Review Article

SnO₂ Nanostructure as Pollutant Gas Sensors: Synthesis, Sensing Performances, and Mechanism

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A significant amount of pollutants is produced from factories and motor vehicles in the form of gas. Their negative impact on the environment is well known; therefore detection with effective gas sensors is important as part of pollution prevention efforts. Gas sensors use a metal oxide semiconductor, specifically SnO₂ nanostructures. This semiconductor is interesting and worthy of further investigation because of its many uses, for example, as lithium battery electrode, energy storage, catalyst, and transistor, and has potential as a gas sensor. In addition, there has to be a discussion of the use of SnO₂ as a pollutant gas sensor especially for waste products such as CO, CO₂, SO₂, and NO_x. In this paper, the development of the fabrication of SnO₂ nanostructures synthesis will be described as it relates to the performances as pollutant gas sensors. In addition, the functionalization of SnO₂ as a gas sensor is extensively discussed with respect to the theory of gas adsorption, the surface features of SnO₂, the band gap theory, and electron transfer.

1. Introduction

In recent years, the growth of the human need for goods from factory production has dramatically increased. In the process of making goods, a lot of waste is dumped directly into the environment. This has a direct impact on the environment because the use of fossil fuels produces exhaust gases that are ultimately harmful to the natural ecosystem. Processing extras that are discarded and can cause pollution to the environment are called pollutants. Currently, the most widely produced forms of pollutants are gases. CO, CO₂, SO₂, and NO_x are pollutant gases which are produced by factory processes [1–3]. Many efforts are being made to reduce the impact of pollution gases, one of which is the implementation of gas sensors as a means of prevention.

The use of sensors to detect gas is widely considered as a means of prevention. In the last few decades, several types of gas sensors have developed with different materials and transduction platforms. The main substances used as a gas detector include metal oxide semiconductors,

intrinsic conduction polymers, conductive composites polymers, metal oxide/composite polymers, and other new materials. These materials can be used on different transduction units, otherwise known as chemiresistive surface acoustic waves (SAW), quartz crystal microbalance (QCM), optical transducer, and metal oxide semiconductor field-effect transistor (MOSFET) [4, 5]. Based on the research that has been done, the chemiresistive metal oxide semiconductor is a material that has the greatest potential for gas sensor technology.

Metal oxide semiconductor gas sensors have several advantages, including low production cost, high sensitivity, fast response and recovery time, simple electronic interface, ease of use, low maintenance, and the ability to detect large amounts of gas. In general, metal oxides are classified into two types: nontransition and transition. At the same time, metal oxide semiconductors have two types: n-type (the majority of carriers are electrons) and p-type (the majority of carrier is the hole). Most of the metal oxide semiconductors are n-types due to electrons produced naturally by oxygen [6, 7].

However, the p-type semiconductor has a lower working temperature when compared to the n-type [4, 5, 8]. Sensor-based metal oxide semiconductors are used to detect the target gases through a redox reaction between the target gases with the oxide surface [5]. Tin oxide (SnO_2) has been identified as a metal oxide semiconductor with great sensitivity to the target gases, when compared with other oxide semiconductors [9].

SnO_2 is an n-type semiconductor that has a wide band gap (3.6 eV at 300 K) so that it can be utilized in a variety of technologies [31–35]. SnO_2 is used in lithium battery electrodes, electrochemical energy storage, catalysts, and sensors [8, 31, 34]. The working principle of SnO_2 as gas sensors comes from changes in the electrical conductivity of SnO_2 grains, which result from the reaction between oxygen and gas reduction. In general, SnO_2 nanoparticles, which have large surface areas, make for higher sensitivity on gas sensor. The good performance of the sensors can be achieved by minimizing the size of the particles [36]. Many efforts have been made to improve the sensitivity of SnO_2 , including modifying its morphology. For example, some morphologies that have been obtained are nanoparticles [31, 36], nanowires [32], nanotubes [35], nanoneedles [37], nanoflowers [38], nanosheets [24], and granular [24].

The harmful gases that are reviewed in this paper are the gases CO , CO_2 , SO_2 , and NO_x . Carbon monoxide (CO) is a colorless and tasteless gas. The CO gas can cause death for humans if the gas is inhaled for 8 hours with a concentration of 10 ppm [4]. In general, CO gas is produced by incomplete combustion of fossil fuels from motor and vehicles [4]. Carbon dioxide (CO_2) is a colorless gas, is nonflammable, and is a major cause of the greenhouse effect. The gas is generated from human respiration, combustion of fossil fuels, and forest fires. This gas can be recycled into oxygen through photosynthesis process by plants [4]. Sulfur dioxide (SO_2) is a gas that is colorless and smells like burnt matches. If the gas is inhaled in large quantities, it can lead to respiratory problems, pain in the respiratory system, changes in lung resistance, and cardiovascular disease. For the environment, SO_2 gas released into the atmosphere can lead to the greenhouse effect and acid rain [4]. Nitrogen oxides (NO and NO_2) are toxic gases produced by the burning of plants. Nitrogen dioxide (NO_2) at 3 ppm is the most dangerous type of NO_x gases. This gas causes the ozone layer to form at a lower than normal altitude [4]. While NO gas is relatively less hazardous compared to NO_2 , it produces acid rain that is harmful to the environment and living organisms; therefore its detection is essential for environmental protection [4].

This paper will review SnO_2 nanostructure in its applicability as a pollutant gas sensor. Different aspects of SnO_{2a} as a pollutant gas sensor in regard to the synthesis, morphology, and its performance will be discussed. In addition, the theory of adsorption process on the surface of SnO_2 will be presented, as well as discussions on band gap and the electron transfer process at the surface of SnO_2 . An understanding of this theory provides a useful framework in order to further understand the potential of SnO_2 as a gas sensor. The gas sensitivity of SnO_2 can be analyzed through the theories that have been mentioned above.

2. The Preparation Method of SnO_2

Recent developments in synthesis and morphology techniques are described below.

2.1. Synthesis. Various synthesis methods (chemical and physical) have been developed to obtain SnO_2 structures that have better characteristics than previous efforts. To enhance the characteristics even further, scientists tested different parameters such as the morphology, particle size, and composition.

2.1.1. Synthesis Method

(a) Solution-Based Method. Solution-based methods are commonly used and have been proven as an effective way to obtain metal oxide nanostructures with good control over shape, composition, and reproduction. Usually, this method involves low temperature reactions, with certain flexible parameters that are suitable for large production [38]. With this method, the size, composition, and dimensions of the material can be controlled easily [38]. Several techniques often used to make SnO_2 nanostructures include the hydrothermal method and chemical precipitation method.

In the hydrothermal synthesis method, the reaction is performed in a pressurized, sealed container and set to a certain temperature where the reaction solution exceeds a critical point using water as a solvent. This process has been widely used to obtain nanoscale materials because of the following advantages [38]:

- (1) Many inorganic salts are compatible, which can be reconstituted with ether. It may be easier to set the source of metal ions that can be tailored to the needs.
- (2) Water is nontoxic and safe for the environment and is usually cheap to obtain.
- (3) Molecules can easily be used in regulating the growth of nanocrystals.
- (4) The strong polarity of water is very beneficial for the growth of nanocrystals.

Firooz et al. [10] have experimented with the hydrothermal method at low temperatures to obtain SnO_2 nanoparticles and nanorods. The solution used is made of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH , which stirred until the solution becomes clear. Then, the surfactant CTAB (cetyltrimethyl ammonium bromide) is inserted into the solution and stirred again while being heated. Having seen the homogeneous solution, the solutions are inserted into the autoclave with a temperature of 130°C for 24 hours.

Firooz et al. [10] conducted experiments to obtain SnO_2 nanostructures through hydrothermal synthesis method with microwaves assisted. The solution is made with a mixture of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, urea, and water while stirring at room temperature. After that, citric acid is added and stirred until clear. The clear solution is poured into five double-walled vessels that are coated with Teflon. Vessels that have been filled solution were then closed and inserted into the Microwave Accelerated Reaction System (MARS-5) with

FIGURE 1: General chemical precipitation synthesis method.

temperatures at 90°C, 120°C, and 160°C for 30 min and 120°C for 10 and 60 minutes. Wu et al. [12] experimented to get some morphological nanostructures using hydrothermal method. A solution made of water, ethanol, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, NaOH, and HMT was stirred for 30 minutes. Afterwards, it was inserted into an autoclave for 24 hours at 180°C. In addition, other solutions are also made by replacing HMT with PEG or oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) with the same treatment. Guan et al. [13] synthesized with the substances $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, and NaOH. They were stirred with water and ethanol. Having seen a homogeneous liquid, Guan et al. added $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Then, the solution was similarly inserted into a Teflon container and processed in an autoclave at 180°C for 12 hours.

The experiments to establish its morphology by hydrothermal synthesis method have been conducted by Talebian and Jafarinezhad [14]. In this process, the temperature, decomposition time, and ageing time were parameters that were subject to experimental change. The solution was made from precursors $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, NaOH, water, and ethanol (solution was stirred until the solution became white). Parameters changed were temperature and time [temperature (°C) : time (hour), 190 : 48, 190 : 24, 160 : 20, and 100 : 20]. As a consequence, morphology of material was varying. For material which was warmed for 48 hours at the temperature of 190°C, a nanoflower formed; for 24 hours and 190°C, a nanorod formed; for 20 hours and 160°C, nanocauliflower formed, while for a temperature of 100°C for 20 hours a nanosphere formed. Chemical precipitation based solution methods are similar to the hydrothermal method using a solution as the reaction process, but the chemical reactions process can be set up in an open container at low temperatures (typically below 100°C). This process can be interpreted as a chemical reaction between the precursors to produce monomers that later grew into the final material or in accordance with the desired product [14]. An illustration of the chemical precipitation method can be seen in Figure 1.

Xu et al. [15] introduced the preparation of SnO_2 nanosheets via precursor precipitation with a solution made of $\text{SnCl}_2 \cdot 5\text{H}_2\text{O}$, water, and $\text{CO}(\text{NH}_2)_2$ dissolved in water. The material is stirred and then the Al_2O_3 tube dipped into the solution for 6 hours at a temperature of 95°C. SnO_2 grew on the Al_2O_3 tube. Chikhale et al. [16] conducted experiments to compare the precipitation method detection properties of pure SnO_2 nanocrystals and plastered by lanthanum. The solution is made of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3$, water, and

ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$). The precursor is stirred in water until the solution looks clear or transparent then dropped into ammonia until pH >8. Under these conditions, precipitation is formed. The final product is then washed several times with water and heated for 2 hours at a temperature of 450°C.

Tian et al. [17] conducted experiments to determine the structure and magnetic properties of Mn doped SnO_2 by chemical precipitation synthesis method. The solution consists of SnCl_2 and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ that dissolved into ethanol. During the mixing process at a temperature of 60°C, NH_4HCO_3 and HCl are dropped into the solution until pH 9. The solutions were then dispersed by ultrasonicator for 30 minutes while the precipitation results are washed and dried at 150°C to obtain nanocrystal powder. Then the powder is heated in different temperatures (450–800°C) for 3 hours. Baitha et al. [18] conducted experiments with chemical precipitation synthesis method to make ZnO- SnO_2 nanocomposite. The solution used is made of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ precursors that are dissolved in water for a few minutes until the solution is mixed. Then, NaOH is dropped into the solution until reaching different pH targets (3, 5, 7, 9, and 11). Once the consistency looks like porridge, the solution is filtered using a filter paper and washed with water to remove SO_4^{2-} and Cl^- ions. The filtered product is then oven-dried for one hour at 100°C.

(b) *Thermal Conversion Based on Precursor Solids.* Another method that can be used to form nanostructures is through thermal conversion of precursor solids. Morphological forms can be obtained very well by heating the solution at the right heat. This method is similar to the chemical precipitation synthesis method, but the process of thermal dehydration of precursors is performed in solid form with a relatively higher treatment temperature. One important synthesis parameter that must be set properly is the acidity (pH) of the solution during hydrolysis because it affects the morphology and size of the structure. Then, after a proper heat treatment process, a good morphological sample will be formed [38]. The thermal conversion method based on precursor solids has the advantage of being simpler and more controllable for large scale production, which makes it more practical and promising in producing material for catalyst and gas sensors [38].

(c) *Electrochemical Methods.* Electrochemical method is widely used for the manufacturing of nanoporous metal oxide

FIGURE 2: Diagram of the electrochemical method.

because it is a very simple process at low temperatures, making it feasible for commercial production [38]. This method is very advantageous because of the orientation of the growth, morphology, and size, allowing for strict control of the deposition parameters (deposition voltage strength, current density, and temperature) [38]. A diagram of the electrochemical method can be seen in Figure 2.

Jeun et al. [19] performed the experiments with electrochemical deposition method to obtain nanohybrid foams of SnO_2/CuO . The process occurred over Sn/SnO_2 -coated substrate in an electrolyte solution containing sulfuric acid, lead sulfate, and copper sulfate. Electrodeposition is performed at a current density of 0.667 A cm^{-2} for 10 seconds. For the oxidation, the foam is heated at 700°C for 1 hour. Lai et al. [20] conducted experiments to manipulate the morphology of SnO_2 nanotubes by controlling their size through the electrochemical deposition method. SnO_2 nanotubes were synthesized using a polycarbonate membrane with a pore diameter of 50 or 100 nm as a template. The thickness and pore density are $6 \mu\text{m}$ and $6 \times 10^8 \text{ pore/cm}^2$, respectively. One side of the polycarbonate is coated gold with a thickness of 500 nm by sputtering to make the seed layer. Electrical contact is made to the membrane as an electrode using copper tape. The resulting sample is then placed in the electrolyte cell. The electrodes used were platinum and Ag/AgCl using SnCl_2 , NaOH , and nitric acid as the electrolyte solution. SnO_2 deposited on the template using a voltage of -0.4 V with variation of the deposition time. After deposition, the sample was washed using dichloromethane and isopropanol and purified by heating it at 400°C for 4 hours.

Jeun et al. [21] conducted experiments to create SnO_2 porous foams using electrochemical deposition synthesis methods on a SiO_2/Si substrate and to determine its performance on pollution gas detection. Before the deposition process started, the substrate was first cleaned with acetone, ethanol, and water, as well as being coated through the atomic layer deposition method (ALD). SnO_2 thin layer is made using precursor dibutyltin diacetate (DBTDA) which is the precursor of Sn. Time durations used are 3 seconds (for source pulses), 12 seconds (first cleaning), 2 seconds (oxygen pulse), 10 seconds (plasma pulse), and 12 seconds (second cleaning). The substrate is heated to temperatures between 70 and 100°C . The electrolyte solution is made of sulfuric acid and lead sulfate. Substrate that has been coated serves as the cathode and SUS as the anode. The distance between the

cathode and the anode is 35 mm. The value of current density that is used in the deposition process is about 2 A/cm^2 . The as-deposited sample is then heated at 700°C for 1 hour. Figure 3 describes the electrochemical deposition technique.

(d) *Thermal Oxidation Method.* The thermal oxidation method is used to obtain 1D morphology of metal oxide [38]. Obtaining the unique desired morphology form can only be accomplished by heating the metal substrate in order to transform it into metal oxide. This process also requires an atmosphere of a particular air composition (air, i.e., O_2 and N_2) [38]. Morphological growth is dependent on the temperature, typically from 400 to 700°C , growth time, and gas flow rate [38].

Lu et al. [22] conducted experiments to obtain SnO_2 nanoparticles by using the thermal oxidation method and the resulting layer was then used for H_2 gas sensors. Preparation of SnO_2 nanoparticles in these experiments used a substrate made of SiO_2 with a thickness of 100 nm. Tin (Sn) was deposited on substrates of different thicknesses (10–100 nm) by electron beam. After that, the thermal oxidation process is carried out by heating Sn films (at 200°C for 2 hours, 40°C for 2 hours, and 600°C for 8 hours) in an atmosphere of pure oxygen gas flow (flow rate of 200 mL/min). A diagram of the experiment can be seen in Figure 4.

Zhou et al. [23] made SnO_2 films through thermal oxidation synthesis process. At first, tin nitride (SnN_x) was deposited on Si and quartz substrates through the sputtering method. The film thickness is 150 nm. After deposition, the samples are given a thermal oxidation treatment with different temperatures (400 – 800°C) for 2 hours. During this process, the form of the morphological structure of SnO_2 would change.

Several researchers have conducted some thermal methods. Arafat et al. review some of SnO_2 nanostructures synthesized [39]. Some of those methods are hydrothermal, electrospinning, molten salt, vapor assisted growth process, and thermal evaporation. Among those method, hydrothermal method offers inexpensive, rapid fabrication, and low temperature process. Arafat et al. in their research grow SnO_2 nanowires/nanoneedles on Si/SiO_2 substrates at 95 – 98°C using hydrothermal method [39]. The characteristic of the resulting nanowires/nanoneedles depends on some parameters which are growth time, temperature, and $\text{Sn}^{4+}/\text{OH}^-$ in solution. Besides, they report that decreasing

FIGURE 3: Electrochemical deposition of SnO_2 on Si/SiO_2 substrate.

FIGURE 4: Diagram of thermal oxidation synthesis.

concentration of SnCl_4 can make nanowire become thinner [39]. Arafat et al. [39]. They used $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and NaOH as a precursor. Precursor dissolves in water/ethanol and heated up at 190°C . Besides, they load La_2O_3 to SnO_2 nanorod where the nanorod disperses in alcohol followed by adding $\text{La}_2(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Another simple method of growth of SnO_2 is thermal evaporation [39]. In this method, nanowire SnO_2 grows on Au deposited substrate. Sn powder heated up at 800°C and the substrate kept away from Sn source at certain distant. SnO_2 evaporated at certain interval. The longer the evaporation takes, the longer the length of nanowire gets [39].

Kim et al. [40] offer the new chemical route to produce hierarchical and dense SnO_2 sphere. They used solutions that contain $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{H}_2\text{C}_2\text{O}_4$, and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ [40]. The dense sphere was synthesized with concentration of $\text{H}_2\text{C}_2\text{O}_4$ and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ higher than in hierarchical sphere [40]. At first, each solution heated up hydrothermally at 180°C for 14 h and yields low yellow precipitate. Then the precipitate was washed and was calcined at 600°C for 2 h and yielded powder. The difference of $\text{H}_2\text{C}_2\text{O}_4$ and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ caused the difference of SnO_2 structure [40]. Hierarchical porous spheres were formed from nanosheet while dense spheres

formed smooth surface. For sensing characterization, powder mixed with organic vehicle to form paste and then deposited on substrate [40]. In their report, Kim et al. compared hierarchical and dense sphere sensing performance to ethanol, H_2 , and C_3H_8 at 400°C [40]. Response hierarchical sphere films to all gases are higher than the dense one [40]. Besides, hierarchical sphere film shows faster response than the dense sphere film. This phenomenon is caused by the porosity of hierarchical sphere that provides more diffusion path and faster surface reaction [40]. Moreover, the specific surface area of hierarchical sphere is higher than dense sphere [23].

(e) *Other Methods.* Dinan and Akbar review some method of growth of one-dimensional nanostructure. Among them, vapor-liquid-solid method was used to grow SnO_2 nanowire [41]. Dinan and Akbar used this method to grow SnO_2 nanowire. In their work, disk SnO_2 was used as source material and substrate for growing SnO_2 nanowire. At first, Au catalysts were deposited on SnO_2 disk and anneal at $700\text{--}800^\circ\text{C}$ [41]. At this temperature, dewetting of Au film into nanoparticles occurred. Then the substrates that contain Au nanoparticles were heated at $700\text{--}800^\circ\text{C}$ under

FIGURE 5: The SnO₂ decomposition mechanism on the substrate.

H₂ atmosphere at certain pressure [41]. In this process, nanowires of SnO₂ were formed and the longer the exposure time takes, the longer the length of nanowire gets. Au nanoparticles were observed at the tip of nanowire [41]. The presence of Au is important because it provides site for growing nanowire. SnO₂ will grow on the substrate just in case there are Au nanoparticles on the substrate.

Carney et al. in their report tried to combine the advantage of TiO₂ and SnO₂ in sensing performance by mixing them [42]. In their experiment, TiO₂ and SnO₂ were mixed using ball milling method with isopropanol for 4 h [42]. Isopropanol then evaporated and resulted in mixing powder. The powder then compacted at certain pressure resulting in compact disk. Disk of TiO₂ was also made to compare with mixed one. Disks then were sintered at 1450°C and 1200°C for 6 h and 2 h. Nanofibers were produced by nanocarving process [42]. In this method, disks were heated at 700°C for 8 h under H₂/N₂ atmosphere. TiO₂-SnO₂ that sintered at 1450°C for 6 h shows nanofibers structure on the surface while the other that sintered at the same temperature for 2 h shows no fibers [42]. TiO₂-SnO₂ that sintered at 1200°C for 6 h and 2 h did not show fibers but formed groove on grain. The H₂ sensing characterization at 400°C results in the idea that TiO₂-SnO₂ that sintered at 1200°C for 6 h is more sensitive to H₂ than others except pure TiO₂. TiO₂-SnO₂ is more stable than pure TiO₂.

There are also several other synthesis methods that have been used to yield SnO₂ nanostructures. Some of these include sonochemical method [43, 44], microwave irradiation synthesis [45, 46], template-assisted method [47–49], sol-gel [50, 51], microemulsion [52], electrospinning technique [53], spray pyrolysis [54], chemical vapor deposition [55, 56], and arc plasma source [57]. Table 1 is featuring a review of various methods that have been discussed.

2.1.2. Decomposition. One recent development in synthesis of SnO₂ nanostructures uses a water solvent, utilizing the hydrothermal synthesis process. With the mixing process, hydrolysis between salt Sn precursors and water occurred, with the chemical reaction shown as follows [25]:

In open systems, most of the Sn(OH)₂ is hydrolyzed into Sn²⁺ (1). Meanwhile, some are oxidized into the precipitation of Sn(OH)₄ (2). Part of Sn(OH)₂ undergoes the hydrolysis process and is oxidized to SnO₂ (3), accelerating the hydrothermal process [25]. When the NaOH catalyst is inserted into the precursor solution with Sn salt and water, Sn(OH)₄ directly interacts with OH[−] ions to form Sn(OH)₆^{2−}:

When experiencing the hydrothermal process in an autoclave, temperature and high pressure decomposition of Sn(OH)₆^{2−} became crystal SnO₂ as shown in (5) [25]. If the decomposition process occurs over the substrate, the decomposition mechanism can be described as can be seen in Figure 5.

3. SnO₂ Performance as Pollutants Gas Sensors

Performance of semiconductors used as gas sensors is measured by means of sensitivity, response time, and recovery time. These depend on how much electron activity takes place on the semiconductor surface and the amount of chemisorbed oxygen species (O[−] and O^{2−}) from the targeted pollutants gases.

3.1. CO Gas. When CO gas detection is performed with SnO₂, reactions occur on the surface of SnO₂ between CO with oxygen species (O[−] and O^{2−}). CO reaction with oxygen species is given as follows [4]:

Firooz et al. [24] reported that the sensitivity of SnO₂ (sheet-like, nanogranular, and nanoflower-like), which is made by solid-state reaction method, to CO gas has a maximum value at working temperature of 275–300°C. When comparing the sensitivity of all three morphological forms with the same calcination temperature at 400°C, SnO₂ nanoflower-like form (16.78 nm crystal size) has a higher sensitivity. Sensitivity of SnO₂ nanoflower-like form is 71.5 at the maximum temperature 250°C; the sheet-like SnO₂ sensitivity (19.26 nm crystal size) is 17.7 at a temperature of

TABLE 1: Fabrication method of SnO₂-based materials.

Method	Material	Substance	Condition	Reference
Hydrothermal	SnO ₂	SnCl ₂ ·2H ₂ O, NaOH, and CTAB	In autoclave at 130°C for 24 hours	[10]
		SnCl ₂ ·2H ₂ O, urea, and citrate acid	Entered into microwave accelerated reaction system at temperature of 90, 120, and 160°C for 30 minutes and at 120°C for 10 and 60 minutes	[11]
		SnCl ₄ ·5H ₂ O, NaOH, HMT, PEG, and H ₂ C ₂ O ₄	Entered into autoclave at 180°C for 24 hours	[12]
		SnCl ₂ ·H ₂ O, Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O, NaOH, and Zn(NO ₃) ₂ ·6H ₂ O	Entered into autoclave at 180°C for 12 hours	[13]
		SnCl ₄ ·5H ₂ O, NaOH	Entered into autoclave (temperature (°C) : time (hours), 190 : 48, 190 : 24, 160 : 20, and 100 : 20)	[14]
Chemical Precipitation	SnO ₂	SnCl ₂ ·5H ₂ O, CO(NH ₂) ₂	Al ₂ O ₃ tube is entered into solution for 6 hours at 95°C.	[15]
		SnCl ₄ ·5H ₂ O, La(NO ₃) ₃ , and NH ₃ ·H ₂ O	Dropped NH ₃ ·H ₂ O into solution till pH >8, washed with water and heated for 2 hours at 450°C	[16]
	Mn doped SnO ₂	SnCl ₂ , Mn(CH ₃ COO) ₂ ·4H ₂ O, HCl, and NH ₄ HCO ₃	Stirred at 60°C, dropped HCl and NH ₄ HCO ₃ into solution till pH 9 Dispersed with ultrasonic for 30 minutes and dried at 150°C. heated at 450–800°C for 3 hours	[17]
	ZnO-SnO ₂ nanocomposite	SnCl ₄ ·5H ₂ O, ZnSO ₄ ·7H ₂ O, and NaOH	Dropped NaOH into solution for different pH (3, 5, 7, 9, and 11). Dried at 100°C for 1 hour	[18]
		Sn/SnO ₂ -coated substrate, sulfuric acid, lead sulfate, and copper sulfate	Electrodeposition is done with current density 0.667 A cm ⁻² for 10 seconds and then heated at 700°C for 1 hour	[19]
Electrochemical	Nanohybrid foams SnO ₂ /CuO	Polycarbonate membrane coated with gold, copper band, SnCl ₂ , NaOH, and nitrate acid	V = -0.4 V; after deposition, washed by dichloromethane and isopropanol; the last process, heated at 400°C for 4 hours	[20]
Electrochemical	SnO ₂ foams	SiO ₂ /Si substrate, <i>dibutyltin diacetate</i> (DBTDA), sulfuric acid, and lead sulfate	Current density 2 A/cm ² , after deposition, heated at 700°C for 1 hour	[21]
Thermal oxidation	SnO ₂	SiO ₂ substrate, Sn, and oxygen	Deposited Sn on substrate by electron beam, heated Sn film with O ₂ atmosphere (flow speed, 200 mL/minutes) at 200°C for 2 hours, 400°C for 2 hours, and 600°C for 8 hours	[22]
		SnN _x , Si substrate	Deposited SnN _x on Si substrate by sputtering; heated film at 400–800°C for 2 hours	[23]

about 275°C, while for nanogranular morphology (crystal size of 10.59 nm) it is 16 at maximum temperature of 300°C.

In another paper, Firooz et al. [25] reported experimental results on the effect of nanostructured SnO₂ morphology to its CO gas exposure sensitivity. Comparisons show that the resulting nanostructure of SnO₂ would yield various morphologies at nanoscale including prism-like SnO₂ (crystal size 128 nm), mixed nanoflower-like, prism-like (crystal size 62 nm), nanoflower-like (crystal size 39 nm), cubic-like (crystal size 60 nm), and nanosheet-like (particle size 26 nm). The sensitivities and maximum working temperatures for each form are 38 at 300°C, 847 at 300°C, 1217 at 275°C, 73 at 300°C, and 119 at 300°C. Lu et al. [57] reported that nanoporous SnO₂ has the highest sensitivity (45%) when 1000 ppm CO gas is exposed to its surface. In addition, this study showed that when SnO₂ was tested for 120 hours, the sensor capabilities still turned out well indicating that the sensor has good stability.

3.2. CO₂ Gas. When SnO₂ is used to detect CO₂, a reaction occurs on the surface of SnO₂ between CO₂ gas and the oxygen species (O⁻ and O²⁻). Equation (8) and (9) shows the reaction [4]:

The above reaction affects metal oxide performance as a gas sensor. Luan et al. [26] reported the results of research for SnO₂ sensitivity towards CO₂ (100, 300, and 700 ppm). When 100 ppm CO₂ is exposed on SnO₂, the sensitivity is 0.05 at a maximum temperature of 303 K. For the 300 ppm CO₂, the sensitivity was 0.09 with a temperature of 323 K, while for the 700 ppm CO₂ gas the sensitivity of SnO₂ is 0.18 with a working temperature of 343 K.

3.3. SO₂ Gas. Similar to what was explained above, reactions between SO₂ gas and the oxygen species occur on SnO₂ surface, shown as follows [4]:

The above reaction affects metal oxide performance as a gas sensor. Das et al. [28] reported the results of their research about this phenomenon. At working temperature 350°C, SnO₂ has a different percentage response towards different concentrations of SO₂. At 5 ppm SO₂ concentration, the SnO₂ sensitivity became 20%. When concentration is increased to 100 ppm, the sensitivity is 37%. If SnO₂ is added with 0.15 wt% vanadium, the percentage response, respectively, became 47% and 70%.

Lee et al. [58] also conducted experiments on SnO₂ mixing with other materials, namely, magnesium oxide (MgO) and vanadium (V₂O₅), and how they affect SO₂ gas detection. Table 2 shows MgO-mixed and V₂O₅-mixed SnO₂ performance results towards SO₂ gas detection.

3.4. NO_x Gas. In NO_x gas detection by SnO₂, the surface reactions between NO_x (NO₂, NO, and N₂O) gases and the oxygen species (O⁻ and O²⁻) are shown as follows [4]:

(i) For NO₂ gas,

(ii) For gas NO,

(iii) For gas N₂O,

Khuspe et al. [29] reported the experimental results about SnO₂ based SO₂ sensors where SnO₂ had a sensitivity of 19% at 100 ppm NO₂ gas and working temperature at 200°C. In addition, recovery time and response time differed, depending on NO₂ concentration (10, 20, 40, 60, 80, and 100 ppm). The greater the NO₂ concentration, which is exposed to SnO₂, the shorter the response time—there was a 90% reduction from 30 to the 7 seconds. The recovery time increased 90% from 302 to 1202 seconds. Cho et al. [30] found that the percentage of SnO₂ hollow nanofibers has a better response towards 2 ppm of NO₂ gas when compared to planar SnO₂. Hollow SnO₂ nanofibers sensitivity came in at 81.4% while planar SnO₂ reached only 19.9% at a maximum working temperature of 300°C. The hollow nanofibers response time for NO₂ gas with a concentration of 0.5; 1; and 2 ppm is 79, 57, and 55 seconds, respectively. Moreover, for SnO₂ planar, the results were 96, 56, and 55 seconds, respectively.

Kanazawa et al. [9] studied which SnO₂ pure metal oxide semiconductors are best for N₂O gas sensors. With regard to SnO₂ performance towards N₂O gas sensitivity, results showed 1.66% at 300 ppm N₂O with an operating temperature of 450°C. Sensitivity increased to 4.5% at a temperature of 500°C after 0.5 wt% SrO was added, while the response time became 180 seconds. Table 3 provides a summary of SnO₂ performance towards pollutants gases.

4. Review of Sensing Mechanism

4.1. Gas Adsorption on SnO₂ Surface. The process of adsorption on the surface of metal oxides affects the working mechanism of metal oxide gas sensors. In general, there are two types of reactions that occur on the surface of metal oxides. One is a reaction between the molecules of the target gas and preabsorbed oxygen [4]. Oxygen is absorbed on

TABLE 2: Response and recovery times, (P)-based SnO₂ for SO₂ gas sensors.

Senors	Composition		Sensor response (%)	40% recovery time (s)	70% recovery time (s)
	MgO	V ₂ O ₅			
SnO ₂ (p)Mg ₅	5	—	52,1	1255	—
SnO ₂ (p)Mg ₁ V ₁	1	1	18,2	130	325
SnO ₂ (p)Mg ₅ V ₁	5	1	38,4	250	770
SnO ₂ (p)Mg ₁₀ V ₁	10	1	51,3	1940	—
SnO ₂ (p)Mg ₅ V ₂	5	2	44,2	230	625
SnO ₂ (p)Mg ₅ V ₅	5	5	24,4	180	415

TABLE 3: Performance of SnO₂ toward main pollutants gases.

Gas	Concentration	Morphology	Particle size (nm)	Sensing performance	Reference
CO	n/a	Sheet-like	19,26	Sensitivity = 17,7 at 275°C	[24]
		Nanogranular	10,59	Sensitivity = 19 at 300°C	
		Nanoflower-like	16,78	Sensitivity = 71,5 at 250°C	
	n/a	Prism-like	128	Sensitivity = 38 at 300°C	[25]
		Mix Prism-like and nanoflower-like	62	Sensitivity = 847 at 200°C	
CO	n/a	Nanoflower-like	39	Sensitivity = 1217 at 275°C	[25]
		Cubic-like	60	Sensitivity = 73 at 300°C	
		Nanosheet-like	26	Sensitivity = 119 at 300°C	
	1000 ppm	Nanophorus	n/a	Sensitivity = 45	[26]
CO ₂	100 ppm	n/a	n/a	Sensitivity = 0,05 at 303 K	[27]
	300 ppm	n/a	n/a	Sensitivity = 0,09 at 323 K	
	700 ppm	n/a	n/a	Sensitivity = 0,18 at 343 K	
SO ₂	5 ppm	n/a	n/a	Response 20%	[28]
	100 ppm	n/a	n/a	Response 37%	
NO ₂	100 ppm	n/a	n/a	Sensitivity = 19% at 200°C	[29]
	10–100 ppm	n/a	n/a	Response time is 30 till 7 seconds and the recovery time is 302 till 1202 seconds	
				Response percentage 81,4 Response time = 55 seconds	
	2 ppm	Hollow nanofibers	n/a	Response time = 57 seconds	[30]
	1 ppm	Hollow nanofibers	n/a	Response time = 79 seconds	
	0,5 ppm	Hollow nanofibers	n/a	Response percentage 19,9 Response time = 55 seconds	
	2 ppm	Planar	n/a	Response time = 56 seconds	
	1 ppm	Planar	n/a	Response time = 96 seconds	
	0,5 ppm	Planar	n/a		
N ₂ O	300 ppm	n/a	n/a	Sensitivity = 1,66 at 450°C	[9]

the surface of metal oxide that has a high electronegativity and then the adsorbed oxygen serves as a trap for SnO₂'s conduction band electrons. As a result, the energy barrier increases. The chemical reaction that occurs on the surface is oxidation and reduction reaction of oxygen gases, O₂⁻, O⁻, or O²⁻ [4].

The occurring processes on the surface of metal oxides depend on the type of gas and the type of semiconductor. SnO₂ is an n-type metal oxide semiconductor. Interactions that occur in this type involve the conduction band and the metal oxide surface. Because the type of gas in adsorption process depends on the process of reduction or oxidation

gas, oxygen is initially adsorbed on the surface of metal oxides when heated in air. Oxygen ions are absorbed, that is, O_2^- , O^- , and O^{2-} . This process can occur with the help of electron capture from the conduction band of the metal oxide. Kinematics of adsorption is described by the following reaction [4]:

For oxidizing gases in the adsorption process of a SnO_2 (n-type) semiconductor, electrons are absorbed by the gas and result in ion gases. Then, the oxidation gas ions capture the oxygen ions (O_2^- , O^- , or O^{2-}) and subsequently the electron would stabilize itself into a stable gas [4]. The result is a new stable release of gas and O^{2-} . Oxygen ions are absorbed by the SnO_2 surface for further processing. The reaction can be explained by the following reaction:

In gas reduction, the reduction process begins with the reduction of oxygen ions (O_2^- , O^- , or O^{2-}) from the surface of SnO_2 . The adsorption oxygen ions make the gas become unstable until triggering gas to release electrons in order to become stable again. Ejected electron gas is absorbed by the surface of SnO_2 . In general, the kinematics process of the gas adsorption can be explained by the following reaction:

The adsorption or release process of electrons in SnO_2 leads to the changes in its resistivity [4, 5, 8].

4.2. Band Gap. Material band gap affects the electrical properties of these chemicals. The band gap is located between the valence band and the conduction band. The gap between the two bands is a function of energy, the Fermi level, which describes the electron energy levels that exist at a given temperature [5, 8].

Based on the band gap theory, materials are divided into three categories: insulators, conductors, and semiconductors. The insulator has the largest wideband gap, resulting in an energy level where the electrons cannot move. Wide band gap in the insulator is more than 10 eV. Transferring electrons from the insulator material requires enormous energy. Semiconductors have band gap energies in the range of 0.5 to 4.5 eV so that the conduction below these values is not visible. Above the Fermi level, electrons can fill the conduction band resulting in an increase in the conductivity of semiconductor material. Normally, the conductor has a Fermi level below the conduction band [5, 8].

Band gap theory is also used in working mechanism of gas sensors for SnO_2 which has a band gap at 3.6 eV [24, 31–37]. Target gases interact with the metal oxide surface, usually through the adsorption of oxygen ions, the results of which lead to changes in the concentration of the materials. The changes of charge concentration affect the conductivity or resistivity of materials. The majority of n-type semiconductor charge carriers are electrons, whereas the p-type is a positive hole. In SnO_2 , charge carriers are electrons (including itself among the n-type semiconductors).

In the sensing mechanism of metal oxide gas sensors, oxygen chemisorption becomes important phenomenon. In ambient atmosphere, oxygen molecule will adsorb on surface of metal oxide and transform to oxygen ion by trapped electron from conduction band of metal oxide. Electron can be transferred from metal oxide to oxygen molecule only if the lowest lying unoccupied molecule orbits of O_2 complex lie below the Fermi level. When oxygen adsorbs to the surface, negative surface charge formed and created electron depletion zone. The ion-sorption of oxygen creates an acceptor level that bends the bands upward. This bending is proportional to the built-in potential that increases the resistance of sensor. Built-in potential can change with the presence of gas. When reduction gas is present, gas will react with oxygen ion and release electron back to conduction band, decrease the built-in potential, and cause the resistance decrease. When oxidation gas is present, gas will react with oxygen ions, use the electron together, and cause the built-in potential to increase and lead to increase in resistance [59, 60]. The changing of band gap before and after the exposure of gas can be seen in Figure 6.

Improving sensitivity of SnO_2 can be done by modifying the band gap [61]. SnO_2 can be modified or mixed with other oxides like ZnO , TiO_2 , or CuO to build p-n junction or n-n junction [61]. These ways are proved to increase sensing performance of metal oxide gas sensor.

4.3. Transfer of Electrons. The basic mechanism that creates the response of the metal oxide semiconductor to target gases is still debated; however, the trapping process of electrons to adsorbed molecules and subsequent band bending are understood to be caused by charge molecules (these same molecules are understood to be responsible for the change in conductivity) [62]. The negative charge trapped in the oxygen species causes band bending to curve upwards, revealing the conductivity of the material when compared to band bending under normal circumstances [62]. Figure 7 shows that when the O_2 molecules are adsorbed on the surface of metal oxides, they would extract the electrons from the conduction band E_c and catch them on the surface in the form of ions. This will drive band bending and create electron-depleted regions. Electron-depleted regions are also known as the space-charge layer, where the thickness is the length of the band-bending region [62]. Reaction between oxygen species and reducing gases can restore band bending, resulting in an increase of conductivity of the metal oxide. The number of O^- becomes excessive at temperatures 300–400°C, the working temperature for most metal oxide gas sensors [62].

FIGURE 6: Band bending before (left) and after (right) SnO_2 exposure to reduction (a) and oxidation gas (b). V : built-in potential, Φ : work function, and χ : affinity electron.

FIGURE 7: Schematic diagram of band bending after chemisorption of charge species (here the adsorption of oxygen ions) E_c , E_v , and E_f which shows the energy in the conduction band, valence band, and Fermi level, respectively, where Λ_{air} shows the thickness of space-charge layer and eV_{surface} shows Barrier potential.

5. Conclusions

SnO_2 as a gas sensor has been briefly explored in differing morphological forms, synthesis methods, and sensitivity to certain target gases. In making SnO_2 nanostructures, the easiest method is solution-based synthesis methods, especially the hydrothermal synthesis method. Through this method, the parameters in the process of forming nanostructures are easily regulated, are safe for the environment, and have salt precursors that can be dissolved. In the manufacture of SnO_2 , widely used precursors are $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ with NaOH as a catalyst.

SnO_2 semiconductor performance (n-type) towards many gases has been studied. This paper reviews the pollutant gases CO , CO_2 , SO_2 , and NO_x . For CO gas, the best performance is shown by nanoflower-like SnO_2 with sensitivity 119% at a temperature of 300°C . Unfortunately for this data, the response and recovery time are not shown. For CO_2 gas, SnO_2 shows the best performance at room temperature. Towards 100 ppm CO_2 gas, the sensitivity was 0.05 (303 K) and 300 ppm CO_2 sensitivity was 0.09 (323 K), whereas towards 700 ppm CO_2 gas sensitivity of SnO_2 is 0.18 (343 K). This data also did not include the response and recovery time. For SO_2 gas, the SnO_2 which is mixed with MgO or V_2O_5 with a composition ratio of 10:1 shows the best performance. Its sensitivity was 51.3 and the recovery time (40%) is 1940 seconds, while the other recovery time (70%) is not shown. For NO_2 gas, the best performance is shown by SnO_2 hollow nanofibers whose percentage is 81.4% at the maximum working temperature of 300°C . Meanwhile, the response time towards NO_2 gas with a concentration of 0.5; 1; and 2 ppm, respectively, is, for the morphology of hollow nanofibers, 79, 57, and 55 seconds. For the latter gas, N_2O , sensitivity of SnO_2 , with an additional 0.5 wt% SrO , towards SO_2 gas is 4.5% with a working temperature of 500°C and the response time is 180 seconds. As reviewed, for most SnO_2 gases, the working temperatures are above 250°C . This relatively high temperature needs to be corrected for real world application by lowering its temperature. Adding other substances like metal oxide to SnO_2 could lower its working temperature. One could also develop the SnO_2 in various morphological forms, such as in the form of hollow SnO_2 nanofibers, nanosheet, nanorod, or nanoneedle.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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