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Gas sensitivity enhancement of WO₃ nano-rods by gold nanoparticles

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Abstract

Tungsten oxide nano-rods were prepared by acidic precipitation from sodium tungstate solution and sensitized with gold nanoparticles prepared by Turkevich method from tetrachloroauric acid trihydrate. In order to prevent aggregation the gold nanoparticles of 18 nm characteristic size were stabilized by methoxy-polyethylene glycol (mPEG-SH) and mixed with hexagonal WO₃. Suspension drops of doped and non-doped WO₃ were deposited on micro-hotplates with interdigitated gold electrodes to measure sensing layer conductivity. Sensor responses of pure and doped WO₃ were measured for NH₃ and H₂S in synthetic air up to 100 ppm at the operation temperature of 140-200 °C. The presence of gold nanoparticles significantly increased the sensitivity for H₂S, whereas for NH₃ the response was not affected. Test results are compared in terms of sensitivity, response time and operating temperature.

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1. Introduction

Nanostructured conductivity type gas sensors in principle exhibit high sensitivity but suffer from lack of selectivity, moderate response and recovery time. Therefore, modification of the crystal structure or surface characteristics may

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lead to improvement of essential sensor parameters, such as selectivity or dynamic properties. In our previous work [1] we described a hydrothermal method for the uniform formation of WO_3 nano-rods and tested their gas sensing properties. It is well-known that addition of nano-sized catalyst such as noble metals and transition metal-oxides typically enhances the gas sensitivity of the layer. The present work describes the effect of the addition of gold nanoparticles to WO_3 suspension. In a first demonstration the sensitivity for H_2S and NH_3 was investigated and compared with the non-sensitized reference.

2. Experimental

2.1. WO_3 nano-rods

In our previous work we synthesized uniform WO_3 nano-rods of 80-120 nm diameter and 4 μm length by hydrothermal method.

WO_3 sol was prepared by dissolving 4,075 g sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) in 100 ml distilled water. Then, the solution was acidified by HCl solution (3 mol/l) to set the pH 1.2. The precipitate was generated by oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) in the mixture and was stirred for 30 minutes at room temperature. A 50 ml volume of the obtained WO_3 solution was transferred to an autoclave, and 3.33 g Na_2SO_4 was added to the sol, and maintained sealed at 180 $^\circ\text{C}$ for 24 h. The precipitates were filtered, washed with water and ethanol carefully to remove possibly remaining ions from the final products. The material was finally dried at 60 $^\circ\text{C}$ [1].

2.2. Gold nanoparticles doped WO_3 nano-rods for sensing

Gold nanoparticles were synthesized by the traditional Turkevich method [2]. A solution made from 222 ml DI water and 6 ml 0.01 M HAuCl_4 trihydrate was heated to boil. 6 ml sodium citrate solution (containing 0.0684 g sodium citrate trihydrate) was added into the boiling solution and boiled continuously for 15 minutes before cooling it down to room temperature. The nanoparticles in large excess were PEGylated using thiol functionalized mPEG-SH, with 2000 Da average molecular weight. The PEGylated nanoparticles were cleaned by centrifuging and re-dispersing in water [3].

The WO_3 powders prepared were dissolved in ethylene-glycol-water-ethanol solution and the solution containing 1nM of stabilized nanoparticles was added to the WO_3 suspension. The mixture was agitated by stirring for 3 minutes, then a single drop was transferred onto the surface of each micro-hotplate. The applied micro-capillary transfer method forms ca. 200 μm diameter spot of the sensing layer (Fig. 1). Applying 15 $^\circ\text{C}/\text{min}$ ramp up heating the chip was annealed at 200 $^\circ\text{C}$ for 20 minutes to remove the solvent and mPEG-SH leading to the formation of separated gold nanoparticles on the WO_3 nano-rods.

3. Results

Functional tests were carried out by depositing hexagonal WO_3 on MEMS based conductivity type sensor structures. Our device is a sandwich structured non-perforated membrane with embedded Pt heater and gold interdigitated electrodes on top. The membrane was released by deep reactive ion etching of Si underneath. The Pt filament and the Au interdigitated electrodes were positioned in the middle of the membrane (Fig. 1b).

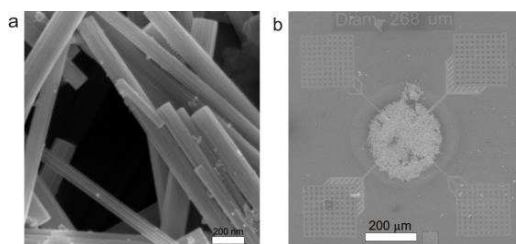


Fig. 1. (a) SEM image of WO_3 nano-rods decorated by separated gold nanoparticles; (b) Top-view of the gas sensor

For NH_3 both sensors exhibited the same response according to the characteristics measured up to 100 ppm (Fig. 2). Due to the geometric constrains and characteristic width of the space charge layer the signals show saturation at around 100 ppm. While the performance of the non-doped sensor is best at 200 °C, the gold sensitized layers require 180 °C for optimum operation.

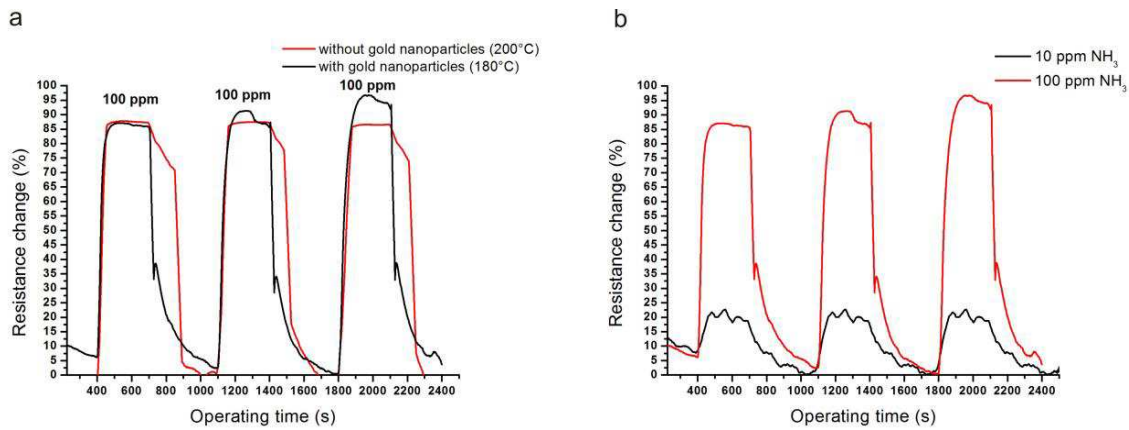


Fig. 2. (a) Relative resistance change profile of non-doped and gold doped WO_3 gas sensors in 100 ppm NH_3 ; (b) Relative resistance change profile of gold nanoparticle-doped WO_3 gas sensors at 180 °C

For H_2S the sensitivity is significantly higher. In this case the effect of gold nanoparticles is obvious: the catalyst sensitized sensors deliver approximately 40% higher signals compared to the non-doped reference (Fig. 3). The geometric constrains of the WO_3 nano-rods in combination with the significant catalytic effect of gold nanoparticles result in a saturation starting around 60 ppm. Sensitized sensors exhibit favourable reproducibility (Fig. 4).

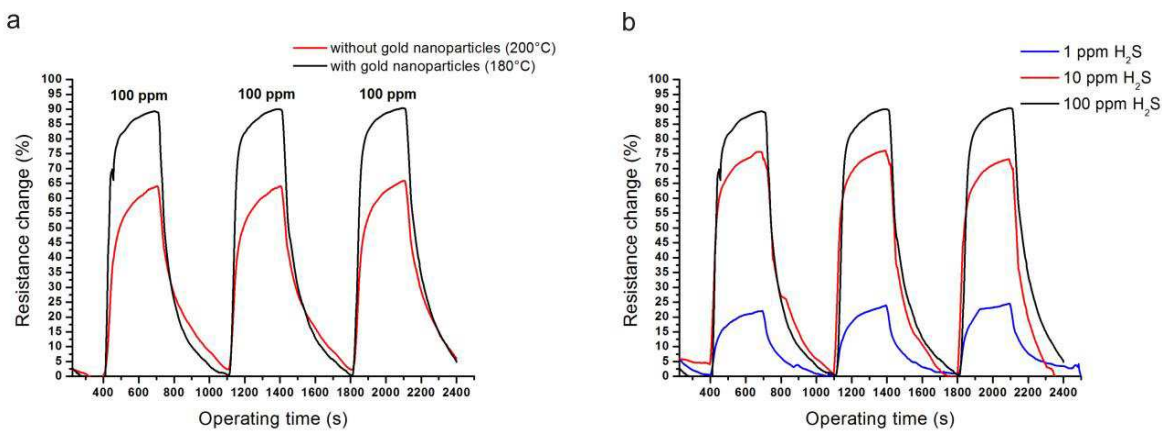


Fig. 3. (a) Relative resistance change profile of non-doped and gold sensitized WO_3 gas sensors in 100 ppm H_2S ; (b) Relative resistance change of gold nanoparticle-doped WO_3 gas sensors at 180 °C

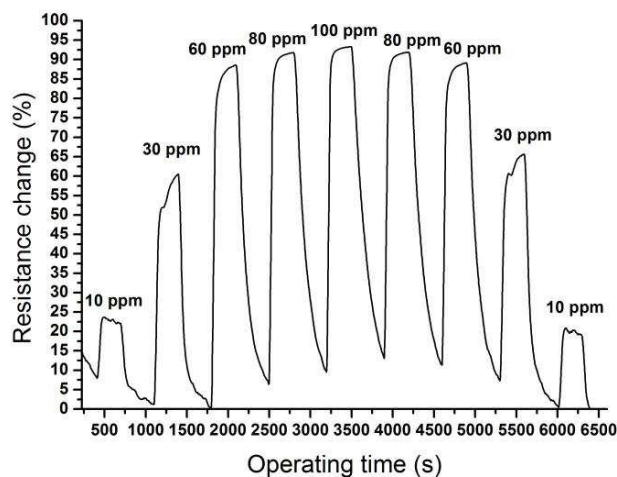


Fig. 4. Relative resistance change of gold nanoparticle-doped WO_3 gas sensors in H_2S gas at $180\text{ }^\circ\text{C}$.

4. Conclusion

The performance of non-doped and gold sensitized WO_3 nano-rod sensors was tested for NH_3 and H_2S response in the concentration range of 1-100 ppm in synthetic air. Gold nanoparticles prepared by the Turkevich method were added to the hydrothermally synthesized hexagonal WO_3 nano-rod suspension to form the sensing layers. Gold doped sensors exhibit higher sensitivity and better reproducibility for H_2S . This property is indicating the potential capability of early alarm in leak-detection. Humidity effects and the detection of NO_x will be the subject of further detailed investigations.

Acknowledgements

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