A Low Temperature Formaldehyde Gas Sensor Based on Hierarchical SnO/SnO₂ Nano-flowers Assembled from Ultrathin 2D Nano-sheets

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Abstract:
In the field of gas sensors, semiconductor metal oxide with high temperature, high energy consumption is an important issue that we need to pay attention to. In this paper, we have successfully synthesized low-temperature formaldehyde gas sensors using hetero-junction generation. Hierarchical SnO/SnO₂ Nano-flowers assembled from ultrathin Nano-sheets were obtained via facile and one-step hydrothermal approach by adjusting the solvent ratio. XRD, FESEM, and FETEM analysis were carried out to investigate the element composition and morphology of hierarchical SnO/SnO₂. The diameter of hierarchical SnO/SnO₂ Nano-flowers is approximately 400-500 nm and the thickness of ultrathin 2D Nano-sheets is about 20nm. Compared with pure hierarchical SnO₂ Nano-flowers, the SnO/SnO₂ gas sensor shows excellent selectivity, good stability, and high response for formaldehyde detection at the best working temperature of 120 °C. The response value can be 8.5 when the concentration of formaldehyde down to 1ppm, moreover, the sensor showed low detection limit (4.96ppb) to formaldehyde. This excellent gas sensing properties of SnO/SnO₂ Nano-flowers can be attributed to hetero-junction of SnO/SnO₂ and unique hierarchical structure assembled from ultrathin 2D Nano-sheets, which can provide more active sites when in contact with formaldehyde. Finally, sensing mechanism can be proved by BET, XPS, and mass spectrometry in detail.

Key words: SnO/SnO₂, Nano-flowers, formaldehyde, gas sensing, ultrathin Nano-sheet

Results and discussion
Fig.1a shows the typical XRD patterns of the as-prepared S2, S4, S4-300 and S6 samples (S2, S4, S6 represents the molar ratio of stannous chloride and sodium citrate are 2: 10, 4: 10, 6: 10, respectively. S4-300 is obtained by calcinating S4 at 300 °C for two hours). Interestingly, the diffraction peaks of S2 and S4 not only be indexed to the SnO₂ (JCPDS file no. 41-1445), but also can be indexed to the SnO (JCPDS file no. 24-1342). The diffraction peaks of S6 and S4-300 could be well indexed as SnO₂ indicating high purity of the products.

The overall morphology (FESEM images have been colored for clarity of observation) of S4 is shown in Fig.1b, indicating that the samples are composed of a large number of Nano-flowers with ultrathin 2D Nano-sheets. The diameter of hierarchical S4 Nano-flowers is approximately 400-500 nm. As shown in Fig.1c, the thickness of all the ultrathin 2D Nano-sheets is about 20nm.

Fig. 2(a, b) show the response of the S4 and S4-300 gas sensor under the nine different formaldehyde concentrations ranging from 1 to 50 ppm at 120°C. It is clearly evident that the response amplitude of the sensor increases gradationally with increasing the gas concentration from 1 ppm to 50 ppm. The response value can be 8.5 when the formaldehyde concentration as low as 1 ppm. Compare with S4 and S4-300, it is worth mentioning that S4 is nearly twice as sensitive as S4-300 for formaldehyde detection at 120°C.

The response and recovery times of gas sensor utilizing S4 and S4-300 as sensing material were investigated toward formaldehyde with the concentration of 50 ppm at 120°C. According to data of Fig. 3, the response time and recovery time of S4 gas sensor are approximately 3 s and 42 s, respectively. At a low temperature of 120°C, S4's extremely excellent gas sensitivity sufficient to prove its significance in the detection of formaldehyde.
Fig. 1 (a) XRD patterns of S2, S4, S4-300 and S6. (b, c) FESEM image of S4 NFs

Fig. 2 (a, b) Dynamic response of the gas sensor under the different formaldehyde concentrations at 120 °C.

Fig. 3 Response and recovery characteristic of the gas sensor under formaldehyde concentration of 50 ppm at the operating temperature of 120 °C.

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**References**

