Metal Oxide Nanostructures-Based Gas Sensor for Ethylene Detection: A Review

Yanxia Xing¹, He Zhu¹,², Guifang Chang¹, Kexue Yu¹ and Fengli Yue¹, *

¹Key laboratory of Shandong Provincial education department: Past-harvest QC and multi-utilization of characteristic agricultural products, Shandong agriculture and engineering university, Jinan 250100, China
²National Engineering Laboratory of Rice and By-Products Deep Processing, Central South University of Forestry and Technology, Changsha 410000, China

*Corresponding author e-mail: sdau_zhuhe@126.com

Abstract. Increased ethylene content may induce the synthesis of respiratory enzymes and enhance respiration, which accelerated fruit ripening. Monitoring of ethylene concentration is critical in the fruit industry, avoid the fruit from passing through. Research interest has focused on the utilization of nano-sized semiconductor to monitor the ethylene through various processes. As detection for ethylene with excellent sensitivity, superior quantum efficiency, and fast response speed, nano-sized semiconductors are regarded as the most promising directions for nanomaterials. We review the latest achievements with nano-sized material gas sensors as for ethylene detector in the article. Firstly, the classification and structure of semiconductor detectors are introduced (such as resistive transducer; non-resistive transducer; organic semiconductor gas sensor), Then we present several kinds of and their performance, focusing on binary oxides with wide band gap (such as ZnO, SnO2, Ga2O3, Nb2O5, and WO3) and ternary oxides (such as Zn2SnO4, Zn2GeO4, and In2Ge2O7) Eventually, finally, we review and summarize the perspectives in this field and the prospects for future research. Perspectives and outlook on future research directions in this field.

1. Introduction
Ethylene has been confirmed the mainly material regulates fruit ripening as the plant hormone all along [1-3]. Its detection and measurement are virtual to food storage application. The traditional of detection and evaluation method of ethylene is chemical analysis methods(including GC [4-5] and photoacoustic detection systems [6], which require sample pretreatment, and then with the help of analysis instrument to detection and analysis. Moreover, which contain the professional operation, process complex, cumbersome and time-consuming. Hence, there is an increased demand for simple, affordable and reliable ethylene sensors that could be used in conjunction with equipment for detecting ethylene concentrations.

Analysis ethylene based on gas sensors belongs to nondestructive determination technology (NDT), apply methods of physics to analysis ethylene. While the sample information is obtained, the integrity
of the test sample is guaranteed, and the detection speed is faster than the traditional chemical method, and the sample can be checked repeatedly.

At present, there are many kinds of gas sensors, no matter which gas sensors have their respective advantages and disadvantages. The liquid electrolyte electrochemical gas sensor has good stability and lower zero drift, however, the evaporation changes the electrolyte concentration, which affects the accuracy of the measurement and the lifetime needs to be improved. Contact combustion type gas sensor has been used as a combustible gas detector for a long time. It has lower price and high precision, but its sensitivity is low, and the catalyst is easier to be poisoned for a long time, which makes the performance of the component decreased. Solid electrolyte gas sensor has good selectivity, however, it has poor sensitivity and stability. Semiconductor gas sensor possessed high sensitivity (general detection limit is as low as 10⁻⁶ (V/V) and 10⁻⁸ (V/V) of trace gases); the response and recovery time is short, the general response time for a few seconds, tens of seconds, and the recovery time only costs tens of seconds; low cost and stable performance (General life expectancy for several years, and some as high as ten years or more). Due to the above characteristics, semiconductor gas sensor is the most widely studied and widely used gas sensor at present.

![Gas Sensor Diagram](image)

**Figure 1.** Types of gas nano-sensors being evaluated for assessing the ethylene in fruit samples.

Since 1962, Taguch and Seiyama [7] reported the use of metal oxides to detect reducing gases. From then on, gas sensors have been rapid developed, such as Xing Jianping [8] used powder sputtering method prepared thin film gas sensing materials and components, and E.Comini [9], etc., to improve the sensitivity of metal oxide gas sensors by illumination instead of traditional heating wires [10]. Noboru, Yamazoe and [11, 12] has been studied in detail of principle of semiconductor oxide sensor, and the test of the SO₂ under UV irradiation have been tested by K. and Anothainart at room temperature [13, 14].

At present, there is still a lot of room for the development of semiconductor gas sensors. From the current trend of development, the material is mainly based on composite materials, P type materials and other techniques, such as Study on NH₃ thick film gas sensors made of La Co₀.8Fe₀.2O₃ composite with G.N. and the P type semiconductor material was prepared by the gum method and its gas sensing characteristics were investigated.

From the view of detection objects and application fields, the application of gas sensors in fruits and vegetables preservation and food safety is increasing day by day. With the deep research and rapid development of semiconductor gas sensor, the semiconductor gas sensor will be more perfect and be applied in every aspect of people's social life in the near future.

Therefore, in recent years various types of nano-sized including TiO₂ [15], ZnO [15], SnO₂ [16], WO₃ [17], MoO₃ [18] has been adopted as food ethylene related semiconductor testing materials. The
aim of this review is to highlight the best semiconductor material suited for detection of low dose ethylene to ensure the application in detection of fruit ripeness.

This article suggests a comprehensive summary of the conclusions of the recent literature on several oxide materials adopted in ethylene detection, and their prepare methods. Finally, we make a prospect of the future research.

2. Main characteristic parameters of gas sense

2.1. Sensitivity (S)
The sensitivity of a gas sensor means the degree to which the element is sensitive to the gas, which usually be defined as the ratio of the resistance in the air to the resistance in the gas.

2.2. Response time (Tres) and recovery time (Trec)
The corresponding recovery performance is a critical parameter to gas sensors. In general, the component resistance is defined as Tres from the resistance value R0 in the air to the time of R0-90% (R0-Rg); the component resistance is defined as Trec from the resistance Rg to Rg+90% (R0-Rg) in the gas to be measured.

2.3. Selectivity α
Selectivity means the selective ability of different gas according to the gas sensor, the parameter is known simply as α.

$$\alpha = \frac{S_1}{S_2}$$

S1 and S2 means different sensitivity of two gases. If the α is larger, means the better selectivity of the gas sensor.

3. Semiconductor gas sensor

3.1. SnO2-based gas sensor
The most common material used in ethylene sensors for detecting ethylene is tin doxide [19, 20]. Fabricate technology was shown as follows: ceramic paste, thick film printing, solgel, and chemical vapor deposition which requires high-temperature heating and complex material mixing techniques.

The traditional SnO2 milling technology can’t satisfy the requirements of particle size, and the purity is difficult to guarantee [21]. In the past decades, various processes for preparing ultrafine powders have been developed, which can be classified into gas phase, liquid phase and solid phase according to the state of the raw materials.

3.1.1. Synthetic methods gas method.
(1)Arc gasification synthesis
This method is a new method for producing nano SnO2 powder, its characteristic is that the metal tin used is not only an electric conduction conductor, but also an object to be gasified, the utility model has the advantages of high heat utilization rate, high product quality, high purity and whiteness, small particle size, and simple equipment. The average particle size is 42.9nm.

The morphology of SnO2 particles obtained by this method is mainly square and rectangular. When the particle size reaches 20nm, the shape of the particles has a regular shape and the particles smaller than 20nm are spherical.

The single powder can be synthesized at one time and the cost is low; the production process can be automated. The scale of production is limited by equipment and is only suitable for small batch production.

(2) LICVD
Laser induced chemical vapor deposition (LICVD) was set by the reaction of gas molecule on the specific wavelength of laser beam absorption caused by chemical synthesis reaction induced by laser
photolysis and laser pyrolysis, laser and laser photosensitized reaction gas molecules under certain technological conditions (control of laser power density, reaction pressure, temperature, gas ratio and velocity) ultratine particle nucleation and growth. The purity of SnO2 prepared by this method can be guaranteed, but the preparation equipment can’t be available and the output is smaller.

Although the product purity and particle size is ideal according the gas phase synthesis, from a technical device view, preparation of the system stability need to develop high precision equipment, or difficult to develop large-scale production.

![Figure 2. SEM image and XRD patter of the sno2 powder](image)

(3) Liquid method
The liquid phase refers to: metallictin dissolved in concentrated nitric acid, then, the SnO2 powder is obtained by heating and dewatering.

(4) Sol-gel
Rutile rutile SnO2 nanocrystals were obtained by this method, particle size is about 10nm, the material possess high uniformity and purity.

(5) Hydro-thermal method
The size distribution of nanocrystalline powders prepared by hydrothermal method is narrow; the phenomenon of hard agglomeration in the roasting process is overcome by crystallization at high temperature, when the reaction strip changed (temperature, pH, etc.), may have different crystal structures and crystalline morphology, moreover, the yield of single pure water thermal method is not high. In the acid medium, SnO2 was formed as tetragonal crystal. If reduce the acidity of the reaction medium appropriately, it helps to reduce particle size and increase yield.

The reaction temperature increased (pH=1.45), the average size of particles increased from 2nm (120°C) to 6nm (220°C). Figure 2 shows the size distribution of the SnO2 nanocrystals, which have a diameter ranging from 2.5 to 4.1nm.

![Figure 3. (a) TEM image (b) HR-TEM and patter of the SnO2 powder. (C) XRD](image)

3.1.2. Solid phase
Solid phase method mainly includes solid phase reaction, mechanical pulverization, metal salt decomposition and mechanochemical method.

It is difficult to prepare uniform ultrafine particles by solid phase reaction and mechanical commination, SnO2 powder prepared by metal salt decomposition method, which dependent on thermal decomposition temperature and atmosphere, often reunited or excessive particle size (20-50nm).
3.1.3. **Gas sensing mechanism of SnO2.** SnO2 belongs to the N type semiconductor, often used as a resistive gas sensor. The gas sensing mechanism is surface conductance model, therefore, when C2H4 in the air is chemically adsorbed on the surface of the semiconductor, resistivity will decrease. Sensing function of semiconductor is closely related to grain size and Debye length, when the grain size drops to a certain value, the sensitivity of the material increases rapidly.

\[
\text{SnO}_2(\text{O}^-\text{ad}) + \text{C}_2\text{H}_4 = (\text{SnO}_2 + \text{e})^- + \text{CO}_2
\]

Usually, the relationship between the resistance (R) and gas concentration (C) is logarithm.

\[
\log R = m \log C + n \quad m \text{ and } n \text{ are constants.}
\]

3.1.4. **Dope effect.** At present, most gas sensors were made by SnO2, however, it is not a ideal material in sensitivity, stability [16], selectivity. Doping is granted a significant subject to improve the function of the element and keep it working steadily. Such as, doping v2o5 into SnO2 improved the element stability. Effect of sensitivity on ethylene of sno2 improved when doped with Alkaline Earth Oxides, the order of sensitization is consistent with the oxidation activity of alkaline earth metal: MgO > CaO > SrO > BaO. However, alkaline earth oxides performed worse in sensitivity and stability than other materials for detect ethylene.

Other materials included PDCl2, AuO, CO2O3, Bi2O3, THO2 and Pt usually.

(1) Pd-sno2 semiconductor gas sensors

In 2014, a comprehensive research on ethylene detection according to Pd-Sno2 was published, in which the performance of Sio2-based detectors were well summarized. In this article, it compared different Pd-sno2 sensors and found PdCl2 possessed most powerful ability to increasing the sensation of this sensor.

![Figure 4. Characters of Pd-sno2 sensors and 5% PdCl2 possessed the best sensitivity.](image)

(2) Pb synthesized sno2 from sol-gel method (Average particle =10nm), then the particles was doped with different metals. Sensitivity was detected under the experimental conditions: experimental ethylene gas was 10ppm, the heating current ranged 80mA-180mA, doped content both at 2wt%. Figure XX shows the sensitivity of different dopants, which was 4.2 under the 120mA. It can be clearly seen that both pure and Pd-doped SnO2 crystal particles are uniform in size and shape. The micro morphological structures of the SnO2 samples before and after doping are almost similar, which indicates that doping rare noble metallic ion Pd2+ only has a slight impact on the morphologies of pure SnO2 samples. The above values suggested that the incorporation of Pd ions causes a large number of active sites on the surface of the semiconductor, which reduces the activation energy of the reactivity of ethylene and semiconductor surfaces and increases the sensitivity.

Consequently, doped sno2 with 5wt% PdCl2 possessed the best sensitivity at 5 under 100mA under 10ppm ethylene. After the treatment (soaked with ethanol which has been magnetically stirred with...
4A Molecular Sieves decorated at 7 times), the selectivity possessed 1.33, 2.47 with the C2H4/C2H6O group and C2H4/H2S group. Meanwhile, $T_{res}$ and $T_{rec}$ reduced to 60s and 110s, respectively. This work indicates that effect of Pd doped Sno2 nanoparticles is helpful in development of high performance gas sensor.

3.2. Carbon Nanotube-based gas sensor

Recently, the importance of Carbon nanotube-based devices in applications as gas sensors for ethylene detection has become increasingly apparent.

Since it was discovered by Iijima Sumio, the sensing mechanism relies on the high sensitivity in resistance of Carbon nanotube-based has been a topic research object of gas sensors. These principles have been employed in a variety of sensing applications.

Carbon nanotubes can be considered as tubes made of graphite sheets twisted around a central axis by a certain degree of helicity. The ends of the tube are usually sealed by a hemispherical grid with pentagon.

3 carbon atoms of each carbon atom and adjacent carbon nanotubes connected to form hexagonal grid structure, so the carbon atoms in carbon nanotubes by SP2 hybridization, but the hexagonal structure of carbon nanotubes will produce a certain bending, forming space topology, which can form a SP3 bonded [24], so it is the SP2 hybrid, SP3 hybrid also contains certain. The carbon nanotubes with smaller diameter have larger curvature, and the ratio of SP3 hybridization is also large. On the contrary, the ratio of SP3 hybridization is small, and the deformation of carbon nanotubes will change the ratio of SP2 and SP3 hybridization [25].

As figure 5 shows carbon nanotubes are generally composed of single layers or multilayer layers, corresponding to single wall carbon nanotubes (SWCNT) and multi walled carbon nanotubes (MWCNT).

![Figure 5. Carbon tubes sensors.](image)

3.2.1. Synthetic methods. Carbon nanotubes, as one of the most promising materials in nanometer materials, have attracted wide attention. The preparation of carbon nanotubes are the main method of arc discharge, laser evaporation method [26-28] and catalytic pyrolysis method, catalytic pyrolysis method with which the reaction process is easy to control, strong applicability, simple preparation method, the product purity is high, and is widely used in the preparation of carbon nanotubes.

4. Conclusion

This review discussed the typical kinds of sensors which would be the most potential and valuable developing perspectives, and argued that the analysis and processing methods.
With the analysis and processing methods, doped SnO2 with 5wt% PdCl2 is the best gas sensors with in the Pd-SnO2 types, and multi-walled carbon nanotubes is the valuable type to promote in the ethylene sensors industry.

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