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The Influence of SnO$_2$ Nanoparticles on Electrical Conductivity, and Transmittance of PANI-SnO$_2$ Films

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Abstract. The study of the potency of conductive polymer and its combination with a various dopant of metals, oxides, and other radicals is significantly improved. We report the results of the study to determine the effect of SnO$_2$ addition on the microstructure, absorbance, and electric conductivity of PANI-SnO$_2$ films. In this work, we also report the effect of variations of light intensity on its electrical conductivity of the same films. The results showed that the addition of mass SnO$_2$ affecting the structure of the PANI-SnO$_2$ bonding function group in which indicated by the appearance of Sn-O-Sn peak at the wave number of 601.79 cm$^{-1}$. The addition of SnO$_2$ affects the crystallinity ratio of PANI-SnO$_2$ films shown by the crystallinity of PANI-SnO$_2$ films by 53.16 %. The addition of SnO$_2$ reduces the porosity of morphological shape of the PANI-SnO$_2$ film surface. It is surprising that addition of mass SnO$_2$ significantly increases the electric conductivity of PANI-SnO$_2$ films by (4.24 × 10$^2$) S·cm$^{-1}$. The addition of SnO$_2$ increases the transmission by 35.48 %. Light irradiance on PANI-SnO$_2$ film decreases the conductivity of the PANI-SnO$_2$ film.

Keywords. Electrical conductivity, nanoparticle, PANI, SnO$_2$, transmittance.

1. Introduction
Optoelectronic materials of organic materials have been widely developed as substitutes of inorganic-based optoelectronic materials [1]. The use of inorganic materials poses a problem because it cannot be deciphered naturally by soil microbes [2]. Polyaniline (PANI) is one of the conductive organic polymers which can be controlled by electronic and optical properties as optoelectronic materials [3]. So far PANI has been applied as an optoelectronic material resulting in low conductivity and transmittance [4, 7]. Therefore, it is necessary to increase the conductivity and transmittance of PANI. Moreover, the increasing electrical properties of PANI can be done by inducing another material to its such as PANI-Fe$_2$O$_4$ [8]. One of them with the addition of a class of oxides is Tin Oxide (SnO$_2$) [9, 11]. Based on the other works, the synthesized PANI-SnO$_2$ showed allow conductivity, wave number absorbance, and band gap respectively of (6.4 × 10$^3$) S·cm$^{-1}$, 300 nm, and 4.1 eV [12]. Therefore, further research is needed to improve the conductivity and transmittance of PANI-SnO$_2$ film. So far, there is no study of the synthesis of SnO$_2$ incorporated into one-phase of PANI reported.

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comprehensively. A composite material which was synthesized from different materials intrinsically consist of two materials which will show a combined property of the constituent [13]. So that PANI-SnO$_2$ system proposed in this research uses an in-situ polymerization method for the development of an optoelectronic material which shows a high conductivity and high transmittance. The fabrication of PANI-SnO$_2$ in the form of the film will increase the crystallinity [14]. The growth of this crystallinity will enhance the desired properties of the material.

2. Materials and methods

PANI-SnO$_2$ films have been prepared for the following procedure. First, we developed a solution made of 0.927 g of aniline hydrochloride, 80 mL of distilled water and 14 g SnCl$_4$·5H$_2$O. The second solution consists of 2.28 g (NH$_4$)$_2$S$_2$O$_8$ which were dissolved in 20 mL deionized water and then stirred it for 30 min. Subsequently, both aniline and SnCl$_4$ solutions were mixed with (NH$_4$)$_2$S$_2$O$_8$ into one container, stirred using a magnetic stirrer for one hour then precipitated for six hours. This precipitation for aniline polymerization process becomes PANI ES I. The result of polymerization of the precipitate was then filtered and rinsed using distilled water for three times and deionized water for three times then followed by an acid-base chemical process to form PANI EB. The preparation of PANI EB is done by adding 15 % ammonia in PANI-SnO$_2$ solution, after which the solution was kept to stand for 24 h. After that, the blue sediment filtered and rinsed using distilled water as much as three times and deionized water as much as three times. Then the resulting PANI-SnO$_2$ precipitate was dried at 180 °C with an XD-1700 electric furnace for 1 h. The final result of the process was PANI-SnO$_2$ powder (PANI ES II) purplish blue.

Next, the film PANI-SnO$_2$ using a spin coating. First, is 0.15 % of the yield of PANI-SnO$_2$ powder added 20 mL of distilled water and 0.05 % PVA of PANI-SnO$_2$ powder mixed in one container [2]. Before mixing, PVA is first dissolved in distilled water and stirred for 6 h at room temperature. Addition of PVA will make PANI-SnO$_2$ in the form of ready-to-use solution to obtain the PANI-SnO$_2$ film. Preparation of the film used glass substrate size 2 cm × 2 cm was washed using acetone for 15 min, then dried at 80 °C heated temperature using the hot plate. The next step is the growth of thin film, PANI-SnO$_2$ solution dripped on the glass substrate (2 to 3) drops, and then spinner is rotated at 1500 rpm for 1 min. After the growth process is complete, the coating is dried with an automatic furnace at 100 °C for 1 h. We further analyzed its crystallinity, conductivity, and transmittance of the films.

3. Results and discussion

The addition of SnO$_2$ to PANI-EB produces the FT-IR PANI-SnO$_2$ spectrum shown in Figure 1. PANI-EB synthesis into PANI ES (II) is a doping process performed by addition of SnO$_2$ doping to PANI. The addition of doping makes Sn$^{4+}$ atoms entering the bond. This bond is indicated by FT-IR peak appear at 601.79 cm$^{-1}$, 505.35 cm$^{-1}$, and 410.84 cm$^{-1}$. At the band of 601.79 cm$^{-1}$ suggests the occurrence of Sn-O-Sn vibration [15], 505.35 cm$^{-1}$ is the Sn-O-Sn bond of the asymmetry strain [12]. While at the peak of 410.84 cm$^{-1}$ occurs the bond of Sn-OH [13].
Figure 1. FTIR spectra of PANI-SnO₂ Film

Based on the result of explanation of FT-IR data above can be concluded match PANI-SnO₂ based on reference data from the previous research article. There is an insignificant shift in the order of 0.1 from the database. So, it can be concluded PANI-SnO₂ successfully synthesized in this study through in-situ polymerization method. The Sn bond shown in the aniline bond is shown in Figure 2.

Figure 2. Possible Sn bond on the aniline chain in the PANI chain [16].

3.1. The diffraction of Polyaniline-SnO₂ analyses

The diffraction pattern of the PANI-SnO₂ film with the mass variation of SnO₂ doped PANI is shown in Figure 3. The phase analysis of PANI-EB formed at peak = 19.68° and 22.5° with the size of lattice parameter a = 7.7 Å, b = 5.8 Å, c = 4.8 Å with orthorhombic crystal structure [17, 18] using cell ref software. The model data is used as a refinement of PANI-SnO₂ data where SnO₂ itself has the peak intensity of 2θ at 26.49°, 33.77°, 54.78°, 57.95°, and 61.86° [19]. Based on the refinement results obtained the peak of refinement results on PANI-SnO₂ at 19.05°, 23.06°, 26.65° with error R² of 0.04821. There is no other peak of SnO₂ appear. It reflects the formation of a single phase. The grain size was obtained from FWHM data using Scherrer formula. The result of the calculation was performed under Gaussian profile-fitting analysis using software Origin 8. The average size was about 14.25 nm. The crystallinity of the material was calculated using the formula of Equation 1.
Figure 3. Pattern of XRD Result a) SnO$_2$, b) PANI-EB (aniline HCL), c) PANI-SnO$_2$ doping 0.02 g, d) PANI-SnO$_2$ doping 0.05 g, e) PANI-SnO$_2$ doping 0.10 g, f) PANI -SnO$_2$ doping 0.15 g, g) PANI-SnO$_2$ doping 0.2 g.

We found that the crystallinity of PANI-EB film is 22.79 %, and increase up to 53.169 % for doped PANI-SnO$_2$ film. The structural changes this research demonstrates, are closely related to the improvement of the resulting physical properties. This result, revealing the fundamental nature of Polyaniline where the features of the crystal structure can be controlled through doping.

3.2. Micro structure analyses
PANI-SnO$_2$ film image based on the result of SEM characterization and EDAX element shown in Figure 4. Based on the above SEM image can be presented a form of PANI morphology of fibers having pivot structures interconnected with other fiber networks [20]. The fiber network interconnected due to the result of polymerization, which results in additional new aniline molecules interacting with the new subsequently aniline groups. The protonation caused by the acid compound makes the structure of the fiber hollow [21]. Based on Figure 4.b the addition of SnO$_2$ to the PANI film results in the closing of PANI polymerization cavities. The inclusion of SnO$_2$ in the PANI cavity reduces the porosity of microstructure of PANI surface morphology. The microstructure shows that Sn is entering on the surface morphological structure of the PANI-SnO$_2$ film. EDAX supports the presence of a Sn element in the film on PANI-SnO$_2$ film shown in Figure 4.c. Based on the cross-section of SEM images, it is obtained that PANI-SnO$_2$ film thickness is in the order of 16.32 μm.
3.3. Electric conductivity

The results of the PANI-SnO$_2$ thin film conductivity of four-point probe measurements shown in Table 1.

| SnO$_2$ mass (g) | conductivity (S·cm$^{-2}$) |
|------------------|-----------------------------|
| 0                | 0.21                        |
| 0.02             | $2.6 \times 10^2$           |
| 0.05             | $3.1 \times 10^2$           |
| 0.10             | $3.37 \times 10^2$          |
| 0.15             | $4.12 \times 10^2$          |
| 0.20             | $4.24 \times 10^2$          |

Based on Table 1, it is shown that the electrical conductivity of undoped PANI films was 0.21 S·cm$^{-1}$ as other previous reports. The induced of SnO$_2$ in the PANI-SNO$_2$ film increase to $(2.6 \times 10^2)$ S·cm$^{-1}$. The highest conductivity was reached by the sample with 0.2 g dopant with a conductivity of $(4.24 \times 10^2)$ S·cm$^{-1}$. The conductivity of PANI-SnO$_2$ films is higher compared to PANI due to the increased of its crystallinity of the system supported by previous XRD analyses.

3.4. Transmittance and UV-Vis measurement

The result of characterization of UV-vis PANI-SnO$_2$ with various levels of addition of SnO$_2$ is shown in Figure 5. The addition of SnO$_2$ resulted in the decrease in absorbance of PANI-SNO$_2$ film. The highest absorbance result is inversely proportional to the transmittance, the higher the absorbance turns, the lower film’s transmittance. Table 2 shows the calculation of transmittance based on UV-Vis data in Figure 5.
The increased of PANI-SnO$_2$ film transmittance is caused by several factors, including the number of doping atoms that enter the film grid, the grain size, the thickness and the roughness of the film. Those factors are presumably present due to the addition of oxide level dopant that makes the transparency of material also increase. Based on the results of Table 2, we found that the highest transmittance is obtained by 0.2 g PANI-SnO$_2$ film with the transmittance of 35.48 %.

Table 2. Results of Transmittance Calculations from Various Levels of PANI-xSnO$_2$.

| Mass (g) | Wave number (nm) | Absorbance max. | %Transmittance |
|---------|------------------|-----------------|----------------|
| 0       | 769              | 0.67            | 21.3796        |
| 0.02    | 758              | 0.61            | 24.5471        |
| 0.05    | 763              | 0.61            | 24.5471        |
| 0.10    | 756              | 0.52            | 30.1995        |
| 0.15    | 742              | 0.49            | 32.3594        |
| 0.20    | 745              | 0.45            | 35.4813        |

3.5. Optoelectronic properties of PANI-SnO$_2$

The effect of light intensity on the PANI-SnO$_2$ film for all ranges of dopant level is drawn in Figure 6. The measurement condition was performed similarly to the result as presented in Table 1 with additional various light intensity impinged on to the samples. Figure 8 tells us that the higher the dopant give rise to the increase of electrical conductivity as in Table 1. Further measurement by exposing light makes the conductivity significantly reduced and strictly independent of intensity at the higher intensity. This phenomenon may be due to the increase of thermal energy in the film PANI-SnO$_2$. The decrease of electrical conductivity looks to follow the electronic mechanism of conductivity due to the rise in energy level of electrons in the oxide semiconductor.
Figure 6. Effect of Light Intensity on PANI-SnO$_2$ film.

4. Conclusions
Based on the analysis, we can draw the following conclusions. The addition of mass SnO$_2$ affects the rise of SnO$_2$ intensity peaks, as well as the crystallinity of PANI-SnO$_2$. The addition of SnO$_2$ also changes the morphological structure of the PANI-SnO$_2$ film, i.e., decreases its porosity. A significant increase of transmittance and electrical conductivity as the increase of SnO$_2$. On the other hand, we obtain that the electrical conductivity of PANI-SnO$_2$ films decreases linearly with increasing intensity of light.

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