Chapter 1
Introduction

1.1 Background of Research

1.1.1 Significance of Fuel-Powered Automobile Exhaust Detection

Since the twenty-first century, the Chinese economy has increased rapidly and the pace of urban construction at all levels in the country accelerated gradually. Meanwhile, the development of industrial production has brought great pressure to the urban environment, and the problem of urban pollution has become increasingly prominent. Of all the environmental pollution, air pollution is the most closely related to human life and should be paid great attention to. According to the data in the *Report on the State of the Environment in China 2016* issued by the Ministry of Ecology and Environment of the People's Republic of China, 254 of 338 cities at prefecture level and above nationwide failed to meet the national air quality standard, accounting for 75.1% [1]. In recent years, the frequent occurrence of smog, PM2.5, and other words in media reports, as well as the frequent occurrence of respiratory diseases in the urban population, have pushed the air pollution problem to the forefront and become the most important urban air pollution problem in Beijing even the whole country [2, 3]. The major air pollutants commonly referred to include: fine particulate matter (PM2.5), inhalable particulate matter (PM10), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), carbon monoxide (CO), and ozone (O_3). These pollutants not only affect the ecological environment but also directly endanger human health. The main pollutants that have a larger impact on human health include: particulate matter, SO_2, and NO_x. Inhalable particulate matter contains many toxic substances and is also the carrier of other pollutants. If it enters the respiratory tract of the human body, it will irritate and corrode the lung wall, thus causing bronchitis, asthma, and other diseases. If SO_2 dissolves in water, it forms sulfurous acid (the main component of acid rain). It is easily absorbed by the mucosal surface of the human body and generates strong

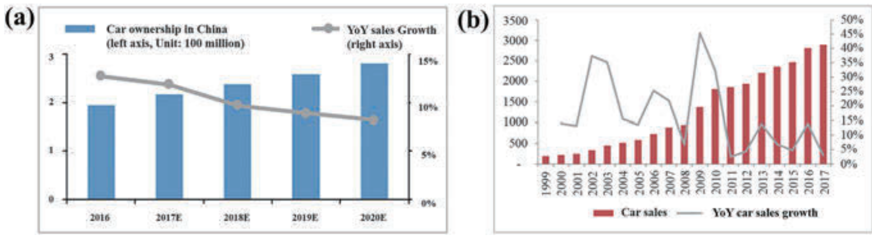

Fig. 1.1 **a** The car ownership and sales growth of China; **b** The car sales and growth rate of China over the years [7]

irritation, thus causing severe respiratory tract disease. But NO_x is more serious. A small amount of NO is easily combined with hemoglobin. It is more likely to cause hypoxia and nerve paralysis than what CO does. NO_2 can be an element of the photochemical reaction in the atmosphere, forming photochemical smog (the main source of PM2.5). It also can cause air pollution problems such as acid rain and ozone hole. The national health department (OSHA, ACGIH) stipulates that the maximum allowable concentration of NO_2 is 1 ppm. When the concentration is higher than 5 ppm, it will cause irritation to mucous membranes and slight discomfort. But when the concentration is higher than 100 ppm, it may cause respiratory disease and even death. This will seriously endanger human health [4, 5].

Nitrogen oxide pollution sources in urban air are mainly generated by fuel combustion. Compared with traditional industrial air pollutant emissions, nitrogen oxide emission from fuel-powered automobiles is dominant, special, and serious [6]. For the Chinese, the population base is large and grows fast. Therefore, the car ownership is high. Car ownership in China exceeded 200 million by 2017, accounting for 20% of the world's total; from 2006 to 2017, the compound annual growth rate of car sales was 15.3% and will continue to grow in the future, as shown in Fig. 1.1. The rapid growth of pollution sources has further worsened the air pollution, endangering the ecological environment and human health.

On the other hand, according to the *2017 Annual Report on Vehicle Exhaust Emission Control* released by the Ministry of Ecology and Environment of the People's Republic of China, the total amount of exhaust pollutants emitted by motor vehicles is estimated to be nearly 44.725 million tons in 2016, while the major pollutants NO_x and PM particles are calculated to be 5.778 million tons and 534 000 tons, respectively, accounting for 90% of the total air pollutants, especially those generated by heavy-duty diesel vehicles (HDDV) [8]. According to the statistical analysis of data in the *2017 Annual Report on Environmental Management of Motor Vehicles in China*, China has been the top producer and seller of motor vehicles in the world for eight straight years, and as a result, automobile exhaust has become an important source of air pollution and shows an increasing trend year by year, as shown in Fig. 1.2. So, it is increasingly pressing to prevent and control vehicle pollution. Because the working condition of an automobile engine is complicated, and it is often operated in moving status, it is extremely difficult to detect and treat automobile exhaust. In

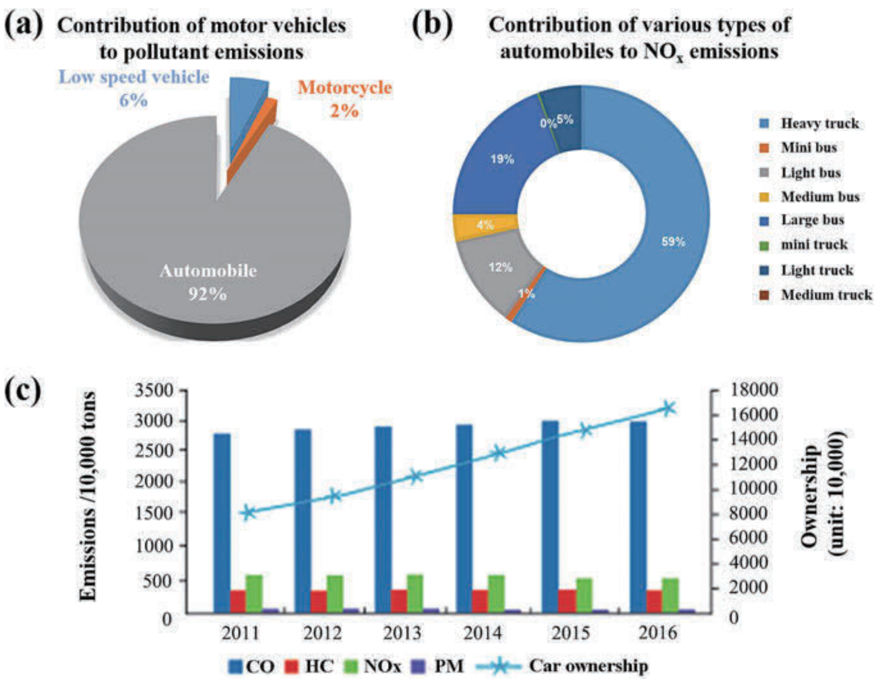

Fig. 1.2 **a** The statistics of the contribution of motor vehicles to NO_x emission in 2017; **b** The contribution of various types of automobiles to NO_x emissions; **c** The growth trend of vehicle pollutant emission in China [9]

addition, most detection methods cannot meet the requirements of online detection of automobile exhaust due to the actual cost and the limited space of the automobile. Therefore, it is significant to study the detection of NO_2 pollutants in automobile exhaust.

In summary, automobiles have become the primary mobile pollution source in modern developed cities and a social consensus has been reached on energy saving and emission reduction of automobiles. Therefore, developing energy-saving and new energy vehicles is an inevitable solution for the society today. However, with a market share of less than 2%, now new energy vehicles are still in the infancy of development in China. An independent and controllable complete energy-saving automobile industry chain is not expected to be formed until 2025. Therefore, the current work is still focusing on strict monitoring and control of the exhaust emissions of existing fuel vehicles.

1.1.2 Overview of Gas Sensors

As most gases exist in special forms, it is difficult to quantify and measure them accurately by conventional methods. Therefore, more professional instruments and test methods are needed for gas detection. Currently, the primary gas detection methods are based on instrumental analysis, and the detection techniques that can be performed by large analytical instruments mainly include spectrometry, mass spectrometry, gas chromatography and ion mobility spectroscopy. The main advantage of these special instrumental analysis techniques is that with high-performance equipment, high-precision and high-sensitivity gas measurement and good gas selectivity can be achieved. However, special instruments are often high in price, expensive to be used, not easy to be carried, and difficult to perform long-term online detection of gas. On the other hand, gas sensors based on various working principles have shown obvious advantages in terms of integration, miniaturization, response speed, and cost. These devices can be complementary to large analytical instruments and used on different occasions, playing an important role in industrial production and daily life.

A gas sensor is defined as a device that converts gas information such as composition and concentration into voltage, resistance, and current, which can be used by a detector, an instrument, or a computer. Generally, gas sensors can be classified as chemical sensors. Detailed classification can be performed by detection mechanism, working principle, material technology, etc. As shown in Fig. 1.3, the working principles of gas sensors can be divided into chemical principles and physical principles. By summarizing and analyzing the research work where the gas sensors are applied, they can also be divided into seven categories: resonant sensors, surface acoustic wave sensors, optical sensors, semiconductor sensors, solid electrolyte sensors, catalytic combustion sensors, and electrochemical sensors [10, 11].

Among these gas sensors of various types, sensors based on chemical principles are the focus of current research and are also the mainstream devices used in applications on the market. In scientific research work in recent years and from the perspective of practicality, semiconductor sensors and solid electrolyte sensors are at the center of the stage. Research on semiconductor gas sensors can be traced back to the last century. Gas sensors based on oxide semiconductors have become a research hotspot in recent decades since Seiyama T et al. reported for the first time the development of semiconductor sensors based on zinc oxide (ZnO) thin film materials in 1962 [12]. Such sensors use semiconductor oxides (mostly metal oxides) as sensitive materials, and detection is realized by taking advantage of the phenomenon that the gas will interact with the gas-sensitive material on the surface or body of the element, which causes changes in the resistance value of the sensitive element. Tin oxide (SnO_2) is a typical n-type semiconductor oxide material. Research is carried out around the blending of tin oxide materials (noble metals, semiconductor metal oxide graphene, etc.), the synthesis of special morphologies (multidimensional nanostructures), etc., and has greatly improved the performance of such sensors and realized commercialization [13–17]. So far, semiconductor sensors have been widely used

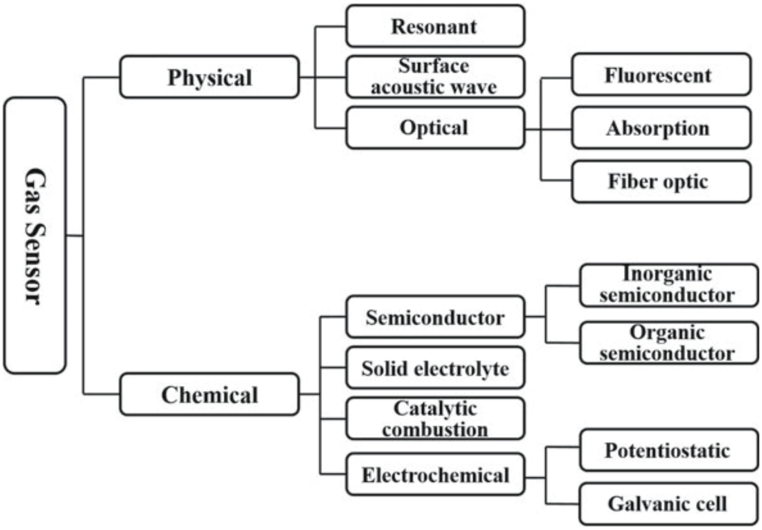

Fig. 1.3 Classification of gas sensors

and occupied nearly 60% of the sensor market due to their simple processing method, low cost, low detection limit, and high sensitivity.

Solid electrolyte gas sensors, as an important branch of chemical gas sensors, are produced with solid ion conductors and gas-sensitive materials. The principle is that a solid electrolyte generates ions through a reaction with the gas to be measured, and the ions move inside the solid electrolyte to form a potential, which is used to characterize the concentration of the gas. Compared with liquid electrolyte sensors, the use of solid electrolyte materials avoids the problems of electrolyte packaging and pollution, which can better ensure the performance of electrolyte materials and extend the life of the sensors. As shown in Table 1.1, by comparing the characteristics of the two types of sensors, it can be seen that solid electrolyte gas sensors have a wider detection range, better response and recovery properties, and incomparable advantages in terms of selectivity and long-term stability relative to semiconductor sensors [18–22]. Therefore, solid electrolyte sensors are often used for gas detection in special environments with high temperature and high humidity, such as automobiles, boilers, and chemical plants. Gas sensors developed with yttria-stabilized zirconia (YSZ), a solid electrolyte material, have been widely used in exhaust emission treatment technology, and are a gas detection solution with great significance in research [23–27].

Regardless of the type of gas sensor, research focuses on the main characteristics of a sensor, which are the criteria for evaluating the performance of the sensor. For example, the main characteristic parameters of solid electrolyte gas sensors include:

Table 1.1 Comparison of characteristics between semiconductor and solid electrolyte gas sensors

	Semiconductor type	Solid electrolyte type
Charge carrier	Electron and hole	Anion and cation
Limit of detection	Extremely low (ppb level)	Low (ppm level)
Detection Range	Low	High
Response and recovery speed	Slow	Fast
Gas selectivity	Poor	Good
Stability	Poor	Good
Integration degree	High	Low
Research direction	Semiconductor material	Solid electrolyte materials, gas-sensitive materials

(1) Response value

Response value most intuitively reflects the corresponding relationship between a sensor's output signal and the concentration of the gas to be measured. Generally speaking, the greater the amplitude of the response value of the gas sensor, the more sensitive the device is to the gas to be measured. Response value represents the amount of change in the output signal, which can be used to obtain parameters such as the sensitivity of a sensor through fitting calculation. Taking a solid electrolyte sensor as an example, the response value of the device is the potential value of the gas to be measured minus the potential value of the air, expressed as $\Delta V = V_{\text{test gas}} - V_{\text{air}}$.

(2) Sensitivity

Sensitivity refers to the ratio of the change in the output signal of a device to the change in the input of the gas measured within a certain range of gas concentration. Sensitivity is a key parameter in the evaluation of gas sensor performance. Taking a mixed potential solid electrolyte gas sensor as an example, its sensitivity can be expressed as the Tafel slope of the response value with the logarithm of the gas concentration measured within a certain gas concentration range, and specifically represents the amount of potential change when the current density increases or decreases by ten times. The internationally common unit is mV/dec.

(3) Response and recovery properties

Response and recovery properties generally include two parameters: 1. response and recovery time. As stipulated in the standards, response time usually refers to the time it takes for the sensor response value to reach 90% of the last stable value in the gas to be measured from the steady state in the air; recovery time refers to, in the gas to be measured, the time it takes for the sensor response value to return to 90% of the stable value from the steady state in the air. 2. Repeatability. Repeatability refers to the error (consistency) between multiple response and recovery values of the sensor during continuous response. Generally speaking, smaller error represents better repeatability.

(4) Selectivity

Selectivity can also be expressed as cross-sensitivity, which can be determined by the response value of a sensor to an interfering gas with a certain concentration. Generally, selectivity will affect the measured response value and repeatability; therefore, an ideal gas sensor must have a high selectivity.

(5) Stability

Stability is usually expressed as the zero drift and interval drift of a sensor within a certain working period while the working conditions remain unchanged. Zero drift refers to the amount of change in the output response value during a certain continuous working period when the sensor is in a steady state in the air. Interval drift refers to the amount of change in the output response value during a certain continuous working period when the sensor is placed in the gas to be measured. Generally speaking, for a qualified sensor, the annual zero drift during continuous working should be less than 10%. There are many factors that may affect the stability of a sensor, while environmental factors such as temperature and humidity play a major role. Stability is also the most critical criterion for determining whether a sensor has practical application value.

Although gas sensors have been widely used in daily life and production, efforts have never stopped to improve their performance. Research on gas sensors should also be developed in three directions: new gas-sensitive materials, new sensors, and smart sensing, to realize the optimization of gas sensor performance and functional expansion and better combination with technologies in other fields to meet the growing market demands.

1.1.3 Application Status of Exhaust Detection Sensors

Automobile manufacturing embodies the comprehensive application of modern science and technology. A major feature of the development of automobile technology is the increasing use of electronic control systems. On-board sensors, as the information source of the electronic control system, are the focus of research and key devices in the field of automotive electronics technology and have been increasingly used in automobiles. By function, on-board sensors can be classified as temperature sensor, pressure sensor, gas sensor, position and speed sensor, flow sensor, etc. [28–30]. Among them, on-board gas sensors are of great significance to the operating conditions of automobile engines and the exhaust emission treatment technology and are a core technical device for achieving efficient and environmentally-friendly working of automobiles. With increasingly serious air pollution, the energy saving and emission reduction of automobiles, and the strict control of pollutants in exhaust emissions have become necessary administrative measures. Therefore, the research and development of on-board gas sensors have profound significance.

On-board exhaust sensors are mainly used in two applications: oxygen sensing and nitrogen oxide sensing.

(1) Oxygen sensor

Figure 1.4 shows the structure and working principle of an oxygen sensor. The main working principle of oxygen sensors is to detect the oxygen concentration in the exhaust of the engine. The deviation of the actual air–fuel ratio of the engine from the theoretical value is determined according to the oxygen concentration, then the detection signal is sent back to the corresponding electronic control unit to adjust the fuel injection quantity and control the concentration of the combustible gas in the engine, so that the air–fuel ratio of the engine converges, close to the expected theoretical value (14.7: 1). The main function of oxygen sensors can be summarized as detecting the air–fuel ratio and achieving closed-loop control. The ultimate goal is to improve the engine's exhausting performance and reduce exhaust emissions. At present, zirconia and titania structural materials are mainly used in the on-board oxygen sensors. As the product maturity is relatively high, they have been an indispensable part of on-board gas sensors [31–34].

(2) Nitrogen oxide sensor

In the automotive industry, in order to effectively reduce fuel consumption and emissions of harmful gases, the development of new engine combustion technologies is critical in research. "Lean burn" is the most typical one. The engine lean burn technology refers to the reduction of the fuel content in the mixed gas (fuel–air ratio above 1:25) in order to increase the output power of the engine and improve fuel efficiency, economy, and environment-friendliness. As shown in Fig. 1.5a, the gaseous pollutants in the exhaust products of general gasoline vehicle engines mainly include HC, CO, and NO_x (mainly NO_2). Three-way catalyst (TWC) devices are needed in exhaust treatment to help dispose of these pollutants. During the treatment process,

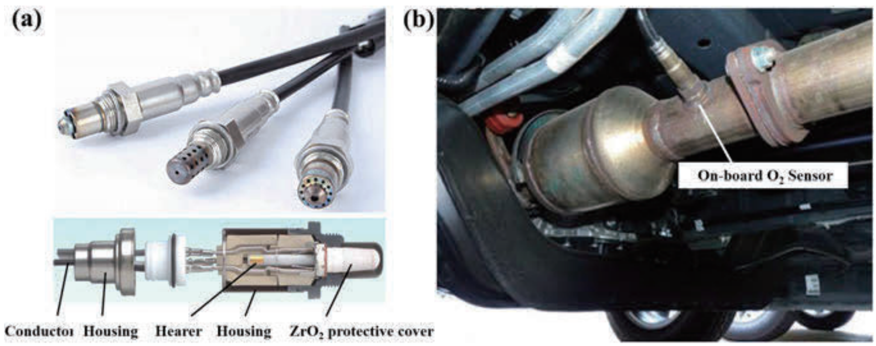

Fig. 1.4 **a** Structural diagram of on-board oxygen sensor; **b** Working principle of oxygen sensor in automobile exhaust system

HC and CO reduce NO_x to N_2 to achieve non-toxic emissions. However, during the lean burn in the engine, a lot of oxygen will be left in the exhaust system. Therefore, the system will always stay in an oxygen-rich state, greatly reducing the reduction of NO_x. In order to ensure the exhaust treatment with a low conversion efficiency, a nitrogen oxide storage catalyst (NSC) assembly is needed at the rear end of the three-way catalyst device to perform secondary reduction. The NSC has the best catalytic activity in the operating temperature range of 250–500 °C. Generally, the operating temperature of a vehicle is higher during normal driving. When the gas adsorption capacity of the NSC is nearly saturated, the electronic control unit will adjust the engine to rich burn mode. In this state, a large amount of CO and HC generated in a short period of time is used to reduce the NOx adsorbed by the NSC to form a cyclic operation. The timing of this adjustment is determined by the NOx gas sensors installed before and after the NSC. When the vehicle is idling or stationary, the catalyst's operating temperature falls down. Now in order to ensure that the NSC will not adsorb excessive sulfide to cause poisoning, it is necessary to raise the operating temperature to more than 650 °C to activate the desulfurization effect. The main function of the NOx sensor now is to monitor the degree of sulfide attachment, and perform timely high-temperature desulfurization according to the monitoring results [23, 35].

Compared with gasoline vehicles, diesel vehicles have higher NOx emissions, so special exhaust treatment is required. Figure 1.5b is a schematic diagram of the exhaust treatment technology of diesel vehicles. The main functions of the front diesel oxidation catalyst (DOC) and diesel particulate filter (DPF) are to realize the oxidation evolution process of the gaseous pollutants CO and HC and soluble organic matter (SOM) in the exhaust of diesel engines and filter the particulate matter in it at the same time. As the NSC cannot remove NOx gas in an oxygen-rich atmosphere like the exhaust, a selective catalytic reduction (SCR) system is used for purification. A metering injection device is mainly used in this system to quantitatively inject

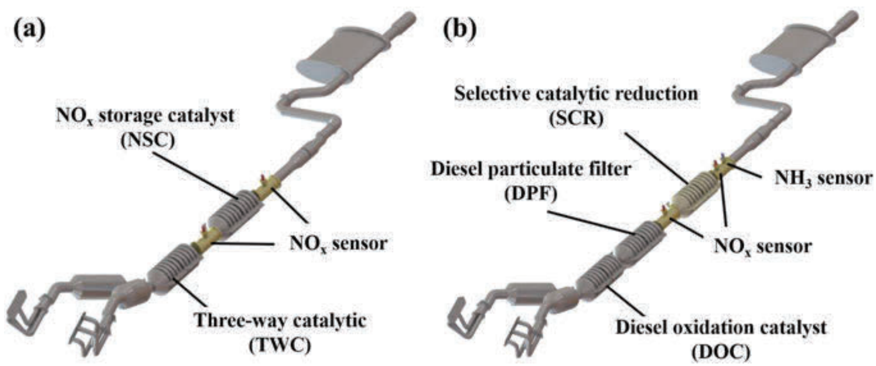

Fig. 1.5 **a** Lean combustion technology of gasoline vehicle exhaust purification system; **b** Diesel vehicle exhaust purification system

the urea aqueous solution. The urea will undergo a hydrolysis reaction in a high-temperature environment to generate ammonia gas (NH_3), and then the NH_3 will reduce the NO_x attached to the surface of the SCR catalyst to N_2. Excess NH_3 will also be reduced to N_2 and discharged together. Therefore, it is necessary to install nitrogen oxide gas sensors both before and after the SCR system to achieve real-time monitoring of gas concentration, and an additional NH_3 sensor is needed to control the injection amount of urea-reducing agent [36–38]. With the continuous raising of international automobile emission standards, in the future, according to China VI (Euro VI) emission standards, all diesel vehicles must also be equipped with an SCR assembly, and the emission limit of NO_x will be tightened by more than 42%. Therefore, the key role of NOx sensors has become self-evident.

On-board NO_x sensors play an indispensable part in the automobile exhaust emission treatment process. In order to ensure the accuracy and reliability of online measurements of sensors, the research and development of new sensors must enable them to adapt to the special and harsh working environment of automobile exhaust emission systems. The main requirements are listed below:

(1) Since most on-board gas sensors need to work in a high-temperature gaseous environment for a long time, the base material of the sensor needs to have good thermal conductivity and high-temperature resistance;
(2) The oxygen concentration in the exhaust is greatly affected by changes in the operating conditions of the vehicle. The dependence of the sensors on the oxygen concentration should be as low as possible, and it should be capable of operating normally in a wide range of oxygen concentrations;
(3) As the composition of gaseous pollutants in the exhaust is quite complex, the sensor materials need to have good selectivity for the gases to be measured;
(4) The sensors used should have good long-term stability, and the influence of humidity and temperature changes and thermal shock in the exhaust emission system on the test signal should be reduced to the minimum;
(5) The device structure should be as simple as possible to reduce cost and facilitate maintenance and replacement.

In summary, solid electrolyte gas sensors can better meet the special application requirements for on-board gas sensors from device performance to operating characteristics, and the gas sensors mainly composed of yttria-blended zirconia material, as the only commercial on-board exhaust detector, have been successfully applied in automobile exhaust treatment technology. However, the current exhaust detection sensors are mainly used for pollutant detection in the tube and catalyst control. Limited by the function, principle, and design method of the devices, outstanding technical problems such as high power consumption, complex structure, low sensitivity, and short life also exist. Based on theoretical analysis and research on solid electrolyte gas sensor-related technologies, new functions, new structures, and directions of performance improvement of devices are proposed in this paper to meet the needs of more comprehensive exhaust detection application development.