

# Synthesis And Characterization Of Electrodes N-TiO<sub>2</sub>/Ti For Chemical Oxygen Demand Sensor With Visible Light Response Flow

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**Abstract:** There had been done a thin layer preparation of N-TiO<sub>2</sub> nano-sized, which is attached to the substrate Ti Plat. Preparation of thin layers (films) N-TiO<sub>2</sub> was done by dip coating into the sol-gel prepared by reflux and then calcined at 450°C. Characterization was conducted towards the film by DRS, XRD, FTIR, SEM, and potentiostat. DRS measurement results indicated wavelength in the visible region, XRD measurement showed that the resulting film was dominated by the N-TiO<sub>2</sub> in the anatase form and has a crystal size (crystallite size) of 13.47 nm. While the results of the FTIR characterization indicated Ti-O bond, -NO and Ti-N. Meanwhile, SEM measurements showed a small crystal size. Photoelectrochemical test with potentiostat, by placing the film N-TiO<sub>2</sub>/Ti as the working electrode produces light flow response to N-TiO<sub>2</sub>/Ti. This system can be developed into a useful sensor for determining COD in a way that has never existed before.

**Keywords:** Nitrogen doped, titanium dioxide, Chemical Oxygen Demand, Visible.

## INTRODUCTION

Development of the industry is very rapid in addition to providing many benefits in improving the quality of life also have a serious impact on the surrounding environment. The use of toxic and hazardous chemicals, waste and pollution generated in a large amount had damaged and threatened the stability of the ecosystem. It prompted scientists to innovate more good for environmet, by introducing the principle of optimization and efficiency of industrial processes which were known as the concept of green chemistry. Since the publication of the phenomenon of photocatalytic titanium dioxide by Fujishima and Honda (1972) was splitting water into oxygen and hydrogen by semiconductor TiO<sub>2</sub> under ultraviolet light [1], TiO<sub>2</sub> material had been studied to help address environmental problems. Even in low concentrations, most of the natural water, domestic water, and industrial water containing organic substances that could caused decrease in oxygen levels in the water. Therefore, the determination of organic substances in water and wastewater is one of the important parameters to determine water quality. Currently there are two standard methods of analysis that have been used for the determination of oxygen demand in the water BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) [2]. Determination of COD with standard methods, it was currently used method involved the use of a strong oxidizing agent potassium bichromate, sulfuric acid, and silver sulfate as catalyst [3].

Environmental aspects of health care will push the need for a critical review of the standard method of determining COD, because of the involvement of hazardous materials and toxic in the analysis process. Various attempts have been made to find a better alternative methods and good for environmet. The development of methods for the determination of COD could be classified into two categories. First, the method is based on the principle of conventional chemical oxidation and simple in its analysis process. Secondly, methods is based on the electrocatalytic oxidation of organic matter and accompanied by electrochemical measurements [4]. Meanwhile, Zhao et al have reported a new method as an alternative method of measuring COD. [5] The proposed method is based on the combined photocatalytic and electrochemical, with an entirely new approach. They use the TiO<sub>2</sub> films were coated on ITO-coated glass substrate (Indium Tin Oxide), which functioned as the anode in the photoelectrochemical system. Light flow that arises when the system has been evaluated and executed photoelectrochemical used as the amount that can be correlated with the COD value. However, these methods still work areas to narrow the range of COD values up to 60 mg/LO<sub>2</sub>. Besides, the design direction of the electrode where the photons to activate photoelectrocatalist of direction must pass through bodies of water samples vulnerability to disruption invite high uptake by the water sample matrix (UV-chromophore, suspended particles and floating solids). Sunlight energy that reaches the earth is one of the energy sources that are abundant in the earth's surface. This abundance will be very advantageous if available a photocatalyst that can be activated by using the sun light. Several researchers had conducted a photocatalyst TiO<sub>2</sub> matrix modifications that could be activated by visible light. One of the modifications made was to insert an other atoms (dopants) into the TiO<sub>2</sub> crystal matrix, wherein the matrix elements of the dopant makes the new catalyst has a value smaller energy gap equal to visible light energy. Efforts to use the N dopant serves to increase the photocatalytic activity of TiO<sub>2</sub> in visible light radiation sensors for application development COD, have not been studied so far. In this study, TiO<sub>2</sub> will be modified with non metallic dopants N (nitrogen) at the plate substar Ti and ITO

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glass. The addition of N dopants in TiO<sub>2</sub> catalyst system is expected to improve the performance of the process of reform-in application for the development of photocatalytic COD sensor that can be used in the visible light region. The addition of N dopant on the one hand can serve as the core active on TiO<sub>2</sub> photocatalytic process as well as to prevent the recombination of electron trapper electron - hole so as to improve the photocatalytic performance in the measurement of oxygen content in waste water [6], [7]. Crucial point in the development of photoelectrochemical cell system mentioned above is the preparation of N-TiO<sub>2</sub> films are nano-sized anode in order to obtain films that have a large surface area and very active. Sol-gel method and calcination used to obtain N-TiO<sub>2</sub> films as desired. This paper will report the results of characterization of N-TiO<sub>2</sub> films were produced and used as the working electrode in the photoelectrochemical determination of COD based.

## METHODS

### Materials Research

The materials used in this study is Titanium Tetra Iso propoxide (TTIP) 97% Aldrich, 95% ethanol, 0.1 M NaNO<sub>3</sub>, distilled water, 31% HCl, 40% HF, concentrated HNO<sub>3</sub>, acetylacetonate, Urea, Plat Ti, glucose, distilled water.

### Synthesis of N-TiO<sub>2</sub> Sol-gel method

The initial step in the synthesis of N-TiO<sub>2</sub> sol-gel method, created two solutions, where solution A solution in the form of colloidal TiO<sub>2</sub> prepared by controlled hydrolysis of titanium tetra iso propoxide (TTIP) was taken as the acetylacetonate 4 mL and 0.5 mL of ethanol 15 ml were included in the reflux flask. Solution B in the form of 15 ml of ethanol and 2 mL of distilled water with the addition of 1 mL of 0.5 M acetic acid were put into a separating funnel and then solution B was added to a solution of A in stages through a separating funnel while stirring using a magnetic stirrer, measuring the desired pH. Solution mixture was refluxed for 2 hours with a temperature of 50°C. The next step for mendoping TiO<sub>2</sub> with urea as a nitrogen source, the same sol was stirred using a magnetic stirrer, followed by the addition of a nitrogen source with a concentration of 1.0 M, 1.5 M and 2.0 M to produce TiO<sub>2</sub> sol containing nitrogen for 1 hour with a temperature of 50°C. The resulting partial solution dianginkan at room temperature to form a gel, and then dried in an oven at a temperature of 80°C for 30 min, and calcined at 450°C to produce crystalline TiO<sub>2</sub> or N-doped TiO<sub>2</sub> sol and partly used for superimposed on Ti plate.

### Electrode Preparation

#### a. Ti Plate (titanium)

Plate of Ti (titanium) which has been previously prepared by sol immobilized TiO<sub>2</sub> and N-TiO<sub>2</sub> by superimposing on the plate surface evenly with a deep coating technique. Then the plate was allowed to dry and calcined using a furnace at a temperature of 450°C. that the formation of crystalline anatase going well. In order to obtain a uniform thin layer on the surface of the plate.

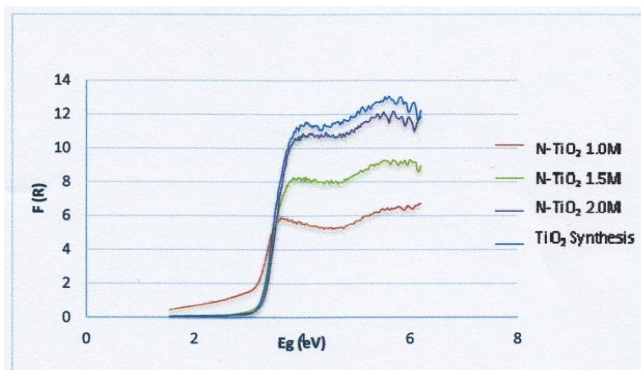
### b. Characterization of N-TiO<sub>2</sub> Catalysts

Characterization is performed to determine whether the products are in accordance with its intended purpose or not. Products may include TiO<sub>2</sub> and N-TiO<sub>2</sub> films synthesized and N-TiO<sub>2</sub> and TiO<sub>2</sub> were successfully prepared. Characterization using UV-Vis DRS, XRD, SEM, and FTIR for TiO<sub>2</sub> and N-TiO<sub>2</sub> synthesis, whereas the film TiO<sub>2</sub> and N-TiO<sub>2</sub> were characterized using electrochemical or potentiostat system.

## RESULTS AND DISCUSSION

### Characterization by UV-Vis DRS

Characterization by means of UV-Vis DRS conducted to obtain information bandgap crystal TiO<sub>2</sub> and N-TiO<sub>2</sub> synthesis results are used. Results of analysis of UV-Vis DRS catalyst TiO<sub>2</sub> and N-TiO<sub>2</sub> shown in Figure 1. In Figure 1, it showed that the smallest band gap value of 3.06 obtained in the synthesis of nitrogen doped TiO<sub>2</sub> with the addition of urea 1.0 M.



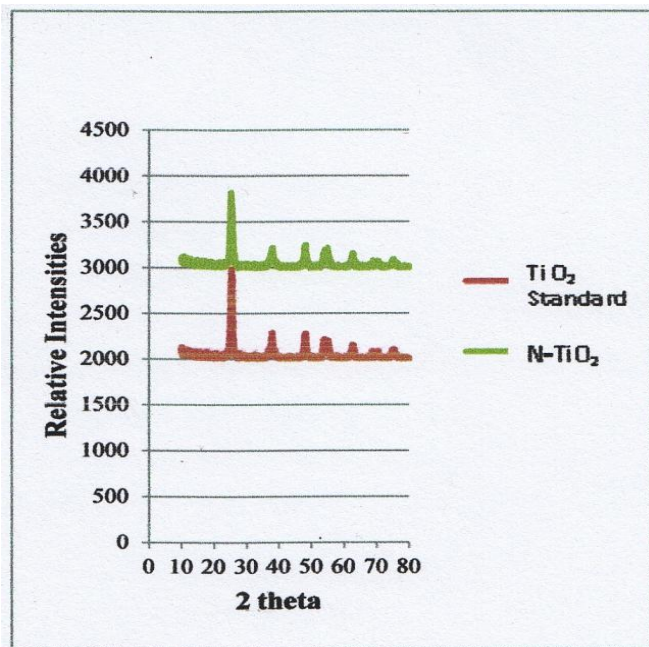
**Figure 1.** The band gap could be used to calculate the wavelength by the formula:

$$E_g = \frac{hc}{\lambda_g} = \frac{1239.8}{\lambda_g} = (\text{eV})$$

Optimum band gap values obtained at a concentration of 1.0 M. Urea mean wavelength of 405 nm. With the decline in the value of the band gap energy of light is needed to form photohole (conduction band) and photoelectron (valence band) will be smaller, for example, simply by using a visible light source.

### Characterization by Xray Diffractometer (XRD)

Characterization by means of XRD performed to obtain information crystal structure of TiO<sub>2</sub> and N-TiO<sub>2</sub> synthesis results. Materials TiO<sub>2</sub> and N-TiO<sub>2</sub> were analyzed are not the result of calcination gel coated on Ti plate substrate, but get the same heat treatment on the substrate coated with the Ti plate.

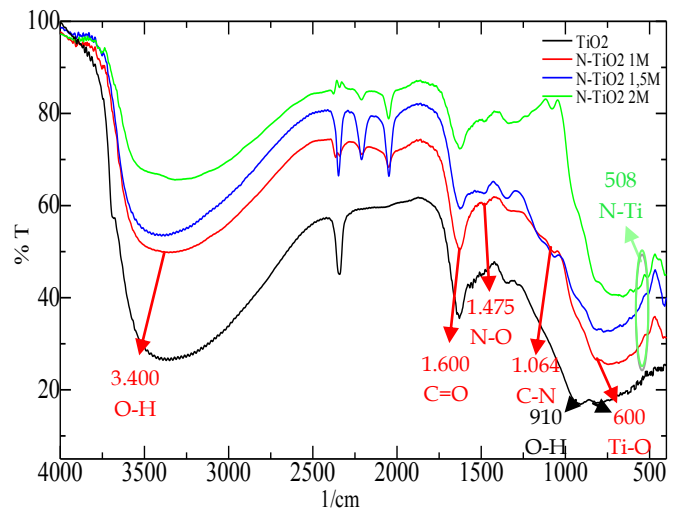


**Figure 2.** Diffractogram X-rays  $\text{TiO}_2$  and  $\text{N-TiO}_2$

Figure 2. an X-ray diffractogram analysis  $\text{TiO}_2$  catalyst and  $\text{N-TiO}_2$ . The images seen on the tops of which can provide identifying information from crystalline  $\text{TiO}_2$  and  $\text{N-TiO}_2$  were made in this study. Crystal shape can be determined by comparing the value of  $2\theta$  or  $d(\text{\AA})$  the results of measurements with data interpretation card crystalline  $\text{TiO}_2$  standard. XRD analysis of the results of  $\text{TiO}_2$  catalysts are shown in Figure 2. It could be seen that the X-ray diffractogram pattern gave nine diffraction peaks with the diffraction  $2\theta$  pattern  $25.34^\circ$  with indicating that the  $\text{TiO}_2$  and  $\text{N-TiO}_2$  were measured dominated by anatase crystals. From the top diffractogram obtained and with the help of Scherrer equation calculated crystalite size or crystal size is equal to 14.01 nm for  $\text{TiO}_2$  catalyst and 13.47 nm for  $\text{N-TiO}_2$  catalyst.

#### Characterization of FT-IR (Fourier Transform Infra Red)

Characterization using FTIR results in Figure 3. obtained a spectrum, which indicated the presence of the OH stretching absorption peak marked the emergence of about  $910\text{ cm}^{-1}$  (bending vibration) with a weak signal around  $3400\text{ cm}^{-1}$  (stretching vibration) with a strong signal. The presence of OH groups thought to have come from the group titanil as Ti-OH terminal of the crystal phase of  $\text{TiO}_2$  and water are absorbed on the surface. Indication of the presence of the C-N group stretching probably derived from aliphatic amine group characterized by a peak around  $1064\text{ cm}^{-1}$ . In addition, the presence of the C = O stretching absorption peak located at  $1600\text{ cm}^{-1}$  allegedly derived from ketone group.

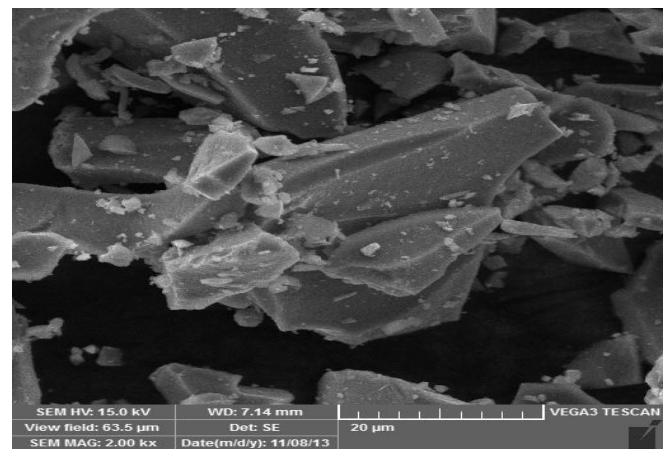


**Figure 3.** FT-IR spectra of  $\text{TiO}_2$  and  $\text{N-TiO}_2$

Indication of the presence of Ti-O bond is thought to occur at  $600\text{ cm}^{-1}$  absorption peak. While the appearance of the peak absorption at  $1475\text{ cm}^{-1}$  (symmetric vibration) indicating the presence of the NO. This allegedly occurred on the uptake of nitrogen insertion into  $\text{TiO}_2$  matrix. In addition, the presence of a Ti-N bonds are at the height of  $508\text{ cm}^{-1}$  with a weak signal. Anticipated amount of nitrogen contained in the catalyst very little.

#### Characterization by SEM

SEM measurement results provide information about the surface topography on the surface of a crystal. In Figure 4 crystal has a very small size and well spreadly, although there were still some large clumps. This could be caused by the presence of solvent trapped in the crystal structure of  $\text{TiO}_2$  could be explained from the emergence of OH vibrational peaks related to previously obtained FTIR spectra. The small crystal size affects the activity of the catalyst. This is because, the photocatalyst takes place on the catalyst surface, the smaller the particle size the greater the surface area of the active collide with the substrate to accelerate the photocatalytic reaction.



**Figure 4.** SEM characterization results of  $\text{N-TiO}_2$

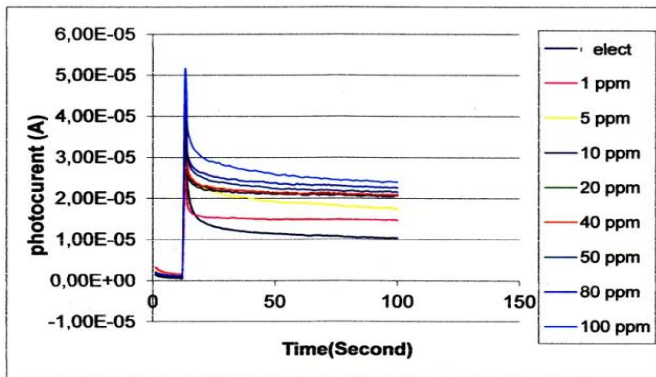


### Photoelectrocatalyst assay towards solution

This study, measured light flows generated from photoelectrocatalyst system developed at the time of test solutions containing some organic compounds. To determine the response to weak adsorbate compound with a compound of glucose is carried out while the strong adsorbate compound then performed with oxalic acid compounds. Current measurement was done by using a potentiostat light by Multi Pulse amperometric method (MPA). Bias potential remains in use were 200 mV. It was done based on the results of previous optimizations that bias 200 mV to 500 mV in capturing light and prevent the flow of electrochemical directly processes [8].

#### a. Glucose

In this experiment, used 1000 ppm glucose that has been diluted before. Glucose was a compound commonly used as a model compound in photoelectrocatalyst system as weak adsorbate. Glucose is one of the compounds photohole good catcher so hopefully these compounds can be degraded either.



**Figure 5.** Response of light flow on Ti plate with thermal compound glucose samples

Figure 5. showed that the higher concentration of organic matter, the higher the resulting current, because the current was proportional to the charge that generated charge was also greater with increasing concentration. Based on the theory that had been explained that the greater the concentration of the light generated current will be greater. The resulting current response of the measurement MPA (multi pulse amperometry) could be seen in Figure 5, from 1 ppm to 100 ppm glucose. Light of the current glucose concentration showed a light increase in line with increases in the current glucose concentration. Difference of total flow of light oxidation steady state ( $i_{tot}$ ) against current light blank 0.1 M  $\text{NaNO}_3$  steady state ( $i_{blank}$ ) was a net flow of light organic compounds ( $i_{net}$ ).

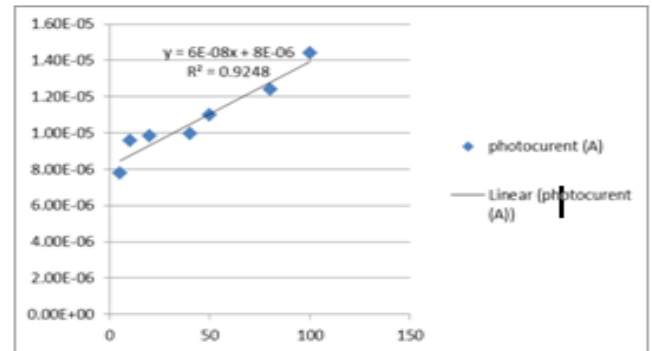
$$i_{net} = i_{st} - i_{blank}$$

This method was used to calculate the  $i_{net}$  value of  $i$  at later stages. Results showed above, will appear when the tabulated current trend of rising net ( $i_{net}$ ) due to higher concentrations. Can be seen in Figure 6. Figure 5. showed that the higher concentration of organic matter, the higher the resulting current, because the current was proportional

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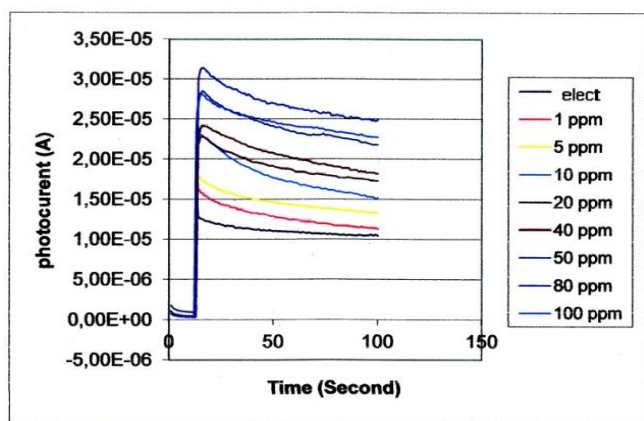


**Figure 6.** Linearity net flows ( $i_{net}$ ) the concentration of glucose in the Ti plate thermal

Figure 5. showed that the steady state photocurrent ( $i_{st}$ ) will further increase as the concentration of glucose. This was consistent with Figure 6, where the net flow ( $i_{net}$ ) increased along with the increase of glucose concentration. This was in accordance with the laws of Faraday who explained that the current would be proportional to the concentration of the solution [8]:

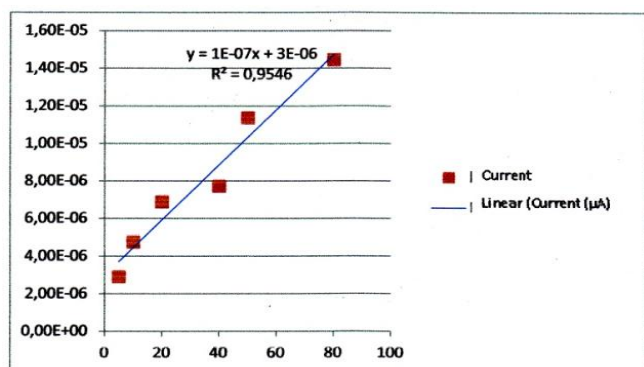
$$i_{net} = \frac{nFAD}{\delta} C_b$$

net flows ( $i_{net}$ ) will rise up at certain concentrations up to saturation where net flows ( $i_{net}$ ) would not increase even if the concentration increased. It could be seen that the increase in net flows ( $i_{net}$ ) is due to the increased of concentration with a value of  $R^2 = 0.9248$ .



**Figure 7.** Current response of Ti plate light on immobilized N-TiO<sub>2</sub> samples with glucose compounds.

Figure 7. indicated that the current value at a certain concentration would saturated where steady state photocurrent ( $i_{st}$ ) would not rise again but will be a constant or dropped at a certain value. This phenomenon was caused by the nature of glucose which is as a weak adsorbate. Weak adsorbate is adsorbate with a weak interaction with the surface of TiO<sub>2</sub>. Degradation in the weak adsorbate type, electron transfer occurs via outer sphere and generally did not form complexes on the surface of the catalyst [9].



**Figure 8.** Linearity net flows ( $i_{net}$ ) the concentration of glucose in the Ti plate immobilized N-TiO<sub>2</sub>.

It could be seen that the increase in net flows ( $i_{net}$ ) due to the increase concentration has a value of  $R^2 = 0.9546$ .

## CONCLUSION

Synthesis of N-TiO<sub>2</sub> was done by adding urea with various concentrations of 1M, 1.5M, and 2M. Where the addition of nitrogen in TiO<sub>2</sub> catalyst could reduce the energy of band gap, the band gap is the smallest value is 3.06 eV in the N-TiO<sub>2</sub> 1M. N-TiO<sub>2</sub> synthesis results could be active in the region based on data from the Visible Characterization of UV-Vis DRS, band gap of 3.06 eV ( $\lambda = 405$  nm); XRD anatase crystalline form on TiO<sub>2</sub> and N-TiO<sub>2</sub>; FTIR, the data binding Ti-O (600 cm<sup>-1</sup>), -NO bond (1475 cm<sup>-1</sup>), Ti-N bond (508 cm<sup>-1</sup>) showed the presence of N on N-TiO<sub>2</sub>; SEM, the size of very small crystals.

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