

The Effects of Al-doped ZnO (AZO) as Anti-reflection Agent for Dye Sensitized Solar Cells System

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Al-doped ZnO (AZO) nanoparticles have been synthesized as anti-reflection agent for dye sensitized solar cells system. Al-doped ZnO was prepared by sol-gel method at 60 °C for 3 hours with variation of Al (0, 2, 3 and 4 %). XRD pattern of AZO shows that the addition of Al affected the structural properties, such as decrease in the crystallinity and crystallite size from 10 nm to 28 nm. The optical properties of AZO were characterized by UV-Vis Spectrophotometer. Al-doped ZnO exhibited the red shift phenomenon at wavelength 320-375 nm. AZO of 3 % and 4 % show 2 peaks considered as the impurities of Mg-doped ZnO. The transmittance spectra of AZO show the increase of transmittance in the visible light region of 50-95 %. The reflectance spectra show the reflectance value increasing in the UV area and decreasing in the visible area (< 50 %). Band gap energy of AZO was calculated with Tauc Plot Method. The addition of Al can decrease the band gap energy of AZO from 3.45 eV to 3.23 eV. Al-doped ZnO is used as anti-reflection agent for Dye Sensitized Solar Cells (DSSCs). Performance of DSSCs system with AZO has higher efficiency than that without anti-reflection coating. The efficiency of the solar cell system without AZO anti-reflection layer is 0.18 %, while the efficiencies with 2, 3 and 4 % AZO anti-reflection layer were 0.28, 0.68 and 0.85 %, respectively. The maximum performance of DSSCs system with AZO 4 % (0.85 %) as anti-reflection agent was shown by the improved efficiency up to 372 times compared to that without anti-reflection agent.

Keywords: Al-doped ZnO, Structure properties, Optical properties, Anti-reflection, DSSCs.

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1. INTRODUCTION

As semiconductor materials, ZnO has typical properties such as a wide band gap, good transparency, refractive index of 2.01 and is similar to TiO₂ properties [1]. Therefore, ZnO can be potentially applied in optoelectronic devices, such as ultraviolet (UV) photodetectors, photocatalytic, sensor, water treatment, transparent conducting oxide, and dye sensitized solar cells (DSSCs) [2]. In the DSSCs, ZnO acts as photoanode and anti-reflection coating [3]. However, the efficiency of ZnO material based DSSCs is still low due to the instability of the oxide surface and surface density [4]. ZnO bulk has chemical instability and low band gap energy when applied to visible light [5], so it needs method enhancement to reduce those disadvantages of ZnO. Doping is one of the methods which can reduce the band gap energy, increase the absorption of light and modify its electronic characteristics [6]. The dopant materials usually used are trivalent atoms, such as elements of group IIIA (Al, In, Ga) through cation substitution [7]. Aluminum (Al) is one of the dopants, which can produce ZnO film with high conductivity and good transparency to form Al-doped ZnO (AZO).

The structural modification of AZO from bulk materials to nanosize materials can improve the performance of DSSCs. Al-doped ZnO nanoparticles can serve as a good electron transport and injection material in optoelectronic devices [8]. Djelloul et al. [9] reported that the

presence of Al was able to decrease the size of crystal and increase the transmittance of visible light. The increase of Al concentration will provide the high crystallinity and good transparency materials.

Al-doped ZnO nanoparticles were synthesized by sol-gel, vapor deposition, microwave, spray pyrolysis, coprecipitation, and hydrothermal processes methods. Sol-gel method is the simplest and low-cost method which can produce high homogeneity and purity, good optical, electrical and magnetic properties of nanoparticles [10]. These properties will affect the ability of AZO as an anti-reflection to improve the ability of solar cells for harvesting light [11].

In this study, AZO nanoparticle was coated with TiO₂ nanorods by sol-gel method at low temperature and short time reaction. The optimization of AZO concentration was discussed to compare the contribution of Al-doped ZnO as an anti-reflection in the DSSCs. In order to get high-efficiency of DSSCs, the particle size of AZO should be small with high transparency and light absorption ability. The presence of AZO layer as an anti-reflection on DSSCs is expected to provide maximum absorption and the best efficiency.

2. EXPERIMENT DETAILS

2.1 Materials

The materials used are Zn(CH₃COO)₂·2H₂O (Aldrich), Al(OH)(CH₃COO)₂ (Aldrich), Polyethylene glycol

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1000 (HO(C₂H₄O)_nH (Merck), Etanol p.a. (Merck), electrolyte for DSSCs (Aldrich), Platinum (Brataco), dye of Ruthenium (Aldrich), TiO₂ nanorods [12] and aquadest.

2.2 Synthesis of Al-doped ZnO (AZO) Nanoparticles

Al-doped ZnO (AZO) nanoparticles were synthesized by sol-gel methods [13]. Zinc acetate dehydrate (0.1 M) was mixed with 0.1 M of polyethylene Glycol 1000 (PEG) in the 40 mL ethanol. The mixture was stirred for 2 hours at 60 °C and was added with Aluminum acetate (Al(OH)(CH₃COO)₂) with variations of concentration 0, 2, 3, 4 at. %. The solution was stirred at 60 °C for 1 hour until it became a gel. Then, it was heated at 60 °C until it turned to be powder. Finally, the product was calcinated at 600 °C for 3 hours. The characterization of material was conducted using X-Ray Diffraction Bruker type D8 with anode Cu to determine the structure properties and UV-Visible spectrophotometer Perkin Elmer Lambda 25 to investigate the optical properties of AZO.

2.3 Preparation of Dye Sensitized Solar Cells

Fabrication of DSSCs used ITO (Indium Thin Oxide) glass as the substrate. Al-doped ZnO (1 g) was dissolved in 2 mL ethanol to form a paste. The paste was coated on ITO glass using the slip casting method in the active layer around 1 cm × 1 cm. The film was then heated at 300 °C for 30 min to obtain AZO thin film. TiO₂ paste was made by dissolving 1 g of TiO₂ in 2 mL ethanol. Then, TiO₂ was coated in the top of AZO thin film to form the AZO/TiO₂ thin films. Thin films of AZO/TiO₂ were soaked in ruthenium complex dyes for 24 hours.

Here, platinum was used as counter electrodes. It was coated on another ITO glass and was heated at 300 °C for 30 min. The active layer of AZO/TiO₂ was arranged with platinum electrodes to form a sandwich structure. On the edge of the structure, a gap of around 0.5 cm was given for electrical contact and to soak the electrolyte solution. The electrolyte solution was then dropped into the gap of the sandwich. The arrangement of the DSSCs system is: ITO/AZO/TiO₂/Dye/Electrolyte/Platinum/ITO. DSSCs system was tested using Keithley 2602 A (1000 W/m²). The efficiency of solar cells was calculated by Eq. 1:

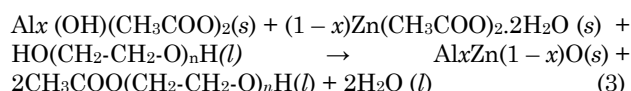
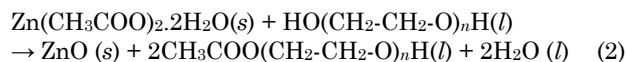
$$\eta = (P_{out}/P_{in}) \times 100\%, \quad (1)$$

where η is the efficiency of solar cells (%), P_{out} is the maximum electrical power output (W/m²), P_{in} is the solar power input (W/m²).

3. RESULTS AND DISCUSSION

3.1 XRD Pattern of AZO Nanoparticles

Al-doped ZnO (AZO) nanoparticles have been synthesized by sol-gel method. Zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O) and Aluminum acetate (Al(OH)(CH₃COO)₂) were used as precursor, and polyethylene glycol (PEG) was used as surfactant in the formation of Al-doped ZnO. The proposed mechanism of the formation of AZO is shown in Eq. 2 and Eq. 3:



XRD pattern of AZO with variation of aluminum was shown in Fig. 1. The crystal structure of AZO according to the ZnO standard (JCPDS 80-0075) was hexagonal wurtzite structure [13]. The peaks were not included by impurity as Al₂O₃ because Al is inserted in the ZnO lattice in which Al is smaller in ion size (0.54 Å) than Zn (0.74 Å). The aluminum was substituted with Zn without changing the structure of ZnO. The addition of Al (2-4 %) obtained lower XRD pattern than pure ZnO (Al 0 %). The increase of Al can decrease the crystallinity of ZnO, which shows the decrease of peak and a wider diffraction gap. Al dopants were able to cause stresses of ZnO and it was formed in grain boundaries, so it could decrease the crystallinity of Al-doped ZnO [14]. The highest crystallinity of AZO was obtained by adding 2 % of Al dopants with sharp and high intensity of peak compared to the crystallinity of 3 % and 4 % AZO. The addition of Al dopant affects crystal growth and crystallite size. The crystallite sizes of AZO 0 %; 2 %; 3 %; 4 % are 28.65 nm; 20.24 nm; 20.21 nm; 10.77 nm, respectively. The substitution of Al in the ZnO lattice can inhibit the growth of ZnO crystals where the radius of Zn²⁺ ion is greater than Al³⁺, so it causes the decrease of crystallite size [14].

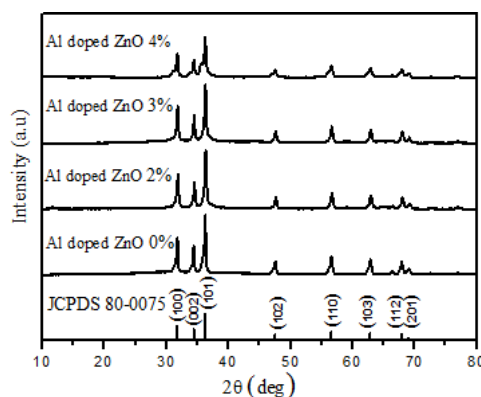


Fig. 1 – X-ray diffraction pattern of Al-doped ZnO with variation of Al

3.2 Optical Properties of AZO Nanoparticles

Optical properties of AZO nanoparticles were characterized using UV-Visible spectrophotometer and shown in Fig. 2. The addition of Al affected the absorption peak to larger wavelength (red shift phenomenon) [15]. The peak of AZO was shown at 320-375 nm. In the UV region, spectra of AZO 3 % and 4 % displayed 2 peaks which were Mg-doped ZnO as impurities [13, 16].

High transmittance spectra of AZO in the visible light area were shown in Fig. 3. The transmittance value of AZO in the visible light region was 50-95 %. The transmittances (%) of AZO at each Al variation of 0 % to 4 % were 60.95 %, 62.83 %, 66.37 %, and 70.46 %, respectively. The increase of Al concentration could improve optical transmission of AZO where the average of transmittance in the visible area was 70-90 % [9]. The

particles were completely distributed to AZO thin film, so it could increase the light transmittance.

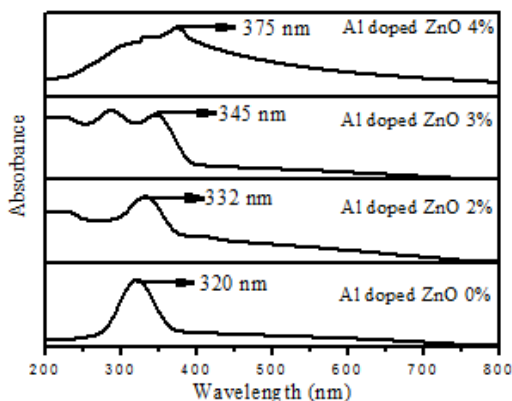


Fig. 2 – Absorbance spectrum of Al-doped ZnO

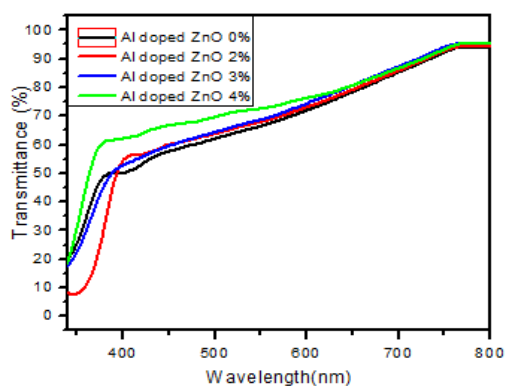


Fig. 3 – Transmittance spectrum of Al-doped ZnO

The reflectance spectrum of AZO was shown in Fig. 4. The greater Al concentration caused a decrease in the reflectance value. Al ions (Al^{3+}) were successfully doped in ZnO and formed the defects in ZnO crystals. The reflectance value increased in the UV area and decreased in the visible area [17].

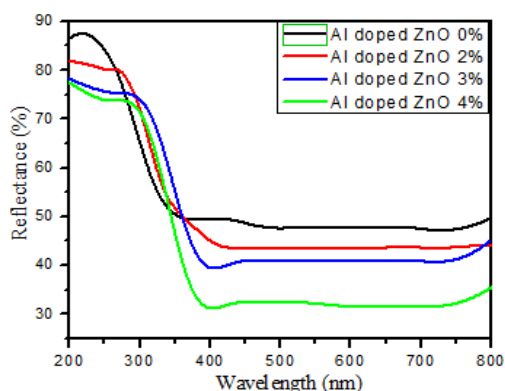


Fig. 4 – Reflectance spectrum of Al-doped ZnO

The reflectance percentages of AZO at each Al variation were 47.70, 43.51, 40.96 and 31.64 %, respectively. The difference of the light scattering is due to the effect of different dopant concentrations. In this study, 4 % AZO has lower reflectance and greater transmittance.

Bandgap energy of AZO was calculated by Tauc Plot method. The value of the band gap energy (E_{gap}) was shown in Fig. 5, where the band gap energy decreased as the Al content increased. The band gap energy of 0 % AZO was 3.45 eV, but by adding Al, it reduced to 3.23 eV. The Al ions diffused in the ZnO lattice caused the decrease of the distance between the valence and conduction bands. In addition, interaction of ZnO and ion dopants caused additional bands (bands of impurities that were below the conduction band) [18]. The additional band made the electrons excited easily into the conduction band.

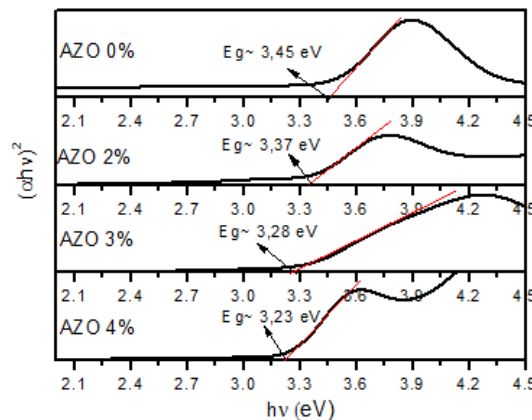


Fig. 5 – Optical band gap calculation of Al-doped ZnO

3.3 Al-doped ZnO Nanoparticles as Anti-reflection Agent in DSSCs

Al-doped ZnO was used for anti-reflection agent in the DSSCs system. The sandwich layer of DSSC without using AZO anti-reflection agent, namely ITO/TiO₂ nanorods/electrolyte/Platinum/ITO and DSSCs coated using AZO anti-reflection was ITO/AZO anti-reflection agent/TiO₂ nanorods/electrolyte/Platinum/ITO. The DSSCs systems were characterized using the Keithley 2600A I-V measurement type ($P = 1000 \text{ W/m}^2$). From I-V, data show the value of V_{max} , I_{max} , P_{out} , and efficiency (η) as in Table 1.

The efficiency of the solar cell system without AZO anti-reflection layer was 0.18 %, while the efficiencies with 2 %, 3 % and 4 % AZO anti-reflection layer were 0.28 %, 0.68 % and 0.85 %, respectively. The use of AZO as anti-reflection layer increased efficiency of DSSCs compared to those without AZO layers. The current-voltage (I-V) curves of DSSCs system with 4 % AZO anti-reflection agent was shown in Fig. 6. The efficiency value of DSSCs using AZO anti-reflection layer 4 % has the best efficiency (0.85 %) with an efficiency improvement of 372 times.

Table 1 – The efficient of DSSCs without and with anti-reflection layer

Materials	Parameter			
	I_{max} (A)	V_{max} (V)	P_{out}	η (%)
Without AZO	9.6×10^{-4}	0.190	1.8×10^{-4}	0.18
AZO 2 %	1.1×10^{-3}	0.235	2.8×10^{-4}	0.28
AZO 3 %	4.2×10^{-2}	0.159	6.8×10^{-4}	0.68
AZO 4 %	5.3×10^{-2}	0.160	8.5×10^{-4}	0.85

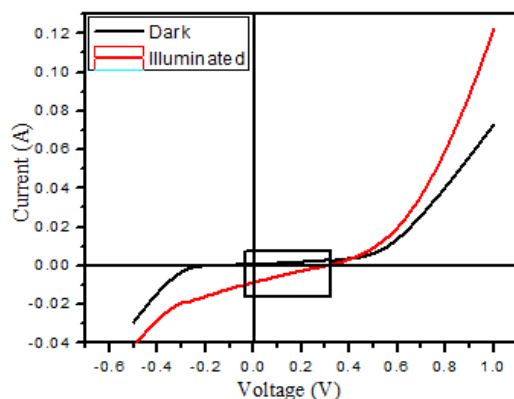


Fig. 6 – Current-voltage (I-V) curves of DSSCs system with Al-doped ZnO 4% as anti-reflection agent

The effect of reflectance on DSSCs efficiency showed that the lower reflectance value could increase the efficiency of DSSCs. The presence of ZnO as anti-reflection agent on the thin layer surface of TiO₂ could absorb maximum photons so that the interaction between dye and photons would be optimized, and the efficiency of the solar cell system would be risen [3]. The crystallite size of ZnO was very influential on anti-reflection properties [19] where the addition of 4% AZO emerged the smallest crystallite size that presented maximum absorption. Besides, the band gap energy of 4% AZO was lower than of 0%, 2% and 3% AZO, so that the excitation of electrons would be easier, and the absorption of light became greater.

REFERENCES

1. R. Vittal, K. C. Ho, *Renew. Sustain. Energ. Rev.* **70**, 920 (2017).
2. J. Wang, R. Chen, L. Xiang, S. Komarneni, *Ceram. Int.* **44**, 7, 7357 (2018).
3. S. Wahyuningsih, G. Fadillah, R. Hidayat, A. H. Ramelan, *Procedia Chem.* **19**, 632 (2016).
4. A.B. Lavand, Y.S. Malghe, *J. Asian Ceram. Soc.* **3**, 305 (2015).
5. M.A Mahadik S.S. Shinde, Y.M. Hunge, V.S. Mohite, S.S. Kumbhar, A.V. Moholkar, K.Y. Rajpure, C.H. Bhosale, *J. Alloy. Compd.* **611**, 446 (2014).
6. M. Sajjad, I. Ullah, M.I. Khan, J. Khan, M.Y. Khan, M. Tauseef, *Result. Phys.* **9**, 1301 (2018).
7. B. Paul, B. Singh, S. Ghosh, A. Roy, *Thin Solid Films* **603**, 21 (2016).
8. Y. Sun, J. Wei, P. Liu, S. Chen, S. Zhang, *ACS Appl. Mater. Interf.* **10**, 18902 (2018).
9. A. Djelloul, Y. Larbah, M. Adnane, B. Labdelli, M.I. Ziane, A. Manseri, A. Messaoud, *J. Nano- Electron. Phys.* **10** No 2, 02036 (2018).
10. S. Thiagarajan, A. Sanmugam, D. Vikraman, *Recent Applications in Sol-Gel Synthesis, Intechopen* (2017).
11. A. Verma, N. Vijayan, *J. Mater. Res.* **28** No 21, 2990 (2013).
12. S. Wahyuningsih, A.H. Ramelan, L.N.M.Z. Saputri, *IOP Conf. Ser. Earth Environ.* **75**, 1 (2017).
13. H. Munawaroh, S. Wahyuningsih, A.H. Ramelan, *IOP Conf. Ser. Mater. Sci. Eng.* **176**, 1 (2017).
14. E. Gungor, T. Gungor, *J. Turkish Chem. Soc. Chem. A* **3** No 3, 453 (2016).
15. M. Vadivel, R.R. Babu, K. Ramamurthi, *Int. J. Chem. Tech. Res.* **7** No 3, 1206 (2015).
16. E.B. Manaia, R. Cristina, K. Kaminski, B.L. Caetano, *Eur. J. Nanomed.* **7** No 2, 109 (2015).
17. E.M. Mkawi, K. Ibrahim, M.K.M. Ali, M.A. Farrukh, A.S. Mohamed, *Appl. Nanosci.* **5**, 993 (2015).
18. A.S. Hossain, M.O. Rahman, D.K. Shaha, *Aus. & NewZe J. Soci. Busi. Env. Sus.* **3** No 1, 18 (2017). <http://www.anjsbes.net.au/index.php/ANJSBES/article/view/17>
19. A. Bedia, F.Z. Bedia, M. Aillerie, N. Maloufi, B. Benyoucef, *Energ. Procedia* **74**, 529 (2015).

Вплив ZnO легованого Al (AZO) як антирефлекторного реагента для системи сонячних елементів, сенсibilізованої барвником

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Наночастинки ZnO, леговані Al (AZO), були синтезовані як антирефлекторний реагент для системи сонячних елементів, сенсibilізованої барвником. ZnO, легований Al, готували методом золь-гелю при 60 °C протягом 3 годин змінюючи концентрацію Al (0, 2, 3 і 4 %). XRD картина AZO показує, що додавання Al впливає на структурні властивості, такі як зменшення розміру кристалітів від 10 нм до 28 нм. Оптичні властивості AZO характеризувалися UV-Vis спектрофотометром. ZnO, легований Al, демонструє явище червоного зсуву на довжині хвилі 320-375 нм. 3 % і 4 % AZO показують два піки, розглянуті як домішки ZnO, легovanого Mg. Спектри пропускання AZO показують збільшення пропускання в області видимого світла на 50-95 %. Спектри відбиття показують величину відбиття, що збільшується в УФ області і зменшується у видимій області (< 50 %). Енергію забороненої зони AZO розраховували за допомогою методу Tauc Plot. Додавання Al може зменшити енергію забороненої зони AZO від 3.45 еВ до 3.23 еВ. ZnO, легований Al, використовується як антирефлекторний реагент для сенсibilізованих барвником сонячних елементів (DSSCs). Система DSSCs з AZO має більш високу ефективність, ніж елементи без антирефлекторного покриття. Ефективність системи сонячних елементів без антирефлекторного шару AZO становить 0.18 %, тоді як ефективність з 2, 3 і 4 % антирефлекторним шаром AZO склала 0.28, 0.68 і 0.85 % відповідно. Максимальна продуктивність системи DSSCs з 4 % AZO (0.85 %) як антирефлекторним реагентом була продемонстрована поліпшеною ефективністю до 372 разів порівняно з системою без антирефлекторного реагента.

Ключові слова: ZnO, легований Al; Структурні властивості, Оптичні властивості, Антирефлексія, DSSCs.