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Highly sensitive gas sensor based on stabilized zirconia and $CdMoO_4$ sensing electrode for detection of acetone

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ABSTRACT

A highly sensitive mixed potential type gas sensor based on stabilized zirconia (YSZ) and $CdMoO_4$ sensing electrode (SE) was developed and used for detection of acetone at 625 °C. By comparing the sensing performance for different devices fabricated, the sensor utilizing $CdMoO_4$-SE exhibited the highest response value (−133.5 mV) to 100 ppm acetone at 625 °C, and even could achieve low detection limit of 500 ppb at 625 °C. The sensor attached with $CdMoO_4$-SE displayed high sensitivity of −84 mV/decade to acetone in the range of 5–300 ppm at 625 °C. The present device also showed good repeatability, selectivity to certain deleterious gases, moisture resistance and acceptable drifts in 10 days measured period at 625 °C, demonstrating great potential for practical application in acetone sensing detection. Additionally, the sensor involving mixed potential mechanism was proposed and further clarified by polarization curve.

1. Introduction

Air pollution associated with photochemical smog and haze-fog, characterized by high levels of ozone (O_3) and fine particulates (PM2.5), has emerged as one of the most severe environmental pollution issues owing to the process of accelerated urbanization and industrialization in China [1,2]. As key precursors of O_3 and PM2.5, volatile organic compounds (VOCs) are composed of hundreds of species, which are directly emitted into the atmosphere from a variety of natural and anthropogenic sources. The major anthropogenic emission sources of VOCs include vehicular exhaust, fuel evaporation, industrial processes, household products and solvent usage, etc. [3–5]. Among different of species, acetone as a kind of important material of VOC, not only cause serious environmental damage but also cause a loose to human body when long-term inhalation or contact. Although some expensive and cumbersome analysis detection technology has been widely used [6–8], but the new effective method and strategy characterized with cost-effective, portable and real-time detection are still expected. The miniaturized and robust mixed potential type solid-state electrochemical gas sensing device based on yttria-stabilized zirconia (YSZ) electrolyte has great potential in aspect of monitoring acetone owing to good stability as well as high sensitivity and selectivity.

So far, the mixed potential type gas sensor based on YSZ and metal oxides sensing electrode has been extensively investigated and developed to detect different kinds of poisonous and detrimental gases, such as NO_x [9–11], NH_3 [12–14], CO [15,16], H_2S [17] and VOCs [18–20]. Additionally, our group developed successively two kinds of YSZ-based mixed potential type gas sensor utilzing $Zn_3V_2O_8$-SE [21] and $NiNb_2O_6$-SE [22] to monitor acetone. The sensor attached with $Zn_3V_2O_8$-SE exhibited response value of −69 mV to 100 ppm acetone and sensitivity of −56 mV/decade to acetone concentration in the range of 10–400 ppm at 600 °C. The sensor using $NiNb_2O_6$-SE showed the sensitivity of −79 mV/decade to acetone in the concentration range of 5–500 ppm and the response value of the sensor to 100 ppm acetone was approximately −113 mV at 650 °C. Based on previous research result, some excellent works have been done. Nevertheless, further development of acetone sensor with higher sensitivity still faces great challenges in the process of practical application. According to mixed potential type model, however, the enhanced sensitivity was depended on the electrochemical catalytic activity of sensing electrode material to target gas at TPB. Therefore, investigation on new

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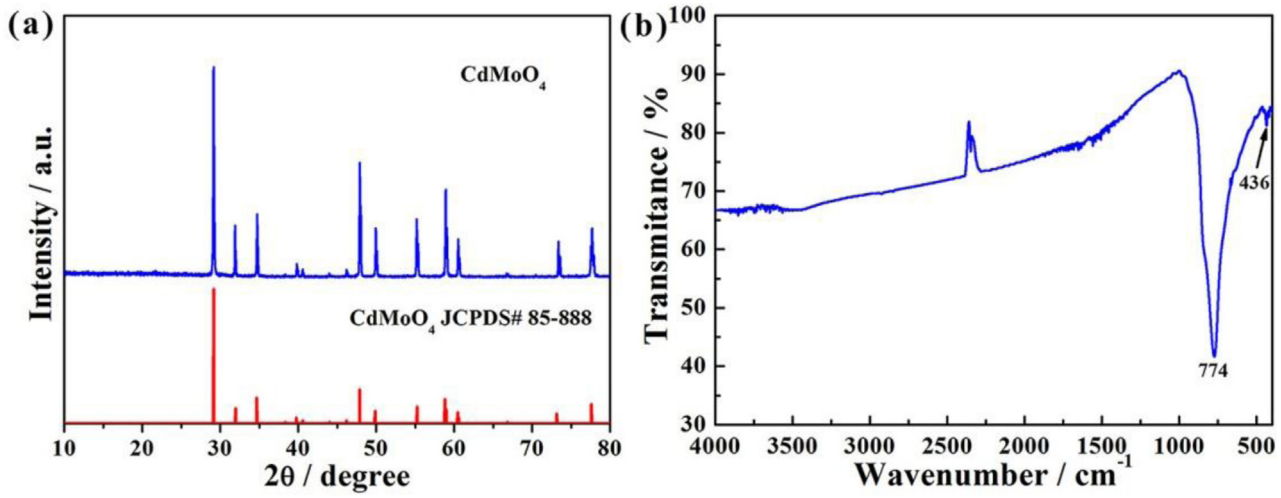

Fig. 1. (a) XRD pattern and (b) FT-IR spectrum of $CdMoO_4$ composite oxide material.

type sensing electrode material is an effective way to achieve highly sensitive acetone sensor.

In this work, three kinds of mixed potential type stabilized zirconia (YSZ)-based acetone sensors using new type sensing electrodes ($CdMoO_4$, $CoMoO_4$ and $NiMoO_4$) were developed successfully, aiming at fast and available detection of acetone in the atmosphere environment. For three sensing devices fabricated, the sensor attached with $CdMoO_4$-SE achieved the highest response value to 100 ppm acetone at 625 °C. Moreover, the corresponding sensing characteristics for the present sensor, such as sensitivity, selectivity, repeatability, moisture resisitance and stability, were studied in detail and sensing mechanism involving mixed potential was discussed.

2. Experimental

2.1. Preparation and characterization of $CdMoO_4$ sensing electrode material

Cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$) and Sodium Molybdat Dihydrat ($Na_2MoO_4{\cdot}2H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. $CdMoO_4$ nanoparticles were synthesized via a facile magnetic stirring method. Typically, 3 mmol $Na_2MoO_4{\cdot}2H_2O$ was dissolved in 20 mL of deionized water under magnetic stirring vigorously. Then, 10 mL of aqueous solution containing 3 mmol $Cd(NO_3)_2{\cdot}4H_2O$ was dropwise added into above solution and stirring for 3 h. The precipitate was collected via centrifugation and washed with deionized water and absolute ethanol several times, and dried at vacuum drying oven of 80 °C. Finally, the target product was sintered at 800 °C for 2 h using a muffle furnace. $MMoO_4$ (M: Ni, and Co) sensing materials were obtained with the same method according to above-described procedure, respectively.

The structural properties of the products were characterized with Rigaku wide- angle X-ray diffractometer (D/max rA, using Cu Kα radiation at wave length = 0.1541 nm) in the angular range of 10–80°. Fourier transform infrared spectroscopy (FTIR) of the $CdMoO_4$ sensing electrode material was recorded in the wavenumber range of 4000–400 cm^{-1} with a PE-400 spectrometer at room temperature. A technique of power pellets with KBr at a mass ratio of 1:200 was applied. Field-emission scanning electron microscopy (FESEM) measurements of surface morphology of the $CdMoO_4$-SE materials were performed using a JEOL JSM-7500F microscope with an accelerating voltage of 15 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB250 spectrometer equipped with an Al-Kα ray source.

2.2. Fabrication and measurement of gas sensor

The sensor was fabricated using the YSZ plate (8 mol% Y_2O_3-doped, 2 mm × 2 mm square, 0.2 mm thickness, provided by Tosoh Corp., Japan). A point-shaped and a narrow stripe-shaped Pt electrode (reference electrode, RE) were formed on two ends of the YSZ plate using a commercial Pt paste (Sino-platinum Metals Co., Ltd.). The various sensing electrode materials ($CdMoO_4$, $CoMoO_4$ and $NiMoO_4$) were mixed with a minimum quantity of deionized water, respectively. Then, the resultant paste was applied on the point-shaped Pt to form stripe-shaped sensing electrode (SE), and then the device was sintered at 800 °C for 2 h to gain good contact between the sensing electrode and electrolyte. The Pt heater printed on Al_2O_3 substrate was then fixed to the YSZ plate by the inorganic adhesive, which provided the required heating temperature for the sensor. The schematic of the fabricated sensor as shown in our previous papers [21,22], the YSZ as the electrolyte and the $MMoO_4$ (M:Cd, Ni and Co) and Pt are sensing electrode and reference electrode, respectively.

The gas sensing characteristics of the fabricated sensors were measured by a conventional static method. The detailed gas sensing measurement process was performed according to our previous work [23,24]. The electric potential difference (V) between the SE and the RE was measured with a digital electrometer (Rigol Technologies, Inc., DM3054, China) when the sensor was exposed to air or sample gas. The results obtained were recorded with a computer connected to the electrometer. The same times exposed to air and different concentrations of sample gases are kept consistent in each measurement concentration situation and the response signal exposed to sample gas at last minute as the calibration of potential value to assure the accuracy. The current–voltage (polarization) curves of the sensor were carried out via the potentiodynamic method (CHI650C, Instrument corporation of Shanghai, China) using a two-electrode configuration in the base gas (air) and the different concentrations of acetone gas (20, 50 and 100 ppm) at 625 °C. The sensing electrode connector of CHI600C Instrument linked with sensing electrode of the sensor, and the reference and counter electrodes simultaneously connected to the same reference electrode of the sensor. The complex impedance measurements of the sensors in air and 100 ppm of various deleterious gases were performed by using an impedance analyzer (Solartron, 1260 and