

Incorporation of Plasma Modified Multi-Walled Carbon Nanotubes into TiO₂ Photoanode for Dye-Sensitized Solar Cells (DSSC)

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ABSTRACT

Dye-sensitized solar cells (DSSC) are fabricated with photoanode comprises of nanocomposite material of TiO₂ and multi-walled carbon nanotubes (MWNT) treated *in situ* by plasma and subsequent functionalization by grafting of maleic anhydride (MA). The functionalized MWNTs enable the nanotubes to disperse homogeneously among the TiO₂ nanoparticles and become an integral part of the nanocomposites. As a result, MWNTs-MA/TiO₂ nanocomposites presented obvious improvements in photocurrent and solar power conversion efficiency as the CNT provides efficient electron transfer through the film as well as the charge collection at the surface of counter electrode due to its excellent conductivity. At an optimum incorporation of 0.075wt.% MWNTs into the working electrode, the photo conversion efficiency of the DSSC was improved by more than 30%.

Keywords: TiO₂, MWNTs, DSSC, nanocomposites

1 INTRODUCTION

Numerous studies related to the development of dye-sensitized solar cells (DSSC) have emerged ever since it was first reported by Grätzel in 1991 [1]. Meanwhile, carbon nanotubes (CNTs) have attracted massive amount of attention in various applications due to their unique properties, inclusive of excellent electrochemical stability, low resistivity and high surface area [2-5]. Efforts have been made to incorporate CNTs into component of DSSCs, for example, the working and counter electrode, in order to improve the cell performance. The presence of CNTs in TiO₂ matrix [6] or ionic liquid electrolyte [7] shows limited improvement in the power conversion efficiency. The underlying problems can be attributed to the difficulty to obtain homogeneously dispersed CNT nanocomposites arising from the non-reactive nature of the CNT surface and the unavoidable bundle formation due to van der Waals attraction during synthesis [8-10]. Most published works have focused on chemical modification of the CNT to improve dispersion through functionalization, oxidization, melt mixing, and compounding [11-13]. In order to improve the dispersion of CNT in titania nanoparticles, we use "grafting to" method or functionalization of carbon nanotubes by making use of plasma [14-17]. Here we report a simple method to improve the DSSCs performance by the incorporation of multi-walled carbon nanotubes (MWNTs), of which the surface was grafted with maleic acid (MA) via plasma treatment, into the front electrode using a direct mixing method. The morphology of TiO₂-MWNTs film was observed by Scanning Electron

Microscope (SEM) and Transmission Electron Microscope (TEM). The presence of MWNTs-MA into the film was confirmed by the Raman Spectroscopy and the photochemical performance of the solar cells fabricated with these nanocomposites was examined.

2 EXPERIMENTAL

2.1 Materials

Multi-walled carbon nanotubes (MWNTs) used in this work were purchased from the Industrial Technology Research Institute in Taiwan and were synthesized by ethylene CVD using Al₂O₃ supported Fe₂O₃ catalysts (purity >95%). Prior to plasma modification, the MWNTs were purified by sonicating in ethanol for 1 hr to remove the catalysts and then diluting with deionized water by filtration through a filter paper. Maleic anhydride (MA) (Aldrich Co.), ethanol (99.99%) (J.T. Baker) and the TiO₂ powder (P25 degussa) were used as received.

2.2 Preparation of MWNTs Grafted Maleic Anhydride (MWNTs-MA) by Plasma Treatment.

The plasma treatment (Ar, 50W, 13.56MHz, 10min) was carried out in a stainless steel reactor (6x10³ cm³) at a vacuum level of about 10⁻⁴ torr. The electrodes were made of circular Cu plates and kept at a distance of 3cm. The MWNTs were spread evenly inside the chamber. After the plasma treatment, a large number of radicals were generated on the surface of the MWNTs, and the maleic anhydride (MA) with a concentration of 0.1 M dissolved in dimethylacetamide (DMAC) was immediately injected into the reactor to graft onto the MWNTs at room temperature for 3 h. After the grafting polymerization, the MWNTs grafted maleic anhydride, MWNTs-MA, was washed by DMAC repeatedly and subsequently separated by filtration. The sediments were dried in a vacuum oven at 80 °C overnight to get rid of the residual solvent. The resulting products obtained were the functionalized MWNTs, or known as MWNTs-MA for abbreviation.

2.3 Preparation of the MWNTs-MA/TiO₂ Nanocomposites

The MWNTs-MA was immersed in 0.1N HNO₃ and ultrasonicated for 3 hours to achieve maximum dispersion. TiO₂ powder was added into the solution, and the mixture was stirred vigorously for 3 h before adding the surfactant

to form the paste. The paste of MWNTs-MA/TiO₂ was now ready for subsequent DSSC fabrication.

2.4 DSSC Fabrication

The MWNTs-MA/TiO₂ composite films were obtained after annealed at 350°C for 0.5 h in air. When cooled to 100°C, the MWNTs-MA/TiO₂ films were immediately soaked in an ethanol solution of ruthenium complex dye, N3 (cis-di(thiocyanate)- bis(2,2'-bipyridyl, -4,4'-dicarboxylate) ruthenium (II); ruthenium 535, Solaronix SA, Switzerland). Pt-coated FTO glass substrates were used as the counter electrode. The acetonitrile solution of LiI, I₂, 1-methyl-3-propyl-imidazolium iodide, and 4-tert-butylpyridine was used as an electrolyte. In the DSSC photocurrent performance test, a 100W/cm² Xe lamp (AM1.5) was served as a light source in conjunction with a potentiostat/galvanostat (PGSTAT 30, Autolab, EcoChemie, Netherlands). FT-IR spectra were recorded at room temperature in the range 700 – 4000 cm⁻¹ using a Bio-Rad FT-IR system coupled with a computer.

3 RESULTS AND DISCUSSION

Fourier transform infrared (FT-IR) was used to characterize the functional groups on the surface of the MWNTs. Figure 1 shows the FTIR of MWNTs treated with and without the plasma treatment followed by MA grafting. Characteristic bands at 1719 and 1735cm⁻¹ that represents the C=O and O-C=O groups from MA can be clearly seen from the one of MWNTs- MA. This indicates that the maleic acid has been successfully grafted onto MWNTs after the Ar plasma treatment that created lot of free radicals inside the chamber. The carboxyl groups attached on the tube wall of the MWNTs grafted with MA (MWNTs-MA) enable the bonding with Ti when mixed into TiO₂ matrix through the O-C=O opening and dehydration reactions among the groups. The electrodes were fabricated with nanocomposite obtained by a direct mixing method of MWNTs-MA into TiO₂ (Degussa P25) with aid of organic surfactants (Triton X-100)

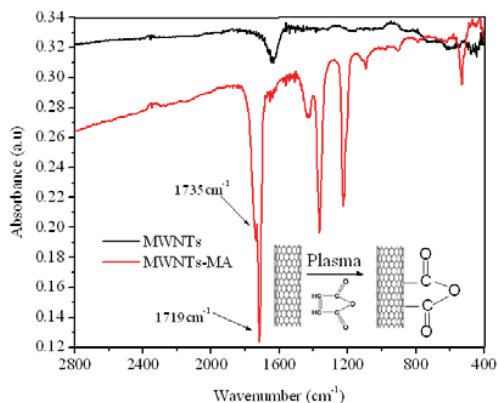


Figure 1: FT-IR for MWNTs before and after the plasma treatment followed by grafting with MA (maleic anhydride)

Figure 2 illustrates the snapshot of the MWNTs-MA nanocomposites prepared from direct blending method via

maximum ultrasonication and mechanical mixing. Without the CNTs addition, the nanocomposite appear as white color, which is solely the nanocrystalline titania. As the amount of CNTs added increased, the color of the mixture solution approaches greysi color, which was primarily attributed to the all-black CNTs. It can also been seen that the CNTs were well mixed with the titania, wherein no aggregation is observed.



Figure 2: Snapshot of nanocomposite paste of MWNTs-MA/TiO₂ of various CNTs weight percent

Figure 3 displays the SEM and TEM images of the MWNTs-MA/TiO₂. Both SEM and TEM images illustrate the well dispersion of the MWNTs-MA among the nanocrystals of TiO₂. Since the amount added into the TiO₂ matrix was relatively small, CNTs could not be identified from the XRD data obtained, as shown in Figure 4(a). The TiO₂ after annealed showed mainly the anatase phase. Therefore, Raman spectroscopy was used and it confirmed the presence of TiO₂ and CNTs in the prepared front electrodes. Three Raman peaks at approximately 395, 518, and 642 cm⁻¹ indicate the anatase form of TiO₂, while the other two peaks at approximately 1348 and 1624 cm⁻¹ represent the D and G bands of MWNTs, respectively (Figure 4 (b)).

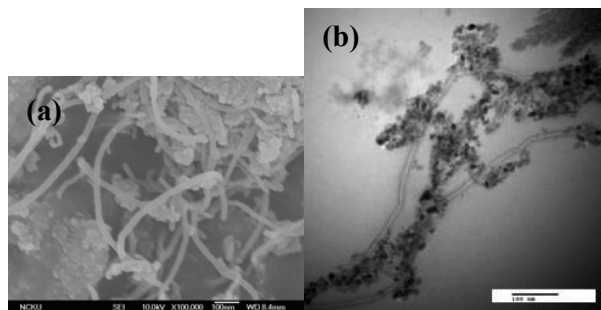


Figure 3: (a) SEM, and (b) TEM images of the nanocomposite material of functionalized multi-walled nanotubes (MWNTs-MA) and TiO₂

J-V characteristics of DSSCs fabricated with MWNTs-MA electrodes were exhibited in Table 1. The photovoltaic performance was measured under the AM 1.5 illumination standard with an active area of 0.25 cm². The solar cell based on 0.075 wt.% MWNTs-MA in TiO₂ working electrode displayed the greatest light harvesting ability with a fill factor (FF) of 61%, short-circuit current (*J*_{sc}) of 14.7 mA/cm², open-circuit voltage (*V*_{oc}) of 0.77 V, and an overall light to electricity conversion efficiency 6.9%. Open-circuit voltage and fill factor remain nearly the same for all conductive CNTs concentration. Compared to a cell fabricated with conventional TiO₂ film, TiO₂ electrode incorporated with 0.075 wt.% MWNTs-MA shows an enhancement of short-circuit photocurrent and overall conversion efficiency of 25% and 32%, respectively.

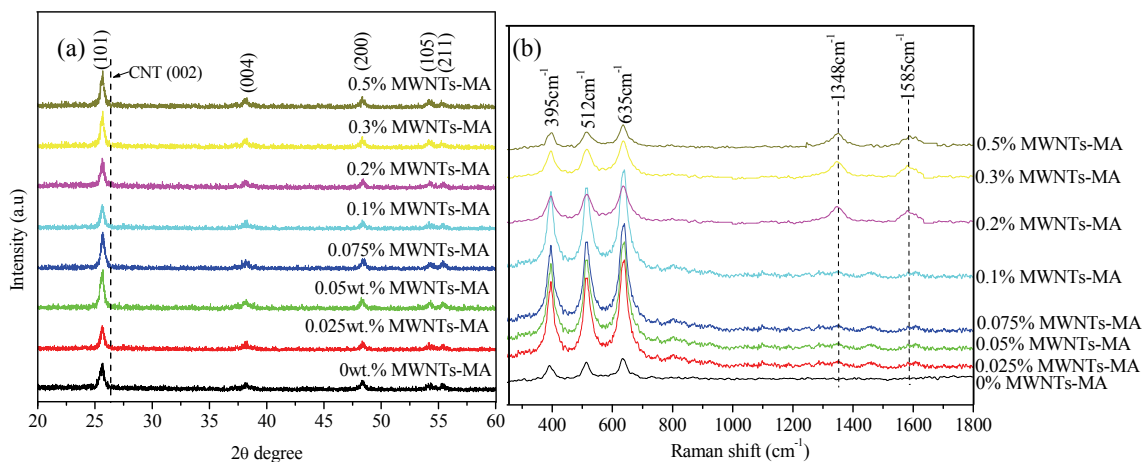


Figure 4: (a) XRD pattern, and (b) Raman spectra of TiO₂ and MWNTs-MA/TiO₂ nanocomposite

Weight percent of MWNTs-MA in TiO ₂ (wt.%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	Efficiency, η (%)
0.000	0.77	11.8	0.58	5.26
0.025	0.76	11.3	0.57	5.31
0.050	0.81	14.5	0.58	6.82
0.075	0.77	14.7	0.61	6.93
0.100	0.76	13.1	0.66	6.52
0.200	0.80	10.8	0.70	6.02
0.300	0.79	11.0	0.60	5.17
0.500	0.80	10.4	0.63	5.28

Table 1: *J-V* characteristics of the MWNTs-MA/TiO₂ photoanode of the DSSCs. V_{oc}, J_{sc} and FF are the open circuit voltage, the short-circuit current, and the fill-factor of the DSSCs, respectively.

Further increase in the amount of MWNTs-MA resulted in a gradual decrease, owing to and losses in optical transparency, decrease of electron injection to the conduction band of TiO₂ particles since the CNTs in black absorb some of the light illuminated. As a consequence, reduced of short circuit current, followed by degradation of the DSSCs performance was observed.

4 CONCLUSION

Improvement of the power conversion efficiency of DSSCs was demonstrated by the incorporation of plasma-modified MWNTs in the TiO₂ photoanode using a direct mixing method. At the best conditions, the MWNTs-MA/TiO₂ DSSCs attained in the short-circuit current density of 14.7 mA/cm², leading to the overall power conversion efficiency of 6.93% under the AM 1.5 illumination standard with an active area of 0.25 cm². An excess amount of MWNTs-MA in the electrode led to degradation of the DSSC performance due to optical transparency losses as well as agglomeration of the CNTs. The plasma modification process that is more environmental-friendly can serve as an alternative to replace the conventional wet-chemical

method that might alter their unique characteristics by shortening and damaging the tubes. Future work should focus on further optimization of the MWNT DSSC fabrication processes and detailed studies of the mechanisms for the solar power conversion efficiency enhancement.

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