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Preparation of ZnO/TiO_2 Nanocomposite Sensitized Mangosteen Rind *(Garcinia mangostana L)* Dye for Light Harvesting Efficiency in Solar Cell

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Abstract

The preparation of ZnO/TiO_2 nanocomposite is done using the sol-gel method for light harvesting in dye-sensitized solar cell (DSSC). The titanium dioxide (TiO_2) compound was added with different ratios to the ZnO matrix and measured its effect on solar cells based on the DSSC system. The powder X-ray diffractions of nanocomposite revealed anatase (TiO_2) and wurtzite (ZnO) phases have the highest peak at 25.26° and 36.97°, respectively. The energy gap was observed by diffuse reflectance-ultra violet (DR-UV) spectroscopy and it revealed that the optimum performance of nanocomposite was 3.16 eV for the 1:2 ratio. The optimum power efficiency was 2.4% with 3.6 cm^2 active area, V_{oc}= 788 mV and I_{sc}=3.39 mA, respectively. The scanning electron microscope-energy dispersive X-ray (SEM-EDX) demonstrated the diversity of surface morphology depends on the ratio of TiO_2 in the nanocomposite. This shows the addition of TiO_2 to the ZnO matrix influenced the structure of the nanocomposite, which can be applied as DSSC electrodes.

Keywords: Ratio, ZnO/TiO_2 nanocomposite, sol-gel, solar cell, DSSC

INTRODUCTION

The world's energy demand increased rapidly along with the progress of human civilization. The utilization of conventional energy sources such as coal, fuel oil, natural gas, and others has a low operating cost. However, it creates greater problems such as limited natural resources and emitting pollution to the environment. Therefore, the study and development of renewable and alternative energy sources were important aspects (Saleem et al., 2021).

Solar energy was known as green-friendly energy (Chamanzadeh, Ansari, & Zahedifar, 2021). In this case, Indonesia has a big potential market and resources to develop its solar cell. To reach this goal, dye-sensitized TiO_2 and ZnO were introduced as an alternative to conventional photovoltaic devices. This development was important due to the high cost of conventional photovoltaic fabrication. The dye-sensitized TiO_2 has several advantages such as a simple fabrication process, low production cost and is economically acceptable in the market (Senthil, Muthukumarasamy, & Kang, 2013).

To improve the efficiency of the TiO_2 electrode, some modification was performed, such as the formation of the nanocomposite. There are several TiO_2 based composites were reported, such as TiO_2/SiO_2 (Nguyen et al. 2007), TiO_2/Al_2O_3 (Zhang et al., 2003), $TiO_2/CaCO_3$ (Lee et al., 2006), TiO_2/SnO_2 (Pham et al., 2021), non-metallic elements (Khan et al., 2021) and polyoxometalates (Gu et al., 2020; Wihadi & Sadakane, 2020).

Mane and team reported DSSC electrodes using thin-film of ZnO/TiO_2 nanocomposite and demonstrated the energy conversion gain was 0.67% (Mane, Lee, Pathan, & Han, 2005). However, their result has not been described in detail on the ratio of the nanocomposite. Song`s group showed that the composite ZnO/TiO_2 with a ratio of 1:0 and 4:1 revealed efficiency of 4.39% and 0.25 %, respectively (Song et al., 2014). To enhance the energy efficiency of a solar cell, the study before about calcined the core-shell ZnO/TiO_2 nanocomposite at 500 °C and obtained a crystal size of 40 nm has been done (Golobostanfard, Ebrahimifard, & Abdizadeh, 2011).

An alternative method to tune the efficiency of DSSC is the sensitization of the electrodes using natural dyes such as extract of mangosteen (Male, Sutapa, & Ranglalin, 2015). Mursal et al. performed the Mg and La-doped TiO_2 photoelectrodes and extracted mangosteen rind (Mursal, Malahayati, Azmi, & Fatmiyah, 2021). Ismail et al. (2020) investigated the electrochemical and photovoltaic properties of the natural photosensitizer using mangosteen fruit (Ismail et al., 2020). Therefore, the presence of mangosteen as natural dyes in photosensitizer was important. To the best of our knowledge, there is no report ZnO/TiO_2 nanocomposite sensitized with mangosteen rind (*Garcinia mangostana L*) dye for DSSC application.

In this study, we reported the preparation of ZnO/TiO_2 nanocomposite with different ratios of TiO_2 and ZnO. The nanocomposite coupled with mangosteen rind (*Garcinia mangostana L*) dye for the solar cell performance.

METHODOLOGY

Materials and Instrumentals

The chemicals such as $Zn(CH_3COO)_2$-$2H_2O$, $Ti[OCH(CH_3)_2]_4$ (TIPP) 97%, ITO glass substrate (8-12 Ω/sq), triethanolamine (TEA), isopropanol, graphite, chloroform, acetone, ethanol, acetic acid, methanol, ethylene glycol, PEG 4000 ($HOCH_2(CH_2OCH_2)_mCH_2OH$), Iodolyte (KI and I_2), and polyvinyl alcohol (PVA) were purchased from Merck and Sigma Aldrich (Germany) and used without further purification. The mangosteen rind *(Garcinia mangostana L*) was purchased from the traditional Indonesian market.

The size and surface morphology of ZnO/TiO_2 nanocomposite was obtained by Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy (SEM-EDX), X-ray diffractometer (Shimadzu XRD-6000), diffuse reflectance UV spectrophotometer (Shimadzu UV 1700 Pharmaspec UV-Vis), UV lamp (365 nm; 12 lux (Goldstar)), multimeter (Heles UX 839TR), shear resistance 20 kV.

Methods

The ZnO/TiO_2 nanocomposite was prepared based on ZnO and TiO_2 ratio. This ratio was 1:0; 1:1; 1:2. The samples were calcined at 500 ^oC; the time of light exposure was 2 hours, and the pH was 3-4. The photon source was obtained from a UV-VIS lamp (λ = 365 nm). The resistance was used according to: 0.5, 1.0, 1.5, 2.0, 4.0, 8.0 and 1000 **Ω**, respectively.

Preparation of ZnO and TiO_2

Four grams of $Zn(CH_3COO)_2$-$2H_2O$ were dissolved in isopropanol and stirred for 60 minutes. TEA as a stabilizer was added to the solution. This mixture was aged for 24 hours and then dried at 120 ^0C for 3 hours. The sample calcination was performed at 500 ^oC for 2 hours. TiO_2 powder was prepared by dissolving 1 mL of TIPP into 10 mL of isopropanol. This mixture was dried at room temperature. The drying substance was calcinated at 500 ^0C for 2 hours. The substrate was washed using ethanol, acetone, and water for 3 minutes in the reactor.

Preparation of the electrode with dye

The dye was prepared from mangosteen rind *(Garcinia mangostana L*) by dissolving the sample in the solvent containing ethanol: acetic acid: and water (25:4:21 ratio). Then, the mixture was filtered off. The maximum wavelength of dye extract was measured using UV-Vis spectroscopy. The dye was immersed in the working electrode for 24 hours.

Preparation of the reference electrode

The graphite was prepared by grinding until 100 mesh and contacting 50 mL PVA 5% on the ITO substrate (150 ° C for 3 minutes). This graphite was used for the reference electrode. The electrolyte gel was prepared by dissolution of 7 g of PEG 4000 in 25 mL of chloroform-filled Iodolyte (KI/I_2). The electrolyte solution was heated at 60 ° C for 10 min to form a gel. In the final step, the working electrode and cells have merged.

The XRD technique characterized the nanocomposite. The band-gap energy of the nanocomposite was measured by a DR-UV spectrophotometer and analyzed by the Kubelka-Munk equation (Equation 1) (Klaas, Schulz-Ekloff, & Jaeger, 1997).

$$F(R\infty) = \frac{K}{S} = \frac{(1-R\infty)^2}{2R\infty} \quad (1)$$

$R_\infty = \frac{Rsample}{Rstandard}$ is the reflectance of an infinitely thick specimen, K and S are absorption and scattering coefficients, respectively.

Preparation of DSSC electrode

The preparation of the DSSC electrode following the condition in scheme 1 (Figure 1). The front and back layer was ITO substrate, and the other layer was carbon, electrolyte and ZnO/TiO_2 nanocomposite-dye, respectively.

RESULTS AND DISCUSSION

Preparation of ZnO/TiO_2 nanocomposite

The ZnO/TiO_2 nanocomposite have prepared by the sol-gel method. The white emulsion was shown when TIPP and isopropanol were mixed in the solution. This indicated the hydrolysis reaction occurred. The preparation method was followed in the experimental section.

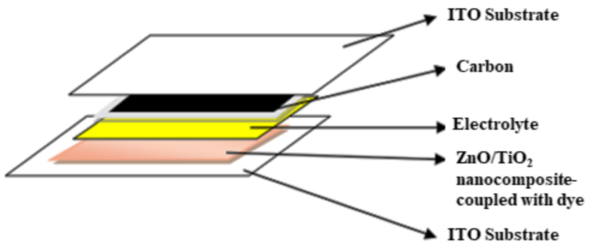

Figure 1. Layered formation in the preparation of DSSC electrode

Figure 2 shows the XRD profile of ZnO, TiO_2, and the nanocomposite, respectively. The diffractogram profile of ZnO was compared to the ZnO standard (JCPDS No. 36-1451) and showed the similarity to the standard [2θ = 31.77° (100); 34.42° (002); 36.25° (101); 56.60° (110); 62.86° (103); 67.96° (112) and 69.10° (201)]. The anatase phase was detected at 25.26° (101) and 48.03° (200) and confirmed by standard (JCPDS No. 21-1272). The rutile phase was detected at 43.2° in TiO_2 due to the effect of the hydrolysis reaction of TIPP in the preparation and changed when the calcination occurred. ZnO/TiO_2 nanocomposite crystallinity decreased when TiO_2 was added to the ZnO matrix.

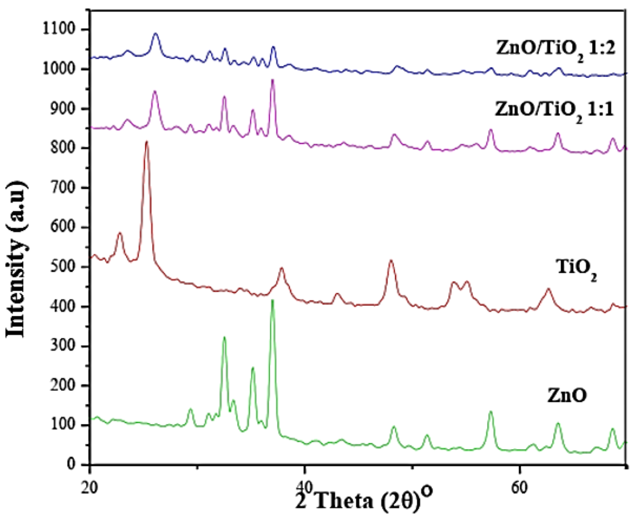

Figure 2. X-ray diffraction pattern of ZnO/TiO_2 nanocomposite with different ratio

The signal corresponding to $ZnTiO_4$ at 36.97° was also detected. This might be caused by reduced crystallinity in the nanocomposite and changed crystal structure.

Energy Gap of ZnO/TiO_2 nanocomposite

Figure 3 shows the reflectance UV-Vis spectra of ZnO/TiO_2 nanocomposite. The additional TiO_2 on the ZnO matrix influenced the decreasing absorbance. Therefore, the band gap value will decrease, and the electron will easily jump to the conduction band. We have calculated this energy gap using equation 1 (Table 1). The gap energy for 1:0, 1:1 and 1:2 ratio was 3.46, 3.51 and 3.16 eV, respectively. Rajaram and team (2005) reported that the photon energy of ZnO/TiO_2 thin films was 3.26 and 3.58 eV. The band gap energy decreased due to the crystallinity of the composite film being low. In our case, additional TiO_2 on the ZnO matrix also decreases the composite's crystallinity and is confirmed by XRD profiles of ZnO/TiO_2 in 1:1 and 1:2 ratios (Figure 2).

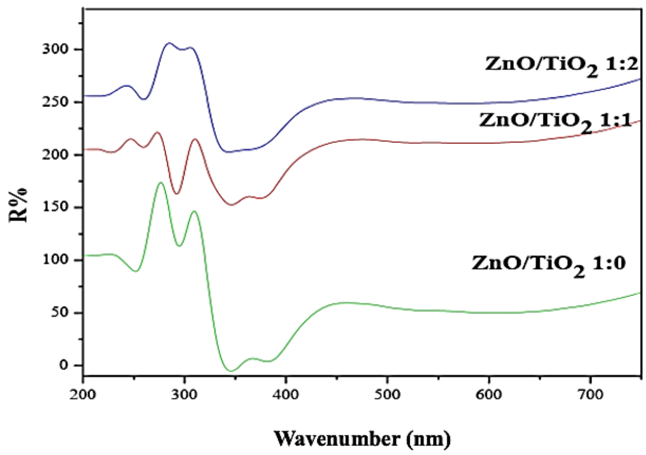

Figure 3. The reflectance spectrum of ZnO/TiO_2 nanocomposite.

Table 1. Energy Gap of ZnO/TiO_2 nanocomposite.

ZnO/TiO_2 ratio	E_g (eV)
1:0	3.46
1:1	3.51
1:2	3.16

Surface morphology of ZnO/TiO_2 nanocomposite

Figures 4 and 5 revealed that the nanocomposite has a pore. We have observed the morphological characteristics of the nanocomposite by SEM in magnification of: 2000X, 10000X, and 20000X, respectively.

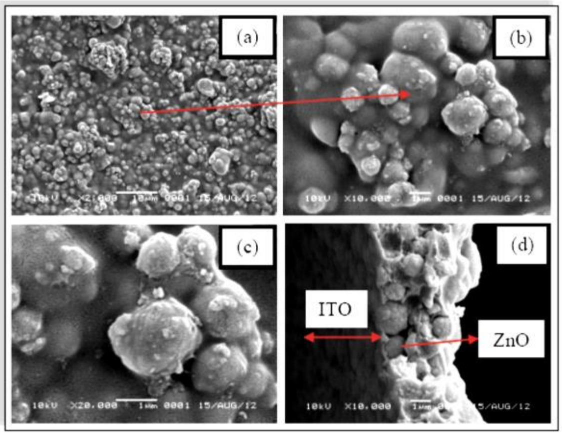

Figure 4. SEM images for ZnO/TiO_2 1:0 with magnification of: a). 2000x, b). 10000x, c). 20000x and d). 10000x (ZnO on ITO substrate)

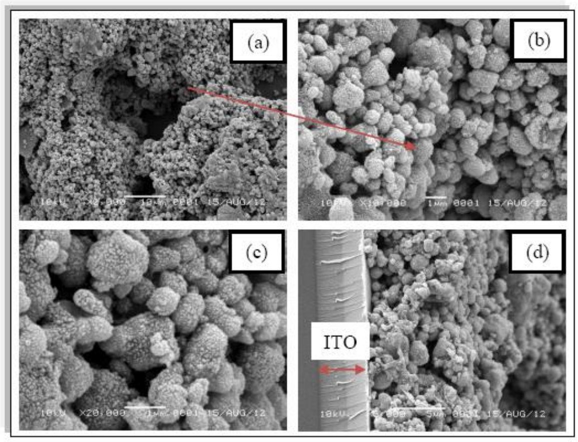

Figure 5. SEM images for ZnO/TiO_2 1:2 with the magnification of: a). 2000x, b). 10000x, c). 20000x and d). 10000x (ZnO/TiO_2 on ITO substrate)

We believed that the difference might be caused by long exposure to ultrasonic waves during ITO substrate laundering and degradation of ITO structure occurred.

Voltage current characteristics (I-V)

The current and voltage testing have been performed to nanocomposite in the dark conditions by UV light (wavelength= 365 nm, light intensity = 12 lux) generated by Luxmeter. The light conversion was 1.405 Watt/cm^2. The result was resumed in Table 2. This research used the liquid-gel electrolyte to avoid the oxidation-reduction reaction to occur. Small value of V_{oc} (open circuit voltage) might be caused by leak electrolyte in the solar cell.

Electrolyte leakage would inhibit the exchange of electrons between the working and reference electrodes. Therefore, this condition is unable to keep pace with the speed of electron generation injected into the side of the working electrode after the photosensitization process. The efficiency and gap energy of the ZnO/TiO_2 nanocomposite 1:0 ratio minor compare to 1:1 ratio. This energy can facilitate the electron from the ground state to the excited state by dye stimulation.

The electrons jump to the hole of semiconductors; then the hole is left with a chemical process where the reaction produced continuous light intensity-dependent, which illuminated the semiconductor surface. Lee and team (2005) reported that the energy conversion gain was 1.78% for 1% w/w TiO_2 and the ZnO matrix with the active area was 0.226 cm^2.

Table 2. The current and voltage testing of ZnO/TiO_2 nanocomposite.

Sample	Parameters							
	V_{oc} (mV)	I_{sc} (μA)	V_{mpp} (mV)	I_{mpp} (μA)	FF (%)	P_{max} (μW.cm^{-2})	Light Intensity (Lux)	η (%)
ZnO/TiO_2 (1:0)	778	1.76	650	1.08	54.63	0.01881	12	1.34
ZnO/TiO_2 (1:1)	789	1.59	680	1.11	60.16	0.02150	12	1.52
ZnO/TiO_2 (1:2)	788	3.39	518	2.37	46.54	0.03410	12	2.40

Figure 4 shows the morphological characteristics of ZnO/TiO_2 nanocomposite with 1:2 ratio and uniform sizes. The pore images were clearly observed at 20000 magnifications. Figure 4 (d) show that the ITO layer is different from the 1:0 ratios in Figure 3 (d).

Our conversion gain was 0.16% which was lower than the previous report. The low value was attributed to the instability of ZnO against dye molecules, presenting the partial termination of Zn^{2+} ions from the surface.

CONCLUSION

The ZnO/TiO_2 nanocomposite was prepared by the sol-gel method. The powder X-ray diffractions of nanocomposite revealed anatase (TiO_2) and wurtzite (ZnO) phases have the highest peak at 25.26° and 36.97°, respectively. This indicated that calcination at 500 °C for 2 hours described the stability of anatase and wurtzite phases. The ratio of TiO_2 on ZnO/TiO_2 nanocomposite influenced solar cell performance. The optimum performance was obtained at a 1:2 ratio. Increasing the ratio of TiO_2 on the ZnO matrix affects decreasing gap energy of ZnO/TiO_2 nanocomposite at 3.16 eV. The crystal was photoactive for absorption of UV-visible light range spectrum with expected phase in wurtzite (ZnO) and anatase (TiO_2) by sol-gel method.

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