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Effects of Multi-walled Carbon Nanotube Incorporation in ZnO Photoelectrode on the Efficiency of Dye-Sensitized Solar Cells

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) are one-dimensional nanostructured materials with many interesting properties such as high thermal and electrical conductivities. Our groups have recently demonstrated that the presence of MWCNT conductive scaffolds in a titanium dioxide-based photoelectrochemical cell can boost the photoconversion efficiency by a factor of more than 1.3. Here, we report the effects of the incorporation of MWCNTs into the ZnO active layer on the photocurrent-voltage (*J-V*) characteristics of dye-sensitized solar cells (DSSCs). Compared to the conventional ZnO electrode, the composite film containing 0.05 wt.% MWCNTs increased the short-circuit photocurrent (J_{sc}), consequently enhanced the energy conversion efficiency (η) by a factor of approximately 1.42. The enhancement of the solar energy conversion may be attributed to an increase of the electrical conductivity of ZnO film containing MWCNTs electrode.

Key words: dye-sensitized solar cells, carbon nanotube, front electrode, electrochemical impedance spectroscopy.

INTRODUCTION

Photovoltaic devices provide clean energy that is able to reduce global dependency on conventional energy sources. Dye-sensitized photo electrochemical cells are a promising low-cost solar energy conversion device, which has been intensively investigated. Typically, nanocrystalline TiO_2 has been used as a photo-anode material in the dye-sensitized solar cell (DSSCs) since the first demonstration by O'Regan and Grätzel (O'Regan and Grätzel, 1991; Nazeerudin *et al*., 1993). Alternative wide band gap metal oxide semiconductors such as ZnO and Nb_2O_5 prepared as porous electrodes in the same manner have also exhibited decent performance (Sayama *et al*.,1998; Tennakone *et al*., 2001). ZnO is a promising alternative material toTiO_2 because of the higher electronic mobility than the former, with similar energy levels of the conduction band. (Bauer *et al*., 2001) Recently, many research groups have attempted to increase the light-to-energy conversion efficiencies of the dye-sensitized ZnO solar cells (Gerischer and Tributsch, 1969; Matsumura *et al*., 1980; Rensmo *et al*., 1997). To gain a high efficiency DSSC, the photoanode must provide a large dye-adsorbing surface area and high photo-induced

electron transportation with low recombination (Baxter and Aydil, 2005; Law *et al*., 2005; Paulose *et al*., 2006). The potentials of the DSSCs depend on the properties of the photoanode. The electron conductivity can be improved by decreasing the thickness of the semiconductor films. ZnO photoanodes fabricated by a chemical deposition method at a thickness of 4 μm have been demonstrated to exhibit an overall photoconversion efficiency of 3.3% (Kakiuchi *et al*., 2008). Carbon nanotubes have been reported as a composite material that can increase the performance of photoelectrochemical cells (Jang *et al*., 2004; Kim *et al*., 2006). We have recently demonstrated that the addition of multi-walled carbon nanotubes (MWCNTs) to the TiO_2 photoelectrode decreases the charge transfer resistance of the TiO_2 electrode, consequently enhances the power conversion efficiency of DSSCs (Sawatsuk *et al*., Accepted).

Here, ZnO-MWCNTs electrode were prepared by direct-mixing and then screen-printing techniques. The effect of MWCNTs on the properties of ZnO films for the dye-sensitized solar cell application was investigated by means of scanning electron microscopy (SEM), UV-Vis spectroscopy, electrochemical impedance spectroscopy (EIS), and transient photocurrent measurements.

METHODOLOGY

Materials

The multi-walled carbon nanotubes (MWCNTs, Bayers Company) were used without further purification. Zinc oxide nanoparticle (<100 nm) and ethyl cellulose (EC) were purchased from Sigma Aldrich. Terpineol was purchased from Fluka. The commercial ruthenium dye (N719) was purchased from Dyesol Ltd. (Australia). Fluorine-doped SnO_2 glass substrates (FTO, sheet resistance: 10Ω/square, Bangkok Solar Cell Ltd., Thailand) were used as transparent conductive oxide (TCO) electrodes.

Preparation of ZnO-MWCNTs front electrode

The ZnO-MWCNTs composited were prepared by dispersing ZnO nanopowder, MWCNTs (0-10 %wt.) and ethyl cellulose in terpineol using ultrasonication for 1 hour. The mixture was vigorously stirred, heated at 80 ^{o}C for 1 hour and then screen-printed on FTO glass substrates with an active area 0.36 cm^2. The ZnO-MWCNTs films were annealed at 450 ^{o}C for 1 hour.

Fabrication of DSSCs

The annealed ZnO-MWCNTs film were soaked in an ethanol solution of $Ru(II)L_2(NCS)$:2TBA (L = 2,2′-bipyridyl-4,4′-dicarboxylate, TBA = tetrabutyl-ammonium). The ZnO-MWCNTs composited electrode and conventional Pt electrodes were attached face-to-face, then filled with a liquid electrolyte containing 0.05 M I_2, 0.1 M LiI, 0.4 M *tert*-butylpyridine (TBP) and 1 M 1-propyl-3-methylimidazolium iodide (PMImI) in acetonitrile solution.

Characterization

The surface morphology and the optical properties were investigated by a scanning electron microscopy (HITASHI, S-3400N) and UV-Vis spectrometer (Perkin Elmer Lambda 650). In addition, the electrochemical impedance analyses of the entire fabricated DSSCs were investigated using the potentiostat/galvanostat (Eco Chemie Autolab PGSTAT302 with a Frequency Response Analyzer (FRA2) module). The spectra were recorded over a frequency range of 1 MHz to 0.1 Hz with an ac amplitude of 10 mV under the white light irradiation. The measurements were carried out after the open circuit voltage was stabilized. The power conversion efficiency of DSSCs was measured from the photocurrent-voltage characteristics with a transient photocurrent under AM 1.5 irradiation (100 mW/cm^2).

RESULTS AND DISCUSSION

ZnO-MWCNT films coated on the TCO glass were used as the DSSC photoanode. From the previous investigation with the TiO_2 system, the addition of highly conductive MWCNT is expected to lead to an enhancement of the electron transport in the semiconductor films, a reduction of charge transfer resistance of the electrodes and an improvement of the conversion efficiency. In this study, the ratio of MWCNTs with respect to ZnO nanoparticles was optimized.

SEM images of the ZnO electrodes containing 0 and 0.05 wt.% MWCNTs have revealed a porous surface with approximately 100 nm spherical ZnO particles (Figure 1(a) and (b), respectively). At the MWCNTs concentration of 1.00 wt.% or higher, SEM images (Figure 1(c) and (d)) have suggested that the segregated tubular structure of MWCNTs may result in agglomerated ZnO particles. Consequently, an increase of the number of cracks and a decrease of necking structures in the porous ZnO electrode surface have been observed, leading to a reduction in the overall surface area of the electrode films.

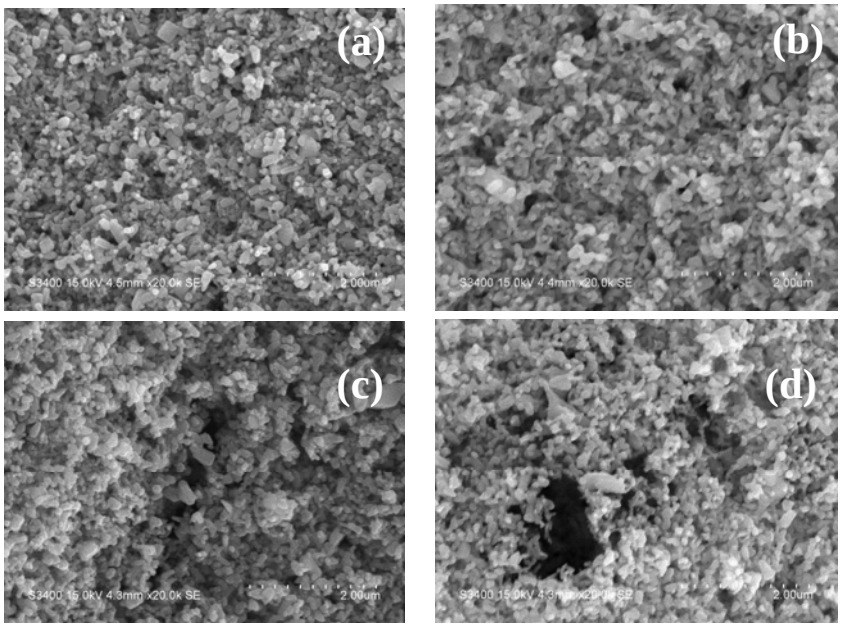

Figure 1 SEM images of (a) bare ZnO film, (b) 0.05 wt.% MWCNTs, (c) 1.0 wt.% MWCNTs and (d) 10.0 wt.% MWCNTs

Optical absorption measurements of the ZnO-MWCNT films on the conductive substrates have revealed that the presence of MWCNTs led an increase in the absorption of the metal oxide films (Figure 2). The more MWCNTs in the composite films, the lower the transparency of the semiconductive electrodes.

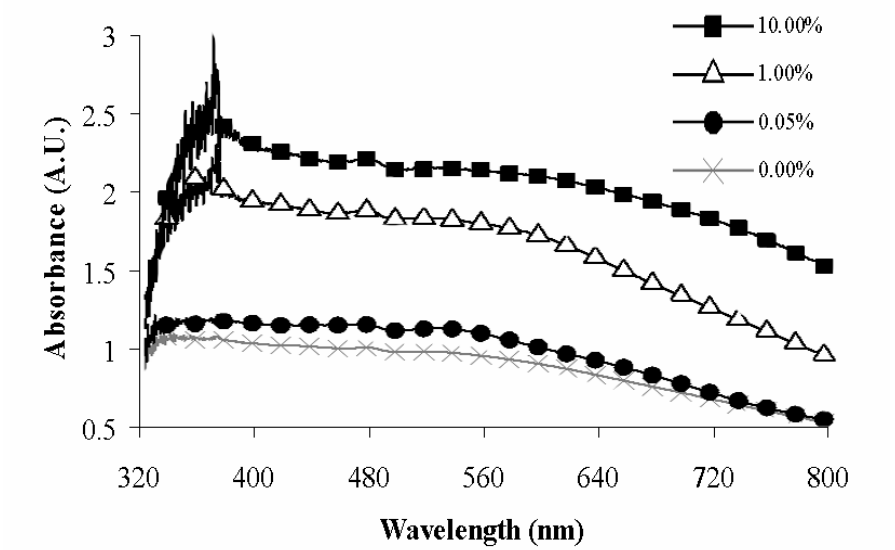

Figure 2 Optical absorption spectra of ZnO-MWCNTs electrode at different MWCNTs loadings.

The electrochemical impedance spectroscopy (EIS) of the entire fabricated cells has been investigated to correlate the device structure with an equivalent circuit model, and to gain understandings of the kinetics of electrochemical processes (Bard and Faulkner, 2001; Wang *et al*., 2005). The EIS analysis of the ZnO DSSCs containing various amounts of MWCNTs is shown in Figure 3. The Nyquist diagrams consist of three semi-circles, which represent the redox reaction at the platinum counter electrode, the electron transfer at the ZnO|dye|electrolyte interface and the carrier transport by ions in the electrolyte in the high, medium and low frequency range. The impedance in the medium frequency range of the fabricated cell containing 0.05wt.% MWCNTs in the ZnO film is smaller than that of the cell without MWCNTs, resulting in the lowest charge transfer resistance at the electrode interface. The decrease of the charge transfer resistance of the composite film suggests that the short-circuit photocurrent (J_{sc}) of the fabricated cell should also be improved, leading to a higher performance of the photovoltaic device. The charge transfer resistance obviously increases as a function of the MWCNTs when the content of the conductive carbon materials is greater than 1 wt.%. The lower conductivity may result from the decrease in the surface area and the necking features of the composited films.

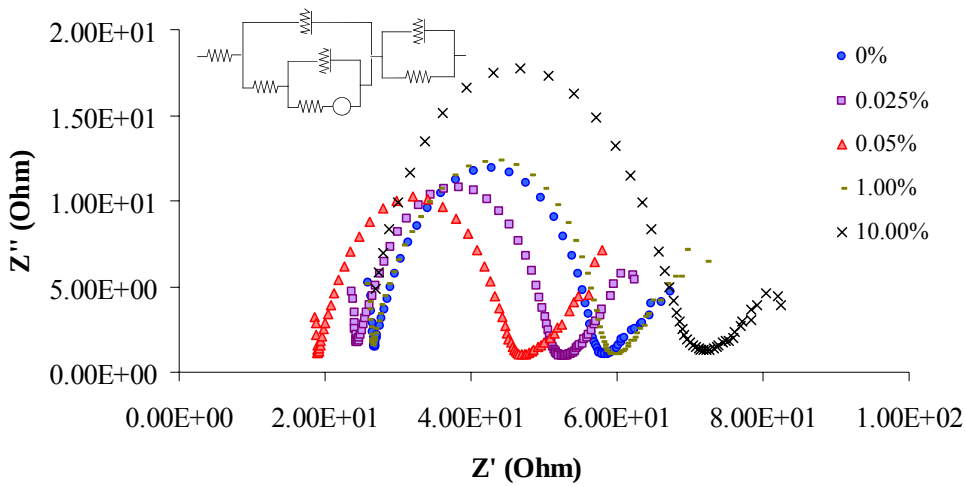

Figure 3 Nyquist plots of DSSCs with ZnO-MWCNTs electrode at different MWCNTs loadings. In set: the equivalent circuit model of DSSCs based ZnO-MWCNTs electrodes.

The *J-V* characteristics of the DSSCs based ZnO-MWCNTs front electrode under the AM1.5 illumination standard with an active area of 0.36 cm^2 are shown in Figure 4 and summarized in Table 1. The open-circuit voltage (V_{oc}) and the fill factor (*FF*) remain nearly the same for all MWCNTs loadings, except for those at the 10 wt.%. The composite film containing 0.05wt% MWCNTs shows an improvement of short-circuit photocurrent (J_{sc}) by a factor of 1.32, consequently an enhancement of the overall energy conversion efficiency (η) by a factor of

approximately 1.42. The *J-V* results of the DSSCs can be related to the electrical and optical properties of the front electrode, as discussed in the electrochemical impedance and optical absorption results. The addition of MWCNTs in the ZnO electrode initially enhances the short-circuit currents and the efficiency at low MWCNT contents. However, above the optimum MWCNT content at 0.05 wt.%, the DSSC performance diminishes owing to both the loss of optical transparency and the decrease in the surface area of the ZnO composite films.

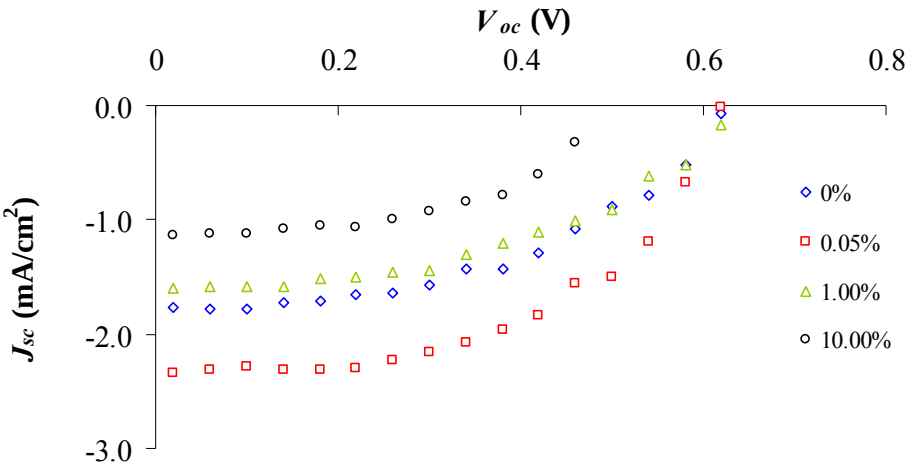

Figure 4 *J-V* characteristics of the ZnO-MWCNTs front electrode of the DSSCs

Table 1 *J-V* characteristics of ZnO-MWCNTs front electrode of the DSSCs

MWCNTs (Wt.%)	*J-V* characters			
	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
0.000	0.63	1.77	0.49	0.54
0.025	0.62	2.07	0.48	0.61
0.050	0.62	2.33	0.53	0.77
0.100	0.62	2.03	0.51	0.65
0.500	0.63	1.79	0.51	0.57
1.000	0.63	1.61	0.46	0.47
10.000	0.49	1.15	0.53	0.30

CONCLUSION

In summary, this study has demonstrated the improvement of the energy conversion efficiency of DSSCs by the incorporation of MWCNTs in the ZnO active layer using a simple direct mixing method. SEM images have revealed the segregation and agglomeration of ZnO on the conductive substrate. The absorption measurements of the composite films suggest that an increase in MWCNTs loading leads to a decrease in optical transparency. EIS analysis have demonstrated that ZnO film containing 0.05wt.% MWCNTs has the lowest charge transfer resistance at the electrode-electrolyte interface. The transient photocurrent measurements were performed under the AM 1.5 illumination standard with an active area of 0.36 cm^2. In comparison with the conventional ZnO film, the 0.05 wt.% MWCNTs-incorporated ZnO films have shown an increase in short-circuit photocurrent (J_{sc}) by a factor of approximately 1.32, resulted in an increase in overall energy conversion efficiency (η) by a factor of up to 1.42. The *J-V* characteristics results can be explained by the surface, optical and electrochemical information. This investigation, together with our previous TiO_2 study, confirms that a direct mixing method for the fabrication of MWCNT composite DSSC electrodes is a simple, yet general and effective to improve the performance of the conventional DSSCs.

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