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Excellent Formic Acid Sensors Based on CuO Loaded SnO_2/Zn_2SnO_4 Hollow Nano-cubes

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Abstract :

Formic acid is a flammable substance, and gaseous formic acid is easy to cause human skin itching. An explosive mixture will form when formic acid vapor is mixed with air. It can cause an explosion once the mixture is exposed to open flame and high heat. In this article, $ZnSn(OH)_6$ hollow nano-cubes were prepared by a simple co-precipitation method, and then CuO loaded SnO_2/Zn_2SnO_4 were synthesized by impregnation and high temperature calcination method. FESEM and FETEM analysis demonstrate that the diameter of CuO loaded SnO_2/Zn_2SnO_4 hollow Nano-cube is about 700nm and the thickness of the hollow Nano-cube is 100nm. Gas-sensing properties of the CuO loaded SnO_2/Zn_2SnO_4 hollow Nano-cubes were tested and analyzed. The results indicated that this composite had a good response towards formic acid. At the same time, the optimal operating temperature, detectable concentration range, detection limit, and response recovery characteristics were evaluated. It was found that the gas-sensing properties of CuO loaded SnO_2/Zn_2SnO_4 hollow Nano-cubes on formic acid were significantly improved compared with SnO_2/Zn_2SnO_4(named Z/S_0) hollow Nano-cubes without CuO, and the gas sensitivity is highest when 1.0mol％ CuO loaded SnO_2/Zn_2SnO_4(named $Z/S_{1.0}$) at best operating temperature 220℃. This excellent gas-sensing enhancement is due to the special contact of CuO with SnO_2/Zn_2SnO_4 hollow nano-cubes, such contact can provides hetero-junction between CuO and SnO_2/Zn_2SnO_4. Therefore, the formation of hetero-junction is very responsible for enhancement of gas sensitivity.

Key words: formic acid, CuO, Zn_2SnO_4/SnO_2, gas sensor, hetero-junction

Results and Discussion

The crystallographic structure of the products including the Z/S_0 and the final products were examined by XRD shown in Fig.1. As can be seen from Fig.1, small peak of CuO gradually appears on the diffraction peak as the increases of CuO.

The SEM image of the synthesized Z/S_0 samples was provided in Fig.2. It can be seen that the synthesized Z/S_0 cube is uniform and the particle diameter is about 700 nm. And the obtained cube has a pronounced hollow structure, the wall thickness of a single cube is about 100 nm.

From Fig. 3 it can be seen that the responses of the Z/S_0 and $Z/S_{1.0}$ vary with operating temperatures. At operating temperatures lower than 220℃, the response gradually rises with the increase of the operating temperature, and the response reaches the maximum value of 66.2 at 220℃. However, above 220℃, the response decreases on increasing the operating temperature. So the best working temperature of sensors is 120℃. And $Z/S_{1.0}$ response to 50 ppm formic acid is much higher than Z/S_0, more significantly, the former responds twice as fast as the latter.

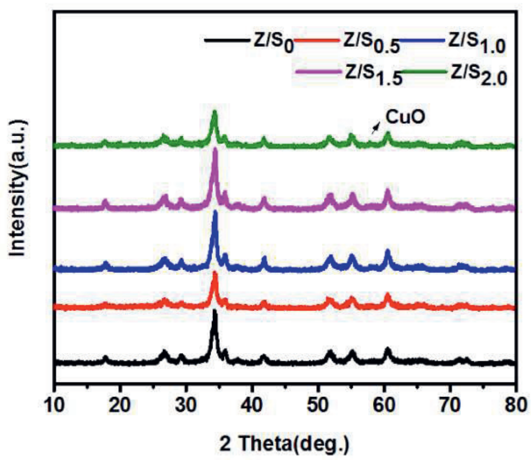

Fig.1 The xrd image of the synthesized sample.

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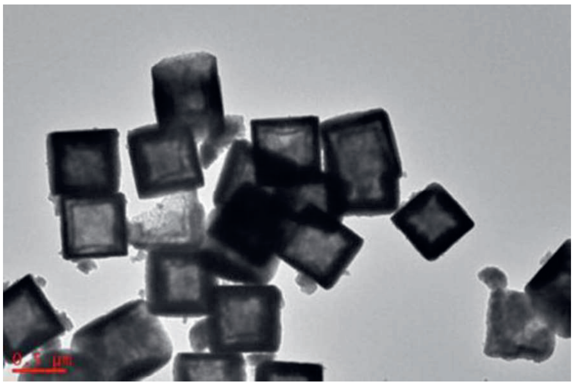

Fig.2 TEM image of Z/S$_0$.

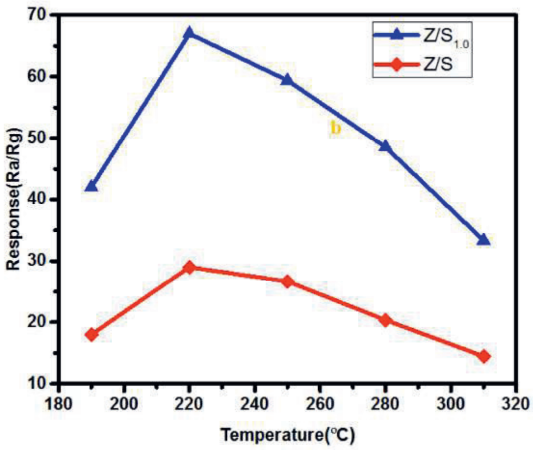

Fig.3 Responses of the Z/S$_0$ and Z/S$_{1.0}$ vary with operating temperatures.

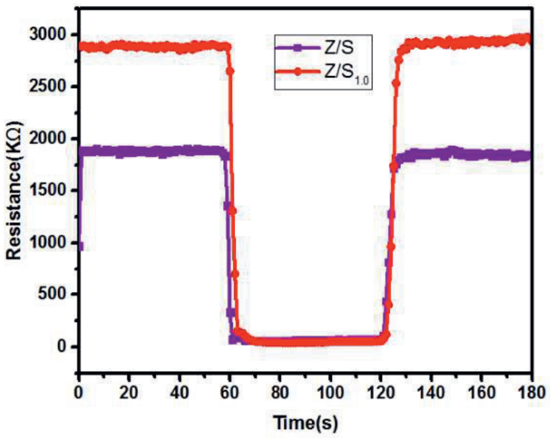

Fig.4 Resistance curve of the sample to 50 ppm formic acid at 220℃.

Fig.4 shows the resistance curves of the two sensors in response to 50 ppm formic acid. From the figure, we can see that the resistance of Z/S$_{1.0}$ in air is far higher than Z/S$_0$, which can visually prove that there is a PN junction in material of Z/S$_{1.0}$. Since the presence of PN junction increases and the increases Ra of the sensor, the sensitivity to formic acid which calculated as S = R_a/R_g will increased.

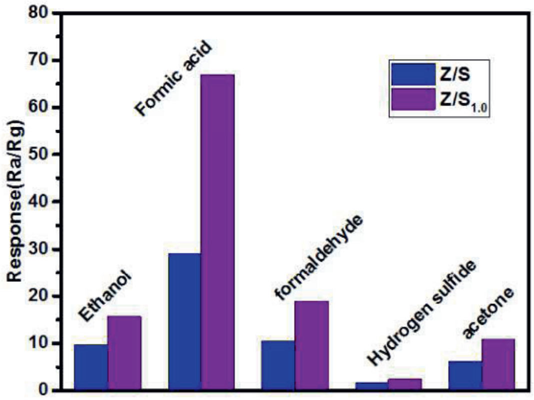

Fig.5 The response of the sample to different gases of 50 ppm at 220℃.

Fig.5 shows the selectivity of the two gas sensors for five different gases at 220℃. From Fig. 5, it can be concluded that among all the five tested gases, the response of the Z/S$_{1.0}$ to formic acid is the highest, and is approximately 2–3 times than to other gases. These phenomena show that the Z/S$_{1.0}$ material has very good application prospects for the detection of formic acid.

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