in order to understand the effect of different iodides, electrolytes with and without Li^+ were also studied based on the TiO_2 electrode containing 0.1 wt% of MWCNT. Herein, LiI was replaced by THI, and the effect of THI on the DSSC performance had previously been studied in our laboratory [30]. The electrolyte containing LiI was named “electrolyte A” and the one with THI, “electrolyte B”. In the Nyquist plot, the DSSC containing electrolyte B had a smaller R_{ct2} than electrolyte A, but in the Bode plot, the characteristic frequency peak shifted to a high frequency when electrolyte B was used (Fig. 6). This observation suggests that more electrons were injected in the TiO_2 electrode, but the electron recombination proceeded more easily in electrolyte B than electrolyte A. The J - V characteristics of the DSSCs based on those electrolytes are shown in Fig. 7. It was found that the J_{SC} was 9.96 mA/cm^2 , V_{OC} was 0.756 V , η was 5.15% , and FF was 0.683 , using electrolyte B. Although the value of V_{OC} decreased a little to 0.756 V , the J_{SC} increased from 9.08 to 9.96 mA/cm^2 , and the DSSC showed a better cell performance of 5.15% .

4. Conclusions

DSSCs incorporated with TiO_2 porous films prepared at a low temperature (150°C) along with MWCNT containing two different electrolytes (LiI and THI) were investigated. The charge transport resistance at the $\text{TiO}_2/\text{dye}/\text{electrolyte}$ interface (R_{ct2}) increased as a function of the MWCNT from 0.1 to 0.5 wt%, due to a decrease in the surface area and less dye adsorption. With 0.1 wt% MWCNT/ TiO_2 , the DSSC had the highest cell performance and the longest electron lifetime in the TiO_2 electrode. Finally, using THI instead of LiI in the electrolyte with a TiO_2 electrode containing 0.1 wt% MWCNT, it was found that the J_{SC} increased, while the V_{OC} decreased and η reached 5.15% . This result suggests that more electrons were injected in the TiO_2 electrode and the electron recombination reaction was faster in the DSSC with THI than that with LiI.

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