Highly Sensitive and Selective NiO Film / K⁺-Exchanged Glass Composite Optical Waveguide Sensor for Chlorobenzene Vapor Detection

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Abstract. In this paper, we propose a new and simple NiO-based Chlorobenzene vapor optical waveguide (OWG) sensor. The highly sensitive element of this sensor was made by coating the nickel oxide film over a single-mode potassium ion (K⁺) exchanged glass OWG. Sensitivity of the NiO film composite OWG sensor was estimated by the change of absorption properties of the film. The sensor has a linear response to Chlorobenzene concentration, and sensitivity up to 1.8ppm. Moreover, it shows a satisfactory repeatability and a low sensitivity to common interfering gases such as benzene, toluene, xylene and ethanol vapors.

1. Introduction
Environmental pollution has increased considerably during the last few decades [1]; Volatile organic compound (VOC) emissions from industrial and commercial processes are very dangerous for human health and environment [2]. Thus, it is very important to develop chemical sensors that allow the measurement of volatile organic compounds in a fast, in situ and continuous way. Optical waveguide (OWG) sensor have received particular interest for biomedicine [3, 4], environmental monitoring [5], and process control and safety, particularly for the detection of gaseous analytes in trace concentrations [6-11]. In this paper, we propose a new and simple NiO-based Chlorobenzene OWG sensor, and then report several characteristics of the device; finally, provide results for the detection of parts-per-million levels of Chlorobenzene vapor as an example of VOC gases detection.

2. Experimental Section
Nickel oxide powder was synthesized by the coprecipitation method [12]. The NiO film was
preparing vacuum evaporation of NiO powder onto K⁺ exchanged glass substrates. The thickness of the NiO film was about 160nm. To taper the ends (slopes) of the thin film, a mask with a rectangular window was mounted at a distance of several mm from the substrate during vacuum evaporation. The mask can be made of a metal plate, an alumina ceramic plate, or slide glass. For a typical experimental configuration, see Figure 1. The K⁺-exchanged glass OWG device is made on a soda-lime glass substrate (76 mm×26 mm×1 mm), which were immersed in molten KNO₃ salt at 400 °C for 40 min. Since the polarizability of K⁺ is considerably greater than that of Na⁺ on glass, K⁺ can be easily incorporated in glass [13]. After ion exchange process, the substrate was taken out of the molten KNO₃, cooled at room temperature, and then washed with distilled water in order to remove the solid KNO₃ on its surface.

![Figure 1. NiO Film / K⁺-Exchanged Glass Composite Optical Waveguide](image)

3. Results and discussion
The VOC gases-testing apparatus (Figure 2a) was constructed from compressed air sources, a flow meter, a diffusion tube, and gas that contained VOC gases. A gas mixing manifold was used to mix the air stream that contained VOC gases with a stream of pure air and to introduce the mixture into the flow cell, which enclosed the waveguide sensor. The NiO film/K⁺-exchanged glass composite OWG gas sensor device in a flow cell (2 cm × 1 cm × 1 cm) was mounted on a rotational stage equipped with X–Y–Z translation. A He–Ne laser (λ= 632.8 nm) beam was introduced into the OWG using a prism coupler (glass prism: n = 1.78 and a matching liquid, diiodomethane: n = 1.74), and it emerged from another prism coupler. The intensity of the output light was monitored by using a radiometer, and the signal was recorded by a computer program. In every measurement, a new syringe was used to inject 10 ml of the Chlorobenzene vapor sample into the flow chamber, and then out from the vent (Figure 2b). Pure air that functioned as a carrier and dilution gas flowed through the cell at a constant rate of 30 ml/min in order to transfer the Chlorobenzene vapor to the sensor. All measurements were made at room temperature.
The typical reversible response of the NiO film/ K\(^+\)-exchanged glass composite OWG sensor to Chlorobenzene vapor is given in Figure 3. As the NiO film was exposed to Chlorobenzene vapor the sensor baseline steadily decreased. Upon exposure to Chlorobenzene vapor, the sensor response returning to dry air results in partial recovery of sensor signal. The extent of reversible signal decrease seems to increase as the Chlorobenzene vapor concentration increases and constitutes a dosimetric response. The response and recovery times of the NiO film/K\(^+\)-exchanged glass composite OWG Chlorobenzene sensor were fast.

As can be seen from Figure 3 the intensity of output light decreases with the increase in the concentration of Chlorobenzene vapor in the range of 1.8-18500 ppm and decreased when the concentration of Chlorobenzene vapor was increased. The recovery time was found to increase with an increase in Chlorobenzene vapor concentration, by means of dry air. The recovery time of the sensor was longer than its response time because the oxidant (oxygen) concentration was lower and a longer time was required for a sufficient amount of oxidant to reach the indicator in the flow chamber. The response and recovery times of the Metal oxide planar OWG Chlorobenzene sensor were fast and less than 6 s and 17 s, and highest output light intensity of this vapor is 1.8ppm.
Several OWG sensors were fabricated and tested for response to gaseous Chlorobenzene. The repetitive responses of typical sensor exposed alternately to pure air and 1.8 ppm and 18500ppm Chlorobenzene vapor is shown in Figure 4. At this concentration the Relative Standard Deviation of output light intensity is ± 0.75%. The response time was rapid (6s) and fully reversible (17 s) after two times consecutive injected 1.8 ppm and 18500ppm of Chlorobenzene vapor, respectively. These results demonstrated that the OWG sensor was fully reversible and reproducible for Chlorobenzene vapor sensing.

Figure 3. Typical response of NiO film / $K^+$-exchanged glass OWG sensor when exposed to Chlorobenzene vapor in air

Figure 4. Repetitive response curve of OWG sensor to two different concentration of Chlorobenzene vapor
Figure 5. Response curve of NiO film/ K⁺-exchanged glass composite OWG sensor to various gases of 2000ppm

For applications in environmental monitoring, a selective fast response to NiO film/ K⁺-exchanged glass composite OWG in the presence of some interference like benzene, toluene, Xylene, Ethanol and Chlorobenzene is describable. The OWG sensor was tested for the experimental result shows that the OWG sensor has not any considerable response to benzene, Xylene, Ethanol, even at same concentrations. Figure 5 shows the response of OWG sensor to 2000 ppm benzene, toluene, Xylene, Ethanol and Chlorobenzene Among same consistence, the sensor has higher response to Chlorobenzene vapor.

4. Conclusion

A novel simple-structure optical waveguide sensor for Chlorobenzene vapor detection has been proposed and characterized. We measured the detection limit of the device under operating conditions that are determined according to the investigations described above. We succeeded in detecting parts-per-million Chlorobenzene vapor, which is a typical example of VOC vapor; it exhibits general sensitive and reversible response to the Chlorobenzene vapor. The detection limit for Chlorobenzene vapor is <1.8 ppm, it shows very good characteristics in terms of response repeatability, response time and a low sensitivity to common interfering gases. Moreover, it has a simple structure, and requires a simple front end optical waveguide.

This OWG system proved to be fast in response, reversible, and highly sensitive for Chlorobenzene vapor, and this NiO film/K⁺-exchanged glass composite OWG sensor is inexpensive and reusable. It will be possible to achieve a parts-per-billion detection limit by controlling the adsorption properties of the sensing layer and its absorption properties. We believe the proposed technique should be very attractive for the eventual realization of a compact and inexpensive distributed alarm VOC optical waveguide sensor.

Acknowledgment

The authors acknowledge the Natural Science Foundation of China for the support of this project under the 20965008 grants.

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