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Synthesis Sensitive Layer of Ethylene Gas Sensor Based Tin Oxide Nanoparticles Using Water as Solvent In Precipitation Method

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Abstract. Ethylene gas is a gas naturally released by fruits. The maturity level of these fruits could be predicted from the amount of ethylene around them. To maintain the freshness of these fruits, the concentrations of surrounding ethylene need to be monitored. Therefore, suitable gas sensor ethylene were still in progress to get good respond. In this paper systhesis of pure SnO2 nanoparticle from $SnCl_2.2H_2O$ and water solution in precipitation method was held. The tin oxide powder was obtained in good distribution with nanoparticle size. This nanoparticle powder was formed into thick film, using ethylene glycol as solvant. To observe this sensor characteristics, several test was held in various conditions. Gas testing used pure ethylene gas show better respond at higher than room temperature but recovery time still unsatisfying.

1 Introduction

Since 1934, fruit's porter known ethylene was emitted by tropical fruit while shipping them from Jamaica to Europe. In plants, ethylene was emitted by flowers, seeds, especially fruits. In fruits, ethylene was indicator of initiation ripening. There are two type of fruits, climacteric and non-climacteric. Most of fruits harvested in Indonesia are climacteric type. In the climatric fruit, the concentration of ethylene gas will raise up until it reaches the peak. So, they continue ripen as ethylene existence. When fruits had uncontroll ethylene concentration environment, it will spoiled. Less than 1 ppm by volume of ethylene can trigger the process of climacteric fruit ripening. This fact made important to monitoring ethylene gas during storage and distribution. If these fruit products are left too long, they would get fermented and rotten. Fruits can emit ethylene in range ppb scale to around 140 ppm [1, 2].

Ethylene is an invisible, colorless, and odorless gas. As in container or the other transport, many other organic substance may exist, then potential sensing methods need good

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sensitivity as well as good selectivity. Then, we must understand the characteristics of ethylene gas. Ethylene molecular weight is 28.05 g mol^{-1}. As its specific weight (1.178 kg m-3 at 15ºC) is similar to that of air (1.225 kg m-3 at 15ºC), ethylene freely diffuse in storage [2].

Several technologies have been proposed in order to monitoring concentration of ethylene. Hence, there is a need for simple, compact, inexpensive, portable, and reliable ethylene sensors that could be used parallel in controlling ethylene concentration systems. The technologies that have been commonly used include gas chromatography [3], optical sensors [4], colorimetric sensors [5], amperometric sensors [6], photoluminescence sensors [7], gravimetric sensors [8], and chemoresistive and capacitive sensors [9, 10]. From technologies has been mentioned, chemoresistive can meet criteria desired

One of material frequently used as sensitive layer in gas sensor is tin oxide (SnO_2), because of its properties including fast–response speed, high chemical stability, and prominent selectivity. SnO_2 is a n-type semiconductor metal oxide with band gap 3,6 eV at 300 K, making it favorable material for sensing device [11]. As n-type materials major carriers in SnO_2 is electrons. In the air condition, when layers of nanoparticles absorbs oxygen, a depletion layer of species O- was formed. As more oxygen was absorbed, the depletion region increase and the conduction region decrease in thickness. [9] When reductive gas like ethylene was presented, the active sensitive layer with oxygen adsorbates will react with the gas and permit electrons inject back into the active material, causing an increase in electronic conductivity or decrease in resistivity. The depleted electrons were replenished back to the SnO_2 surface, thereby increasing the conduction region and reducing depletion region. While this process occur, the sensing performance was determined by the diffusion of gas throughout the pores of the sensing layer. To improve the sensor performance, some research did focusing on controlling SnO_2 nanostructure, develop method of producing the sensitive layer improve the porosity of the material, which obtain better performance in gas sensing behaviors [12]. One of modification was fabricating SnO_2 in nanoscale so that interaction area between etilen and sensitive layer become larger. This condition effected much detected gas adsorbed into SnO_2 and produce higher sensitivity. [13]

Some research about ethylene gas sensor based metal oxide already done several time, as we could see below :

1) Passive capacitive gas sensor based SnO_2 (10-15 nm) detected 0-100 ppm of ethylene in room temperature with sensitivity 39% [9].
2) Thick film gas sensor from WO_3/SnO_2 nanoparticle was made to detect 2-8 ppm ethylene at optimum operating temperature of 300ºC with best respond at 37,5%[10].

From informations above, SnO2 was successfully detect gas ethylene in lowconcentration. The development capacitive gas sensor was rare, then we develop pure SnO_2 nanoparticles with chemo resistive gas respond to detect ethylene. The methode of synthesis was precipitation, which promising decrease the particle size to decrease optimum operating temperature.

2 Detail Experiment

Fig.1 shows a flowchart of the method used for synthesis of SnO_2 sensitive layer and the characterization. This section was divide to some parts. Powder preparation, powder characterization, thick film fabrication, and characterization gas sensor.

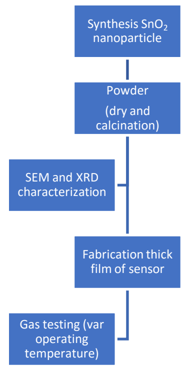

Fig. 1 Experimental Flowchart

2.1 Powder Preparation

SnO_2 nanoparticles obtain were prepared by precipitation method using 0,4 gram $SnCl_2.2H_2O$ in 40 ml water as solvent and amount of NaOH was dropped as precipitant agent to stirred solution until pH condition wanted. This solvant colored like watery milk, not so white. Proof that from this solution will get nanoparticle powder. As we know from data solubility of metal hydroxide compound, that $Sn(OH)_2$ will dissolve around pH 3.5 to 11. This research using condition above pH 11. This condition permit the solution into sol condition, which the result is not like ordinary precipitation. Then, the obtain precipitant was centrifuged and washed several time with aqua bides until neutral condition obtained. The samples was dried in furnace a night to remove water, then calcinated for 2 hours. Powder obtain will be characterized to observe the properties.

2.2 Powder Characterization

SnO_2 nanoparticles was investigated by scanning electron microscopy (SEM, Hitachi 9100 0005) to analyze morphology and structure which operating in 5 kV.
The crystal structures of tin dioxide powder was analyzed using X-ray diffraction (XRD) using a Advanced Bruker with Cu-Kα radiation (1.54439 Å) and LynxEye detector. The pattern of sample was collected from 20° to 80° as 2θ with step size of 0.019°.

2.3 Thick Films Fabrication

The obtained powder was added by ethylene glycol to form white paste. Before this paste was smeared on alumina. Firstly, alumina was coated by silver paste to get electrodelayer. Using doctor blade method white paste was smeared on alomina. To remove the impurity drying samples at 200ºC for 2 hours. Then we get thick film senstive layer of gas sensor.

2.4 Characterization Gas Sensor

Gas sensing performance of SnO_2 based gas sensor was evaluated with pure ethylene gas in test chamber. The electrical resistances in air and in present of ethylene were measured at

100 ppm from room temperature to 200 ºC. The exposure time was for 10 minutes. The response towards ethylene were calculated and expressed in percentage as follows :

$$\%S = \frac{|R_{gas} - R_{air}|}{R_{gas}} \quad (1)$$

Where, R_{air} and R_{gas} are the sensor resistance in air and in the presence of gas target, respectively at the same operating temperature.

3 Result and Discussion

3.1 Morphology and Structure Characterization

In **fig 2** was shown the XRD pattern of samples having tetragonal rutile structure (Joint Committee on Powder Diffraction Standards Card no 41-1445). Peaks that showed indicate materials was a tetragonal rutile crystal structure. Where the diffraction peaks are (110), (101), and (211). [14] Based on peak (211), using Scherre's equation obtain crystallite size 12,61 nm. The result of crystallite size was better than using 1-buthanol as solvent with same calcination temperature [15].

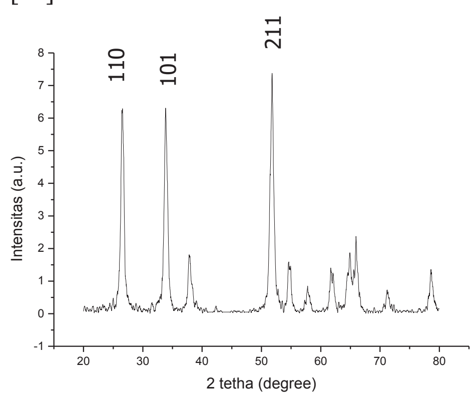

Fig. 2 XRD result of SnO_2

From **fig 3** SnO_2 samples has good homogenity and distribution, with average particle size 30 nm. This nanoparticle material size provide many site for reaction between gas target and oxygen ion. Although, agglomeration happen in many place as one of SnO_2 problem. From this result of characterization we decide to make SnO_2 thick film as sensitive layer and test it in chamber.

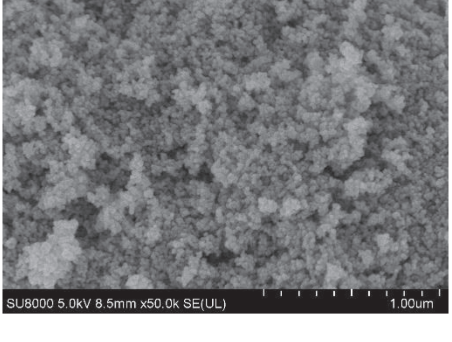

Fig. 3 SEM result of SnO_2

3.2 Sensor Gas Testing

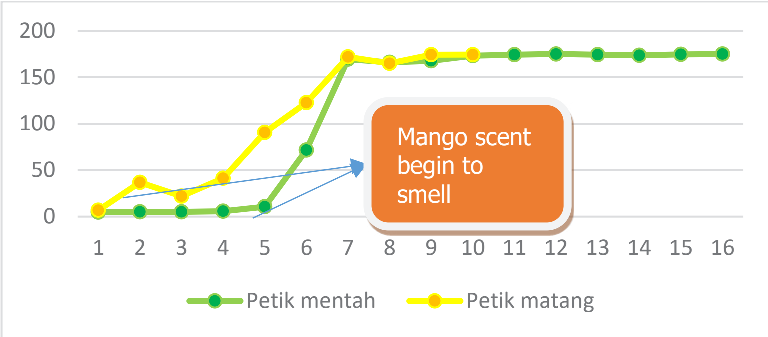

Fig. 4 Ethylene emition from a mango.

The mechanism of detection ethylene at the surface sensitive layer SnO_2 thick film can observe by chemical surface interaction. Firstly, initial physisorption occured, then ethylene gas bonded with O^-_{ads} to formed C_2H_4O and released e^-. The change in resistance would occur simultaneously with exposure to ethylene gas in the gas sensor. We used two operation temperature as comparison, in low temperature and in high temperature. From fig. 1 we know that mango started ripe stage while ethylene concentration around 20 ppm indicated by smell mango flavor. And the point above 150 ppm of ethylene mango reach full ripe stage, usually at this stage we called rotten. So we tested the sensor on 40-100 ppm based on concentration of ethylene while mango best at flavour.

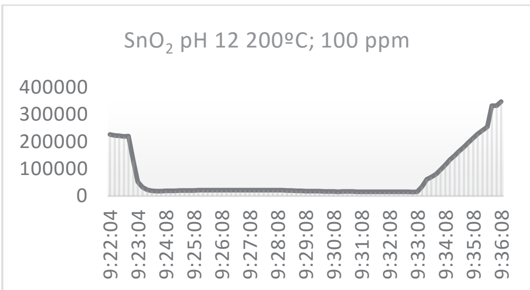

Fig. 5 Gas sensing respond to 100 ppm pure ethylene at 200ºC

Firstly, we tested SnO_2 gas sensor in 100 ppm pure ethylene at moderate temperature (50ºC) and get S = 19.8%. Then, we would like to get better sensitivity. Fig 5 show the respond of SnO_2 gas sensor when we increase the temperature became 200ºC obtain S = 92.68%. If we compared to ref 10, material we made much better, because get 92.68% at 200ºC. But, as higher operating temperature we used the recovery time show unstatisfying result. At moderate temperature, need 1.5 minutes to back in air condition. But at higher temperature need 3 minutes to back, but the resistance not stable as we see in figure 5, the resistance still increase. It was happened because at high temperature sensor the chemisorption dominate the interaction as said before [16]. Then we asume, there was ethylene trap in material site.

4 Conclusion

We had been successfully synthesized the SnO_2 nanoparticles with average size 30 nm by precipitation method using $SnCl_2.2H_2O$ and NaOH as precipitate agent in water solution. The formation of crystalline tin dioxide nanoparticles had been confirmed by XRD patterns and FE-SEM. Through gas testing we were informed that increase the temperature comparable with sensitivity. But took longer to recovery back in air condition. Portable gas sensor to monitoring rippening fruit needs sensor's material that high sensitivity and fast respond also recovery in low temperature.

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