

Electrochemical Characterization of Tubular Structured PANI/Ni-TiO₂-based Photoanodes

S.N.F. Zainudin, H.Abdullah and A.A. Abdul Aziz

Abstract— Dye-sensitized solar cells (DSSC) offer a promising route for low-cost and transparent solar cells, flexible applications with automotive integrated electricity generation. In this study, PANI/Ni-TiO₂ hybrid nanocomposite based photoanodes were synthesized by using sol-gel chemical method to let the oxidative polymerization between polyaniline and Ni-doped TiO₂ nanoparticles. The effects of Ni²⁺ doping on the morphology, optical characterization, electrochemical behaviour and electrical conductivity of PANI/TiO₂ were investigated using field emission scanning electron microscopy (FESEM), UV-vis spectroscopy, electrochemical impedance spectroscopy (EIS) and photocurrent density-photovoltage (J-V) analysis. The FESEM images exhibits the modification of morphology from nanospherical structure into nanorod-like structure as more aggregation takes place with the addition of Ni²⁺ and TiO₂ nanoparticles on the surface of PANI. The UV-vis light absorption spectra of both PANI/TiO₂ and PANI/Ni0.4-TiO₂(0.6) hybrids revealed the higher light absorption peaks affected by the decreasing size of particles (2.75nm and 2.84nm), resulted with higher bandgap energies (4.37eV and 4.31eV, respectively). The maximum frequency of intermediate semicircles of EIS Nyquist curves for all synthesized hybrid nanomaterials are within range 0.599Hz to 1.501Hz, resulted with electron lifetime (τ) values ranged from 0.266ms to 0.106ms. Both PANI/TiO₂ and PANI/Ni0.4-TiO₂(0.6) hybrids achieved higher photoconversion efficiencies than other synthesized hybrid nanocomposite materials which at 1.28% and 2.07%, respectively.

Keywords—Dye-sensitized solar cells, EIS analysis, Polyaniline, Thin film.

I. INTRODUCTION

In contrast to the growing global energy demands, the decreasing reliability on fossil fuels can be replaced with other renewable energy. The solar energy is one of the renewable energies that became an alternative to the fossil fuels that dissipates carbon dioxide (CO₂), hence reduces global warming issues. Dye-sensitized solar cell (DSSC) is a type of solar cell that have been developed by Grätzel [1] in 1991 which a combination of nano-structured electron and dye-sensitizer for electron charge adsorption. DSSC have its advantages in research field due to low cost fabrication, high photocurrent efficiency (*PCE*) and environmental-friendly. Polymer / inorganic hybrid material has excellent electrical properties because of the direct interface reaction between polymer as donor with inorganic material as acceptor [2]. The employment of DSSC can be an alternative to the massive application of conventional silicon based solar cell, but the difference in energy exchange efficiency rate and solar cell lifetime have to

be considered. Usually, the effective lifetime of solar cell can up to 25 years. The biggest challenge is that the photocurrent efficiency of DSSC is much lower than conventional solar cell. In order to increase the *PCE*, suitable method needs to be utilized to enhance the capabilities and improves the DSSC components such as dye-sensitizer, photoanode, electrolyte, and counter electrode [3]. In addition, the electrocatalytic activity of the nanocomposite material can be improved from the aspect of electrical properties by increasing the specific surface area of the material, [4]. The doping addition to the nanocomposite material also increase the porosity and the morphology of specific surface area [5]. The conducting polymer (PANI) also shows higher electrical conductivity and excellent heat stability, however, the shortcoming in chemical solubility and mechanical properties of the conducting polymer have lessen the process ability (Deivanayaki & Selvan 2016). The studies conducted by [7] shows the result of the doping conducting polymer of PANI-Ni formed a complex polymer and increase the electrochemical activity. The comparison between electrical conductivity of PANI-Ni (0.22 S.cm⁻¹) and PANI (0.13 S.cm⁻¹) shows that Ni-doped increase the electrical conductivity of PANI. The proper amount of dopant Ni and TiO₂ could increase the conducting properties of PANI up to 10 S.cm⁻¹[8]. In the present work, we reported a novel fabrication of PANI/Ni-TiO₂ hybrid structure by sol-gel method, and employed as photoanode in dye-sensitized solar cells application. Titanium dioxide (TiO₂) was selected because of the matching conduction band to the lowest unoccupied molecular orbital of PANI which increase the electron mobility properties. The nickel doping also has been added to the PANI/TiO₂ hybrid material resulting a higher electrical conductivity. The electrochemical impedance analysis is utilized to further understand the electron transfer behaviour in PANI/Ni-TiO₂ hybrid structure.

II. METHODOLOGY

PANI/Ni-TiO₂ hybrid photoanodes were prepared by using sol-gel method. In this process, titanium (IV) tetra-isopropoxide, TTIP (Aldrich) and nickel-(II)-acetylacetone, Ni-acac (Merck) were used as the precursors. Isopropanol, IPA acts as the catalyst to prepare Ni-TiO₂ sols was added with deionized water, H₂O for the hydrolysis of TTIP and Ni-acac in the solution at 60°C for 5 hours. 0.05M aniline, 0.5ml HNO₃, and 30ml H₂O were used in vaporization and hydrolysis process which was stirred at 60°C for 5 hours to formed the PANI sols. Then, 0.301g (NH₄)₂S₂O₈ was dissolved in 30ml H₂O and 0.92ml HCl through hydrolysis reaction which was stirred at 60°C for 5

hours into the solution. All solutions that have been prepared separately were combined and continuously stirred at 30°C for 12 hours to let the oxidative polymerization of aniline on the surface of the Ni-TiO₂ nanoparticles which is assisted by the oxidizing agent, ammonium persulphate, (NH₄)₂S₂O₈. The resulted dark-green hybrids gel of PANI/Ni-TiO₂ was layered on on indium tin oxide (ITO) substrate at 200rpm for 15 seconds and annealed at 300°C for 2 hours. The PANI/Ni_x-TiO_{2(1-x)} molar ratio was used to prepare the synthesis of different solutions which ($x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0$). Pure PANI was also synthesized via the same procedure without anticipating the Ni-TiO₂ sols. The morphology and the nanostructured PANI/Ni-TiO₂ hybrid materials were observed by using Field Emission Scanning Electron Microscopy (FESEM Carl Zeiss Supra 55VP). The Perkin Elmer Lambda 950 UV-Vis spectrophotometer was used to measure the light absorption spectra of PANI/Ni-TiO₂ hybrid materials. Electrical impedance spectroscopy (EIS) were used to analysed the electrochemical activity of PANI/Ni-TiO₂ hybrids with proper linear equivalent circuit. The electrical properties and the photocurrent efficiency of nanocomposite materials were measured through the photocurrent density-photovoltage (J-V) analysis.

III. RESULTS AND DISCUSSION

The surface morphology has been observed through FESEM images as shown in Figure 1(a-d). It is observed that the addition of Ni²⁺ reduced the size of particles and modified the morphological structure of the particles form non-uniform size to a tubular structure as clearly observed in Figure 4 (b) and (d). The addition of Ni²⁺ reduced the aggregation and resulted with evenly distributed particles on the thin film. Both PANI/TiO₂ and PANI/Ni0.4-TiO_{2(0.6)} thin films were analyzed with UV-Vis spectroscopy with absorbance ranged from 300-800nm at visible light condition. The characteristic absorption edges for PANI/TiO₂ and PANI/Ni0.4-TiO_{2(0.6)} were at 332 nm and 364 nm, resulted with the quantum confinement effect on the nanoparticles as shown in Figure 2. The absorption edges of PANI/TiO₂ (332 nm) showed a larger blueshifts than PANI/Ni0.4-TiO₂ (364 nm) which defines the decreasing in wavelength which corresponds to the increased absorbance. The PANI/TiO₂ showed a sharp and apparent excitation peaks corresponds to narrower size distribution than PANI/Ni0.4-TiO₂ nanoparticles. From Table 1, it shows that the optical bandgap energy of PANI/TiO₂ (4.37eV) was slightly higher than PANI/Ni0.4-TiO_{2(0.6)} (4.31eV) corresponding to its narrow particle sizes and higher absorption peak values (364nm).

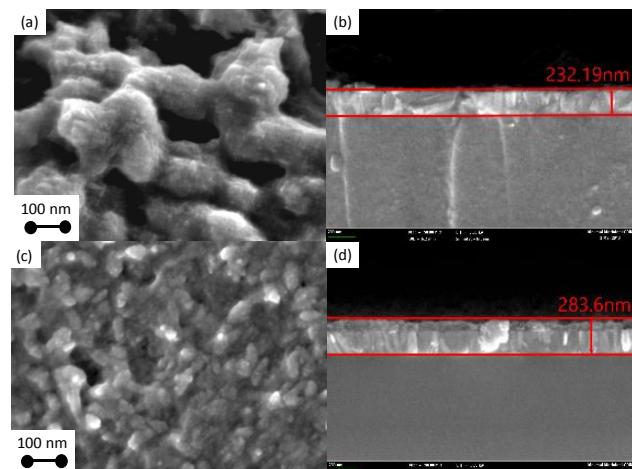


Fig. 1. FESEM images taken on the surface; PANI/TiO₂ (a) 30KX magnification (b) Cross-sectional thickness and PANI/Ni_{0.4}-TiO_{2(0.6)} (c) 30KX magnification (d) Cross-sectional thickness.

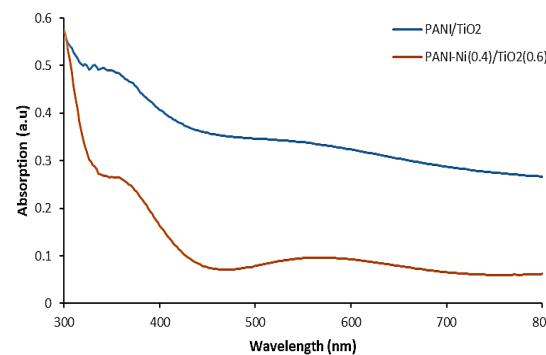
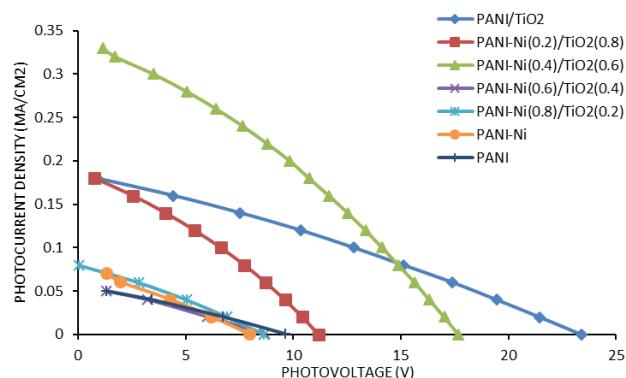


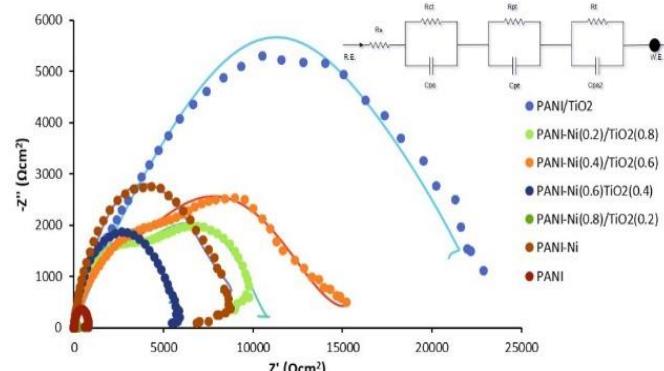
Fig. 2. UV-Vis absorption spectra of (a) PANI/TiO₂ and (b) PANI/Ni_{0.4}-TiO_{2(0.6)}.

The J-V curves shown in Figure 4 (a) indicate that as the photovoltage, V_{oc} of the hybrid PANI/Ni-TiO₂ nanocomposite increased, the photovoltaic performance of DSSC dropped sharply as the photocurrent density, J_{sc} decreased. The result of the overall performance of different hybrid nanocomposite thin films based DSSC are shown in Table 3 and the comparison of J-V curves between all the hybrid nanomaterials were shown in Figure 5. Both PANI/TiO₂ and PANI/Ni_{0.4}-TiO_{2(0.6)} exhibit higher V_{oc} and J_{sc} compared to the other utilized hybrid which were at 0.33V and 0.18V, and at 30mA/cm² and 35mA/cm², resulted with higher photocurrent conversion efficiency at 1.28% and 2.07%, respectively. PANI/Ni_{0.2}-TiO_{2(0.8)} based DSSC showed similar value of V_{oc} (0.18V) as PANI/TiO₂ but lower value of J_{sc} obtained at 11.19mA/cm², which then resulted with lower PCE at 0.66%. Besides that, the other four hybrid exhibit much lower overall performance of V_{oc} , J_{sc} and PCE could be due to formation of larger and dense hybrid nanostructured which could lower the reachable surface areas for dye loading as well as electron mobility [9].

Fig. 3. J-V curves under simulated sunlight irradiation (100mW/cm²).TABLE I: PHOTOVOLTAIC PERFORMANCES OF DIFFERENT HYBRID NANOSTRUCTURED PANI-Ni/TiO₂ AND PURE PANI

Sample	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
PANI/TiO ₂	0.18	23.38	30	1.28
PANI-Ni	0.07	7.95	35	0.20
PANI	0.05	9.63	34	0.16
PANI-Ni _(0.2) /TiO _{2(0.8)}	0.18	11.19	33	0.66
PANI-Ni _(0.4) /TiO _{2(0.6)}	0.33	17.67	35	2.07
PANI-Ni _(0.6) /TiO _{2(0.4)}	0.05	8.67	31	0.13
PANI-Ni _(0.8) /TiO _{2(0.2)}	0.08	8.63	31	0.21

The EIS Nyquist curves of different hybrid photoanodes are shown in Figure 4. The initial gap indicates the sheet resistance on ITO substrate (R_s), which is related to the contact resistance between ITO and Ni-TiO₂ metal. The first semicircle assigned for electron transfer and recombination at the TiO₂/dye/electrolyte interface (R_{ct}), the second semicircle which in high frequency region represents the charge transfer resistance at the electrolyte/counter electrode interface (R_{pt}), and the third semicircle which in low frequency region represent the electron transport resistance (R_t) correspond to the characteristics of the I/I³⁺ redox electrolytes electron [10]. The fitting of the electrochemical impedance spectra was interpreted by using the equivalent circuit model as shown in Figure 4. The characterization parameters were summarized in Table 2. Based on Table 2, PANI/Ni_{0.8}-TiO_{2(0.2)} hybrids showed lowest R_{ct} (10 Ω). The low R_{ct} could be due to the formation of the large and dense structure of Ni-TiO₂ metal which could enhance the electron mobility in the hybrid nanostructures. The peak frequency shifted to a lower value as Ni-doped decreased and TiO₂ increased in the hybrid nanostructures which increases the recombination resistance (R_{ct}) and elongate the electron lifetime.

Fig. 4. Impedance spectra of different PANI/Ni-TiO₂ hybrids and the equivalent circuit model.TABLE II: EIS PARAMETERS FOR PANI-Ni/TiO₂ HYBRID BASED DSSC.

Sample	R _s (Ω)	R _{ct} (Ω)	R _{pt} (Ω)	R _t (Ω)	f _{max} (Hz)	τ _{eff} (ms)
PANI	0.05	60	450	750	0.60	0.27
PANI-Ni	0.06	800	3500	9000	1.50	0.11
PANI/TiO ₂	0.1	1418	3000	18000	0.60	0.27
PANI-Ni _(0.2) /TiO _{2(0.8)}	0.5	850	2950	14000	0.75	0.21
PANI-Ni _(0.4) /TiO _{2(0.6)}	0.6	1050	4100	20000	0.75	0.21
PANI-Ni _(0.6) /TiO _{2(0.4)}	0.1	400	1750	7000	1.19	0.13
PANI-Ni _(0.8) /TiO _{2(0.2)}	0.07	10	80	115	1.19	0.13

IV. CONCLUSION

The PANI/Ni-TiO₂ hybrids were synthesized by sol-gel method through the oxidative polymerization of aniline by adding well-dispersed Ni-doped and TiO₂ nanoparticles. The morphology of the hybrids changed from nanospherical structure into nanorod-like structure as more aggregation takes place with the presence of Ni²⁺ and TiO₂ nanoparticles onto the surface of PANI. The nanorod-like structure was excellent in terms of electrochemical stability and exhibits higher photocurrent conversion efficiency at 2.07% compared to other hybrid materials. This enhancement of the stability of the hybrid was contributed by the realization of the chemical bonding between the PANI and the TiO₂ with the Ni-doped. By synthesizing longer hybrid with higher aspect ratios or branched complex nanostructures, the reachable surface areas can be increased for dye loading as well as high electron transport ability improving DSSC performance.

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S.N.F. Zainudin received the B.Eng degree in Biochemical Engineering and M. Sc. degree in Chemical Engineering from Universiti Kebangsaan Malaysia, in 2009 and 2012, respectively. She is a former lecturer at UCSI University. Currently, she pursues her postgraduate studies in dye-sensitized solar cells application involving nanocomposite thin films. Her current research interest is towards thin films modifications for solar cells.



H. Abdullah received the B.Eng degree in Biochemical Engineering and M. Sc. degree in Chemical Engineering from Universiti Kebangsaan Malaysia, in 2009 and 2012, respectively. She is an Associate Professor for Functional Nanomaterials at Universiti Kebangsaan Malaysia (UKM). Her research interest focused on analyzing the basic optical, structural, electronic and chemical properties of metal oxides as a base material for high efficiency and low cost solar cell and on sensor based conducting polymer-metal and polymer-metal oxide nanocomposite thin films. The research works were supported by various research grants from government, local and international research institutions. In 2007, she was awarded For Women In Science (FWIS2007) award and a research grant from L'Oreal Malaysia. In June 2011, she obtained an international grant, COMSTECH-TWAS Research Grants for dye-sensitized solar cell project awarded by The World Academy of Sciences (TWAS). In 2012, she was awarded as a Young Excellent Researcher by Malaysian Solid State Science and Technology Society (MASS).

A.A. Abdul Aziz received the B.Eng degree in Electrical and Electronics Engineering from Universiti Kebangsaan Malaysia 2018.