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WO_3/ SnS_2 Hybrid Material for ppb-level NO_2 Detection

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Summary:

Heterostructures exhibit superior performance, due to strong interfacial interactions, compared to their single-component structures. Herein, we demonstrate the effectiveness of a hybrid structure of tungsten trioxide (WO_3) nanoneedles loaded tin disulfide (SnS_2) nanosheets, for NO_2 detection at law temperature. The co-existence of both materials is confirmed by FESEM and EDX. Furthermore, the impact of SnS_2 material on the WO_3 gas-sensing performance was demonstrated by the sensor's response to 800 ppb of NO_2 at law temperature, where the response of WO_3/SnS_2 was amelioration by 5 folders compared to bare WO_3. Notably, the WO_3/SnS_2 heterostructure exhibited high sensitivity toward NO_2 at the ppb level, operating efficiently at room temperature.

Keywords: Gas sensors; TMDs; SnS_2; WO_3; AACVD; APCVD; nanomaterials.

Background, Motivation and Objective

Tungsten oxide (WO_3) is a versatile n-type semiconductor with a band gap of 2.6–2.8 eV, which is a conventional type of gas-sensing material. Its wide band gap and excellent gas-sensing properties make it a strong candidate for detecting various gases such as NO_2, H_2S, acetone, NH_3, CO, and others [1]. Nonetheless, its high operating temperature, high power requirements, and lack of selectivity have triggered a hunt for new gas-sensing materials or structures with better response and selectivity at room temperature. Transition metal dichalcogenides (TMDs) nanostructured materials possess unique physical and chemical properties, making them promising candidates for electrically transduced gas sensors. Among TMDs, tin disulfide (SnS_2) nanostructure demonstrates excellent characteristics for gas sensing applications, such as a large surface area, abundant active sites, high selectivity, as well as long-term stability [2]. In an attempt to address the shortcoming observer in WO_3 and inherent its limitations for gas sensors, scientists have focused on creating hybrid nanocomposites of metal oxides and Transition metal dichalcogenides (TMDs) nanomaterials in order to produce heterojunctions and attain enhanced gas-sensing performance with tunable electronic properties that surpass the capabilities of a single material. NO_2 is one of the most hazardous air pollutants, that poses serious risks to soil, water, and the atmosphere. It plays a significant role in the production of ozone layers, acid rain, and photochemical smog. Extended exposure to NO_2 concentrations above 3 ppm can lead to severe respiratory illnesses and even death. Therefore, it is crucial to monitor NO_2. Here, we report the successful synthesis of WO_3\SnS_2 heterostructure using the combination of aerosol assisted and atmospheric pressure chemical vapor deposition methods, (AACVD and APCVD), for ppb traces level detection of NO2 at temperatures near the one of the ambient.

Description of the New Method or System

The first step is the direct growth of WO_3 nanoneedles onto alumina substrate via aerosol-assisted chemical vapor deposition (AACVD) of 50 mg tungsten hexacarbonyl ($W(CO)_6$) dissolved in a mixture of 20 mL of acetone and methanol, at temperature of 400ºC. Herein, 0.5 L/min of nitrogen was used as a carrier gas. Subsequently, SnS_2 nanosheets were synthesized via an ambient-pressure chemical vapor deposition (APCVD) sulfurization process, using SnO_2 and sulfur powders as precursors, with argon as a carrier gas. In the final step, the SnS_2 nanosheets are airbrushed onto the surface of the pre-grown WO_3 nanoneedles to form the hybrid heterostructure.

Results

First, we investigated the morphology of the WO_3 nanoneedles, grown directly on top of the alumina substrate with AACVD, displayed in Fig. 1(a). The results prove the formation of WO_3 nanoneedles, with a regular morphology and uniform size, distributed homogenously over the electrode area. Fig. 1(b) represents the FESEM image of the structure WO_3\SnS_2 which confirmed the successful growth of SnS_2 nanosheets, with a good hexagonal shape, on top of WO_3.

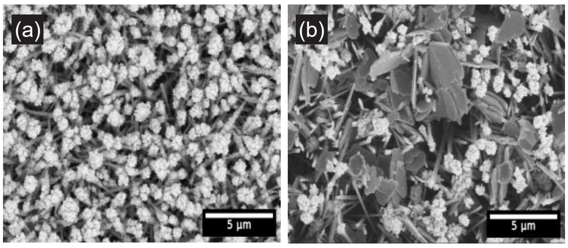

Fig. 1. FESEM images of (a) WO_3, (c) WO_3/SnS_2 nanostructures.

In order to verify the composition and the structure of our materials we examined our samples using energy-dispersive spectroscopy (EDX) techniques. WO_3 spectra is represented in Fig.2(a) and WO_3\SnS_2 spectra is represented in Fig.2(b). The results confirm the growth of WO_3 in the first stage, then the simultaneous presence of multilayers of WO_3 and SnS_2 materials proven the formation of the WO3/SnS2 heterostructure.

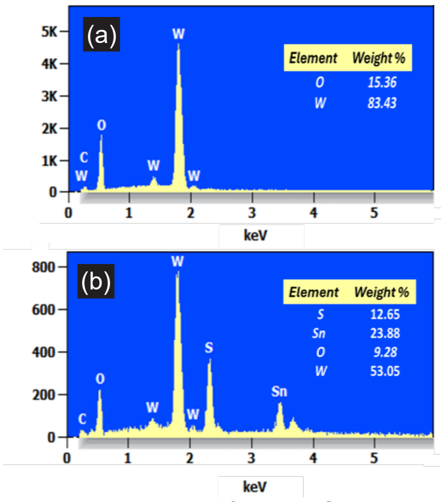

Fig. 2. EDX spectra of (a) WO_3, (b) WO_3/SnS_2 nanostructures.

For gas sensing measurement, we tested bare WO_3 and hybrid WO_3\$SnS_2$ sensors towards 800 ppb of NO_2, at different operating temperatures (RT, 100, and 150ºC). At low operating temperatures, bare WO_3 exhibited significant baseline resistance drift, and even at 150 °C, its sensitivity remained insufficient, as illustrated in Fig. 3. In contrast, the hybrid WO_3\$SnS_2$ sensor demonstrated improved stability and significantly higher sensitivity at low temperatures, achieving its optimal response at 150 °C. Moreover, at room temperature, WO_3\$SnS_2$ was able to detect the target gas at ppb-level, with enough sensitivity. Fig. 4 shows the real sensors responses as a function of time toward 800 ppb of NO_2 at 150ºC. Both sensors exhibited an n-type semiconductor behavior, increasing resistance upon exposure to oxidizing gas and decreasing it upon exposure to dry air.

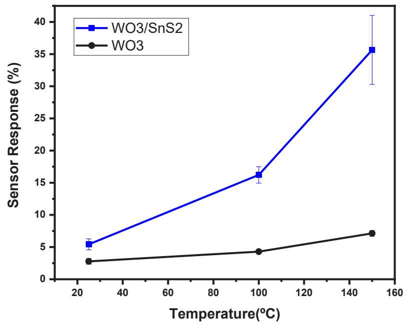

Fig. 1. Sensors responses toward 800 ppb of NO_2 as a function of temperature.

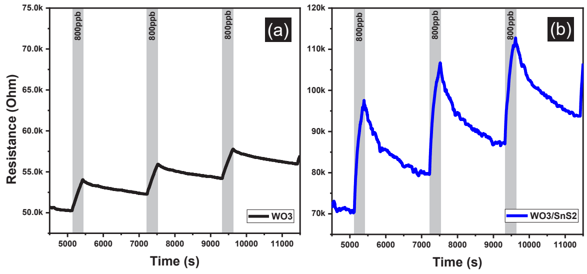

Fig. 2. Responses of sensors (a) WO_3, and (b) WO_3\SnS_2 at 150ºC toward 800 ppb of NO_2.

At low temperatures, the bare WO_3 sensor showed two primary limitations which are poor response and slow recovery. The sensitivity of the sensor was greatly increased by the addition of SnS_2 nanosheets. The WO_3\SnS_2 hybrid sensor's response was five times greater than that of pristine WO_3, as seen in Fig. 4. Efforts are ongoing to further improve the recovery characteristics through extended recovery times and the application of UV illumination. Investigations into humidity cross-reactivity are also in progress; more information will be provided at the conference.

Conclusions

This study presents a facile and scalable method for synthesising a WO_3\SnS_2 heterostructure, demonstrating its enhanced selectivity, response speed, and stability for ppb-level NO_2 detection at low operating temperatures.

References

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