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Short communication

Mixed-potential type NO_x sensor using stabilized zirconia and MoO₃-In₂O₃ nanocomposites

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ABSTRACT

Highly sensitive mixed-potential-type NO₂ sensors based on yttria-stabilized zirconia (YSZ) electrolyte and In₂O₃-MoO₃ nanocomposite electrode were fabricated. The In₂O₃ doped with 2%, 5%, 10% MoO₃ and pure In₂O₃ were synthesized by sol-gel method, and these materials were applied to sensing electrode (SE). The effects of doping amount of MoO₃ on NO₂-sensing properties were investigated. It was found that the sensor using In₂O₃ sensing electrode doped with 5 wt% MoO₃ exhibited larger sensitivity to NO₂ in the range of 10–200 ppm than the other sensors using In₂O₃ doped with 0%, 2% and 10% MoO₃. The sensor using In₂O₃ sensing electrode doped with 5% MoO₃ showed high sensitivity (59 mV/decade), good stable and repeatable performance at elevated temperature. The electric potential difference (ΔV) of the sensor varies almost linearly with the NO₂ concentrations in the examined range of 10–200 ppm. Moreover, it is noteworthy that the influence of relative humidity on NO₂ sensitivities at 500 °C is little. Combined with the XRD analysis, XPS analysis, ICP analysis of the sensing materials and modified-polarization curves of the sensors, it could be speculated that the MoO₃, doped to the In₂O₃ sensing electrode, plays a significant role in sensing performance, and a possible mechanism for the improvement of NO₂-sensing properties was proposed here.

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1. Introduction

As the amount of vehicles increases fast and the modern industries develop rapidly, there is a strong concern about air pollution by the exhaust emission, which causes adverse results such as acid rains and photochemical smog in the environment ecosystem. In order to detect the NO_x emission from cars, high performance NO_x sensors are urgently demanded. Among the existing sensors, the mixed potential type NO_x sensors using yttria-stabilized zirconia (YSZ) captured people's attention and have been widely reported before [1–6].

The mixed potential type NO_x sensor using yttria stabilized zirconia (YSZ) and oxide electrode has been considered to be one of the best candidates for monitoring the exhaust emissions on account of its excellent durability, high temperature tolerance, chemical and mechanical stability, and low fabrication cost [7–14]. Many studies have focused on sensing electrode materials, device structure and sensing mechanism [15–34]. An army of metal oxides and mixed oxides, such as NiO [35], Cr₂O₃ [36], In₂O₃ [37] and

CdCrO₄ [38], have been investigated in YSZ-based potentiometric sensors in some early researches. The use of the sensing electrode consisting of these oxides was reported to exhibit good sensitivity to NO₂, since they were considered to act as an electrochemical catalyst for the decomposition of NO₂. On the other hand, the doping of noble metal or other oxides to the oxide electrodes is an effective method to improve the sensing property. Miura et al. doped WO₃ [39], MoO₃ and Au [40] to the sensing electrode to improve the response and selectivity of the sensors. Inspired by these works, we decide to dope different amount of MoO₃ to In₂O₃ for improving the sensing property of In₂O₃.

In this work, we synthesized MoO₃-In₂O₃ as sensing electrode for YSZ-based potentiometric sensors, and the NO₂ sensing property was tested. The effects of the doping amount of MoO₃ on the NO₂-sensing property were investigated.

2. Experimental

MoO₃-In₂O₃ nanocomposites were prepared from their nitrates by sol-gel method, which could provide homogeneous mixing MoO₃-In₂O₃ nanocomposites. In a typical synthesis process, In(NO₃)₃ and MoO₃ were dissolved in nitric acid. The molar ratio of In and

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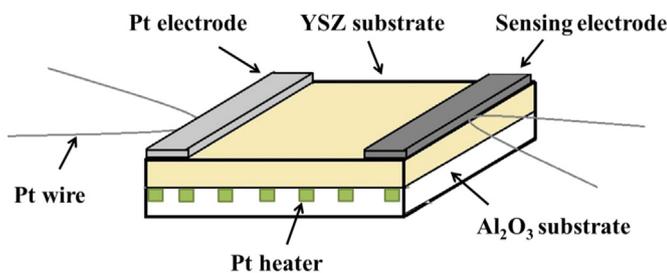


Fig. 1. Schematic structure of the sensor.

Mo was 9:1, 19:1 and 49:1, respectively. Then ethylene glycol was added to the above solution (the nitric acid/ethylene glycol volume proportion of 3:4). The resulting solution was maintained at 80 °C to form a polymeric gel. The polymeric gel was initially sintered at 350 °C for 2 h in the tubular furnace to remove the NO_3^- , and then sintered at 600 °C for 2 h to remove the polymer.

The schematic cross-sectional view of the planar sensor using YSZ and oxide electrode was shown in Fig. 1. The components, parameters and fabrication process of sensor as a traditional device structure was described in our previous paper [41]. The device was sintered at 550 °C in order to fit the sintering temperature (600 °C) of $\text{MoO}_3\text{-In}_2\text{O}_3$ nanocomposites.

The obtained powder was characterized by XRD, XPS and ICP measurement. XRD patterns were tested by Rigaku wide-angle X-ray diffractometer (D/max rA, using $\text{Cu K}\alpha$ radiation at wavelength=0.1541 nm). XPS (VG ESCA LAB MK II, Mg $\text{K}\alpha$, 10^{-7} Pa) was utilized to analyze the doped species in In_2O_3 . Moreover, A Perkin-Elmer Optima-3000 was used to detect the chemical composition of the samples by inductively coupled plasma analysis (ICP).

The NO_2 sensing characteristics were measured with increasing NO_2 concentration from 10 ppm to 200 ppm ($\text{NO}_2+21\text{ vol}\% \text{O}_2+\text{N}_2$ balanced) at the operating temperature of 550 °C. The electric potential difference between SE and RE was recorded by the digital electrometer (Digital Multimeter; Rigol Technologies, Inc., DM3054, China) as the testing signal.

The current-voltage (polarization) curves were measured by means of potentiodynamic method (Instrument corporation of Shanghai, China, CHI600 C) at a constant scan-rate of 3 mV/min using a two-electrode configuration in the base gas (21 vol% O_2+N_2 balance) and the sample gas (20 and 50 ppm $\text{NO}_2+21\text{ vol}\% \text{O}_2+\text{N}_2$ balance). The current axis of the anodic polarization curve was subtracted from that of the cathodic polarization curve at each potential so as to obtain the modified polarization curve.

3. Results and discussion

Fig. 2 shows the XRD patterns of samples In_2O_3 doped with 2%, 5% and 10% MoO_3 , respectively. It could be easily seen that all the diffraction peaks of each sample were indexed to In_2O_3 (JCPDS PDF # 65-3170). However, there is no obvious diffraction peak indexed to MoO_3 . One reason for this is the low molecular proportion of MoO_3 . In addition, the low sintering temperature might lead poor crystallinity of MoO_3 . For the above reasons, the MoO_3 showed no obvious diffraction peak.

In order to verify the existence of Mo^{6+} , XPS was applied for measuring the In_2O_3 powders doped with 2%, 5% and 10% MoO_3 , respectively, as shown in Fig. 3. As a result, it was found that the the strongest peak of $\text{Mo}3d_{3/2}$ appeared at 232.9 eV and 235.9 eV, which accords with that of MoO_3 and Mo^{6+} , respectively. Moreover, with the ICP technique, the amounts of In and Mo in the samples were determined, and the result was shown in Table 1. By calculation, the molecular proportion of MoO_3 is 2.3%, 5.2% and

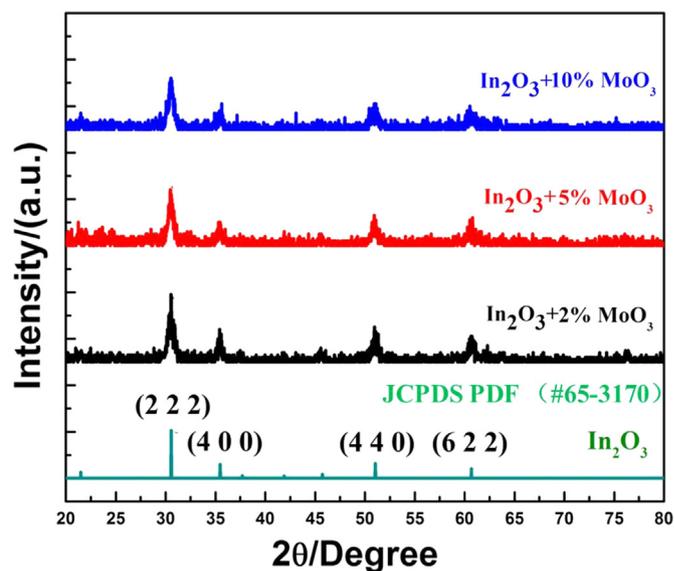


Fig. 2. XRD pattern of NiO powders doped with 2%, 5% and 10% MoO_3 , respectively.

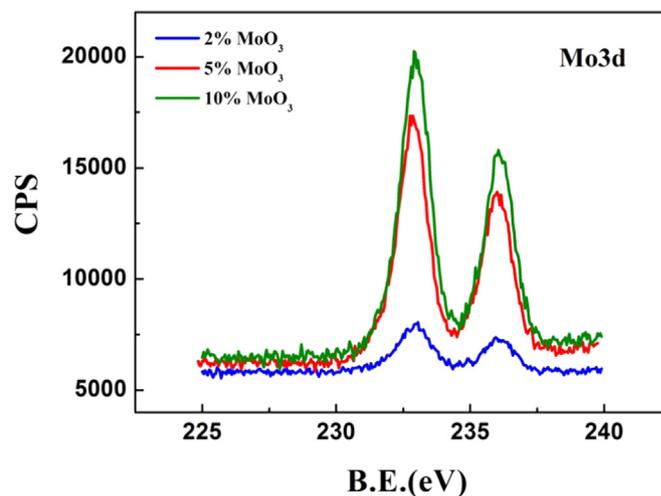


Fig. 3. XPS spectra of samples doped with 2%, 5% and 10% MoO_3 , respectively.

Table 1
Sample analysis of results (mg/L).

	Mean concentration (In)	Mean concentration (Mo)
Sample 1	134 mg/L	2.79 mg/L
Sample 2	140 mg/L	6.77 mg/L
Sample 3	118 mg/L	9.93 mg/L

8.8%, respectively, which is close to the proportion of the material input.

The response transients of the sensors attached with In_2O_3 doped with 2%, 5%, 10% MoO_3 and pure In_2O_3 to various NO_2 concentrations were exhibited in Fig. 4. The operating temperature for these sensors was set to 500 °C. It could be seen that the sensor attached with In_2O_3 doped with 5% MoO_3 as sensing electrode have highest electric potential difference (ΔV) (electric potential difference (V_{NO_2}) – electric potential difference (V_{air})) and the ΔV of this sensor to 100 ppm NO_2 is 101 mV, which is about 1.19, 1.51 and 1.35 times higher than those for the sensors doped with 2% MoO_3 , 10% MoO_3 and no doped, respectively.

The dependence of ΔV on the logarithm of NO_2 concentration

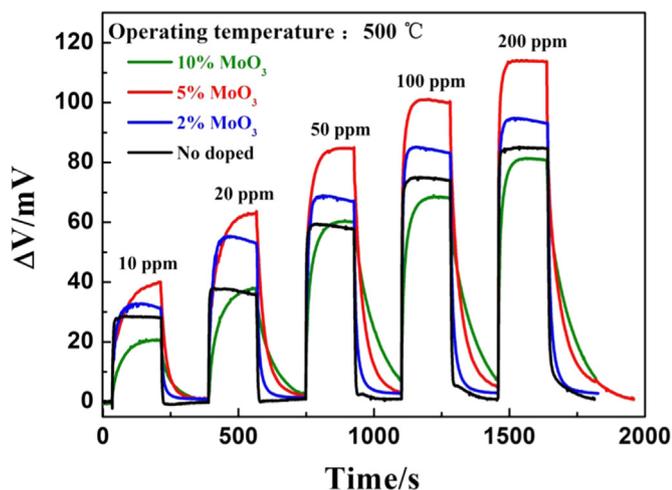


Fig. 4. Response transients of the sensors attached with In_2O_3 which was doped with 2%, 5%, 10% MoO_3 and pure In_2O_3 to various NO_2 concentrations in the range from 10 ppm to 200 ppm at 500 °C.

for sensor doped with 5% MoO_3 and no doped was also shown in Fig. 5a. The ΔV values are almost linear to the logarithm of NO_2 concentration. The slope is promoted from 47 mV/decade (for no doped ones) to 59 mV/decade (for doped with 5% MoO_3 ones). The continuous response-recovery transients (Fig. 5b) show the stable and repeatable performance of sensor doped with 5% MoO_3 . By calculation, the mean squared error of these continuous responses to 100 ppm NO_2 was 0.745 mV, which indicated that sensor doped

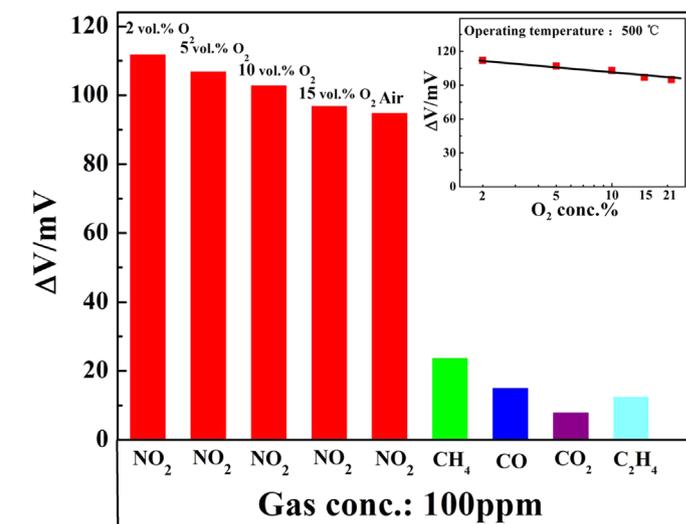
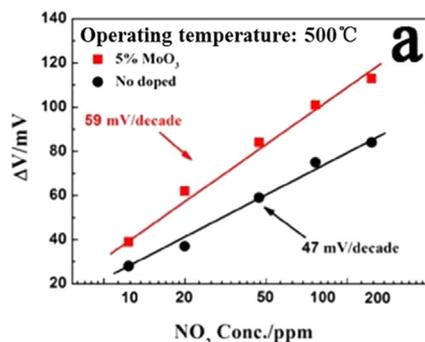


Fig. 6. Cross-sensitivities to various gases and dependence of the ΔV on the logarithm of O_2 concentrations for the sensor attached with 5% MoO_3 -SE at 500 °C.

with 5% MoO_3 showed superior repeatability. In addition, the response for the sensor attached with 5% MoO_3 -SE to 100 ppm NO_2 in the relative humidity range of 15–100% at 500 °C was measured and the results obtained are shown in Fig. 5c. It can be seen that the effect of relative humidity on the response of the sensor is small in the examined range.

Furthermore, the cross-sensitivities of the sensor doped with 5% MoO_3 is shown in Fig. 6. It can be observed that the sensor

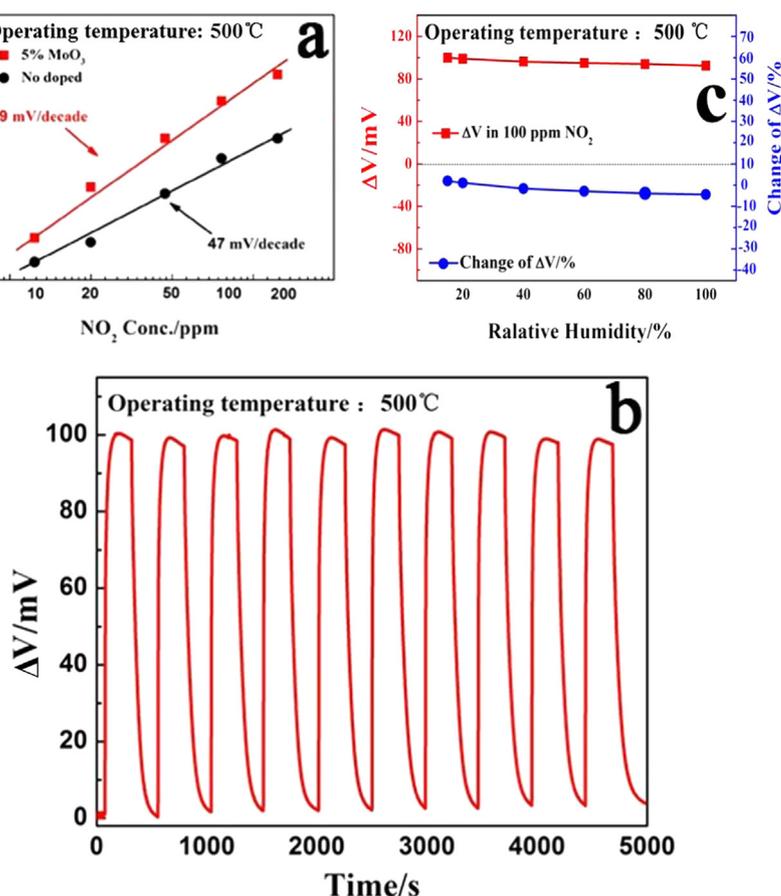


Fig. 5. (a) The dependence of the ΔV on the logarithm of NO_2 concentrations for sensor attached with In_2O_3 doped with 5% MoO_3 and pure In_2O_3 , (b) continuous response-recovery transients of sensor attached with In_2O_3 doped with 5% MoO_3 to 100 ppm NO_2 at 500 °C, (c) the response for the sensor attached with 5% MoO_3 -SE to 100 ppm NO_2 in the relative humidity range of 15–100% at 500 °C.

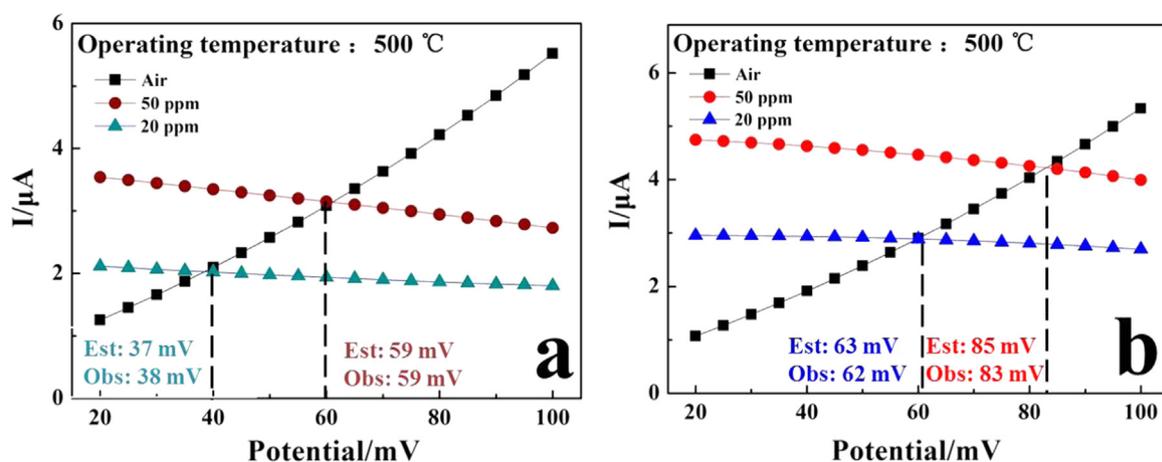


Fig. 7. Polarization curves recorded in air, in 20 and 50 ppm NO₂ at 500 °C for (a) sensors attached with pure In₂O₃ and (b) sensors attached with In₂O₃ doped with 5% MoO₃.

shows favorable selectivity to NO₂ among other gases which may exist in vehicle's exhaust. Responses of the sensor utilizing 5% MoO₃-SE to 100 ppm NO₂ at different concentrations of O₂ at 500 °C were measured and shown in Fig. 6. It can be seen that the response to 100 ppm NO₂ for the sensor decreased with the increasing of oxygen partial pressure, and the response was almost linear to the logarithm of O₂ concentrations. Therefore, this result could be regarded as an evidence for the mixed-potential potential theory, the reasons were discussed in the following.

The mechanism of mixed-potential-type zirconia-based NO₂ sensor has been reported in our earlier work [41,42]. This sensing mechanism could be described by the following electrochemical cells:

In air: O₂, In₂O₃/YSZ/Pt, O₂

In sample gas: O₂ + NO₂, In₂O₃/YSZ/Pt, NO₂ + O₂

In air, the electrons in the equilibrium transferred between electrodes and YSZ. At sensing electrode (SE) and reference electrode (RE), the equilibrium took place at different rates, inducing an electric potential difference (V_{air}) between SE and RE. For the case of the insensitivity of RE to NO₂, the potential of RE was fixed by constant O₂ concentration under the coexistence of NO₂ and O₂. On the other side, due to SE's high electrochemistry catalytic activity to NO₂, the potential of SE could be changed by NO₂ and a local cell was formed at the sensing electrode by the following electrochemical reactions:

Cathodic: NO₂ + 2e⁻ → NO + O₂²⁻(_{YSZ})

Anodic: 2O₂²⁻(_{YSZ}) → O₂ + 4e⁻

When the rates of the two electrochemical reactions were equal, the potential of SE was the so-called mixed-potential. The electric potential difference between SE and RE was V_{NO_2} . The response for this kind of sensor to NO₂ was depended on the rate of the cathodic and anodic electrochemistry reactions occurred on three-phase boundary (TPB). In this case, the sensor attached with In₂O₃ doped with 5% MoO₃ gave larger response to NO₂, implying that the In₂O₃ doped with 5% MoO₃ gave fairly high electrochemistry catalytic activity to the reaction occurred on TPB.

For further investigating the mechanism of the improvement of the electrochemistry catalytic activity, the modified polarization curves of the sensor attached with 5% MoO₃-In₂O₃ and pure In₂O₃ as sensing electrodes were shown in Fig. 7. Both of the sensors were measured in 20 ppm NO₂, 50 ppm NO₂ and air. The anodic polarization curve was obtained in air, and the cathodic polarization curve was obtained by subtracting the one in air from the one in NO₂+air. The mixed-potential can be estimated from the

intersection of the anodic and cathodic polarization curves. It can be seen that the sensor attached with 5% MoO₃-In₂O₃ as sensing electrode shows larger catalytic activity for the cathodic electrochemical reaction than the sensor attached with pure In₂O₃-SE, leading to a larger potential value. Hence, it is reasonable to believe that the response of the sensor to NO₂ is enhanced by the addition of MoO₃ to In₂O₃, due to the comparative increment on catalytic activity for the cathodic electrochemical reaction. Moreover, the mixed potentials estimated by intersecting the anodic polarization curve with the cathodic polarization curve were in good agreement with the measured ΔV values, which confirms a new evidence for that the present sensors are working based on the mixed-potential mechanism.

4. Conclusions

In this work, the MoO₃-In₂O₃ SE layer was formed on the YSZ plate. It is found that the sensor attached with 5% MoO₃-In₂O₃ as sensing electrode has the highest sensitivity among the sensors doped with 0%, 2% and 10% MoO₃ in molecular proportion. Further tests were taken with a concentration range of 10–200 ppm, and agree with the linear relationship between the response and logarithm of the concentration. The selectivity and repetitiveness tests have been carried out and the results are promising. The high sensitivity could be attributed to the increment on catalytic activity for the cathodic electrochemical reaction. These positive sensing performances indicate that the sensor using 5% MoO₃-In₂O₃ has potential application in car emission control system.

Acknowledgments

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