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A novel mixed potential NH_3 sensor based on TiO_2@WO_3 core–shell composite sensing electrode

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ABSTRACT

The TiO_2@WO_3 core-shell composite with mass ratio of core and shell4:1 was prepared by a hydrothermal synthesis method using sodium tungstate dehydrate, nitric acid and commercial TiO_2 powder as raw materials. A novel mixed potential NH_3 sensor was fabricated by using above-mentioned TiO_2@WO_3 as sensing electrode and $La_{10}Si_{5.5}Al_{0.5}O_{27}$ as solid electrolyte. X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM) were used to characterize the morphology and structure of the samples. The sensor response to NH_3 was examined at 400~550 °C. The experimental results indicated that the sensor based on TiO_2@WO_3 sensing electrode possessed greatly enhanced NH_3 sensing properties including higher and more stable response value and faster response rate compared to the sensor using TiO_2, WO_3 or TiO_2-WO_3 mixture sensing electrode under the same conditions. The responding potential values of the sensor with TiO_2@WO_3 sensing electrode exhibited a linear dependence on the logarithm of the NH_3 concentrations. The highest NH_3 sensitivity of 74.8 mV/decade was achieved at 450 °C. In the meantime, the sensors also showed well anti-interference capability to CH_4, CO_2 and H_2, but noticeable cross sensitivity toward NO_2 was observed. O_2 effect on responding signal could be calibrated by predetermining O_2 content.

1. Introduction

Recently, the diesel cars are substantially introduced because of their high fuel efficiency and low CO_2 emissions. However, compared to gasoline automobiles, the diesel cars produce higher emissions of NO_x because three-way catalysts for NO_x removal do not work in oxidizing atmosphere [1,2]. NO_x emissions result in serious environment problems, including photochemical smog and acid rain. Therefore, suitable advanced after-treatment technology is needed to reduce NO_x into N_2 in order to meet the upcoming more stringent emission standards. Selective Catalytic Reduction (SCR) using NH_3/urea has been recognized as an effective technology for the removal of NO_x emissions from heavy-duty diesel engine cars [3,4]. In SCR system, NH_3 as a reducing agent produced by injecting urea into a catalytic converter successfully reduces NO_x to N_2 over catalysts in a wide range of temperature [5,6]. The amount of urea injection must be strictly controlled in order that redundant NH_3 will not cause new air pollution [7]. So NH_3 concentration in down-stream needs monitoring continuously.

Several analytical techniques have been developed for detecting NH_3, including gas chromatography, ion chromatography and electrochemical methods. Compared to other approaches, electrochemical detection shows the advantages of simple experimental procedures, short response time, and feasibility for building portable sensors. Fortunately, the smart NH_3 sensor technology is available for vehicle applications [8]. Up to now, the main types of NH_3 sensors mostly investigated by researchers are semiconductor-type sensors [9,10] and solid electrolyte type sensors [11–28]. However, the semiconductor-type gas sensors for NH_3 detection in the presence of various interfering gases remain challenging [29]. In contrast, solid electrolyte type gas sensors have advantages of simple structure, good selectivity and high sensitivity, especially excellent stability under high temperature, showing a wide application prospect [30].

The solid electrolyte type NH_3 sensors include Nerstian type [11–13] and mixed potential type [14–28]. Nagai et al. developed Nernstian NH_3 sensors based on two types of auxiliary sensing electrode of $Pr_2(SO_4)_3{\cdot}(NH_4)_2SO_4$ or $0.7La_2O_2SO_4{-}0.3NH_4H_2PO_4$.

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The sensors showed superior sensing performances such as rapid, continuous and reproducible response to NH_3. But because of the stability problem of the auxiliary electrodes, the NH_3 sensors could not be utilized at high temperature [11–13]. The sensors based on ammonium hydrogermanate electrolyte could be used at a limited temperature range [14,15]. The mixed potential type NH_3 sensors based on solid electrolyte have been extensively reported by some groups. Häfele et al. proposed a mixed potential type sensor using zirconia electrolyte. The sensing signal of the sensor was a result of catalytic and adsorptive interactions between the gas and the sensing electrode [16]. Kida et al. fabricated a mixed potential sensors by depositing MoO_3 layer with a thickness of 200 nm on a YSZ tube, which showed considerably high sensitivity toward NH_3 (10–100 ppm) in air at 500 °C. The sensing signal ΔEMF of the sensor was still as high as 30 mV even to 10 ppm NH_3 [17]. Wang et al. presented various metals and metal oxides as sensing electrodes, including V_2O_5, MoO_3 and/or WO_3 that are doped with materials like Bi and with stabilizers to improve the long-term stability for ammonia sensors and declared that doped V_2O_5, $BiVO_4$, MoO_3 and WO_3 are effective for the sensing to NH_3 [18]. A YSZ-based mixed potential type NH_3 sensor attached with an Au-electrode covered with vanadia–tungstenia–titania-based SCR catalyst was fabricated and displayed good sensitivity and long-stability to NH_3 [20]. The planar sensors using Au or NiO/Au as the sensing electrode also exhibited good sensitivity to NH_3 at 600 and 700 °C [19,21,22]. Teranishi et al. demonstrated an approach to impart both proton conduction and solid acidity to the surface of YSZ by the surface treatment of YSZ with H_3PO_4, the sensor showed a remarkably sensitive and selective response to low concentrations (10-200 ppm) of NH_3 [23]. Satsuma et al. fabricated mixed potential sensors using YSZ as the solid electrolyte and a mixture of Au and various metal oxides (e.g., V_2O_5, Bi_2O_3 or MoO_3) as the sensing electrode. The effects of calcination temperature and acid-base properties of the metal oxides on the sensing properties were examined. The results showed that the acidity of metal oxides closely correlated with the NH_3 selectivity and the sensors with metal oxides calcined at nearly melting points displayed optimal properties [24]. Plashnitsa et al. prepared a planar sensor using a nano-structured Au sensing electrode and found that its performance was greatly modified by nano-SiO_2 particles. As a consequence, the sensor exhibited great selectivity to NH_3 ascribed to the strong acid–base interaction between nano-SiO_2 and gaseous NH_3 molecules [25]. The YSZ-based mixed potential sensors attached with $CoWO_4$ gave the fast response. The 90% response and recovery time to 100 ppm NH_3 were 3s and 1s, respectively. The sensor also exhibited outstanding selectivity to NH_3 against the interference gases [26]. The NH_3 sensor with In_2O_3 sensing electrode showed a excellent response to NH_3 but serious cross-sensitivity to NO_2. In order to minimize the interference from NO_2 of the above sensor, the $LaCoO_3$ reference electrode was used instead of Pt. The result showed that the interfering effect of 150 ppm NO_2 to the new sensor was reduced by five times [27]. Recently, the NH_3 sensor based on YSZ electrolyte and $Ni_3V_2O_8$ sensing electrode exhibited good sensitivity, repeatability, long-term stability, and selectivity against various interfering gases [28].

Obviously, the improvement of NH_3 sensor is mainly depended on the design of sensing electrodes. The sensitivity of the NH_3 sensors has room to be further enhanced by tuning chemical composition and microstructure of sensing electrode. Recently, core–shell nanostructure composites substituting single metal oxide for gas sensors have attracted great attention due to their unique properties, which give more versatile functions [31,32]. As far as we know, the core shell structure composite materials as the sensing electrode for solid electrolyte-based mixed potential type NH_3 sensors has received less attention and need further investigation

WO_3 and TiO_2 as common sensing materials had been employed for NH_3 detection in semiconductor sensors and showed excellent response properties [33,34]. In this work, we synthesized TiO_2@ WO_3 core shell composite via the hydrothermal method. A mixed potential type NH_3 sensor was prepared by using the TiO_2@ WO_3 as sensing electrode and $La_{10}Si_{5.5}Al_{0.5}O_{27}$ as electrolyte. The morphology and structure of the samples were characterized and the performance of the sensors was examined.

2. Experimental

2.1. Preparation and characterization of materials and sensor

The TiO_2@WO_3 core-shell composite was prepared from $Na_2WO_4·2H_2O$(AR), and TiO_2 (AR, 150 nm for diameter) by the hydrothermal process similar to what reported by Xu et al. [35]. Typically, Na_2WO_4 solution was first prepared by dissolving 1.000 g $Na_2WO_4·2H_2O$ into 40 ml deionized water and then 2.8115 g TiO_2 were added into the Na_2WO_4 solution under constant magnetic stirring to keep the final mass ratio of $TiO_2/WO_3 = 4{:}1$. Then 20 ml 5 M HNO_3 was dropped into the mixture with constant magnetic stirring. As a result, the white suspension was turned into yellow color, indicating that H_2WO_4 was formed. The suspension was transferred into a Teflon-lined autoclave and maintained at 180 °C for 24 h, and then cooled to room temperature. The resulting yellow precipitate was extracted by filtering and dried in vacuum at 80 °C for 12 h. After the precipitate was calcined in air at 500 °C for 2 h, TiO_2@WO_3 core-shell composite was obtained. For comparison purposes, WO_3 powder was prepared by the same method except for no TiO_2 addition. Finally, yellow WO_3 powder was obtained by calcination in air at 500 °C.Furthermore, the physical mixture of TiO_2 and WO_3 (TiO_2/WO_3) was obtained by mixing TiO_2 powder and the obtained WO_3 powder with mass ratio of $TiO_2{:}WO_3 = 4{:}1$.

$La_{10}Si_{5.5}Al_{0.5}O_{27}$ (LSAO) electrolyte with porous layer was prepared by solid state reaction method in combination with screen-printing technology. The analytical grade La_2O_3, Al_2O_3 and SiO_2 powders were used as raw materials. It was noted that La_2O_3 powder needed to be treated at 900 °C for 3 h before weighing in order to eliminate the lanthanum hydroxide or lanthanum hydroxyl present in La_2O_3 powder [36]. The stoichiometric

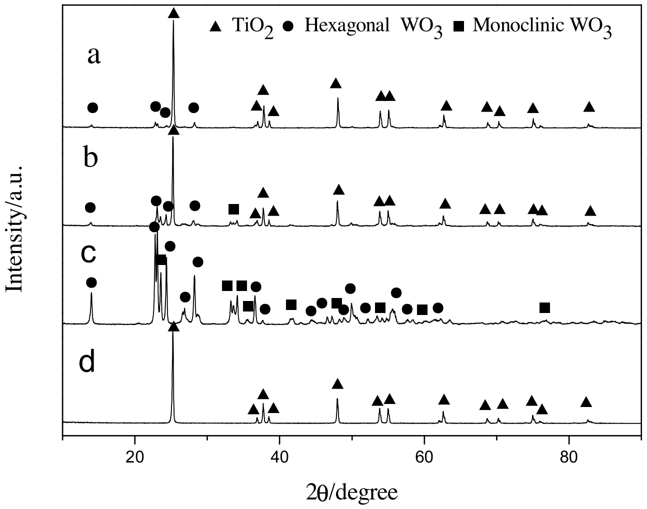

Fig. 1. XRD patterns of the prepared powder samples (a) TiO_2@WO_3, (b) TiO_2/WO_3, (c) WO_3, (d) TiO_2.