Efficiency of Nb-Doped ZnO Nanoparticles Electrode for Dye-Sensitized Solar Cells Application

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Abstract. The technological of Dye-sensitized solar cells (DSSCs) had been improved for several years. Due to its simplicity and low cost materials with belonging to the part of thin films solar cells. DSSCs have numerous advantages and benefits among the other types of solar cells. Many of the DSSC devices had use organic chemical that produce by specific method to use as thin film electrodes. The organic chemical that widely use to establish thin film electrodes are Zinc Oxide (ZnO), Titanium Dioxide (TiO\textsubscript{2}) and many other chemical substances. Zinc oxide (ZnO) nanoparticles had been used in DSSCs applications as thin film electrodes. Nanoparticles are a part of nanomaterials that are defined as a single particles 1-100 nm in diameter. From a few year ZnO widely used in DSSC applications because of its optical, electrical and many others properties. In particular, the unique properties and utility of ZnO structure. However the efficiency of ZnO nanoparticles based solar cells can be improved by doped various foreign impurity to change the structures and properties. Niobium (Nb) had been use as a dopant of metal oxide thin films. Using specification method to doped the ZnO nanoparticles thin film can improved the efficiencies of DSSCs. The efficiencies of Nb-doped ZnO can be compared by doping 0 at wt% to 5 at wt% in ZnO nanoparticles thin films that prepared by the spin coating method. The thin film electrodes doped with 3 at wt% represent a maximum efficiencies with the lowest resistivity of 8.95×10\textsuperscript{-4} Ω cm.

1. Introduction
Solar energy is one of the most essential energy source for renewable energy. This solar energy is the clean energy with a substantial renewable resources. Dye-sensitized solar cells (DSSCs) seem to be fond of commonly, this is because of the cost value to prepared the materials and invent the device is less than any other solar cells application. DSSCs were first studied and researched vastly after B. O’Regan et al. [1] reported the efficiency of DSSCs in 1991. The technology that attractive for established DSSCs is the synthesis of thin films electrode. There are so many preparation method to prepare compounds materials and many method for electrode fabrications. The usage of ZnO nanoparticles is attractive for thin film electrodes to prepared the thin films electrodes [2],[3],[4],[5],[6] and [7] because of its good characteristics[8],[9] and [10]. Even though ZnO nanoparticles is a part of nanomaterials that has a crystal structure of wurtzite (B4) at ambient conditions. The ZnO wurtzite structure has a hexagonal unit cell of two lattice parameters. However, hexagonal structure has lo efficiencies in such a way of one-dimentional (1D) nanostructures had less surface area. Therefore, the used of ZnO nanoparticles based solar cells can be improved by optimize the crystal srutecture of active layer. Zno is the II-VI semiconductor group with a wide bandgap about 3.2 - 3.4 eV and the wurtzite structure by lattice parameters of a = b = 0.325 nm and c = 0.520 nm.
Various foreign impurity had doped into ZnO nanoparticles thin films to changed its characteristics and properties. Many of compound materials had been use for doping to improve efficiencies of thin films electrode. Especially, an elements from Group IIIA (B, Al, Ga, In, etc.), IVA (Si, Ge, Sn, etc.), IIIB (Sc, Y, etc.) and IVB (Ti, Zr, etc.). Furthermore, the transition metals has been researched for using as dopant material for instance Mn, T, La, Fe, etc. Meanwhile, using Niobium (Nb) as dopant material is very attractive by Nb$^{5+}$ and Zn$^{2+}$ there is only 3 valence difference, thus, Nb atom can be grant more than 1 electron to the electrical conductivity. Also Nb have a smaller ionic radius of 0.64 Å and higher covalent radius of 1.34 Å compared to Zn values that have an ionic radius of 0.74 Å and covalent radius of 1.25 Å.

In this article, we reported the effect and efficiencies of Nb-doped ZnO nanoparticles (Nb:ZNP) electrode based on DSSCs. In the usage as thin film electrode in DSSCs, we focusing on the scope of structural and electrical properties with a good efficiencies to using for DSSCs applications. Although the amount of Nb dopant is different at wt% of percentages from 1 at wt% to 5 at wt%.

2. Experimental details

2.1 Electrode and Counter electrode preparation

In order to fabricated the thin film electrode for DSSCs. A ZnO nanoparticles solution were prepared by dissolved 2 g of zinc acetate, anhydrous [Zn(CH$_3$COO)$_2$, Wako] in 50 mL of 1 M methanolic solution and keep under stirring for 24 hours. Then add a few drops of sodium hydroxide 1 mol/L solution (NaOH, Junsei) while keep stirring the solution and mix it up well into a white suspension solution. Then keep it under stirring for 24 hours at room temperature. Then drop wired with niobium (V) ethhoxide in a different weight percent of solution from 0 at wt% to 5 at wt% and mix it well. The Nb:ZNP solution will get into a viscous suspension paste.

For the fabrication of thin film counter electrode using Platinum paste. By dissolved 3 g tetraammine platinum(II) chloride [Pt(NH$_3$)$_4$Cl$_2$.H$_2$O, Kaida] in 50 mL of 0.1 M Hydrochloric acid solution [HCl, Sigma-Aldrich] and stirred for 2 hours at room temperature until it get into sticky paste.

Nb:ZNP paste and Pt paste were adopted on 5 x 4 cm$^2$ conducting fluorine-doped SnO$_2$-(FTO)-coated glass substrate (resistance sheet: ~7 Ω/sq, Pilkington). FTO glass sheets were first washed with DI water then sonicate in ultrasonic cleaner (JAC4020, Ultrasonic) in acetone solution (CH$_3$COCH$_3$, Duksan) for 1 hour. Then drying under dry air jet. The FTO were coated with Nb:ZNP paste and Pt paste. Using spin coating technique to figure 2 x 2 cm$^2$ layers. Then the layers were heating at 450°C for 1 hour.

2.2 Fabrication of DSSCs

Nb:ZNP coated on FTO glasses with difference wt%, used as an electrode were fixed with a distance of 50 µm by spacers (Himilian). For counter electrode using Pt coated on FTO glass as a counter electrode. The Nb:ZNP electrode and Pt counter electrode are put together into DSSCs in the structure of FTO glass/ Nb:ZNP electrode/ Electrolyte/ Pt counter electrode/ FTO glass. The schematic of DSSCs can be shown in figure 1.

![Figure 1. The schematic of DSSCs](image-url)
3. Result and Discussion
The chemistry analytical to analyze the crystalline structure of the thin film electrode can be analyzed by XRD analysis. The XRD pattern is shown in figure 2. The XRD patterns are exposes that it belong to the crystal structural of the hexagonal structure of wurtzite (B4) structure which growth through (002) and (101) orientation plan. The normally ZnO films that prepared by annealing at the temperature about 400 °C to 500°C normally growth through (002) orientation plan. The strongest intensity of Nb:ZNP films have the peak at an angle of 36.21° (2θ) corresponding to the ZNP (002) and (101) plan and observed corresponding to the Nb (010) plan.

Figure 2. The XRD pattern of Nb-doped ZnO nanoparticles at difference wt% 

In figure 3 is shown the SEM images of Nb:ZNP thin film electrodes that coated on FTO glasses. The morphology of Nb:ZNP were observed as clear spherical particles. The figures of SEM micrographs show the morphologies of Nb:ZNP in different doping wt%. All the result show as nanoparticles in the uniform spherical morphology with the size distribute at diameter about 25 nm.
Figure 3. SEM images of Nb-doped ZnO nanoparticles at difference wt%

The electrical properties of Nb:ZNP thin film electrodes can be analyse by the I-V curve of Nb:ZNP in different doping wt% from 1 at wt% to 5 at wt%. in figure 4.

Figure 4. I-V curve of Nb-doped ZnO nanoparticles at difference wt%

All the DSSCs which was tested under a solar simulation AM 1.5 light illumination at 200 mW/cm². The open circuit voltage (VOC), current density (JSC), fill factor (FF) and efficiency (η) can summarize in table 1. The conversion efficiency of DSCs with Nb:ZNP and ZNP film electrode can calculated in equation (1),

$$\eta = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}}$$

Table 1. Solar cells parameter characteristics of DSSCs using Nb:ZNP thin film electrodes

| Sample | $V_{OC}$ (V) | $J_{SC}$ (mA/cm²) | FF (%) | Efficiency (%) |
|--------|--------------|-------------------|--------|----------------|
| B      | 0.452        | 11.4              | 19.32  | 8.18           |
| C      | 0.536        | 13.6              | 22.82  | 8.48           |
| D      | 0.627        | 16.3              | 38.26  | 9.02           |
| E      | 0.582        | 15.1              | 26.84  | 8.68           |
| F      | 0.524        | 14.3              | 24.22  | 8.52           |

The DSSCs using Nb:ZNP in sample D (3 wt%) was highest energy conversion efficiency of 9.02%, ISC of 16.3 mA/cm², VOC of 0.627 V and FF of 38.26% which more than that other electrodes with different doping wt%.

4. Conclusion

The synthesis and operation of DSSCs with Nb-doped ZnO nanoparticles using as thin film electrode can be improved the electrical properties and performance of ZnO nanoparticles. It can be concluded that Nb did not affect the ZnO structure. It was observed that the absorption intensity of ZnO slightly
increased with increasing Niobium content. Which can improved the advantages of organic semiconductors (flexibility, solutions processing) with those of inorganic semiconductors (stability, high dielectric constant, which facilitates carrier generation processes, a high carrier mobility and thermal morphological stability of the blended materials).

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