

The effects of different precursor in sonicated immersion technique on hematite nanostructure properties

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Abstract. In this work, hematite nanostructures were synthesized through sonicated immersion technique to study the effects of using different precursor on the surface morphologies and the optical properties of the hematite nanostructures. The surface morphologies of the samples have shown different shape of nanostructures grown on the FTO substrates that were probably affecting their optical properties. The ferric nitrate sample has shown granular shape and porous nanostructure and it has a better absorbance in the lower range of wavelength (300-550 nm), meanwhile ferric chloride has been found to cultivate a nanorod-based structure and dominant in the transmittance properties at higher wavelength (550-1200 nm).

1. Introduction

Hematite (α -Fe₂O₃) is II-VI group compound semiconductor becomes a promising material for electronic device applications due to its valuable properties. Hematite (α -Fe₂O₃) is an n-type semiconductor and the most stable iron oxide with energy band gap $E_g=2.1\text{eV}$ in ambient condition. In aqueous solution, it has a good stability, non-toxic, corrosion resistance and abundance. α -Fe₂O₃-based material have been studied for use in many applications, including photo electrochemical water splitting[1]–[3], magnetic devices[4], [5], lithium ion batteries[4]–[7], gas sensors[8], [9], photocatalytics[10], [11], and humidity sensors[12]–[14]. There were a lot of works in controlling the growth of nanomaterials have been implemented to improve the structural and optical properties of hematite nanostructures. Some of the efforts were about to prepare the hematite nanostructures with variety of techniques include spin-coating deposition solution[15], ultrasonic spray pyrolysis[16], electrochemical deposition[17], sol-gel[18], and hydrothermal synthesis[19]. Based on previous works, a few synthesis of hematite nanostructures that were using ferric nitrate (Fe(NO₃)₃·9H₂O) as precursor in solution synthesis have produced porous nanostructures[20][21] which might increase the possibility of absorbing lights or water due to related applications. However, most research works on preparing hematite nanostructures were using ferric chloride in order to produce nanorod-based structures [3], [22], [23] with regards of different stabilizer and solution-based techniques.

The main purpose of this research is to study the effects on surface morphology and optical properties of hematite nanostructures that are prepared using different precursor materials in sonicated immersion technique. In the prepared aqueous solution, we compare the use of 0.2 M ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O) and 0.2 M ferric chloride (FeCl₃·6H₂O) as the precursor, 0.2 M urea



($\text{NH}_2\text{-CONH}_2$) as stabilizer, and deionized water as the solvent at identical molarity. The solutions are going through solution synthesis, which is sonicated immersion process. Then, the prepared nanostructures are characterized to investigate the difference between these two samples in terms of morphology and the optical properties.

2. Methodology

In this study, hematite nanostructures samples were divided into two, the first sample was using 0.2 M ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) as the precursor, meanwhile the second sample was using 0.2 M ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) as the precursor. Both samples have similar composition of the precursor, stabilizer and solvent, and they were also going through similar synthesis process that was sonicated immersion method. The synthesis process was started with substrate preparation, and followed by solution preparation, and material characterizations.

2.1. Substrate preparation

In this process, fluorine doped tin oxide (FTO) coated glass was used as a substrate to grow hematite nanostructures on top of its conductive surface through sonicated immersion process. The ready 2-by-2 cm FTO substrates were cleaned for the purpose of eliminating unwanted dirty particles, oxide layers and chemicals on the surface of substrate to ensure a good quality of growth nanostructures. In the cleaning step, the substrates were sonicated in methanol for ten minutes in an ultrasound bath at 50°C . Then, the substrates were rinsed with deionized (DI) water and sonicated in DI water for ten minutes at the same temperature. The substrates were rinsed with DI water and were blown for drying using a nitrogen blow-gun. The substrates were placed in the Schott bottle for further process.

2.2. Solution preparation

The solution preparation required a few steps, involving the precursors as starting material, stabilizer and solvent. The mixed solutions initially were dissolved in DI water, and went through a sonication process in a sonication waterbath for 30 minutes at 50°C as indicated in Fig 1(a). Next, the solutions were stirred on a hotplate to create homogenous solution and were charged into a Schott vial with FTO glass substrates placed horizontally in the glass vial earlier of that, and the conductive edge facing up of the vial. The mixture solutions in the Schott vial were going through sonication immersion in a water bath for 4 hours at 95°C as shown in Fig 1(b). The samples with nanostructured films formed on FTO-coated substrate were rinsed with DI water and dried at room temperature prior to a thermal annealing process for 1 hour at 500°C for surface modification.

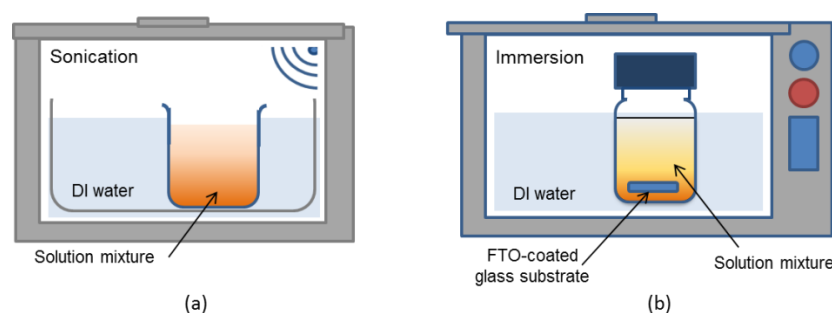


Figure 1 Experimental setup for sonicated immersion synthesis technique, (a) sonication process in an ultrasonic waterbath, and (b) immersion process in an immersion waterbath.

2.3. Material Characterizations

With the aim of analysing the surface morphology and the optical properties of the samples in different precursor, the material characterizations were conducted in two different parts; structural and optical characterizations. The field-emission scanning electron microscopy (FESEM) was used to observe the surface morphology of the hematite nanostructures, meanwhile ultraviolet-visible (UV-VIS) was used to observe the optical properties, which are absorbance and transmittance profile of the samples.

3. Results and discussions

The FESEM images in Fig 2 indicate the surface morphologies of the synthesized hematite nanostructures using two different precursors at low (30,000x) and high (50,000) magnifications. Fig 2 (a) and (b) display the hematite nanostructures that prepared using ferric nitrate as precursor that produces a granular shape and porous nanostructures. In another sample, Fig 2 (c) and (d) show the shape of nanorod hematite structure that prepared using ferric chloride as the precursor. Fig 2(c) also shows a uniform nanorod-array were grown with average diameter 67 nm and average thickness 250 nm.

The optical absorption properties within the spectrum range reveal where light is being absorbed to excite the electrons from the source of electricity. As shown in Fig 3(a), the absorbance properties of hematite nanostructures for both samples were illustrated in the range of 300-1200 nm wavelength. From the results, an intense absorbance can be seen in both samples between 300-550 nm wavelengths. However, the sample of precursor ferric nitrate has displayed higher absorbance properties compared to the sample that using precursor ferric chloride. In another optical measurement, the transmittance spectrum displays that the sample ferric chloride has a higher transparency in comparison with ferric nitrate sample as depicted in Fig 3(b). The transmittance spectrum shows a strong transparency within 550-1200 nm wavelength. The ferric chloride sample has achieved a good transmittance at visible region about 80-100% in a range of 700 to 1200 nm wavelength.

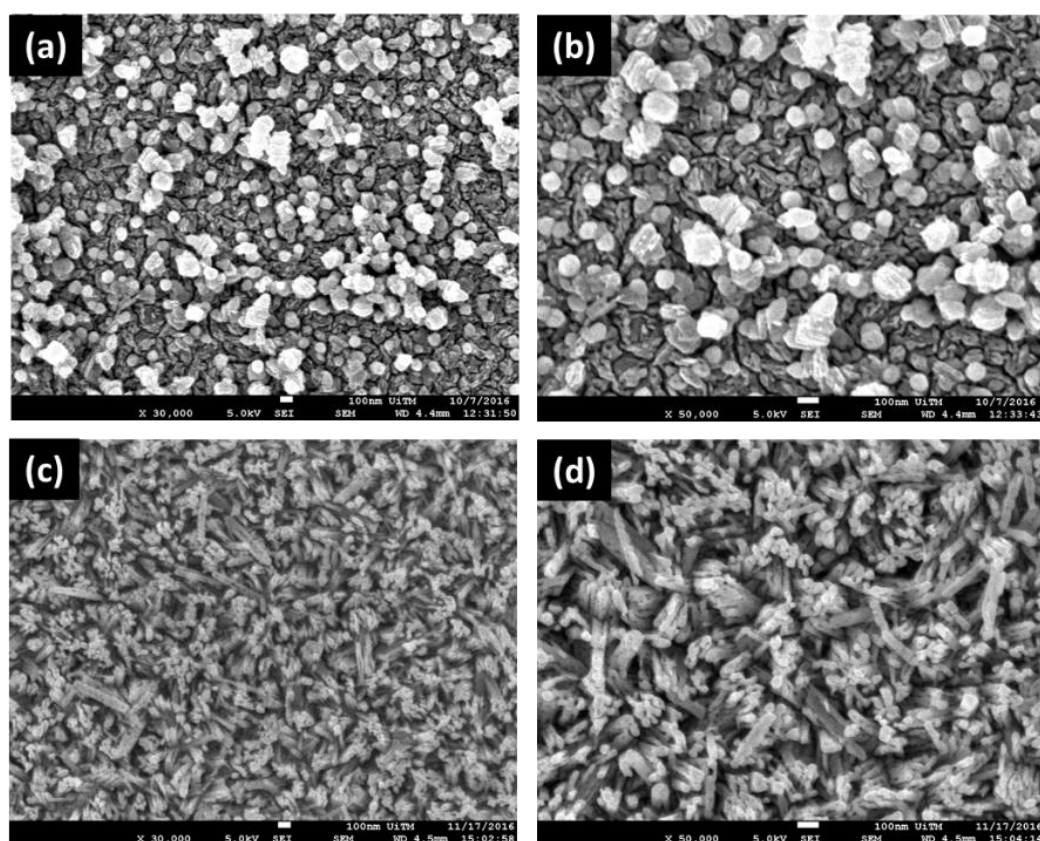


Figure 2 Surface morphologies of the hematite nanostructures using precursor ferric nitrate (a)&(b), and ferric chloride (c)&(d).

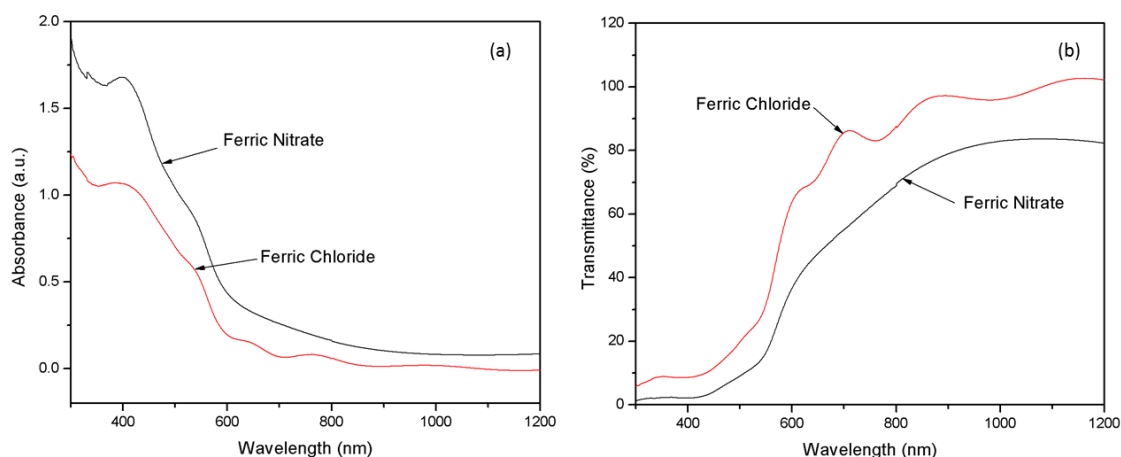


Figure 3 The optical properties of the hematite nanostructures; (a) absorbance, and (b) transmittance.

4. Conclusions

In this study, we have successfully prepared hematite nanostructures to investigate the effects of using different materials as precursor through sonicated immersion technique on the surface morphology and its optical behaviours. From the obtained results, it was found that the different precursor materials used in the immersion method would produce different shape of nanostructures on the FTO substrate. Additionally, these nanostructures also result in different behaviour of the optical properties, as we can see that the hematite nanostructure prepared using ferric nitrate has a good absorbance, meanwhile the hematite nanostructure prepared using ferric chloride offers a better transparency. In this observation, we believe that ferric nitrate causes a higher porosity of hematite granular nanostructure grown on FTO substrate, thus increases the rate of light adsorption on top of it. The nanorod profile of the nanostructures prepared using precursor ferric chloride provided a good transmittance at wavelength above 600 nm probably due to its one dimension architecture.

Acknowledgments

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