IJIREEICE

ISSN (Online) 2321-2004
ISSN (Print) 2321-5526

International Journal of Innovative Research in
Electrical, Electronics, Instrumentation and Control Engineering

Vol. 7, Issue 4, April 2019

Effect of Molarity on Acid-assisted Hydrothermal Routed TiO_2 Thin Films

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Abstract: This research article presents on the experimental study of the Influence of Hydrochloric Acid Concentration on the TiO_2 Thin Films. The microstructures and nanostructures TiO_2 thin films were grown directly on the surface of fluorine-doped SnO_2 (FTO glass substrate) by using simple aqueous chemical growth technique through single step surfactant free hydrothermal method with a steel made autoclave. The chemical solution was prepared by mixing titanium butoxide (TBOT) used as precursor, Hydro Chloric Acid (HCL) as catalyst, and the de-ionized water as solvent. Field-emission scanning electron microscopy (FE-SEM; JOEL JSM-6320F) with an accelerating voltage of 20 kV was used to analyse the morphological of the nanostructures TiO_2 thin films through the surface morphology images and cross section images. Meanwhile, the thickness of each nanostructures TiO_2 thin films was evaluated by using the cross section images. Then, Micro-Raman spectrometer-In-Via reflex Raman spectroscopy system operated with 514 nm wavelength of argon (Ar+) laser was used to study the crystalline structure of the nanostructures TiO_2 thin films. Lastly, LAMBDA 750 UV/Vis/NIR Spectrophotometer (UV-Vis) was used to study the optical property in this study. It was found that the morphologies of the synthesized microstructures and nanostructures TiO_2 thin films can be controlled by the hydrochloric acid concentration to obtain the complex nanostructures for boosting the photo catalytic performance. These microstructures and nanostructures TiO_2 thin film also indicate the good optical properties in the optical absorption measurement. Experimentally, it has been well established that the single-step hydrothermal synthesis method has demonstrated a high-yield fabrication process for creating large-scale production of microstructures and nanostructures TiO_2 thin films.

Keywords: Microstructures and Nanostructures; Titanium Dioxide; Hydrothermal method; Thin films

I. INTRODUCTION

Over the past few decades, nanoparticles like metals oxide, semiconductors and metals have attracted great attention in the environmental applications, energy applications and the fields of information. The interest in the research field of nanoparticles has seen rapidly developed due to their unique size-dependent optical, catalytic and electronic properties. Among all the nanoparticles, Titanium Dioxide (TiO_2) is known as a crucial semiconductor material which has been extensively investigated and applied in (photo)electrochromic devices, paints, pigment, photovoltaic cell, additive, gas sensors and photocatalysis applications. [1] According to the literature, nanoscale TiO_2 has demonstrated the peculiar properties which much better compared to its bulk materials.

Generally, TiO_2 is an anisotropic material occurs naturally in three different phases, such as rutile anatase and brookite. Among these three phases, the rutile is the most stable phase and rutile phased TiO_2 obtains a good expertise in photocatalytic effect, high refractive index, light scattering efficiency, and chemical inertness which reported in the research works of Zhou et al. 2011.[2] The properties of TiO_2 are usually dependent on its optical energy bandgap, size, morphology, crystal structure, shape, surface area and porosity. Therefore further investigations have been done on the microstructures and nanostructures titanium dioxides (TiO_2) such as microspheres, nanorods, nanotubes, and nanoflowers have been widely studied in determining the efficiency in specific applications. One dimensional nanostructures TiO_2 in thin film form have demonstrated the good optical and electrical properties and low recombination rate for electron-hole pair compared to TiO_2 nanoparticles which according to the research works of M.K.Ahmad et al. 2018.[3]

In later years, the nanoparticles synthesis methods become one of the most popular topics of concern regarding nanotechnology since it act as an important role in controlling the nanoparticles shape, size and its distribution for the specific practical applications. For example, a few fabrication methods have been employed to synthesize the research

IJIREEICE

ISSN (Online) 2321-2004
ISSN (Print) 2321-5526

International Journal of Innovative Research in
Electrical, Electronics, Instrumentation and Control Engineering

Vol. 7, Issue 4, April 2019

nanostructures TiO_2 thin films including sol-gel [4], spray pyrolysis deposition (SPD) method[5], electrochemical method[6], hydrothermal method[7], chemical vapor deposition (CVD)[8], and spin-coating [9] to enhance TiO_2 performance as photocatalyst by modifying and tuning it such as through fabrication methods including thermal treatment or dopant introduction during the synthesis system. Some of these fabrication methods request for the high operating cost and also might involve for the complex systems setup. Meanwhile, some of these chemical and physical fabrication methods will directly produce toxic by-products which are considered to be ecologically hazardous and it cannot be used in medical applications.

Therefore, the main purpose of this study is to demonstrate the economical and simplicity synthesis method of nanostructures of TiO2 thin film among the various fabrication methods available today. In this paper, the nanostructures of TiO_2 thin films were prepared using single step surfactant free hydrothermal process where it is a liquid-deposition process using soft chemistry (bottom-up approach) that provides a homogeneous thin film assisted with stable temperature and pressure. The growth mechanism of nanostructures of TiO_2 thin films with the effect of different concentration of hydrochloric acid molarity will also investigated.

II. EXPERIMENTAL SETUP

2.1 Materials

All the analytical reagent grade chemicals were purchased from Sigma Aldrich and used as received without any further purification. All aqueous solutions were prepared using deionized water. The titanium butoxide (TBOT) solution will used as a precursor; the deionized water as solvent; hydrochloric acid (HCL) as catalyst to increase conductivity of thin film.

2.2 Substrate

In present study of nanostructures TiO2 thin film using hydrothermal method were growth on the surface of fluorine-doped SnO_2 (FTO glass substrate) with the dimension of 10 mm x 25 mm. Before the preparation of chemical solution, the FTO-coated substrates were cleaned with acetone, ethanol, and deionized water with the volume ratio of 1:1:1 in an ultrasonic bath about 30 minutes and then dried in air.

2.3 Preparation of TiO2 Solution

The chemical solution was prepared to grow the nanostructures TiO2 thin film by hydrothermal process. First the acid solution was prepared by dissolving the 16.40 ml concentrated hydrochloric acid (HCl) (37%) into 25 ml deionized (DI) water in a beaker, then adjust the final volume of solution to 100 mL with deionized water to make the 2.0 M acid base solution. In present work, the different concentrations of hydrochloric acid (HCL) molarity from 2.0 M to 8.0 M were be prepared in order to study the effects of HCl concentration. Then this acid base solution was vigorously stirred with the speed around 300 RPM at 35 °C for 5 minutes with using heating magnetic stirrer. After that, around 5.8 mL of titanium butoxide (TBOT) was added drop wise by using a capillary tube into the prepared acid base solution and keep stirred for 20 minutes to form a homogeneous solution.

Table 1 shows the samples prepared at different concentration of hydrochloric acid (HCL) molarity (a) 2.0 M, (b) 4.0 M, (c) 6.0 M, and (d) 8.0 M.

Sample	Molarity of HCL (M)
H1	2.0
H2	4.0
H3	6.0
H4	8.0

2.4 Hydrothermal Process

After the ultrasonic bath, the FTO glass substrates were placed into the steel made autoclave with Teflon made liner (300 mL) with the conducting FTO surface facing upwards. Then, the homogeneous mixing solution was kept into the Teflon made liner (300 mL) for hydrothermal process. The process was carried on for 10 hours reaction times at 150 °C. After the hydrothermal process, the autoclave was taken out from the oven and the autoclave was let to cool to room temperature.

2.5 Annealing Process

After the autoclave was cooling down to room temperature, the prepared samples were rinsed with deionized water for 5 min and left to dry at room temperature. Then, the prepared samples were ready for annealed at 450°C for 30 minutes. Through the annealing process, it will improve the electronic contact between all the nanoparticles of the thin

IJIREEICE

ISSN (Online) 2321-2004
ISSN (Print) 2321-5526

International Journal of Innovative Research in
Electrical, Electronics, Instrumentation and Control Engineering

Vol. 7, Issue 4, April 2019

films and therefore produces better physical attachment. After the annealing process, the prepared samples were undergoing slow cooling at room temperature.

2.6 Characterization Method

Finally, the morphological of the prepared samples were analyzed by using field-emission scanning electron microscopy (FE-SEM; JOEL JSM-6320F) at an accelerating voltage of 20 kV on the surface morphology view and cross section view. Meanwhile, the thickness of each nanostructures TiO2 thin films was evaluated by using the cross section images. Then, Micro-Raman spectrometer-In-Via reflex Raman spectroscopy system operated with 514 nm wavelength of argon (Ar+) laser was used to study the crystalline structure of the nanostructures TiO_2 thin films. Lastly, LAMBDA 750 UV/Vis/NIR Spectrophotometer (UV-Vis) was used to study the optical property in this study.

III. RESULT AND DISCUSSION

3.1 Morphological properties

From the results shown by the FE-SEM images in Figure 3.1 (a) below, the random TiO_2 micro size crystals aggregations are obtained at a low acid concentration where the concentration of hydrochloric acid is around 2.0 M. These TiO_2 microspheres are obtained on the top of FTO substrate are observed in the Figure 3.1 (e) below after the hydrothermal process. The diameter of these microspheres are found in the ranges of sizes approximately 0.2–1 µm which portrayed in the histogram in Figure 3.2 (a) below based on their frequency distributions.

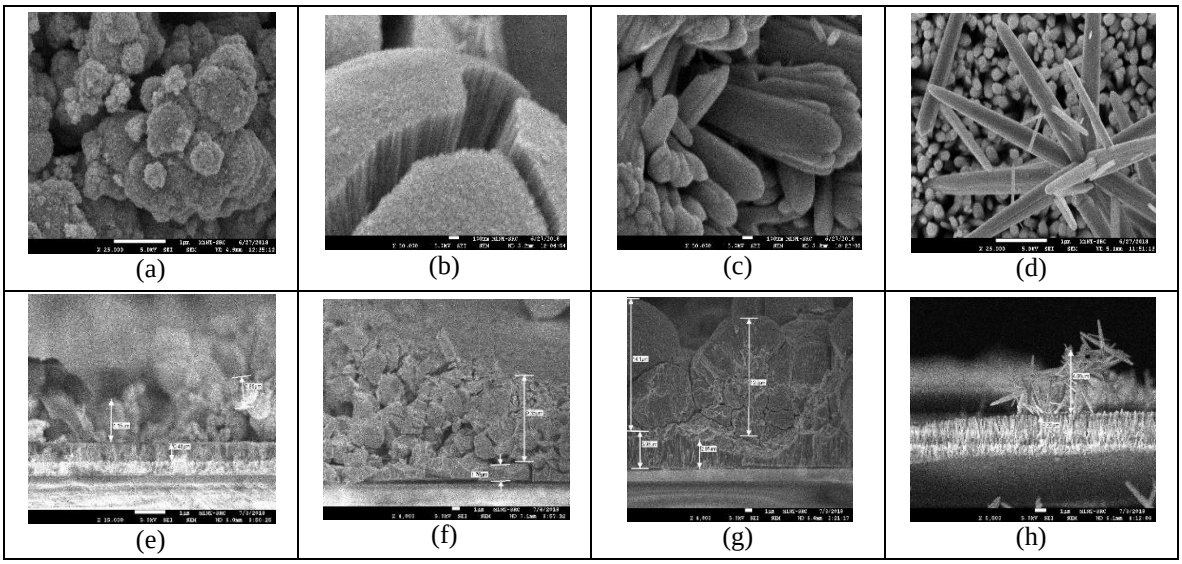

Figure 3. 1 - FESEM result for hydrochloric acid-hydrothermal process varying with HCL molarity (a) 2.0 M, (b) 4.0 M, (c) 6.0 M, and (d) 8.0 M, and the corresponding cross-section view respectively.

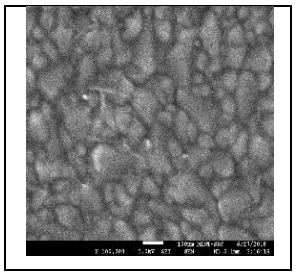

Figure 3. 1 (i) FESEM result for 10.0 M hydrochloric acid-hydrothermal process

Meanwhile, the same microspheres morphology is also observed with the 4.0 M hydrochloric acid-hydrothermal process, which shown as the Figure 3.1 (b) and (f) above. The size of about 2–6 µm TiO_2 microspheres are found which are bigger compared with that of 2.0 M hydrochloric acid-hydrothermal process above. However, there are a lot of cracks can easily found on the surface of these TiO_2 microspheres.

With the high-magnification of field emission scanning electron microscopy, these microspheres composed of radially aligned TiO2 nanorods are observed on these rough surfaces. These crystal rods are aligned perpendicularly to the

IJIREEICE

ISSN (Online) 2321-2004
ISSN (Print) 2321-5526

International Journal of Innovative Research in
Electrical, Electronics, Instrumentation and Control Engineering

Vol. 7, Issue 4, April 2019

spherical surface, pointing toward the common centre. The same cauliflower-like morphology is also obtained on the top of FTO substrate by using the 6.0 M hydrochloric acid-hydrothermal process, but the petals separate each other more obviously as shown in Figure 3.1 (c) above. The average size of nanorods are simulated approximately equal to 134.21 nm based on the frequency distributions in histogram in Figure 3.2 (c) below. The length of these nanorods crystallites are in the ranges of approximately 2.5-3 µm can obviously found with the cross section view in Figure 3.1 (g) above.

Lastly, the 8.0 M hydrochloric acid-hydrothermal process successfully produced the complex nanostructures TiO2 multi-level branched structures which are shown in Figure 3.1 (d) and cross section view in Figure 3.1 (h) above. Based on the showed FE-SEM images, the numerous TiO2 crystalline nanotree structure with trunks and branches are uniformly synthesized on the top of the layer of nanorods layer. The thickness of these nanorods layer is in the ranges of approximately 2-2.5 µm and the average diameter size of these nanorods are approximately equal to 98.82nm which portrayed in the histogram in Figure 3.2 (d) below based on their frequency distributions.

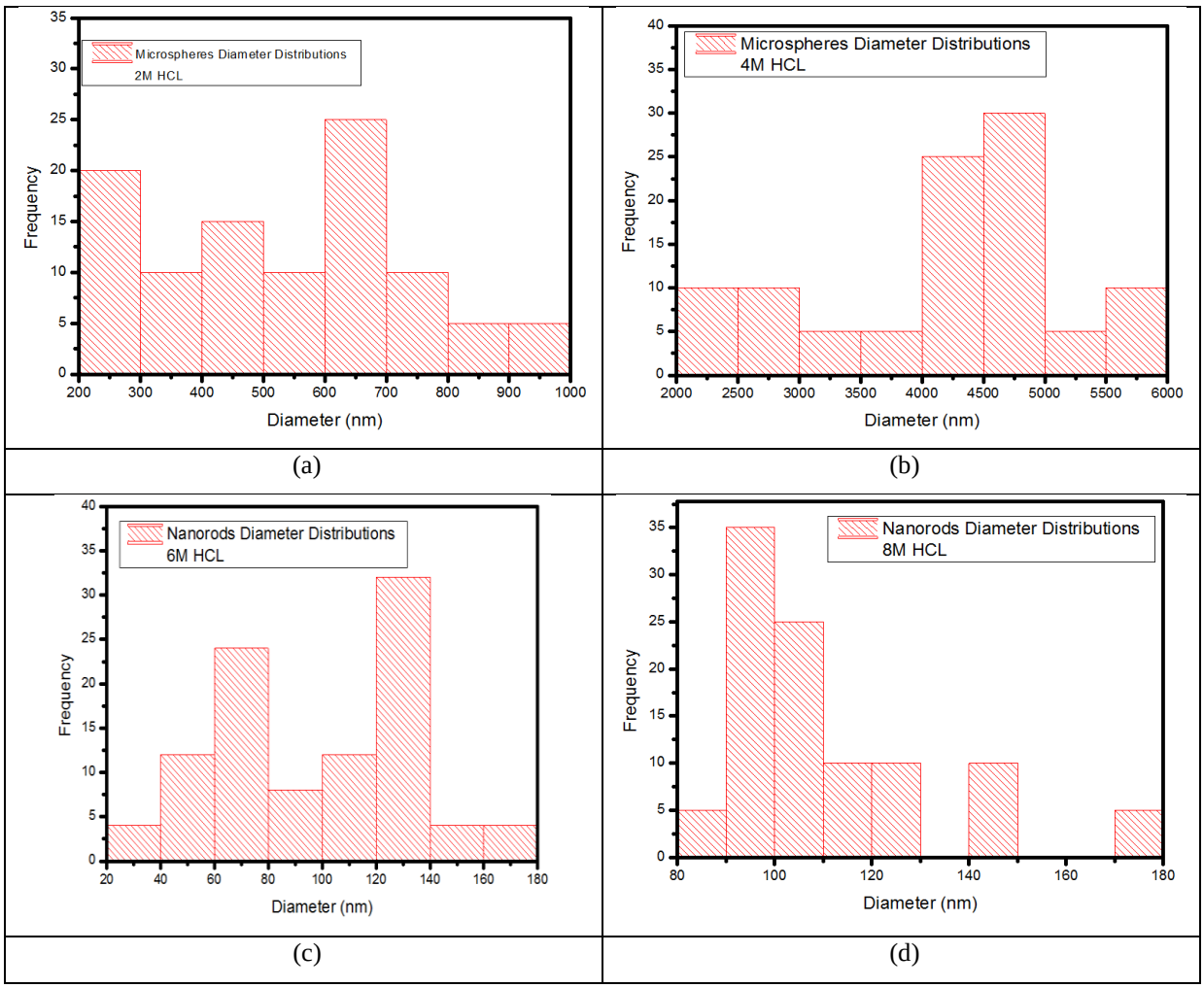

Figure 3. 2 - Frequency distributions of microstructured and the nanostructured TiO2 thin films with varying hydrochloric acid (HCL) molarity (a) 2.0 M, (b) 4.0 M, (c) 6.0 M, and (d) 8.0 M

The experimental study results above show that the control of different morphologies on the TiO_2 thin films from microstructure (microspheres) to nanostructures (such as nanoflowers, and nanobranches), can be tuned by varying the concentration of hydrochloric acid (HCL) molarity. During the hydrothermal process, the concentration of chloride ions in the initial acid solution play the vital role in the nucleation and crystal growth according to the literature. It is believed that the different concentration of hydrochloric acid (HCL) molarity leads to a different hydrolysis rate of titanium butoxide. Based on the experiments and analysis above, when the concentration of hydrochloric acid in the solution increased, the increased chloride ions around the titanates nucleus lead to the improvement for thickness of nanorods layer (the length of the nanorods) and also the surface area of nanostructured TiO_2 thin films. However, when the concentration of hydrochloric acid in the solution reach extreme levels, this phenomenon will dramatically change.

IJIREEICE

ISSN (Online) 2321-2004
ISSN (Print) 2321-5526

International Journal of Innovative Research in
Electrical, Electronics, Instrumentation and Control Engineering

Vol. 7, Issue 4, April 2019

The highly concentrated chloride ions will restrict the hydrolysis of titanium and restrains homogeneous nucleations which mentioned by Guo et al. (2012) through their study.[10] This was also supported by the FESEM result for 10.0 M hydrochloric acid-hydrothermal process which shown as Figure 3.1 (i) above, the distribution of TiO2 nanorods diminished on the surface of FTO substrate.

3.2 Micro-Raman spectroscopy

In this section the variation of intensity versus Raman shift of the microstructured and the nanostructured TiO_2 thin films that fabricated with varying the molarity of HCL will be discussed and the overall Raman spectra in the range of 0 to 1500 cm^{-1} portrayed in Figure 3.3 below. According to the literature, the first-order Raman spectrum of single crystal and coarse (micrometer-sized) polycrystalline rutile TiO_2 shows four Fourier Transform (FT) Raman-active fundamental modes: B_{1g} (143 cm^{-1}), E_g (447 cm^{-1}), and A_{1g} (612 cm^{-1}), and B_{2g} (826 cm^{-1}) which expressed as A_{1g} + B_{1g} + B_{2g} + E_g.[11] In addition, there are second-order scattering features, the most prominent one at ~237 cm^{-1} (E_g) peak due to the multiple-phonon scattering processes, which is also considered as a characteristics Raman peak of rutile phase TiO_2.

The Raman spectra of four samples varying the different hydrochloric acid (HCL) concentration which portrayed in Figure 3.3 below show E_g and A_{1g} modes, as well as the second-order effect at ~237cm^{-1}, as the major features; the B_{1g} and B_{2g} modes are extremely weak or absent. All these microstructures and the nanostructures TiO_2 thin films exhibit dominant peaks in rutile crystalline by the existence of three different peaks that were belong to rutile properties. It is noteworthy that only rutile TiO_2 microstructures and the nanostructures thin films were synthesized since the obtained results on their graphs will start from zero and followed with the three different peaks which within the range of rutile then it can be verified the crystalline of that particular sample is in rutile phase. On other hand, if the obtained results on its graph start with the high peak and no higher peak found after that particular peak, then it will be concluded as anatase crystalline.[12]

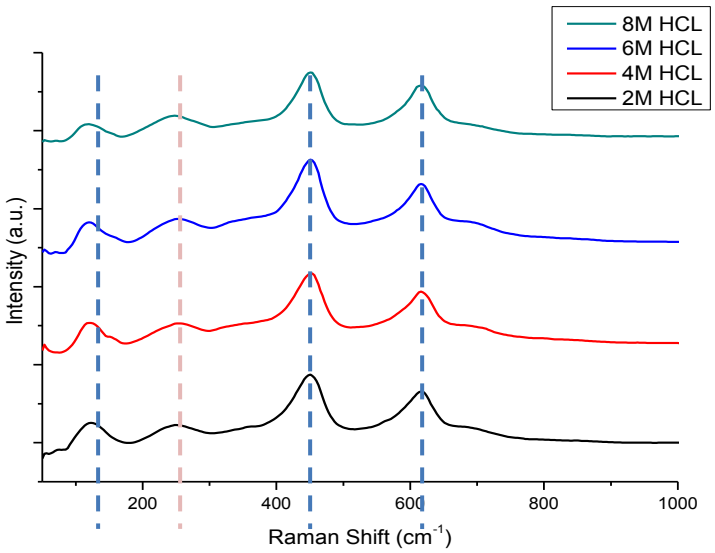

Figure 3.3- The Raman spectra of the fabricated microstructured and the nanostructured TiO2 thin films with varying the different hydrochloric acid (HCL) concentration.

3.3 Optical properties

In this optical study, the UV-1800 UV-Vis Spectrophotometer has been used with the setting of wavelength range 290 and 800nm at room temperature collect the data of light absorbance of the prepared microstructured and the nanostructured TiO_2 thin films. In order to analyse the optical properties of the prepared microstructured and nanostructured TiO_2 thin films, the collected light absorbance data are used to determine the extrapolated optical energy band gap (E_g). All the absorbance spectra and the extrapolated optical energy band gap of 4 different samples that subjected to different hydrochloric acid (HCL) molarity are portrayed in Figure 3.4 below. In present works, all the microstructured and nanostructured TiO_2 thin films exhibit their high absorbance properties around wavelength below than 400nm which is within the ultraviolet spectrum and their energy band gap were estimated using the Tauc plots.[13] The optical energy band gap of these prepared microstructured and nanostructured TiO_2 were calculated on the basis of optical absorption by using Tauc relationship which can be express by equation as the following[14]:

$$\alpha h\upsilon = K(h\upsilon - E_g)^n \quad \textbf{Equation 1.1}$$

IJIREEICE

ISSN (Online) 2321-2004
ISSN (Print) 2321-5526

International Journal of Innovative Research in
Electrical, Electronics, Instrumentation and Control Engineering

Vol. 7, Issue 4, April 2019

Where α is the absorption coefficient which defines how far into a material of a certain wavelength of light can penetrate before it was absorbed, meanwhile hυ represent the photon energy, E_g is optical band gap energy and K is a constant or Tauc parameter.[13] The exponent 'n' is parameter connected to the distribution of the density of states during the absorption process. For the direct allowed transition n= ½ and n= 2 for the indirect allowed transition. Thus, the optical energy band gap will be estimated by extrapolating the linear portion of $(\alpha h\upsilon)^2$versus photon energy (hυ) shown in Figure 3.4 below showing direct and allowed optical transition. The extrapolated optical energy band gap (E_g) obtained in this experiment are varying between 2.89 eV up and 3.18eV which is consistent with the optical energy bandgap of rutile TiO_2 according to the literature review.[15]

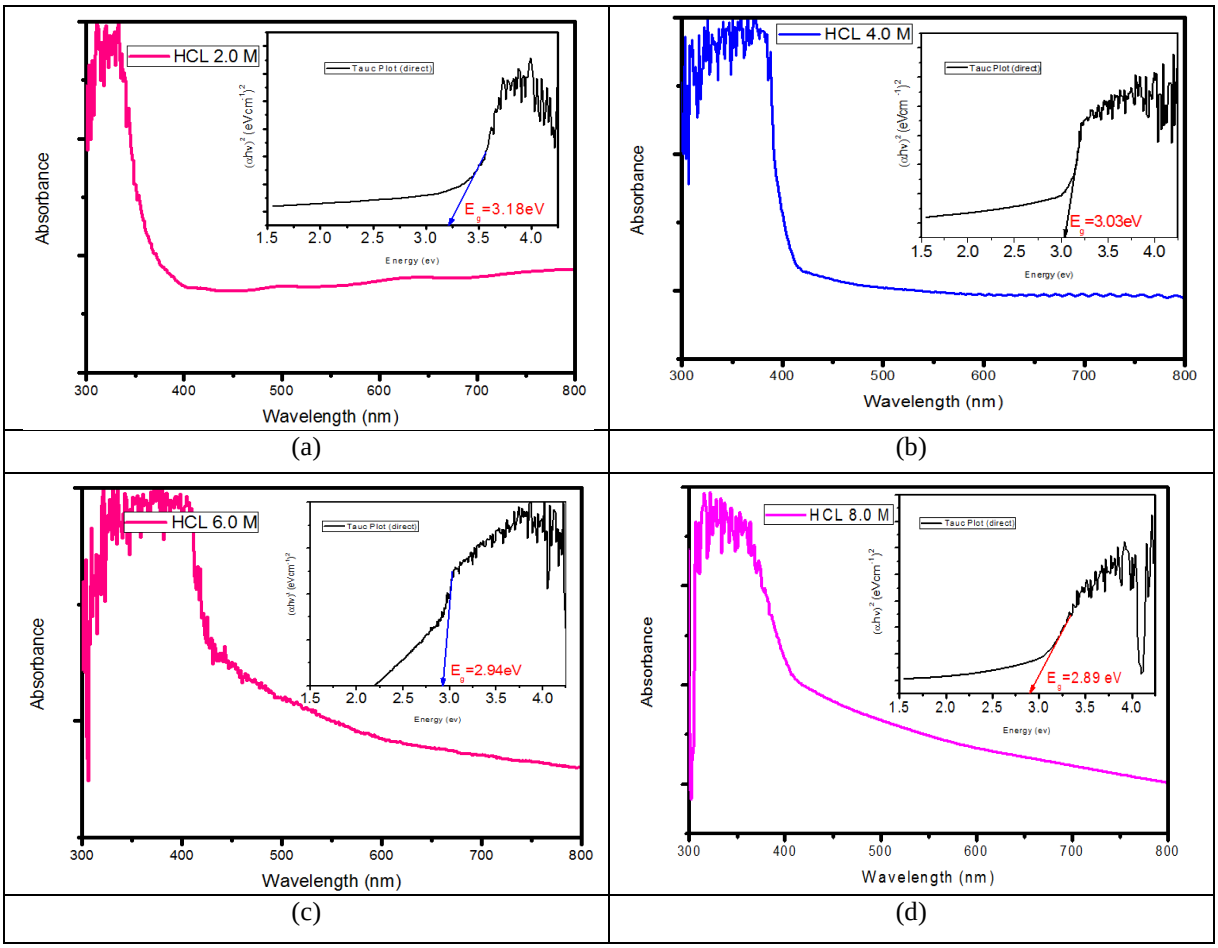

Figure 3.4 - The absorbance spectra and the extrapolated band gap of microstructured and nanostructured TiO_2 thin films with varying hydrochloric acid (HCL) molarity.

IV. CONCLUSION

In this study, single step low-cost hydrothermal process without any surfactant was implemented to demonstrate the effects of concentration of hydrochloric acid (HCL) on the morphologies control of microstructures and nanostructures TiO_2 thin films for boosting the photocatalytic performance. Under FE-SEM observation, the results demonstrate that the morphologies of the synthesized microstructures and nanostructures TiO_2 thin films can be controlled by the hydrochloric acid concentration to obtain the complex nanostructures which including the microspheres, nanoflowers, and nanobranches. The selection of nanorods and nanoflowers structure for nanostructures TiO_2 thin films are due to the ability in providing a larger surface area for light absorption and offers good electron mobility transfer. Optical absorption measurement for these microstructures and nanostructures TiO_2 thin film indicate that all the samples having good optical properties. Thus, it's very positive that these microstructures and nanostructures TiO_2 thin films can offer tremendous potential in future applications of electronic and magneto–electric devices, as well as applied for gas sensing, biomedical device and sun screen applications. This synthesis method has demonstrated that the hydrothermal method can obtain a high yield and suitable be used for large scale synthesis of microstructures and nanostructures TiO_2 thin films in near future.

ISSN (Online) 2321-2004
ISSN (Print) 2321-5526

IJIREEICE

International Journal of Innovative Research in
Electrical, Electronics, Instrumentation and Control Engineering

Vol. 7, Issue 4, April 2019

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