

WO₃ Nanowires Loaded with Cobalt Oxide Nanoparticles, Deposited by a Two-Step AACVD for Gas Sensing Applications

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Abstract: A two-step procedure was implemented to obtain tungsten oxide nanowires (WO₃) doped with cobalt oxide nanoparticles employing W(CO)₆ and the metal-organic precursor Co(acac)₂. In the first step, tungsten oxide nanowires were grown at 400 °C using an aerosol assisted chemical vapor deposition system (AA-CVD) and subsequently annealed at 500 °C for 2 hours in dry air. Then, cobalt oxide loading (at different dose levels) of the nanowires was performed via a second AA-CVD process. These hybrid nanomaterials were grown on top of commercial alumina substrates that comprised interdigitated electrodes and a heating element. The response of these nanomaterials toward H₂S, ethanol H₂

and ammonia is investigated and discussed. Co-loaded tungsten oxide is well suited for detecting ammonia under dry conditions and hydrogen sulfide in humid environments.

Keywords: Nanowires; Tungsten trioxide; Cobalt oxide; Gas sensors.

1. Introduction

Air quality monitoring both indoor and outdoor have become a major issue nowadays due to the global industrial growth and the rise of emissions of harmful gases, such as NO_2 , H_2S , or VOCs, which, at high enough concentrations, represent a threat to the environment and human health [1]. Major efforts have been employed for developing new gas sensors with the ability to monitor such gases at low concentrations. Nowadays there are different types of sensor technologies that may possess, at least in part, the requirements to perform a widespread monitoring of harmful gases and vapors. These comprise calorimetric, electrochemical, photoionization detectors (PID) or metal oxide semiconductor gas sensors [2]. Metal oxide semiconductor gas sensors (MOXs) have been continuously researched in the last decades due to their cost-effectiveness, their high sensitivity and their suitability for miniaturization [3]. Among the most popular MOXs are n-type semiconductors such as SnO_2 , ZnO , In_2O_3 or WO_3 . The main drawback of MOXs remains their lack of selectivity and, very particularly, cross-sensitivity to ambient moisture. Different strategies have been reported to fight cross-sensitivity. Namely, the use of filters to prevent specific gases from reaching the gas sensing surface and thus, interfering in the measurement process [4], the use of sensor arrays with overlapping selectivity and pattern recognition [5] [6] or the use of advanced sensor operation techniques such as temperature cycling [7]. However, the major efforts to tackle this problem have consisted of loading MOXs with different metal or metal oxide

nanomaterials in an attempt of tailoring gas sensing properties and selectivity towards specific targets [8] [9]. In particular, nanoparticles of noble metals such as platinum, palladium or gold nanoparticles have been employed for enhancing gas detection, since these metals display interesting bulk properties and catalytic activity [10]. In addition, the loading of n-type metal oxide nanomaterials with p-type metal oxide nanoparticles has been explored in the last few years because this is a route to achieve both chemical and electronic sensitization effects. For example, upon the formation of many n-p heterojunctions in n-type nanowires decorated with p-type nanoparticles, electronic charge is injected from the nanowires to nanoparticles and depletion zones develop at the interfaces [4-6]. In addition, p-type nanoparticles may help increase the amount of oxygen species that end-up trapped at the surface of the n-type nanowire via their catalytic activity and a spill-over effect [7,9,10]. While these two effects combined translate in an increase in the electrical resistance of decorated nanowire films (in comparison to the resistance for bare nanowire films) when in clean air, they also play a role in the enhancement of sensitivity and selectivity to gases. This result involves different mechanisms occurring at the surface of the hybrid nanomaterial, which alter the overall electrical conductance of the gas-sensitive film. Namely:

- The adsorption of gaseous species onto p-type nanoparticles involves charge-transfer mechanisms that eventually affect the width of the depletion zones.
- Gaseous species can interact directly with oxygen adsorbates on n-type MOX, and we should keep in mind that there is an increased amount of oxygen surface species in hybrid nanomaterials due to the presence of p-type MOX nanoparticles, as stated above.

- Gaseous species can react with p-type nanoparticles resulting in highly reactive radicals that can further react with oxygen adsorbates via a spill-over effect.

It is the choice of the particular p-type MOX to be employed in the hybrid nanomaterial that enables tailoring the system selectivity towards specific targets. Employing this approach Llobet and coworkers reported the use of copper oxide nanoparticles for selectively detecting hydrogen sulfide through a reversible sulfurization of copper oxide upon exposure to H₂S [11]. Similarly, palladium oxide nanoparticle decorated tungsten oxide nanowires have been also reported for the selective detection of H₂ [12]. Hydrogen dissociation at the p-type PdO nanoparticles, followed by spill over onto the n-type nanowires (at high/ moderate operating temperatures) or the reversible formation of palladium hydride upon hydrogen exposure (at near room-temperature operation) are the reported sensing mechanisms. More recently, the loading of tungsten oxide nanowires with nickel oxide nanoparticles was found to be of interest for the selective detection of H₂S [13].

Following the approach described above, this paper is focused on the decoration of tungsten oxide nanowires with p-type cobalt oxide nanoparticles. At first, the suitability of the aerosol assisted chemical vapor deposition (AACVD) for growing the hybrid nanomaterial with different cobalt oxide loadings is studied via a morphological and compositional study of the nanomaterials grown. Then, the gas sensing response is investigated and discussed in detail. Here, a two-step AACVD procedure in which WO₃ nanowires are grown at first and subsequently loaded with cobalt oxide nanoparticles was implemented to ensure that the loading could be performed effectively in wide concentration range.

The use of cobalt oxide as a gas sensing material, either standalone or supported by different n-type metal oxides has been reported in the literature

and Table 1 summarizes the state of the art. To the best of our knowledge, this is the first time that the growth of tungsten oxide nanowires decorated with cobalt oxide is reported and their use as gas sensing nanomaterial investigated. Cobalt oxide supported on tungsten trioxide nanowires was only reported before in a conference work [14] in which we presented preliminary and incomplete results.

Table 1. Summary of results reported for chemo-resistive sensors employing cobalt oxide.

Nanomaterial	Operating temperature	Gas/Range (ppm)	Response (R_{air}/R_{gas})	Response time	Relative humidity	Reference
Co₃O₄ nanoparticles	240°C	CO / 6.7	1.9 ^a	110 s	60 %	[15]
Co₃O₄ nanorods	300°C	EtOH / 100	25.7 ^a	29 s	DA	[16]
CuCo₂O₄ nanosheets	23°C	NH ₃ / 400	1.07 ^a	120 s	57 %	[17]
Co₃O₄/TiO₂ nanotubes	100°C	H ₂ / 1000	7 ^a	660 s	50 %	[18]
CoO_x/SnO₂ nanocomposite	250°C	H ₂ S / 2	10 ^a	NS	DA	[19]
Co/SnO₂ NPs	320°C	H ₂ / 40	15.7 ^a	NS	DA	[20]
0-2 wt% Co/SnO₂	350°C	NO / 1000				
		C ₃ H ₆ O / 2000	1637 ^a	75	NS	[21]
		EtOH / 1000	660 ^a	5		
			806 ^a	1		
0-1wt% Co/CdO	130°C	HCHO / 100	23 ^b	82	DA	[22]
Co/WO₃ thin film	250°C	O ₃ / 0.8	1.33 ^a	-	DA	[23]
WO₃ nanowires/ Co₃O₄ loaded	250°C	H ₂ / 20	1.7	819 s	DA & 50%	This work
		EtOH / 20	3.2 ^a	150 s		
		H ₂ S / 50	5.4 ^a	40 s		
		NH ₃ / 25	12 ^a	308 s		

Notes: **a** (R_{air}/R_{gas}); **b** (%); **DA**: Dry Air Conditions; **NS**: Not Specified.

2. Experimental

2.1. Sensing layer synthesis

The AACVD methodology was employed to grow, on top of alumina transducers, a first layer of pristine tungsten oxide. Some of the layers grown

underwent a second AACDV process to be loaded with different concentrations of cobalt oxide nanoparticles. The first step consisted of the synthesis of pure WO_3 nanowires employing 50 mg of $\text{W}(\text{CO})_6$ as precursor. Such precursor was solubilized in a mixture of methanol and acetone with a 1:3 volume ratio. It has been studied experimentally that higher amounts of methanol lead to the formation of tungsten oxide nanoparticles instead of the desired nanowires, the main reason for this effect is the lower solubility of the organic precursor in methanol than in acetone, leading to a less homogenous solution that, once used in the aerosol generator results in a less effective precursor delivery. The solution was sonicated until all the precursor material was fully solved and then, was placed in an aerosol generator, which used a bath and ultrasonic waves to convert the solution into a micro-droplet spray that contained the precursor. This spray is conveyed via a connecting pipe system using nitrogen as an inert carrier gas at a flow of 1 L/min towards a 400°C preheated CVD hot-wall reactor where the substrates are placed. Typically, the process for growing tungsten oxide samples took 20 to 30 minutes to complete and is run at atmospheric pressure. With this procedure and considering the reactor dimensions, up to 3 samples can be produced at the same time. The commercially available alumina substrates employed have interdigitated platinum electrodes screen-printed on the front side and a platinum heating resistor printed on the backside. Three of these substrates placed and kept face up in the reactor chamber during and AACVD process. The resulting tungsten oxide nanowire layers fully coat the electrode are of the substrates. Such layers have a dark-blue color, which is indicative of tungsten oxide being highly oxygen sub-stoichiometric and that some amorphous carbon residues left by the organic precursor and solvents are present. To remove such impurities and enhance oxidation, an annealing step is performed right after the deposition, which is conducted in a muffle at 500°C for 2 hours, with a temperature ramp of $5^\circ\text{C}/\text{min}$, under pure dry air. After this step,

the films show a green-yellowish color, indicative that a slightly oxygen defective tungsten oxide is achieved.

For some of the previously grown tungsten oxide nanowire samples, a second AACVD process is performed for loading them with cobalt oxide nanoparticles. In the first place, different amounts of a cobalt organic precursor, $\text{Co}(\text{acac})_2$, are weighed. Here 5 mg or 10 mg of the Co precursor were used to produce sensors with different loading levels. The organic precursor is mixed with 10 ml of methanol and subsequently sonicated until its full solubilization. The sensor substrates comprising annealed WO_3 nanowires are placed again inside the CVD reactor and preheated at 350°C . The solution of the Co precursor is placed at the aerosol generator and delivered into the CVD reactor via a nitrogen flow of 1 L/min. The typical duration of this second AACVD step is 10 to 15 minutes. Finally, similarly to what was implemented for the first process, an annealing step is performed to clean the surface from carbon residues.

In addition to this two-step approach, a one-step approach for achieving cobalt oxide decorated tungsten oxide nanowires was checked as well. In the one-step approach both the precursors for tungsten and cobalt oxide are mixed and dissolved together. However, the overall efficiency of the cobalt oxide loading achieved in this way was very poor in comparison to the two-step approach described above. This lack of efficiency, which is in agreement with the findings for the AACVD decoration with nickel oxide reported in [13], can be attributed to the difficulty in achieving a good, simultaneous dissolution of the two precursors in the solvent mixture. Therefore, the one-step approach is not discussed further in this paper.

2.2. Material Characterization

The nanomaterials had their crystalline phase characterized through X-ray diffraction (XRD), their structural morphology was studied employing scanning

electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM). Finally, their chemical composition was characterized using energy-dispersive X-ray spectroscopy (EDX) and X-Ray photoelectron spectroscopy. A Bruker-AXS D8-Discover diffractometer with a parallel incident beam was used to perform the XRD analysis. SEM was carried out using a SU8020 Microscope from Hitachi (Tokio, Japan) operated at 30 kV. XPS was conducted on the sensing layers using a VERSAPROBE PHI 5000 from Physical Electronics, equipped with a monochromatic Al K α X-ray source. The X-ray photoelectron spectra were collected at the take-off angle of 45° with respect to the electron energy analyzer operated in the CAE (constant analyzer energy) mode. For the compensation of built-up charge on the sample surface during the measurements, a dual beam charge neutralization composed of an electron gun (≈ 1 eV) and an Ar ion gun (≤ 10 eV) was used. Binding energies are all referred to the C1s peak at 284.6 eV. TEM analysis was carried out using a JEM-2100 (Jeol, Japan, 200 keV) equipped with an energy dispersive X-ray spectrometer (EDXS). The specimens for TEM investigation were mechanically removed from the growth substrate and ultrasonically dispersed in MeOH and a drop of the dispersion was deposited onto a lacy carbon film supported by a copper grid. In addition, room-temperature photoluminescence (PL) measurements were made with a chopped Kimmon IK Series He-Cd laser (325 nm). Fluorescence was dispersed with an Princeton Instruments Acton SP2750 0.750 m imaging triple grating monochromator, detected using a Hamamatsu H8259-02 with a socket assembly E717-500 photomultiplier, and amplified through a Stanford Research Systems SR830 DSP. A 360 nm filter was used to filtering the stray light. Finally, A cross-section and element mapping was performed employing a FESEM-FIB-field emission gun SEM-focused ion beam.

2.3. Gas sensing studies

These comprised testing the response for four different species (i.e., hydrogen sulfide, ethanol, hydrogen and ammonia vapors) at different concentrations and for three different operating temperatures (150, 200 and 250 °C). The concentrations tested were 10, 15, 25, 50 ppm for hydrogen sulfide, 5, 10, 15 and 20 ppm for both ethanol and hydrogen, and 25, 50 and 100 ppm for ammonia. These species were in calibrated gas cylinders balanced in dry air. The total flow was kept constant at 100 mL/min throughout the measurements. In a typical experiment sensors were exposed to a given species and concentration for 30 minutes, which was followed by 30 minutes of dry air for recovering the baseline. The DC resistance of the sensors was recorded. Sensors were placed inside an airtight test chamber made of Teflon®, which was connected to a mass-flow controlled dilution system that delivered reproducible concentrations of the species tested. All sensors were manufactured in duplicate (to test reproducibility). In a standard measurement, each sensor was exposed to 5 cycles of pulses of increasing gas concentration (to check repeatability). On the other hand, to test the reproducibility, two sensors of each type (i.e. 2 pure WO₃, 2 Co/LC and 2 Co/HC) were tested and the responses for each concentration were compared. Finally, when all the response values for each concentration had been gathered, a Q Dixon test was run to find possible outliers; and the mean values were calculated together with the standard deviation associated for each concentration to a given operating temperature and plotted in accordance. For the detection of the different species, the cross-sensitivity of ambient moisture was studied. A mass flow controller for liquids was added to the dilution system and samples could be humidified to 50% R.H. at 25°C.

3. Results and discussion

Figure 1 shows typical successive response and recovery cycles of pure and cobalt oxide loaded tungsten oxide nanowire sensors to increasing concentrations of ethanol. As it could be expected, the loading of n-type tungsten

oxide nanowires with increasingly high amounts of p-type cobalt oxide nanoparticles results in an increase of the baseline resistance. This increase can be due to space charge regions developing at the interfaces between p-type cobalt oxide nanoparticles and n-type tungsten oxide nanowires, but also to cobalt oxide nanoparticles favoring an increase in the concentration of oxygen adsorbates at the nanowires (oxygen surface species trap electrons of the n-type nanowires increasing overall resistance).

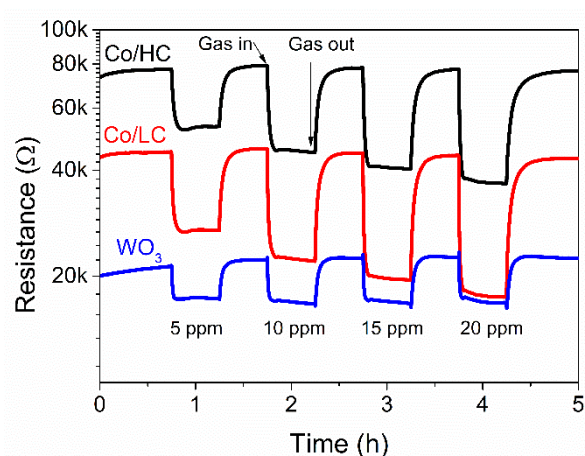


Figure 1. Typical cycles of response and recovery to increasing concentrations of ethanol pulses for three tungsten oxide nanowire sensors with different loading levels of cobalt oxide nanoparticles. Namely, bare WO_3 , low cobalt loaded WO_3 (Co/LC) and high cobalt loaded WO_3 (Co/HC). Sensors were operated at 200°C under dry air conditions.

The effect of having different amounts of cobalt oxide loading on the sensing properties was screened (see the Supporting Information, Figure S1). In accordance to the results obtained, two loading levels were considered for further analysis. These corresponded to using either 5 mg or 10 mg of $\text{Co}(\text{acac})_2$ during the synthesis step. These low and high loading levels are referred to as Co/LC and Co/HC, respectively.

3.2. Material characterization

The different nanomaterials were characterized by means of XRD to study their crystallinity. All nanomaterials presented peaks in agreement with those

reported in ICDD card n° 43-1035 corresponding to monoclinic WO_3 . In addition, cobalt loaded samples showed peaks that corresponded to cobalt oxide. XRD spectra (Figure S2) and a discussion of these results can be found in the Supporting Information. Tungsten oxide nanowires were single crystalline monoclinic and some peaks recorded in the XRD spectra indicated the presence of Co in Co-loaded samples. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to understand their morphology.

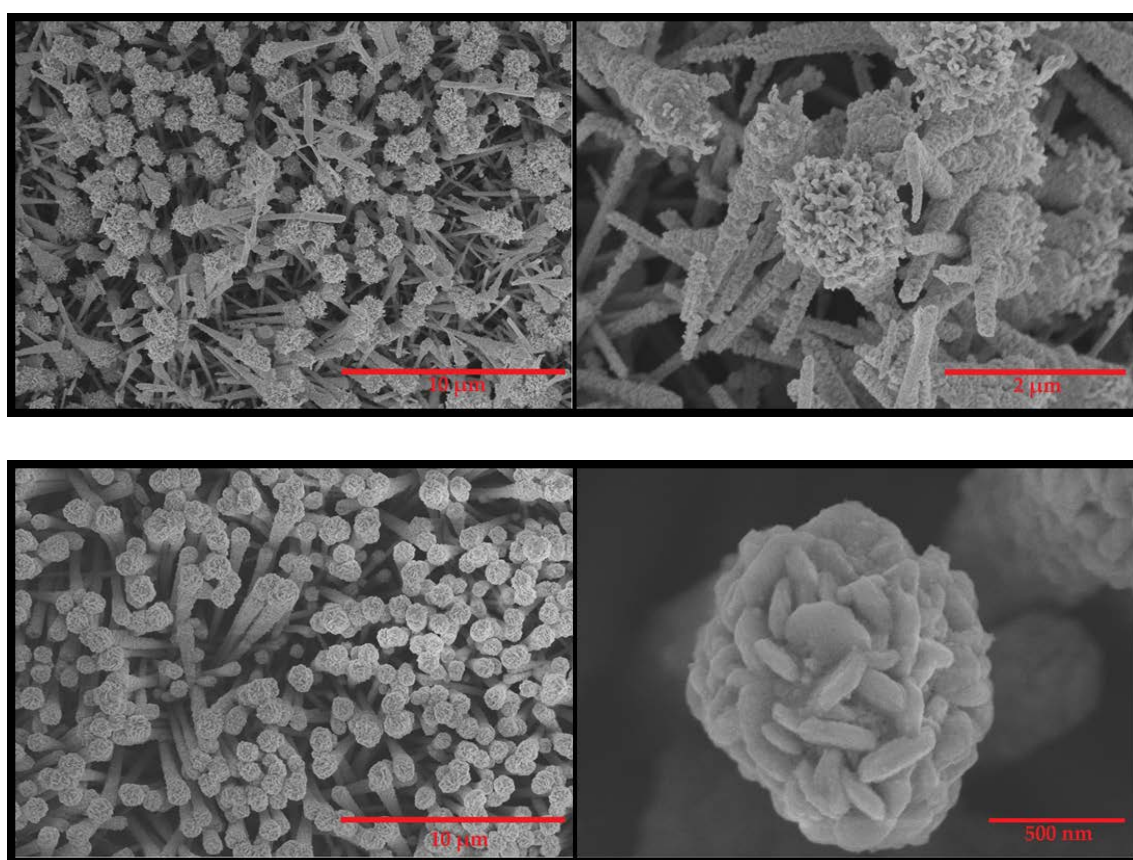


Figure 2. SEM results. Co/LC tungsten oxide nanowires appear almost covered by clustered cobalt oxide resembling to petal like structures (upper left panel). Close look at the tips (upper right panel). Co/HC tungsten oxide nanowire tips are covered by clustered cobalt oxide with nanoflake-like structure (lower left panel). Close look at the tip of a Co/HC tungsten oxide nanowire (lower right panel).

Figure 2 shows typical SEM images of tungsten trioxide nanowires loaded with low and high concentrations of cobalt. Nanowires grow randomly oriented, their

length ranges from 4 to 12 μm and they are between 50 and 150 nm in diameter. The SEM images indicate that even though cobalt is distributed along the whole length of tungsten oxide nanowires, more cobalt is present at the nanowire tips (see Supporting Information). At high loading levels, cobalt oxide clusters at the tips in a nano-flake morphology. EDX studies confirm the presence of cobalt in both Co/LC and Co/HC samples (see Supporting Information). TEM microscopy of a Co/HC sample confirmed SEM results and further revealed that nanoparticles covering WO_3 nanowires have diameters ranging from 20 nm to 80 nm (see Figure 3). WO_3 nanowires are crystalline with no amorphous edge observed proving that annealing step at 550°C in air was efficient. Clear lattice fringes of 0.36 nm are observed (inset in Figure 3c) corresponding to the interplanar spacing of (200) planes in monoclinic WO_3 (ICDD no. 43-1035), thus supporting XRD results. Nanoparticles deposited at the upper tip of the WO_3 nanowire are polycrystalline, as concluded from selective area electron diffraction (SAED) pattern (see the Supporting Information, Figure S3a and b). EDX spectrum taken over this area (see the Supporting Information, Figure S3c), reveals the presence of wolfram, oxygen, and cobalt. In addition, the interplanar spacing measured in some of the deposited CoO_x nanoparticles is 0.46 nm (inset in Figure 3b), which could correspond to the interplanar spacing of (111) planes in Co_3O_4 (ICDD no. 01-073-1701).

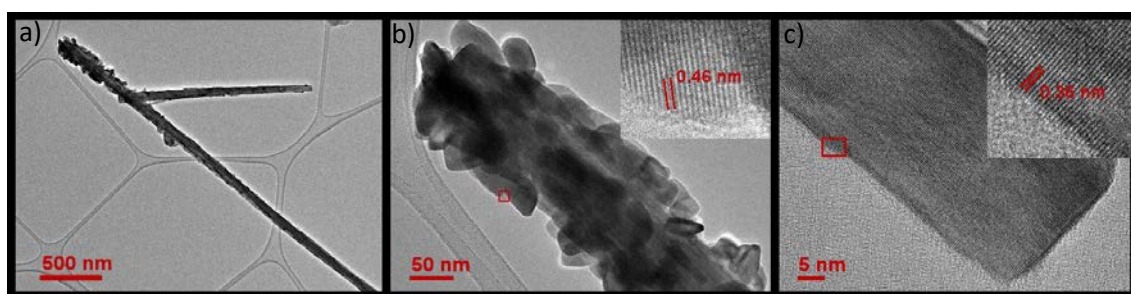


Figure 3. TEM images of Co/HC sample: (a) TEM image of an individual WO_3 nanowire where (b) the upper end is thickly covered with CoO_x nanoparticles (b) while the bottom end is not (c). HR-TEM inset in figure (c) reveals that the WO_3 nanowire is crystalline. The measured lattice fringes, inset to figure (b) and (c), are 0.46 nm and 0.36 nm, respectively, which corresponds to the interplanar spacing of (111) planes in Co_3O_4 (ICDD no. 01-073-1701) and (200) planes in

monoclinic WO₃. (ICDD no. 43-1035). The red frames in images (b) and (c) indicate areas of the HRTEM insets in images b and c.

In contrast, on the Co/LC sample, characteristically smaller cobalt-containing agglomerates are found at the surface of WO₃ nanowires (Figure 4). Also these agglomerates are less densely distributed over the WO₃ nanowires than in the case of the Co/HC sample.

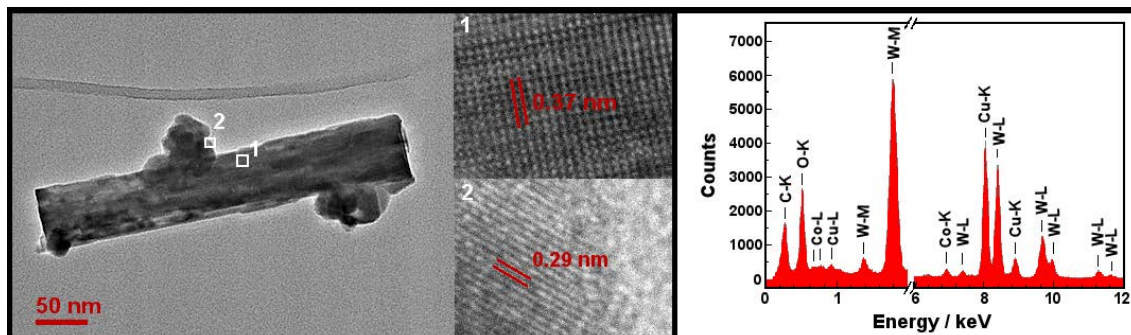


Figure 4. TEM image of the Co/LC WO₃ nanowire with a corresponding EDX spectrum. HRTEM images of WO₃ nanowire (1) and nanoparticle attached to the surface of WO₃ nanowire (2) reveal that both WO₃ nanowires and nanoparticles are crystalline. The measured lattice fringes in 1 is 0.37 nm, which corresponds to (200) planes in monoclinic WO₃ (ICDD no. 43-1035). The EDX spectrum indicates that the nanoparticle agglomerate at the surface of the WO₃ nanowire contains cobalt.

Additionally, an element mapping was performed to confirm the material distribution as well as room-temperature photoluminescence study (these results can be found in the supporting information). The elemental mapping confirms that cobalt is well distributed along the full length of the tungsten oxide nanowires, with higher presence at the nanowire tips. The PL study indicates that Co-loaded tungsten oxide nanowires have higher number of defects than pure tungsten oxide nanowires.

To investigate the surface composition and chemical states of the elements in the samples synthesized with different cobalt loading, XPS spectra were recorded. A typical survey spectrum is shown in Figure 5a. It indicates that the surface of the samples is composed of tungsten and oxygen elements with carbon contamination. In addition, the peaks generated by photoelectrons emitted from cobalt atoms are evident. The relative concentration of elements is shown in the Supporting Information (Table S1), it is clear that by increasing the amount of

cobalt loading, the amount of Co incorporated into the material increases. It was observed that the Co/HC sample loaded with the higher concentration of cobalt oxide presented two different regions having dark grey and a light grey colors in SEM images (see Supporting Information, Figure S4). By studying the concentration of Co in these areas, it is clear that the amount of Co incorporated is higher in the dark grey region.

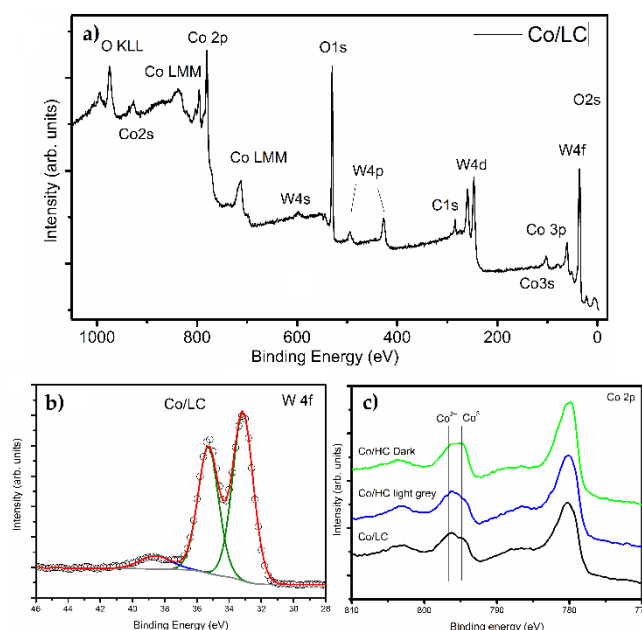


Figure 5. a) XPS survey showing the composition at the Co/LC sample surface. b) XPS spectrum recorded in the binding energy range of the 4f core level. The spectrum is characterized by a doublet $W4f_{5/2}$ and $W4f_{7/2}$ and a singlet loss feature centered at 38.7 eV. c) Co 2p XP spectrum on both samples Co/LC and Co/HC in the light and dark regions.

The high-resolution spectrum of the $W4f$ core level (Figure 5b) shows a doublet with components at 35.3 and 33.1 eV, which are assigned to $W4f_{5/2}$ and $W4f_{7/2}$, respectively. These peaks can be associated to the presence of W atoms with oxidation state 6+ (WO_3) [13]. The detailed inspection of the XPS Co 2p spectra recorded on the different samples and regions (Figure 5c), shows that for sample Co/LC and light grey region of sample Co/HC, cobalt has the oxidation state 2+, while in the dark grey region of sample Co/HC the oxidation state is 3+ [24] [25].

This supports the HRTEM findings, indicating the polycrystalline nature of cobalt oxide in Co/HC samples.

3.2. Gas sensing results

The responses of the different materials to ethanol, hydrogen, hydrogen sulfide and ammonia were studied under dry and humid conditions (50% R.H.). Hydrogen and ammonia detection results can be found in the Supporting Information.

3.2.1. Ethanol

The sensors were exposed to different concentrations of ethanol vapors, namely, 5, 10, 15 and 20 ppm in a balance of dry air. Each sensor was exposed to a cycle of four pulses of increasing gas concentrations. Between two consecutive concentration pulses, dry air was used to clean the sensor surface. To test the repeatability of the measurements, such cycle was repeated five times (see Figure 6). Results indicate that measurements were highly repeatable.

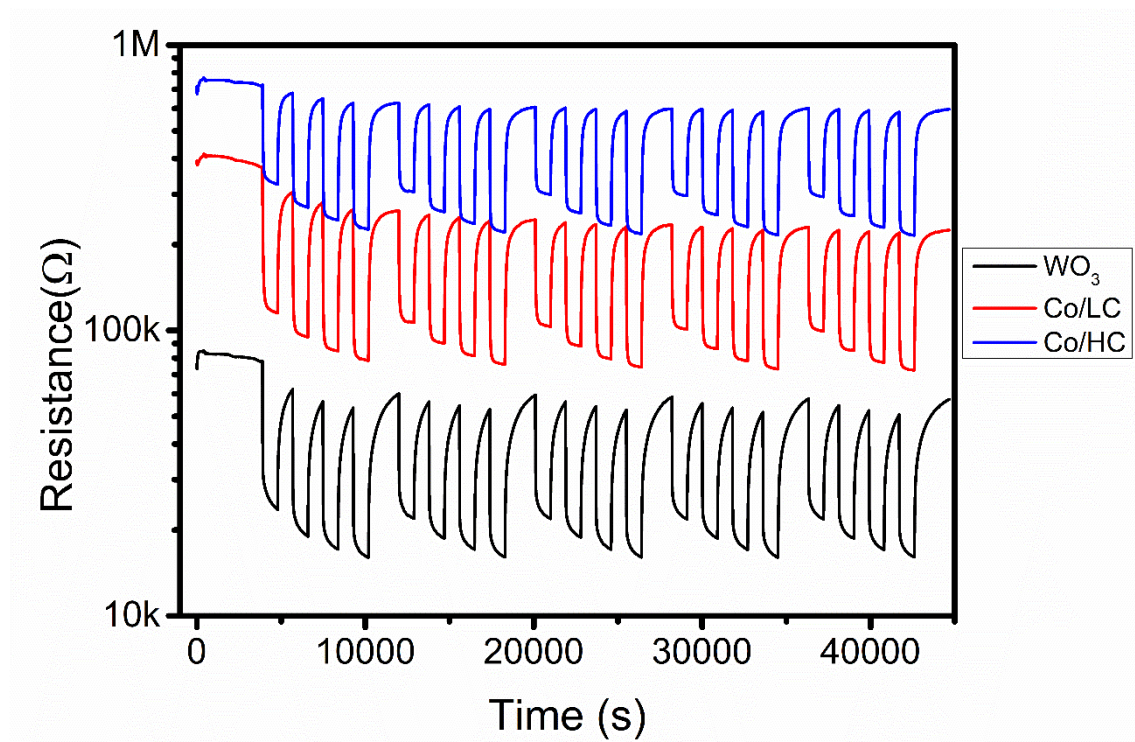


Figure 6. Sensor resistance behavior when sensors were exposed to 5, 10, 15 and 20 ppm of ethanol while operated at 250°C. The measurement cycle was repeated 5 times.

Figure 7 reports these results for pure tungsten oxide samples operated at three different temperatures (i.e., 150, 200 and 250°C). Figure 8 shows that loading tungsten oxide with cobalt has a positive effect in the sensitization towards ethanol vapors. In particular, when loaded at the higher level (Co/HC sample), the higher responsiveness towards ethanol under dry conditions is reached at the lowest operating temperature tested (i.e., 150°C). The improvement in responsiveness in Co/HC samples is roughly 80% (compared to the responsiveness of pure tungsten oxide samples). Figure 8 reports as well the responses to ethanol vapors of cobalt loaded tungsten oxide samples, when measured under humid conditions. At 50% R.H., the response towards ethanol is negatively affected. The comparison of the slopes of the curves shown in Figure 8 clearly indicate that slopes are lower under humid conditions, which is indicative of a decrease in ethanol sensitivity. Figure 8 shows as well that Co/HC samples operated at the higher temperature tested are more resilient to the presence of moisture, since responsiveness to ethanol remains remarkably high.

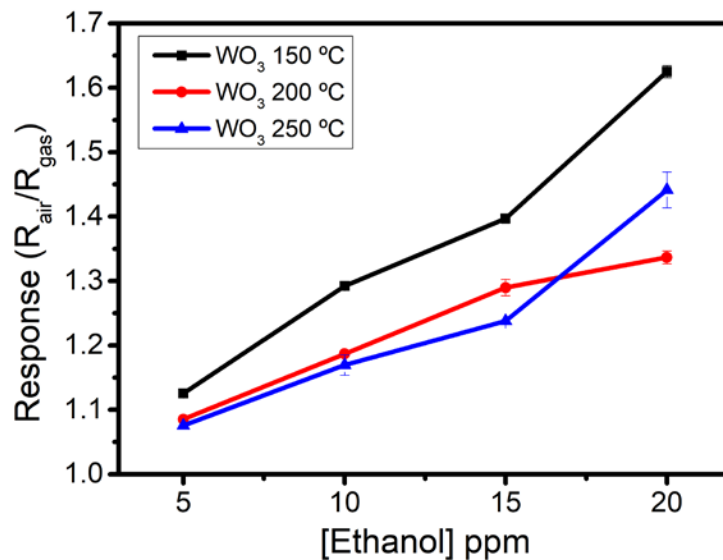


Figure 7. Effect of the working temperature, to pure WO₃ sensor, on the response to different concentrations of ethanol (diluted in dry air).

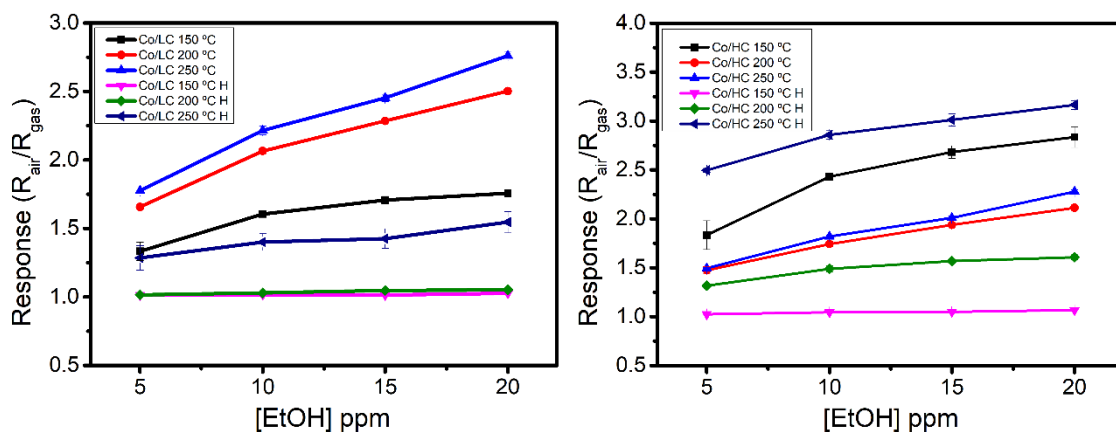


Figure 8. Humidity effect on ethanol sensing at different operating temperatures for cobalt-loaded samples. Left panel Co/LC results; Right panel Co/HC results.

3.2.2. Hydrogen sulfide

Finally, the response of the different nanomaterials to hydrogen sulfide was investigated. In the first step, sensors were exposed to hydrogen sulfide at 10, 15, 25 and 50 ppm under dry conditions. These results are summarized in Figure 9 and Figure 10. The loading of tungsten oxide nanowires with cobalt results in an enhanced response towards H_2S . The improvement in responsiveness towards hydrogen sulfide in Co/HC samples is roughly 60% (compared to the responsiveness of pure tungsten oxide samples). The effect of the operating temperature is very different in pure and cobalt-loaded samples. While the responsiveness towards hydrogen sulfide decreases with the operating temperature in pure tungsten oxide samples, responsiveness increases when the operating temperature is raised for cobalt-loaded samples. This is indicative that the contribution to the response of cobalt oxide nanoparticles decorating tungsten oxide nanowires is a temperature-activated process (catalytic effect). When in the presence of background humidity (see Figure 10), cobalt-loaded sensors, especially those employing Co/HC samples, remarkably retain high responsiveness towards hydrogen sulfide, provided they are operated at high temperatures (i.e., 250°C).

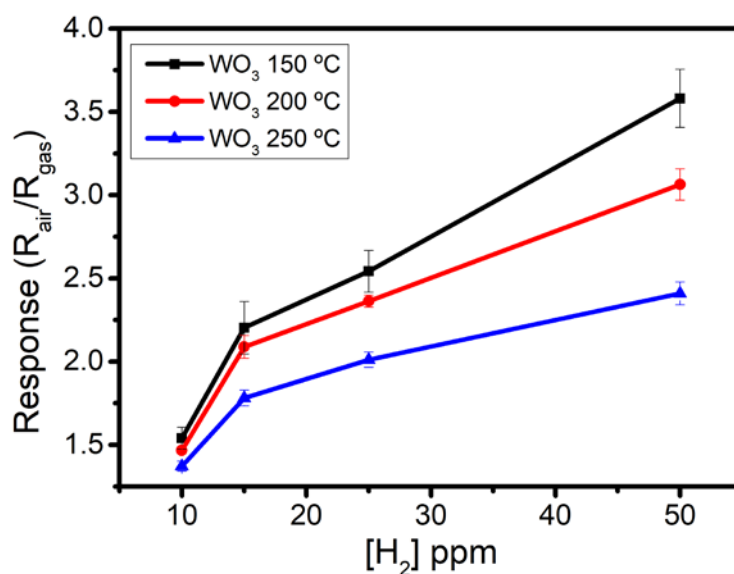


Figure 9. Effect of the working temperature, to pure WO₃ sensor, on the response to different concentrations of hydrogen sulfide (diluted in dry air).

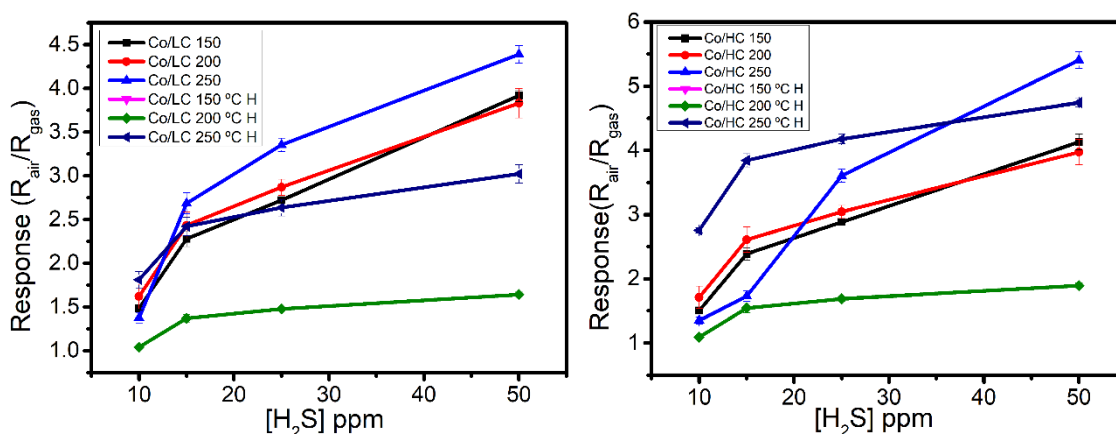


Figure 10. Humidity effect on hydrogen sulfide sensing at different operating temperatures for cobalt-loaded samples. Left panel Co/LC results; Right panel Co/HC results.

The low standard deviations (error bars) associated to the measurements reported in this section are indicative, not only of the good repeatability of measurements, but also of the fair reproducibility of sensors since Figures 7 to 10 summarize the results for two sensors per material considered. The gas sensing properties towards hydrogen and ammonia are fully discussed in the Supporting Information. A short summary of these results is as follows. Co-loaded sensors show small responsiveness towards hydrogen. In contrast, under dry conditions,

Co/LC sensors operated at 250°C were found to be remarkably selective to ammonia, since the response to this vapor was 4 times higher than for any of the other species tested (see Figure 11). However, the presence of ambient moisture heavily influenced (diminished) the response towards ammonia.

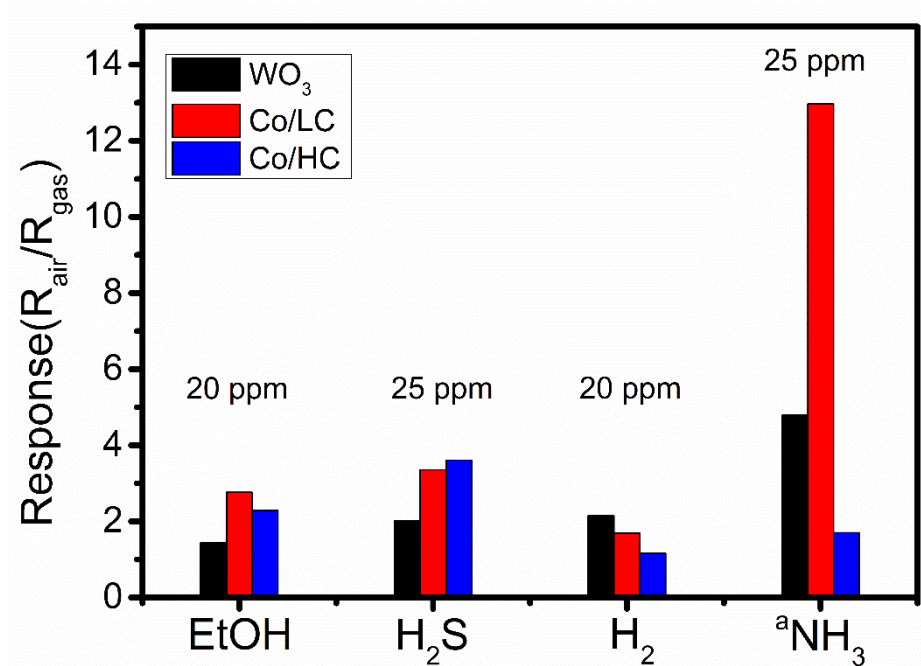


Figure 11. Sensor response (R_{air}/R_{gas}) comparison for the different species and different nanomaterials used (under dry air conditions). Operating temperature was set to 250°C. ^aSensor response calculated as R_{gas}/R_{air} .

Since Co/LC sensors operated at 250°C were the most promising devices, a long-term stability test was performed for these sensors. Long-term stability measurements consisted of measuring ethanol during November 2018 and then repeating these ethanol measurements in May 2019, after 6 months of continuous operation in which other species such as hydrogen, hydrogen sulfide or ammonia had been measured. Long-term stability results are summarized in Figure 12, which shows a normalized response towards ethanol (a baseline correction was applied). Results indicate that a fair long-term stability is achieved over a 6-month period.

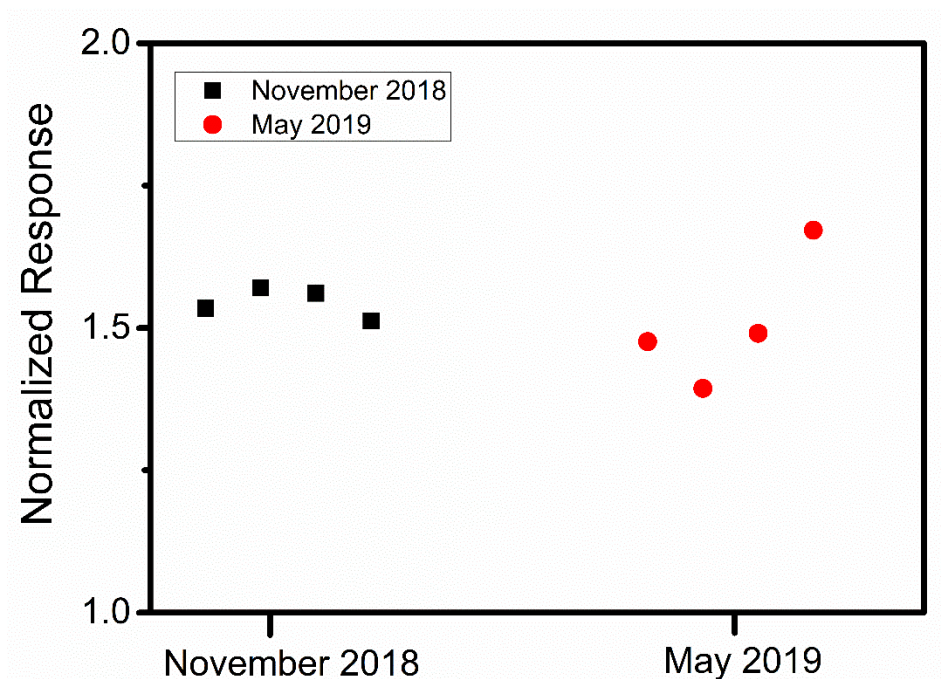


Figure 12. Long-term stability study for Co/LC sensors operating at the optimal working temperature of 250°C and detecting ethanol vapors.

If compared to the state of the art results reported in Table 1, our Co-loaded sensors have undergone a more in depth study (gas sensing properties, moisture cross-sensitivity and long-term stability). They show promise in the selective detection of low levels of ammonia (if background humidity is filtered out) and in the detection of hydrogen sulfide (in this case with the clear benefit of showing low moisture cross-sensitivity).

3.3. Gas sensing mechanisms

It is generally accepted that, reducing species such as ethanol, hydrogen or hydrogen sulfide are adsorbed on metal oxides and react with oxygen surface species. Electrons trapped at oxygen adsorbates are then freed and contribute to the increase in the electrical conductance that is observed in n-type metal oxide films. As discussed in the introduction, the decoration of an n-type metal oxide (e.g. tungsten oxide) with p-type (e.g. cobalt oxide) nanoparticles can tune the sensitivity and selectivity of the n-type metal oxide via electronic and chemical sensitization effects. In particular, the use of catalytically active metals can

enhance sensitivity towards reducing species by increasing the amount of oxygen surface species in their n-type metal oxide host (via a spillover effect). However, this does not seem to be the case here, because such an increase in the number of adsorbed oxygen species would have been very favorable for increasing the response towards hydrogen, which was not observed. Therefore, we have to conclude that the main reasons for the observed enhancement in responsiveness of cobalt oxide-loaded samples towards ethanol and hydrogen sulfide are related to:

- Charge-transfer mechanisms triggered by the adsorption of ethanol or hydrogen sulfide on cobalt oxide nanoparticles, which affect the width of the depletion zones that develop at the p-n interfaces.
- Ethanol or hydrogen sulfide reacting with cobalt oxide nanoparticles and, producing highly reactive radicals that can further react with oxygen species located at the surface of the n-type tungsten oxide via a spill-over effect.

At the operating temperatures tested, we can assume that the dominant oxygen species at the surface of tungsten oxide are O^- [26]. The presence of cobalt oxide nanoparticles could help breaking down the ethanol molecule, favoring its complete oxidation and maximizing the number of electrons released to the conduction band of tungsten oxide (see Equation 1).

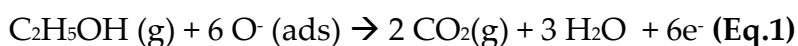


Figure 13 shows a cartoon of the detection mechanism for ethanol or hydrogen sulfide in which the presence of cobalt oxide nanoparticles contributes to the effective oxidation of ethanol and thus, to response enhancement.

a)

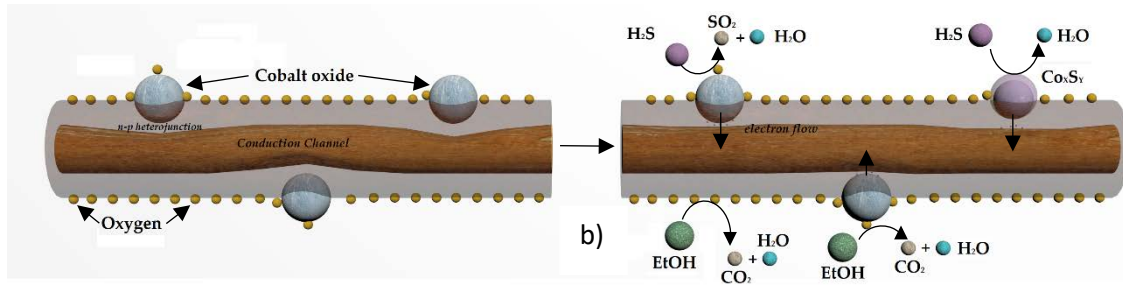
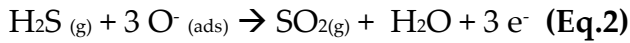
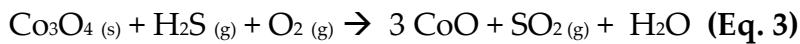


Figure 13. Representation gas sensing mechanisms for ethanol and hydrogen sulfide. a) Representation of oxidation of H₂S molecules via reaction with adsorbed oxygen species (upper left) and partial cobalt oxide sulfurization (upper right). b) Reaction of ethanol molecules with oxygen molecules adsorbed both at cobalt oxide nanoparticles and the nanowire surface (bottom).

For H₂S, a similar mechanism than the one describe for ethanol applies [17] in which hydrogen sulfide molecules react with oxygen surface species present on tungsten oxide nanowires, releasing electrons as reported in Equation 2.



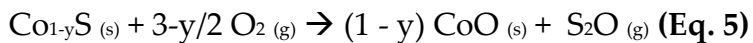
According to Eq. 2, a hydrogen sulfide molecule reacts with oxygen adsorbates and undergoes an oxidation that leads to the formation of sulfur dioxide, water and the transferring of three electrons towards the conduction band of tungsten oxide. Furthermore, cobalt oxide nanoparticles can suffer a sulfurization process as expressed by Equations 3 and 4, leading to a response enhancement due to electronic sensitization. The width of the depletion layers at the n-p interfaces is altered (reduced) upon this sulfurization process. Such a process is similar, but to a much lower extend, to the one described in tungsten oxide nanowires decorated with copper oxide nanoparticles [9].



The XPS analysis performed after H₂S detection indicates the presence of Sulphur at the sensing layer surface. A close analysis of the S 2p core level spectrum

(supplement Figure S10) suggests the presence of S-O and S-Co supporting the assumptions in Eq.3 and Eq.4.

This sulfurization of cobalt oxide nanoparticles can be reversed (at least in part) when the gas sensitive films are cleaned using a flow of pure dry air, as shown by equation 5, [25]:



In a humidified background, water molecules compete with target molecules for the adsorption sites available. Exposure to ambient moisture leads to formation of surface hydroxyl groups. In comparison to a dry surface, a hydroxylated surface has a significantly lower number of surface oxygen species that are free to react with ethanol, hydrogen or hydrogen sulfide. This is why the observed responsiveness and sensitivity decreases in a humid atmosphere. When operating at high temperatures (e.g. 250°C) the desorption of water from the gas-sensitive surface is favored, which explains why at higher operating temperatures, the response towards target species is restored, at least in part. The reversible sulfurization mechanism described above, a detection mechanism that does not rely on the direct interaction of hydrogen sulfide with oxygen surface species, could explain why cobalt-oxide loaded tungsten oxide is quite resilient to the presence of ambient moisture in the detection of hydrogen sulfide.

4. Conclusions

AACVD has been employed in a two steps process to successfully grow tungsten oxide loaded with different amounts of cobalt oxide nanoparticles. ESEM, HR-TEM, XRD, EDX and XPS analysis confirm that single crystalline tungsten oxide nanowires loaded with cobalt oxide nanoparticles are obtained.

The gas sensing properties of the different nanomaterials grown have been studied. There is a clear modification in the gas sensing behavior between films of pure tungsten oxide nanowires and those obtained with cobalt oxide loaded

tungsten oxide nanowires. While the loading did not have a positive effect for detecting hydrogen, the presence of cobalt oxide nanoparticles clearly had a positive influence in enhancing responsiveness to ethanol (80% increase) and hydrogen sulfide (60% increase). Co-loading at low levels also had a positive effect for achieving remarkable selectivity towards ammonia. The presence of humidity is, in general, detrimental for the detection of the four reducing species tested. However, it was found that by loading tungsten oxide nanowires with cobalt oxide nanoparticles resulted in a clear decrease in the moisture cross-sensitivity, especially in the detection of hydrogen sulfide at an operating temperature of 250°C. This result can be attributed to an electronic sensitization mechanism in which a reversible sulfurization of cobalt oxide occurs upon exposure of the gas sensitive film to hydrogen sulfide. Cobalt oxide is regenerated during the recovery phase in which sensors are flown with pure air. In addition, the sensors tested show very good repeatability and good long-term stability.

Conflicts of interest

There are no conflicts of interest to declare.

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