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Effect of Morphological Properties on the Performance of the ZnO-DSSC

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In this study, ZnO nanopowders were synthesized by MW-HTS method using different zinc source and hydroxide sources. The structural and morphological properties of these nanopowders were studied using XRD and SEM. In order to investigate the photoelectrochemical properties of the obtained ZnO nanopowders, ZnO anodes were prepared on the FTO by using the doctor blade method. Solar cell performance of these DSSCs has been analyzed by calculating some solar cell parameters (η%, Voc, FF and Jsc).

Keywords: Zinc oxide, MW-HT, SEM, XRD patterns.

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1. Introduction

One of the technologies used to obtain electricity from solar energy is solar cells. Solar cells (photovoltaic cells) are semiconductor devices that convert sunlight coming into their surface directly into electrical energy. Very little of the energy spent today is produced from solar cells. This is because the efficiency of solar cells is very low and production costs are too high. Therefore, it is necessary to find cheap methods to make solar cells and to increase the efficiency of solar cells produced with existing methods. If we classify solar cells taking into account the technological development until today; Dye-sensitive solar cells (DSSCs), a third generation photovoltaic device, are important devices that are expected to respond to many environmental and energy problems. DSSCs have many advantages. Among these advantages; it is cheap, does not require cleanroom technology and can operate in low light conditions and in full sunlight. One of the closest alternative materials to TiO_2 as semiconductor material for DSSCs is ZnO. A lot of work has been done on ZnO-DSSCs, since they can be easily synthesized in different morphologies (nanorod [1], nanoflower [2], nanotube [3] , nanowire [4], etc.) using different methods and have higher electron mobility than TiO_2.

The surface structure, particle size and shape of the semiconductor material used are very important parameters in terms of the performance of DSSCs. By changing the solution preparation parameters and the production parameters of the used chemical method, semiconductor materials with the desired properties can be easily produced. One of the methods used in the production of nanoparticles (nanopowders) used in the fabrication of DSSCs is the microwave-assisted hydrothermal method (MW-HT). The synthesis of nanoparticles with the MW-HT method has been quite common in recent years. High-quality nanoparticle production can be achieved by simple operations compared to more traditional nanoparticle synthesis methods. What makes this method attractive is the use of microwave radiation, which both shortens the synthesis time and allows the synthesis of high-quality nanoparticles [5].
In this study, ZnO nanopowders were obtained by using different hydroxide source and zinc source. The synthesis of ZnO nanopowders was carried out using the microwave-assisted hydrothermal synthesis (MW-HTS) method. It has been investigated how the photovoltaic performance of the fabricated ZnO-DSSCs is affected by the structural and morphological properties of ZnO nanopowders.

2. Material and Methods

ZnO nanopowders were synthesized by microwave assisted hydrothermal (MW-HT) method. For this, zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) (ZnAc) and zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$ (ZnNt) were used as zinc precursors, respectively. As a source of hydroxide anion, solutions were prepared using sodium hydroxide (NaOH, 98%, Sigma Aldrich) and urea (NH_2CONH_2, UE; ≥99%; Sigma-Aldrich). The codes of the nanopowders are given in Table 1. As indicated in Table 1, zinc nitrate was used as the zinc precursor and urea as the alkaline agent to prepare the sample code Z1. 1.12g zinc nitrate was dissolved in 200ml deionized water, then 24g urea was added. It was observed that the prepared solution was a transparent solution. Zinc acetate as the zinc precursor and urea as the alkali material were used to prepare the Z2 coded sample. Zinc acetate as the starting salt and urea as the alkali material were used to prepare the Z2 coded sample. The solution was prepared by mixing 0.012 mol urea and zinc acetate in deionized water in equal proportions, and the mixture was stirred at 30oC for 15 minutes. The pH value of the mixture was determined to be 7. A transparent solution was obtained by adding KOH to pH = 12. Zinc acetate as the zinc precursor and NaOH as the source of hydroxide were used to prepare the Z3 coded sample. The solution was prepared by mixing 18.4 g NaOH and zinc acetate in deionized water and the mixture was stirred at 30°C for 15 minutes. This solution was also seen to be a transparent solution. Mixing times were set as optimum time intervals from which homogeneous solutions were obtained, and the preparation temperature of the solutions was chosen below the boiling temperature of the solvent. After these solutions were irradiated with microwaves at 300W (150°C) for 10 minutes, the precipitates formed were filtered. After filtration, the washing was carried out using deionized water and ethanol, respectively. The resulting homogeneous precipitates were calcined in an oven at 60°C for 24 hours and then in the air at 500°C for 1 hour to obtain the ZnO nanopowders. For the fabrication of DSSC's, fluorine-doped tin oxide (FTO) glass substrates were chemically cleaned previously. The process of cleaning the substrates was given in detail in our previous work [6]. The paste, which will be used in the DSSC fabrication, was prepared by mixing Zinc nanopowder, Triton-X 100 and acetyl acetone in certain proportions and spread on the surface of the FTO by the doctor blade method. The DSSC assemble process was detailed in our previous study [6]. The active area of the DSSC was about 0.25 cm^2. The CEM Mars 6 model microwave oven was used to produce nanopowders. For structural analysis, BRUKER D2 Phaser model XRD was used. ZEISS Ultraplus model SEM was used to determine surface morphology. FYTRONIX FY-9000 solar simulator I-V measurement system was used for current-voltage (I-V) measurements of DSSC.

Table 1. Deposition parameters of ZnO powders.

Sample Code	Zn Source	Source of Hydroxide
Z-1	$Zn(NO_3)_2$	NH_2CONH_2
Z-2	$Zn(CH_3COO)_2.2H_2O$	NH_2CONH_2
Z-3	$Zn(CH_3COO)_2.2H_2O$	NaOH

3. Results and discussion

X-ray diffraction (XRD) analysis of the powders were carried out with an X-ray powder diffractometer in air with CuKα radiation (wavelength λ=1.5406). XRD patterns of ZnO nanopowders obtained using different solutions are given in the Fig.1. The characteristic peaks of the zincite phase were confirmed with the JCPDS Card (36-1451). The direction of the (1 0 1) was observed in all patterns. Since the peaks of the Z3 have a higher intensity and smaller half-peak widths, they are better crystallized than other powders. In Table 2, crystallite sizes (*D*) calculated using the Scherrer Equation [7] are given. The *D* value for Z3 is greater than that calculated for the other two samples.

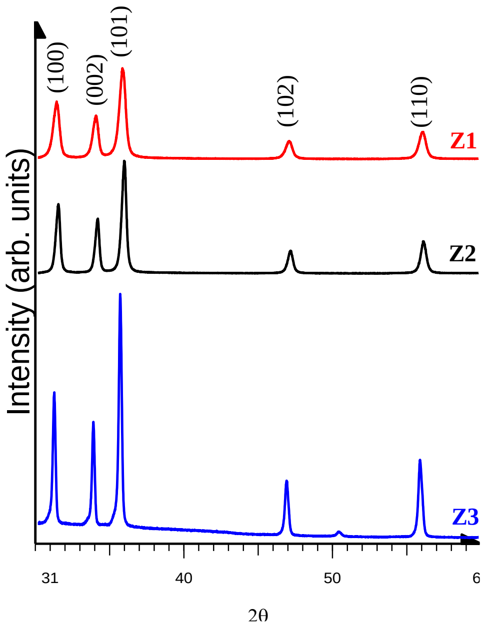

Figure 1. XRD spectra of ZnO nanopowders

Table 2. Structural parameters of ZnO nanopowders

Sample Code	(hkl)	2θ (degree)	d (Å)	D (nm)
Z-1	100	31.289	2.85878	18
	002	33.961	2.63972	
	101	35.784	2.50930	
	102	47.107	1.92920	
	110	56.184	1.63717	
Z-2	100	31.399	2.84902	25
	002	34.071	2.63147	
	101	35.889	2.50221	
	102	47.193	1.92590	
	110	56.244	1.63556	
Z-3	100	31.114	2.87442	38
	002	33.779	2.65350	
	101	35.613	2.52099	
	102	46.931	1.93604	
	110	56.009	1.64187	

Morphological structure is a highly influential parameter on the performance of DSSCs. Since the morphological parameters of the semiconductor material used as photoanode (such as porosity, surface area, pore size, particle diameter, particle shape, and faces) greatly affect the electron diffusion coefficient, many studies have focused on synthesizing ZnO nanostructures with various morphologies for DSSCs [8]–[13]. Fig. 2 shows SEM images of nanopowders. All of the ZnO nanopowders have grown in nanoflower shape. However, the nanoflowers in each sample are formed of different structures. It is observed that the nanoflowers in the Z1 sample are formed of nanoplates, the nanoflowers in the Z2 sample are formed of triangular structures, and the nanoflowers in the Z3 sample are formed nanorods. Rod structures in the Z3 sample are approximately 1 mm in length and approximately 100 nm in diameter. As a result, it can be said that different solvents and salts affect the morphological properties of the produced ZnO nanoparticles.

At a DSSC, J_{sc} and V_{oc} are short circuit current, open circuit voltage, respectively. FF is the filling factor and is a measure of the quality of the cell. FF is expressed by Equation 1.

$$FF = \frac{I_{max} x V_{max}}{I_{sc} x V_{oc}} \quad (1)$$

where V_{max} and I_{max} are voltage and current values at the maximum output power point, respectively. The ratio between the maximum generated power ($Pmax$) and the electrical input power (Pin) is defined as the power conversion efficiency (η%) and is expressed by Equation (2).

$$\eta(\%) = \frac{FF x I_{sc} x V_{oc}}{I_{max} x V_{max}} x 100 \quad (2)$$

From Fig. 4, DSSC parameters of the Z1-DSSC, Z2-DSSC and Z3-DSSC such as Voc , Jsc, FF and η% values are estimated using Equation (1) and (2) [14]. It was seen that the Jsc value calculated for Z3-DSSC was higher than that calculated for other DSSCs. The increase in the value of Jsc can be associated with small nanoparticles and hence large surface area. This results in an increase of Jsc, as the larger surface area provides more dye adsorption [15]. If the power conversion efficiency of the DSSCs fabricated with ZnO powders deposited using different hydroxide source and zinc source are compared, the η values calculated for Z1-DSSC and Z3-DSSCs are two times higher than the η value calculated for Z2-DSSC. These different η values may be related to changing morphology and the improvement in the crystal structure because the morphological features are directly related to dye absorption. In addition, this situation is very important in terms of facilitating electron transfer [16]–[18].

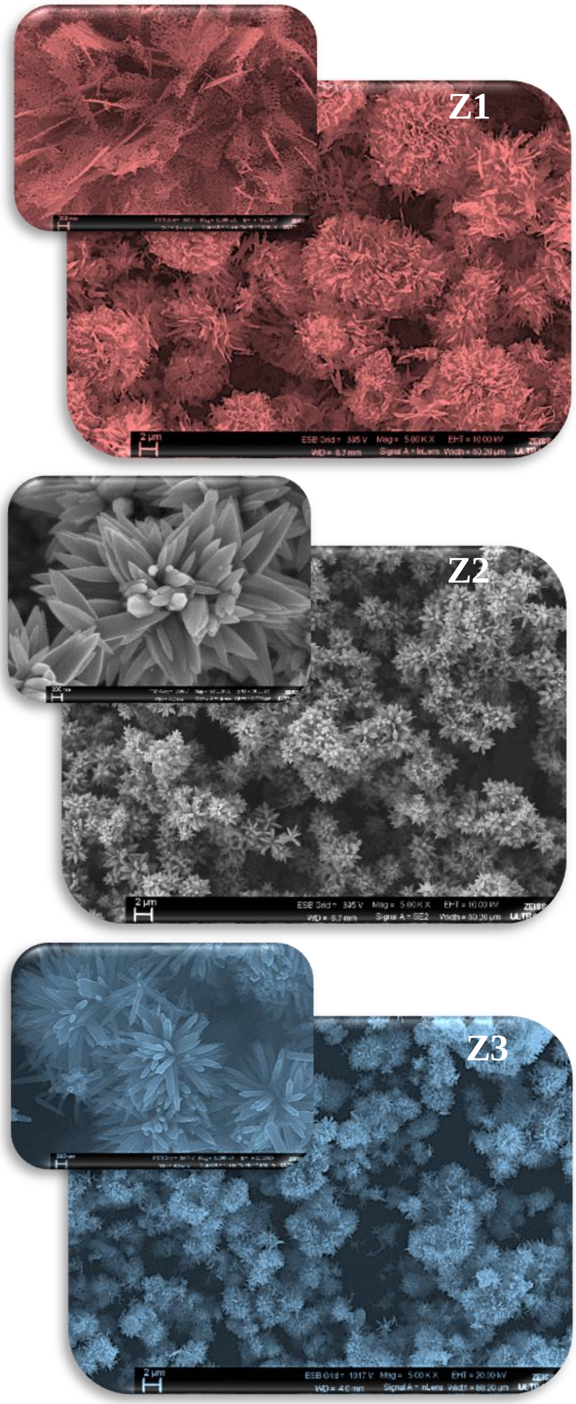

Figure 2. SEM images of the ZnO nanopowders (5.00K and 50.00K)

Table 3. The photovoltaic parameters of ZnO-DSSCs

DSSC	Jsc (mA/cm^2)	Voc (V)	FF	η%
Z1-DSSC	0.66	0.58	0.58	0.23
Z2-DSSC	0.45	0.58	0.42	0.11
Z3-DSSC	1.36	0.46	0.36	0.23

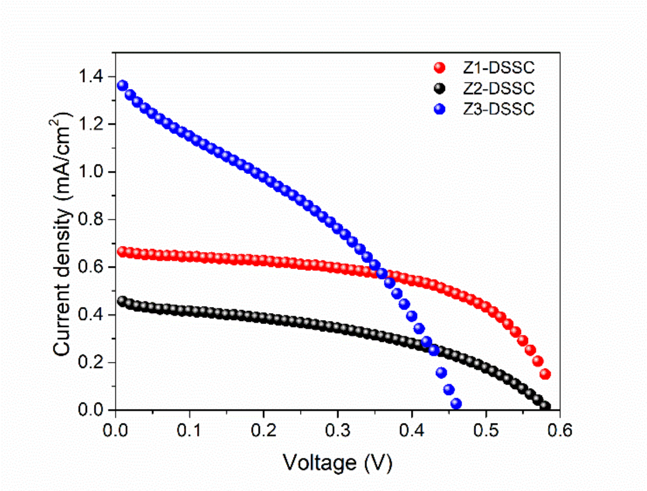

Figure 3. J-V graph of DSSCs at 100 mW/cm^2 power density of light.

4. Conclusion

In this study, ZnO nanopowders were synthesized by the MW-HTS method. The results of the XRD studies indicate that Z3 has the best crystallization among the synthesized powders. It was observed in this study that the zinc source and hydroxide source used in preparing the solutions have a direct effect on the morphological properties of ZnO nanopowders. ZnO-DSSCs were fabricated with these ZnO nanopowders whose structural and morphological characterizations were completed, and then electrical measurements were carried out under simulated sunlight at 100 mW/cm^2. As a result of these measurements, the highest short circuit density was calculated for Z3-DSSC with 1.36 mA/cm^2. Z1-DSSC and Z3-DSSC were found to have the highest efficiency values among the fabricated cells. This may be because the change in morphology increases dye absorption, resulting in more light absorption. Consequently, the η improvement can mainly be attributed to the effect of morphological structure on light trapping of ZnO nanostructures.

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References

[1] Z. Zhang, Y. Chen, and J. Guo, "ZnO nanorods patterned-textile using a novel hydrothermal method for sandwich structured-piezoelectric nanogenerator for human energy harvesting," Phys. E Low-Dimensional Syst. Nanostructures, vol. 105, pp. 212–218, 2019.
[2] Y. Xu J. Jin, X. Li, Y. Han, H. Meng, T. Wang, X. Zhang, "ZnO nanorods patterned-textile using a novel hydrothermal method for sandwich structured-piezoelectric nanogenerator for human energy harvesting," Phys. E Low-Dimensional Syst. Nanostructures, vol. 105, pp. 212–218, 2019
[3] P. Samadipakchin, H. R. Mortaheb, and A. Zolfaghari, "ZnO nanotubes: Preparation and photocatalytic performance evaluation," J. Photochem. Photobiol. A Chem., vol. 337, pp. 91–99, 2017.
[4] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H.Jin Choi, "Controlled growth of ZnO nanowires and their optical properties," Adv. Funct. Mater., vol. 12, no. 5, pp. 323–331, 2002.
[5] S. Horikoshi and N. Serpone, Microwaves in Nanoparticle Synthesis. Wiley-VCH Verlag GmbH & Co. KGaA, 2013.
[6] S. Aksoy, K. Gorgun, Y. Caglar, and M. Caglar, "Effect of loading and standbye time of the organic dye N719 on the photovoltaic performance of ZnO based DSSC," J. Mol. Struct., vol. 1189, pp. 181–186, 2019
[7] B. D. Cullity, Elements of DIFFRACTION. 1978.
[8] M. Abd-Ellah, N. Moghimi, L. Zhang, N. F. Heinig, L. Zhao, J. P. Thomas, K. T. Leung, "Effect of electrolyte conductivity on controlled electrochemical synthesis of zinc oxide Nanotubes and nanorods," J. Phys. Chem. C, vol. 117, no. 13, pp. 6794–6799, 2013.
[9] A. Lamberti, A. Sacco, M. Laurenti, M. Fontana, C. F. Pirri, and S. Bianco, "Sponge-like ZnO nanostructures by low temperature water vapor-oxidation method as dye-sensitized solar cell photoanodes," J. Alloys Compd., vol. 615, no. S1, pp. S487–S490, 2015.
[10] C. Pei Lee, J. Chieh Lin, Y. Chun Wang, C. Yu Chou, M. Hsin Yeh, R. Vittala and K. Chuan Ho, "Synthesis of hexagonal ZnO clubs with opposite faces of unequal dimensions for the photoanode of dye-sensitized solar cells," Phys. Chem. Chem. Phys., vol. 13, no. 47, pp. 20999–21008, 2011.
[11] L. Bahadur and S. Kushwaha, "Structural and optical properties of tripod-like ZnO thin film and its application in dye-sensitized solar cell," J. Solid State Electrochem., vol. 17, no. 7, pp. 2001–2008, 2013.
[12] Y. Wang, X. Cui, Y. Zhang, X. Gao, and Y. Sun, "Preparation of Cauliflower-like ZnO Films by Chemical Bath Deposition: Photovoltaic Performance and Equivalent Circuit of Dye-sensitized Solar Cells," J. Mater. Sci. Technol., vol. 29, no. 2, pp. 123–127, 2013
[13] Y. Zhou, C. Liu, M. Li, H. Wu, X. Zhong, D. Li, D. Xu, "Fabrication and optical properties of ordered sea urchin-like ZnO nanostructures by a simple hydrothermal process," Mater. Lett., vol. 106, pp. 94–96, 2013.
[14] T. Marimuthu, N. Anandhan, R. Thangamuthu, and S. Surya, "Influence of solution viscosity on hydrothermally grown ZnO thin films for DSSC applications," Superlattices Microstruct., vol. 98, pp. 332–341, 2016.
[15] H. Abdullah, S. Mahalingam, and I. Ashaari, "Morphological, photovoltaic, and electron transport properties of In2O3-based DSSC with different concentrations of MWCNTs," Ionics (Kiel)., vol. 22, no. 12, pp. 2499–2510, 2016.
[16] R. Vittal and K. Ho, "Zinc oxide based dye-sensitized solar cells : A review," Renew. Sustain. Energy Rev., vol. 70, no. March 2016, pp. 920–935, 2017.

[17] S. Aksoy, O. Polat, K. Gorgun, Y. Caglar, and M. Caglar, "Li doped ZnO based DSSC: Characterization and preparation of nanopowders and electrical performance of its DSSC," Phys. E Low-Dimensional Syst. Nanostructures, vol. 121, no. April, p. 114127, 2020.
[18] S. H. Jeong, B. N. Park, S. B. Lee, and J. H. Boo, "Study on the doping effect of Li-doped ZnO film," Thin Solid Films, vol. 516, no. 16, pp. 5586–5589, 2008.