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NO_2 gas response of WO_3 nanofibers by light and thermal activation

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Abstract

Aim of this paper is to compare the electrical responses to sub-ppm NO_2 gas concentrations of WO_3 electrospun nanofibers both activated by thermal (in the temperature range 25°C - 150°C) and/or light-radiating conditions (Red λ=670nm, Green λ=550nm, and Purple Blue λ=430nm). Blue light resulted the most effective light source with respect to the others. Light illumination at room temperature improves the 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 despite the reduction of sensor gas sensitivity. Light induced electrical response mechanisms are presented and discussed.

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Keywords: Light activation; WO_3; Nano fibers; Metal oxide; NO_2.

1. Introduction

Thermal activation mode at different operating temperatures (OT) represents up to date one of the most common ways to increase the catalytic activity of metal oxides sensors (MOX) toward gas response. In previous studies we demonstrated that WO_3 thin film is suitable to detect sub ppm concentration of NO_2 if thermally activated at operating temperatures (OT) in the range 150°C – 200°C [1-2]. Drawbacks of the thermal activation mode are jet 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 ZnO_2 [3], TiO_2 [4], In_2O_3 [5], and WO_3 [6] respectively. It was demonstrated that by illuminating the WO_3 thick film sensors surface by UV or visible light sources, recovery of the base line as well as the speed of response was improved [6]. Room temperature light

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activated gas sensitivity could be further enhanced in terms of relative response (RR), response time (RT) and recovery of the base line (BLR), by scaling down from 3D (thick) to 2D (thin) and eventually to 1D (Fibers) nanostructures. Considering that literature reports have already shown that visible light activation can be easily achieved at room temperature by utilizing WO_3 thick films [6], in this paper we report room temperature NO_2 gas responses of 1D electrospun WO_3 nanofibers thermally and light activated at different wavelengths.

2. Experimental

WO_3 nanofibers were fabricated by dissolving 0.4g of WCl_6 in 5mL of ethanol in a glow box under nitrogen flow. After 3 days refluxing the transparent precursor solution was mixed with polymeric solution prepared by dissolving 0.17g of polyvinylpyrrolidone (PVP) in 1mL of dimethylformamide (DMF). The final solution was electrospun on rotating silicon nitride (Si_3N_4) substrates with Pt patterned electrodes with an applied tension, distance and flow rate of 14kV, 10cm and 1µl/min, respectively. After spinning, fibers were annealed in an oven for 1 hour at 450°C with a heating rate of 2°C/min. Microstructural investigation was carried out by means of Optical, SEM and XRD techniques. Electrical responses to NO_2 gas (100ppb – 400ppb) were measured at different operating temperature (25°C – 100°C) and at different visible light sources (at the wavelength λ=670nm, λ=550nm and λ=430nm).

3. Morphological characterization

As reported in the experimental section the electrospinning process requires liquid solutions which have been obtained by mixing tungsten alkoxide with a polymeric carrier solution made of PVP solubilized in DMF. After electrospinning deposition, fibers have been thermally treated in order to burn out the polymeric carrier and to enhance WO_3 crystallization. Figure 1 shows the percentage of weight loss versus temperature plots (heating rate 2°C/min) of the polymeric and final solutions. It turns out that by annealing at 450°C for 1 hour, almost all the polymeric carrier is removed whereas the 15% weight left can be assigned to WO_3. This hypothesis is confirmed by XRD of the annealed since a well-developed crystalline WO_3 structure is formed at this temperature.

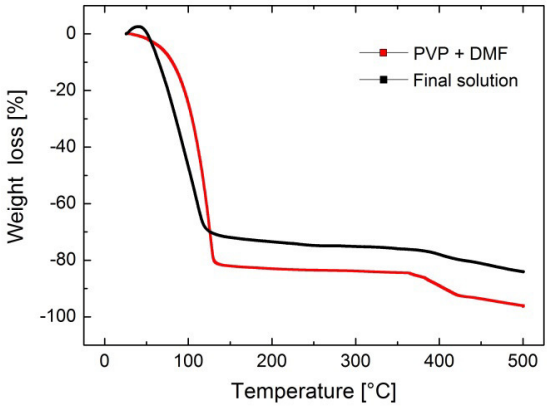

Fig. 1. Percentage of weight loss as function of temperature of the: (red) polymeric solution (PVP+DMF) and (black): final solution (polymeric solution + tungsten alkoxide) up to 500°C.

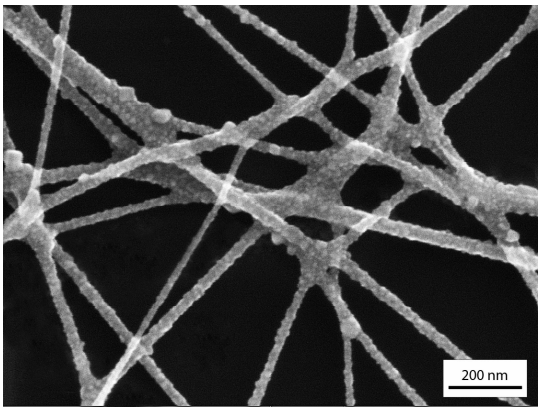

Fig. 2. SEM image of WO_3 nanofibers highlighting the occurrence of a continuous network of fibers, with nanograins of around 20nm.

Figure 2 shows a SEM high magnification picture of WO_3 nanofibers deposited on silicon nitride substrate. The formation of a continuous 3D-network of interconnected homogenous nanofibers of around 50nm diameter is highlighted. After annealing at 450°C for 1 hour, fine nanograins of around 20nm are visible with a well-developed crystalline structure. XRD investigation, carried out on a massive sample fabricated by electrospinning technique under the same experimental parameters, shows the formation of a fine texture of WO_3 crystallites at 450°C.

4. Electrical response

Figure 3 shows the electrical responses of WO_3 to 400ppb NO_2 at 25°C in dark and illuminated conditions. Light sources were set at wavelengths equal to λ=670nm (Red), λ=550nm (Green) and λ=430nm (Purple Blue), respectively. The base line resistance (i.e., the resistance in dry air here identified as BLR) decreases by switching from dark, red, green and blue light respectively. If we define the relative response (RR) as the ratio R_G/R_A (where R_G and R_A are the resistances in gas and in dry air respectively), the RRs values slightly decrease by exposing the WO_3 fibers from dark to blue light conditions according to the first column of Table 1.

Table 1. Sensing characteristics of WO3 fibers as respect to Base line resistance (BLR); Relative Response (RR); Recovery Percentage (RP) and response times (τ_{ads}/τ_{des}) to 400ppb NO_2 at room temperatures and different light wavelengths.

Light source	BLR (Ω)	RR	RP (%)	τ_{ads} (*min*)	τ_{des} (*min*)
Dark (D)	8.9 x 10^5	1.55	9	/	/
Red (RL)	4.5 x 10^5	1.57	38	/	/
Green (GL)	2.5 x 10^5	1.56	55	/	/
Purple-Blue (PB)	1.2 x 10^5	1.48	92	51	60

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 have introduced the recovery percentage (RP) given by the percentage ratio (Δ_D/Δ_A,) x 100, where D and A stands for desorption and adsorption respectively (see Fig. 3). It turns out, according to Table 1, that the RPs increase from 9% (dark), to 38% (Red), 55% (green) and 92% (blue).

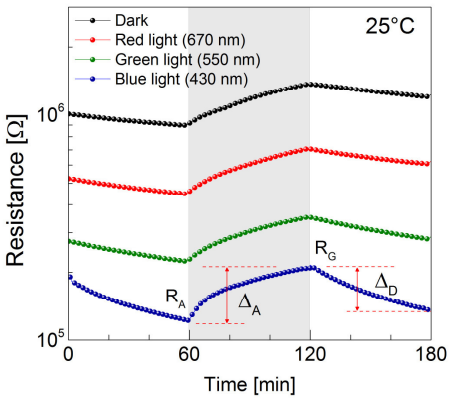

Fig. 3. WO_3 nanofibers electrical responses at 25°C to 400ppb NO_2 under different illuminating conditions.

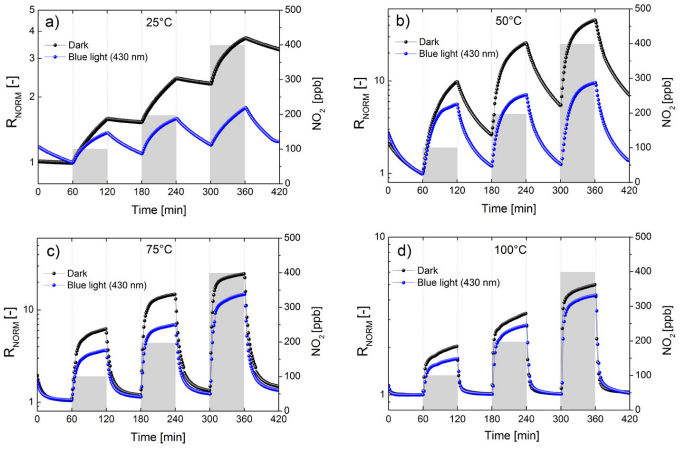

Fig. 4. Comparison of the electrical responses in dark condition and under purple-blue light (λ=430nm) at different temperatures and NO_2 gas concentrations.

There are interesting features worth of discussion to explain the decrease of the base line resistance (BLR), the change of the RRs and the RPs respectively. Regarding the BLR, considering that O_2^- is the prevailing oxygen adsorbed species up to 150°C, considering that the desorption energy of an oxygen atom on a metal oxide material is around 1.5eV it turns out that all the investigated light sources yield enough energy (Red 1.85eV, Green 2.25eV, Blue 2.9eV) to desorb oxygen according to reaction (1):

$$O_2^- + h\nu = O_2 + e\downarrow \qquad (1)$$

According to this reaction an impinging photon is directly adsorbed by surface O_2^-, causing desorption of O_2 and release of the trapped electron into the conduction band of the material. Blue light resulted to be the most effective in reducing the base line resistance according to its superior light energy (2.9eV). Figure 4 shows a comparison between the electrical responses of WO_3 nanofibers under dark and purple blue light at different operating temperatures (OT) in the range 25°C - 100°C and different NO_2 gas concentrations (100ppb - 400ppb). The main numerical figures in terms of RRs, RPs and adsorption/desorption times ($\tau_{ads/des}$), are reported in Table 2. At room temperature (25°C) the sensor resistance increases with increasing the NO_2 concentration both in dark and blue light

conditions. According to Table 2, at 25°C and 400ppb, the RRs yield 1.55 and 1.48 in dark and blue light respectively. At 25°C the base line recovery is very poor when desorbing in dark, but it significantly improves under blue light. This behaviour is numerically highlighted at 25°C by the increase of the Recovery Percentage from RP=9% (dark) to RP=92% (light) as shown in Table 2. 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. Moreover at 75°C the relative response yield RR=18.4 (dark) and RR=12.4 (light), showing an inhibiting influence played by light on the relative response. We may conclude that light activation mode increases the recovery percentage, whereas thermal activation enhances the relative response. To explain the higher RRs in dark as respect to light illumination conditions, we have to consider that light is expected to activate the desorption of adsorbed oxygen from WO_3 surface according to reaction (1). Considering now that NO_2 reacts with the adsorbed oxygen on WO_3 surface according to reaction (2):

$$NO_2 + O_2^- = NO_2^- + ½\ O_2 \qquad (2)$$

by illuminating the sensor surface, less oxygen species are available to react with NO_2 to form NO_2^- eventually decreasing the relative response. Moreover both temperature and light play a positive effect on the recovery percentage (RP) as shown in Table 2. RPs values increase from 9% to 98% in dark and from 92% to 99% under light, if temperature is increased from 25° to 100°C. The interesting thing is that under light conditions the RP yields 92% of its full response at 25°C as respect to 9% of the recovery in dark conditions. This behaviour can be explained again considering that independently from the activation mode, reaction (2) shift always from right to left increasing the O_2^- concentration on sensor surface if desorbing in dry air. Under light conditions, in contrast, as soon as new O_2^- is available on the surface, more oxygen is desorbed according to reaction (1) (which shift from left to right), boosting additional electrons in the WO_3 conduction band, thus decreasing the sensor resistance to its base line faster and more effectively. Finally adsorption and desorption times (τ) are also shown in Table 2. Some of their values are not reported (n.d., not defined in the table) only in case, by definition, the 90% of the response was not achieved. Both temperature and light enhance adsorption/desorption rates, thus decreasing response time.

Table 2. Sensing characteristics in terms of Relative Response (RR), Recovery Percentage (RP) and response times (τ_{ads}/τ_{des}) to 400ppb NO_2 at different operating temperatures (25°C, 50°C, 75°C and 100°C).

Temperature	DARK CONDITION				PURPLE BLUE LIGHTING CONDITION			
(°C)	$RR=R_G/R_A$	$RP\ [\Delta_D/\Delta_A]*100$	τ_{ads} (*min*)	τ_{des} (*min*)	$RR=R_G/R_A$	$RP\ [\Delta_D/\Delta_A]*100$	τ_{ads} (*min*)	τ_{des} (*min*)
25	1.55	9	n.d.	n.d.	1.48	92	51	60
50	8.29	81	n.d.	n.d.	7.62	95	49	52
75	18.42	96	38	42	12.46	97	33	38
100	4.95	98	31	32	4.32	99	30	31

5. Conclusion

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 ppm NO_2 detection at room temperature.

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