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Sensitive and Selective H_2S Gas Detection at Low Temperature Employing In_2O_3 Quantum Dots

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Abstract:

Indium oxide (In_2O_3) has been employed for gas sensors as an important candidate. Here we demonstrated the sensitive gas sensors based on In_2O_3 quantum dots synthesized via solvetheramal methodology. A room-temperature films deposition was utilized for sensor fabrication, followed by the Cu salt surface ligand exchange with a moderate annealing treatment. The In_2O_3 CQD-based gas sensors exhibited an excellent H_2S-sensing performance with the response up to 90 upon 5 ppm H_2S with a fast response and recovery time being 72 s and 200 s at the low operating temperature of 37 °C. Their sensitive response and recovery properties combined with the low-temperature fabrication and operation, rendering the devices amenable to rapid H_2S detection with lower power consumption in practical application.

Keywords: Indium Oxide Quantum Dots; Gas Sensor; Ligand Exchange Treatment; Hydrogen Sulfide, Low Temperature.

Introduction

Metal oxide semiconductor nanomaterials has been investigated extensively as promising participants for gas sensor applications contributing to their excellent sensitivity, high response and long-term stability. Among them, In_2O_3 as an important semiconductor with a wide direct bandgap of 3.55 eV-3.75 eV [1] exhibits potential applications for gas sensors, such as for the detection of H_2S. However, both the sensor device fabrication and operating temperatures were high (usually at 200-500 °C) that set a huge obstacle for the realization of miniaturization and integration [2].

Colloidal quantum dots (CQDs) have been studied as an ideal cooperator for applications in solar cells [3], light emitters [4], photodetectors [5] and especially recent years for gas sensors [6-8]. Most importantly, the operating temperature of gas sensors based on CQDs nearly reduced to room temperature. Motivated by this, we presented In_2O_3 CQDs employing a solvothermal processing at 240 °C in oleic acid and oleylamine of indium acetate solution. The as-obtained In_2O_3 CQDs was deposited onto ceramic substrates at room temperature, followed by the surface ligand exchange treatment with a gentle annealing treatment. The In_2O_3 CQDs-based gas sensor devices showed an excellent H_2S-sensing performance with the operating temperature down to 37 °C while the sensor response was up to 90 toward 5 ppm H_2S with a fast recovery time being 200 s.

Experimental details

In_2O_3 CQDs were synthesized following the reference [9]. Generally, 1 mmol (0.292 g) of indium acetate was dissolved in 30 mmol (10 mL) OA and 76 mmol (25 mL) OLA at room temperature and stirred continuously under vacuum for 1 h. Then, the mixture was heated to 240 °C and kept under nitrogen atmosphere for 30 min. After cooling down to the room temperature, the product was transferred to centrifuge and wash with ethanol and N-hexane and eventually, dispersed in N-henane. All the chemicals were employed without any further treatment.

The obtained In_2O_3 CQDs were dripped onto the commercial sensor substrates to fabricate the devices inside a fume hood in air atmosphere at room temperature. Then, an annealing treatment in ambient air at 130 °C for 2 h was carried out after the ligand exchange treatment followed an encapsulation of the devices using a spot welding.

Results

The X-ray diffraction patterns of In_2O_3 powder was showed in Fig. 1. The diffraction peaks

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appeared at Bragg angles (2θ) of 20.9°, 30.62°, 35.48°, 51.04°, 61.02°, corresponding to the (211), (222), (400), (440), (622) planes of the cube In_2O_3 structure. All the peaks were matched with the In_2O_3 and no any additional phase diffraction peaks were detected, indicative of the formation of their perfect crystallization.

Then, we constructed a detail investigation upon In_2O_3 CQDs devices fabricated through the $Cu(CH_3COO)_2$ ligand exchange treatment with a mild annealing at 130 °C for 2 h and the successive dynamic response curve on H_2S exposure/release cycles toward 0.5, 1, 2, 5, 10, 30 and 50 ppm were recorded in Fig. 2. At all the detected gas concentration range, the gas-sensing response tended to saturation upon higher concentration, exhibiting a power law relationship. As demonstrated previously, the sensor response reached to 90 toward 5 ppm H_2S with a fast recovery time being 200 s as the operating temperature down to 37 °C.

Conclusions

Gas sensors based on colloidal In_2O_3 quantum dots were fabricated by a simple drip-coating method in ambient air. Solution processing and low temperature annealing were used to improve the gas sensing performance towards H_2S. The In_2O_3 CQD based gas sensors exhibited excellent H_2S-sesing performance with the response up to 90 upon 5 ppm H_2S with a fast response and recovery time being 72 s and 200 s at a low operating temperature of 37 °C after the surface ligand exchange treatment with a moderate annealing treatment.

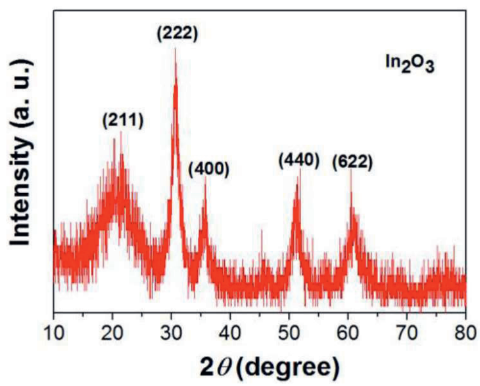

Fig. 1. The XRD pattern of In_2O_3 CQDs

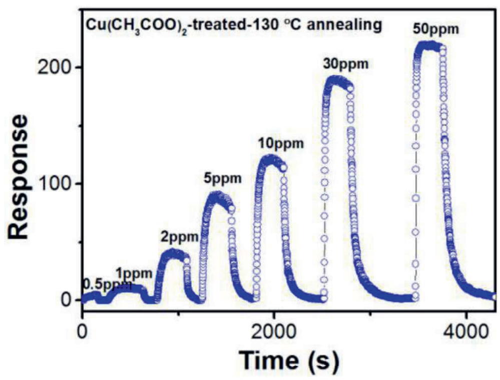

Fig. 2. Response curves of the $Cu(CH_3COO)_2$-treated CQDs sensor toward increasing H_2S gas concentration at the annealing temperature of 130 °C.

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