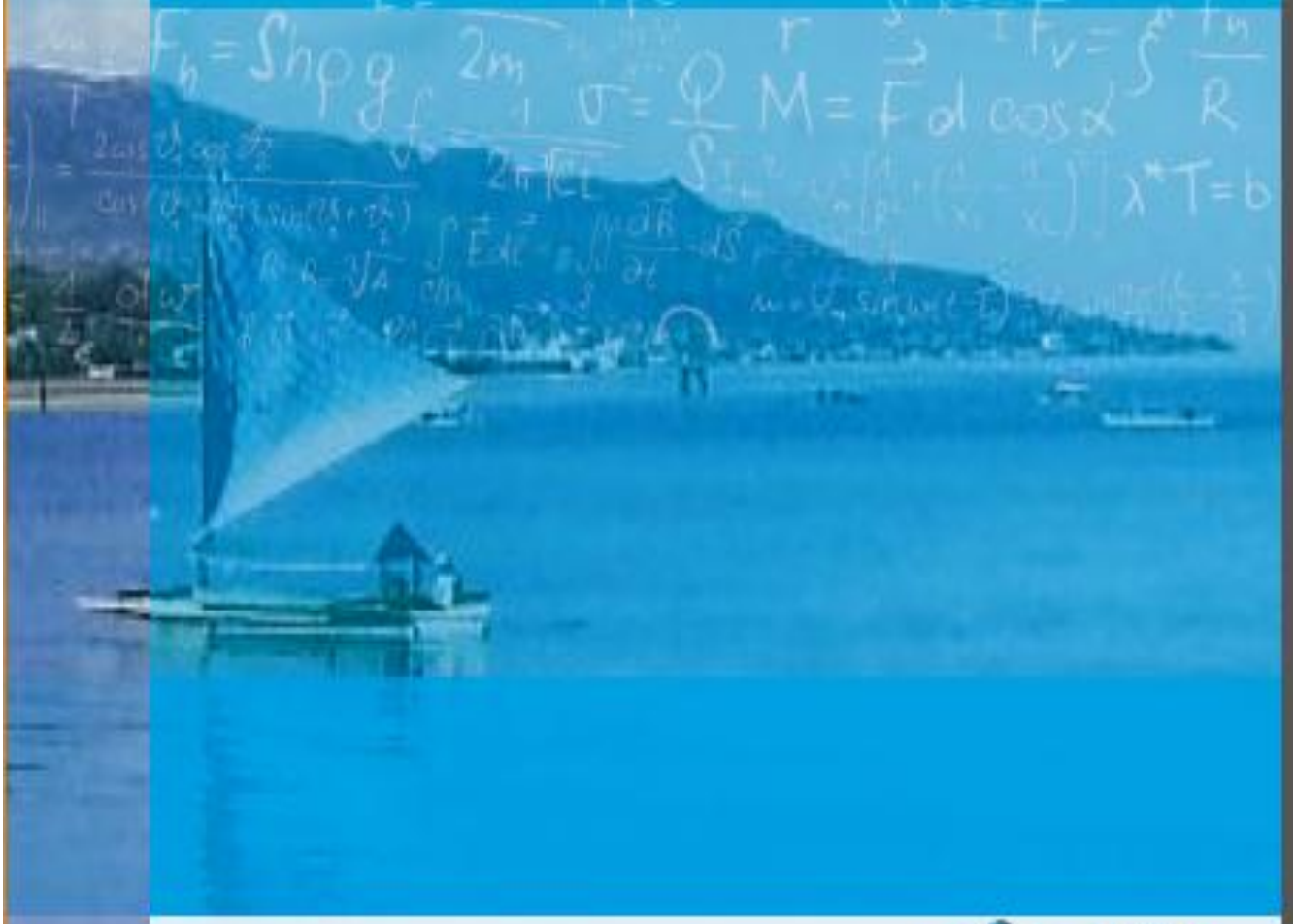
Basic Science
for Sustainable Marine Development

PROCEEDING
INTERNATIONAL SEMINAR 2015

Ambon, 3-4 June 2015



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Welcoming Address by The Organizing Committee

The honorable, the rector of Pattimura University

The honorable, the vice rector of academic affair, Pattimura University

The honorable, the vice rector of administration and financial affair, Pattimura University

The honorable, the vice rector of planning, cooperation and information affair, Pattimura University

The honorable, all the deans in Pattimura University

The honorable, the key note speakers and other guests.

We have to thank The Almighty God for the blessings that allow this International seminar can be held today. This is the first seminar about MIPA Science in which the Faculty of MIPA Pattimura University becomes the host. The seminar under the title Basic Science for Sustainable Marine Development will be carried out on 3 June 2015 at Rectorate Building, the second floor. There are 250 participants from lecturers, research institute, students, and also there are 34 papers will be presented.

This International seminar is supported by the amazing people who always give financial as well as moral supports. My special thanks refer to the rector of Pattimura University, Prof. Dr. Thomas Pentury, M.Si, and the Dean of MIPA Faculty, Prof. Dr. Pieter Kakissina, M. Si. I also would like to express my deepest gratitude to Dr. Kotaro Ichikawa, the director of CSEAS Kyoto University, Prof. Bohari M. Yamin, University of Kebangsaan Malaysia, Prof. Dr. Budi Nurani Ruchjana (Prisident of Indonesian Mathematical Society/Indo-MS), Dr. Ir. A. Syailatua, M.Sc (Director of LIPI Ambon), and Hendry Ishak Elim, PhD as the key note speakers. We expect that this international seminar can give valuable information and contribution especially in developing basic science for sustainable marine development in the future.

Last but not least, we realize that as human we have weaknesses in holding this seminar, but personally I believe that there are pearls behind this seminar. Thank you very much.

Chairman

Dr. Netty Siahaya, M.Si.

Opening Remarks
By Dean of Mathematic and Natural Science Faculty

I express my deepest gratitude to The Almighty God for every single blessing He provides us especially in the process of holding the seminar until publishing the proceeding of International Seminar in celebrating the 17th anniversary of MIPA Faculty, Pattimura University. The theme of the anniversary is under the title Basic Science for Sustainable Marine Development. The reason of choosing this theme is that Maluku is one of five areas in Techno Park Marine in Indonesia. Furthermore, it is expected that this development can be means where the process of innovation, it is the conversion of science and technology into economic value can be worthwhile for public welfare especially coastal communities.

Having the second big variety of biological resources in the world, Indonesia is rich of its marine flora and fauna. These potential resources can be treated as high value products that demand by international market. Basic science of MIPA plays important role in developing the management of sustainable marine biological resources.

The scientific articles in this proceeding are the results of research and they are analyzed scientifically. It is expected that this proceeding can be valuable information in terms of developing science and technology for public welfare, especially people in Maluku.

My special thanks refer to all researchers and reviewers for your brilliant ideas in completing and publishing this proceeding. I also would like to express my gratefulness to the dies committee-anniversary of MIPA Faculty for your creativity and hard working in finishing this proceeding, God Bless you all.

Dean of Mathematic and Natural Science Faculty

Prof. Dr. Pieter Kakisina, M.Si.

Contents

Synthesis and Modification of Ni-N-TiO_2/Ti for Chemical Oxygen Demand Sensor with Visible Light Response Flow

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ABSTRACT

Preparation has been carried out Ni-N-TiO2 thin film nano-sized , which is attached to the glass substrate. Preparation of thin layers (films) N-TiO_2 done by dip coating into the sol-gel prepared by reflux and then calcined at 450°C. The film characterization is with DRS, XRD, FTIR, SEM, BET, and potentiostat. DRS measurement results indicate wavelength in the visible region, XRD measurements showed that the resulting film is dominated by the Ni-N - TiO2 in the anatase form and has a size of 15.56 nm crystallite size. While the results of the FTIR characterization indicates Ti-O, -NO and Ti-N bond. Meanwhile SEM measurements show that small crystal size. Pore surface area of composite Ni-N-TiO_2 from the result of measurement has a surface area of 92.79 m^2/g Photoelectrochemical test with potentiostat, by placing the film Ni-N-TiO2/Ti as the working electrode and the Nirrent response of light to produce Ni-N-TiO2/Ti. This system can be developed into a useful sensor for determining COD in a way that has never existed before.

Keywords: *Doped Ni-N, titanium dioxide, Chemical Oxygen Demand, Visible.*

INTRODUCTION

The development of the industry rapidly in addition providing many benefits to improve the quality of life which being serious impact on the surrounding environment. The use of toxic and hazardous chemicals as well as waste and pollution generated overwhelmed amount and it has been damaged and threatened the stability of the ecosystem even at low concentrations, most of the natural water, domestic water and industrial water containing organic substances that can cause a decrease in oxygen levels in the water. Since the determination of organic substances content in water and waste water is one of the important parameters to determine the quality of the water. Currently there are two standard analytical methods that have been used for the determination of oxygen demand in water is BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) [1-3].

The method for determining COD can be classified into two categories. First, the method is based on the principle of conventional chemical oxidation and simple in process analysis. Second, the method based on electro catalytic oxidation of organic matter and accompanied electro chemical measurements[4].

Meanwhile, Zhao *et al* had reported a new method as an alternative method of measuring COD. The proposed method was based on the combined photo catalytic and

electrochemical, with a completely new approach. They used the TiO_2 films coated on ITO-coated glass substrate (Indium Tin Oxide), as an anode in a photo electrochemical system. Light currents rose when running a photo electrochemical system had been evaluated and used as a quantity that could be correlated with the value of COD. However, these methods still work area narrower, the COD value range to 60 mg/L of O_2. On the other hand, the design of the electrode where the data direction of photons to activate photo electro catalysis of direction must pass through the body of water sample inviting vulnerability to disruption of high absorption by water sample matrix (UV-chromospheres, suspended particles and floating solids)[5-7].

Sunlight reaches the earth as an abundant source of energy in the Earth's surface. This abundance would greatly beneficial if available a photo catalyst that could be activated by using the sun light. Several researchers had done a matrix modified TiO_2 photo catalyst that could be activated by visible light. One modification was done by inserting another atom (dopants) into the TiO_2 crystal matrix, where in the dopant elements to make new catalyst matrix has a value smaller energy gap equivalent to the visible light energy[8].

Dopants could be used by dividing into two types, namely as the dopant metal and non-metal. Non-metallic dopants were used to modify the energy band gap of TiO_2 to be active against visible light. N dopant substitution on TiO_2 catalyst was the most effective used to reduce the energy band gap. Morikawa *et al*, 2001 reported that mixing of p states and N 2p states of O could raise the valence band to be able to reduce the band gap of TiO_2, while the position of the conduction band remains. This leads were more active TiO_2 photo catalysts for visible light. However, Jinlong *et al* in 2010 reported that the addition of dopants N into TiO_2 photo catalyst system into N-TiO_2 composite still had many obstacles such as the difficulty of generating a composite catalyst with high N concentrations, low photo catalytic activity in the UV wavelength range, instability species N in catalyst system after the photo catalytic process, weak oxidation power generated and the high hole recombination rate as a result of the narrowing of the band gap and impurity catalyst factor [9,10].

Efforts to incorporate dopants N which can increase activity of TiO_2 photo catalyst in the visible light radiation with metal dopants could prevent recombination between electrons and holes for COD censor application development, has not been widely studied. In this study, TiO_2 will be modified with a non-metal dopant N (nitrogen) and Ni metal. The addition of additional Ni dopant in the N-TiO_2 catalyst system is expected to improve the performance of the process of reform-photo catalyst in its application to the development of sensors COD. The addition of Ni dopant on the one hand can serve as the active core on TiO_2 photo catalytic process as well as the electron trapper to prevent recombination of electron-hole so as to improve the photo catalytic performance in the measurement of the oxygen content in the waste water. On the other hand, the addition of Ni dopant can improve the stability of nitrogen species in the nanocomposite catalyst system to be prepared.

In this study, TiO_2 will be modified with the dopant metal and non-metallic Ni N (nitrogen) in the Ti plate substar. The addition of additional dopant N on TiO_2 catalyst system is expected to improve the performance of the process of reform-photo catalyst in its application to the development of COD sensors that can be used in the visible light region. The addition of dopants N on one side can function as an active nucleus in TiO_2 photo catalytic process as well as the electron trapper to prevent recombination of electron-hole so as to improve the photo catalytic performance in the measurement of the oxygen content in the waste water [6] [7].

Crucial point in the development of photo electrochemical cell systems mentioned above is the preparation of the film Ni-N-TiO_2 nano-sized in order to obtain the film anode

having a large surface area and very active. Sol-gel method and calcinations used to obtain films of Ni-N - TiO_2 as desired. This paper will report the results of the film characterization of Ni-N-TiO_2 produced and used as the working electrode in the determination of COD-based photo electrochemical.

METHODS

Materials Research

The materials used in This research is Titanium tetra iso Proposida (TTIP) 97% aldirch, Ethanol 95%, Aceton, 2-propanol, 0.1 M NaNO3, distilled water, HCl 31%, 40% HF, HNO3, acetylacetonate, Urea, $Ni(NO_3)_2.3H_2O$, Plate Ti, NH_3, aquabidest.

Synthesis of Ni-N-TiO_2 Sol-gel Method

The initial step in synthesizing Ni-N-TiO_2 sol-gel method is to make two solutions, where a solution of 1 in the form of a colloidal solution of TiO_2 prepared by controlled hydrolysis of titanium tetra iso-propoxide (TTIP) taken in a total of 5 mL and 0.5 mL ethanol acetylacetonate or 2-propanol 15 ml were included in the reflux flask. Two solutions in the form of 15 ml of ethanol and 1 mL of distilled water with the addition of 10 drops of acetic acid were put into a separating funnel and then a solution of 2 is added to a solution of 1 gradually through the funnel while stirring using a magnetic stirrer. The mixture solution was refluxed for 2 hours at 40^oC.

The next step is continued for doping of TiO_2 with urea as a nitrogen source, the same sol was then stirred using a magnetic stirrer followed by the addition of a nitrogen source mole ratio of N: Ti 1%, 2% and 3% to produce TiO_2 sol containing nitrogen for 2 hours at 40^oC. After the addition of Ni mole ratio of Ni: Ti is 1%, 2% and 3%.

Electrode Preparation

a. Ti Plate (titanium)

Plate Ti (titanium) which has been previously prepared by sol immobilized TiO_2 and N¬TiO_2 superimposing manner on the surface of the plate evenly with deep technical coatings. Then the plate was allowed to dry and calacinated using furnace at a temperature of 450^oC for 2 hours to allow the formation of anatase crystals is progressing well. In order to obtain a uniform thin layer on the surface of the plate, the coating process is repeated three times.

b. Catalyst Characterization of Ni-N-TiO_2

Characterization is performed to determine whether the products are in accordance with the intended purpose or not. Products may include TiO_2, N-TiO_2 and Ni-N-TiO_2 and TiO_2 films synthesized, N-TiO_2 and Ni-N-TiO_2 were successfully prepared. Characterization used UV-Vis DRS, XRD, SEM, FTIR and BET for TiO_2 and N-TiO_2 synthesized, whereas the film of TiO_2 and N-TiO_2 were characterized using electrochemical system or a potentiostat.

RESULTS AND DISCUSSION

Characterization by UV-Vis DRS

Characterization by means of UV-Vis DRS conducted to obtain information band gap crystal TiO_2 and N-TiO_2 synthesis results are used. The results of the analysis of UV-Vis DRS TiO_2 catalyst, N-TiO_2 and Ni-N-TiO_2 were showed in Table 1.

Tabel 1. Band Gap Energy Calculation Results TiO_2, N-TiO_2 (Urea-dope TiO_2) and Ni-N-TiO_2

No	Cuplikan	Gap Energy
1	TiO_2 Degussa P-25	3.35
2	TiO_2 pH 3	3.20
3	N (Urea 2 %)-dope TiO_2	3.00
4	Ni (1 %)-dopeN- TiO_2	2.55
5	Ni (2 %)-dope N-TiO_2	2.60
6	Ni (3 %)-dope N-TiO_2	3.06

In Table 1, it can be seen that the value of the band gap of, TiO_2 synthesis and nitrogen doped TiO_2 and N-TiO_2 with addition of dopants Ni variations have different values.

The band gap can be used to calculate the wavelength of the formula:

$$Eg = h\frac{c}{\lambda} = (eV) \quad (1)$$

The optimum value of the band gap is obtained at a concentration of 1% urea. Mean wavelength of 486 nm. With the decline in the value of the band gap energy of light is then required to establish photohole (conduction band) and photoelectron (valence band) will be smaller, for example, simply by using a visible light source.

Characterization by X-ray diffract meter (XRD)

Characterization by means of XRD performed to obtain information TiO_2 crystal structure, the N-TiO_2 and Ni-N-TiO_2 synthesis results. Material TiO_2, N-TiO_2 and Ni-N-TiO_2 were analyzed are not the result of calcinations gel coated on Ti substrate plate, but get the same heat treatment with the Ti coated on the substrate plate.

Figure 1 is an XRD spectrum analysis results TiO_2 catalyst, N-TiO_2, and Ni-N-TiO_2. In the image showed the peaks that can provide identity information crystalline form of TiO_2, N-TiO_2, and Ni-N-TiO_2 prepared in this study. Crystal shape can be determined by comparing the value of 2θ or d (A) the results of measurements with data interpretation card standard TiO_2 crystals.

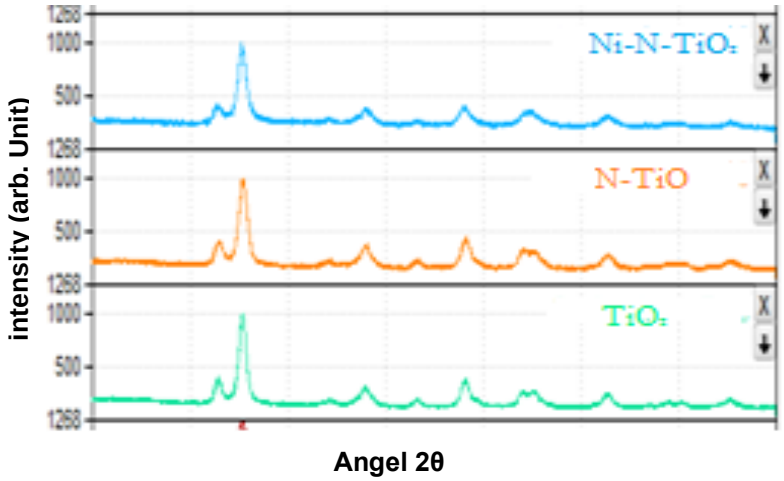


Figure1. XRD spectrum of TiO_2, N-TiO_2, and Ni-N-TiO_2

The peak of diffract gram obtained with the help of Scherrer equation, can be predicted crystallite size of each crystal, which is 17.89 nm for TiO_2 catalyst, 15.43 nm for N-TiO_2 catalysts, catalyst and 15.56 nm for Ni-N-TiO_2.

The results of XRD analysis showed the peak 2θ = 25.3° which is the peak of anatase. And absence of peak 2θ = 27.4° which marks the rutile crystal type, so it can be concluded crystals formed a kind of anatase crystals. In addition, the crystal form can be determined by comparing the value of 2θ or d (A) the results of measurements with data interpretation card standard TiO_2 crystals.

Characterization of FT-IR (Fourier Transform Infra Red)

A measurement with FTIR aims to identify indications of the existence of a bond between the Ti-O-, and the presence of nitrogen or Ni in the TiO_2 matrix synthesis results. Measurements with FTIR aim to identify indications of the presence of the Ti-O bond, the presence of nitrogen and Ni in the TiO_2 matrix synthesis results.

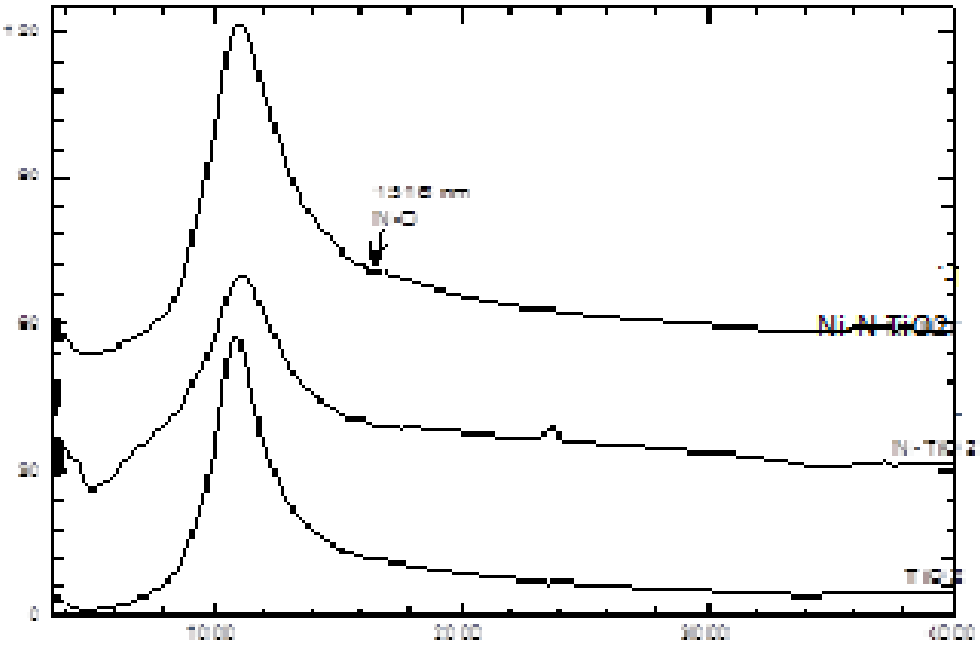


Figure 2. FT-IR spectra of TiO_2, N-TiO_2, and Ni-N-TiO_2

In Figure 2. it could be observed the characteristics of the bond O-Ti-O munNil the wave number region 400-1250 cm^{-1}. There was also an absorption peak at 3500-3000 cm-1 which was a characteristic of the OH stretching vibration and 1625-1650 cm^{-1} indicates peak OH bending vibrations emanating from the solvent is trapped in the crystal structure of TiO_2, or group titanol and 1000-1300 cm^{-1} is the absorption peak for CO stretching vibration originating from combustion is less than perfect [11],[12].

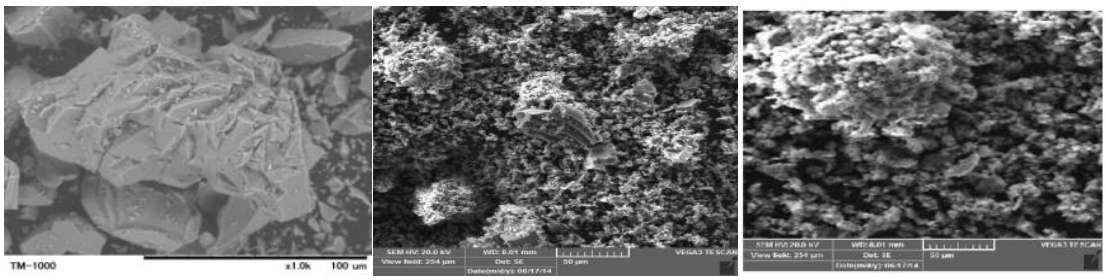
J.Sabataityté, *et al* (2006) reported the bond absorption in the Ti-O-Ti is at 440 cm^{-1}. In the area were also reviewed in the crystal, found that the absorption peak profile resulting from the synthesis of TiO_2 results similar to the profile of the TiO_2 Degussa P25, but there are some differences in the absorption peak of N-TiO_2, and Ni-N-TiO_2 was the catchment area 430 cm^{-1} which indicates the role of N, and Ni in Ti bond [13].

Indication of the presence of Ti-O bond is thought to occur in the absorption peak of 600 cm^{-1}. Meanwhile appearance peak absorption at 1510 cm^{-1} (symmetric vibration) which indicates the existence of groups -NO. Allegedly on nitrogen uptake occurs insertion into the

TiO_2 matrix. In addition, an indication of the presence of Ti-N bonds are at the height of 508 cm^{-1} with a weak signal. Allegedly the amount of nitrogen present in the catalyst is very little[14],[15].

Characterization by SEM

The results of SEM measurements provide information about the surface topography on the surface of a crystal.



(a) (b) (c)

Figure 3. SEM Characterization Results: (a) TiO_2, (b) N-TiO_2, (c) Ni-N-TiO_2

In Figure 3. (a) crystalline form of large size and large blob, this can be caused by the presence of the solvent is trapped in the crystal structure of TiO_2 which can be explained from the appearance of the peak related to the OH vibration FTIR spectra obtained previously. In figure 3 (b) crystal sizes smaller than TiO_2, this is due to the effect of nitrogen doping, whereas in Figure 3 (c) shows the shape of the porous crystalline structure and this affects the activity of the catalyst. Photo catalytic process takes place on the catalyst surface, the smaller the particle size the more active surface area collides with the substrate to accelerate the photo catalytic reaction.

Characterization by BET

Isothermal adsorption BET used to characterize the surface of Ni-N-TiO_2 synthesis results. BET also known as nitrogen adsorption focusing on bond style gas adsorbed on the surface of the absorbent, is not only limited to a single layer only. Characterization of pore properties and specific surface area of the sample studied by the BET adsorption isotherm analysis on Ni-N-TiO_2, which was produced from the sol-gel process (from precursor TTIP), each with the help of reflux hydrothermal process and help acetyl acetone, and calcinations 450^oC showed that the Ni-N-TiO_2 used in this study has a specific surface area of 92.79 m^2/g. The obtained surface area was smaller than the Degussa P25 with a broad 53,60m^2/g. The pore volume of 0.0042 cm^3/g, and 15.97Å pores diameter. A decrease in the surface area of the composite Ni-N-TiO_2 are thought to originate from Ni metal ions and non-metallic ions N immobilized on TiO_2 composite structure causes a decrease in surface defects. Elements Ni and N were immobilized on TiO_2 framework would lead to changes in the bond that can alter the structure of the arrangement of atoms less regulated so that the surface area decreases.

CONCLUSIONS

Synthesis of Ni-N-TiO_2 had done by adding urea mole ratio of 1%, 2%, and 3%. Where the addition of nitrogen in TiO_2 catalyst capable of lowering the energy band gap, with the smallest value of the band gap was 3:00 eV in the N-TiO_2 2% and the addition of Ni metal

was able to reduce the band gap of 2.55 eV with a comparison to Ni: Ti 1%. Ni-N-TiO_2, and N-TiO_2 synthesis results could be active in the visible area based on data from the characterization of UV-Vis DRS,; XRD on TiO_2 anatase crystalline form, the N-TiO_2 and Ni-N-TiO_2; FTIR data Ti-O bond (600 cm^{-1}), -No bond (1475 cm^{-1}), Ti-N bond (508 cm^{-1}) showed the presence of N on N-TiO_2; SEM for Ni-N-TiO_2 had a porous structure and small size.

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REFERENCES

[1]. Fujisima, A., and Honda, K., *Electrochemical Photolysis of Water at A Semoconductor Electrode*. Nature, 1972, 238, 37- 38.
[2]. Nurdin, M., *Pengembangan Sistem Sensor Chemical Oxygen Demand Berbasis Elektrokatalisis Menggunakan Elektroda Berlapis Partikel Titanium DioksidaBerukuran Nano ,* D. Universitas Indonesia, 2008.
[3]. Christina, M., Mu'nisatun, S., Saptaaji, R., Marjanto, D., *Studi Pendahuluan Mengenai Degradasi Zat Warna Azo (Metil Orange) dalam Pelarut Air Menggunakan Mesin Berkas Elektron 350 keV/10 mA*, BATAN, Yogyakarta.2007.
[4]. APHA: *"Standard Methods for the Examination of Water & Wastewater*" 18th Ed. Washington, 1992.
[5]. Y.C. Kim, S. Sasaki, K.Yano, K.Ikebukuro, K. Hashi moto, and I. Karube: "*Relationship between Theoretical Oxygen Demand and Photocatalytic Chemical Oxygen Demand for Specific Classes of Organic Chemicals*". *Analyst,* 2000, 125, 1915-1918.
[6]. H. Zhao, D.Jiang, S.Zhang, K.Catterall, and R.John: "*Development of Direct photoelectrochemical Method for Determination of Chemical Oxygen Demand*". *Anal. Chem*, 2004, 76: 155-160.
[7]. He, C., X.Z. Li, X.Z., Graham, N., and Wang, Y. 2006, *Preparation of TiO_2/ITO and TiO_2/Ti photoelectrodes by magnetron sputtering for photocatalytic application*, Applied Catalysis A: General, 2006, 305, 54–63.
[8]. Ruslan and Mirzan, *Sintesis dan Karakterisasi Elektroda N-TiO_2 dan N-TiO_2/ITO untuk Sensor Chemical Oxygen Demand dengan Respon Arus Cahaya Visible,* Hibah Bersaing, Universitas Tadulako, 2013.
[9]. Morikawa, T., Asahi, R., Ohwaki, T., Aoki, K., and Taga, Y., *Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides,* Jpn. J. Appl.Phys, 2001, Vol. 40: L561.
[10]. Jinlong Zhang, Yongmei Wu, Mingyang Xing, Leghari, Sajjad Ahmed Khan, Sajjad Shamila. *Development of modified N doped TiO_2 photocatalyst with metals, nonmetals and metal oxides*. Energy Environ. Sci., 2010, Volume 3, 715-726.
[11]. Jagadale, T. C., Takale, S. P., Sonawane, R. S., *N-Doped TiO_2 Nanoparticle based Visible Light Photocatalyst by Modified Peroxide Sol-Gel Method*, J. Phys. Chem. C, 2008, 112 (37), 14595-14602.
[12]. Wang, J.; Zhu, W; Zhang, Y.; Liu, S, *An Efficient Two-Step Technique for Nitrogen-Doped Titanium Dioxide Synthesizing: Visible-Light-Induced Photodecomposition of Methylene Blue*, J. Phys. Chem. C, 2007, 111 (2), pp 1010–1014.

[13]. J. Sabataityte, I. Oja, F. Lenzmann, O. Volobujeva, and M. Krunks, *Characterization of nanoporous TiO_2 films prepared by sol-gel method*, Comptes Rendus Chimie, 2006 vol. 9, no. 5-6, pp. 708–712.
[14]. Slamet, H.W. Nasution, E. Purnama, S. Kosela, J. Gunlazuardi, *Photocatalytic Reduction of CO_2 on Copper-Doped Titania Catalysts Prepared by Improved-Impregnation Method*, Catalysis Communication, 2005, 6 (5), 313-319.
[15]. Nolan, N.T., Synnott, D.W., Seery, M.K., Hinder, S.J., Wassenhoven, A.V., Pillai, S.C., 2012, *Effect of N-doping on the photocatalytic activity of sol–gel TiO_2*, Journal of Hazardous Materials**,** 211– 212: 88– 94.