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# Application of $TiO_2$ to amperometric $NO_x$ sensors based on NASICON

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ABSTRACT

The work focused on improvement of the current response to NO and the reduction of response time of both NO and $NO_2$. By adding a layer of $TiO_2$ catalyst layer, the shortcoming of NO insensitivity of traditional NASICON based amperometric $NO_2$ sensor was solved. $TiO_2$ was known as an n-type semiconductor and a high-performance NO oxidation catalyst. We separately applied different types of $TiO_2$ (rutile and Degussa P25) on the device and compared the test results with the traditional type without a catalyst layer. The results showed that the $TiO_2$ attached device exhibited a significant improvement to NO response, and P25 was better than rutile $TiO_2$ on account of the higher activity of anatase $TiO_2$. In addition, $TiO_2$ also played a role of a semiconductor electrode, resulting in the increase of response to $NO_2$. The response time of NO and $NO_2$ was separately shrunk from 153 s, 70 s to 77 s, 43 s owing to the P25 layer. The current responses were found to be barely affected by the coexistence of $CO_2$.



## 1. Introduction

Nitrogen oxide ($NO_x$: NO and $NO_2$) exhaust from combustion devices and vehicles causes acid rain and photochemical smog, both of which have a major impact on the environment [1–2]. Analytical instruments based on chemical luminescence and the Saltzman method has been used to detect $NO_x$, but they are either too expensive or too large, or not sufficiently sensitive to low concentrations of $NO_x$. Therefore, researchers have recently been paying considerable attention to the development of compact, low-priced, and high-sensitivity solid-state sensors which can detect in-situ $NO_2$ (or NO) in real-time. $NO_x$ is emitted into the environment mostly as NO from combustion devices and automobile engines. In the atmosphere, some of the NO is gradually converted to $NO_2$ to establish a dynamic balance. The composition and concentration of NO and $NO_2$ in the air varies because of the differences in humidity, temperature, location, and weather conditions [3–9]. Thus, there is a need for a sensor capable of detecting $NO_2$ (or NO) in the parts-per-billion (ppb) range.

Yttria-stabilized zirconia (YSZ) [10–12] and sodium super ionic conductor (NASICON) [13–15] are solid-state electrolytes which are widely used in the field of gas sensors. Given that automobile emission standards continue to become stricter, mixed potential-type sensors based on YSZ have been the subject of intense research as such sensors can detect nitrogen dioxide in automobile exhaust [16–17]. Bosch in Germany and NGK in Japan have produced YSZ-based $NO_2$ sensors for automobile applications. However, these products were designed to monitor parts per million (ppm) concentrations of $NO_2$. They are unable to measure ppb levels. To monitor these lower concentrations of $NO_2$, NASICON-based amperometric solid-electrolyte sensors [18] have been shown to be advantageous. This kind of sensor was first proposed by Miura et al. in 1997 [19]. The device could detect sub-ppm levels of $NO_2$ but could not detect NO. To enable the simultaneous detection of the concentration of $NO_2$ and NO, Miura et al. applied a layer of $WO_3$ oxidation catalyst to convert the NO to $NO_2$ [20]. Therefore, they successfully developed a device capable of detecting both NO and $NO_2$.

$TiO_2$ is widely applied to heterogeneous photo-catalytic oxidation because of its excellent photo-catalytic effect, and because it is an excellent n-type semiconductor [21–22]. Degussa P25 (20% rutile and 80% anatase) is a standard material in the field of catalytic reactions [23]. P25 has large specific surface area and crystalline imperfections, giving it the ability to capture $O_2$ from the air [24–26]. For this study, we employed Degussa P25 as a catalyst for amperometric $NO_x$ sensors, which exhibit an excellent response to both NO and $NO_2$.

## 2. Experimental

### 2.1. Materials synthesis

NASICON was synthesized by means of a high-temperature solid-state method using $Na_2CO_3$, $SiO_2$, $ZrO_2$, and $NH_4H_2PO_4$ powders, which were commercially sourced from Sinopharm Chemical Reagent Co., Ltd. The substrates were weighed and mixed according to the mole ratio of the $Na_3Zr_2Si_2PO_{12}$, and then heated in air to 1125 °C for

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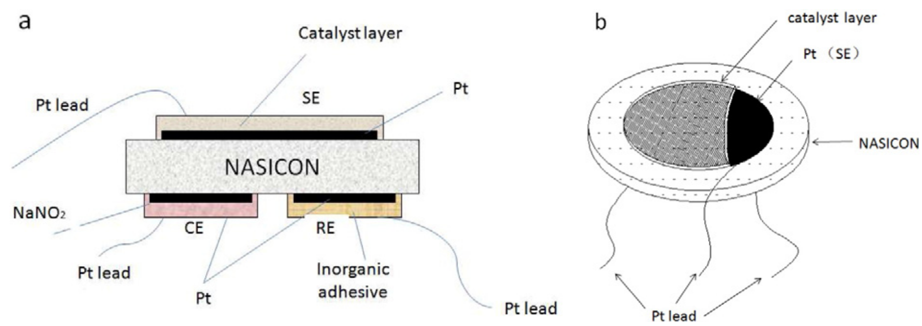


**Fig. 1.** Schematic view of sensor with $TiO_2$ oxidation layer: side view (a) and cross-sectional view (b).

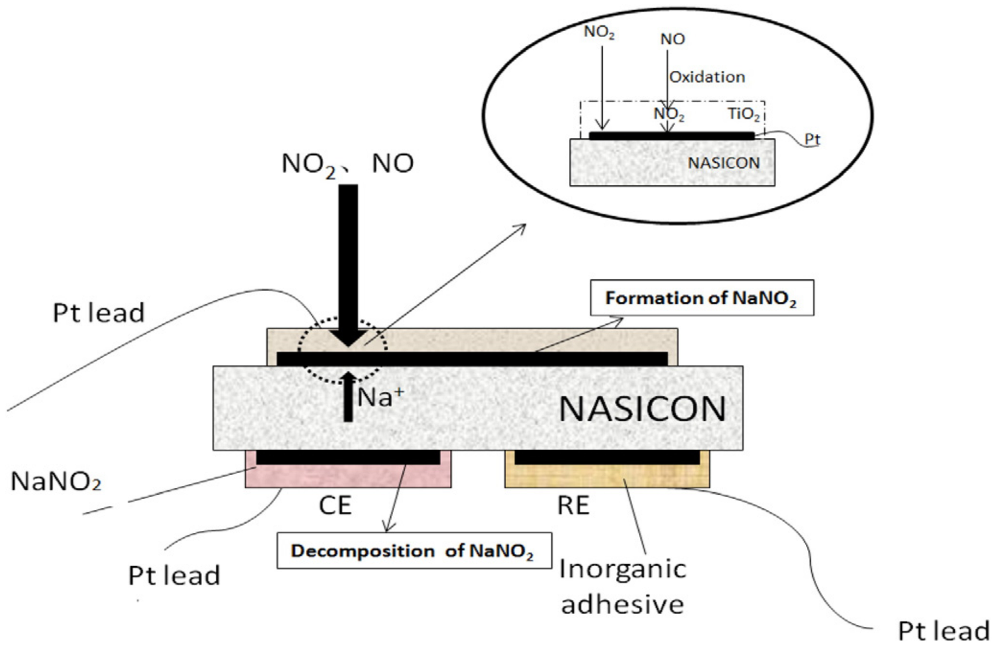


**Fig. 2.** Schematic sensing model of amperometric $NO_x$ sensor.

12 h. Owing to the volatility of the phosphorus, a 5 wt.% excess of $NH_4H_2PO_4$ was applied. The resulting material was then ground in a mortar to identify the NASICON phase, which was then further milled for 24 h with zirconia balls in anhydrous ethanol to produce a fine powder. A certain amount of powder was cold-isostatic pressed at 160 MPa into 12-mm diameter uniaxial pellets. Finally, NASICON disks were produced by sintering these pellets at 1175 °C for 12 h. The SE oxidation catalyst was obtained by mixing $TiO_2$ powder with terpineol and ethyl cellulose, then ball-milling for 1 h in a vibratory mill.

### 2.2. Fabrication of sensors

As shown in Fig. 1, the sensor was fabricated by screen-printing Pt paste (Pt 7850, Sino-platinum Metals Co., Ltd.) on both sides of the

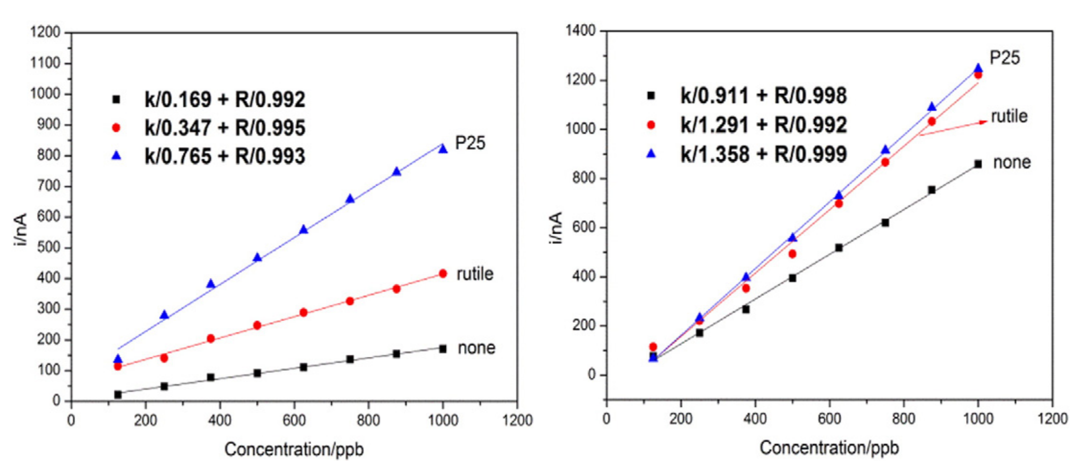


**Fig. 3.** Calibration curves for NO (a) and $NO_2$ (b) for three devices either with or without catalyst layers (−200 mV, 150 °C).