PHOTOCATALYSIS ACTIVITY NANOTITANIA UNDER SUNLIGHT IRRADIATIONS

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Abstract - The synthesis of nanotitania was prepared using the sol gel method with the addition of ethanolamine as a surfatan. This research was conducted to determine the effect of ethanolamine addition on the photocatalyst activity and energy gap of nanotitania. In this study, the use of titanium butoxide acts as a precursor, ethanol as a solvent and HCl as a converter for sol to gel. The addition of varied ethanolamine is 0; 0.5; 1; 1.5; and 2 ml. The sample was calcined at 500ºC for 4 hours. Nanotitania were characterized using Raman Spectroscopy, UV-Vis Spectrophotometry, and UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS) using the Kubelka-Munk method. The results of the characterization of Raman spectroscopy showed that the C-1 sample formed anatase, rutile and brookite phases. Test the photocatalyst activity by degrading remazole yellow solution using sunlight as the trigger. The results of the UV-Vis DRS characterization of the energy gap of each samples are 3.18; 3.2; 3.03; 3.15 and 3.2 eV for samples of A-0, B-0.5, C-1, D-1.5 and E-2 respectivly.

Keywords - Energy gap, Ethanolamine, Nanotitania, Photocatalyst, Remazol Yellow.

I. INTRODUCTION

The rapid development of research on nanomaterials is caused by the desire to change technology, which is generally micrometer-sized materials, into nanometer-sized materials [1]. Nano-sized materials have superior physical, chemical and mechanical properties than bulk materials [2]. Some of the common materials found in nano form are nanosilica, nanotitania and nanomagnetite. Nanotitania is a nano material derived from TiO_2 which has stable chemical properties, is insoluble in water, non-toxic, environmentally friendly, and non-corrosive [3]. TiO_2 has 3 types of crystal structures, namely anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). TiO_2 is a semiconductor metal oxide which is often applied as a gas sensor, photovoltaic cell, pigmentation, and photocatalyst [4].

Photocatalyst is a process from a combination of photochemical processes and catalysts, namely a chemical synthesis process that involves light as a trigger and a catalyst as an accelerator of the transformation process [5]. Factors that influence the occurrence of photocatalysts are particle surface area [6], crystal structure, phase composition, particle size [6], and energy gap [7], [8]. Band gap energy or also known as band gap energy is the minimum energy required to excite electrons from the valence band to the conduction band. If a semiconductor is subjected to an energy corresponding to the bandgap energy, then the electrons in the valence band will move to the conduction band to form holes in the valence band. Some of the holes and electrons will be stuck on the semiconductor surface, the holes will undergo an oxidation reaction and the electrons will experience a reduction reaction with chemical compounds that are around the surface of TiO_2. This principle is used as an active compound in degrading pollutants and microorganism compounds. Bandgap energy contained in the anatase, brookite, rutile phases were 3.21, 3.13, 3.00 eV [9]. The formation of the nanotitania phase can be influenced by the synthesis process of its manufacture.

Synthesis in the formation of nanotitania can use several materials such as titanium tetra isopropoxide (TTIP), $TiCl_4$ and titanium butoxide (Chen and Mao, 2007). The use of titanium butoxide has the advantage of being environmentally friendly, has a high metal content in the environment, has a high metal content and is easily dissolved [11]. The nanotitania synthesis method can be carried out using the sol-gel method, the hydrothermal method, the solid reaction and the solvothermal method [10], [12]. The method used in this research is the sol-gel method. The sol-gel method has the advantage that the synthesis process of nanotitania can be carried out at low temperatures and has high homogeneity. Based on research conducted by Galkina *et al.*[6], the addition of surfactants in the synthesis of nanotitania using the sol-gel method at calcination at a temperature of 500ºC can produce anatase, rutile, and brookite phases. The surfactant used in this study is ethanolamine (MEA) which is a weakly alkaline surfactant solution.

The results of the synthesis of nanotitania with the addition of ethanolamine will be tested for the photocatalyst activity of the Cary 100 UV-Vis tool to determine the absorption of the wavelength, the analysis is carried out at a wavelength of 200-550 nm, to determine the energy gap, the test will be carried out using UV-Vis DRS Spectrophotometry, and to determine The formation phase was tested using Raman Spectroscopy. The tools used in the Raman Spectroscopy test are LabRAM HR Evolution Raman Microsopes which have a multilaser and a multidetector capable of covering UV to NIR wavelengths, namely 532 nm and 758 nm wavelengths. Raman spectroscopy is a microscopic technique that is able to identify various forms of bonds between atoms, this is confirmed based on the

absorbance electron structure of a molecule. In addition, Raman spectroscopy is also used as a supporting analysis of the XRD test results. This happens because UV Raman spectroscopy is more sensitive in detecting the small phases that are formed [13].

II. DETAILS EXPERIMENTAL

2.1 Preparation Sample

The preparation of titanium dioxide powder is carried out by synthesizing a mixture of titanium butoxide ($C_{16}H_{36}O_4Ti$) Sigma Aldrich (≥97%), Emsure's ethanol (C_2H_5OH) (99.9%), Merck brand ethanolamine (99%), and Merck brand HCl (37%) with the composition in Table 3.1. In this case, titanium butoxide ($C_{16}H_{36}O_4Ti$) functions as a precursor, ethanol (C_2H_5OH) functions as a solvent, ethanolamine functions as a surfactant and HCl functions as a pH converter in the sol to gel solution. The synthesis process is carried out by making a titania solution. The process of making a titania solution by mixing 60 mL of ethanol with 5.25 mL of titanium butoxide using a micro pipette, stirring for 20 minutes with a magnetic stirrer. Then add ethanolamine drop per drop using a micro pipette with variations (0 mL; 0.5 mL; 1 mL; 1.5 mL; and 2 mL) stirred for 30 minutes and the next step is adding HCl 2.45 mL drop per drop using pipette and keep stirring for 24 hours until a solution of gel nanotitania forms. Nanotitania gel solution in an oven with a temperature of 100-150°C for 24 hours and calcined at a temperature of 500°C for 4 hours.

Sample	Ti-butoxide (mL)	Ethanol (mL)	HCl (mL)	MEA (mL)
A-0	5.25	60	2.45	0
B-0.5	5.25	60	2.45	0.5
C-1	5.25	60	2.45	1.0
D-1.5	5.25	60	2.45	1.5
E-2	5.25	60	2.45	2.0

Table 1. Composition without addition and addition of ethanolamine nanotitania.

The nanotitania powder is crushed using a mortar agate for 30 minutes until the particles become fine. Table 1. Sample variations of differences in the addition of ethanolamine.

2.2 Preparation of characterization

Raman spectroscopy using LabRAM HR Evolution Raman Microsopes with a laser source wavelength of 532 nm (maximum power 100 mW), objective lens set at 10 x Vis (NA = 0.25, WD = 10.6 mm) and CCD detector. UV-Vis and DRS spectrophotometry using Cary 100. UV-Vis measures absorbance at a wavelength of 200-550 nm and DRS looks at the reflectance value at a wavelength of 200-800 nm. Nanotitania photocatalyst activity with the addition of ethanolamine was carried out in a solution of 10 ppm golden yellow remazole with a concentration of 10 ppm made from mixing 3 ml of remazole yellow (1000 ppm concentration) and 297 ml of aquabides. In the irradiation under the sunlight, it is carried out at around 11-12 am.

III. RESULT AND DISCUSSION

3.1 Raman Spectroscopy

Raman spectroscopic analysis shows on Fig. 1 of the nanotitania samples with the addition of 1 ml MEA (C). According to previous research conducted by Beltran *et al.* (2017) synthesizing nanotitania using titanium butoxide obtained the anatase phase at shifts of Raman 149, 197, 398, 513, 519, and 637 cm^{-1}, whereas based on the research of Jing *et al.* (2011) synthesis of nanotitania can produce anatase, rutile and brookite phases. The Raman shift of the rutile phase is located at 235, 444, and 612 cm-1, the anatase phases 143, 195, 395, 514, 519, and 635 cm^{-1}, and for the brookite phase 121, 150, 244, 284, 321, 363, 402, 487, 542, and 630 cm^{-1}. Fig. 1. the peaks appear at the raman shifts of 146, 197, 245, 444, 502 and 612 cm^{-1}. The raman shift at the 146, 197, 245 cm^{-1} peaks defined as the anatase phase, the 444, 612 cm^{-1} peaks defined as the rutile phase, and the 502 cm^{-1} peaks defined as the brookite phase. Based on the test results using the DRS UV-Vis Spectrosphotometry shown in Fig. 2.

3.2 DRS UV-Vis Spectrophotometry

On the y-axis is the reflectance (% R) data of the sample to light with a wavelength of 180-800 nm as the x-axis. Based on the results of the DRS UV-Vis Spectrophotometry, it can be seen that there is not much difference between the samples. Based on research conducted by Muthee *et al.* (2020) determining the bandgap energy can be done by changing the% R (reflectance) quantity with the Kubelka-Munk method (F (R)), as in eq. 1

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (1)$$

where, F (R) is the Kubelka-Munk factor, K is the absorbance coefficient, S is the scattering coefficient, and R is the reflectance value. Bandgap energy is obtained from then perform linear extrapolation $(F(R)hv)^2$ against hv (eV) cutting the abscissa, this cut value which is the value of the gap energy is shown in Figure 3. The value of hv (eV) can be determined by eq. 2.

$$E_g = hv = \frac{hc}{\lambda} \qquad (2).$$

Where: E_g = bandgap energy (eV),
h = Planck's constant (6,624 x 10-34Js),
c = the speed of light in air (3x 108 m/s),
λ = wavelength (m).

Based on the results of calculations using the Kubelka-Munk method, it is known that the energy gap is shown in Fig 4.

3.3 Photocatalyst activity
Photocatalyst activity by doing the exploration using remazol golden yellow irradiation under sunlight as a trigger for the reaction. Irradiation under the sun is carried out for 50 minutes with 10 minutes of sample taken as much as 10 ml. Based on the results of UV-Vis
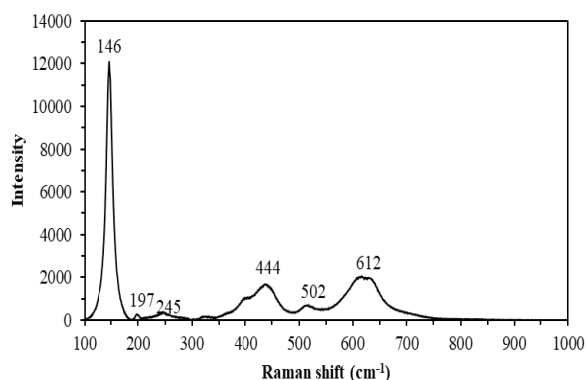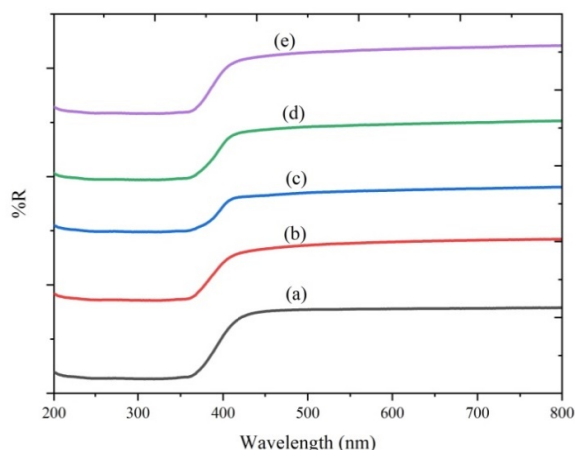

Fig. 1. Raman spectroscopy on sample C-1 with MEA dopping 1 ml.

Fig. 2. UV-Vis DRS Spectrophotometry results from samples (a) A-0, (b) B-0.5, (c) C-1, (d) D-1.5 and (e) E-2.
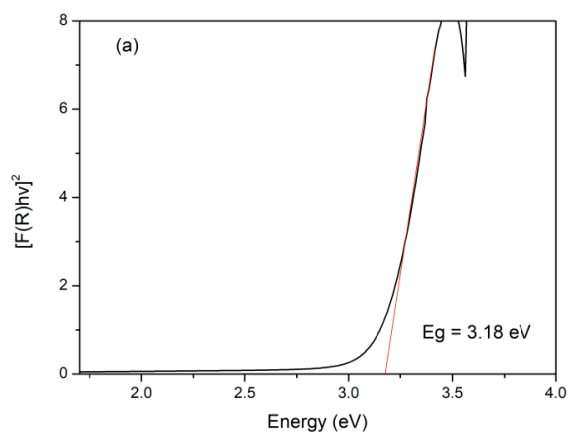

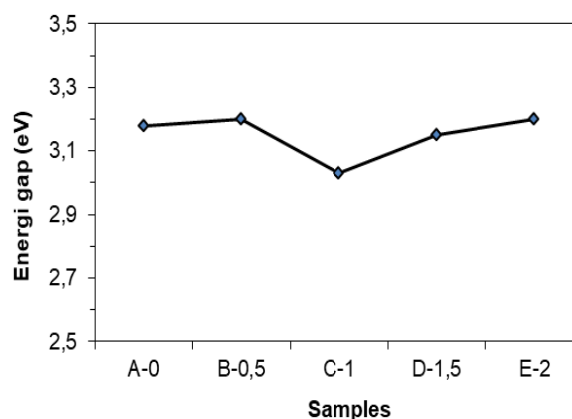**Figure 3. Results of the energy gap sample A.**

Fig. 4. Energy gap of samples A, B, C, D, and E.

spectroscopy, it is known that the maximum peak position of the wavelength is at 411 nm and the longer the exposure time will make the absorbance decrease as in Figure 5. The activity of photocatalysts that experienced the most significant photodegradation of remazole golden yellow in sample C with the addition of 1 ml of MEA, this is influenced by sample C which has the largest surface area [16].
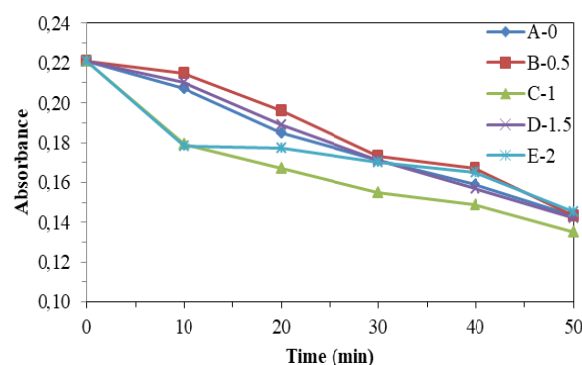

Fig 5. Photodegradation of nanotitania with the addition of ethanolamine under sunlight irradiation on samples A-0, B-0.5, C-1, D-1.5 and E-2 at the peak position λ = 411 nm.

IV. CONCLUSION

Results Characterization of nanotitania with the addition of ethanolamine / MEA using the sol gel method and calcined at a temperature of 500 ^{o}C influenced the phase formation. From the results of the Raman spectroscopy analysis on the sample C-1, the anatase, rutile, and brookite phases were obtained. The results of the UV-Vis spectrophotometer showed that samples A-0, B-0.5, C-1, D-1.5 and E-2 were able to degrade remazol golden yellow solution and the highest photoactivity was found on samples MEA dopping 1 mL. The results of the UV-Vis DRS characterization showed that the energy gap of each samples are 3.18; 3.2; 3.03; 3.15 and 3.2 eV for samples of A-0, B-0.5, C-1, D-1.5 and E-2 respectively.

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