Effect of SnO$_2$ Nanoparticles on Band Gap Energy of $x$(SnO$_2$)-$y$(Ag)-β-Carotene/FTO Thin Film

Solehudin$^1$, Markus Diantoro$^{1,2,*}$, Ulwiyatus Sa’adah$^1$, Arif Hidayat$^{1,3}$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia
$^2$Center of Advanced Materials for Renewable Energy, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia
$^3$Optics and Computational Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5 Malang 65145, Indonesia

*Corresponding author’s email: markus.diantoro.fmipa@um.ac.id

Abstract. SnO$_2$ shows higher electron mobility (100–200 cm$^2$V$^{-1}$s$^{-1}$) than TiO$_2$ (0.1–1.0 cm$^2$V$^{-1}$s$^{-1}$), indicated that it has higher electron diffusion transport. As a result, it may minimize interfacial charge recombination losses to oxidized redox species in the electrolyte or solid-state hole transporter, thus enhancing solar cell device performance. Many researchers have done the synthesis of SnO$_2$ by controlling morphologies and architectures to optimize solar cells performance. Unfortunately, it’s just view of them investigated the properties of the composite SnO$_2$ with metallic materials and its potentials for solar cell devices. In this work, SnO$_2$ nanoparticles, Ag nanoparticles, and β-Carotene were composited with a various mass portion of SnO$_2$ nanoparticles to control the band gap energy and the other optoelectronic properties. The composites subsequently were deposited on FTO substrates using spin coater. The thin film of SnO$_2$-Ag-β-Carotene/FTO composites were characterized by UV-Vis, FTIR spectroscopy, and XRD measurements. We found that the maximum direct band gap energy of 3.74 eV was reached by the sample 20, while the minimum direct band gap energy of 3.54 eV was achieved by sample 15. The maximum indirect band gap of 1.59 eV resulted in sample 20. On the other hand, the minimum value of the indirect band gap is 1.27 eV achieved by sample 25. Both direct and indirect Tauc plot analysis showed that there was no significant influence of SnO$_2$ mass portion on the band gap energy of SnO$_2$-Ag-β-Carotene composite thin film. But it was a fact that each mass fraction composites had different band gap energy. This fact can be used to control the band gap energy to optimize the use of SnO$_2$ composite as DSSC electron transporting electrode. The FTIR spectroscopy and XRD result were also detail examined in this work.

Keywords: SnO$_2$-Ag-β-Carotene/FTO composites, UV-Vis spectroscopy, band gap energy, DSSC

1. Introduction

In the past several decades, Dye-Sensitized Solar Cells (DSSCs) emerged as a generation of cost-effective solar cells with the highest performance have been those fabricated using TiO$_2$ nanoporous films as the electron transporting electrode [1]. However, further performance of the TiO$_2$-based DSSCs was limited due to TiO$_2$ low electron mobility. SnO$_2$ has over two orders of magnitude higher
electron mobility (−100 – 200 cm²/(V.s)) than TiO₂ (0.1 - 1.0 cm²/(V.s)) in their bulk single crystal phases [2], indicated that it has higher electron diffusion transport. As a result, it may minimize interfacial charge recombination losses to oxidized redox species in the electrolyte or solid-state hole transporter, thus enhancing solar cell device performance [3]. SnO₂ is also has a larger band gap (3.6 eV) than TiO₂ (3.2 eV), which would create fewer oxidative holes in the valence band (VB), thereby minimizing the dye-degradation rate and facilitate the long-term stability of DSSCs [4]. On the other hand, larger band gap also means that higher energy was necessary to exciting the electron of SnO₂.

Many researchers have reported the synthesis of SnO₂ with different morphologies and architectures ranging from zero-dimensional (0D) [5,6], one-dimensional (1D) [7–10], and two-dimensional (2D) [11,12] structures to complex three-dimensional (3D) architectures assembled from nanoparticles (0D) [13], nanorods (1D) [14], nanosheets (2D) [15] and core-shell as building blocks [16]. Unfortunately, it's just view of them investigated the properties of the composite SnO₂ with other materials such as polymer [17], metallic and its potentials for solar cell devices. In this work, SnO₂ nanoparticles, Ag nanoparticles, and β-Carotene were composited with the various mass fraction of SnO₂ to control the band gap energy to optimize its application in Dye-Sensitized Solar Cells (DSSC). This work is closely related to our previous research on the synthesis of Ag NPs [18] and its usage in electrical properties modification [19,20]. The competition of SnO₂ NPs and Ag NPs is studied related to its structure as well as band gap.

2. Materials and Methods

Silver nanoparticles (Ag NPs) was prepared according to the chemical reduction method. The materials used are silver nitrate (AgNO₃) as a precursor, sodium borohydride (NaBH₄) as a reducing agent, and Mercaptosuccinic acid (MSA) as a stabilizer to prevent the nanoparticle from agglomerating. Tin oxide nanoparticles (SnO₂ NPs) have been obtained by a sol-gel method from stannic chloride dihydrate (SnCl₂·2H₂O). In a typical synthesis procedure, 8 g SnCl₂·2H₂O was dissolved in 25 ml methanol under continuous stirring at 400 rpm. After 30 minutes, 0.1 M polyethylene glycol (PEG, Mw=6000) added into the solution. The next step was refluxed at 200 rpm for 5 hours till and the temperature maintained at 120 °C. After the solution transformed into amber one, keep it to obtain the precipitate. Further, the yellowish precipitate was filtered and annealed at 100 °C for 3 hours. Finally, the precipitate calcined for 1 hour at 350 °C resulting the SnO₂ nanoparticles.

The composite of x(SnO₂)-y(Ag)-β-Carotene solutions were prepared by adding 0.04 Ag NPs into one mL H₂PO₄ stirred for 1 hour at 1000 rpm. 0, 0.005, 0.010, 0.015, 0.02 and 0.025 g of SnO₂ was added into the solutions then stirred for 1 hour at 1000 rpm. The fraction of SnO₂ NPs also followed by AgNPs of 0.04, 0.045, 0.050, 0.055, and 0.060 g. Subsequently, about 0.013 g of β-Carotene in 0.1 M solutions were added into the SnO₂-Ag solutions and then stirred and sonication each for 2 hours. The fraction of β-Carotene was kept constant. The composite thin films were deposited on FTO substrate by using a spin coating method for 10 seconds at the speed of 1500 rpm. The produced film was then annealed at 100 °C for 4 hours. These samples are labelled as 0, 5, 10, 15, 20, and 25 or associated to the fraction of SnO₂ respectively as 0, 0.09, 0.16, 0.23, 0.28, and 0.33 to the total mass.

The functional chemical bonds that were appeared in the sample was characterized using spectrophotometer Shimadzu IR Prestige-21. The crystallinity, grain size, and phase that was formed in the samples. Characterized using diffractometer x-ray PanAnalytical XPERT-type Pro with Cu-Kα radiation sources (λ = 1.54060 Å). The optoelectronic property (band gap energy) was characterized using spectrophotometer UV-1700 Series. The UV-Vis spectrophotometer results were then analyzed using Tauc plot linear fitting with both direct and indirect approach. The fitting processes were a done using Microcal Origin software.
3. Results and Discussion

Figure 1 represents the XRD patterns of the (Ag-SnO₂) NPs-β-Carotene thin films. Generally, it could be seen that four peaks appear at 37.80°, 44.87°, 64.53° and 77.53° belong to silver with low intensity. There are peaks appear at 26.60°, 33.90°, 37.94°, 51.75°, and 64.77° belong to SnO₂ NPs detected in the sample 0, 5, 10, and 15. The 26.60°, 33.90° peaks on 0 g SnO₂ shows that the SnO₂ of the FTO substrate was detected due to the thickness of the film was very thin.

![X-ray diffraction patterns of SnO₂-Ag-β-Carotene/FTO composite thin films with various SnO₂](image)

Figure 1. X-ray diffraction patterns of SnO₂-Ag-β-Carotene/FTO composite thin films with various SnO₂.

FTIR measurements were carried out to find the functional groups of films. Some peaks according to the functional groups of chemical bonds are drawn in Figure 2. The results of the analysis show that some peaks identified as C-H, O-H, N-H, O-Sn-O, and M-O. The peaks at a wave number of 592.15 cm⁻¹ belong to the type of (M-O) metallic oxygen bond; it assigns to silver which is bond the oxygen. Stretching modes of the O-Sn-O functional group shown by existing at wave number 827.46 cm⁻¹. The wave number about 3496.94 cm⁻¹, which is in the range of 3349-3409 cm⁻¹ related to stretching vibrations of the O-H bond. Beside, O-H stretching vibration also identified at 359 cm⁻¹ indicating the presence of hydroxyl group. The peak at 1319.31 cm⁻¹ suggests the appearance of a C-H bond corresponds to the β-carotene functional group. At wave number 2833.43 cm⁻¹, investigated as N-H functional group. There are no remarkable differences since SnO₂ NPs added in a tiny portion.
The optoelectronic property represented by band gap energy of SnO$_2$-Ag-β-Carotene/FTO composite thin films was characterized using UV-Vis spectrometer. The UV-Vis Spectra of SnO$_2$-Ag-β-Carotene/FTO composites thin film with various SnO$_2$ mass portions were shown in Figure 3. The band gap energy data can be extracted from UV-Vis spectra using Equation (2) based on linear fitting.

\[
\alpha = A \frac{(h\nu - E_g)^2}{h\nu} \quad (1)
\]

\[
(\alpha h\nu)^2 = A^2 h\nu - A^2 E_g \quad (2)
\]

\[
y = hx + a \quad (3)
\]

where \(a\) is the absorption coefficient, \(h\) is Planck constant, \(\nu\) is UV-Vis electromagnetic frequency, and \(E_g\) is the band gap energy. Equation (1) can be rearranged into Equation (2) which is analog to a linear of Equation 3. From Equation (2) we can make \((\alpha h\nu)^2 - h\nu\) plot called the Tauc plot from which we can get the band gap energy information. The band gap energy then is

\[
E_g = b/m \quad (4)
\]

where \(b\) is \((\alpha h\nu)^2\) value when \(h\nu\) equal to zero and \(m\) is the gradient of the linear fit of the Tauc plot. The Tauc plot (direct), Tauc plot (indirect), band gap energy (direct), and band gap energy (indirect) of SnO$_2$-Ag-β-Carotene/FTO composite thin films are shown in Figure 4, 5, 6, and 7 respectively.

Figure 2. FTIR spectra of SnO$_2$-Ag-β-Carotene/FTO thin films with 0 g (black), and 25 g of SnO$_2$ (red).
Figure 3. UV-Vis data plot of various SnO$_2$ in SnO$_2$-Ag-β Carotene/FTO thin films
Figure 4. Tauc plot (direct) analysis result of UV-Vis data plot of various SnO₃ in SnO₂-Ag-β Carotene/FTO thin films.
Figure 5. Tauc plot (indirect) analysis result of UV-Vis data plot of various SnO$_2$ in SnO$_2$-Ag-β Carotene/FTO thin films
Figure 6. Band gap energy (direct) as the function of mass portion of SnO$_2$ in SnO$_2$-Ag-β Carotene

Figure 7. The band gap energy (indirect) as the function of mass portion of SnO$_2$ in SnO$_2$-Ag-β Carotene

Figure 6. shows that the maximum direct band gap energy of 3.74 eV was achieved by sample 20 of a SnO$_2$ fraction, while it showed a minimum value of direct bandgap energy of 3.54 eV by sample 15. Figure 7. shows that the SnO$_2$:Ag:β-Carotene mass portion gave maximum indirect band gap energy of 1.59 eV yielded by sample 20, while a minimum value of indirect band gap energy of 1.27 eV was reached by sample 25. For direct Tauc plot analysis, the slope of the linear fitting curve was 0.10454 and -0.13739 for indirect Tauc plot analysis. These results showed that there was no significant influence of SnO$_2$ mass portion on the band gap energy of SnO$_2$-Ag-β Carotene composite thin film for both direct and indirect Tauc plot analysis. But it was still an important fact that each mass variation composites had different band gap energy. In the case of indirect analysis, the SnO$_2$
fraction tends to decrease the band gap. This fact can be used to control the band gap energy to optimize the usage of SnO$_2$ composite as DSSC electron transporting electrode.

4. Conclusion

We have successfully fabricated a thin film of x(SnO$_2$)$_y$(Ag)$_z$-β Carotene/ITO PET at the different SnO$_2$ portion. The maximum direct band gap energy at 3.74 eV was reached by the sample 20, while the minimum direct band gap energy of 3.54 eV was achieved by sample 15. The maximum indirect band gap of 1.59 eV resulted in sample 20. On the other hand, the minimum value of the indirect band gap is 1.27 eV achieved by sample 25. Both direct and indirect Tauc plot analysis showed that there was no significant influence of SnO$_2$ mass portion on the band gap energy of SnO$_2$-Ag-β Carotene composite thin film. But it was still a remarkable fact that each mass variation composites had different band gap energy. This fact can be used to control the band gap energy to optimize the use of SnO$_2$ composite as DSSC electron transporting electrode. The competition between SnO$_2$ NPs and Ag NPs may take a role in this composite film.

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