

Near room temperature operable H₂S gas detection employing In₂O₃ Quantum Dots

Introduction

Gas sensors provide fast, real-time and in-situ information of gas species and concentration, playing a significant role in detecting hazardous and explosive gas in the environment. As an important semiconductor, In₂O₃ exhibits potential applications for gas sensors, such as for the detection of H₂S owing to its nonstoichiometric chemical form due to O₂ vacancy and its relatively low work function and low electron affinity. In addition, colloidal quantum dots (CQDs) have been studied as an ideal cooperators for applications in gas sensors. Most importantly, the operating temperature of gas sensors nearly reduced to room temperature [1]. The In₂O₃ CQD-based gas sensors exhibited an excellent H₂S-sensing performance with the response up to 90 upon 5 ppm H₂S with a fast response and recovery time being 72 s and 200 s. The corresponding limit of detection was as low as 4.3 ppb. Theoretical analysis results revealed that the main oxygen species (O₂⁻, O⁻) adsorbed on the surfaces with the ratio of 1:1 which plays an important role in gas-sensing properties and is helpful for making a deep understanding of the sensing mechanism.

Results

In₂O₃ CQDs were synthesized via a modified method based on reference [2]. The successive dynamic response curve on H₂S exposure/release cycles toward 0.5-50 ppm were recorded in Fig. 1. In all the detected range, the gas sensing response tended to saturation upon higher concentration, exhibiting a power law relationship, as in detail fitted in Fig. 1 based on the log-linear plot. The exponent value was 0.75, corresponding to the fitting equation being $y=ax^b$.

Since the power law exponent may be decided by the type of gases as well as sufficiently high gas concentration, we could calculate the proportion ratio of oxygen deposited on surfaces based on the power law [3]. As above discussed, the fitting exponent value was about 0.75, which is between the theoretical values of 1 and 1/2, indicating oxygen species being O₂⁻ and O⁻ involved in the interaction with H₂S[3]. Thereby, we could describe the dependence through the power law as $S=aP^{0.75}$. Furthermore, we could calculate the ratio of O₂⁻ and O⁻ as: $H_2S+O_2-H_2+SO_2$

Where x and y are the ratios of H₂S participated in O₂⁻ and O⁻ reaction, and hence $x + y = 1$. Further, we could obtain that $S=aP^{1/(x+2y)}$, according to reference [3]. Then, inserting the exponent value 0.75, we obtain $x = 2/3$ and $y = 1/3$. A significant result can be got that the proportion (x:2y) of O₂⁻ and O⁻ existing on the In₂O₃ surfaces was 1:1.

As shown in Fig. 2a, the coexistence of its shakeup satellites peaks further indicated the formation of CuO on the surfaces [1]. In the H₂S-exposed case, the Cu 2p_{3/2} and Cu 2p_{1/2} peaks slightly shifted to lower binding energy. This could be explained by the mixture of CuO and CuS, suggestive of the transformation of CuO to CuS [1]. It could also be observed in Fig. 2b that there is a peak at 161.67 eV in the Gaussian-resolved spectra after exposure of H₂S, which could be assigned to S 2p, corresponding to S₂⁻ of sulfide S species.

The feasible p-n heterojunction will generate between p-type CuO and n-type In₂O₃. On the other hand, the CuO might also be introduced as the catalysts not only to provide an alternative reaction pathway for the chemisorbed oxygen species with lower activation, but also active the species of chemisorbed analytes. In addition, quantum dots possess surface effects capable of high surface activities owing to a large amount of unpassivated dangling bonds, which provide favorable sites for gas adsorption and gas-solid interaction reducing the adsorption and desorption energy demand for the reaction, thereby resulting in the better interaction with target gas at a low temperature.

References

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Summary

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