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Aliovalent-Doping-Strengthened Ethylene Sensor

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Summary:
A simple and reliable ethylene sensor was fabricated based on W-doped Sb_2MoO_6, which presented excellent responses toward 2-10 ppm ethylene, with high sensitivity, good selectivity, low LOD (24 ppb), excellent repeatability (~100 cycles) and long-term stability (within 45 days). The decreased grain size, abundant defects, proper size mismatch and increased charge separation capability contribute to the enhanced sensing properties. Besides, the sensors were applied in VOCs detection of unhusked rice to demonstrate the practical application potential in rice mildew evaluation.

Keywords: gas sensor, ethylene, rice mildew, heteroatom dopant, room temperature

Background

Ternary extrinsic semiconductor intentionally inserted by transition metal dopants as ionized donors through the substitution of the original atom position and interstitial doping in crystal structure has been reported as a feasible approach for strengthening the electronic properties [1, 2]. Compared with native transition metal atoms, the d-orbitals of transition metal dopants show various localizations, impacting the spatial delocalization of the discrete energy level, and thus resulting in the alteration of the band structure, and the redistribution of the density of states (DOS) around the Fermi level which is in proportion to the electron transition probability [3, 4]. It is worth stressing that, an evident drop in ionic conductivity will happen accompanied by the dopant concentration and atom size exceeding the optimum [5].

Ethylene was identified as a typical volatile organic compound (VOC) from the metabolism of several common fungi. The specific role of ethylene in fungal metabolism remains unclear at present. On the whole, the ethylene production has been demonstrated displaying upwards tendency parallel with the growing fungi quantity, which serves as a valuable point of reference for identifying moldy grain.

Description of the New Method or System

A facile one-step solvothermal approach was used to synthesize W-doped Sb_2MoO_6 (SMO) with different W:Mo molar ratios of 2.5%, 5%, 7.5% and 10%, named as W-2.5, W-5, W-7.5 and W-10. The sensing layers were coated onto an alumina substrate (6*30 mm) with Pt electrodes by a droplet coating method. The gas-sensing test was performed via a four-channel gas sensing testing instrument, which measures electrical resistance signals of the corresponding channel in highly pure air and target gas. All the experiments conducted in dry air were carried out at RT.

Results

Fig. 1 displays the EBSD image and line-scan analysis, signifying that the W atoms are successfully doped and uniformly dispersed.

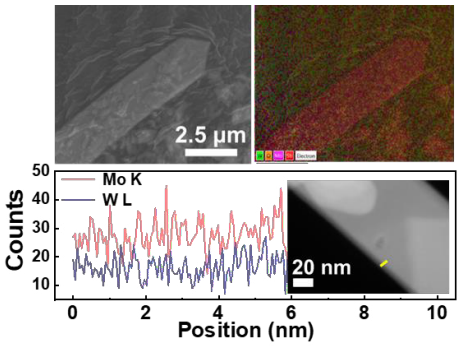

Fig. 1. EBSD and line-scan analysis of W-5.

Fig. 2 shows that the content of doped W^{4+} obviously enhances the sensing performance due to the proper size mismatch compared with Mo^{6+}, contributing to distortion in the crystal lattice, improving carrier mobility and strain-induced changes in conductivity. Besides, effect of doping W ions with various valence states on the adsorption energy was explored through DFT calculation.

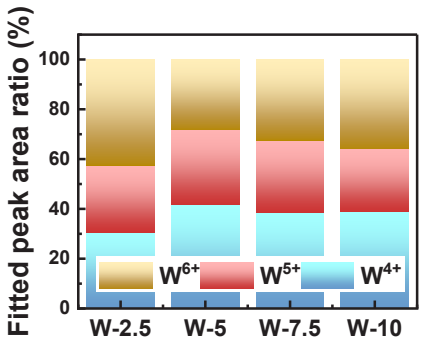

Fig. 2. Fitted peak area ratios of different W dopants with various valence states for W-doped samples.

It can be intuitively observed in Fig.3 that the W-5 shows the best response signature to ethylene molecules ahead of the other four sensors, and all the W-doped samples appear to have higher response values than pure Sb_2MoO_6. LOD of W-5 reached ~24 ppb under RT. Besides, response deviation is below 1 within a 100 repetition cycles.

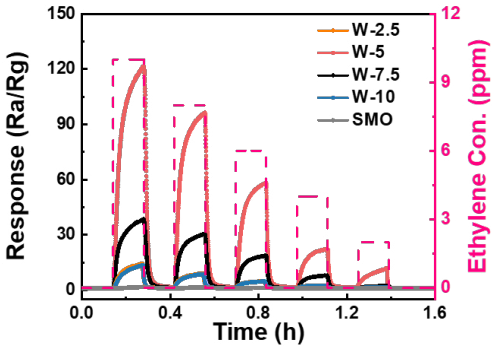

Fig. 3. Transient responses of 10-2 ppm ethylene for all samples at RT.

The response first increases till 40%RH and then decreases. There is an excellent linear relationship between response and ethylene concentrations, and the calculated LODs are all at the ppb levels. Besides, low response drifts were calculated of ~0.2% and ~5.0% under 20%RH and 60%RH.

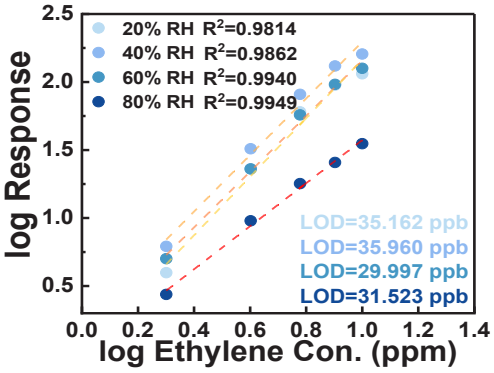

Fig. 4. Linear relationship between response and gas concentration for W-5 under various RH and corresponding calculated detection limit.

Fig. 5 exhibits exponential relationship between response and storage time during 120 days with R^2=0.972, demonstrating that fabricated sensors proved to be highly sensitive to the change of mildew smell of unhusked rice during different storage periods. Besides, excellent selectivity towards other interfered gases generated during rice storage ($S_{ethylene}/S_{interference\ gas}$ > 10^2) was exhibited, which further confirmed feasibility of practical application.

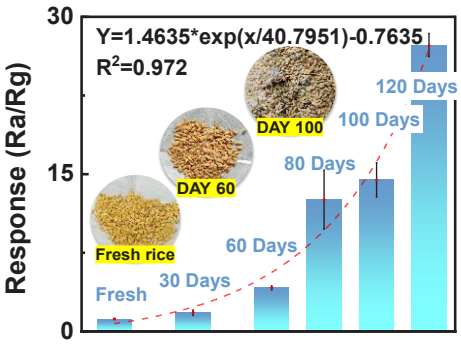

Fig. 5. Responses of the W-5 sensor as a function of storage time measured at RT under exposure to odors from 50 g in a 100 ml cell unhusked rice and the corresponding released ethylene concentration.

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