# Effect of substrate placement in schott vial to hematite properties

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**ABSTRACT**

In the present study, hematite ($\alpha$-$Fe_2O_3$) nanostructures were deposited on fluorine doped tin oxide (FTO) coated glass substrate using sonicated immersion synthesis method. The effect of FTO glass substrate placement in Schott vial during immersion process was studied on the growth of the hematite nanostructure and its properties. XRD pattern has revealed seven diffraction peaks of $\alpha$-$Fe_2O_3$ for both hematite nanostructures samples attributed to polycrystalline with rhombohedral lattice structure. The surface morphologies from FESEM have shown that the hematite nanostructures were grown uniformly in both samples with FTO conductive layer facing up and down. Hematite sample with FTO facing down exhibits a smaller size of nanorod, 26.7 nm average diameter, compared to the hematite sample that FTO face up with 53.8nm average diameter. Optical properties revealed higher transmittance in the sample with FTO facing down, probably due to smaller size of nanostructure. The optical band gap energy plotted and extrapolated at 2.50eV and 2.55eV for FTO face up and FTO face down hematite samples respectively, presenting the sample with FTO face up has a lower optical bandgap energy.



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## 1. INTRODUCTION

Hematite ($\alpha$-$Fe_2O_3$) is the most stable iron oxide and becomes a promising material for electronic device applications due to its stability and low-cost mining. Hematite is an n-type semiconductor with energy band gap $E_g$=2.1eV in ambient condition. It has a good stability, non-toxic, corrosion resistance and abundance. Many studies have been reported the use of hematite nanostructures in variety applications, for instance photoelectrochemical water splitting, humidity sensor, lithium ion battery, photocatalyst, and magnetic devices[1-4]. Different methods and route to synthesize hematite nanostructures, were also described in the literatures which controlling the hematite nanostructure growth to enhance the structural, optical and electrical properties. The regulatory synthesis methods include spin-coating deposition[5], spray pyrolysis[6], magnetron sputtering[7], sol gel[8], and hydrothermal [9, 10] synthesis. In many research works that synthesize hematite through hydrothermal, they have constrain with high temperature, high pressure and a long synthesis process which increase the fabrication cost [11, 12]. On the other hand, some research works have reported that the angle of FTO substrate does affecting the growth of nanostructures, such as the synthesis of dandelion-like $TiO_2$ nanorods were obtained with substrate placement angle of 75 degrees in a vial through hydrothermal method [13]. To the best of our knowledge, there are no reports on the study of the substrates placement to the properties of hematite nanostructure growth through solution based method. Thus, in this work, we present the study of hematite nanostructure growth on FTO glass substrate, a transparent conductive layer on glass for two different placements in Schott vial immersed in aqueous solution. The synthesis method that we use in this research is sonicated immersion method, which is merely require low temperature and short duration synthesis process.

## 2. EXPERIMENTAL WORK

In this research work, we investigate how the placement of the substrate where the conductive layer (FTO) surface facing to in the Schott vial might influence the growth of hematite nanostructure on FTO coated glass substrate. We study the structural, optical and electrical properties of hematite nanostructures by characterizing two samples that have been placed horizontally facing up and down in separated Schott vials. Those substrates need to be cleaned prior to the solution synthesis to eliminate unwanted material and contamination on its surface. Therefore, the growth of hematite can be done without the presence of other materials. In the process of substrate cleaning, FTO substrates were sonicated in methanol for 10 minutes at 50°C in ultrasonic waterbath equipment. Then, the substrates were discharged from the beaker and rinsed with DI water. The substrates were next sonicated in DI water at 50°C for 10 minutes. The substrates were rinsed and dried by using nitrogen blow. For solution synthesis, the FTO substrates were placed in two different Schott vials with one substrate contains the FTO conductive layer facing up, and the other one facing down. Figure 1 shows the placement of FTO substrate in Schott vial.

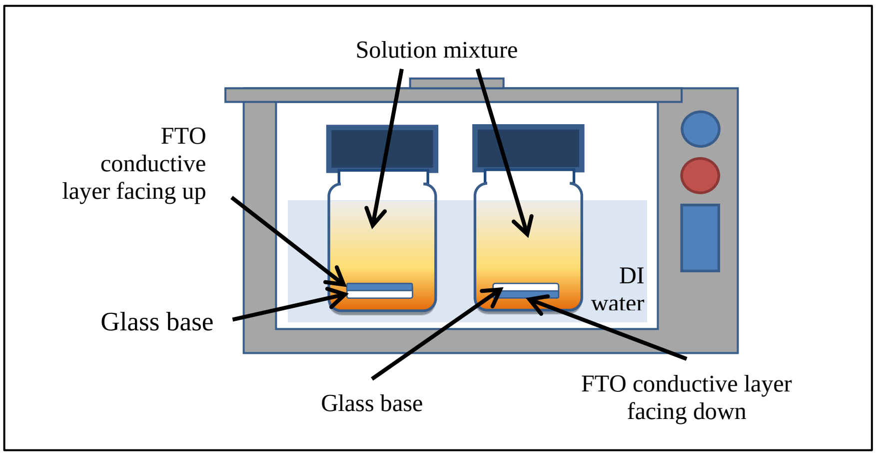



Figure 1. The placement of FTO substrate in Schott vial; FTO conductive layer facing up (left vial) and FTO conductive layer facing down (right vial)

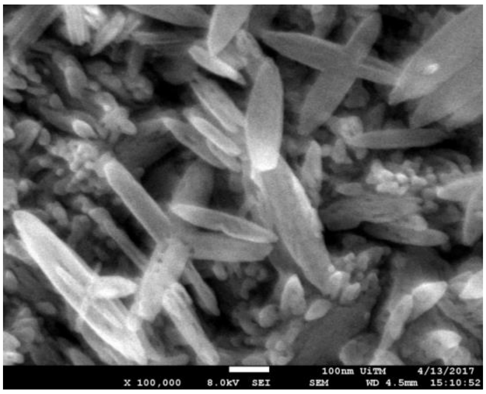
In the solution synthesis, hematite nanostructures were grown on FTO substrate via sonication and immersion technique. 0.2 M ferric chloride ($FeCl_3{\cdot}6H_2O$) was used as starting material, 0.2 M urea ($NH_2CONH_2$) as the stabilizer and deionized (DI) water as the solvent. The substances were mixed to 200 ml aqueous solution, sonicated in ultrasonic waterbath at 50˚C for 30 minutes and stirred on a hotplate at room temperature for 5 minutes at 250 rpm to blend it well. The aged solutions were immediately poured into Schott vial in which FTO substrate were placed at the base of the vial. The solutions in the Schott vials were immersed in a waterbath at 95˚C for 2 hours. After discharging the substrates from the immersed solution, the samples were rinsed using DI water and dried at 150°C for 15 minutes in a furnace. The samples then were thermally annealed at 500°C for 1 hour to improve the crystallinity of the hematite nanostructure films that were grown during the immersion process. The samples were cooled down and ready for characterizations. One of the FTO substrates for each sample was deposited with Platinum (Pt) metal contact for electrical characterization purpose, meanwhile the other one was left for structural and optical characterizations.

In this work, several characterizations were done to analyze the difference of hematite nanostructure growth effect due to placement of FTO substrate in Schott vial during immersion process. For the structural characterization, the crystallinity of the hematite nanostructures was analyzed through X-Ray Diffraction (XRD; PANalytical X'Pert PRO) and the surface morphology was examined by Field Emission Scanning

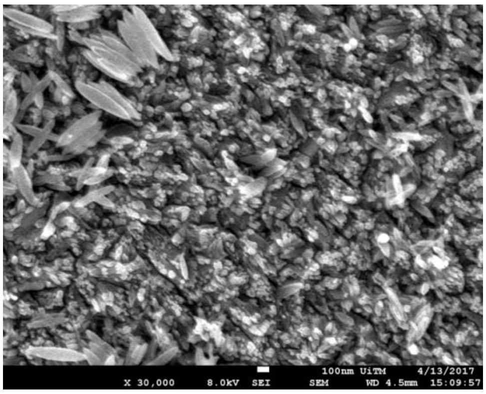
Electron Microscopy (FESEM; JEOL JSM-7600F). Ultraviolet Visible Spectroscopy (Varian Cary 5000) was used to characterize the optical properties, and thus from the transmittance (%) value, the optical band gap was calculated and plotted. The electrical behavior of the hematite nanostructure was characterized by using two-probe current-voltage (I-V) measurement system with voltage biasing ranging from -6V to 6V supplied to the metal contact and the FTO conductive layer as the second contact.

## 3. RESULTS AND DISCUSSION

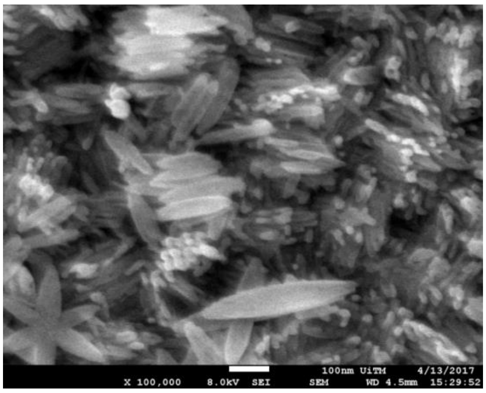
The FESEM images in Figure 2 illustrate the surface morphology of two samples, FTO facing up and FTO facing down. The FESEM images of sample with FTO facing up during immersion are presented by Figure 2(a) at 100,000×magnification and 2(b) 30,000×magnification, meanwhile the images of sample with FTO facing down are presented by Figure 2(c) 100,000×magnification and 2(d) 30,000×magnification. The surface morphology images indicate that the deposited hematite nanostructure with FTO facing up is denser and high uniformity with nanorod shape respected to the FTO surface. Figure 3(a) exhibits nanorod structure in the sample with FTO facing up with a larger in average diameter, 53.8nm. The average diameters of sample with FTO facing down was observed lesser to 26.7nm, as indicated in Figure 3(b), which is about half of the size in the first sample.



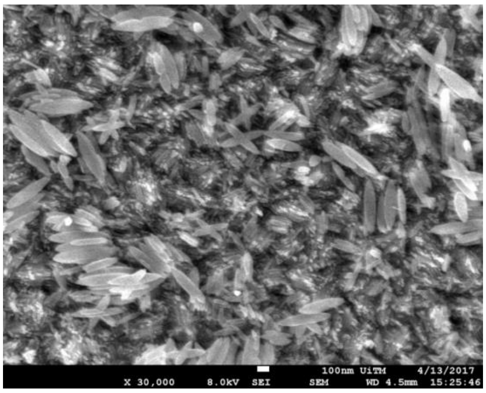

(a)




(b)



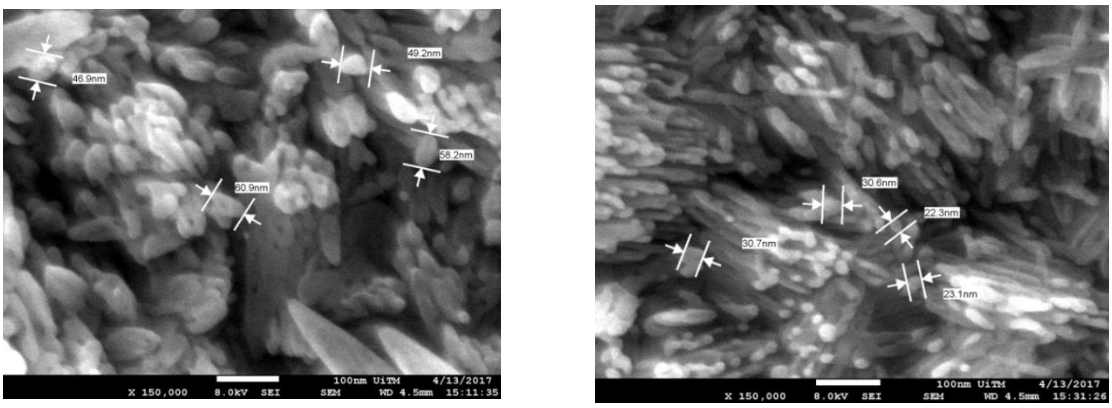

(c)




(d)

Figure 2. The surface morphology of hematite nanostructure samples with FTO facing up, (a) 100,000× magnification, (b) 30,000× magnification, and sample with FTO facing down during immersion process, (c) 100,000×magnification, (d) 30,000×magnification

The crystallinity of the prepared hematite nanostructures was analyzed using X-ray diffraction (XRD). The XRD pattern of hematite nanostructures for both samples correspond to seven diffraction peaks of $\alpha$-$Fe_2O_3$ hematite phases for two theta ($2\theta$) angles measured from 20˚ to 90˚, namely, (104), (110), (116), (214), (125), (223) and (128), as illustrated in Figure 4(a). The observed peaks for both samples of hematite nanostructure are attributed to a polycrystalline structure with rhombohedral hematite structure films (hematite phase JCPDS #33-0664). The high diffraction peaks at 26˚, 38˚, and 53˚ observed in both XRD pattern due to X-ray penetration into the FTO layer on the glass substrate. There is merely slightly difference of either the number of peaks or the intensity of hematite diffraction peaks comparing both samples, as the peak (214) and (128) of the facing down FTO sample can be seen to reveal a slightly higher intensity.




(a) (b)

Figure 3. The average diameter of hematite nanorods that creates the nanostructures; (a) Sample with FTO facing up, the average diameter is about 53.8nm, and (b) Sample with FTO facing down, the average diameter is 26.7nm

The optical properties of hematite nanostructures for samples with FTO facing up and FTO facing down during immersion process were determined from the transmittance spectrum in the range of 300-800 nm wavelengths, as depicted in Figure 4(b). Both samples exhibit a high transmission of higher than 80% in the 600–800 nm wavelengths with a gradual increment between 400 nm to 600 nm. Moreover, the hematite sample with FTO facing down was found to exhibit higher transmittance, with the value of transmittance exceeds 100% at 730nm wavelength, meanwhile the other sample was found has reached 100% transmittance at the same wavelength. The smaller grain size probably might lead to higher porosity in the surface of hematite sample with FTO facing down. Thus, it increases the optical scattering effect and improving the transmission of the lights through the sample[14]. From the transmittance spectra, the absorption coefficient of hematite nanostructures has been calculated using Lambert's law as shown in (1):

$$\alpha = \frac{1}{t} ln\left(\frac{1}{T}\right) \quad (1)$$

where $\alpha$ is the absorption coefficient, $t$ is the film thickness and $T$ is the transmittance of the nanostructure film in %. The optical band gap energy, $E_g$ is derived by assuming a direct transition of electron between the edges of the valence band and the conduction band, for which the variation in the absorption coefficient with the photon energy. The relation of direct band gap energy with the absorption coefficient and photon energy is given by (2):

$$\alpha hv = A\left(hv - E_g\right)^{\frac{1}{2}} \quad (2)$$

where $A$ is the constant and $hv$ is the photon energy [15]. The direct band gap of hematite nanostructure is estimated by plotting $(\alpha hv)^2$ vs. $hv$ as shown in Figure 4(c). From the figure, extrapolation of the linear part near the onset of absorption edge to the $hv$ axis offered the band gap energy value of 2.50 eV and 2.55 eV for FTO face up and FTO face down hematite samples respectively. It could be agreed that the hematite nanostructure grown with FTO facing down during immersion process performed wider optical band gap energy compared to hematite nanostructure grown with FTO facing up.

Figure 4(d) shows electrical properties (I-V) curve of hematite nanostructures deposited with FTO conductive layer facing up and facing down measured under room illumination at room temperature in the range of -6V to 6V. Platinum (Pt) contacts were deposited onto the thin films using Electron Beam Thermal Evaporator as electrode for electrical characterization purpose of two-probe IV measurement. From the data obtained, the IV properties exhibit Ohmic characteristic in both samples. The high current characteristic might be caused by the improvement carrier concentration in hematite nanostructure. These results have proved that both placement of conductive surface in FTO glass substrate does not contribute significant difference to the optical and electrical properties that were synthesized using sonicated immersion method. Both samples have indicated a strong potential to be applied in electronics device applications.

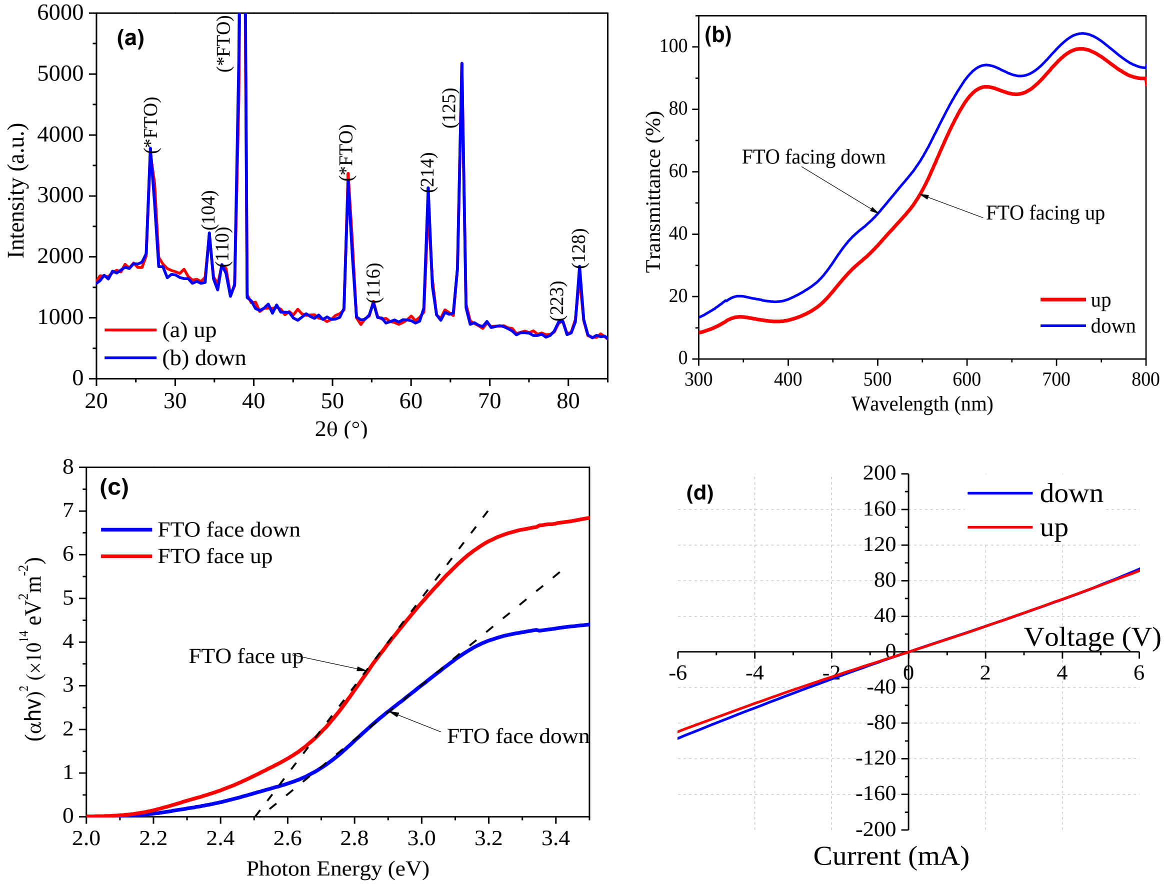



Figure 4. The properties of deposited hematite nanostructures films; (a) X-ray diffraction patterns, (b) transmittance spectra, (c) estimation of optical energy band gap, and (d) I-V characteristic

## 4. CONCLUSION

In conclusion, we successfully synthesized two samples of hematite nanostructures that were deposited in different placement of FTO conductive layer in Schott vial during immersion process. The crystalline properties show seven diffraction peaks of $\alpha$-$Fe_2O_3$ for both samples however the peak (214) and (128) of the facing down FTO sample is slightly more intense. The hematite nanostructures with FTO conductive layer face down exhibit a smaller size in average diameter that leads to higher transmittance and slightly wider optical band gap found. In electrical characterization, Ohmic characteristic obtained for both samples indicating that the both samples have potential to be applied in electronic devices.

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