Development of a ZnO-modified Light-Scattering Sensor for the Detection of Alcohols

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A light-scattering sensor that incorporated zinc oxide (ZnO) nanoparticles was developed and characterized in this study. Evenly distributed nanostructured ZnO materials were formed on the sensing elements through the calcination of zinc acetate-treated sensing elements in a high-temperature oven. There was a large change in the scattering properties of the nanostructured ZnO materials after adsorption of the target compounds; this behavior was exploited for quantitative purposes. To investigate the detection of volatile compounds using this method, both static and flow cell-type devices were constructed. To determine the most suitable nanostructured ZnO material for the light scattering sensors, several factors that influenced their morphologies, including the calcination temperature, calcination time, and the amount of ZnO colloidal solution for calcination, were examined. Fiber-like ZnO structures were produced at temperatures below 400°C. Above 400°C, particles having round shapes were observed; the higher the calcination temperature, the larger the particle sizes. Based on an examination of the signals from several volatile organic compounds, the prepared ZnO sensor was selective for the detection of alcohols, and the observed signals followed the surface-adsorption mechanism. The prepared sensor is fast in response, and the detection time can be shorter than 2 min. For quantitative purposes, the linear range was limited to low concentrations of alcohols, *i.e.*, up to *ca.* 200 ppm.

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Introduction

ZnO exhibits unique chemical properties, and can exist in a wide range of nanostructural forms.¹ Nanostructured ZnO materials can be prepared in the form of nanoparticles,^{2,3} nanorods,^{4,5} nanowires,^{6,7} and other morphologies^{8,9} through the use of vapor deposition or wet chemical methods. These materials have been used in devices, such as field-effect transistors,^{10,11} solar cells^{12,13} and as photocatalysts.^{14–16} One of the most interesting uses of ZnO is in the field of sensing technology. For instance, taking advantage of the catalytic behavior of ZnO, sensors have been developed for the detection of NO_x,¹⁷ alkanes,¹⁸ ethers,¹⁹ amines,^{20–22} ketones,^{23–25} aromatic volatile compounds,²⁶ and alcohols.^{27–31} Unfortunately, these sensors are typically operated at temperatures above 250°C to trigger catalytic reactions that allow electronic sensing. The need for extreme sensing conditions and catalytically reactive molecules limits the application of these types of detection systems. To increase the ability to detect under milder conditions, ZnO nanowires³² and ZnO nanoparticles³³ have been prepared directly on the surfaces of infrared sensing elements; these systems allow for the highly sensitive detection of volatile organic compounds (VOCs) in gas atmospheres, particularly for those compounds bearing hydroxyl groups.³³ To simplify the sensing system while utilizing the unique interactions between ZnO and alcohols, in this study we developed a light-scattering sensor. This device is simple in terms of the instrumentation required, and is effectively operational for the selective detection

of alcohols. Conceptually, the analytical signals in this new detection scheme are based on changes that occur to the light-scattering properties of ZnO particles after they have interacted specifically with the target compounds.

Experimental

Materials and reagents

Zinc acetate dihydrate (99.6%, Sigma), 2-methoxyethanol (99.5%, Riedel-De Haën), ethanol (anhydrous, J. T. Baker), and monoethanolamine (99%, Riedel-De Haën) were used to prepare zinc colloidal solution. The six VOCs examined as analytes (chloroform, carbon tetrachloride, trichloroethylene (TCE), methanol, ethanol, and propanol) were obtained from Acros Organics (Geel, Belgium) in reagent grade.

Apparatus

Two sensing systems were prepared: a static system and a flow-cell system. Figure 1A displays a schematic illustration of the experimental setup for the static system. The volume of the cell was 70 mL. To prevent gas molecules from leaking through or adsorbing onto the sample cap, the cap of this cell was formed from a thick Teflon film, a rubber pad, and a stainless-steel plate; it was tightened to the cell body using four screws. A quartz rod of diameter of 3 mm was placed at the center of the sample cell to direct the laser radiation. In the middle of the quartz rod, a region of 6 mm in length was further treated with ZnO nanoparticles to scatter the propagated laser radiation out of the quartz rod. A silicon detector (DP01-39, Duma Optronics) having a sensing area of 5 mm² was used to detect the scattered radiation. A 660-nm diode laser (30 mW,

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Fig. 1 Schematic illustrations of (A) static and (B) flow cell-type sensing systems.

E-Laser Enterprise, Taichung, Taiwan), used as radiation source, was operated at 4.5 V so as to increase its lifetime. Figure 1B provides a schematic illustration of the experimental setup of the flow-cell system; its components were the same as those in the static sensing system. Glass wool was placed at the bottom of 7-mL sample vial so as to reduce the flow pulse after injection of the samples into the flow cell.

Preparation of a zinc oxide colloidal solution and ZnO-modified sensing element

A zinc colloidal solution was prepared using a modified sol-gel approach. Zinc acetate dihydrate was mixed with 2-methoxyethanol and ethanol (70:30, v/v), followed by the addition of monoethanolamine; the Zn^{2+} -to-monoethanolamine molar ratio was 1:1. The final concentration of Zn^{2+} was 0.25 M. This mixture was heated at 70°C for 2 h to ensure the formation of a colorless solution.

Portions of the prepared zinc colloidal solution (volumes of 10 to 60 μL) were coated on a quartz rod (diameter: 3 mm); the coated area had a length of 6 mm. After drying for 30 min in a fume hood, the surface-coated sensing element was placed into a high-temperature furnace for calcination of the coated zinc solution. The calcination temperature, the volume of the coating zinc colloidal solution, and the calcination time were modified to determine their effects on the sensing properties and morphologies of the ZnO nanomaterials. Field emission scanning electron microscopy (FESEM), using a JSM-6700F microscope (JOEL, Japan), was employed to examine the morphologies of the ZnO nanoparticles.

Results and Discussion

Morphologies of the prepared ZnO nanostructural materials

To optimize the conditions for the preparation of suitable nanostructured ZnO materials for light-scattering sensing devices and to observe the morphologies of the materials prepared under different calcination conditions, ZnO solutions were calcined at various temperatures and for different calcination times. Figures 2A to 2C display SEM images of ZnO solutions calcined at 300°C for 1, 1.5, and 2 h. As can be seen in these images, non-regular fiber-like structures can be observed for the ZnO solution calcined at 300°C; when the calcination time was extended to 2.5 h, the morphologies of the resulting ZnO materials remained as non-regular fibers, but with decreased size. When the calcination temperature was raised to 400°C (Figs. 2D to 2F), the ZnO particles that formed had round shapes; extending the calcination time from 1 and 1.5 h increased the diameter of the nanoparticles slightly.

To further examine the effect of temperature on the formation of ZnO nanoparticles, SEM images (Figs. 2G to 2I) of the products of ZnO solutions calcined at 200, 500 and 600°C for 1 h were further acquired. As can be seen in these images, the ZnO materials formed at calcination temperatures lower than 400°C tended to form in non-regular shapes. When the calcination temperature was higher than 400°C, the nanoparticles that formed were round; a higher calcination temperature provided larger nanoparticles. This behavior presumably arose as a result of incomplete decomposition of the organic species in the ZnO solution when the heating temperature was lower than 400°C. As evidenced in a previous study, we observed infrared absorption bands for carboxylic groups after ZnO solutions had been calcined at temperatures lower than 300°C.³³

Characterization of scattering sensing systems

Based on their shapes and sizes, we believed that these ZnO nanoparticles would be suitable for the direct monitoring of targeted analytes that specifically adsorb onto and modify the light-scattering properties of the ZnO nanoparticles. To increase the effect of light scattering, the incident angle of the diode laser was first examined using a static detection system. As an example, Fig. 3A presents a typical plot of the dynamic signals detected after ethanol had been injected at a volume of 1 μL utilizing static cell for detection; for this experiment, a ZnO sensor that had been prepared through calcination at 400°C for 1 h was used. Based on the intensity of the detected signal with respect to the detection time, the rate of detection was quite rapid, with the time required to reach maximum signals being *ca.* 1 min. Considering the time delay necessary for evaporation of the ethanol sample, the real rate of detection was probably considerably shorter. To examine the influence of the incident angle, Fig. 3B presents the signals detected at a detection time of 5 min as a function of the incident angle. An angle of incidence of *ca.* 20° provided detected signals having the highest intensity. Therefore, in the following experiments, the incident angle of the diode laser was maintained at 25°.

Effect of calcination temperature

To examine the effect of the calcination temperature on the light-scattering properties of the nanostructural materials, ZnO samples through 1-h calcination at various temperatures were prepared and used to detect ethanol by a static cell. The injected volume was 1 μL . Three sensing elements for each calcination temperature were prepared to obtain the standard deviation (plotted as error bars) of the signals. Figure 4A plots the signals

Fig. 2 SEM images of ZnO solutions calcined at 300°C for (A) 1, (B) 1.5, and (C) 2 h and at 400°C for (D) 1, (E) 1.5, and (F) 2 h. SEM images of ZnO solutions calcined at temperatures of (G) 200, (H) 500, and (I) 600°C for 1 h.

Fig. 3 (A) Time profiles for the detection of 1 µL of ethanol after 20 µL of ZnO solution had been calcined at 400°C for 1 h. The angles of incidence of the diode laser were 5° (■), 15° (●), 25° (▲), and 35° (▼). (B) Signals recorded at a detection time of 5 min, plotted against the angle of incidence of the diode laser.

Fig. 4 (A) Signals of 1 µL of ethanol recorded at a detection time of 5 min, plotted against the calcination temperature. The sensor had been prepared from the calcination of 20 µL of a ZnO solution for 1 h. The angle of incidence of the diode laser was 25°. (B) Signals of 1 µL of ethanol recorded at a detection time of 5 min, plotted against the calcination time, for the sensor prepared from the calcination of 20 µL of a ZnO solution at 400°C.

Fig. 5 (A) Time profiles for the detection of 1 μL of ethanol using sensors calcined at 400°C for 1 h after coating with 10 (■), 20 (●), 30 (▲), 40 (▼), and 50 μL (◀) of the ZnO solution. (B) Signals of 1 μL of ethanol recorded at a detection time of 5 min, plotted against the volume of the ZnO solution used for coating.

obtained after 5 min against the calcination temperature. Although the ZnO samples calcined at 300°C gave the highest-intensity signals, their reproducibility was the lowest among the tested samples. Based on these findings, it appeared that nanostructured ZnO materials possessing fiber-like forms would be most suitable for light-scattering measurements, but their low reproducibility might limit their applicability. The signals obtained at a calcination temperature of 400°C had lower intensity than those of the samples calcined at 300°C, but much better reproducibility; the intensity of the signals decreased upon further increasing the calcination temperature. Based on our findings from the SEM measurements, the ZnO materials tended to form rounder nanoparticles with larger particle sizes as the calcination temperature was increased and, hence, a reduction of the scattering properties.

Effect of calcination time and volume of coating

To examine the effect of the calcination time, ZnO sensors were calcined by various durations at a temperature of 400°C and used to examine their analytical performances. Figure 4B presents a plot of the signals detected at 5 min after the injection of 1 μL of ethanol. The signals obtained from each sensing element were similar. Based on Figs. 2D–2F, the calcination temperature at 400°C resulted in films of having round-shaped ZnO nanostructures and the extending the calcination time did not alter the shape or size of these ZnO nanoparticles significantly. Thus, although the morphologies of these ZnO nanoparticles and the signals detected from them were both temperature-dependent, the duration of the calcination process had little effect on either of these properties.

Fig. 6 (A) Detection time profiles of 1- μL samples of methanol (▲), ethanol (●), propanol (■), carbon tetrachloride (◀), and trichloroethylene (▼), using the sensor prepared through a process of coating with 30 μL of the ZnO solution and calcining at 400°C for 2.5 h. (B) Signals recorded at a detection time of 5 min for the examined VOCs.

The thickness of the ZnO layer on the surface of the sensing element is also an important parameter. For example, we expected that a thin layer of ZnO might result in a low degree of light scattering and, hence the changes to the scattering properties in the presence of the analyte might be too small to detect. On the other hand, a layer of ZnO that is too thick might also exhibit ineffective scattering of light. Therefore, we optimized the thickness of the ZnO layer by treating the surface of the sensing elements with different amounts of the ZnO solution while maintaining the length of the treated region at 6 mm. After air-drying, we calcined these sensing elements at 400°C for 1 h. Figure 5A displays the time profiles for the detection of 1 μL of ethanol using the sensors prepared with coating volumes ranging from 10 to 50 μL . A static cell was used in this study. The time required to reach the optimal signals was similar in each case, but the intensities varied with respect to the amount of coating. Figure 5B presents the signals obtained after 5 min as a function of the coating volume. The signal of the sensing element coated with 30 μL of the ZnO solution was the most intense.

Selectivity in the detection of alcohols

According to literature,^{21–31,33} ZnO interacted uniquely with VOCs bearing hydroxyl groups. Therefore, in this study, the behaviors of our ZnO nanoparticles were examined their responses to six compounds (methanol, ethanol, propanol, TCE, carbon tetrachloride (CCl₄), and chloroform (CHCl₃)) each injected at a volume of 1 μL into the static cell. The sensing element for this study was prepared by coating with 30 μL of

Fig. 7 Detection time profiles obtained using the flow cell-type system after (A) individual injections of 1 μL of ethanol and CCl_4 and (B) four consecutive injections of 1 μL of ethanol.

the ZnO solution and then heating at 400°C for 2.5 h. Figure 6A provides the resulting response profiles for these compounds; Fig. 6B plots the signals obtained at a detection time of 5 min. It is clear that the ZnO sensing element could detect the alcohols selectively, and that the responses toward the other three VOCs were too weak to interfere.

As can also be seen in Fig. 6B, the order of the selectivity among three alcohols is propanol > ethanol > methanol. This order can be explained by the electron donating-effect of gas molecule, as indicated by Cheng *et al.*²⁶ For instance, the propanol bears a longer hydrocarbon chain than that of methanol, resulting in that the negative charge of the oxygen atom would increase with an increase of the electron-donating effect. Hence, the gas molecules are easier to be adsorbed on the film surface and the sensitivity increases.

Flow-cell detection system

To demonstrate that the type of light-scattering sensor developed in this study could be simplified further in terms of the detection procedure, a flow system was further constructed utilizing an air pump to pass the vaporized samples into the flow cell, as shown in Fig. 1B. After the injection of 1 μL of a liquid sample into the sample vial and waiting for 5 min for complete evaporation, an air flow was used to purge the vaporized sample into the flow-cell device; the air flow rate was maintained at 15 mL/min. Figure 7A displays the typical response after one injection of neat ethanol and CCl_4 ; Fig. 7B presents a plot of the response to a consecutive injection of ethanol. As is evident in Fig. 7A, the injection of CCl_4 caused a rapid response in the first minute. As in the static system, the ZnO-treated sensor exhibited no response toward CCl_4 ; therefore, response of CCl_4

Fig. 8 Concentration-response curves for the detection of ethanol diluted in CCl_4 . The responses were calculated using the (A) time-delay and (B) band-area techniques. For the time-delay technique, the response at 110 s was selected to minimize the shearing effect, and used to plot against the concentration of ethanol. For the band-area technique, the area under the entire response in each injection was integrated and used to subtract the area when only CCl_4 was injected. The subtracted values were plotted against the concentration of ethanol.

is most likely to be due to the flow pulse during the injection process (shearing effect). When comparing the band caused by this shearing effect with that of ethanol, the shearing effect could be completely eliminated when the analytical signals were recorded after a time delay of *ca.* 110 s. When detecting a low concentration of ethanol, however, this time delay might not be feasible, because the rate of decay would be too fast to obtain an appropriate signal. Therefore, a method to extract the analytical signals was further developed and named the band-area technique. In this method, the responses during detection were integrated. By subtracting the integrated area of the response curve caused by the shearing effect (with injection of CCl_4 only), the subtracted areas could be used to indicate the amount of ethanol and the concentration-response curves for quantitative purposes could be constructed. To obtain higher accuracy for the analysis, ethanol, was diluted in CCl_4 , and then 1 μL of the diluted solution was injected. Figures 8A and 8B compare the results obtained using a time-delay the band-area techniques, respectively. For both cases, the linear range was limited to concentrations lower than *ca.* 200 ppm. Because there appears to be a bias in the curve for the time-delay technique, we suggest the use of the time-delay technique to obtain more-accurate quantitative results when the concentration of the analyte is relatively high. On the other hand, for low concentrations of analytes, the subtracted band-area technique appears to be more suitable for use.

Conclusion

In this work, a light-scattering sensor that integrates the specific interactions between nanostructured ZnO materials and alcohols was developed. Both static and flow cell-type detection systems were performed. For the static sensing system, the effects of the parameters employed to prepare nanostructured ZnO materials for light scattering were investigated. Results indicated that ZnO nanoparticles formed when the calcination temperature was higher than 400°C, with the calcination time having little influence on their morphologies. For calcination temperatures below 400°C, the ZnO materials obtained possessed fiber-like shapes, for which the reproducibility in the detection of ethanol was worse than that of samples prepared at higher calcination temperatures. The thickness of the ZnO layer on the sensing element also influenced the analytical properties; the optimal conditions were obtained after 30 µL of the ZnO solution had been applied to the sensing element. From a study of the response of a sensing element to various concentrations of ethanol and propanol, the detection behavior appeared to follow a surface adsorption mechanism with a linear range of up to 200 ppm. To accelerate the rate of detection, a flow cell-type sensing system was also constructed, which provided results similar to those of the static system, but with the time required to finish one sample being significantly reduced. Taken together, our results reflect the successful construction of a ZnO-modified light scattering sensor that was selective for alcohols.

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