

Hexagonal WO₃ nanorods for Selective H₂S Detection: Synthesis, Characterization, and Gas Sensing Properties.

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Summary:

Hydrogen sulfide (H₂S) is a hazardous gas that necessitates reliable detection in industrial and environmental settings. Hexagonal tungsten oxide (h-WO₃) has gained attention as a promising sensing material due to its high surface reactivity and structural stability. This study presents the hydrothermal synthesis of h-WO₃, characterized by XRD, Raman spectroscopy, and SEM. The material exhibited outstanding selectivity and sensitivity toward H₂S, attributed to its porous structure and surface chemistry. These findings underscore the potential of h-WO₃ for effective H₂S gas sensing applications.

Keywords: Hydrogen sulfide (H₂S), Hexagonal tungsten oxide (h-WO₃), Metal oxide semiconductors (MOS), gas sensor.

Hydrogen sulfide (H₂S) is one of the most common highly toxic, flammable, and corrosive gas emitted from industrial processes, natural gas production, and wastewater treatment, posing severe risks to human health and the environment [1]. Effective detection of trace amount H₂S is crucial for workplace safety and environmental monitoring. Metal oxide semiconductors (MOS), such as WO₃, have gained attention as gas-sensing materials due to their structural defects, high sensitivity, stability, oxygen vacancies [2]. Among various WO₃ phases, hexagonal tungsten oxide (h-WO₃) exhibits superior gas-sensing performance compared to monoclinic (m-WO₃). While m-WO₃ has been widely studied due to its high stability, bulk m-WO₃ exhibits poor gas sensitivity at 25–500°C, particularly toward gases like CO and H₂S. This limitation has driven the need to enhance WO₃'s gas-sensing performance. Szilágyi et al. demonstrated that h-WO₃ outperforms m-WO₃ in detecting low concentrations (10 ppm) of H₂S [3]. The unique structural advantages of h-WO₃ such as its large hexagonal and trigonal tunnels contribute to a high specific surface area, facilitating superior gas adsorption and reactivity. In the current research, h-WO₃ was synthesized by a hydrothermal process and carefully examined by X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM) and transmission

electron microscopy (TEM) to define its structural and morphological features against sensing performance.

Synthesis of pure h-WO₃

For synthesis of pure h-WO₃ 285 mg of ammonium metatungstate hydrate (AMT) were dissolved in 10ml of water. The pH of the final solution was kept in the range of pH=1.8-2.0 by adding nitric acid. The prepared solutions have been transferred into Teflon lined autoclaves and kept in a furnace at 180°C for 24 hours. The autoclaves were cooled down to the room temperature. The obtained product was rinsed by water and ethanol 3 times and freeze dried.

Gas sensor preparation

The fabrication procedure for the solid-state gas sensor electrode was as follows: First, the powder material was dispersed in distilled water to form a paste, which was then deposited onto an alumina ceramic substrate with interdigitated Pt electrodes and heating elements. The deposited layer was dried on a hotplate at 100°C for 5 min to evaporate water.

Results and discussion

SEM image of the h-WO₃ nanorods is reported in Fig.1. In the inset is also reported TEM image shows the nanoscale dimension of the nanorods,

consisting of one-dimensional needle-like structures. Linear dimensions of the h-WO₃ rods were 406±100 nm in length and 38±14 nm in diameter.

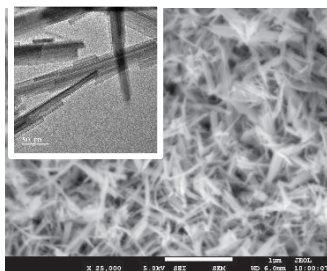


Fig. 1. SEM and TEM images of h-WO₃ sample.

The microstructural characterization by XRD (Fig. 2) and Raman (Fig. 3) measurements, confirmed that nanorods display the hexagonal WO₃ phase.

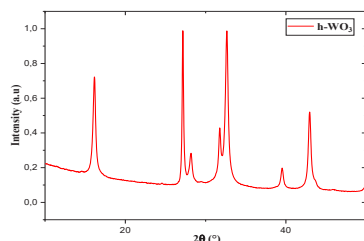


Fig. 2. XRD pattern of h-WO₃ sample.

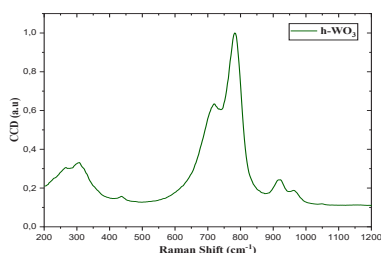


Fig. 3. Raman spectra of h-WO₃ sample.

Gas-Sensing Measurements

Preliminary gas sensing measurements indicated that the h-WO₃ rods based sensor is highly sensitive to H₂S. At the optimal operating temperature of 250 °C, the sensor exhibited a gradual decrease in resistance upon H₂S exposure, followed by a rapid recovery to its baseline resistance (Fig. 4). This behavior confirms the sensor's fast and fully reversible response and recovery to H₂S. Additionally, since the baseline resistance decreased upon H₂S exposure, the sensing mechanism was attributed to n-type semiconductor behavior. Figure 4 presents the calibration curve, where the response (R_a/R_g) is plotted against H₂S concentration (ppm). Based on this curve, the sensor demonstrated a detection limit (LOD) of 11.1 ppb, highlighting its high sensitivity.

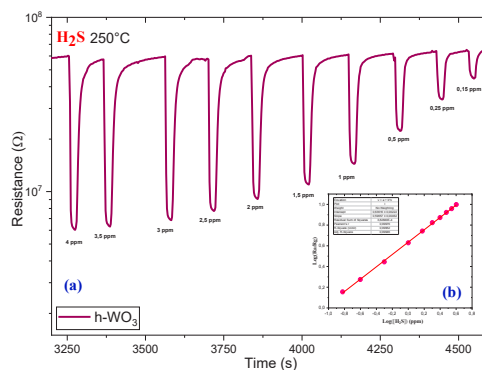


Fig. 4. a) Response of h-WO₃ sensor at the operating temperature of 250°C as a function of H₂S concentration. Inset in b) shows the calibration curve.

Conclusion

h-WO₃ particles were synthesized using an hydrothermal method. Characterization data confirms the hexagonal phase of tungsten trioxide. This material shows promising p-type behavior for detecting reducing gas H₂S with fast response/recovery, making it suitable for environmental and industrial gas sensors. Further studies are finalized to the optimization of sensor performances (sensitivity, selectivity, stability).

References

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