

# Preparation and Application Porous TiO<sub>2</sub> for SO<sub>2</sub> Gas Sensor

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**Abstract**—Air Pollution become one of serious issue that must be deal with. One of them is SO<sub>2</sub> Pollution. This gas is hazardous even in small concentration and can cause inflammation and irritation on respiratory system. Therefore, it is urgent to made an early detection device that can detect the existence and level of SO<sub>2</sub> concentration. This research was successful to find out the performance of TiO<sub>2</sub> material for detection SO<sub>2</sub> gas. SO<sub>2</sub> gas concentration used is 10 ppm. The TiO<sub>2</sub> material was synthesized using solvothermal method at 180 C by varying the reaction time. Sensitive material is made above the FTO glass. The Material Characterization indicate the structure of TiO<sub>2</sub> is rutile which have round structure that covered by nanorods TiO<sub>2</sub>. The size of the diameter of nanorods increases with increasing reaction time. Sensor testing was carried out from 150° C – 350° C using 10 ppm SO<sub>2</sub>. The test results showed that the best sensor response was obtained from samples with a reaction time of 12 hours at working temperature of 350°C.

**Keywords:** porous TiO<sub>2</sub>, solvothermal synthesis, three-dimensional structure, SO<sub>2</sub> sensor

## I. INTRODUCTION

One of problem that needs attention is air pollution. this is due to so many negative effect caused of it. Based on data from the World Health Organization, more than seven million people per year in the worldwide get premature death because of air pollution [1]. Unconsciously, air quality has led to the lower quality of life especially in transportation and industrial areas. Cahyono said that the gas source of SO<sub>2</sub> came from industrial activities, followed by transportation and from settlements. SO<sub>2</sub> is a colourless gas but has a strong odour. This gas can be absorbed by nasal and respiratory system. At high concentrations this gas damage the lungs. Some studies show that the exposure levels of SO<sub>2</sub> more than 5 ppm can cause throat irritation [2]. The reality is not all the areas have been equipped with air monitoring detection systems. Whereas this system is important to protect health and safety of human around that environment.

Gas sensor is a device that generates electrical signal due to interactions with targeted gas or organic compounds. The working principle of metal oxide-based gas sensor is the change of electrical

conductivity because of reaction from oxygen ions with reducing or oxides gas on material surface. If material has large surface area it will cause high sensor sensitivity. This can be achieved by minimizing the particle size of material. Research about sensors has developed rapidly since Brattain and Bardeen find that gas adsorption on the surface SMO can change the resistance of material.

Nowadays, there are many types of technology of sensor developing. Some of them are optical-based sensor, gas chromatography based sensor and electrochemistry based sensor. The working principle of the optical method is absorbing infrared light due to its wavelength that depend on characteristics of target gas. However this method is not very popular because its large energy consumption which effect to high procurement costs. Analyze using chromatography gas is very accurate at low concentrations but it has disadvantage like not real-time result, not portable because of the large device and has high cost per analysis. This study using electrochemical based sensor with chemiresistive parameter.

Material sensor like ZnO, NiO, tiO<sub>2</sub>, SnO<sub>2</sub> are widely used in photocatalyst application, cosmetic ingredients, corrosion protection, solar cells and as an active element of gas sensor [3]. TiO<sub>2</sub> is used for gas sensor manufacturing because of its advantages such as low synthesis temperature, high sensitivity and easily arrange the morphology. There are various type of TiO<sub>2</sub> structure from 0D, 1D, 2D and 3D shape. Made 3D Structure of TiO<sub>2</sub> aims the structure get a specific surface area with high porosity for application gas sensor. TiO<sub>2</sub> have been carried out for hydrogen gas [4], ethanol gas [5], and NO<sub>2</sub> gas[6].

In this research fluorine tin oxide (FTO) substrate is used as the growth media for sensitive material. Based on [7], [8] rutile and FTO structure have small tetragonal lattice mismatch structure less than 2%. These conditions make the process of linear growth of Tio<sub>2</sub> layers on the FTO substrate easier than other substrates such as glass substrate. On the other hand the activation energy on the glass substrate when deposited by TiO<sub>2</sub> is greater than FTO. It indicates

that the energy required by electron to jump to conduction band is greater so that the electron in conduction band become reduced so that cause the small amount of electron will interaction with target gas. Al Humoudi, 2007 also reported the decrease of resistance value on glass substrate is smaller when compared to the FTO substrate so when it used for sensor application.

The synthesis method is solvothermal. It chosen because can produce TiO<sub>2</sub> with high crystallinity, controlled phase and large specific surface area. It is important to control the several parameter such as precursor preparation, reactant composition, reaction temperature, pH and duration of growth. Working principle of sensor gas based on the mechanism of adsorption and desorption of gas molecules on the surface of semiconductor metal oxide. SMO sensor usually operate at high ranging temperature from 200°C until 600°C. when the surface area exposed by oxygen gas, it will be adsorbed on the surface layer and capture an electron and forming the O<sub>2</sub>, O<sup>-</sup>, and O<sub>2</sub><sup>-</sup> ions. When electrons are removed and depleted from surface layer, the concentration of electron valence will decrease and form a depletion layer at grain boundary.

## II. METHOD

All chemical used are from commercial resources. To obtain the TiO<sub>2</sub> sensitive layer that will be used in sensor testing, several stage need to be done. The reagent Titanium dioxide were titanium (IV) isopropoxide (Aldrich, 97% purity), Ethylene Glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) (Merck, 99%), Cetyltrimethylammonium bromide (C<sub>19</sub>H<sub>42</sub>BrN) (Merck, 97%), hydrochloric acid (HCl) (Merck 37%).

### 1) Substrate Preparation and Synthesis of TiO<sub>2</sub>

The substrate is FTO glass. It must be clean so it is washed successively using soap water, technical ethanol and aquabides. Then the substrate is dried at 100 C for 30 minutes. After that the substrate is put into a solution in 100 ml Teflon lined autoclave for 6 hours, 12 hours, after the substrate was deposited with silver paste as electrode on the FTO substrate, then drying the substrate at 100 °C.

There are several steps to made TiO<sub>2</sub> solution. titanium (IV) isopropoxide (TTIP) was count 0.6 grams, Hexacetyltrimethyl bromide (CTAB) 0.5 grams, then Measure 2.5 ml aquabidest, the volume of HCl 17.5 ml, Ethylene glycol 12.5 ml Ethylene glycol was stirring in bottle A for 15 minutes, then in bottle B, put 0.5 grams in 2.5 ml aquabides, stirring for 15 minutes. After that Put the solution from bottle B to A, stirring 30 minutes. the solution is transferred into Teflon lined autoclave 100 ml. after that the FTO glass substrate immersed in a precursor solution at a temperature of 180 C with a time variation of 6 hours, 12 hours. After the solvothermal process, leave the sample to normal temperature. Then remove the

substrate from the Teflon and wash it with ethanol and aquabidest, after washing it is dried for 3 hours at 100°C and the final result is transferred to a ceramic cup to calcined at 550°C for 6 hours. This calcination cause all the acidic and glycolic compounds evaporate and the remaining titanium is oxidized to form titanium dioxide. The next step is to design and manufacturing the sensor. After the material has grown on the FTO substrate, then silver paste deposition on it. The silver paste acts as an electrode. The conductive silver paste was deposited using the doctor blade method and then dried at 400°C for 30 minutes.

### A. Material Characterization

Three characterizations used in this study are X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy and Emmet-Teller (BET). The purpose X-ray Diffraction (XRD) is to determine the crystal structure, crystal phase and crystallite size. When X-rays fall on crystals, a detector will record the angle. the X-rays that was reaching detector must fulfil the Bragg's Law. The results from XRD will compared with the results of XRD materials already in the database, the International Center for Diffraction Data (ICDD) Database. The XRD instrument is from Philips Analytical X-Ray. The diffraction pattern is obtained by Cu radiation ( $\lambda = 1.54060 \text{ \AA}$ ) through a generator voltage of 40 kV and a current of 30 mA. The tool is set in step scan mode with a step size of 0.02 2 $\theta$  and a time per step of 0.2 seconds in an angle range of 20°-80°

SEM characterization used to obtain material morphological images. it can also see the size of the particles. The SEM specification is Hitachi-9100-0005 with a magnification of 4,000 - 20,000 times. Samples of SEM should not contain water, solution and all items that can evaporate when vacuumed. Non-metallic samples must be coated with a conductive coating such as gold. The layer must be conductive in order to reflect the electron beam and drain it to the ground. when made a conductive layer, the sample is placed in a glass tube surrounded by an anode. Between the anode and the cathode, the voltage is paired with a certain value so that ionization of low-pressure air occurs. Electrons move towards the anode with high energy and then hit the cathode. This causes gold particles scattering on the surface of the specimen.

N<sub>2</sub> gas adsorption used to determine the specific surface area, pore size, and pore size distribution. The sample must be vacuum before testing to remove oil and water content. Then the gas is introduced gradually and then gas will form a layer of monolayer throughout the surface of the material.

B. Sensor Gas Testing

For testing using SO<sub>2</sub> 10 ppm gas to regulate the concentration of ppm SO<sub>2</sub> gas using Bacharach PCA3. The air compressor functions to flow air into the test chamber until achieve a stable sensor resistance. To record the resistance using Picotest instrument. The test parameters carried out in this study use operating temperature: 150 °C to 350 °C, the concentration of the SO<sub>2</sub>: 10 ppm with Exposure time 10 minutes

The equation that can be used to calculate the gas respon are given below.

$$\Delta R (\%) = R_g - R_a / R_a \times 100\% \quad (1)$$

$$\Delta R (\%) = R_a - R_g / R_a \times 100\% \quad (2)$$

R<sub>a</sub> is resistance before exposed by gas, R<sub>g</sub> is resistance after Equation 1 is used if the resistance value of the sensor increases and the equation 2 used when the value of resistance decrease while exposed with gas.

III. RESULTS AND DISCUSSION

Synthesis process show that there is a colour change of white sediment in the solution. White sediment show because of reduced volume of the solvent so that the concentration of dissolved compounds becomes more solubility. This reduction occurs due to the evaporation process. The reactions that occur are hydrolysis and condensation reactions as shown. In hydrolysis, the alkoxy group (-OR) is replaced by nucleophilic attack of oxygen atoms from water molecules under the release of alcohol and the formation of metal hydroxides. The condensation process can occur when hydrolysis compounds interact each other and release water molecules.

TiO<sub>2</sub> calcinate for 6 hours at temperature 550 °C, then silver electrode coated on TiO<sub>2</sub> layer by doctor blade. TiO<sub>2</sub> does not have solubility in water so that when the TiO<sub>2</sub> compound is formed in the solvothermal process some TiO<sub>2</sub> will left and some will bound on the surface. Beside the hydrolysis reaction, there is also a reaction between the surfactant and TiO<sub>2</sub>. Surfactants are used as pore-forming agents. This process occurs in an autoclave at 180°C and produces Ti(OH)<sub>2</sub>. Calcination formed TiO<sub>2</sub> rutile. The residual products of calcination will evaporate and leave a small hole that becomes the seed of forming material pore.

XRD results show that the peaks produced have the same orientation but with different intensity values. The highest intensity indicates a high level of crystallinity. The peaks that appear indicate that the samples are TiO<sub>2</sub> with rutile crystal structure. This was confirmed by matching the TiO<sub>2</sub> peak with a database from JCPDS-211276.

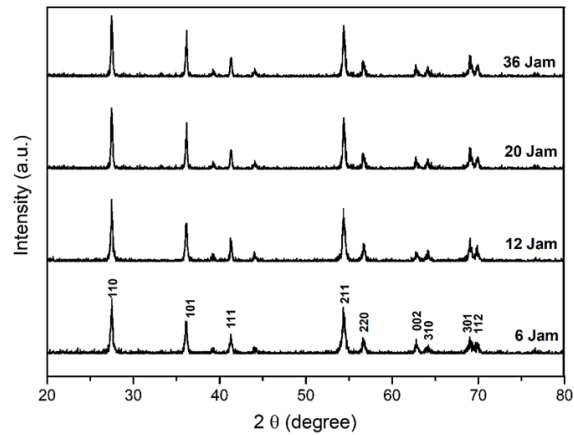


Figure 1. XRD Pattern Of TiO<sub>2</sub>

Morphological structure (a,b,c,d) that appears is a three-dimensional round shape. The longer reaction time the more uniform the particle size and the less agglomeration. The nucleation process of TiO<sub>2</sub> help CTAB template forms a spherical TiO<sub>2</sub> composed by nanorods.

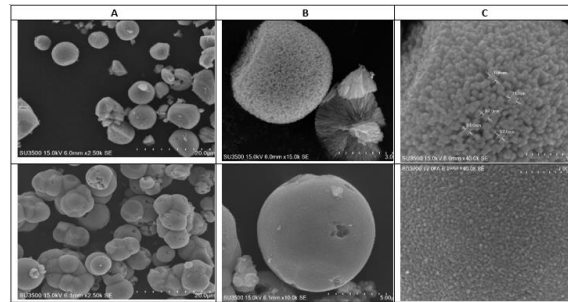


Figure 2. morphology of microsphere TiO<sub>2</sub>

BET results show that specific surface area increase with increasing reaction time. The specific surface with a reaction time of 6 hours and 12 hours is 20,537 m<sup>3</sup>/g and 8,336 m<sup>3</sup>/g . Specific surface area increases with increasing reaction time. This increased surface area is due to the more pores that form on the material.

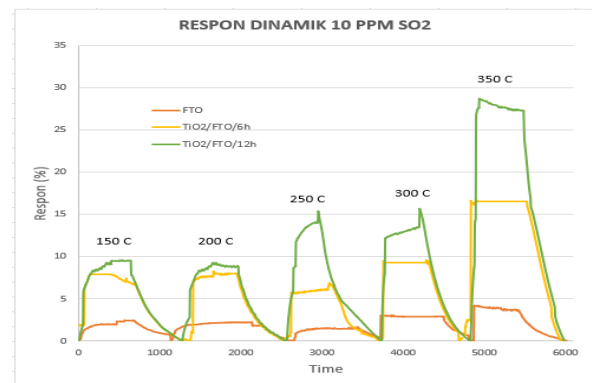


Figure 3. Respond sensor

The graph of the TiO<sub>2</sub> response to 10 ppm SO<sub>2</sub> gas shown in Figure 3 At temperatures of 150 -350°C. When TiO<sub>2</sub> sample is heated, the electrons in the TiO<sub>2</sub> will rise to the conduction band causing the TiO<sub>2</sub> resistance decrease, but at high temperatures exposure Oxygen, the TiO<sub>2</sub> resistance increase. This happens because the electrons in the conduction band are used by oxygen molecules to ionize. After stable resistance, then the sample is exposed to SO<sub>2</sub> gas. SO<sub>2</sub> gas will bond with oxygen ions so the electrons return to the conduction band and the TiO<sub>2</sub> resistance goes back down. Stopping the exposure of SO<sub>2</sub> gas will make the resistance rise again. TiO<sub>2</sub> testing at 150 °C.

Overall, the response to SO<sub>2</sub> gas seems increase with increasing work temperature. The response will increase to the optimal temperature. Optimal temperature is the temperature at which the sensor shows the maximum response. In this study the optimal temperature is at 350°C. This temperature plays a main role in the transfer of electrons to conduction band. The greater the temperature given, the more electrons can move to bond with oxygen so that, more oxygen ions can interact with SO<sub>2</sub> gas. The highest response value is 28,387% obtained by a 12 hour TiO<sub>2</sub> sample. a larger surface area causes the number of molecules absorbed become greater, so that the resulting sensor response is also higher.

#### IV. CONCLUSIONS

This study have been successful to make Three-dimensional spherical TiO<sub>2</sub> layers on the FTO substrate using the solvothermal method. The length of time a solvothermal reaction has effect to the formation of TiO<sub>2</sub> morphological properties and particle size. The longer the reaction time, the sphere size and the diameter of the nanorods surround the sphere also increases. Same with the level of crystallinity. The longer the reaction time, the higher the crystallinity of the sample. Sensor response increases with temperature.

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