CHAPTER II

THEORECTICAL BACKGROUND

2.1 Type of gas sensors

Gas sensor technologies have been developed over the years. Conventionally, gas sensors are separated by the type of detector that are used to interface them [26]. They are categorized into 6 types.

2.1.1 Catalytic and electrocatalytic gas detector

This detector measures the combustible gases in air which occur via catalytic combustion. The combustible gases react with catalyst to generate heat. Then, heat is converted into electrical signal for measurements.

2.1.2 Electrochemical cell sensor

This detector can be considered as transducers which electrical signal has been generated when the target gas molecule reacted with sensing electrode.

2.1.3 Solid state sensor

This detector usually consists of metal oxides from transition metals. The common name of this type is known as metal oxide semiconductor (MOS). Electrical signal is generated by adsorption or desorption of target gas at the metal oxide surface.

2.1.4 Infrared gas detection

Two different wavelengths of infrared radiation are used together in this detector. One has been used for target gas to detect and the other one is the wavelength that absorb by the other component in atmosphere.

2.1.5 Ultrasonic gas detection

This detector measures the sound pressure level of target gas by changing the baseline pattern of ultrasonic wave.

2.1.6 IR gas cloud imaging

This detector differs from the other types that it monitors the detection through images. Infrared camera is used to generate or acquire the image. An IR absorptive gas appears as dark clouds in the video images. The contrast is different when contaminated gas appears.

Table 2.1 Advantages and disadvantages of each type of gas sensor [26]

Types of gas sensor	Advantages	Disadvantages
Catalytic and electrocatalytic gas detection	Robust Simple to operate	Contamination of catalyst Oxygen required for detection
Electrochemical cell sensor	Fast response High accuracy Low power consumption	Operating range is limited to low temperature (< 45 °C) Unsuitable in dry environment Operating in narrow range pressure
Solid state detectors	Robust Able to detect various gases Resistance to corrosive environment Long lasting	High power consumption Low selectivity
Infrared gas detectors	Resistance to corrosion No routine calibration required	The measured gas must be infrared active Large volume of gas required
Ultrasonic gas leak detection	Not influence by fog, heavy rain or other ambient condition	Unable to detect concentration of gas
IR gas cloud imaging	Detection of multiple gas at the same time	Not a small concentration detector Detect gas difficulty when contrast with background is poor

Good characteristics of gas sensor should be low cost, high sensitivity, good selectivity, robustness, and fast response to target gas. There are many sensing materials that show good characteristic of gas sensor, as indicated in **Table 2.2**. One of gas sensor that shows this characteristic is solid state detector, even though it shows low selectivity. Solid state detector is commonly known as metal oxide semiconductors.

Table 2.2 Advantage and disadvantage of sensing materials

Material	Advantage	Disadvantage
Enzyme	High selectivity	Expensive Short life time
Ionic liquid	Robust	Slow response time
Polymer	Wild sensor application	Lower sensitivity than metal oxide Susceptibility to strong oxidizing gas
Metal oxide	Robust Low cost Detection in low concentration	High temperature of operation Low selectivity

2.2 Metal oxide semiconductors

Metal oxide such as ZnO, WO_3, TiO_2, SnO, and so on is considered as semiconductors due to its band gap energy. Semiconductors have energy gap in the range of 0.5-5.0 eV which electron can be promoted from valance band to conduction band through the Fermi level. The Fermi level is the highest occupied state. If energy is above Fermi level, electron occupied in conduction band. Conductivity of semiconductors will increase. Insulators have higher energy gap which is about 10 eV or more. Electron from valance band can be transferred to conduction band via lots of energy. In opposition to insulators, valence band and conduction band of conductors are overlapped. The Fermi level of conductors is in conduction band. Therefore, electron can be transferred easily [2].

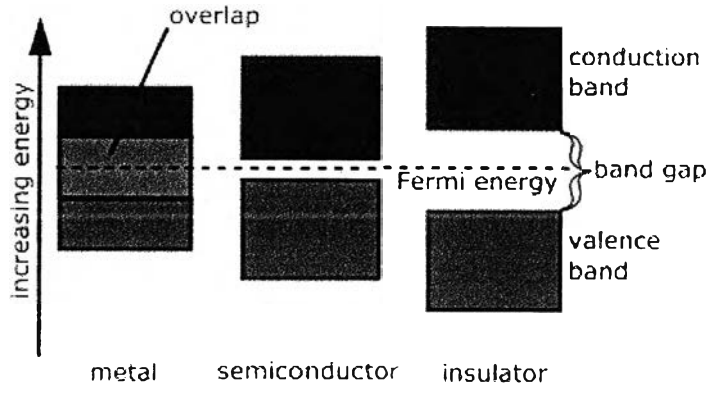

Figure 2.1 Band gap energy of metal, semiconductor, and insulator [27]

Conventionally, principle of metal oxide gas sensor is based on charge-transfer of electron and adsorbed species on metal oxide surface. This phenomenon results in change of conductivity of metal oxide which can be revealed into electrical signal. Change of this electrical signal can be calculated to define the sensitivity of gas detection. For example, Chou *et al.* reported that ZnO:Al thin film showed electrical signal under air and ethanol ambience, as shown in **Figure 2.2** [28].

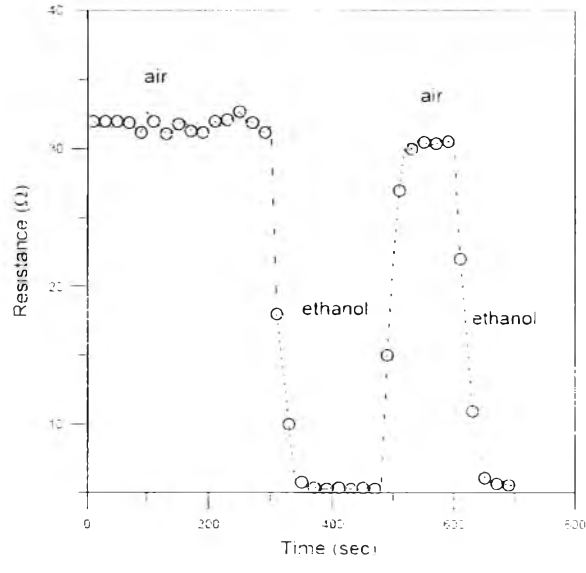

Figure 2.2 Electrical response of the sensor at operating temperature of 250 °C under 400 ppm of ethanol concentration [28]

Resistance of sensor under air and ethanol ambience is about 32 Ω and 5 Ω respectively. Change of resistance can be guaranteed that sensor responded to ethanol gas. This change of electrical signal is explained by following reactions

$$\text{Surface} \xrightarrow{\Delta} h^+ + e^- \quad (1)$$

$$O_{2\,(g)} + e^- \longrightarrow O_{2\,(ads)}^- \quad (2)$$

$$O_{2\,(g)} + 2e^- \longrightarrow 2O_{(ads)}^- \quad (3)$$

$$2C_2H_5OH_{(g)} + O_{2\,(ads)}^- \longrightarrow 2CH_3CHO_{(g)} + 2H_2O_{(g)} + e^- \quad (4)$$

$$C_2H_5OH_{(g)} + O_{(ads)}^- \longrightarrow CH_3CHO_{(g)} + H_2O_{(g)} + e^- \quad (5)$$

When sensor was heated, free electron and positive hole were generated (reaction (1)). Oxygen in air ambience accepted free electron and become oxygen ion species (reactions (2) and (3)). Thereafter, ethanol reacted with oxygen species on sensor

surface to give acetaldehyde, water, and electron as products (reactions (4) and (5)). Electron as product resulted in decreasing of resistance under ethanol ambience. Response and recovery time of sensor to ethanol vapor is 2-4 minutes, as shown in **Figure 2.2**. Response and recovery time is time at 90 % of resistance change. Time that is required for a device to reach at 90 % of its total response of electrical signal when exposed to target gas ambience is the response time. Recovery time is time that the sensor returns to its 90% of baseline electrical signal. According to reaction (1) it can be seen that metal oxide gas sensor needs to be activated in order to be used in gas sensing application. From this principle, many research groups have been proposed their gas sensors based on metal oxide semiconductors, as shown in **Table 2.3**.

Table 2.3 Metal oxide semiconductors as gas sensing application

Gas	ZnO Response (conc. ppm)	TiO_2 Response (conc. ppm)	WO_3 Response (conc. ppm)	SnO_2 Response (conc. ppm)	In_2O_3 Response (conc. ppm)	CuO Response (conc. ppm)
CO	2.2 (20 ppm) [29]	2.6 (15 ppm) [30]	1.4 (100 ppm) [10]	3.8 (500 ppm) [8]	0.47 (200 ppm) [31]	0.07 (30 ppm) [32]
NO_2	0.7 (20 ppm) [29]	38 (2.1 ppm) [33]	1.2 (100 ppm) [10]	422 (50 ppm) [8]	2.6 (1 ppm) [34]	0.15 (2 ppm) [32]
EtOH	24 (100 ppm) [18]	40 (100 ppm) [35]		23 (50 ppm) [36]	2 (100 ppm) [37]	1.2 (5 ppm) [38]
NH_3	5.7 (50 ppm) [39]	0.11 (20 ppm) [40]	4.5 (50 ppm) [10]	11 (1,000 ppm) [41]		
H_2S	19 (10 ppm) [42]	20 (60 ppm) [43]	48 (1 ppm) [44]	9.5 (200 ppm) [45]	150 (600 ppm) [46]	

2.3 Activation of metal oxide semiconductors for gas sensor application

2.3.1 Activation by heat

In the past decade, metal oxide semiconductors have been developed for gas sensor application. The adsorption and desorption of gas molecule on the sensor's surface results in a change in electrical conductivity of metal oxide semiconductors. This phenomenon has been demonstrated in 1962 which zinc oxide thin films were used as sensing materials and temperature of operation was about 400 °C [47]. Leng *et al.* [10] proposed that WO_3 nanofibers were used as sensing materials for ammonia detection at 200 °C of operating temperature. Barreca *et al.* [48] reported that 1D ZnO nano-assemblies which were prepared from plasma enhanced-chemical vapor deposition (PE-CVD) indicated detection of carbon monoxide, methane, and hydrogen gas at operating temperature of 200, 300, and 400 °C respectively. Even though this activation method of metal oxide semiconductors for gas sensor is popular in the past, the danger of this activation is also high. It is awry since high temperature is required. An alternative to avoid this risk is switching from a heat activating source to a low temperature activating source like an ultraviolet light with proper wavelength.

2.3.2 Activation by UV

Although heating is a conventional activation method, an ultraviolet light at proper wavelength has also been reported to activate metal oxide semiconductors. de Lacy Costello *et al.* reported that UV-activated zinc oxide nanoparticles yield high sensing performance for various gases at room temperature [13]. Gong *et al.* reported that UV-activated zinc oxide fibers can be operated for gas sensor application at room temperature [14]. Peng *et al.* proposed ZnO nanorods which were activated via UV light exhibited detection of formaldehyde at room temperature [17]. These are good evidence that UV light can activate metal oxide semiconductors to perform as gas sensors at room temperature. Not only does this alternative method reduce the risk to human and asset, but this also indicates that high energy consumption is not required.

Many metal oxide semiconductors have been utilized as sensing materials for gas sensor application. Examples include ZnO, TiO_2, WO_3, SnO_2, $BaTiO_3$-CuO, and others. ZnO, WO_3, and SnO_2 are sensing materials that have been widely studied in gas sensor scope. $BaTiO_3$-CuO is interesting to be used as sensing materials, however, it showed poor sensing performance [49]. One of metal oxides that has drawn a lot of interest is TiO_2. TiO_2 is generally well known as photocatalyst. Thus, the use of TiO_2 as sensing materials which is activated by UV light is interesting. Furthermore, evidence

of Chen *et al.* report also supported that TiO_2 exhibited the higher sensitivity than ZnO under the same detection parameters.

From such researches, TiO_2 also mostly indicated the higher sensitivity when compared to ZnO, as shown in **Table 2.4**.

Table 2.4 Comparison between TiO_2 and ZnO as sensing materials for gas sensing application

Gas	TiO_2 response (conc. ppm)	ZnO response (conc. ppm)	Metal-doped	Morphology
CO	2.6 (15 ppm) [30]	2.2 (20 ppm) [29]	-	Nanofibers
NO_2	38 (2.1 ppm) [33]	0.7 (20 ppm) [29]	Pd	Nanofibers
EtOH	40 (100 ppm) [35]	24 (100 ppm) [18]	Cr/Cr_2O_3	Film/Nanofibers
CO	0.6 (15 ppm) [35]	1 (100 ppm) [18]	Cr	Film/Nanofibers
H_2S	20 (60 ppm) [42]	19 (10 ppm) [43]	Pt/Cu	Film/Nanofibers
NO_2	9.3 (0.5 ppm) [23]	1 (100 ppm) [18]	$-/Cr_2O_3$	Nanofibers

It can be seen from **Table 2.4** that at 15 ppm of carbon monoxide concentration, TiO_2 exhibits 2.6 of response whereas ZnO indicates 2.2 of response at 20 ppm of concentration. This behavior is mostly similar to other gases, even though hydrogen sulfide detection is different.

2.4 Titanium dioxide (TiO_2)

Titanium dioxide, titanium (IV) oxide, or titania is one of metal oxide semiconductors that have been reported as gas sensor [2-4, 12, 15, 16, 23-25, 30, 33, 35]. TiO_2 in nature occurs in three forms: rutile, anatase, and brookite. Rutile is the most stable form of TiO_2. Anatase and brookite are the metastable form which can be converted to rutile by heating. It has been reported that the two metastable forms become rutile when annealing the material above 700 °C [50, 51]. Rutile and anatase structures are tetragonal while brookite structure is orthorhombic. Even though both rutile and anatase are tetragonal structure, their band gap energy are different. Band gap energy between valance and conduction band of rutile is 3.0 eV whereas that of anatase is 3.2 eV which can be converted to UV absorption at 413 nm and 388 nm respectively. Thus, TiO_2 needs 3.0 or 3.2 eV of energy to be conductive material. Notwithstanding, anatase phase is preferred for sensor application. According to Madare *et al.* report, they proposed that TiO_2 film with different annealing temperature

showed the different sensitivity of sensing materials. TiO_2 film with only anatase phase indicated higher sensitivity than anatase and rutile phases, as shown in **Table 2.5** [52].

Table 2.5 Sensitivity of TiO_2 film with different annealing temperature [52]

Samples	T_a (°C)	W_a (%)	D_A (nm)	D_R (nm)	S_{240}
TiO_2	300	100	17.3	0.0	4.25
undoped	500	74	44.2	40.5	1.74
TiO_2 0.5%	300	100	18.5	0.0	6.92
Pd	500	94	30.7	29.5	4.20

T_a – annealing temperature

W_A – weight percentage of anatase phase

D_A – average crystalline size of anatase phase

D_R – average crystalline size of rutile phase

S_{240} – sensitivity of formaldehyde gas at temperature 240 °C

Both undoped TiO_2 and 0.5 % of Pd-doped TiO_2 at 100 % of weight percentage of anatase phase (W_A) indicated that sensitivity to formaldehyde gas of 240 °C of operating temperature is higher than that lower weight percentage.

In addition, morphology of sensing materials can also affect the sensing property. Fan *et al.* reported that ZnO nanoline showed higher sensitivity in gas detection and faster recovery time than ZnO thin film at room temperature. Large surface-to-volume ratio of sensing materials is an important factor that showed highly sensitivity behavior. Furthermore, ZnO nanoline with smaller particle sizes also indicated higher sensitivity, as shown in **Figure 2.3** [22].

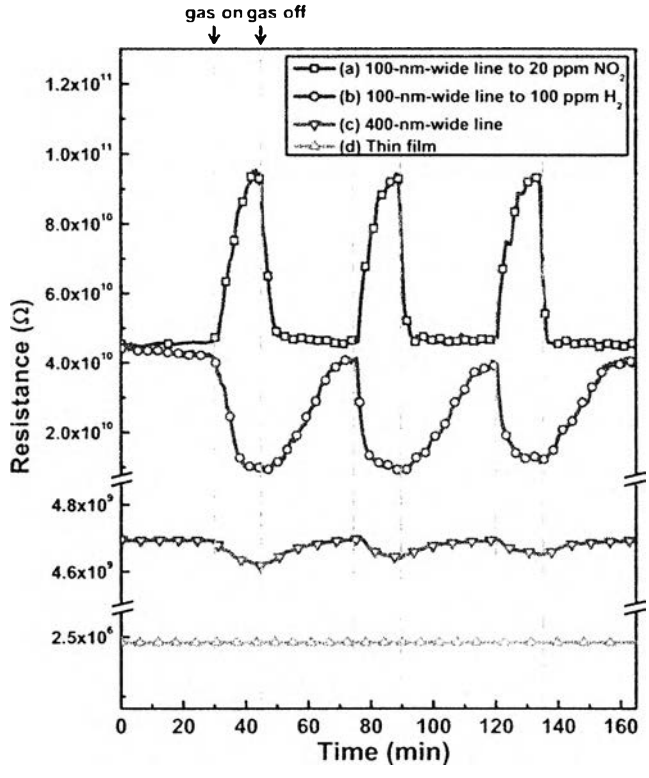

Figure 2.3 Sensor response of ZnO nanoline and ZnO thin film [22]

Moreover, Eriksson *et al.* reported that two different morphologies of ZnO, thin film and nanoparticle, showed differences in sensitivity and stability of sensors. ZnO nanoparticles exhibited higher sensitivity and higher stability than polycrystalline ZnO film, as shown in **Figure 2.4** [53].

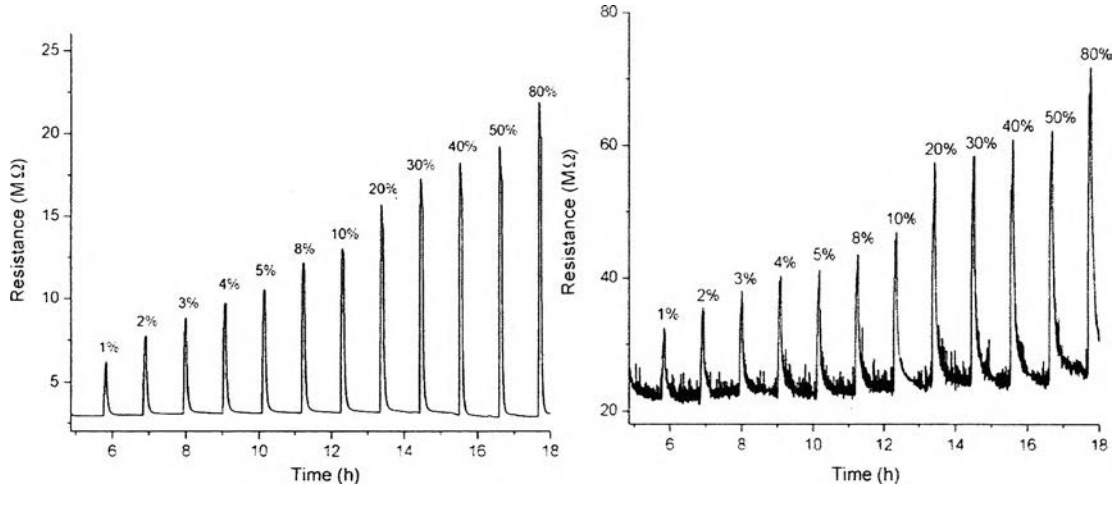

Figure 2.4 Sensor signal of ZnO a) nanoparticle and b) polycrystalline film exposed to 1-80% O_2 at 450 °C [53]

It can be seen that ZnO nanoparticle showed higher sensitivity which are ascribed to large surface-to-volume ratio. Moreover, sensor signal of ZnO nanoparticle also showed lower noise signal than polycrystalline film which ascribed to higher stability.

Nanoscale structure is of high interest to be morphology of sensing materials. Many of morphology of metal oxide such as thin film, nanorods, nanolines, nanoparticles, and nanofibers have been used in gas sensor application due to high surface-to-volume ratios. One of the nanoscale structure that has been reported in such works is nanofibers. One of the processes that can be used to fabricate nanofibers is electrospinning method.

2.5 Electrospinning process

Electrospinning process is a simple, low-cost, and versatile method for fabrication of fibers. Materials such as polymer, ceramic, and composites can be fabricated into nanofibers or microfibers by electrospinning. High surface area is one of the characteristics that can be obtained from electrospinning. Electrospinning has been used to prepare materials for many applications such as medical, environmental, electronic, and so on. For gas sensing application, electrospinning is used for fabrication of nanofibers to be sensing materials. Polymer as template for electrospinning is surrounded by metal oxide particles in the form of a solution. The solution is pushed by electric force that applied to solution and become to fibers. As preparation of nanofibers in Leng *et al.* [10] report, WO_3 nanofibers were fabricated via electrospinning process. Polyvinylpyrrolidone was an example of the polymers that acted as template for metal oxide nanofibers. Afterwards, electrospun WO_3 nanofibers were successfully fabricated. Electrospun WO_3 nanofibers were calcined at elevated temperature of organic compound which removed polymer as template and such organic solvent. Finally, pure metal oxide, WO_3, nanofibers were obtained which is sensing materials for gas sensing application.

High voltage power supply, feeding system, and collector are main components of electrospinning equipment. High voltage power supply is connected to needle tip of electrospinning solution syringe at positive or negative electrode and collector at grounded electrode, shown in **Figure 2.5** [54]. When high voltage is not applied to needle tip, the droplet of electrospinning solution is a semicircular shape due to surface tension of solution. Once high voltage has been applied until conquers the surface tension force, semicircular droplet ejects from the tip and reaches the grounded collector.

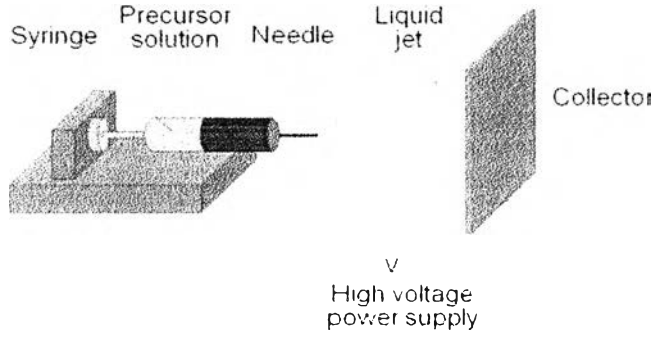

Figure 2.5 Schematic of electrospinning process [54]

Fibers obtained from electrospinning process are nanofibers to microfibers. Controlling of electrospinning parameters such as applied voltages, distance between needle tip and collector, feeding rate, concentration of solution, and many more is necessary to specify diameter of fibers. Many research have reported the roles of each parameter that affect diameter of electrospun fibers [24, 54-57]. Park *et al.* synthesized TiO_2 nanofibers through electrospinning process [55]. Titanium isopropoxide and polyvinylpyrrolidone were the main components of electrospinning solution. Nanofibers with large diameters were found at high concentration of titanium isopropoxide while less titanium content resulted less diameters, as illustrated in **Figure 2.6**.

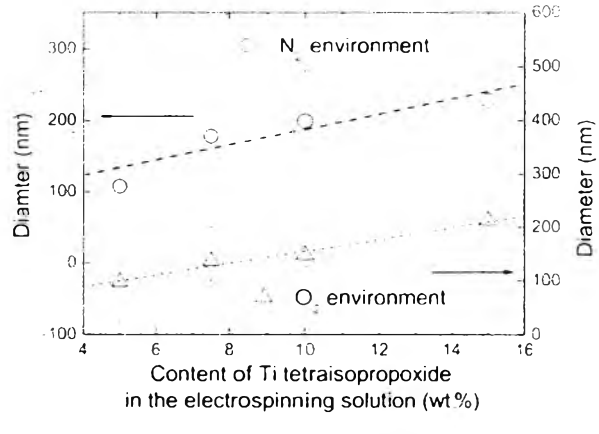

Figure 2.6 Diameter of nanofibers calcined in O_2 and N_2 atmosphere as a function of the Ti tetraisoproxide content [55]

Zhang *et al.* found that an increase in polyvinylpyrrolidone content in electrospinning solution gave larger fiber diameters and higher viscosity of solution, as shown in **Figure 2.7** [24].

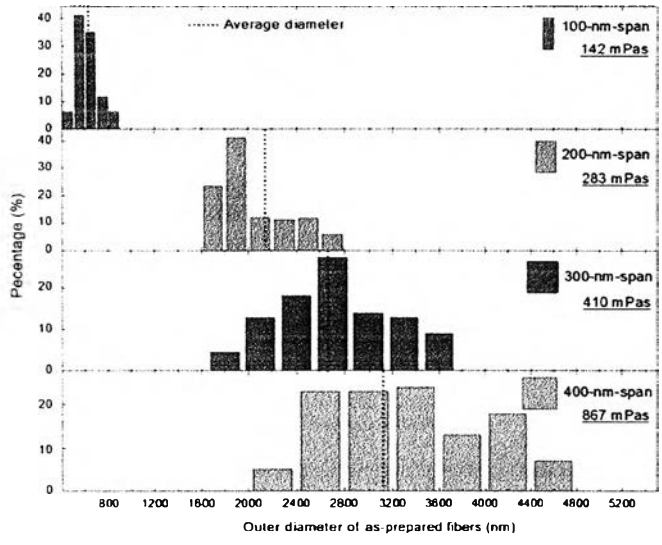

Figure 2.7 A histogram of hollow TiO_2 nanofibers at various solution viscosity [24]

Wang *et al.* proposed the effect of voltages and distance between needle tip and collector to poly(phenylene vinylene) (PPV) nanofibers. Their applied voltages and distance between needle tip and collector were studied at 7.5-15.0 kV and 15-35 cm sequentially. In first case, average diameter of PPV nanofibers was 739 nm at 7.5 kV of applied voltage. At 10.5 kV of applied voltage, the average diameter was found about 706 nm while the broad length of diameter, 492-1279 nm, was found at an increase voltage to 15.0 kV. PPV nanofibers at 7.5-15.0 kV of applied voltage were shown in **Figure 2.8** [56]. Diameter of nanofibers was reduced when increasing applied voltages.

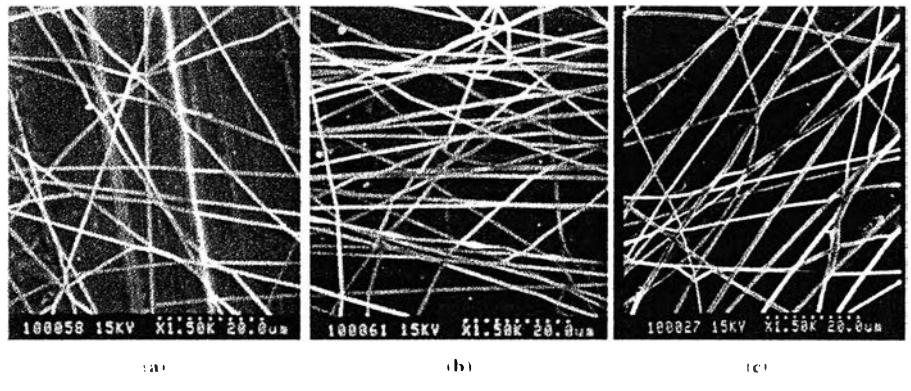

Figure 2.8 Effect of applied voltages a) 7.5, b) 10.5, and c) 15.0 kV to diameter of PPV nanofibers [56]

For latter case, less diameter of nanofibers was found at the longer distance due to evaporation of solvent, as shown in **Figure 2.9** [56].

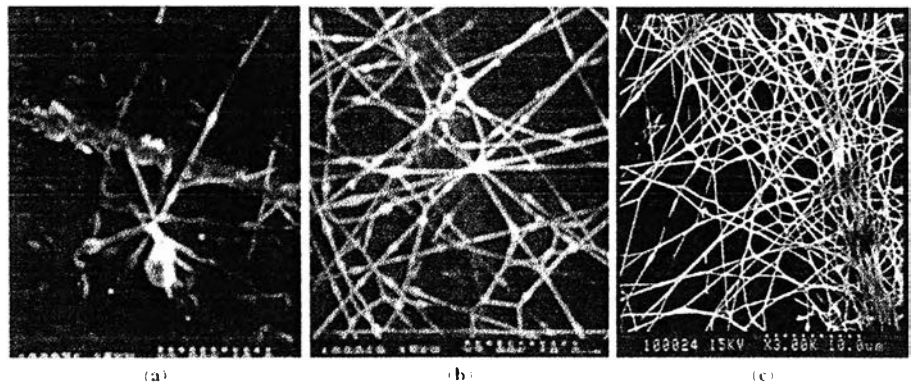

Figure 2.9 Effect of distance between needle tip and collector a) 15, b) 25, and c) 35 cm to diameter of PPV nanofibers [56]

2.6 Hot-pressing process

There are great deal of interest in fabrication parameters which affect the morphology of electrospun nanofibers. Kim *et al.* proposed the method that enhances surface area of nanofibers which is called hot-pressing [23]. Surface area of hot-pressed nanofibers was indicated to be about 4 times higher than electrospun nanofibers without hot-pressing. In 2010, they also reported that hot-pressed SnO_2 nanofibers exhibited attractive sensing characteristic of NO_2 and CO detection [8].

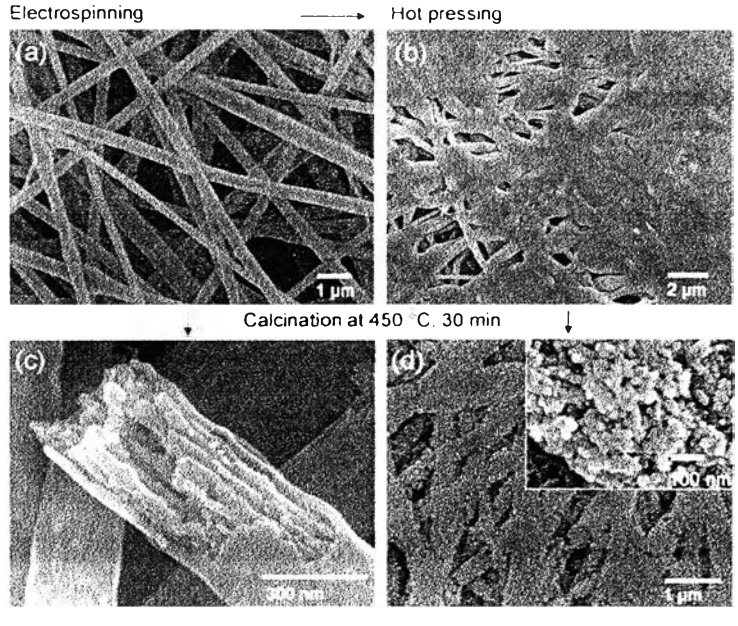

Figure 2.10 (a) SEM image TiO_2/PVAc composite fibers fabricated by electrospinning from a DMF solution. (b) SEM image of TiO_2/PVAc composite fibers after hot pressing at 120 °C for 10 min. (c) SEM image of unpressed TiO_2 nanofibers after calcination at 450 °C. (d) SEM image of hot pressed TiO_2 nanofibers after calcinations at 450 °C [23]

2.7 Sensing materials characterization techniques

2.7.1 Scanning electron microscopy (SEM)

SEM is a technique that reveals morphology of specimen in images. Resolution of this technique is up to nanometer scale which is high magnification. Principle of this technique is that the primary electron beam interacts with the specimen. Thereafter, secondary electrons which ejected from specimen surface are collected. Finally, collected electrons are displayed into image. For example, Kim *et al.* presented ZnO nanorods synthesized at 150 °C for 4 hours which used for gas sensor application, as revealed in **Figure 2.11** [58]. The average length of ZnO nanorods was approximately 1 μm.

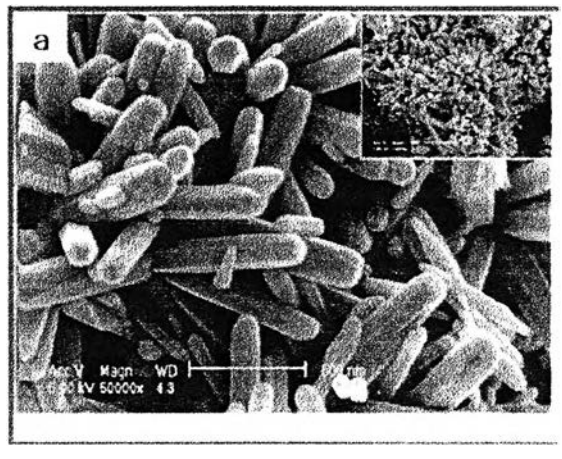

Figure 2.11 SEM image of ZnO nanorods that synthesized at 150 °C over 4 hours [58]

2.7.2 X-ray diffraction analysis (XRD)

XRD is a technique that determines the crystal structure of specimen such as metal, salt, inorganic compound, and semiconductors are mostly crystal form. Principle of XRD technique is diffraction of X-ray beam to crystal structure of specimen. When X-ray beam radiated to crystal structure of specimen, X-ray beam can be diffracted if crystal structure of specimen has the crystalline plain. This diffraction of x-ray beam is shown into peak of 2θ. There are reports about XRD pattern of metal oxide semiconductors for gas sensing application. Kim *et al.* reported that XRD pattern of ZnO nanorods which synthesized at 150 °C for 4 hours, as shown in **Figure 2.12** [58]. Crystal structure of ZnO nanorods was found in many peaks of 2θ. Position of each peak can be referred to crystalline plain of ZnO nanorods.

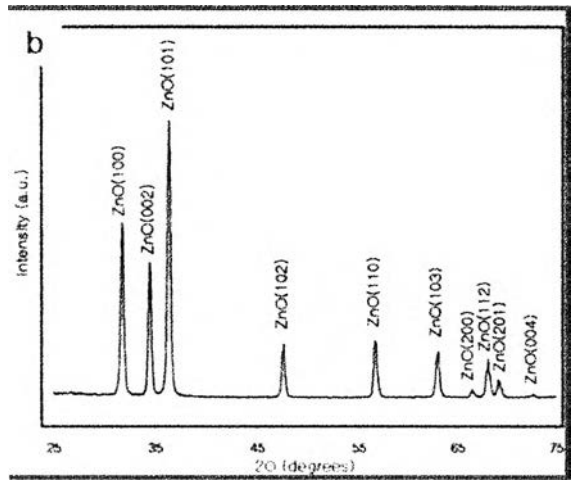

Figure 2.12 XRD pattern of ZnO nanorods synthesized at 150 °C for 4 hours [58]

2.7.3 Brunauer-Emmett-Teller surface area analysis (BET)

BET is a technique that measures the surface area of specimen by adsorption and desorption of gas molecules. Nitrogen is usually used for measurement. Nanoscale materials such as catalyst, nanofibers, cellulose, and etc. are mostly examined by this technique. Zhang *et al.* presented BET analysis of hollow and normal TiO_2 fibers. Hollow TiO_2 fibers exhibited higher surface area than normal TiO_2 fibers which measured surface area was 57.9 and 22.6 m^2/g respectively. This technique usually indicates surface area of sensing materials of gas sensor application. Due to high surface area of sensing materials, high sensitivity of gas sensor is exhibited. Moreover, as mention in Kim *et al.* report [23], hot-pressed TiO_2 nanofibers indicated higher surface area than unpressed TiO_2 nanofibers. Surface area of unpressed and hot-pressed TiO_2 nanofibers was investigated via BET analysis. The measured surface area of unpressed TiO_2 nanofibers was 31.22 m^2/g while hot-pressed TiO_2 nanofibers exhibited 138.23 m^2/g of surface area.

2.7.4 Contact angle measurement

Generally, hydrophilic and hydrophobic properties of specimen are explained by angle of water droplet on specimen surface. This angle is measured from liquid phase on surface. If the angle is equally 0° which means perfect wetting, water droplet fully absorb on specimen surface. The angle is in the range of 0-90° and 90-150° means hydrophilicity and hydrophobicity respectively. Superhydrophobicity is in the range of 150-180° of contact angle. Moreover, perfectly non-wetted is at 180° of contact angle [59], as revealed in **Figure 2.13**.

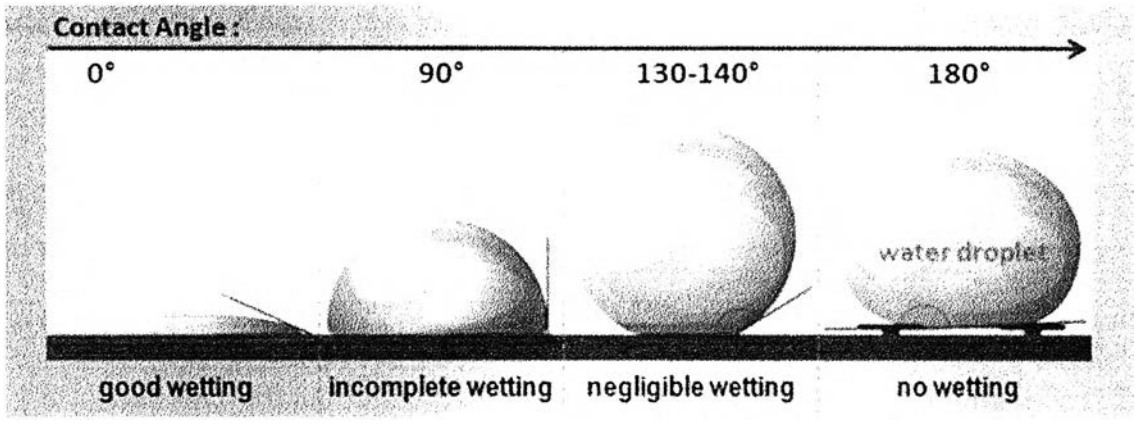

Figure 2.13 Characteristic of contact angle [60]

2.7.5 Sensing performance

Sensing performance of gas sensor is usually defined as sensitivity. Sensitivity is signal-to-noise ratio of electrical signal which mostly compared between electrical signal in air and test gas ambience. Definition of sensitivity (S) or response has been reported in several forms, $S = R_a/R_g$, $S = R_g/R_a$, $S = \Delta R/R_a$, and $S = \Delta R/R_g$, where R_a is resistance of gas sensor in air ambience, R_g is resistance of gas sensor in target gas ambience, and ΔR is absolute of different resistance between two ambience [4]. Nonetheless, some groups reported with other electrical parameters which are current (I) or voltages (V) [13, 14, 35, 47-48, 54, 61-68].

From principle of metal oxide gas detection, there have many research groups wanted to improve the sensing performance of metal oxide gas sensor which is sensitivity, selectivity, fast response and recovery, and many more. Therefore, high sensing performance of gas sensor based on metal oxide semiconductors relies on the following factors:

2.7.5.1 Surface area

It can be considered that high surface area of sensing materials resulted high sensing property. This factor is previously mentioned in section 2.6.3.

2.7.5.2 Morphology of sensing materials

Design of morphology of sensing materials is a challenge in gas sensor application scope. Nanoscale materials is desired because of large surface-to-volume ratio which mostly indicate high sensitivity to target gas. This factor commonly goes together with surface area. As mentioned in Fan *et al.* report [22], ZnO nanoline with smaller particles size indicated higher sensitivity than thin film (**Figure 2.3**). Moreover, this phenomenon also exhibited in Eriksson *et al.* [53] report (**Figure 2.4**).

2.7.5.3 Humidity

There have been reports that humidity affected the gas sensing property of sensing materials. de Lacy Costello *et al*. reported that humidity decreased the sensitivity of ZnO thin film. At room humidity which is about 35%, the sensitivity was found to be 50% lower than in dry condition and 25% at 100% humidity [13]. In contrast, Gong *et al*. reported that humidity can be ignored because the sensitivity at different humidity (53-93%) was similar [14]. Evidence of the importance of humidity in sensing ability of metal oxides includes Herrán's report that CO_2 detection of $BaTiO_3$-CuO thin film was not successful without humidity [49]. Moreover, Ostrick's report also confirmed that $BaCO_3$ sensors for CO_2 detection was blocked without the presence of water [69]. Therefore, the reactions of carbonate and CO_2 needs OH^- group on the surface at low temperature of CO_2 detection. While without humidity, sensitivity of CO_2 detection disappeared,

2.7.5.4 Dopant

Generally, doping is addition of impurities into material which improves the conductivity of material. Nonetheless, there have been reported that doping can also improve the sensing performance of metal oxide gas sensor. One disadvantage of metal oxide semiconductors is low selectivity. Many research groups developed metal oxide semiconductors by metal doping to improve the selectivity of sensing materials. Biao *et al*. reported that Cu-doped TiO_2 nanofibers exhibited high sensitivity to CO detection when compared to undoped TiO_2 nanofibers. Sensitivity of Cu-doped TiO_2 nanofibers at 300 °C was 17 times higher than undoped TiO_2 nanofibers at the same condition. Liu *et al*. reported that 0.5 wt% of Co-doped ZnO nanofibers indicated higher sensitivity of 100 ppm acetone than pure ZnO nanofibers [21]. It is noteworthy that an increase of doping content too much, 1 wt% of Co-doped ZnO nanofibers, decreased the response of acetone detection. In addition, they also indicated the selectivity to acetone when compared to various gases. Response of sensor to 100 ppm of acetone concentration is higher than the other gases. Response of mix gases, which are acetone and ethanol mixed gas, is indicated close to response of acetone gas. Hence, this gas sensor is selective to acetone gas, even though other gases can be detected.

From this background, it can be revealed that there are many types of gas sensors due to their own characteristic. One of them that is of high interest to be used as gas sensor is solid state gas sensor or metal oxide semiconductor. Strong points of this gas sensor are robust, low cost, long lasting, and able to detect various gases,

nevertheless, its weak points are high power consumption and low selectivity. For gas sensor application, metal oxide semiconductors have to activate to be gas sensor. Heating is traditionally required for activation. Alternative to heating is UV light with proper wavelength. TiO_2 as metal oxide gas sensing materials of activated by UV light is of great interest. Moreover, nanoscale morphology is envisaged to increase the performance of gas sensor since high surface area usually result in high sensing performance. Simple, low cost, and versatile method to fabricate nanofibers are electrospinning process. In metal oxide gas sensor scope thus far, there have not been reports on the use of TiO_2 nanofibers which are activated by UV light for gas sensor application. Hence, TiO_2 fabricated via electrospinning and activated by UV light is our main interest to be investigated as gas sensor at room temperature.