Enhanced selective performance of mixed potential ammonia gas sensor by Au nanoparticles decorated CeVO$_4$ sensing electrode

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ABSTRACT

A mixed-potential type sensor using a new sensing electrode (SE) of CeVO$_4$ is developed for NH$_3$ detection. Well-dispersed Au nanoparticles are introduced into the CeVO$_4$-SE by a simple immersion method to further improve the performances, especially the selectivity of the sensor. The sensor using the CeVO$_4$-SE exhibits well response-recovery characteristics to NH$_3$ at 500–600 °C. Good linear correlations between the response potential difference of sensor and the logarithm of NH$_3$ concentrations are obtained. The sensor displays the negligible cross-sensitivities to CH$_4$ and CO$_2$ except NO$_2$ present in the gas mixture. After the introduction of the Au nanoparticles into the CeVO$_4$-SE, the sensitivities of the sensor reach -78.9, -77.3 and -43.1 mV/decade at 500, 550 and 600 °C, respectively, which are much higher than those using the single CeVO$_4$-SE. More importantly, the cross-sensitivity of the sensor with CeVO4/Au-SE to NO$_2$ is almost eliminated. Introduction of 1000 ppm NO$_2$ in sample gas containing 300 ppm NH$_3$ causes a response ΔV from 67.2 (for CeVO$_4$-SE) to 4.6 mV (for CeVO$_4$/Au-SE). The complex-impedance measurements display that introduction of Au can promote electrochemical oxidation reaction of NH$_3$ to TPBs. The results of the temperature-programmed desorption indicate that the improvement of the selectivity is attributed to the effective depression of NO$_2$ adsorption in the sensing electrode by introduction of Au.

1. Introduction

NH$_3$ gas is an important chemical product as well as hazardous material and widely involved in various chemical industries. Therefore, the development of high performance NH$_3$ sensors is in a strong demand to monitor the level of harmful leakage or slip NH$_3$ [1]. Among the various sensors, the NH$_3$ sensors based on solid electrolyte have been attracted special attention because of the advantages of high sensitivity, fast response, and especially the good durability in the harsh conditions at elevated temperatures, such as the Selective Catalytic Reduction (SCR) process in the automotive industry [2–6].

Up to now, the solid electrolyte type ammonia sensors based on different principles have been investigated [6–8]. The mixed-potential type sensor is regarded as the most reliable and realistic sensing device for monitoring NH$_3$ concentration due to several attractive advantages, such as simple structure, portability, good stability, wide operating temperature range and multiple choices of sensing materials [9–11].

Noble metal (such as Au [12]), single metal oxide (such as V$_2$O$_5$ [13], MoO$_3$ [14], In$_2$O$_3$ [15]) and composite metal oxide (such as CoFe$_2$O$_4$ [16], CoWO$_4$ [17] and Ni$_3$V$_2$O$_8$ [18]) have been widely investigated as the sensing materials of the NH$_3$ sensors. Wang et al.

presented a series of SCR-active materials as the SE, which exhibited promising sensing performances in the exhaust of the engine test benches [19]. As one of the most effective SCR catalysts, Vanadate, such as CeVO$_4$, has good stability and excellent resistance to deactivation, low-cost, which is very propitious to the mixed-potential type NH$_3$ sensor used in elevated temperature [20–22].

In addition, the composite sensing electrodes have been identified as the effective means to improve the sensitivity and selectivity of the mixed-potential type NH$_3$ sensor. Miura et al. prepared a NiO layer on the Au-deposited YSZ electrolyte to form NiO/Au composite sensing electrode. It is speculated that the NiO layer may act as a catalyst for the oxidation of CO, NO and hydrocarbons, leading to good performance of anti-interference to the co-existence reducing gases [23]. Moos et al. used a porous commercial SCR catalyst (V$_2$O$_5$–WO$_3$–TiO$_2$ mixtures) to cover the Au sensing electrode for separating the sensing electrode functions of the conductivity, catalytic activity, electrochemical activity and long-term stability [24]. The sensing performances of NH$_3$, NO and NO$_2$ indicate that the cross-interference of NO is almost negligible, while a slight cross-sensitivity to NO$_2$ can be noticed. In literature [25], the nano-structured Au sensing electrode was modified by nano-SiO$_2$ particles, which can effectively improve the selectivity of the mixed-

potential type NH_3 sensor due to the acid–base interaction between SiO_2 and NH_3 molecules. In our previous work [26], the $TiO_2@WO_3$ core-shell composite sensing electrode was prepared for the mixed-potential type NH_3 sensor, the performances of which were much better than those of the sensor using TiO_2, WO_3 or TiO_2-WO_3 mixture sensing electrode. As shown above, most of the composite sensing electrodes are Au based electrodes modified by some oxides, which means the large dosage utilization of noble metal. Therefore, the composite sensing electrode with high sensing performance, low cost and easy preparation still needs to be investigated.

In this paper, $CeVO_4$ was used as the SE for the mixed-potential type NH_3 sensor. In order to further improve the performances of the sensor, the well-dispersed Au nanoparticles were introduced into the $CeVO_4$ sensing electrode by a simple immersion method, because Au nanoparticles are considered to possess excellent sensing performance and high selectivity to NH_3 [27]. The sensitivity and selectivity of the sensors were investigated in detail.

2. Experimental

2.1. Preparation of YSZ electrolyte

All the sensors in the experiment were fabricated using YSZ disks as the electrolyte. YSZ powder (8 mol% Y_2O_3-doped, purchased from SUZHOU UG.NANO MATERIAL CO., LTD) was mixed with 1 wt% polyvinyl butyral (PVB, purchased from Aladdin Industrial Corporation) binder by ball-milling in ethanol for 24 h. After drying, the powder mixture was ground in agate mortar and pressed into disks (13×13 mm, 1 mm thickness) at 20 MPa, and then sintered at 1600 °C in air for 6 h.

2.2. Preparation of sensing materials

$CeVO_4$ powders were prepared by the hydrothermal method. All the raw materials are of analytical grade (purchased from Aladdin Industrial Corporation). In a typical process, 2 mmol of $Ce(NO_3)_3 \cdot 6H_2O$ and 2 mmol of EDTA were dissolved in 80 mL aqueous ammonia (the volume ratio of $NH_3 \cdot H_2O{:}H_2O = 1{:}1$) under vigorously stirring. In another separated experiment, 2 mmol of NH_4VO_3 was dissolved in 10 mL hot deionized water. Then the above two solutions were mixed together and the pH of the solution was adjusted to approximate 9 by aqueous ammonia. This mixed solution was transferred into a Teflon-lined stainless steel autoclave for hydrothermal reaction at 180 °C for 24 h. the precipitates were collected by centrifugation and calcined at 500 °C for 3 h.

$CeVO_4$/Au sensing materials were prepared by the immersion and thermal decomposition method. The preparation process is shown in Fig. 1A. A certain amount of $CeVO_4$ powder was placed in the appropriate amount of deionized water to form a suspension under stirring. A certain amount of citric acid as the complexing agent was added into

Fig. 1. Schematic illustration of (A) the synthesis of the $CeVO_4$/Au composite sensing electrode and (B) the sensor.

the suspension. After stirring for half an hour, a certain amount of $HAuCl_4$ solution was added into the suspension under vigorous stirring. The final mass fraction of Au was adjusted to 5 wt%. After dried, the product was calcined at 800 °C for 3 h in a muffle furnace to form $CeVO_4$/Au composite.

2.3. Preparation of sensors

The sensors consist of $CeVO_4$ or $CeVO_4$/Au sensing electrode, Pt reference electrode and YSZ electrolyte. The sensing electrodes was prepared by screen-printing $CeVO_4$ or $CeVO_4$/Au paste onto one side of the YSZ electrolyte substrates, and then calcined at 800 °C for 3 h. Pt thin film was painted on the other side of the YSZ electrolyte as the reference electrode. After Pt wires were bonded by Pt paste onto the two sides of the sensor, the sensor sample was fired at 800 °C for 1 h. The schematic construction of the sensor was shown in Fig. 1B.

2.4. Characterization and sensing performance of sensors

The phase composition of the samples was determined by X-ray diffraction (XRD, D/MAX2500PC, Rigaku) operated at 45 kV and 40 mA using Cu Kα radiation. Field emission scanning electron microscopy (SEM, S-4800) was used to characterize the microstructure of the samples.

The sensing performance of the sensors was evaluated in a home-made test system at 500–600 °C. The sample gases with 0–400 ppm NH_3 were prepared by diluting 8040 ppm NH_3 standard gas by air. In experiment process, the total flow rate of the sample gas fed to the sensor was controlled at 200 cm^3/min. The current–voltage curves in the potential range of 0 to -100 mV were measured by the potentiodynamic method at a constant scan-rate of 5 mV/s in the base gas and the sample gas containing 100, 150, 200 or 300 ppm NH_3. The complex-impedance measurements of the sensor were carried out in the frequency range of 1 MHz to 0.1 Hz under open circuit voltage using AC amplitude of 50 mV. In this paper, all electrochemical measurements were carried out by Zahner IM6e electrochemical workstation.

The NO_2 temperature-programmed desorption (NO_2-TPD) was conducted on Quantachrome ChemBET Pulsar TPR/TPD Automated Chemisorption Analyzer, and NO_2 were monitored by a thermal conductivity detector (TCD). 100 mg of $CeVO_4$ or $CeVO_4$/Au sample was pre-treated with high-purity (99.99%) He (15 mL min^{-1}) for 30 min. After heating up to 40 °C, the sample was exposed to a flow of 500 ppm NO_2 with high-purity He as base gas for 40 min before the TPD tests. Finally, the temperature was raised to 600 °C at a rate of 10 °C min^{-1}.

3. Results and discussion

Fig. 2 shows the XRD pattern and SEM image of $CeVO_4$ powders prepared by the hydrothermal method. As shown in Fig. 2A, all the diffraction peaks of the calcined sample can be perfectly assigned to tetragonal $CeVO_4$ (JCPDS 01-079-1065). The products consist of relatively irregular particles which exhibit the agglomeration phenomena, as shown in Fig. 2B and C. The average size of the as-prepared $CeVO_4$ is approximately 50–100 nm.

The as-prepared $CeVO_4$ powders were screen-printed on the surface of YSZ electrolyte and then calcined at 800 °C as the SE of the NH_3 sensor. Fig. 3 shows the SEM images of surfaces and fractured cross-sections of the CeVO4 SE on YSZ substrate after screen-printing for 3 times. We can see from Fig. 3A that after the calcination process, the $CeVO_4$ particle size reaches micron-scale, which is much larger than the original $CeVO_4$. The SE layer presents a porous structure, which is beneficial for the diffusion of the gas into the three phase boundaries. Meanwhile, the SE layer is closely combined with dense YSZ substrate and the sensing electrode layer thickness is about 40 μm after screen-printing for 3 times, as shown in Fig. 3B.

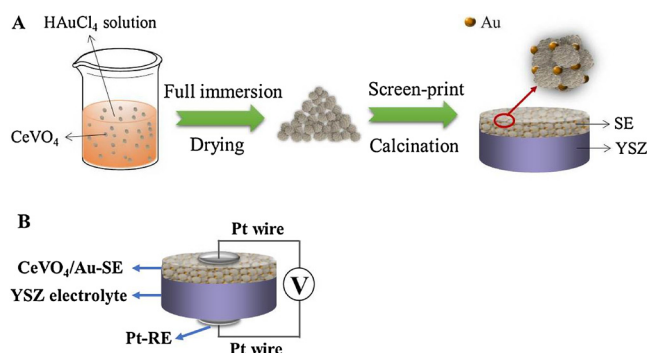Fig. 4A shows the response transients of the sensor based on $CeVO_4$-