

UV-light activated ZnO for ppb level NO₂ detection: influence of modified Pechini synthesis route

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Summary:

Zinc oxide (ZnO) nanoparticles have been successfully synthesized by modified Pechini process. To investigate the effect of additives on low temperature NO₂ detection, citric acid (CA), ethylene glycol (EG) and nitric acid (HNO₃) were used. The results showed that all sensors were able to detect NO₂ at near-room temperature, while the addition of ethylene glycol and nitric acid led to the highest response under UV light illumination. This study provides an easy and efficient way to obtain ZnO nanoparticles highlighting their potential for low temperature gas sensing.

Keywords: ZnO, polymer precursor method, gas sensing, drop coating, light irradiation.

Background, Motivation and objective

Resistive gas sensors based on semiconducting metal oxide are the mainly focus for atmospheric pollutants detection due to their high sensitivity and low cost. However, they present the disadvantage of elevated operating temperatures (up to 500°C) to activate gas-solid interactions [1], leading to high energy consumption and long-term instability.

Light activation has emerged as a promising strategy to enable room temperature gas detection by modulating the concentration of photo-generated electron-hole pairs, thereby enhancing sensing performances. This approach aligns with the growing demand for high precision and low power air quality monitoring networks, driven by concerns over rising global mortality rates linked to environmental risk factors. Thus, the development of low power semiconducting metal oxides sensors (SMOX) with low NO₂ detection limit is of particular importance, given its toxicity at concentrations as low as 100 ppb [2].

This work investigates ZnO thin films synthesized via a modified Pechini method for NO₂ sensing. This polymeric gel route is based on the use of a hydroxyl carboxylic acid (citric acid) and a polyhydroxyl alcohol (ethylene glycol) [3]. While the amount of ethylene glycol and solution pH are known to influence ZnO morphology [4], their role in UV-light assisted gas sensing has received less attention. Therefore, the objective of this work is to correlate Pechini synthesis

parameters with ZnO morphology and NO₂ sensing performance at low operating temperature.

Methodology and experimental setup

All analytic grade reagents were used as received. Zinc nitrate (Zn(NO₃)₂·6H₂O, 99%), and ACS grade citric acid (CA) were obtained from Sigma Aldrich. Ethylene glycol (EG, 99%) and nitric acid (HNO₃, 68%), were acquired from Emplura and VWR Chemicals, respectively. De-ionized water (18 MΩ.cm) was also utilized in preparing solutions. In brief, zinc nitrate was dissolved in 50 mL deionized water and certain amounts of EG, CA, and HNO₃ were added to prepare different sols under constant stirring and heating at 200°C for 2 h until the final solutions were homogeneous and without any precipitation.

The precursors were drop coated onto Si/SiO₂ substrates with 100 nm-thick interdigitated platinum electrodes. After deposition, the wet thin films were dried at 80°C and annealed at 500°C for 2 h in the ambient atmosphere. The sensors were labeled as ZnO:CA, ZnO:CA:EG, ZnO:EG and ZnO:EG:HNO₃ according to the additives used.

All sensors have been measured in an automated gas measurement setup using synthetic air as the carrier gas at a constant flow rate of 250 mL.min⁻¹, while it was adjusted upon the injection of target gas. The resistance changes of the sensor upon exposure to NO₂ were measured at a constant operating temperature

(30±2°C), and continuous UV light irradiation at a wavelength of 395 nm.

The sensor's normalized response was calculated by comparing the fully saturated resistances after exposure to dry air (R_{air}) and NO_2 (R_{gas}), according to (eq.1):

$$\text{Response} = \frac{R_{\text{gas}}}{R_{\text{air}}} \quad (1)$$

Results and discussion

Fig. 1a shows the nanorod like morphology of ZnO:CA , whereas ZnO:CA:EG shows homogeneous spherical nanoparticles (Fig. 1b). It can be observed that grain agglomeration leading to a compact sensing layer, is much more evident in ZnO:EG:HNO_3 (Fig. 1c) than in ZnO:EG (Fig. 1d).

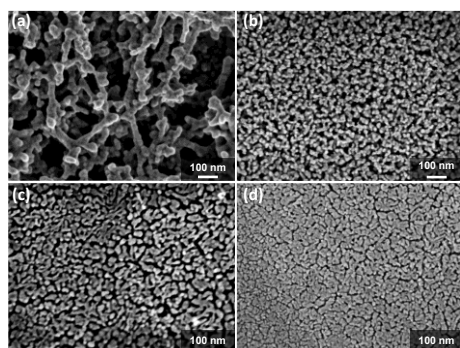


Fig. 1. SEM images of ZnO thin films: (a) ZnO:CA (b) ZnO:CA:EG (c) ZnO:EG and (d) ZnO:EG:HNO_3 .

Fig. 1 illustrates the dynamic resistance changes in the presence of NO_2 of ZnO-based films, prepared using different additives. All sensors presented an increase in resistance independently of the additive, characteristic of n-type semiconducting behavior. The ZnO:EG:HNO_3 sensor showed significantly enhanced response, reaching resistance changes of nearly two orders of magnitude at sub-ppm range, suggesting that the addition of ethylene glycol and nitric acid leads to a higher sensitivity under light illumination.

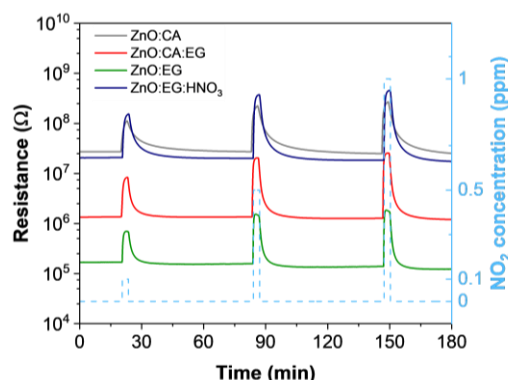


Fig. 2. Resistance variations of ZnO sensors under 395 nm light irradiation at different NO_2 concentrations (0.1, 0.5 and 1 ppm).

The ZnO:EG:HNO_3 sensor was initially exposed to NO_2 at 30°C in the dark, a slight response was observed with a longer recovery time. When exposed to NO_2 under UV illumination, the response was enhanced over that without any illumination.

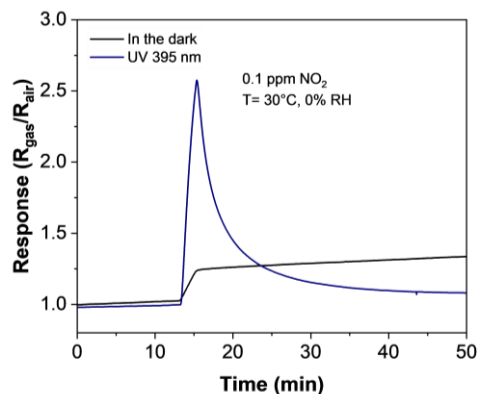


Fig. 3. NO_2 response of ZnO:EG:HNO_3 sensor in dark (black curve) and under UV-light irradiation (blue curve) towards 0.1 ppm of NO_2 .

Conclusion

This work reported a facile and scalable route to synthesize ZnO nanoparticles, for the detection of ppb-level of NO_2 at a relatively low temperature of 30°C. Gas sensing experiments at different operating temperatures, in comparison to operating under LED illumination as well as under humidity conditions, have been performed and will be discussed at the conference.

References

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