Synthesis of nano crystal TiO\(_2\) with modified commercial powder of TiO\(_2\)

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Abstract. Nano crystal TiO\(_2\) was synthesized by modifying the TiO\(_2\) powder (Merck). The powder of TiO\(_2\) was stirred in 1M HCl solution for 2 hours, and then added ammonia solution (NH\(_4\)OH). The suspension of TiO\(_2\) is spread evenly over the substrate glass and then heated to a different temperature. The structure and optical properties of TiO\(_2\) layer were examined using XRD to see the TiO\(_2\) crystal structure and size in heating temperature treatment. The optical properties of TiO\(_2\) observation showing the absorption band edge shifted to the shorter wavelength, it means the energy of band gap increases to heating temperature.

1. Introduction
Titanium dioksida (TiO\(_2\)) is a metal oxide material which is currently examined very intensively because TiO\(_2\) material has specific chemical and physical feature so it is widely applied to various field [1-3]. The features of photocatalytic activity can be used to destructed the chemical and biological pollutant [4-7]. The optical features can be used on photoelectrochemical-based energy conversion technology, especially dye-sensitized solar cell [8-10]. TiO\(_2\) is also widely used as a blech pigmentation, gas censor and so on [11,12].

TiO\(_2\) is a semiconductor material with a wide energy gap, ie about 3.0-3.4 eV which can be specifically absorbed the ultraviolet spectrum [1-3,13]. So, it can be utilized as a photocatalyst for the decomposition of chemical pollutants and the destruction of harmful microorganisms. In addition, it is also suitable for dye-sensitized solar cells. TiO\(_2\) has three main polymorphs which is anatase, rutile and brookite. Anatase and rutile phases are known to be more stable and widely applied to various fields such as the conversion of energy, environmental, and health. However, the used of pure TiO2 or modified with crystal structure for photochatalic system still has a weakness such as low photochatalic efficiency which is only 3-5% of the sunlight spectrum can be absorbed [14]. This research aims to syntesise nanocrystal of TiO\(_2\) by moification of commersial powder of TiO\(_2\) to investigate the optical properties and the crystalisation of the samples.
2. Methods

Please The materials used are TiO\textsubscript{2} powder (Merck), HCl and ammonia solution (NH\textsubscript{4}OH). While the equipment used is hotplate stirrer, furnace, XRD equipment and UV-Vis Spectrophotometer.

Nanocrystal TiO\textsubscript{2} is synthesized by modifying commercial TiO\textsubscript{2} powders (Merck) as follows; Firstly, 2 g powder of TiO\textsubscript{2} was mixed into 1M HCl (50 ml) while stirring strongly using magnetic stirrer for 12 hours on room temperature. Furthermore, ammonia solution (5 ml) was added while stirring for 2 hours until TiO\textsubscript{2} suspension was produced. The suspension is spread over the surface of substrate glass preparations until flat. Three TiO\textsubscript{2} samples were heated in the furnace for 1 hour at different temperatures, i.e. 100, 300, and 500 °C. The produced samples were characterized by XRD to observe the crystal structure and UV-Vis spectrophotometer to observe the optical characteristics.

3. Results and Discussion

The XRD (X-Ray diffraction) characterization result of the three modified TiO\textsubscript{2} samples shown in figure 1. In panel (a) shows the diffraction pattern for the heated sample at 100 °C. The pattern of TiO\textsubscript{2} diffraction with anatase crystalline phase based on very strong diffraction peaks at an angle of 2\theta = 25.20\textdegree followed respectively at 36.84; 37.70; 38.47; and 47.94. There are also peaks at 22.79 and 32.57 that has not been identified. In figure 1 (b), the diffraction pattern for the heated sample at 300 °C shows the peaks at the angle 2\theta = 25.27; 36.92; 37.75; 38.53 and 48.00. There is shift in diffraction peak toward the larger angle but still in the range for the anatase TiO\textsubscript{2} crystalline phase. While in figure 1 (c), the diffraction pattern for the heated sample at 500 °C, the diffraction peaks appear at an angle of 2\theta = 25.22; 36.88; 37.70; 38.48 and 47.95.

![Figure 1](image1.png)

**Figure 1.** The modified of nanocrystalline TiO\textsubscript{2} diffraction pattern : (a). 100 °C, (b). 300 °C and (c) 500 °C

From the diffraction pattern can also be determined the crystal size (crystal size) of TiO\textsubscript{2} by using the Scherrer equation,

\[
\sigma = \frac{0.94\lambda}{\beta\cos\theta}
\]

with \(\sigma\) is crystal size; \(\lambda\) is wavelength of X-ray used; \(\theta\) is diffraction angles and \(\beta\) is max peak width (the peak full-width at half-maximum, FWHM).
Based on the FWHM value for the diffraction peak at an angle of 25.20°, the equation (1) used to calculate the crystal size. The calculation results for the three samples with different annealing temperature showing the value of crystal size (a) for 100 °C, 300 °C and 500 °C are 44.28 nm, 59.05 nm, 59.05 nm, respectively. The values of the crystal size has getting into the nanocrystal region (i.e. <100 nm). Thus, it can be concluded that the nanocrystalline TiO₂ is synthesized by modifying the commercial TiO₂. It also found that the crystal size of TiO₂ increases to heating temperature.

Besides, the characterization of XRD, the modified of TiO₂ samples were also characterized the optical properties using a UV-Vis spectrophotometer. Spectrum refektans and absorbance the modified results of TiO₂ sample with HCl + NH₄OH is shown in Figure 2.

Figure 2 (a) is the spectrum of reflectance of the modified result of TiO₂ samples with a heating temperature at 100 °C, 300 °C and 500 °C, respectively. It appears that TiO₂ samples reflect on strong visible spectrum. While in Figure 2 (b) shows that the absorption area of TiO₂ sample on the ultraviolet region. The interesting part of the reflectance spectrum (figure 2a) and the absorbance (figure 2b) are the occurrence of a shifting spectrum on heating temperature, where the shift occurs towards the shorter wavelength increases to heating temperature. Although the displacement is not very significant, but it gives different optical properties, which the optical gap width increases on heating temperature.

The energy band gap (E₉) of a semiconductor can be determined by using a relation.

$$E_g = h\nu = h\frac{c}{\lambda_{edge}}$$  (2)

where υ is the frequency of photons, c is the speed of light (3x10⁸ m/s), λ_{edge} is the wavelength of the photon at the edge of the absorption band and h is Planck’s constant (4.136x10⁻¹⁵ eVs). Figure 2 shows the spectrum curves of reflectance and absorbance for the sample with heating temperature of 100 °C, 300 °C and 500 °C at wavelength of 401 nm, 394 nm and 394 nm respectively. These wavelengths were used in calculation of energy gap using equation (2) which resulting a value of 3.09 eV for heating temperature of 100 °C, 3.14 eV for heating temperature of 300 °C and for heating temperature of 500 °C. The results showing that the value of energy band gaps increases to heating temperature. The value of this bandwidth gap width still approaching the values that obtained by previous researchers [15].

4. Conclusion
We have synthesised nanocrystalline TiO₂ by modifying the commercial of TiO₂ using HCl and ammonia solution (NH₄OH), resulting TiO₂ powder size of 50 nm which is still within the nanostructure material area. Based on the XRD investigation, it is found that TiO₂ crystal structure and crystal size change to the heating temperature. The Results of optical test shown that optical properties (optical band gap) varies with the heating temperature. The obtained Nanocrystal of TiO₂ can be applied as a photoelectrode on a dye-sensitized solar cell system.
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