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Optical Ammonia Sensor Based on ZnO:Eu$^{2+}$ Fluorescence Quenching Nanoparticles

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Abstract: An ammonia sensor is conceived and constructed using the downconverting ZnO:Eu$^{2+}$ nanoparticles that can be excited by near-ultraviolet (378 nm) light and emit indigo color light. The capability of the ZnO:Eu$^{2+}$ nanoparticles for ammonia gas sensing was studied from fluorescence quenching measurements. When these nanoparticles were exposed to ammonia gas, a significant luminescent intensity variation of the excitation spectra was observed. The detection limit of the proposed optical gas sensor is 20 ppm with a good linearity ($R^2 = 0.9759$) from 0 to 80 ppm of ammonia. The sensor has the advantages of a simple structure, high sensitivity, easy fabrication, and low cost, and can be used for sensing ammonia gas in factories, laboratories, etc.

Keywords: Ammonia Gas; Fluorescence Quenching; Optical Sensor; ZnO:Eu$^{2+}$.

1 Introduction

Ammonia is a compound of nitrogen and hydrogen with the formula NH$_3$. The simplest pnictogen hydride, ammonia is a colorless gas with a strong, pungent odour [1–3]. Ammonia poisoning takes place mainly through the respiratory tract. The toxicity of ammonia to the human body is related to the concentration of ammonia in the environment and the contact time. Low concentration of ammonia is irritating to the mucous membrane, whereas high concentration of ammonia can cause tissue protein degeneration, adipose tissue necrosis, etc. [4, 5]. Ammonia can also cause fatty degeneration of the liver, renal interstitial inflammation, and myocardial injury. Generally, the maximum allowable concentration of ammonia in the indoor air is 0.2 mg/m$^3$, i.e. 26.35 ppm. With the increase of human safety concerns and health consciousness, it is urgent to monitor flammable, explosive, and toxic gases in various production and living places. At present, the common detection methods for ammonia, such as infrared absorption, chromatography, thermal analysis, etc. [6], have disadvantages of the need for bulky equipment, high cost, difficulty in carrying, time consumption, and so on. In addition, among the sensitive materials, nano-semiconductors are widely used in gas sensing. Thus, it is important to develop a semiconductor gas sensor with high sensitivity, low cost, and portability. As is well known, zinc oxide (ZnO) is a wide-bandgap semiconductor that is widely used in solar cells, field-effect transistors, sensors, and other devices [7, 8]. Their different physical and chemical properties and applications can be obtained via doping ZnO [7, 8]. In this work, the downconverting luminescent nanoparticles of ZnO:Eu$^{2+}$ are prepared by a high-temperature solid-state method. The optical ammonia sensor based on ZnO:Eu$^{2+}$ fluorescence quenching nanoparticles is fabricated by connecting a gas chamber with an optical fibre spectrometer. The sensing mechanism for ammonia is also discussed.

2 Experiment

2.1 Synthesis and Characterization of ZnO:Eu$^{2+}$

Zn$_{1-x}$Eu$_x$O luminescent materials were prepared in the carbon monoxide reduction atmosphere by using zinc carbonate (ZnCO$_3$, A.R.) and europium oxide (Eu$_2$O$_3$, A.R.) as raw materials. The reaction is as follows:

\[
(1 - x)\text{ZnCO}_3 + \frac{x}{2} \text{Eu}_2\text{O}_3 \xrightarrow{\text{CO gas}} \text{(Zn}_{1-x}\text{Eu}_x\text{O}) + (1 - x)\text{CO}_2 \uparrow + \frac{x}{4} \text{O}_2 \uparrow
\] (1)
in which the Eu\(^{2+}\) dopant amount is \(x = 0.03\) molar. X-ray diffraction (XRD) of the sample was carried out by a Shimadzu XRD-6000 diffractometer. As shown in Figure 1a, the crystal structure of ZnO:Eu\(^{2+}\) is in good agreement with the standard card (No. PDF\#36-1451 [9]), which indicates that ZnO:Eu\(^{2+}\) crystals were successfully synthesized.

The crystallite size of ZnO:Eu\(^{2+}\) can be calculated by the Scherrer equation [10]

\[
D = \frac{0.89\lambda}{\beta \cos \theta},
\]

where \(D\) is the mean size of the crystallites, \(\lambda (=0.15405\) nm\) is the wavelength of Cu K\(\alpha\) radiation, \(\beta\) is the full width at half-maximum, and \(\theta\) is the Bragg angle.

The three XRD peaks (100), (002), and (101) were used to calculate the average size of ZnO:Eu\(^{2+}\) nanoparticles, resulting in 74.7 nm.

The fluorescent spectrum of ZnO:Eu\(^{2+}\) was studied using a Hitachi F-4600 spectrometer. As shown in Figure 1b, the excitation and emission wavelengths are 378 and 493 nm, respectively.

2.2 Design and Fabrication of the Sensing System

A gas-sensitive film that can produce fluorescence is important for fluorescence quenching-type gas sensors. The ZnO:Eu\(^{2+}\) nanoparticles and ethanol were fully mixed and dispersed by ultrasonication, and then spin-coated on the surface of a quartz slide. After drying at 60 °C for 2 h, the gas-sensitive element was obtained.

As shown in Figure 2, the gas chamber is a glass tube with an inlet and an outlet, which can ensure that NH\(_3\) gas is spreading in the tube. A jack for adjusting depth of the fibre probe and a support base at the bottom of the chamber are used for placing the ZnO:Eu\(^{2+}\) nanoparticles. The optimum depth of the optical fibre probe can be determined when there is no NH\(_3\) gas in the chamber and the luminescent intensity of sample is the strongest. As shown in Figure 2, the optical spectral data are collected by a USB 4000 Ocean micro-fibre spectrometer with a 380 nm light source. The optical fibre probe of the micro-fibre spectrometer can provide the excitation light and collect the light emitted by ZnO: Eu\(^{2+}\) simultaneously.

3 Results and Discussion

3.1 Stability Test

The optical spectral data were recorded every 10 s by the test system. As shown in Figure 3, there is almost no fluctuation in these optical spectra. It proves that the test system is stable and can be used for monitoring fluorescence quenching.

3.2 Fluorescence Quenching Analysis

As shown in Figure 4, fluorescence quenching is investigated at different concentrations of NH\(_3\) gas. It clearly indicates that with increasing NH\(_3\) concentration, the intensity...
of the excitation spectra decreases, which clearly indicates the fluorescence quenching for ZnO:Eu$^{2+}$ nanoparticles when the NH$_3$ gas flows in the chamber.

### 3.3 Sensing Mechanism

The dynamic quenching process is due to the interaction between the quencher and excited molecules of the fluorescent material. During the dynamic quenching process, collisions occur between the excited molecules of the fluorescent material and the quencher molecules. The energy or charge transfer of the excitation energy of the fluorescent material will take place, and then the molecules return to the ground state. In the present experiment, with different concentrations of NH$_3$ in the chamber, the quenching agent (i.e., NH$_3$ molecules) comes into contacting with the ZnO:Eu$^{2+}$ nanoparticles which act as the fluorescent material. The fluorescent material combining with the gas molecule makes the former return to the ground state from the excited state. The dynamic quenching process is shown in Figure 5. In the figure, $E$ is the energy required for the gas-sensitive material to get excited by light irradiation and arrive at the excited state. $R/NR$ are the conversions between the ground and excited states of the fluorescent material. $L$ and $L^*$ are, respectively, the molecular ground state and excited state. $L$-NH$_3$ and $(L$-NH$_3)^*$ denote the gases adsorbed on the gas-sensitive nanoparticles and the formed composite from the ground and excited states. The dynamic quenching efficiency is affected by the concentration of NH$_3$ and the excited state lifetime of the fluorescent material. The dynamic fluorescence quenching Stern–Volmer equation can be expressed as follows [11, 12]:

$$I_0/I = 1 + K_{SV}C[\text{NH}_3],$$

where $I_0$ and $I$ are, respectively, the luminous intensities of the sensing nanoparticles before and after accessing NH$_3$ gas. $C[\text{NH}_3]$ is the NH$_3$ gas concentration, and $K_{SV}$ is a dynamic quenching constant reflecting the relationship of the diffusion and collision of the equilibrium between the fluorescence molecules and the quencher.

The excitation wavelength is 380 nm, and the optical spectrum is recorded. The different concentrations (0–80 ppm) of NH$_3$ gas and the relative luminous intensity ($I_0/I - 1$) were analyzed, and the results are shown in Figure 6. It is found that there is a good linear relationship, which is consistent with the result of the Stern–Volmer equation. According to the fitting result of the Stern–Volmer equation, the slope ($K_{SV} = 0.00238$) is obtained. As shown in Figure 6, the correlation coefficient $R^2$ is about 0.9759.

![Figure 5: Dynamic quenching process of fluorescent substances.](image)

![Figure 6: Fitting curve of fluorescence quenching.](image)
0.9759, which means a very good linear response of the gas sensor in the given concentration range (0–80 ppm) of ammonia. The sensitivity of ZnO:Eu$^{2+}$ nanoparticles to ammonia is 20 ppm.

4 Conclusions

In this work, ZnO:Eu$^{2+}$ nanoparticles were successfully synthesized by the high-temperature solid-phase method, and a fluorescence quenching ammonia gas sensor based on ZnO:Eu$^{2+}$ sensitive material was proposed and constructed. The detection limit was found to be 20 ppm. The relative strength and the concentration of ammonia gas showed a good linear relationship, with correlation coefficient $R^2 = 0.9759$. The gas sensor has the advantages of small volume, easy fabrication, and high sensitivity, and is suitable for the measurement of ammonia in storage or production workplaces.

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