

# Gas Sensing Characterization of Single-Nanowire Sensor Array Systems Based on Non-Functionalized and Pt-Functionalized Tungsten Oxide <sup>†</sup>

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**Abstract:** Here we present the gas sensing characterization of single-nanowire sensor array systems based on either non-functionalized or Pt-functionalized single tungsten oxide nanowires towards various concentrations of nitrogen dioxide and ethanol. The sensor systems demonstrate stable and reproducible responses to the tested analytes, showing consistency with previous systems based on multiple-nanowire based films and validating the fabrication process of these devices.

**Keywords:** gas sensing; single-nanowire; sensor array; tungsten oxide

## 1. Introduction

One-dimensional (1D) semiconducting metal-oxide (MOx) nanostructures in the form of nanowires, nanorods or nanobelts have demonstrated to play a significant role in the functional properties of different components (e.g., photodetectors, biosensors, gas sensors), typically improving their performance, as opposed to bulk MOx. For instance, in gas sensors, 1D MOx have demonstrated to improve parameters, such as the sensitivity and stability of these devices, and also, to certain extent, the selectivity [1]. 1D MOx, such as SnO<sub>2</sub>, WO<sub>3-x</sub> or ZnO, have been used previously to monitor various toxic gases, including CO and NO<sub>2</sub>. In particular, WO<sub>3-x</sub> has been found to be highly sensitive to NO<sub>2</sub>, and recently the functionalization of WO<sub>3-x</sub> with platinum nanoparticles (NPs) has shown to enhance the sensitivity of WO<sub>3-x</sub> to other analytes, including ethanol and hydrogen [2], attributed to the chemical and electronic sensitization of WO<sub>3-x</sub> when functionalized with platinum NPs. These studies also proved that arrays of multiple-nanowire films based on non-functionalized and Pt-functionalized tungsten oxide nanowires could be used to enhance the selectivity of the gas sensor device.

It has also been demonstrated that gas sensors based on a single (or few) nanowire structures connected in parallel are the ideal architecture to achieve well defined conduction channel easy to modulate by external stimuli (e.g., gaseous molecules) [1]. However, yet current methods for the

integration of single nanowire structures in functional devices represent a technological challenge, with most of the methods needing the assistance of techniques, such as focus ion beam (FIB), which restricts the scalability of the process and increases the cost and time of fabrication [3].

In this context, recently, we have achieved the fabrication of nanoelectrode array systems for the integration of single nanowires connected in parallel [4]. These systems proved to be suitable to selectively integrate single nanowires connected across pairs of electrodes using dielectrophoresis method, and here we present the gas sensing characterization of these nanosensors based on either non-functionalized or Pt-functionalized tungsten oxide nanowires synthesized via aerosol-assisted chemical vapour deposition (AACVD).

## 2. Materials and Methods

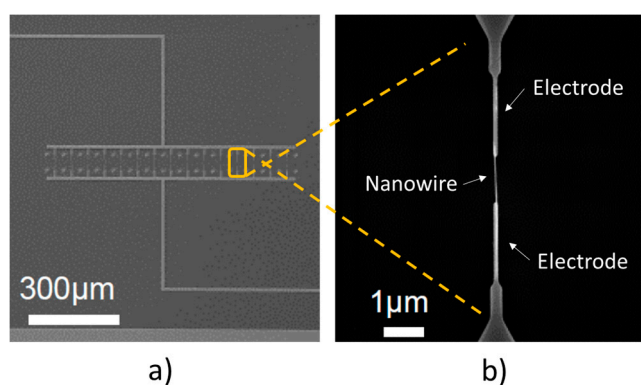
The fabrication of single-nanowire sensor array systems based on non-functionalized or Pt-functionalized tungsten oxide was achieved using various clean room fabrication processes, which included thin film depositions, lithography and etching, followed by dielectrophoresis. A detailed description of the fabrication process of these systems was reported previously [4].

These nanosensors were examined using scanning electron microscopy (SEM; Tescan FE Mira II LMU) equipped with EDX. Further analysis of the non-functionalized and Pt-functionalized nanowires was performed using scanning transmission electron microscopy (STEM; FEI Tecnai F20, 200 kV), and XPS (XPS; Phoibos 150 analyzer IISPECS GmbH, Berlin, Germany in ultrahigh vacuum conditions (base pressure  $1 \times 10^{-10}$  mbar) and a monochromatic  $K\alpha$  X-ray source, 1486.74 eV).

Gas sensing tests of the nanosensors were carried out towards ethanol and nitrogen dioxide by monitoring the electrical resistance changes of the wires while applying different currents in the order of nanoAmpere. The sensors were exposed to various concentrations of the analytes for five minutes in a continuous flow test chamber (200 sccm) provided with mass-flow controllers. Subsequently, the test chamber was purged with synthetic air during five minutes until the initial baseline resistance was recovered [5]. The sensor response was defined as  $R_{air}/R_{gas}$  for ethanol and  $R_{gas}/R_{air}$  for nitrogen dioxide, where  $R_{air}$  is the sensor resistance in air at stationary state and  $R_{gas}$  the sensor resistance after five minutes of analyte exposure.

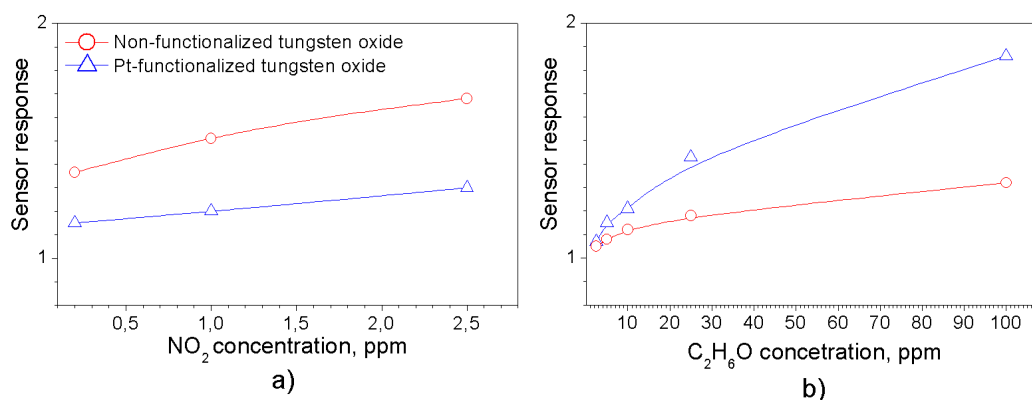
## 3. Results and Discussion

The system array described in this work consisted of single non-functionalized or Pt-functionalized nanowire sensor arrays containing up to five nanowires connected in parallel. Figure 1 displays a view of the system array (Figure 1a) and a single nanowire connected across a couple of electrodes (Figure 1b). Previous analysis of the nanowires using STEM and XPS proved the synthesis of non-functionalized and Pt-functionalized tungsten oxide nanowires with diameters between 50 nm and 100 nm, and the incorporation of well dispersed Pt nanoparticles with diameters between 1 nm and 5 nm along the functionalized wires [6].



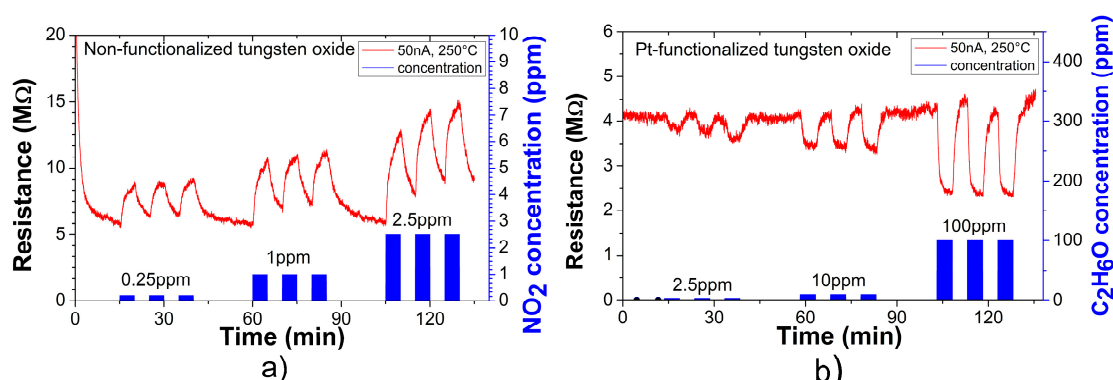
**Figure 1.** View of the single-nanowire sensor array system (a) and a pair of electrodes with a nanowire integrated across (b).

Gas sensing tests of the nanosensors were carried out at 250 °C using a current of 50 nA. Generally, the characterization of the dependency of the sensor's response to analyte concentration proved better responses to nitrogen dioxide when using the non-functionalized nanowires (Figure 2a), as opposed to the sensors based on Pt-functionalized nanowires, which showed better responses to ethanol (Figure 2b). Thus, non-functionalized nanosensors displayed up to 40% higher response to nitrogen dioxide than Pt-functionalized nanosensors, whereas Pt-functionalized nanosensors showed up to 60% higher response to ethanol compared to the non-functionalized nanosensors. These results are consistent with our previous observations on non-functionalized and Pt-functionalized multiple-nanowire based sensors [2].



**Figure 2.** Calibration curves for nitrogen dioxide (a) and ethanol (b) using the non-functionalized and Pt-functionalized tungsten oxide nanowires.

Figure 3a,b show the typical electrical resistance changes when exposing the sensors to different concentrations of nitrogen dioxide and ethanol, respectively. Overall, the responses displayed reproducible behaviours for the same concentration of the analyte, with the electrical resistance increasing or decreasing when the sensors were exposed to nitrogen dioxide or ethanol, respectively. This is consistent with other n-type metal oxides reported in the literature, including tungsten oxide. These results also showed longer response and recovery times for the non-functionalized nanosensors, as opposed to the Pt-functionalized nanosensors.



**Figure 3.** Resistance changes recorded on the non-functionalized systems towards various concentrations of nitrogen dioxide (a) and on the Pt-functionalized for ethanol (b).

#### 4. Conclusions

We validated the fabrication of single-nanowire sensor array systems based on either non-functionalized or Pt-functionalized tungsten oxide. These systems demonstrated better response to nitrogen dioxide or ethanol when using nanosensors based on non-functionalized or Pt-functionalized systems, respectively. Pt-functionalized based systems also proved faster response

and recovery times compared to the systems based on non-functionalized tungsten oxide nanowires. The results suggest that the use of these systems integrated in a monolithic array could allow for the selective detection of other gaseous species. Further work on this line is in progress.

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**Conflicts of Interest:** The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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