Band Gap Shift and Electrical Conductivity of (Ag-xSnO\textsubscript{2})NPs-β-Carotene Thin Film

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Abstract. This research proposed to use β-carotene as a conducting polymer to encapsulate Ag-SnO\textsubscript{2} to enhance the electrical conductivity, so it becomes more new green technology. Initially, the synthesis of Ag and SnO\textsubscript{2} nanoparticles was performed by chemical reduction and a sol-gel method respectively. The (Ag-xSnO\textsubscript{2}) nanoparticles with β-carotene composite were synthesized by the blending method and followed by deposition using a spin coating method. Samples of nanoparticles and films were characterized using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to obtain their structure, morphology, and size. Based on the analysis of XRD pattern, it was shown that the grain size of Ag and SnO\textsubscript{2} are 25.50 nm and 37.79 nm respectively. Optical properties of samples which were investigated by using UV-vis spectroscopy to find out the energy gap based on the Tauc plot method. It was found that the energy gap of (Ag-xSnO\textsubscript{2})NPs-β-carotene thin film reduce which the average of ~3.7 eV. It was also shown that inducing of SnO\textsubscript{2} nanoparticles could enhance the electrical conductivity of films with the increase of SnO\textsubscript{2}. This combination of reducing the band gap and enhancing its electrical conductivity opens this composite for solar cell application.

Keywords: Bandgap shift, electrical conductivity, (Ag-SnO\textsubscript{2})NPs-β-carotene composite, thin film

1. Introduction
Metal-oxide semiconductors such as SnO\textsubscript{2}, TiO\textsubscript{2}, and ZnO are intensively used in photoelectrochemical applications. Among the semiconductor materials, SnO\textsubscript{2} shows relatively high electron mobility (~250 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}), high electron-hole separation ability, and high transport properties [1]. Moreover, SnO\textsubscript{2} as a stable n-type semiconductor with a wide band gap ($E_g = 3.6$ eV) has been used for various applications, including a solid-state gas sensor, photovoltaic devices, transparent conductive films, and dye-based solar cells [2]. In the case of dye-sensitization, the conduction band edge has to match the lowest excited state of the day molecule to enable effective electron transfer from the molecules excited state to the semiconductor’s conduction band [3].

Organic dyes can easily found in nature, such as chlorophyll, anthocyanins, and carotenoid which are contained in any plants and fruits. Carotenoids are lipid-soluble C40 tetraterpenoids. Carotenoid is one of the conducting polymers that can conduct electricity in the range of semiconductors [4]. The
hydrocarbon carotenoids which are known as \( \beta \)-carotene is an asymmetrical molecule with a chemical structure of \( \text{C}_{40}\text{H}_{56} \). \( \beta \)-carotene has conjugated bonds; there are single and double bonds as 11 \[12\]. In conducting polymers, the charge carriers can move easily on the conjugated polymer chain by hopping mechanism. Thus \( \beta \)-carotene is expected to be a good candidate as organic electrical applications. These doped conducting polymers play a key role in the optoelectronic and electrochemical devices. To modify the electrical properties of this material, we can use metallic based materials. Some elements in the transition group such as Mn, Fe, Cu, Zn, Pt, Au, Ag has been used to modifying the material properties \[4\]. Among metallic nanoparticles, the silver nanoparticles have a typical attractive characteristic, they are high electrical conductivity, stable under the chemical environment, and can be used as a catalyst \[5\]. So far there is no intensive study related to synthesis \((\text{Ag-SnO}_2)\) NPs-\( \beta \)-carotene thin film. In this work, we report the band gap shift and electrical conductivity of the films with the various mass of \( \text{SnO}_2 \).

2. Materials and Methods

2.1. Synthesis of \( \text{Ag} \) and \( \text{SnO}_2 \) Nanoparticles

Silver nanoparticles (AgNPs) were prepared according to the chemical reduction method \[5\]. The materials used are silver nitrate \((\text{AgNO}_3)\) as a precursor, sodium borohydride \((\text{NaBH}_4)\) as a reductor, and mercaptosuccinic acid \((\text{MSA})\) as a stabilizer to prevent the nanoparticle from agglomerating. Tin oxide nanoparticles \((\text{SnO}_2 \text{NPs})\) have been obtained by the sol-gel method \[6\] from stannic chloride dihydrate \((\text{SnCl}_2\cdot2\text{H}_2\text{O})\). In a typical synthesis procedure, 8 g \( \text{SnCl}_2 \cdot 2\text{H}_2\text{O} \) was dissolved in 25 ml methanol under continuous stirring at 400 rpm. After 30 minutes, 0.1 M polyethylene glycol \((\text{PEG}, M_s = 6000)\) 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, kept 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 \( \text{SnO}_2 \) nanoparticles.

2.2. Preparation of \((\text{Ag-SnO}_2)\) NPs-\( \beta \)-Carotene Thin Film

Basic of an experimental method for synthesis \((\text{Ag-SnO}_2)\)NPs-\( \beta \)-Carotene composite was blending method. Firstly, 0.04 g AgNPs dissolved in 1 mL of phosphoric acid \((\text{H}_3\text{PO}_4)\) under for 1 hour. \( \text{SnO}_2 \)NPs, as prepared, was added to the solution with the various mass; they were 0.05 g, 0.010 g, 0.015 g, 0.020 g, and 0.025 g. After 2 hours, 0.1 M \( \beta \)-carotene was added into the solution. The important one of this process was sonication to obtain a homogeneous solution with small particles; it ran for 2 hours. For comparison, the control AgNPs without adding of \( \text{SnO}_2 \)NPs was named as 0 g sample. Deposition method used in this current work was a spin coating on the glass substrate. The composite was deposited for 10 s with the rate of 1500 rotation per minute (rpm). A thin film of \((\text{Ag-SnO}_2)\)NPs-\( \beta \)-Carotene obtained after annealing at 100 °C for about 4 hours.

2.3. Characterization of \((\text{Ag-SnO}_2)\) NPs-\( \beta \)-Carotene Thin Film

The phase identification of the resulting samples investigated by X-ray diffraction (X’Pert Pro) measured with Cu-K\(\alpha \) radiation \((\lambda = 1.540598 \text{ Å})\) in the range of 20 10-90° and a step size as 0.02°. The surface morphology and elemental compositions were characterized using SEM-EDAX (FEI INSPECT-S50). Fourier Transform Infrared spectroscopy measurement was recorded by Shimadzu FTIR (IR-Prestige 21). UV-Vis absorption was obtained from (UV-1700 Pharmaspec Shimadzu) UV-Vis spectrophotometer. Electrical properties of the samples were measured by the four-point probe method.

3. Results and Discussion

3.1. XRD Analysis

The phase purity and crystallinity of synthesized products were analyzed by x-ray diffraction (XRD). The diffractogram of silver nanoparticles displayed in Figure 1. Several identified peaks of intensity at 20 are 38.19°, 44.38°, 64.53°, 77.53° and 81.69°, according to Bragg planes of \((111), (002), (022), (113), \)
and (222) respectively. Analyzing was done using Celref with $Fm\bar{3}m$ space group of AMCS 0011135. The lattice parameter of $a = 4.0862$ Å as input model. After the refinement process, we obtained that the lattice parameter decreases to $a = 4.0834$ Å. The crystallite size was calculated using the Scherer equation, where in this case we use (111) plane as the highest plane. The crystallite size of AgNPs falls at 25.20 nm.

The x-ray diffraction pattern of SnO$_2$NPs prepared by the sol-gel method shown in Figure 2. There were several main identified peaks indexed using the Celref software at $2\theta = 26.60^\circ$, $33.90^\circ$, $37.94^\circ$, $51.75^\circ$, $54.77^\circ$, dan $64.77^\circ$ according to Bragg planes of (110), (101), (020), (121), (220), and (112) respectively.

The peaks observed in the XRD patterns are in good agreement with the standard of COD 9007433. It corresponded to the rutile type of SnO$_2$NPs which has a tetragonal crystal structure. Lattice parameters of refinement give $a = 4.7419$ Å and $c = 3.1881$ Å, it was rather difference with input model as $a = 4.7370$ Å and $c = 3.1850$ Å. The crystallite size of the prepared samples is 37.79 nm as calculated by Debye Scherrer equation.
Figure 3. Typical x-ray diffraction patterns of (Ag-SnO$_2$)NPs-β-Carotene thin films with a various mass of SnO$_2$NPs.

Figure 3 represents the x-ray diffraction patterns of the (Ag-SnO$_2$)NPs-β-Carotene thin films. All histogram were rearranged start from 2θ = 10° up to 85°. Generally, it could be observed that two peaks appear at 37.80° and 44.87° belong to silver with low intensity. There are no clear peaks of SnO$_2$NPs detected in the 0 g, 0.005 g, 0.010 g, and 0.015 g of SnO$_2$NPs mass since the film is extremely thin. Specifically, several peaks of SnO$_2$NPs seen in the mass variations of 0.020 g and 0.025 g, two of them are identified at 26.57° and 33.85°, represent two strong peaks of tin oxide. It is revealed that there are small peak shifts in the film. The crystallinity of thin films is obtained by comparing the area of the peaks to the total area under histogram [4]. The crystallinity of the samples relatively low, since the materials contain a polymer which naturally has an amorphous structure.

3.2. FTIR Studies

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 4.

Figure 4. FTIR spectra of (Ag-SnO$_2$)NPs-β-Carotene thin films with a different mass of SnO$_2$NPs

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 [7]. Stretching modes of the O-Sn-O functional group shown by existing at wave number 827.46 cm$^{-1}$ [8]. The wavenumber about 3496.94 cm$^{-1}$, which is in the range of 3349-3409 cm$^{-1}$ related to stretching vibrations of the O-H bond [8]. 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 [7]. At wavenumber
2833.43 cm$^{-1}$, investigated as an N-H functional group [9]. There is no remarkable discrepancy since SnO$_2$NPs added in a very small portion.

3.3. Morphological Analysis
The morphology and microstructure of film were characterized by SEM as shown in Figure 5.

![SEM images of (Ag-xSnO$_2$)NPs-β-Carotene thin films with various mass of SnO$_2$NPs](image)

**Figure 5.** SEM images of (Ag-xSnO$_2$)NPs-β-Carotene thin films with various mass of SnO$_2$NPs a) 0, b) 0.005, c) 0.010, d) 0.015, e) 0.020, dan f) 0.025 g

From the SEM images depicted in Figure 5, it seems that silver and tin oxide nanoparticles are not fully dispersed as expected. The materials agglomerated to form clusters and porous. Further, the agglomeration increases at a higher fraction of SnO$_2$NPs. Surface porosity of (Ag-xSnO$_2$)NPs-β-Carotene thin films are shown in Table 1.

**Table 1.** Surface porosity of (Ag-xSnO$_2$)NPs-β-Carotene thin films at the various mass of SnO$_2$NPs

| SnO$_2$NPs (g) | Surface Porosity (%) |
|---------------|----------------------|
| 0             | 5.15                 |
| 0.005         | 5.94                 |
| 0.010         | 4.80                 |
| 0.015         | 4.00                 |
| 0.020         | 9.68                 |
| 0.025         | 21.60                |

The results of SEM analysis using ImageJ software show that porosity surface of films in the range of 4 to 6% for 0 to 0.015 g. Percentage of porosity surface increase significantly at 0.020 g, and 0.025 g as 9.68, and 21.60% respectively. Higher porosity of films due to higher SnO$_2$NPs added on the films which tend to agglomerate with AgNPs and β-Carotene.

3.4. Optical Absorption Properties
The optical and energy band of the film confirmed using UV-vis spectroscopy. Absorption of the light at certain wavelength related to electron energy needed for excitation from valence band to conduction band [10], thus it is necessary to use Tauc plot method to find out the energy gap of the films. Figure 6 shows the curve of ($\alpha$hv)$^2$ as a function of hv.
Figure 6. Tauc plot curve of (Ag-SnO$_2$)NPs-β-Carotene thin films.

From the specific Tauc plot, we further analyzed by using a linear fit of each curve of Figure 6. One example is shown in Figure 6 for the undoped film. The band gap could be obtained from the linear fit cut to $h\nu$ axis. The film of undoped SnO$_2$NPs exhibit a higher energy gap of 3.8 eV. The results of the bandgap analysis of all samples are shown in Figure 7.

Figure 7. Energy gap range of (Ag-SnO$_2$)NPs-β-Carotene thin films

Introducing SnO$_2$NPs on the films provide a shift the bandgap shift. The (Ag-xSnO$_2$)NPs-β-carotene films show an average band gap around ~3.7 eV as depicted in Figure 7. These values approach the energy gap of the tin oxide nanoparticles as 3.68 eV [7]. The energy gap between samples decreases with the various increasing mass of SnO$_2$NPs, due to several factors as like grain size, morphology, or crystal structure [11]. The wide band gap of this samples corresponds to wavelength absorption in the range of ultraviolet at ~380 nm.

3.5. Electrical Conductivity

Measurement of electrical conductivity has been investigated using four points probe method; it will be provided current and voltage ($I$-$V$) curve relationship. Figure 8 shows the influence of SnO$_2$NPs doping on the electrical conductivity of (Ag-SnO$_2$)NPs-β-Carotene thin films.
Figure 8. The effect of SnO$_2$NPs on the electrical conductivity of (Ag-xSnO$_2$)NPs-β-Carotene thin films.

The addition of tin oxide nanoparticles gives higher electrical conductivity, which is due to the presence of SnO$_2$NPs which provide higher electron mobility. The undoped sample shows a relatively conductive which provided by Ag NPs [4, 15] and other metallic [13], or metal oxides [14] in conducting polymers. This also results Electrical conductivity properties of the films significantly increases from 12.28 S/cm to 15.70 S/cm with the various mass of SnO$_2$NPs as 0.005 g to 0.025 g, while the AgNPs-β-carotene film reaches up to 8.72 S/cm. Although the electrical conductivity of the films is relative low, thus it opens a wide range of research to enhance the electrical properties and modify the films for solar cell applications [16].

4. Conclusion
(Ag-SnO$_2$)NPs-β-carotene thin films have been synthesized using the spin coating method. It is observed that the composite films were clarified according to XRD patterns analysis. Observation using SEM indicates that materials agglomerate and more evident along with the increasing of mass tin oxide nanoparticles. It is found that the film provides the wide energy gap ~3.7 eV, it has been decreased from 3.8 eV without any tin oxide nanoparticles. Moreover, the electrical properties were investigated using four points probe, and it shows that SnO$_2$NPs doping gives rise to the electrical conductivity of the films. The decrease of the band gap and high electrical conductivity make this film possess excellent potential for solar cell applications, mainly for photoanode of DSSC device.

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