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A new and high response gas sensor for methanol using molecularly imprinted technique

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ABSTRACT

A new gas sensor with high response and selectivity was fabricated by using molecularly imprinted powders (MIPs) which provide special recognition sites to methanol. The MIPs were characterized by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectrometer (FT-IR) and transmission electron microscopy (TEM), respectively. The gas sensing properties of MIPs to methanol were investigated. The experimental results indicate that the sensors based on the MIPs show excellent gas sensing properties to methanol vapor, and the properties of the sensor with $x = 1{:}4$ (x = methanol:methyl acrylic acid, molar ratio) are the best. At the optimal operating temperature of 130 °C, the response of the sensor ($x = 1{:}4$) to 1 ppm methanol is 41, and the response and recovery times are 40 s and 50 s, respectively. Those good gas sensing properties make the MIPs the promising candidates for determining methanol vapor in air.

1. Introduction

Methanol is a highly volatile, flammable and colorless transparent liquid. As an important chemical raw material and clean liquid fuels, methanol has been widely applied in organic synthesis, antifreeze, dyes, paints, automobile, etc. [1,2]. However, methanol has strong toxicity, especially on the body's blood system and nervous system. Studies have also shown that methanol is potentially harmful for human optic nerve and retina [3]. And methanol is a less studied organic compound as compared to formaldehyde, ethanol, and toluene. So it is necessary to develop a fast and convenient method for determining methanol vapor at very low concentrations in air.

Now several methods have been developed to determine methanol vapor in air, such as gas chromatography [4], spectrophotometry [5], optoacoustic spectroscopy [6], infrared spectrometry [7] and gas sensor [8–12], etc. Among these methods, gas sensor is thought to be an effective means to determine the methanol vapor in air because it is small, cheap and easy to use [13].

Molecular imprinting is a useful approach in the area of molecular recognition and sensing, in which specific recognition sites are formed in a polymer matrix by polymerization in the presence of a print molecule or template [14]. The approach is receiving increasing attention due to its predetermination, selectivity, and practicability. Molecularly imprinted polymers have been successfully used in the analysis of many classes of molecules including herbicides [15], drugs [16], proteins and peptides [17,18], cholesterol [19]. Generally, molecularly imprinted polymers [20–22] are formed by copolymerizing functional and a large excess of cross-linker monomers in the presence of template molecules and a radical initiator. In this approach, the selected template molecule is first allowed to interact with one or more functional monomers to form host–guest complexes via covalent or non-covalent bond. Subsequently, the host–guest complexes are copolymerized with a large excess of cross-linker to give a rigid polymer. After polymerization, the template molecule is removed from the polymer and leaves cavities, which are complementary in arrangement and functionality to the template. And these cavities not only maintain the integrated shape and size to the template, but also the complimentary chemical functionalities of the target molecule are maintained.

In this paper, we prepared new gas sensors which involve special recognition sites for methanol based on the molecular imprinting technique, and the methanol gas sensing properties were investigated. Effects of template molecule to functional monomer ratio on their sensing properties for methanol vapor were examined.

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2. Experimental

2.1. Preparation of Ag-$LaFeO_3$-based sensing materials

1/99Ag-$LaFeO_3$ (Ag:La = 1:99, molar ratio) was prepared using sol–gel method combining with microwave chemical synthesis [23]. All the chemicals used are analytic grade reagents without further purifications from Tianjin Kermel Chemical Reagents Development Center. 10.00 mmol $Fe(NO_3)_3{\cdot}9H_2O$, 9.9 mmol $La(NO_3)_3{\cdot}6H_2O$ and 10.00 mmol citrate were dissolved in 100 mL distilled water as solution A. 0.1 mmol $AgNO_3$ were dissolved in 10 mL distilled water and then added to the solution A, and subsequently polyethylene glycol (PEG) was added. Finally, the mixed solution was kept stirring at 80 °C for 8 h, and then the solution was put in the microwave chemical device to synthesize for 2 h. The sol was dried at 150 °C and ground, and then heat treated at 800 °C for 2 h. Thus 1/99Ag-$LaFeO_3$ was obtained.

2.2. Preparation of MIPs

First, methyl acrylic acid (MAA) as functional monomer (4 mmol) was mixed with methanol (which acts as a template molecule) at various molar ratios (x = methanol:MAA = 0.1:4, 0.4:4, 0.8:4, 1:4, 4:4, 6:4, 8:4, 10:4) in a reaction vial. Then Ag-$LaFeO_3$ (10 mmol) as cross-linking agent and a small amount of azodiisobutyronitrile (AIBN) as radical initiator were added to the mixture. The solution was stirred for polymerization at 50 °C for 12 h under the protection of N_2. The obtained polymer containing the template molecule was ground and dried at 80 °C to remove the template molecule completely.

2.3. Fabrication of gas sensor

The prepared MIPs were subsequently printed onto an alumina tube with Au electrodes and platinum wires. We controlled both substrate heating and temperature via a resistor which was formed by using a Ni–Cr alloy wire crossing the alumina tube. And in order to improve their repeatability and stability, all the gas sensors were aged at an operating temperature of 150 °C for 170 h in air. The gas response was defined as the ratio of the electrical resistance in gas (R_g) to that in air (R_a) [24].

The gas-sensing properties of the sensors were examined in a chamber, in which the measured gas with defined concentration was obtained by evaporating certain volume of measured gases liquids. The conversion formula between the injected volume of the liquid (U) and defined concentration of the gas (C) as follows [25]:

$$U = \frac{(273 + T_K) \times V \times C \times 10^{-9} \times m}{(273 + T_B) \times 22.4 \times d \times p}$$

where U (ml) refers to the injected volume of the liquid, V (ml) is the volume of the test chamber, C (ppm) represents the measured gas with defined concentration, T_K (°C) is room temperature, T_B (°C) is the temperature of the test chamber, and m, d (g/cm) and p is the ml number, the density and the purity of the liquid, respectively. The electrical response of the sensors was measured with an automatic test system, controlled by a personal computer.

2.4. Characterization

The X-ray diffraction (XRD) patterns were obtained for the phase identification with a D/max23 diffractometer using Cu Kα radiation (λ = 1.54056 Å), where the diffracted X-ray intensities were recorded as a function of 2θ. The accelerating voltage was 35 kV and the applied current was 25 mA, and the sample was scanned from 10° to 90° (2θ) in steps of 0.02°. The infrared spectra were identified by FTS-40 infrared spectrometer (BIO-RAD Corporation, America), and the sample was scanned from 4000 cm^{-1} to 400 cm^{-1} with KBr pellet method. The particle morphology of the sample was tested by transmission electron microscope (TEM, JEM-2100).

3. Results and discussion

Gas-sensing properties of MIPs with x = 1:4 is better than those with x = 0.1:4, 0.4:4, 0.8:4, 4:4, 6:4, 8:4 and 10:4. In this paper, we mainly discuss the material with x = 1:4.

3.1. Characterization of MIPs

The XRD patterns of MIPs with different proportions (x = 0.1:4, 0.4:4, 0.8:4, 1:4, 4:4, 6:4, 8:4 and 10:4) are displayed in Fig. 1. The patterns indicate that the structure of MIPs is orthogonal perovskite, which include only one phase of $LaFeO_3$. This can be explained as follows: (1) the amount of Ag is so small that it can't be detected; (2) the template molecules and azodiisobutyronitrile (AIBN) are removed from MIPs and only parts of the groups of functional monomer are maintained in the MIPs. Fig. 2 shows the Raman spectroscopy of $LaFeO_3$ (a) and Ag-$LaFeO_3$ (b) in the range of 100–1500 cm^{-1}. In curve a, the peaks at 153, 283, 431, 822 and 1154 cm^{-1} are assigned to the one phonon scattering, while 1315 cm^{-1} are assigned to the two phonon scattering. The band at 631 cm^{-1} is related to disordered anion lattice of the $LaFeO_3$ crystallites [26]. Compared with curve a, the curve b shows some differences. First, a new peak appearing at 230 cm^{-1} compared with curve a, which is not appeared in the $LaFeO_3$ sample and it is correlated with local vibrations of Ag atoms in the $LaFeO_3$ host matrix [27]. Finally, another noteworthy difference is that the peak at 822 cm^{-1} has more tense than curve a, which may arise from the defects introduced by Ag doping. Thus, it can be concluded that these differences are correlated with Ag doping and prove the existence of Ag element.

Fig. 3 shows the TEM image of the MIPs (x = 1:4). It can be seen that the MIPs (x = 1:4) is composed of quadrate particles with almost uniform size and the particle sizes ranging from 30 to 40 nm. It also can be seen that the Ag-$LaFeO_3$ particles are coated with a layer of film around 4.98 nm, which are metal carbonyl complexes formed via coordination between functional monomer

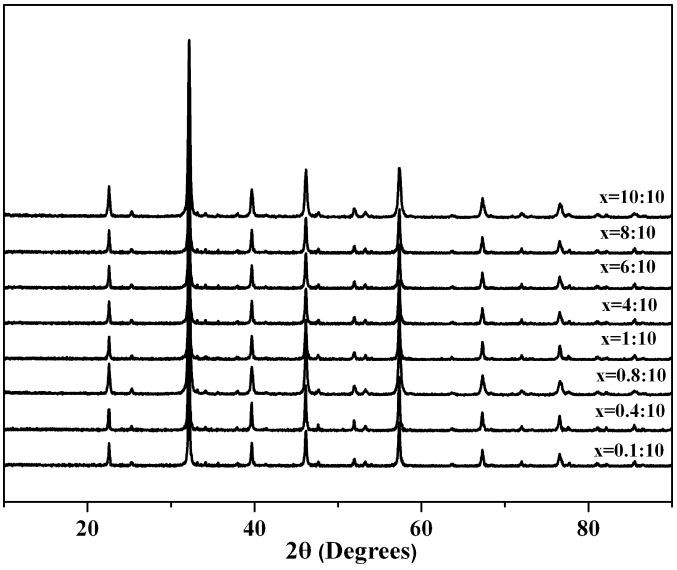

Fig. 1. XRD patterns of MIPs ($0.1{:}4 \le x \le 10{:}4$).