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# High Response and Selectivity Methanol Gas Sensor Using Molecular Imprinting Technique

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**Key words:** Methanol, Gas sensor, Molecularly imprinted powders (MIPs)

**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), transmission electron microscopy (TEM) and fourier transform infrared spectrometer (FT-IR), 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=6:10 (x= methyl acrylic acid: $LaFeO_3$, molar ratio) are the best. At the optimal operating temperature of 130℃, the response of the sensor (x=6:10) to 1 ppm methanol is 21, and the response and recovery times are 57 s and 67 s, respectively.

## Introduction

As an important chemical raw material and clean liquid fuels, methanol has been widely applied in organic synthesis, antifreeze, paints, dyes, 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 procreations and developments [3]. Therefore, to develop a fast and convenient method for determining methanol vapor at very low concentrations in air is of practical significance.

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 [4]. This approach is receiving increasing attention due to its predetermination, selectivity, and practicability. Based on these favorable properties, the molecularly imprinted polymers have been successfully used in solid-phase extraction [5], chromatography [6,7], by-products removal processes [8], pharmaceutical analysis [9], ligand-binding assays [10], immunoassays [11,12,13], and chiral separations [14,15]. Generally, molecularly imprinted polymers [16,17,18] 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. 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. Molecular imprinting can be approached in two ways, covalent and non-covalent, in which the non-covalent imprinting can be further grouped into hydrogen-bond imprinting and even weaker van der Waals imprinting. Covalent imprinting is achieved by a covalent interaction, which is easily cleavable, between a monomeric component of the polymer and the template.

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 functional monomer to cross-linking agent ratio on their sensing properties for methanol vapor were examined.

## Experimental

**Preparation of $LaFeO_3$-based Sensing Materials.** $LaFeO_3$ was prepared using sol-gel method. All the chemicals used are analytic grade reagents without further purifications from Tianjin Kermel Chemical Reagents Development Center. 10.00 mmol $Fe(NO_3)_3 \cdot 9H_2O$, 10 mmol $La(NO_3)_3 \cdot 6H_2O$ and 10.00 mmol citrate were dissolved in 100 mL distilled water and subsequently polyethylene glycol (PEG) was added. Finally, the mixed solution was kept stirring at 80℃ for 8 h. Thus $LaFeO_3$ sol was obtained.

**Preparation of MIPs.** First, methyl acrylic acid (MAA) as functional monomer was mixed with methanol (which acts as a template molecule) in a reaction vial. Then $LaFeO_3$ sol (10 mmol) as cross-linking agent was mixed with MAA at various molar ratios (x= MAA: $LaFeO_3$=1:10, 4:10, 5:10, 6:10, 7:10, 8:10, 9:10, 10:10) and a small amount of azodiisobutyronitrile (AIBN) as radical initiator were added to the mixture. The solution was stirred for polymerization at 50℃ for 12 h under the protection of $N_2$. The obtained polymer containing the template molecule was ground and dried at 80℃ to remove the template molecule completely.

**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℃ 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 ($R_a$) [19].

**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 $cm^{-1}$ - 400 $cm^{-1}$ with KBr pellet method. The particle morphology of the sample was tested by transmission electron microscope (TEM, JEM-2100).

## Results and discussion

Gas-sensing properties of MIPs with x=6:10 is better than those with x=1:10, 4:10, 5:10, 7:10, 8:10, 9:10 and 10:10. In this paper, we mainly discuss the material with x=6:10.

**Characterization of MIPs.** The XRD patterns of MIPs with different proportions (x=1:10, 4:10, 5:10, 6:10, 7:10, 8:10, 9:10 and 10:10) 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 because that 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 TEM image of the MIPs (x=6:10). It can be seen that the MIPs (x=6:10) is composed of quadrate particles with almost uniform size and the particle sizes ranging from 50 to 60 nm.

Fig. 3 shows the FT-IR spectroscopy of $LaFeO_3$ (a), MIPs (x=6:10) (b), MAA (c) in the range of 400-4000 $cm^{-1}$. In curve a, the broad peak occurring at 3490 $cm^{-1}$ is attributed to the stretching vibration of O-H [20,21] of $H_2O$ in air, and the other peaks at 557 $cm^{-1}$ and 2356 $cm^{-1}$ are corresponding to Fe-O vibrations and the gas phase carbon dioxide vibrations, respectively. The peaks at 1412 $cm^{-1}$ and 1587 $cm^{-1}$ represent the La-O vibrations. In curve b, new peaks appearing at 1635 $cm^{-1}$ and 2917 $cm^{-1}$ compared with curve a, which are attributed to the stretching vibration of C=O in carboxylate anion and O-H in carboxylic acid, respectively. Compared curves b and c, the disappearance of the relatively strong peaks of C-O (1210 $cm^{-1}$) stretching vibration in carboxylic acid and C=O (1710 $cm^{-1}$) stretching vibration in carboxylic acid suggests the successful interaction between $LaFeO_3$ and MAA, and the interaction should be ascribed to the coordination between carbonyl groups in MAA and La in $LaFeO_3$, which results in the formation of metal carbonyl complexes [22,23].

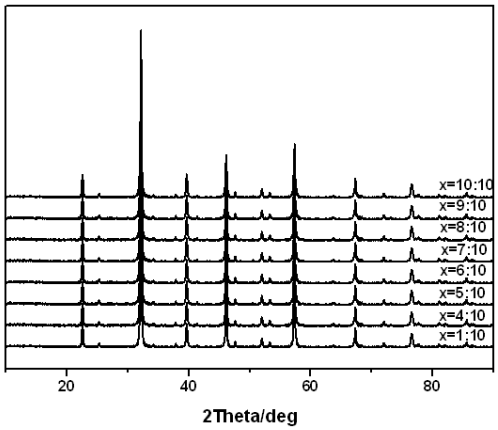


Fig. 1 XRD patterns of MIPs (1:10≤x≤10:10)

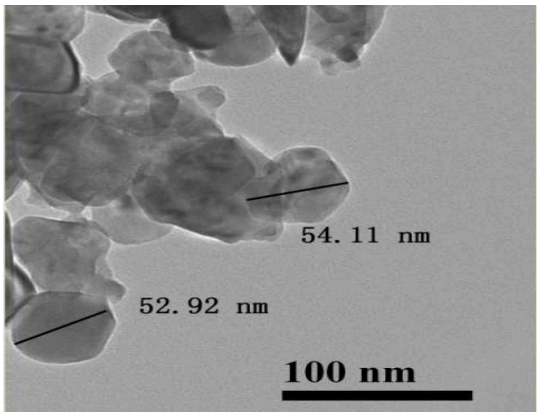


Fig. 2 TEM image of MIPs (x=6:10)

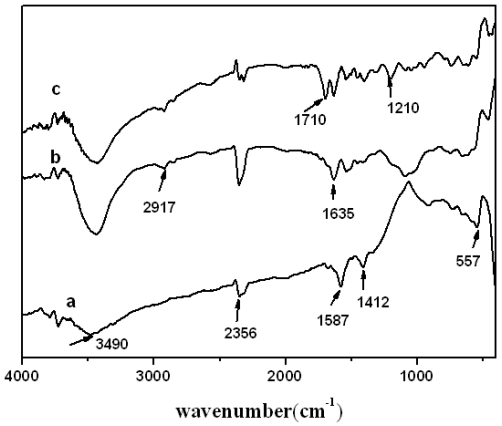


Fig. 3 FT-IR spectroscopy of (a) $LaFeO_3$, (b) MIPs (x=6:10) and (c) MAA

**Gas Sensing Properties.** The response and selectivity of the molecular imprinting sensor is mainly determined by the recognition sites. MIPs usually contain specific recognition sites that can recognize the target molecule and so exhibit a high response and selectivity for reabsorbing the target molecule [24]. In order to study the effect of the concentration of the functional monomer on the response and selectivity, the performance of molecular imprinting sensors prepared with different ratios of functional monomer (1:10 ≤x≤ 10:10) was studied. The results (Fig. 4) indicate that the sensor with x=6:10 exhibit higher response to methanol gas at the operating temperature between 50℃ and 170℃. If the ratio of the MAA is lower (1:10 ≤x≤ 5:10), the interaction between the template molecule (methanol) and functional monomer (MAA) is weakly, and specific recognition sites in the MIPs for the methanol are reduced, which result in bad gas sensing properties. On the contrary, if the ratio of the MAA is higher, MAA molecules will form polymers via auto-polymerization, which lead to poor gas sensing properties. So the optimal ratio is x=6:10.

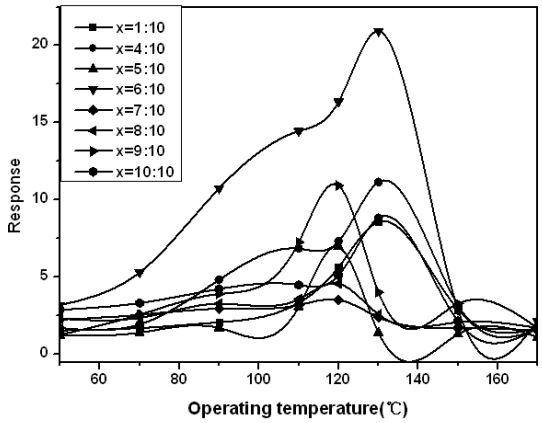


Fig. 4 Response-operating temperature curves for 1 ppm methanol of MIPs (1:10≤x≤10:10) sensors

The correlation between gas response and operating temperature of the sensor based on MIPs (x=6:10) to different test gases is shown in Fig. 5. The sensor was exposed in 1 ppm test gases which include ethanol, formaldehyde, toluene, acetone, ammonia and gasoline. It can be seen that this sensor exhibits the highest response (21) to methanol at the operating temperature of 130℃ while shows a lower response (≤7) to the other test gases. It also clarifies that the sensor has good selectivity to methanol.

The relationship between response and methanol concentration was investigated at 130℃ as illustrated in Fig. 6. It can be seen that the response increasing for the sensor based on MIPs (x=6:10) is near linear with the different concentration of the methanol at the operating temperature of 130℃. At the same time, the sensor response increases nearly linear with gas concentration ranging from 2 ppm to 20 ppm indicates that the sensor can be used as a continuous real-time monitoring at lower concentration of methanol.

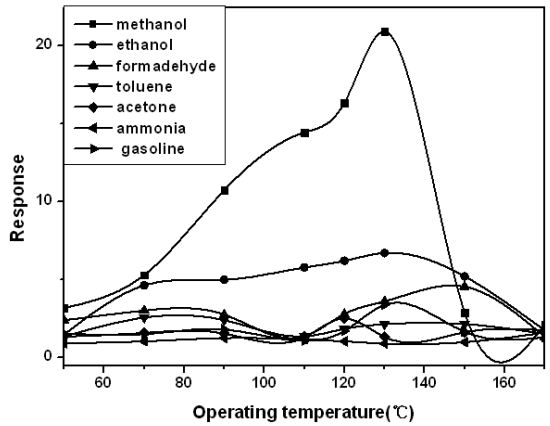


Fig. 5 Response-operating temperature curves for 1ppm different tested gases of MIPs (x=6:10) sensor

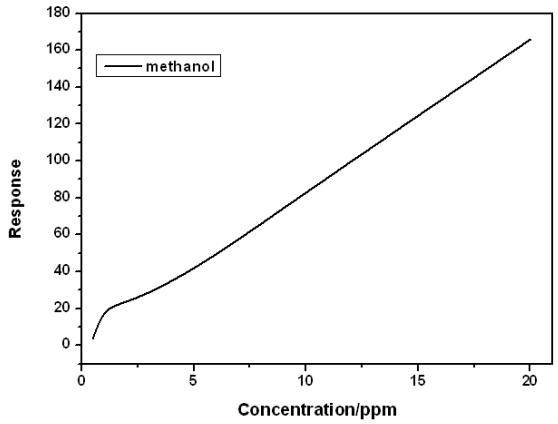


Fig. 6 Variation in response to different concentration of methanol gas at an operating temperature of 130℃

The response-recovery time were observed with the sensor based on MIPs (x=6:10) at the operating temperature of 130℃. The response changes at the different methanol gas concentrations (0.5-20 ppm) are shown in Fig.7. The response time (defined as the time required to reach 90% of the equilibrium after exposure of the sensor surface to a test gas) and recovery time (defined as the time needed to return to 10% above the original resistance in air after stopping the flow of the test gas) are 57 s and 67 s, respectively.

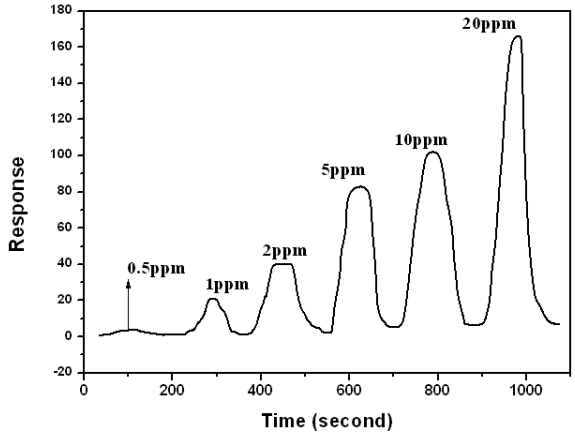


Fig. 7 Response and recovery times of the sensor (x=6:10) to methanol with increasing concentrations operated at an operating temperature of 130℃

## Conclusion

In this study, a new gas sensor that provides recognition sites to methanol with a high response and selectivity was fabricated by using the molecularly imprinted powders (MIPs). The optimal ratio is x=6:10, the average grain size of the MIPs (x=6:10) is about 53 nm. The MIPs (x=6:10) has high response and good selectivity for low concentration methanol. The sensor response based on x=6:10 is 21 to 1 ppm methanol at the operating temperature of 130℃, and the response and recovery times of the sensor to methanol vapor are 57 s and 67 s, respectively. These results indicate that the sensor based on the MIPs is a practical way for determining the methanol at very low concentrations in air.

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## References

[1] N.G. Pramod, S.N. Pandey and P.P. Sahay: Ceramics International, Vol. 38 (2012) No.5, p.4151.
[2] M. Nogami, T. Maeda and T. Uma: Sensors and Actuators B: Chemical, Vol. 137 (2009) No.2, p.603.
[3] C. Director, E.T.P. Director and L. Goldman: Reproductive Toxicology, Vol. 18 (2004) No.3, p.303.
[4] G. Wulff: Angewandte Chemie International Edition, Vol. 34 (1995) No.17, p.1812.
[5] C.F. Poole: TrAC Trends in Analytical Chemistry, Vol. 22 (2003) No.6, p.362.
[6] M.C. Hennion and V. Pichon: Journal of Chromatography A, Vol. 1000 (2003) No.1-2, p.29.
[7] P. Spegel, L. Schweitz and S. Nilsson: Analytical Chemistry, Vol. 75 (2003) No.23, p.6608.
[8] I. Ye, O. Ramtrom and K. Mosbach: Analytical Chemistry, Vol. 70 (1998) No.14, p.2789.
[9] Y. Tan, H. Peng, C. Liang and S. Yao: Sensors and Actuators B: Chemical, Vol. 73 (2001) No.2-3, p.179.
[10] T. Takeuchi, A. Dobashi and K. Kimura: Analytical Chemistry, Vol. 72 (2000) No.11, p.2418.
[11] G. Vlatakis, L.I. Andersson, R. Muller and K. Mosbach: Nature, Vol. 361 (1993), p.645.
[12] S.A. Piletsky, E.V. Piletska, A. Bossi, K. Karim, P.T. Lowe and P.F. Anthony: Biosensors and Bioelectronics, Vol. 16 (2001) No.9-12, p.701.
[13] J.S. Metcalf and G.A. Codd: Chemical Research in Toxicology, Vol. 16 (2003) No.2, p.103.
[14] D. Chamely and C.E.J. Carraher: Polymer News, Vol. 28 (2003) No.3, p.86.

[15] S.V. Martha and D.A. Spivak: Macromolecules, Vol. 36 (2003) No.14, p.5105.
[16] G. Wulff and G. Kirstein: Chemistry & Food Science, Vol. 29 (1990) No.6, p.684.
[17] K. Haupt: Analytical Chemistry, Vol. 75 (2003) No.17, p.376A.
[18] S. Peter, L. Schweitz and S. Nilsson: Electrophoresis, Vol. 24 (2003) No.22-23, p.3892.
[19] Y.M. Zhang, J. Zhang, J.L. Chen, Z.Q. Zhu and Q.J. Liu: Sensors and Actuators B: Chemical, Vol. 195 (2014), p.509.
[20] M. Karlsson, A. Matic and P. Berastegui: Solid State Ionics, Vol. 176 (2005) No.39-40, p. 2971.
[21] X.J. Cheng, K.L. Liang, G. Liu and N. Song: Chemistry Online, Vol.70 (2007) No.11, p.861 (in Chinese).
[22] J.X. Yang, Z. Yi and S.F. Weng: Spectroscopy and Spectral Analysis, Vol. 22 (2002) No.5, p.741.
[23] W.M. Lu, W.G. Chen, X.Y. Luo and N. Dong: Chemical Journal of Chinese Universities, Vol. 18 (1997) No.3, p.337 (in Chinese).
[24] C.Y. Lin, D.F. Tai and T.Z. Wu: Chemistry A European Journal, Vol. 9 (2003) No.20, p. 5107.