

Enhanced acetone sensing properties of Eu-In₂O₃ nanotubes with bumps

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Pure and Eu-In₂O₃ nanotubes with bumps were synthesised via electrospinning and calcination method. The crystal structure and morphologies of the as-prepared materials were characterised by X-ray diffraction (XRD), energy-dispersive spectrometer and scanning electron microscopy (SEM), respectively. The SEM images displayed the unique nanotube structure which is constructed with bumps on the nanotube surface. Tests on gas sensing properties validated that the response of Eu-In₂O₃ nanotube sensors to 20 ppm acetone was up to 20 at 240°C which was 3.4 times larger than that of the pure (5.8) and the response and recovery times were 3 and 90 s, respectively. The sensor could detect 200 ppb acetone with a response of 2. It showed excellent selectivity to acetone and sorted acetone from ethanol successfully which has similar properties with acetone.

1. Introduction: In₂O₃, as an *n*-type oxide semiconductor, has caught the eye for its stable, excellent chemical, low cost and non-toxic nature in recent years. A wide range of one-dimensional In₂O₃ nanostructure such as nanoband, nanoparticle, nanofibre and nanotube were synthesised to fabricate gas sensors for monitoring hazardous [1–3]. Among these structures, nanotubes are much helpful for gas sensing properties because of a relatively large contact area and efficient mass transport compared with other nanostructure. However, the pure In₂O₃ nanotube sensors show poor sensitivity. Doping other elements especially the rare earth elements has been advocated as an effective and simple way to improve gas sensing properties of material because of their good thermal stability and high chemical reactivity. For example, the doping of RE (RE = Gd, Tb, Dy, Ho, Er, Tm, Yb) significantly improved sensitivity of In₂O₃ nanotube sensor to H₂S [4]. Eu is on the lists of rare earth elements and expected to enhance gas sensing properties. However, attention is paid to the effect of Eu doping on electrical conductivity and optical properties rather than gas sensing properties. Therefore the sensor based on Eu-In₂O₃ nanotube is rarely reported. Thus, its instructive to explore the sensing characteristics of In₂O₃ after doping Eu. On the other hand, acetone is highly flammable and has damage to central nervous system. Thus, there is an urgent need for the development of acetone sensor with high sensitivity, good selectivity.

In this work, we fabricated a special structure of Eu-In₂O₃ nanotubes with granular protuberance through the single-nozzle electro spinning and annealing method. Tests showed that gas sensing properties of In₂O₃ nanotube sensor had been improved significantly by doping Eu. This sensor has reached the practical requirements. Compared with other acetone sensors based on such as ZnO, ZnFe₂O₄ and Ag₂WO₄, it owns lower working temperature, better selectivity and higher sensitivity [5–7].

2. Experiment: 0.32 g of In(NO₃)₃, 0.36 g polyvinylpyrrolidone and a certain amount of Eu(NO₃)₃ were added into the mixture of 0.5 g N,N-dimethylformamide and 5.2 g ethanol. The precursor solution was obtained after 8 h for magnetic stirring at room temperature. The precursor solution was injected into a single stainless steel capillary with 12 kv for electro spinning.

The as-obtained samples calcined were mixed with proper amount of deionised water and coated on a ceramic tube to fabricate gas sensors. The sensing measurements of sensors were tested in a closed stainless steel chamber connected to a precision temperature

controller for heating. The real-time change of resistance which changed with operating temperature and gas concentration was synchronously recorded by computer. The response was defined as the ratio of R_a/R_g , which is calculated automatically by computer, wherein R_a and R_g were the resistance of sensor in the air and in tested gas, respectively (RH~20%).

3. Results and discussion: The X-ray diffraction (XRD) pattern of In₂O₃ samples in Fig. 1 is in good agreement with JCPDS card no. 06-0416 and no additional peaks can be observed which indicates that the samples are purity. The XRD pattern has little change after doping Eu. Fig. 1 reveals that Eu was doped in the lattice of In₂O₃. The content of In, O and Eu were 75.79, 18.04 and 6.17 wt%, respectively (Fig. 2).

As can be seen in Figs. 3a and b, In₂O₃ nanotubes with unsmooth surface are long and uniform on the whole. The Eu-In₂O₃ nanotubes were constructed with bumps on the surface shown in Figs. 3c and d. Doping Eu may produce more nucleation sites and gather more atoms, resulting protrusions were much more pronounced than before.

As known, the sensitivity of the sensor is greatly affected by operating temperature [8]. Fig. 4 illustrates the response of pure and Eu-In₂O₃ sensors to 50 ppm acetone under different temperature. The sensitivities of both sensors improve with an increased temperature. At 240°C, In₂O₃ and Eu-In₂O₃ exhibit the maximum sensitivity. As the temperature further increases, the response decreases. This phenomenon can be explained as follows. At low

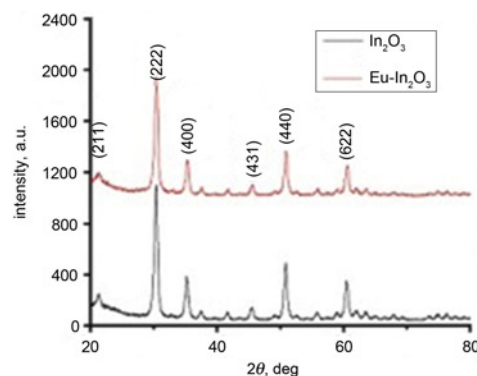


Fig. 1 XRD patterns of In₂O₃ and Eu-In₂O₃ nanotubes

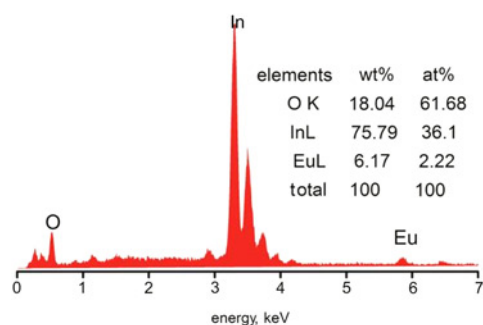


Fig. 2 Energy-dispersive spectrometer spectrum of Eu-In₂O₃ nanotubes

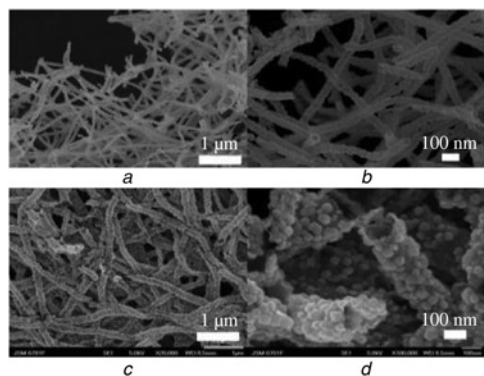


Fig. 3 SEM images of pure (a and b) and Eu-In₂O₃ nanotubes (c and d)

temperature the reaction between oxygen species and target gas is weak. Along with the increase of temperature, the reactive rate is accelerated until a dynamic equilibrium between adsorption and desorption is obtained and the sensors reach the optimal state. If the temperature ascended beyond 240°C, desorption was dominant and the concentration of chemisorbed oxygen decreases, and the response of sensors decreases sharply [9]. Therefore, the optimum operating temperature is 240°C. At 240°C, the response of Eu-In₂O₃ nanotube sensors to 50 ppm acetone was 30 which is 3.4 times higher than that of the pure (8.8). Thus, the acetone sensing properties of In₂O₃ nanotube sensor was enhanced remarkably by doping Eu.

Fig. 5 shows the response and recovery curve of the Eu-In₂O₃ sensor to 20 ppm acetone at 240°C which exhibits an immediate response (3 s) and a good repeatability of the sensor.

When the acetone concentration is in the range of 0.2–100 ppm, the response of Eu-In₂O₃ sensor is linearly correlated to the concentration as shown in Fig. 6. The responses of sensor are up to 59.5

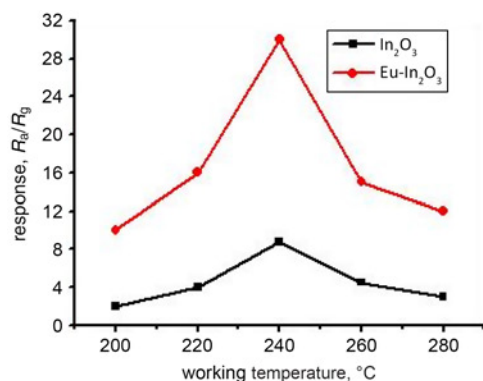


Fig. 4 Response of pure and Eu-In₂O₃ nanotube sensors as a function of working temperature

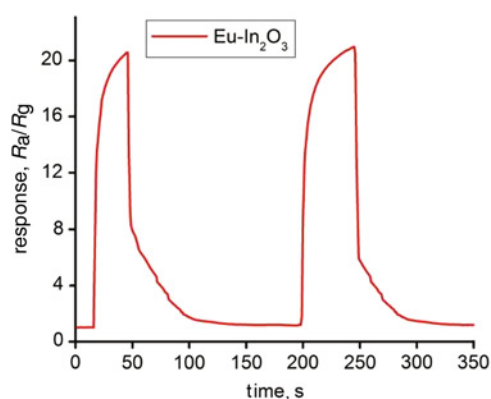
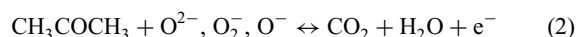
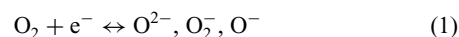


Fig. 5 Response and recovery curve of Eu-In₂O₃ nanotube sensors

and 20 to 100 and 20 ppm acetone, respectively. 200 ppb acetone can be detected with response of 2. Evidence here indicates that Eu-In₂O₃ nanotube sensor is potential for acetone monitoring.

It is seen that Eu-In₂O₃ nanotube sensor had the highest sensitivity to acetone, followed by ethanol (Fig. 7). Generally, it is hard for gas sensor to distinguish acetone and ethanol because of similar properties. For In₂O₃, the ratio of response to 20 ppm acetone and ethanol is 1.8. For Eu-In₂O₃ sensor, the ratio is 2.5 which indicates that In₂O₃ sensor exhibits better selectivity to acetone after doping Eu. This is presumably caused by the functional carbonyl group (C=O) in acetone while ethanol has hydroxyl group (–OH). Acetylbenzene and acetidin have the same C=O bond with acetone. That is why the Eu-In₂O₃ could not select acetone from them. The above results prove that the selectivity of In₂O₃ nanotube sensor is improved by doping Eu.

The mechanism of acetone-sensing is explained as the change in resistance of sensors. In the air, oxygen adsorbs on the surface of nanotubes, and creates chemisorbed oxygen by capturing electrons through (1), leading to increase of resistance. When acetone is introduced, it will react with chemisorbed oxygen, releasing electrons through (2), resulting in a decrease on resistance. A change in resistance is observed.



The enhanced response of Eu-In₂O₃ sensor can be classified into the following aspects. Bump structure makes Eu-In₂O₃ nanotube larger surface-volume ratio for reactions and provides more reactive sites

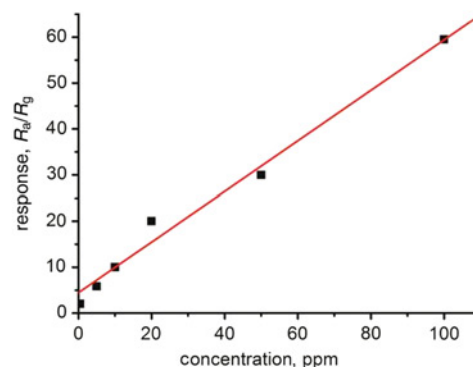


Fig. 6 Response of Eu-In₂O₃ nanotube sensors as a function of acetone concentration

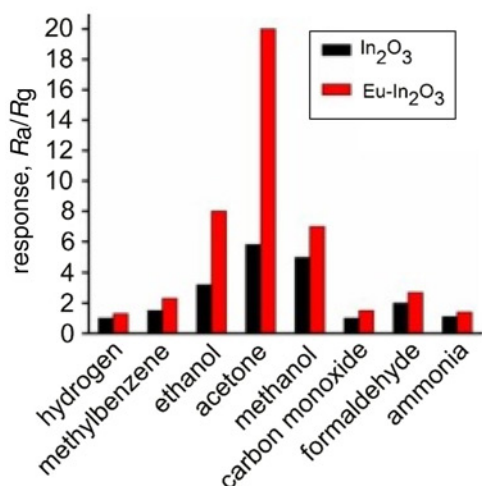


Fig. 7 Response of pure and Eu-In₂O₃ nanotube sensors to 20 ppm different gases

than normal tube [10, 11]. The number of oxygen vacancies will increase due to the substitution of Eu for In. The bump is expected to enhance the efficiency of electron transport. More electrons are trapped by the increased oxygen vacancies during transmission [12]. Thus, the Eu-In₂O₃ sensor has a higher resistance which increases the response. Besides, Europium will speed up the reaction rate as a catalyser which leads to more electrons being released.

4. Conclusion: We fabricated pure and Eu-In₂O₃ nanotubes using electro spinning and calcination method. The scanning electron microscopy (SEM) images revealed that the surface of Eu-In₂O₃ nanotube was distributed with bumps. Studies on gas sensing properties illustrated that the Eu-In₂O₃ nanotube has better acetone sensing properties than pure. The response of Eu-In₂O₃ nanotube sensors was about 20 to 20 ppm acetone at 240°C which is 3.4 times higher than that of the pure (5.8). The sensor could detect 200 ppb acetone with value of 2. Besides, the Eu-In₂O₃ nanotube sensor possesses good selectivity to acetone. It reveals that the Eu-In₂O₃ sensor has potential to be used as acetone sensor.

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6 References

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