PT-MESOPOROUS TIO2 PREPARATION FOR HIGH RESPONSE FORMALDEHYDE SENSOR

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Abstract - Sensing materials of mesoporous TiO_2 were prepared by hydrothermal synthesis from tetrabutyl orthotitanate. For the sensing formaldehyde (HCHO) gas, the sensing materials was characterized by X-ray Diffraction (XRD). It exhibited sensor response of 14.1 to 10 ppm HCHO at room temperature, the response time (T_{90}) and recovery time (T_{r90}) were measured as 80 s and 40 s, respectively. Addition of 1% Pt on mesoporous TiO_2 revealed a promotion of sensor response 71.7 to 10 ppm HCHO, the response time and recovery time were measured as 80 s and 32 s, respectively.

Keywords - mesoporous TiO_2, HCHO sensor, sensor response, response time.

I. INTRODUCTION

Formaldehyde (HCHO) gas is a kind of VOCs, it is emitted from the environment for example indoor construction and decoration materials. Another view of point it is an main chemical has been widely applied in many processes, including wood preservative, dry cleaning detergent, production of fertilizer and petroleum production, as well as paper and pulp production, the cosmetics, rubber industry, and the textile industries [1,2]. It is a hazardous material with negative effect to human body. It includes nasal tumors, irritation of the eyes and respiratory tract, nausea, headache, fatigue, dullness, thirst, skin irritation, central nervous system damage, immune system disorders, as well as asthma and nasopharyngeal cancer [3–5]. It is a very important assay for formaldehyde rapidly and accurately in the atmosphere for its high toxicity.

There are several methods for the detection of formaldehyde gas (HCHO), including spectrophotometry [6], high performance liquid chromatography (HPLC) [7], gas chromatography mass spectroscopy (GC/MS) [8], electrochemical system [9] and semiconductor gas sensor [10–12]. Among these methods, semiconductor type gas sensors with the benefits of low cost, fast response, high sensor response and selectivity for exploration [10-12]. There are several kinds of sensing materials prepared for HCHO sensor, for examples SnO_2 [10], ZnO [11], In_2O_3 [12], Ag-$LaFeO_3$ [13], Ag-In_2O_3/ZnO [14] and Multi-wall carbon nanotube (MWCNT) [15]. But the interferences evaluation test of the semiconductor type gas sensors is lack in literatures [10-15]. Therefore, a sensitive and selective gas sensor for formaldehyde is desirable in application. TiO_2 as one of the semiconductor has been proved to be an excellent candidate to fabricate practical gas sensors for detecting HCHO gas [16]. The various TiO_2 nanostructures have been synthesized and applied for formaldehyde gas sensors, such as hollow microspheres [16], porous nanostructure [17]. Some reductive gases were existed strong interferences and the selectivity was poor on the sensors [17]. In this study, we reported the fabrication, characterization and analytical performance of a semiconductor type formaldehyde sensor based on the mesoporous TiO_2. In addition, a doped Pt on mesoporous TiO_2 (Pt/meso-TiO_2) was used for the sensitive detection of formaldehyde for the first time. Furthermore, the Pt/meso-TiO_2 presented excellent sensitivity to formaldehyde gas at concentration to 10 ppm and good sensor selectivity.

II. EXPERIMENTAL

A. Preperation of sensing materials

The mesoporous TiO_2 was prepared through a hydrothermal method. DI water (1 mL) and CH_3COOH (50 mL) were combined in a beaker, and $Ti(C_4H_9O)_4$ (1.6 mL) was added dropwise to the solution with vigorous stirring for more than 5 min. The aforementioned solution and DI water (10 mL) were then transferred to a 200-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated to 200 °C, and this temperature was maintained for 24 h. After the hydrothermal treatment was completed, the autoclave was cooled to room temperature naturally. The obtained precipitate was washed with DI water through centrifugation and dried in an oven at 60 °C for 24 h. Finally, the product was calcined under air at 500 °C for 2 h and then cooled to room temperature. The obtained powder, denoted as mesoporous TiO_2, was impregnated with an aqueous solution containing a given amount of chloroplatinic acid (H_2PtCl_6) with constant stirring for 1 h at room temperature and then washed with DI water, dried at 60 °C for 24 h, and calcined at 300 °C for 2 h. The final product was denoted as Pt/mesoporous TiO_2. In addition, Pt/mesoporous TiO_2 was impregnated with an aqueous solution of H_2PtCl_6 to obtain samples with 0.5, 1.0, and 1.5 wt% of Pt.

B. Characterization of Sensing materials

The characterization of the crystal structures of sensing materials were characterized using X-ray diffraction (XRD) (Shimadzu XRD 6000, Cu X-ray tube [Cu Kα, 1.54060Å]). Sensing materials were identified using the 2θ angles of diffraction, and the particle planes were characterized using XRD at 40.0 kV voltage and 30 mA current. The scanning 2θ range was between 20° and 80°.

C. Gaseous sensing system

The sensing materials were fabricated by mixing the prepared samples and 5 wt% aqueous PVA, which was added as a binder. The sensing film was fabricated by dip coating it on a pair of comb-like gold electrodes on an alumina substrate with dimensions of 10 mm × 5 mm. The sensing film was heated at 100 °C for 1 h, and calcined at 400 °C for 3 h. The HCHO sensing properties were measured using a formaldehyde sensor system, which system includes an HCHO-sensing chamber, and is associated with a static system, as shown in Figure 1. Based on calculating an ideal gas equation, the concentration of HCHO gas can be determined by injecting an appropriate amount of HCHO solution into a liquid sample inlet. A heater was used to heat the HCHO sample until it transformed into vapor and spread throughout the system using a fan. The system can create a set of concentrations ranging from of 1.0 to 10 ppm. In general, the response time (t_{90}) is defined as the time taken to go from 10 to 90% saturation value, while the recovery time (tr_{90}) is the reverse of the response time.

The sensor response (S) was defined as $S = R_{air} / R_{HCHO}$, where R_{HCHO} is the resistance of the sensor in formaldehyde with air background and R_{air} is the resistance in air, respectively. The temperature of the sensor device was controlled at 25 ± 3 °C, with the humidity maintained at 50 ± 5% RH. Other gas inference tests were performed under the same conditions. Interference gases of 10000 ppm hydrogen, 10 ppm ethanol gas and 10 ppm isopropanol gas were employed for the sensing system. Signals from the sensor head were converted into resistance using a simple circuit.

A computer was employed for data collection and processing. All resistance measurements were performed using a Jiehan 5000 data acquisition system by repeating the test several times, and the input voltage (Vs) was set to 2.0 V by power supply.

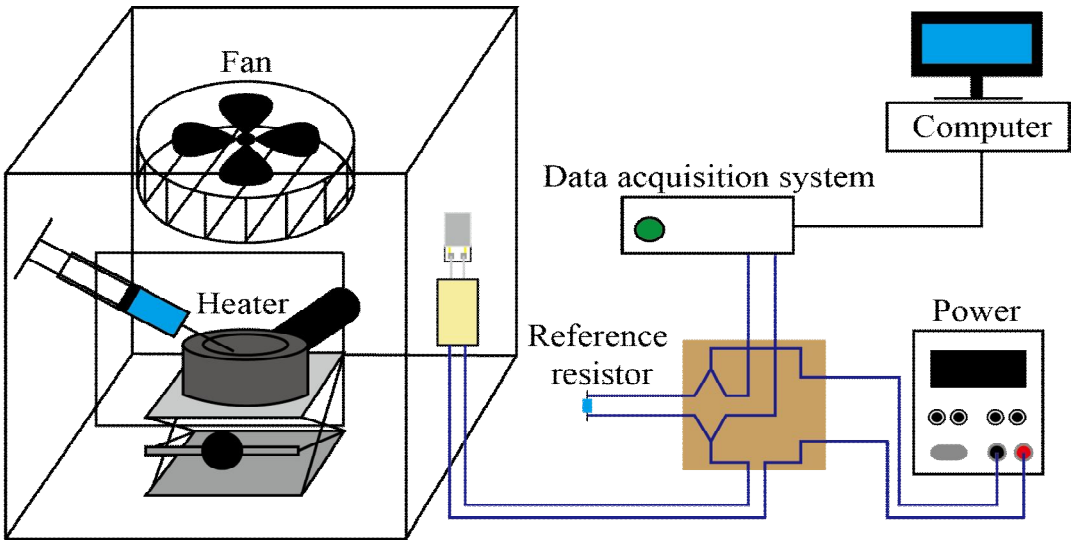


Fig. 1. Sensing system of gaseous HCHO.

III. RESULTS AND DISCUSSIONS

A. Structure characterization

If As shown in Figs. 2 (a)-(d), the XRD patterns were performed on TiO_2, meso-TiO_2, 0.5 wt% Pt/meso-TiO_2, 1 wt% Pt/meso-TiO_2 and 1.5 wt% Pt-meso-TiO_2.

In Fig. 2 (a), several diffraction peaks corresponding to anatase TiO_2 were obviously observed in all the samples and reach agreement with those in the standard JCPSD card No. 21-1272. Furthermore, the deposited Pt does not affect the crystal structure of anatase TiO_2. One distinct additional diffraction peak at 39.76°, corresponding to the (111) plane of the hexagonal face-centered cubic phase of Pt, was found in 0.5, 1, and 1.5 wt% Pt-meso-TiO_2.

The results also approve that the characteristic diffraction peak of platinum oxide was absent in the XRD patterns. Furthermore, with increasing amounts of deposited Pt, the diffraction peak of Pt (111) gradually intensified. Moreover, the mean crystallite sizes of TiO_2 and Pt were calculated using the Debye–Scherrer formula, and were approximately 5.13 and 3.11 nm, respectively.

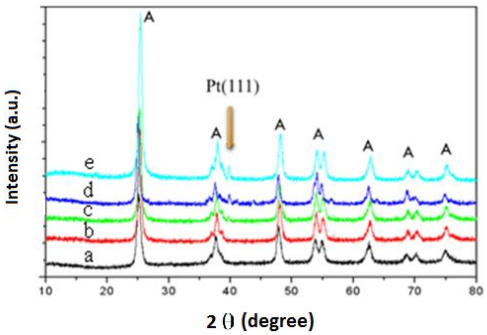


Fig. 2. XRD patterns of (a) TiO_2 (b) meso-TiO_2 (c) 0.5% Pt/meso-TiO_2 (d) 1% Pt/meso-TiO_2 (e) 1.5% Pt/meso-TiO_2.

B. Gas sensing properties

Fig. 3 (a) and (b) presented the sensor resistance versus time to 10 ppm HCHO on TiO_2 and meso-TiO_2, respectively. The resistance was decreased while the HCHO gas input into the system in Fig. 3 (a) and (b), and it revealed the TiO_2 and meso-TiO_2 are n-type semiconductor gas sensors. In Fig. 6 (a), (b) and Table 1, the sensor response of meso-TiO_2 was 14.1 and it was higher than TiO_2 when the HCHO gas concentration was 10 ppm. The reason is the mesoporous TiO_2 possesses more active sites to react to HCHO gas than TiO_2 [17]. The sensor response of meso-TiO_2 can be promotion by appropriate addition of Pt. Sensor responses of 0.5 % Pt/ meso-TiO_2 and 1.0 % Pt/ meso-TiO_2 are 29.5 and 71.6, respectively. Various kinds if precious metals of 1.0 % Au, Pd, Ag and Pt were added on meso-TiO_2 to measure the sensing properties in Table 2. All the metals are possessed the response promotion effect, and among these sensors the response enhancement of Pt metal addition is higher than other metals. The reason is an excellent ability of oxygen adsorption and HCHO oxidation on Pt can explain the promotion effect on the Pt. The relationship between sensor response and concentrations of HCHO is shown in Figure 4 (a), (b) and (c). It can be found that the sensor response enlarged when the HCHO concentration increased from 1.0 to 10 ppm of TiO_2, meso-TiO_2 and 1% Pt/meso-TiO_2. In Fig. 4, the sensor response of 1% Pt/meso-TiO_2 is superior than TiO_2 and meso-TiO_2 from 1.0 to 10 ppm HCHO concentration.

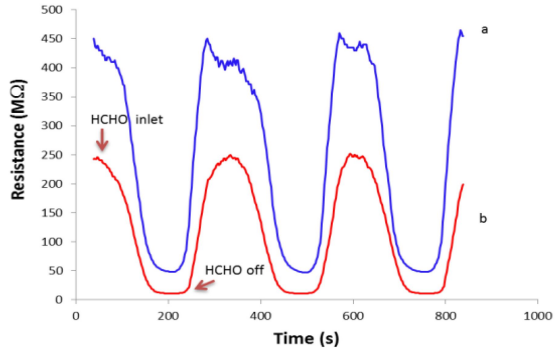


Fig. 3. Sensor resistance versus time on (a) TiO_2 (b) meso-TiO_2 under the HCHO gas concentrations to 10 ppm.

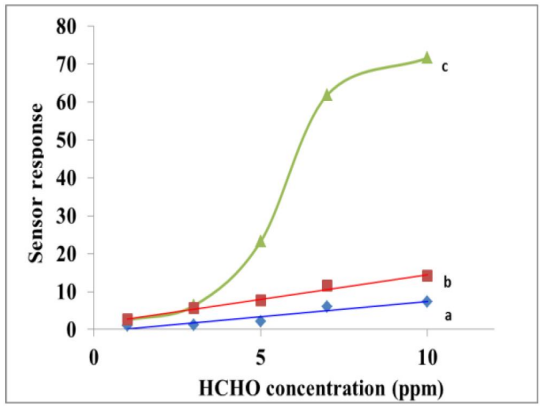


Fig. 4. Sensor response versus various HCHO gas concentrations on (a) TiO_2 (b) meso-TiO_2 (c) 1% Pt/meso-TiO_2.

Table 1: Sensing properties to 10 ppm HCHO on various kinds of sensing materials

Various kinds of sensing materials	Sensor response	Response time T_{90} (s)	Recovery time T_{r90} (s)
TiO_2	7.3	66	140
meso-TiO_2	14.1	80	40
0.5% Pt/meso-TiO_2	29.5	120	38
1% Pt/meso-TiO_2	71.6	80	32
1.5% Pt/meso-TiO_2	5.8	112	42

Table 2: Sensing properties to 10 ppm HCHO on various kinds of meso-TiO_2 materials

Various kinds of sensing materials	Sensor response	Response time T_{90} (s)	Recovery time T_{r90} (s)
meso-TiO_2	14.1	80	40
1% Au/meso-TiO_2	27.6	110	90
1% Pd/meso-TiO_2	36.1	104	38
1% Ag/meso-TiO_2	20.1	100	48
1% Pt/meso-TiO_2	71.6	80	32

CONCLUSION

Sensing material TiO_2 polymeric nanospheres were prepared for detecting gaseous formaldehyde (HCHO), the sensing materials was characterized by XRD. It revealed a very high sensor response of 252.5 to 10 ppm HCHO at room temperature, the response time (T_{90}) and recovery time (T_{r90}) were measured as 74 s and 102 s, respectively. This HCHO sensing material is promising to apply in future.

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