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Review

Development of NOx Emission and Electrochemical Detection in Atmosphere

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Abstract: Reactive NOx is one of the major air pollutants, which also plays a key role as greenhouse gas. Many research efforts have been devoted to not only detection of NOx in air but also abatement of NOx emission. The aim of this mini review is to provide a panoramic snapshot of the electrochemical analysis methods for the emission and detection of NOx in atmosphere, with special emphasis on NOx sensor. The electrochemical detecting mechanism and materials for fabricating electrochemical gas sensors are discussed and the prospects and challenges in this area are also evaluated. This work will serve as a useful source to inform the interested audience of the latest developments and applications in the field of NOx emission and electrochemical detection.

Keywords: NO_2; NO; gas sensor; nitrogen oxide emission; semiconductor; carbon; electrochemical

1. Introduction

As we all know, environmentally hazardous gases can be classified into oxidizing gases (such as CO_2 and Cl_2) and reducing gases (such as H_2S, CO, and C_2H_5OH)[1]. Among these gases, nitrogen oxide (NOx), which is a mixture of nitric oxide (NO) and nitrogen dioxide(NO_2), is well known to be one of the major air pollutants containing oxidizing gas (NO_2) and reducing gas (NO)[2-4]. NOx plays a key role not only in air pollution but also as greenhouse gas, because its multiple effects can sometimes lead to various harmful reactions, such as acidification, haze, summer photochemical smog and the increase of tropospheric ozone level[5-7]. Furthermore, high concentration of NOx in air can cause headaches, various diseases, respiratory distress, and lung tissue damage [8-10]. 53 ppb of NOx concentration in air is highly acute demanded by public the air security applications[2]. So, finding out the emission source of NOx and developing sensitive gas sensors for detecting NOx in the environment are important and critical to human health and ecological balance[11]. However, NOx cannot be avoided to generate in nature, due to it can be produced from the reaction of N_2 and O_2 during high-temperature combustion processes in everywhere, for example, car engines, power plants, industrial processes and even a thunderstorm[12]. So, many research efforts have been devoted to not only detection of NOx in air but also abatement of NOx emission.

Recently, several reviews focused on the development of NOx researches in environmental science. For example, in the aspect of NOx emission, Wilfried and Zbigniew reviewed the role of N-gases (N_2O, NOx, NH_3) in cost-effective strategies to reduce greenhouse gas emissions and air pollution in Europe[5]. They concluded that cost efficient abatement of greenhouse gases needed to include mitigation of nitrous oxide emissions[5]. In the aspect of NOx detection, scientists synthesized various functional materials to fabricate kinds of sensor for sensitively detecting NOx via different techniques[13]. Although NOx is important for both health care and ecological protection, there is no reports to review the development of NOx emission and detection in recent years.

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In this paper, we review 81 reports in recent five years from three aspects: source and approach of NOx emission, mechanism of NOx detection and arrays for NOx detection. Our investigation and conclusion can be essential information both for policy purposes and scientific researches.

2. Source and approach of NOx emission

As we all know, NOx can be generated from the reaction of N_2 and O_2 during high-temperature combustion processes. So, the sources and approaches of NOx emission are very common in our daily lives, which can be divided to two parts: anthropogenic emission and natural generation.

2.1. Anthropogenic emission

With the development of modern science and industry, anthropogenic emission of NOx happens everywhere, such as fuel combustion, industrial manufacture, power plants, vehicle exhaust, aviation emission and so on. Among these sources and approaches, fossil fuel combustion is identified as one of the main contributors to the escalation of NOx emission[14]. For example, China is the largest energy consumer in the world and have contributed amount of various emission during past three decades because of its rapid industrializations and urbanizations. Although China has plenty of strict environment policy in recent years, NO_x emission still keeps an increase trend all the way[15].

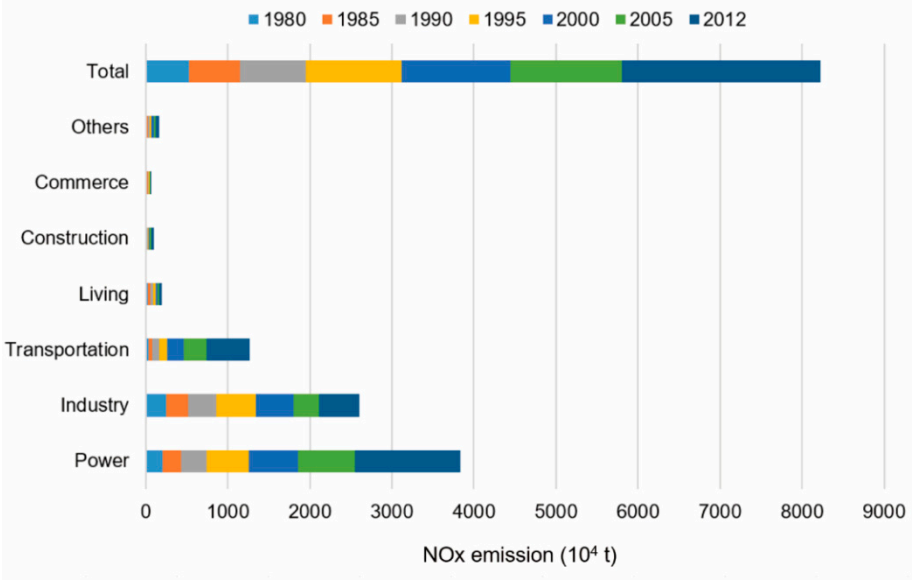

Figure 1 NOx emission of main sectors from 1980-2012 in China

Figure 1 illustrates the emissions and contributions of various sources. It can be found that the total NOx emission from various sources has increased from 446.45×10^4 t to 2499.72×10^4 t and increased 4.6 times from 1980 to 2012, keeping the rapid growth in recent 10 years because of energy consumption increase. Power (i.e. electricity) is the absolutely dominated contributor of NOx all the way in the past three decades, NOx emission from the electricity generating power plants has increased from 145.04×10^4 t to 1311.6×10^4 t. Industry is the second contributor after electricity. NOx emission from industry has increased from 206.75×10^4t to 479.46×10^4 t and increased about 1.31 times than that of 1980. Transportation is the fast-growing source, because NOx emission has increased from 39.44×10^4t to 576.31×10^4t and increased about 13.61 times than that of 1980. NOx emission from other sectors, including construction, residential and others, is little and takes up less than 5% of emission only.

2.2. Natural generation

Although anthropogenic emission is the main source and approach of NOx emission, natural generation of NOx cannot be also neglect. The production of NO_x by lightning represents a large uncertainty in the global NO_x budget with estimates varying by up to two orders of magnitude,

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although the range is likely within 2–20 Tg(N)/year[16]. In addition to naturally generate from lightning during a thunderstorm, NOx can be released from biological metabolism, environmental evolution and so on[12, 17]. For instance, NO is a ubiquitous bioactive signaling molecule. Biological NO is generated in the oxidation of L-arginine to L-citrulline, which is catalyzed by nitric oxide synthases. In general, this process participates in the regulation of a variety of physiological and pathological processes, such as in the control of vascular smooth muscle relaxation and vasodilation, platelet adhesion, regulation of the immune response and as a neurotransmitter in the brain[12].

3. Electrochemical detecting mechanism

The compounds NO and NO_2 are radicals. Many analytical methods for detecting NOx are mainly based on this chemical property. Among the various techniques for NOx detection, electrochemical detection systems received extensive concerns [18-21]. Compared to alternative techniques, such as spectrophotometry[12, 22], tunable diode laser absorption spectroscopy (TDLAS)[23-25], fluorescent probe[26-29], laser diode chemiluminescence based spectroscopy methods[30], and their combined arrays[31-33], electrochemical detection systems can provide the best sensitivity and simple supporting apparatus. For example, Stranzenbach and Saruhan reported impedance-metric detection of NO and NO_2 and yield the best results for detection of total NOx[34]. Furthermore, in these sensing approaches, electrochemical techniques are the most viable for a robust sensor, as they can provide high performance of selectivity, durability, and portability[13]. So, the electrochemical gas sensor is the most studied technique for NOx detection.

Electrochemical gas sensors, which are covered by two catalytic electrodes, consist in a ceramic ion-conducting electrolyte. In the detecting process, the general mechanism is that the response of the sensing materials is based on chemisorptions, i.e. the exchange of charge between absorbed gases and the materials surface. Therefore, the working principle of gas sensor is based on the measurement of gas adsorption and the change of conductivity caused by the surface reaction process[35]. In air, there are several different negatively charged oxygen adsorbates, such as O_2^-, O^- and O^{2-}, which are present in the metal oxide surface. The maximum sensor response observed in the experiments might be related with the following reactions [36]

$$O_2 + e^- \rightarrow O_2^-$$
$$O_2^- + e^- \rightarrow 2O^-$$

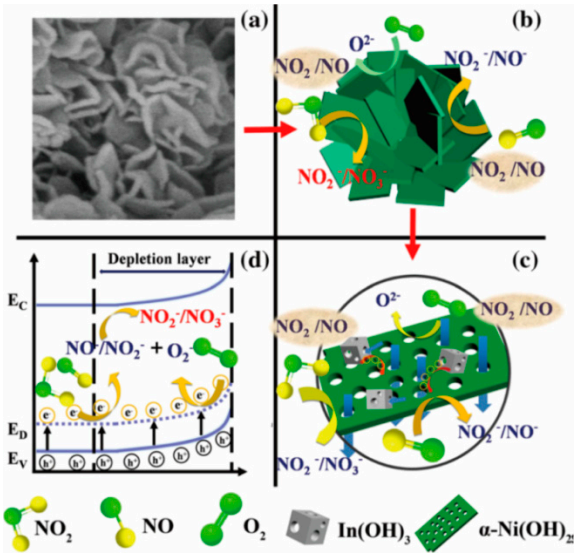

Figure 2 The gas conducting mechanism of the NOx sensor[2].

As detecting NOx in air, the adsorption of NO_2 on the semiconductors leads to NO_2^- and the adsorption of NO on the semiconductors leads to NO^-. Erisman and Fowler indicated that NO and NO2 react with the atmospheric ozone so that the quantities are transitive[37]. The process traps electrons from the conduction band or the donor level of the semiconductors, which finally leads to

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an increase of hole density. It finally results in a rapid decrease of resistances. NO_2 directly adsorbs onto the semiconductors and react with O^- and generate bidentate NO_3^- (s). NO also can adsorb onto the semiconductors and react with O^- and generate NO_2^-. As discussed above, the generation of oxygen adsorbates (O_2^-, O^- and O^{2-}) on the semiconductors surface occurs at high temperatures, and the gas sensing response increases drastically for the metal oxide based gas sensors with particle sizes below the Debye length[38].

So, as shown in Figure 2, there are four sensing processes. First, the oxygen from the air is chemisorbed on the semiconductors surface. Second, the chemisorbed O_2 can react with the electrons near the surface and transform into O_2^- at room temperature, thus decreasing the concentration of electrons near the surface and forming a depletion layer. Third, the generated oxygen adsorbent (O_2^-) at the surface of semiconductors, when exposed to NO or NO_2, the co-adsorption and mutual interaction between the gases and the adsorbed oxygen result in reduction at the surface and a decrease in the chemisorbed oxygen concentration[2]. The reactions are as follows:

$$NO_2 + e^- \rightarrow NO^-$$
$$NO_2 + e^- \rightarrow NO_2^-$$
$$NO + O^- \rightarrow NO_2^-$$
$$NO_2 + O^- \rightarrow NO_3^-$$

In addition to the detection of NOx in gaseous phase, the ability to detect NO in aqueous environments with robust and sensitive sensors would provide a means to monitor levels of dissolved NO emissions and to trace transient concentrations of NO in biomedical applications[13].

Furthermore, the interferences from other components presented in the sensing systems are not totally obviated for the systems with numerous components[39]. Do and Chen illustrated that the sensing properties of an amperometric NO gas sensor were significantly interfered by the presence of NO_2 and SO_2 in gas phase[40]. Xi et al. studied the effects of CO_2 and H_2O on the NO conversion performance and revealed that the presence of CO_2 and H_2O are beneficial to the NO reduction [41]. Moreover, the improvement by H_2O was stronger than that by CO_2. Friedberg and Hansen indicate that the electrochemical reduction of the nitrates when no propene is present is a surface reaction, whereas the propene enables further reduction of the bulk nitrate[42].

4. Electrochemical detection of NOx

Due to the harmfulness to people health and environment, it is important to develop NOx gas sensors to detect its concentrations as quickly and sensitively as possible in air. To realize this purpose, a wide variety materials with hierarchical structure provide more opportunities for exploring novel properties and superior electrochemical device performances more recently[11, 43-45], since this structure is often associated with a large surface area and fast gas diffusion, then leading to a better gas sensing properties in comparison with conventional nanocrystallites[2, 46-48]. At 2007, Fergus reviewed materials for high temperature electrochemical NOx gas sensor with a discussion on potentiometric sensors, impedancemetric and amperometric sensors[49]. To illustrate the methods for fabricating electrochemical NOx gas sensors more clearly, table 1 lists the recent reports on different methods of electrochemical detection of NOx.

Table 1. Different method designed for fabricating electrochemical NOx gas sensor.

Methods	Target gas	Detecting temperature/°C	References
Impedance spectroscopy	NO	300-400	[42]
Amperometric spectroscopy	NO_2	80-160	[50]
Voltammetry	NO	Room temperature	[51]
Pulsed corona discharge	NO	Room temperature	[52]

In order to in-depth analysis, herein, we reviewed recent reports on electrochemical detection of NOx based on different kinds of materials used for fabricating gas sensor.

4.1. Semiconductor oxides based gas sensor

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Semiconductor oxides are famous for their promising gas sensing properties. Tremendous efforts have been devoted to create highly responsive gas sensors based on n-type semiconductors by morphology control, doping and composites, such as ZnO, WO_3, CuO and SnO_2[53].

Zinc oxide (ZnO) has already been utilized in gas sensors for detecting toxic or hazardous gases[54-57]. To enhance the sensitivity and response time of NOx sensors, ZnO was always combined with other materials. Recently, Zhang et al. synthesized 3D graphene aerogel–ZnO (ZnO/GAs) composites via a simple solvothermal route. In this composite, the 3D graphene not only creates a conductive matrix that provides a rapid electron channels to ZnO to assist in sensing process, but also acts as a confined support to prevent agglomeration and growth of the ZnO spheres. Additionally, 3D interconnected macroporous channels provide a large specific surface area which greatly increases the gas contact area, ensuring that the NO_2 molecules easily penetrate the mesoporous. By incorporating 3D interconnected graphene with ZnO as conducting network, they realized rapid detection of NO_2 at room temperature[53].

As another n-type oxide semiconductor, WO_3 has also attracted great attention on account of its good response property to NOx gas[58-60]. To date, various WO_3 nanostructures, including nanoparticles[61], nanowires[62], nanorods[63], nanosheets[64], hollow spheres[65], hierarchical spheres[66], and their hybrid compounds with other nanomaterials[60, 67, 68] have been widely investigated to accomplish high response to ppm or sub-ppm-levels of NOx. Until now, the sensitivity of the NOx sensor based on WO_3 can be achieved to several tens ppb levels[45].

Although semiconducting metal oxides show good response property for NOx detection, tremendous efforts have been made to investigate the micro- or nano- composites to get higher response time and sensitivity, such as indium-doped SnO_2 nanoparticle-graphene nanohybrids[69], In_2O_3-xBaO(x=0.5-5 at.%)[70], SnO_2/3D graphene aerogel[71], ITO-SnO_2[72], Cr-doped CuO nanorods[73], and p-porous silicon(substrate)/ p-TeO_2 (nanowires)[74], etc.

4.2. Carbon materials based gas sensor

As we discussed above, metal oxides are well-known materials suitable for detecting a wide spectrum of gases with enough sensitivity. However, these materials are typically operated at temperatures that range between 200 and 800 °C. The reason is that the mobility of oxygen vacancies becomes appreciable and the mechanism of conduction becomes mixed ionic–electronic at higher temperatures. The diffusion of oxygen vacancies is known to be a mechanism responsible for long-term drift in metal oxide gas sensors [35, 36]. Therefore, a strategy to avoid long-term changes in their response could consist in operating the sensors at temperatures low enough so that appreciable structural variation never occurs, provided that gas reactions occur at a reasonable rate. So carbon micro- or nano- materials can be utilized to composite with other materials to realize this purpose.

Based on multiwall carbon nanotube(MWCNTs), Espinosa et al. prepared oxygen-functionalized MWCNTs composited with three different types of metal oxides (SnO_2, WO_3 and TiO_2) hybrid films[75]. They discovered that the addition of a small quantity of O_2-functionalized MWCNTs to metal oxides can significantly improve the detection capability of a metal oxide based sensor at low operating temperatures. They also concluded that there should be an optimum amount of carbon nanotubes to be added to each particular metal oxide in order to enhance responsiveness.

Graphene based sensors have the ability to detect even a single molecular species due to the tunable electrical conductivity caused by the chemical doping from the adsorbed molecules[76, 77]. Furthermore, due to its good electrical conductivity, it always acts as a conducting channel[69]. For example, because of the extraordinary electrical properties and ultra large specific surface area of graphene, Wang et al. fabricated more excellent gas sensing properties based on the In_2O_3-reduced graphene oxide (In_2O_3–rGO) nanocomposites. They prepared n-type In_2O_3-rGO nanocomposites via a facile hydrothermal method, which exhibited excellent selectivity, high response, and relatively short response/recovery time for the detection of NO_2 at room temperature.

4.3. Other materials based gas sensor

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α-$Ni(OH)_2$ that is composed of NiOH layers or nanosheets has a typical LDH structure. Generally, the layered double hydroxide-like (LDHs-like) structure has always shown a gallery pathway facilitating carrier diffusion/ transportation throughout the entire particle bulk. It is benefit for improving the sensing response time, and the charge carriers only need to diffuse a very short (subnanometer) distance before reaching the surface of the unit sheets in a LDHs-like structure. Therefore, LDHs-like structure materials might be a favorable material for gas detection. Wang et al. prepared a highly mesoporous hierarchical nanostructure $Ni(OH)_2$-$In(OH)_3$ composite assembled by nanosheets via one pot facile reflux method were reported. The gas sensor exhibited excellent sensing properties at ultralow detection limit of 9.7 ppb for detection of NOx and the response toward 97 ppm NOx could reach to 60 % and the response time was 1.2 s.

MoS_2, which is a graphene-like two-dimensional (2D) layered transition metal dichalcogenide material, has attracted enormous interest for its promising semiconducting characteristics and the advantageous band gap than graphene. Compared with graphene of zero band gap, the unique monolayer MoS_2 intriguingly shows a desirable and direct band gap of 1.90 eV. The intrinsic semiconductor nature and large surface-to-volume ratio make monolayer MoS_2 appropriate in chemical sensors. And recently, MoS_2 films based on transistor sensors have been experimentally demonstrated to show stable sensitivity towards NO gas molecules[78, 79].

Based on the above discussion, to illustrate the other materials used to fabricate the electrochemical NOx gas sensors more clearly, table 2 show the recent reports on electrochemical detection of NOx based on other different kinds of materials used for fabricating gas sensor.

Table 2. Other different kinds of materials used for fabricating electrochemical NOx gas sensor.

Type of materials	Representative materials	Target gas	Limit of detection (LOD)	References
Metal organic framework (MOF)	Cu-3(BTC)(2) (copper(II) benzene 1,3,5-tricarboxylate)	NO	5 ppb	[80]
Ionic liquid	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][$N(Tf)_2$])	NO_2	0.3 ppb	[50]
Enzyme	Copper nitrite reductase	NO_2	-	[18]
Metalloporphyrins	Hemin on a ZnO–PPy nanocomposite	NOx	0.8 μm	[81]

5. Conclusion and challenge

In this review, we investigated the source of NOx emission in China from 1980 to 2012, and the results indicated that NOx emission had increased 4.6 times during the past 32 years and had an apparent upward trend in recent years, because of rapid energy consumption industrial development and living improvement. Recent years have also witnessed tremendous advances towards the considerable interest to NOx detection. Of all the NOx detection research, hybrid films based on semiconductor oxides or carbon have been used as gas sensitive materials with improved sensitivity. These works indicate that the detection at ambient temperature of NOx can be highly improved with novel nanomaterial. More importantly, porous materials, especially mesoporous materials, which have been used as not only base substrate but also reactive materials, have emerged to show excellent adsorption and sensitivity towards NOx. However, although these types of devices are highly sensitive to low ppm levels, some limitations such as cross response issues to other gases and humidity levels and limited lifetimes along with the complications in the fabrication should keep on improving.

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