A sensor device with specific recognition sites for formaldehyde based on molecular imprinting technique

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Abstract. A novel gas sensor for the detection of formaldehyde was developed based on molecular imprinting technique (MIT) with formaldehyde as template. The structure of the molecular imprinting nanoparticles (MINs) is of orthogonal perovskite. The MINs with a good dispersion possess high surface-to-volume ratio. The particles are spherical and uniform, and then the MINs are printed onto an alumina tube to form a sensor device. At 92°C, the response to 1 ppm formaldehyde based on the sensor is 8, while the response to the other test gases is less than 3. The response time and recovery time are 40 s and 90 s, respectively.

1. Introduction

Formaldehyde is considered to be one of the most important industrial and commercial chemicals due to its chemical activity, high purity and relative cheapness [1-3]. It is well known that formaldehyde is classified as a mutagen and possible human carcinogen by both the US Environmental Protection Agency (EPA) and the World Health Organization (WHO) for its toxin, anaphylaxis and accumulation [4, 5]. Therefore, it is very necessary to monitor the concentration of formaldehyde in atmospheric environment quickly and accurately. Gas sensors based on semiconducting oxides are thought to be an effective means to monitor the gases because they are small, low cost and easy to use [6]. Peng et al. [7] developed a formaldehyde gas sensor comprising ZnO nanorods deposited on an ITO/glass substrate. The experimental results showed that the response of the nanorods to 110 ppm of formaldehyde was around 120 times higher with UV light irradiation than that without it. However, the minimal detection limit was just 1.8 ppm. Lee et al. [8] presented a gaseous formaldehyde sensor comprising a suspended silicon nitride microstructure with an integrated micro Pt heater, a thin-film NiO sensing layer, and Pt interdigitated electrodes. It was shown that the change in resistance varied linearly with the formaldehyde concentration in the range of 0–5 ppm. Lv et al. [9] developed a formaldehyde gas sensor incorporating a thin film of SnO₂-NiO nanometer polycrystalline composite deposited on a micro-hotplate (MHP). It was shown that the device was capable of detecting gaseous concentrations as low as 0.06 ppm given a MHP working temperature of 300°C. Moreover, the device...
showed good selectivity in the presence of common interferents such as alcohol, toluene, \(\alpha\)-pinene and acetone. Commonly used materials include ZnO [10-14], WO\(_3\) [15], hybrid materials [16], NiO [17-20] and so on.

Molecular imprinting is a means to prepare specific binding sites for given molecules in appropriate solid matrices. In this approach, the shape and functionality of a template can be transcribed onto microporous materials. The configuration of the functional groups in the template may be memorized within the matrix. Today, this field has become dominated by the use of organic polymeric materials for chromatographic separation, enzyme-mimicking catalysts, chemical sensors, and biosensors [21-26]. In this paper, MIT were used to prepare specific binding sites for small organic molecules (such as formaldehyde). The response to 1 ppm formaldehyde based on the as-prepared sensor is 8 at 92\(^\circ\)C, and the response to other test gases is less than 3 to the other test gases. The response time and recovery time are 40 s and 90 s, respectively.

2. **Experimental**

2.1. **Preparation of Ag-LaFeO\(_3\)**

Based on our previous experiments [27], the sample carbon nanotube (CNTs) modified Ag-LaFeO\(_3\) with CNTs: Ag-LaFeO\(_3\) = 0.75\% weight ratio (called Sample A, namely, Sample A = 0.75\%CNTs-Ag-LaFeO\(_3\), the same below) was found to be the most promising for the sensing properties to formaldehyde gas. In this study, Sample A was further modified based on molecular imprinting technique. To prepare MINs, formaldehyde is used as template, acrylamide (AM) as functional monomer, azodiisobutyronitrile (AIBN) as initiator and Sample A as crosslinker. The molar ratio of template to functional monomer was defined as \(x = \text{mol (formaldehyde)} : \text{mol (AM)} = 1:1, 1:2, 1:3 \text{ and } 1:4\). And 1.0 mmol formaldehyde mixed with \(x\) mmol AM was treated by ultrasonic concussion for 30 min, and stood for 8 h as Solution A. Then, 1.0 mmol AIBN was dissolved in 20 mL ethanol and mixed with Solution A and Sample A. The final mixture was treated by ultrasonic concussion for 30 min, stirred at 50\(^\circ\)C for 12 h with the protection of nitrogen and circulating water and then dried. The MINs were finally prepared.

2.2. **Fabrication of gas sensor**

The prepared MINs were further mixed with distilled water and ground to form a paste, which was subsequently printed onto an alumina tube. There are two Au electrodes placed at the both end sides of the tube. The length of the alumina tube is 4 mm and the diameter is 1.2 mm. In order to improve their stability and repeatability, the gas sensors were aged at 150\(^\circ\)C for 170 h in air. The gas response \(\beta\) was defined as the ratio of the electrical resistance in gas (\(R_g\)) to that in air (\(R_a\)).

2.3. **Characterization**

The X-ray diffraction (XRD) patterns were obtained for the phase identification with a D/max23 diffractometer using Cu K\(_{\alpha1}\) radiation (\(\lambda = 1.54056\) \(\text{Å}\)), where the diffracted X-ray intensities were recorded as a function of 2\(\theta\). The accelerating voltage was 35 kV and the applied current was 25 mA, and the sample was scanned from 10\(^\circ\) to 90\(^\circ\) (2\(\theta\)) in steps of 0.02\(^\circ\). The particle morphology of the sample was tested by transmission electron microscope (TEM, JEM-2100).

3. **Results and discussion**

Gas sensing properties of the MINs with \(x = 1:2\) is better than those with \(x = 1:1, 1:3\) and \(1:4\). This paper mainly discussed the MINs with \(x = 1:2\).

3.1. **Structure and micro-morphology characterization**

X-ray powder diffraction patterns of MINs are shown in figure 1. The patterns indicate that the structure of MINs is of orthogonal perovskite, which only includes one phase of LaFeO\(_3\), because the amount of Ag and CNTs is too small to be detected and the template, functional monomer and initiator
are removed, and only some functional groups on the crosslinker are left [28], which can't be detected either. The average crystallite size is estimated by means of Scherrer formula (\(D=k\lambda/\beta\cos\theta\), where \(\lambda\) is the wavelength of X-ray, \(\theta\) is the diffraction angle, and \(\beta\) is the true half-peak width.) through measuring the half-peak widths of the lines in the pattern. The average crystallite sizes for the MINs with \(x=1:1, 1:2, 1:3\) and \(1:4\) are about 29 nm, 29 nm, 31 nm and 33 nm, respectively.

![Figure 1. XRD patterns of MINs (1:4≤x≤1:1).](image)

TEM images for the MINs with \(x=1:2\) are shown in figure 2. For this sample, there are many spherically shaped particles which are uniform in size and well dispersed, and the particle size is in the range of 50 nm-90 nm. The specific surface area of the sample is big, which can adsorb formaldehyde more easily. Compared with the XRD results, TEM images reveal that there are various sizes of particles in the MINs. The big particles are composed of small crystallites.

![Figure 2. TEM images of the MINs with x=1:2.](image)
3.2. Gas sensing properties
Figure 3 depicts the relationship between response and operating temperature of MINs \((1:4 \leq x \leq 1:1)\) sensors to 1 ppm formaldehyde gas. As is shown, the sensor with \(x=1:2\) exhibits higher response to formaldehyde gas at the operating temperature between 40°C and 92°C, respectively. Taking the conception of sensing properties and cost conservation into consideration, the sensor with \(x=1:2\) is chosen as an optimal element to do further study.

![Figure 3](image)

**Figure 3.** Response-operating temperature curves for 1 ppm formaldehyde of MINs \((1:4 \leq x \leq 1:1)\).

To investigate the selectivity of MINs with \(x = 1:2\), the responses of formaldehyde, methanol, toluene, acetone and gasoline were tested for 1 ppm at different operating temperature respectively. It can be found that the sensor behaves well in selectivity to formaldehyde in figure 4. The best response to formaldehyde is 8 at 92°C. To the other test gases, the highest response is lower than 3.

![Figure 4](image)

**Figure 4.** Response-operating temperature curves for 1 ppm different tested gases of the sensor based on the MINs with \(x=1:2\).
Then, the relationship between response and formaldehyde concentration was investigated at 92°C as illustrated in figure 5. It can be seen that the response increasing for MINs with x = 1:2 is almost linear with the concentration of the formaldehyde at the operating temperature of 92°C. This is because there are a lot of formaldehyde-adsorbing vacancies on the surface of the sensor. When the concentration of test formaldehyde increases, the quantity of adsorbed formaldehyde on the surface of the sensor increases unceasingly, the electronics that the sensor has got also increase gradually. Thus, for p-type semiconductors, the resistance value of the sensor also rises, eventually resulting in the increase of the response. The detailed sensing mechanism is discussed in Section 3.3. At the same time, gas concentration ranges from 0.5 ppm to 3 ppm, the element response with formaldehyde concentration in a linear increase also shows that the sensor can be used for a continuous real-time monitoring at a lower concentration of formaldehyde [29].

Figure 5. Variation in response to different concentration of formaldehyde gas at an operating temperature of 92°C of the sensor based on the MINs with x=1:2.

Figure 6. Response-recovery time curve of the sensor based on the MINs with x=1:2 at 92°C.
The response/recovery time are two key quantities for a sensor, which are respectively defined as the time required to reach 90% response/recovery when gas is in/out [30]. Figure 6 presents response-recovery characteristic for the sensor based on MINs with $x=1:2$ operated at 92°C. The resistance of the sensor increases sharply when formaldehyde flow is in but returns to its original state when the gas flow is out although with some delay. When formaldehyde is in, the sensor begins to respond which takes 40 s, and when formaldehyde is out, the sensor begins to recover which takes 90 s. The response and recovery time are about 40 s and 90 s, respectively.

4. Conclusion
The selectivity of sensors can be improved by using molecular imprinting method theoretically. In this paper, the optimal amount of functional monomer-acrylamide is $x=1:2$. The structure of MINs is of orthogonal perovskite and the average grain size of the MINs with $x=1:2$ is about 29 nm. The MINs have good selectivity for low concentration formaldehyde. To 1 ppm formaldehyde, the sensitivity is 8 at the operating temperature 92°C, and the response time and recovery time are 40 s and 90 s, respectively. These finding may present a new feasible way for exploring LaFeO$_3$-based molecular imprinting sensing materials.

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