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Preparation of Zinc Oxide/Titanium Dioxide and Grafted Carbon Nanotube for Dye-Sensitized Solar Cell Performance

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Abstract

Zinc oxide/titanium dioxide (ZnO/TiO_2) nanoparticles and grafted carbon nanotubes (grafted-CNTs) were prepared to fabricate photoelectrode for enhancing the performance of dye-sensitized solar cells (DSSCs). ZnO/TiO_2 nanocomposites were prepared by impregnation method. Grafted-CNTs were prepared by grafting copolymerization of aniline and vinyl acetate. The ZnO/TiO_2 nanoparticles and the grafted-CNTs were characterized by FE-SEM, EDX and TEM. Then ZnO/TiO_2 nanoparticles and grafted-CNTs were assembled with N719 dye as the photoelectrode for light absorption test using UV-vis spectroscopy analyses. The results showed that the prepared photoelectrode from ZnO/TiO_2 and grafted-CNTs had an enhancement of light absorption referring to the efficiency of DSSC.

Keywords: ZnO/TiO_2 nanocomposites, Grafted carbon nanotube, Photoelectrode, Dye-sensitized solar cell

Introduction

With the growing demand for clean and renewable energy, the generation of electricity from solar conversion by photovoltaic devices has attracted much attention [1]. Among various photovoltaic devices, dye-sensitized solar cells (DSSCs) have been investigated extensively because of their relatively high power conversion efficiency, ease of fabrication, and low production costs [1]. In a typical DSSC, fluorine-doped tin oxide (FTO) glass substrates are coated with metal oxide semiconductor material, commonly using TiO_2, which is sensitized with commercial available N719 dye (cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II)) and then it is sandwiched with counter electrode (CE) material coated FTO after that the redox electrolyte (I^-/I_3^- and Co^{2+}/Co^{3+}) can be injected through the predrilled holes [2]. Power conversion efficiency of DSSC fabricated by Gratzel in 1991 was reported as 7.9% and it was increased to 13% in 2014 which was achieved by the same scientist [2]. Many studies on the TiO_2 electrode have been performed to hasten the electron transport in the films and to achieve high-efficiency current collection by the conducting substrate. Typical examples were coating the TiO_2 nanocrystal with a thin layer of another semiconductor oxide, such as zinc oxide (ZnO), niobium oxide (Nb_2O_5), aluminum oxide (Al_2O_3) and so on [3], as insulating layer could inhibit the recombination reactions. Other studies focused on utilizing TiO_2 nanostructures, such as CNTs [3], which were expected to lead to faster electron transport.

Carbon nanotube (CNT) is considered for use as the DSSC electrode because of its unique properties such as good catalytic activity good conductivity, high aspect ratio, stability in ambient conditions [4]. To modify the surface behavior of CNTs for reducing particular aggregation, their surfaces must be needed to improve the compatibility between the interface of CNTs and the main matrix [5]. Additionally in this study CNTs were modified on their surface with grafting copolymerization [6] for improving the electrical conductivity and water dispersion in order to dye-sensitized solar cell (DSSC) application.

On the other hand, ZnO is given attention due to its excellent catalytic activity, diverse morphologies, corrosive resistant and large surface area. Its wider band gap (3.37 eV) makes it transparent in the electromagnetic visible spectrum [7-11]. It is low-cost and bears high electron mobility compared to the TiO_2 based DSSCs. Due to its large surface area, ZnO favours the adsorption of dye molecules. This metal oxide shows a good possibility for application in DSSCs [12].

In the present study, CNTs were modified by grafting polymerization with copolymer of polyaniline and poly (vinyl acetate) for improving their electrical conductivity and water dispersion. After that the grafted CNTs were used to fabricate the photoanodes by mixing with ZnO/TiO_2 synthesized by impregnation method. Moreover, the absorbance of the prepared photoanodes for enhancement of DSSC performance was measured.

Materials and methods

Materials

Carbon nanotubes were purchased from Nano Generation (Thailand). Their dimeters were 27 nm diameter and greater than 10 µm length. Acrylic acid (AC) and vinyl acetate (VAc) used as monomer for copolymerization were purchased from Sigma Aldrich (America). Ammonium persulfate (APS) as an initiator was purchased from Ajax Finechem (Australia). Zinc nitrate hexahydrate ($Zn\ (NO_3)_2.6H_2O$) with 99.8% purity was purchased from Ajax Finechem (Australia). Anatase TiO_2 (98%) from Sigma Aldrich (America) was utilized as a support for synthesis of ZnO/TiO_2 composite. N719 dye was purchased from Solaronix (Switzerland). TEC8 FTO glass and polyethylene glycol were purchased from Sigma Aldrich (America). Triton X-100 was purchased from AppliChem Panreac (German). Other chemicals such as acetylacetone, ethanol and deionized water were also used in this study.

Grafted CNTs Preparation

CNTs were used to chemically modify their surface by grafting copolymerization of vinyl acetated and aniline with varying the monomer ratios at 0.4:1 and 1:1. The grafting copolymerization of CNTs was carried out at room temperature (25 ºC) for 4 hrs using APS as an initiator. After that the grated-CNTs were taken out and washed with distilled water several times. Lastly they were dried in the oven at 60 °C for 24 h.

ZnO/TiO_2 Preparation

Wet incipient wetness impregnation method was used to prepare ZnO/TiO_2 nanocomposites by varying ZnO loading at 30% and 50% on the surface of commercial anatase TiO_2 support. $Zn(NO_3)_2.6H_2O$ was weighted for 1.2 g (30% loading) and 2.0 g (50% loading) and then dissolved in 5 mL deionized water by sonication for 15 min at room temperature. Meanwhile, 4.0 g TiO_2 was dried at 180 °C for 1 h. The dried TiO_2 was further immersed into the ZnO solution (varying % loading) and mixed vigorously for 15 min to achieve homogenous absorption of ZnO over the surface of TiO_2. The ZnO/TiO_2 composites were aged at 110 °C for 24 h inside an oven. After that the synthesized ZnO/TiO_2 nanocomposites were calcined at 400 °C for 5 h.

Characterization

Surface morphology of all prepared nanoparticles was analyzed by field emission-scanning electron microscopy coupled with an energy dispersive X-ray (FESEM-EDX) JSM-7610F detector, and transmission electron microscopy (TEM) JEM-2100 Plus.

Photoanode Preparation and test

ZnO/TiO_2 nanoparticles and grafted-CNTs were used for photoelectrode preparation with other chemical as shown in Table 1. Both pastes of ZnO/TiO_2 in beaker and grafted-CNTs in vial were treated in an ultrasonic bath for 30 min. The pastes were then printed on the FTO coated glass and heated at 450 °C for 30 min. Photoanodes were then soaked in the dye solution (0.3 mM solution of N719 dye in ethanol) for 24 h. T80 UV/VIS spectrophotometer was used to measure the absorbance of the composite film of dye for photoanode proration.

Table 1 Chemical composition of photoelectrochemical composite paste.

Materials	Function	Amount
Semiconductor (TiO_2 and each ZnO-TiO_2)	-	1.5 g
Grafted-CNT	Conduction	0.075 g
Polyethylene glycol	Binder	1 ml
Acetylacetone	Surface modifier	50 µl
Triton X-100	Dispersant	50 µl

Results and discussion

Grafted carbon nanotube

The surface morphology of the bare CNTs and grafted-CNTs were obtained by Fe-SEM and TEM as shown in Figure 1 and 2 respectively. The results clearly showed the difference between the bare and grafted CNTs. The grafted-CNTs were coated by an ultrathin film of copolymer on the surface.

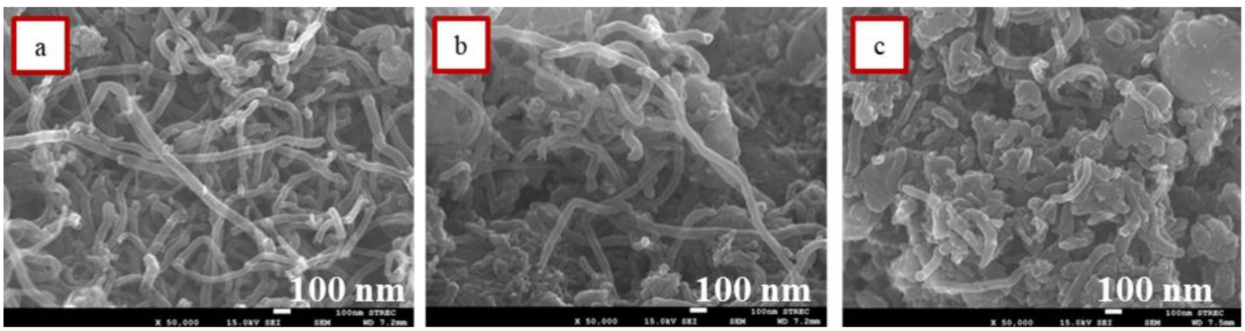


Figure 1 FE-SEM images (scale bar: 100 nm) of (a) bare CNTs and gratefed-CNTs with poly(vinyl acetated):polyaniline at (b) 0.4:1 and (c) 1:1 ratios

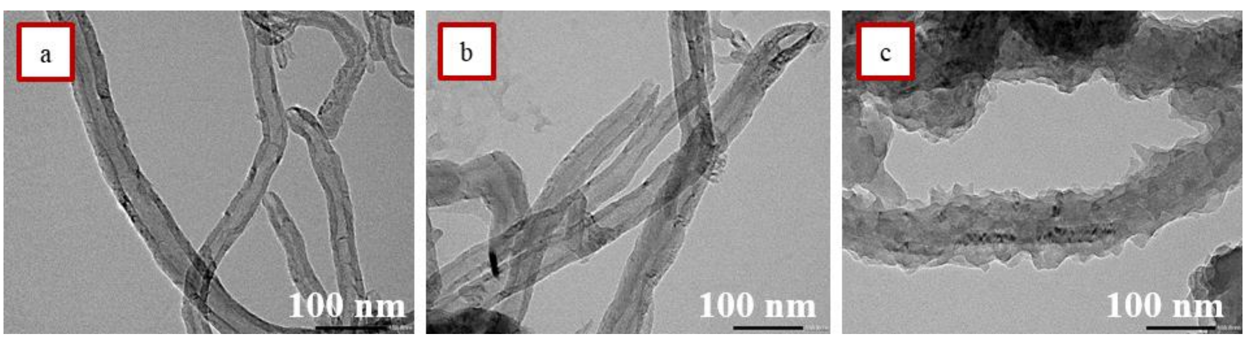
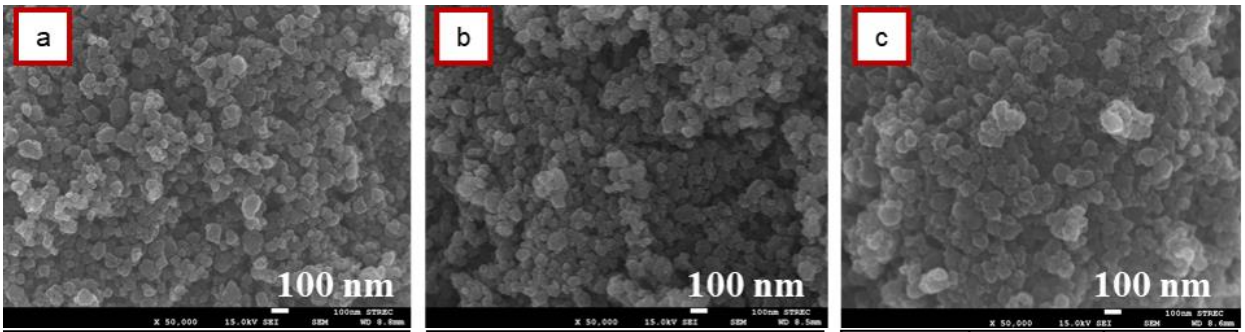


Figure 2 TEM images (scale bar: 100 nm) of (a) bare CNTs and gratefed-CNTs with poly(vinyl acetated):polyaniline at (b) 0.4:1 and (c) 1:1 ratios

The TEM image of the grafted-CNTs at 0.4:1 ratio of vinyl acetate and aniline in Fig 2(b) shows smoothly coated film on CNTs surface that was chosen to prepare the photoanode.

ZnO/TiO2 nanocomposites

The FE-SEM images with EDX analysis of calcined ZnO/TiO_2 nanocomposites at different ZnO loading are given in Fig 3. ZnO/TiO_2 images was evidently different from bare TiO_2 images. It also showed that the dispersion of ZnO was homogeneous over the surface of support for 50%ZnO in TiO_2. Image analysis clearly showed an increase in surface coverage of TiO_2 by ZnO on increasing the loading of ZnO. EDX analysis confirmed the presence of Zn over the surface of TiO_2.



Element	Weight%	Atomic%
O K	54.58	78.25
Ti K	45.42	21.75
Zn L	0.00	0.00
Totals	100.00	

Element	Weight%	Atomic%
O K	53.22	77.83
Ti K	41.55	20.29
Zn L	5.23	1.87
Totals	100.00	

Element	Weight%	Atomic%
O K	51.07	76.78
Ti K	38.81	19.49
Zn L	10.12	3.72
Totals	100.00	

Figure 3 FE-SEM images (scale bar: 100 nm) with EDX analysis of (a) bare TiO_2, (b) 30% ZnO/TiO_2 and (c) 50% ZnO/TiO_2

To clearly confirm the success of ZnO/TiO_2 nanocomposite synthesis, the mapping analysis was used as shown in Fig 4. Mapping images show the dispersion of different elements in nanocomposites. The mapping of each element in the nanocomposites was separately classified for easier observation of its dispersion. Fig4 (a) -the mapping of TiO_2-contains only elemental composition of Ti and O. For Fig4 (b) and (c) show the distribution ZnO in TiO_2 of ZnO/TiO_2 nanocomposites. The results show that when ZnO was added in TiO_2, the ZnO mappings of 50% ZnO addition in Fig4 c was significantly higher amount and greater dispersion than 30% ZnO addition in Fig4 b.

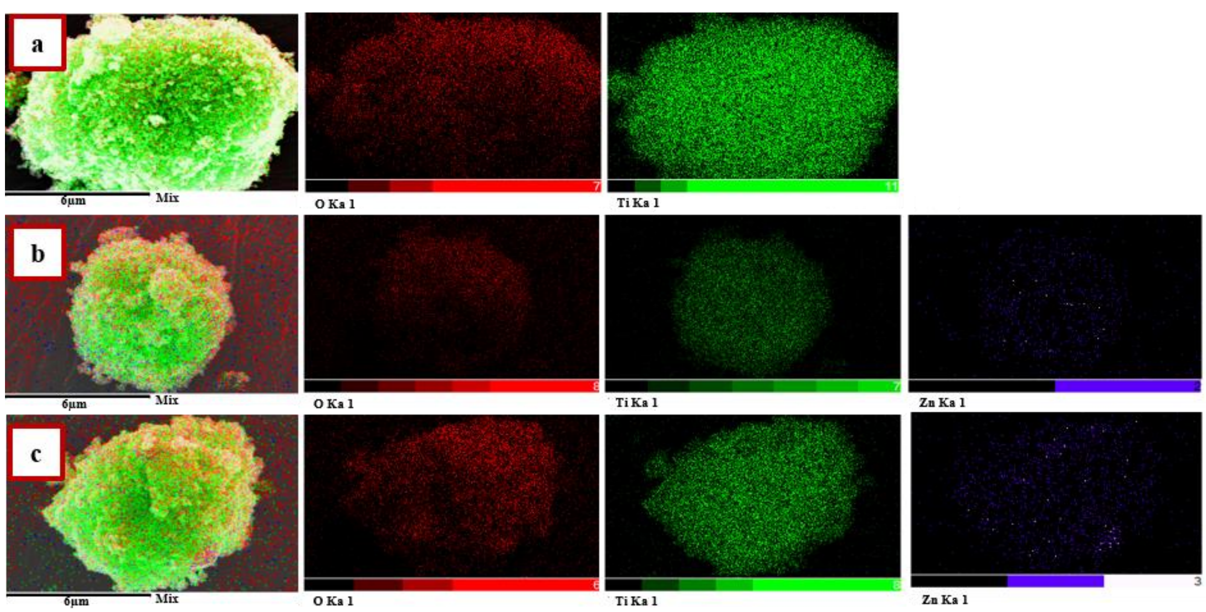


Figure 4 Mapping images of (a) bare TiO_2, (b) 30%ZnO/TiO_2 and (c) 50%ZnO/TiO_2

Photoanodes test

UV-Vis spectra of composite films consisting of dye adsorbed on TiO_2 or ZnO/TiO_2 are shown in Fig. 5. The results demonstrate that the absorbance of photoanode films was increased with carbon nanotube and ZnO addition in composite films. The increase in absorbance could be associated with the increase in the surface area of photoanode films owing to impregnation of ZnO. The absorbance of composite film increased in the order of 30%ZnO/TiO_2 with Grafted CNTs > Grafted CNTs > 50%ZnO/TiO_2 with Grafted CNTs > bare TiO_2. However, an increase in ZnO contents from an optimum level (>30%ZnO) could reduce the charge recombination resistance and electron life-time. It could be attributed to the formation of new defects at the interface between TiO_2 and ZnO (due to high contents of ZnO) that might reduce the fast electron transport and thus increase the recombination rate. ZnO incorporated with TiO_2 as a light scattering layer reflects the incident solar radiationto directly enhance the distance travel by incident light in the photoanode [13].

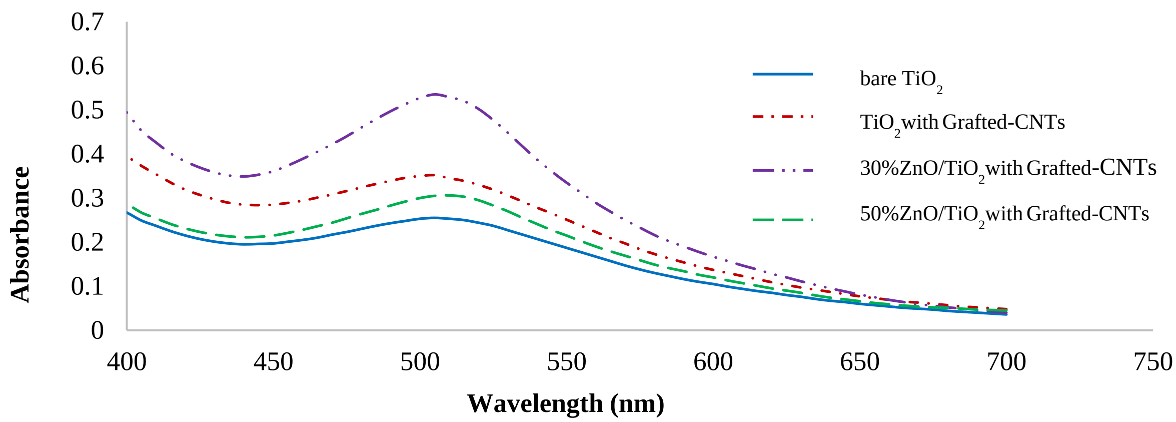


Figure 5 UV–vis absorption spectra of photoanodes.

Conclusion

CNTs were chemically modified by copolymer grafting of poly (vinyl acetated) and polyaniline. At 0.4:1 ratio was uniformly and smoothly coated of copolymer film. ZnO/TiO_2 nanocomposites were successfully synthesized by impregnation method. ZnO/TiO_2 and grafted CNTs added in the composite dye increased the light absorbance that could be employed as photoanodes for high performance of DSSC.

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