The Influence of Temperature and Visible Light Activation on the NO₂ Response of WO₃ Nanofibers Prepared by Electrospinning †

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Abstract: Aim of this work is to compare the electrical responses to 100–400 ppb NO₂ gas concentrations of WO₃ electrospun nanofibers both activated by thermal (in the temperature range 25–100 °C) and/or visible light at different wavelengths (Red λ = 670 nm, Green λ = 550 nm, and Purple-Blue λ = 430 nm). WO₃ nanofibers were prepared by mixing a W-O sol-gel transparent solution with a polymeric solution made of PVP and DMF, electospun and subsequently annealed at 450 °C. Regarding gas sensing measurements, Purple Blue light resulted the most effective light source as respect to the others. Light illumination at room temperature revealed to improve both base line recovery and response time, whereas temperature enhances relative response, with a maximum at 75 °C. Light-radiating room temperature gas detection yields a satisfactory response notwithstanding a slight reduction of sensor gas sensitivity. Light induced electrical response mechanisms is presented and discussed.

Keywords: WO₃; nanofibers; light activation; NO₂ sensor

1. Introduction

Thermal activation mode at different operating temperatures (OT) represents so far one of the most common strategies to increase the catalytic activity of metal oxides sensors (MOX) toward gas response [1]. However, drawbacks of the thermal activation mode are yet represented by power consumption and shortened life time of the components. MOX gas response by light activation mode at room temperature has been more recently reported for NiO [2], TiO₂ [3], In₂O₃ [4], and WO₃ [5] respectively. Considering that literature reports have already shown that visible light activation can be easily achieved at room temperature by utilizing WO₃ thick films [5], in this paper we report room temperature NO₂ gas responses of 1D electrospun WO₃ nanofibers thermally and light activated at different wavelengths.

2. Results and Discussion

Figure 1 compares the SEM images for the as deposited (a,b) and annealed (c,d) WO₃ NFs at low (left side) and high magnification (right side), deposited on Si₃N₄ substrates. The formation of a continuous 3D-network of interconnected homogenous nanofibers of around 50 nm diameter is highlighted. After annealing at 450 °C for 1 h, fine nanograins of around 20 nm are visible with a well-developed crystalline structure.
Electrical responses to NO₂ gas were measured in dark conditions and at different visible light sources (Red $\lambda = 670$ nm, Green $\lambda = 550$ nm, and Purple-Blue $\lambda = 430$ nm) in the temperature range 25–100 °C. Figure 2 shows the electrical responses of WO₃ to 400 ppb NO₂ at 25 °C in dark and illuminated conditions. It turns out that the base line resistance (BLR) decreases by switching from dark, red, green and blue light respectively. This behavior can be explained considering that all the investigated light sources yield enough energy to cause the oxygen desorption from the WO₃ surface with associated release of previously-trapped electrons into the conduction band. Furthermore, another evidence coming out from Figure 2 is that by desorbing in dry air, the recovery of the base line is strongly enhanced by light-radiating the sensor surface. To give a figure of the sensor base line recovery ability we introduce the recovery percentage (RP) given by the percentage ratio ($\Delta D/\Delta A$) × 100, where D and A stands for desorption and adsorption respectively (see Figure 2). It turns out that the RPs increase from 9% (dark), to 38% (Red), 55% (green) and 92% (blue). Figure 3 shows a comparison between the electrical responses of WO₃ nanofibers under dark and purple blue light at different operating temperatures (OT) in the range 25 °C–100 °C and different NO₂ gas concentrations (100 ppb–400 ppb). At 25 °C the base line recovery is very poor when desorbing in dark, but it significantly improves under blue light, as previously demonstrated in Figure 2, thus assigning the best performance to purple blue light. Regarding temperature, under both dark and light conditions, heating resulted to enhance the relative response (RR), with a maximum at 75 °C, and the recovery percentage.

**Figure 1.** SEM images of electrospun WO₃ nanofibers. Panels (a) and (b) are respectively low and high magnification of as deposited NFs. Panels (c) and (d) represent the NFs after 1h annealing at 450 °C.

**Figure 2.** WO₃ nanofibers responses at 25 °C to 400 ppb NO₂ under different illuminating conditions.
Figure 3. Comparison of the electrical responses in dark conditions and under purple-blue light ($\lambda = 430$ nm) at different temperatures and NO$_2$ gas concentrations.

However, an inhibiting influence played by light on the relative response is revealed, in particular at 75 °C. We may conclude that light activation mode increases the recovery percentage, whereas thermal activation enhances the relative response. To explain the higher RR$\$s$ in dark as respect to light illumination conditions, we have to consider again that light is expected to activate the desorption of adsorbed oxygen from WO$_3$ surface. Considering now that NO$_2$ sensing is due to the reaction between NO$_2$ and the oxygen adsorbed on WO$_3$ surface, by illuminating the sensor surface, less oxygen species are available to react with NO$_2$, eventually decreasing the relative response of the sensor.

3. Conclusions

We have prepared WO$_3$ electrospun nanofibers and tested to sub-ppm NO$_2$ concentrations by light and thermal activation modes. Room temperature gas sensitivity was comparable in dark and light conditions. A strong enhancement of both base line recovery and response times was displaced under light conditions, suggesting 2D WO$_3$ fibers to be suitable for ppb NO$_2$ detection at room temperature.

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References


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