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Silver Growth on Tungsten Oxide Nanowires for Nitrogen Dioxide Sensing at Low Temperature [†]

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Abstract: Gas sensors produced and working at low temperatures are particularly interesting for their compatibility with temperature sensitive substrates such as flexible ones or for their use in specific environments. In this work, we present the chemical synthesis of silver nano-islands grown on ultrathin tungsten oxide nanowires (Ag/WO₃ NWs) in order to obtain sensing materials for nitrogen dioxide (NO₂) detection at temperatures below 150 °C. We compare the efficiencies of NO₂ gas sensing, for WO₃ NWs both before and after the silver growth, by drop-casting the nanomaterials from colloidal solutions onto substrates. Interestingly, the working temperature is reduced down to 130 °C even for NO₂ concentrations as low as 0.2 ppm, with a clear improvement in sensitivity in the case of the Ag/WO₃ NWs. Additionally, continuous UV irradiation reduced greatly the recovery time.

Keywords: NO₂ sensors; WO₃ nanowires; low temperature detection; UV irradiation; silver nano-islands

1. Introduction

Nitrogen dioxide (NO₂) is a toxic oxidizing gas considered as one of the main pollutants found in the atmosphere, harmful to human health and environment [1]. It takes its origin mostly from the burning of fuel from cars. For decades, metal oxide semiconductors have been applied increasingly as sensing materials as (i) the gas absorption/desorption on the surface changes its conductivity [2] and (ii) they present high sensitivity and relatively low cost [3]. Great efforts have been made to further improve the performances of n-type semiconductors such as SnO₂, ZnO or WO₃. However, their best gas sensing performances were observed at temperatures higher than 200 °C, which require higher consumption. Recently, scientific researches have been focused on the use of novel nano-materials, especially metal/metal oxide nano-composites, and UV-light excitation as an efficient and inexpensive way for gas sensing performance improvements [4]. Following these directions, we focus on ultrathin and highly reactive tungsten oxide nanowires (WO₃ NWs) and study the potential to chemically reduce silver salts directly on top of their surface to obtain silver nano-islands grown on the nanowires (Ag/WO₃ NWs). Gas sensing experiments were performed using this material and revealed that Ag/WO₃ NWs present higher response to NO₂ than WO₃ NWs even for NO₂ concentrations as low as 0.2 ppm. A recovery time improvement could also be observed under continuous UV excitation.

2. Materials and Methods

- *Synthesis of WO_{3-x} NWs*: Ultrathin WO_{3-x} NWs were synthesized by a solvothermal method using slight modifications from our previous work [5]. Typically, 110 mg of Na₂WO₄ were dissolved in 3 mL of deionized water and 3 mL of 7% HNO₃ aqueous solution were then added. A light-yellow deposition of H₂WO₄ was formed immediately and centrifuged to get a solid which was washed twice with isopropanol. Then, 16 mL of oleylamine was added and the mixture was sonicated for 20 min to get clear solution. The solution was then transferred into a 45 mL autoclave, purged with argon and put into an oven at 220 °C for 12h. The blue WO_{3-x} NWs products were then washed by three centrifugation steps using absolute ethanol. The prepared WO_{3-x} NWs were then redispersed in toluene and kept in an argon-filled glovebox for further use.
- *Synthesis of Ag/WO₃ NWs*: The original synthesis of Ag/WO₃ NWs is based on a controlled reduction of silver ions directly onto preformed WO_{3-x} NWs. This silver growth on the WO_{3-x} NWs was realized following a modified approach from G. Xi et al. [6] A first step involved the creation of silver seeds onto the nanowires by injecting, under argon, 350 μL of AgNO₃ (0.3 mg/mL). The solution turned from blue to green and was kept under stirring for 4 h. Then, the growth of silver islands on the preformed seeds could be obtained by adding drop-by-drop each hour 300 μL of AgNO₃ (3 mg/mL) until precipitation of the Ag/WO₃ NWs. The nanowire precipitate was finally dispersed as a nice brown solution in toluene by adding a minimum of oleylamine (see Figure 1a for color evolution).

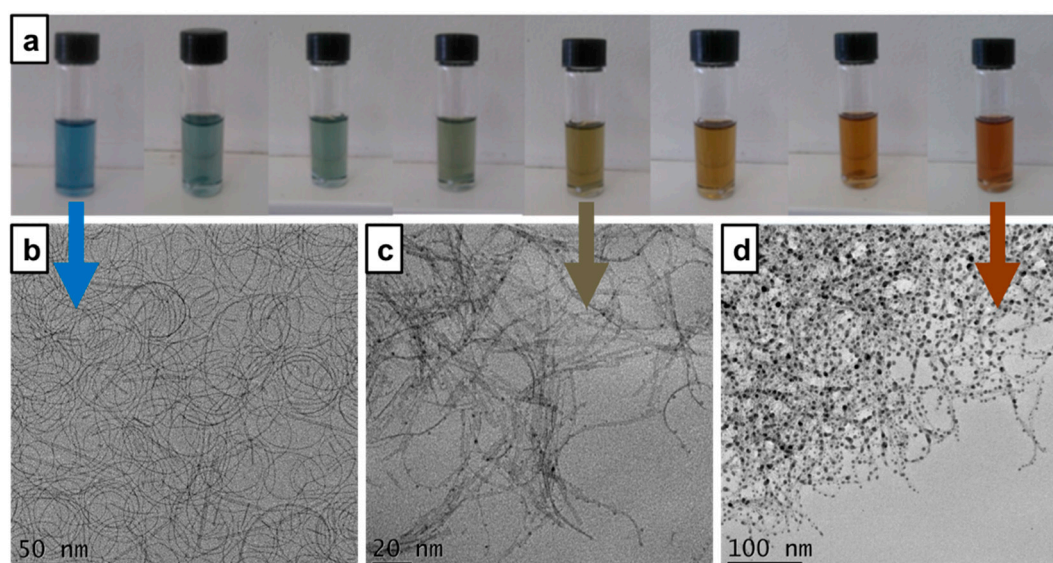


Figure 1. (a) Control of the silver island density from WO_{3-x} NWs (left) to Ag/WO₃ NWs (right) as a function of time. TEM images for WO_{3-x} NWs (b), intermediate density of silver islands on NWs (c) and final Ag/WO₃ NWs (d).

- *Sensor fabrication*: The gas-sensing performances were then studied using Ti/Pt thin interdigitated electrodes (5/100 nm respectively) deposited on Si/SiO₂ by magnetron sputtering. All materials were deposited by drop-casting 10 μL of the solutions (about 1 mg/mL) onto the electrodes followed by drying on a hot plate at 80 °C for 5 min. The films were then exposed to UV-ozone treatment for 15 min before being finally annealed at 150° for 30 min and then used in sensing experiments.
- *Gas measurements procedures and characterizations*: Gas sensing experiments were performed at various working temperature (from 25 to 130 °C) under obscurity or continuous UV-light-emitting-diode excitation (LED, λ_{exc.} = 390 nm; 60 mW) for four NO₂ concentrations (0.2, 0.5, 1 and 2 ppm) using dry air as gas vector. High-Resolution Transmission Electron Microscopy (HR-

TEM) was realized on a JEOL 3010 microscope. UV-vis spectroscopy was recorded using a Varian CARY 50 spectrophotometer.

3. Results and Discussion

In this study, tungsten oxide material was chosen for NO₂ detection as this material is known to be very efficient regarding this gas [7]. Concerning the shape, we focus on nanowires with high aspect ratio as they possess high surface-to-volume ratio which is a parameter known to improve gas sensing properties [8]. As we could synthesize in previous studies ultrathin WO_{3-x} NWs with high aspect ratio and good photocatalytic activity, we chose this material as a good candidate. The main interest of this study was to explore the ability of these ultrathin WO_{3-x} NWs to reduce silver in order to realize Ag/WO₃ nanocomposites formed by silver island grown on the WO₃ NWs surface. This is extremely interesting regarding the potential improvements in gas detection of metal/metal oxides nanostructures, as proven already with Ag/WO₃ materials of higher dimensions [9]. In the present case, we start with monoclinic WO_{3-x} NWs having 2 nm diameter and 120 nm length, as shown on the TEM image on Figure 1b. The blue color of the WO_{3-x} NWs solution is directly connected to the oxygen defects of the materials and appears on the UV-visible absorption spectra as a wide absorption band starting at 500 nm with an increasing intensity towards higher wavelengths (Figure 2a, red line). This reduced form of tungsten oxide is easily oxidized, for instance after air exposure during a day, giving the transparent material referred as WO₃ NWs, which doesn't possess the visible absorption anymore (Figure 2a, blue line) and will be used as a reference for sensing materials. The WO_{3-x} NWs can also be oxidized through the reduction of a metal salt, such as silver nitrate in the present study. The reduction of silver ions into metallic silver can occur directly onto the surface of the NWs, by a classical two-step seed-growth mechanism. Indeed, under the present specific synthesis conditions, homogeneous nucleation of silver nanocrystals is avoided, allowing a controlled heterogeneous growth of islands on the NWs' surface. We thus obtain a control of the size and the density of silver islands on the oxidized tungsten oxide NWs. Figure 1c,d show typical TEM images of these metal/metal oxide nanocomposites during silver growth. In the final stage of the growth (Figure 1d), the material referred as Ag/WO₃ NWs present homogeneous distribution of spherical silver islands having ca. 5 nm diameter. As expected, the brown Ag/WO₃ NWs don't possess the visible absorption due to oxygen defects as it is an oxidized form of tungsten oxide, similarly to the air-exposed WO₃ NWs (Figure 2a, black line). However, Ag/WO₃ NWs have the classical feature of silver plasmon resonance at 450 nm, corresponding well to 5 nm spherical silver particles close to WO₃ environment. Interestingly, it is possible to follow the silver island growth directly on the UV-visible absorption spectra, as shown on Figure 2b, where the plasmon resonance peak intensity increases and slightly shifts (yellow arrow) while the absorption band attributed to oxygen defects decreases (blue arrow).

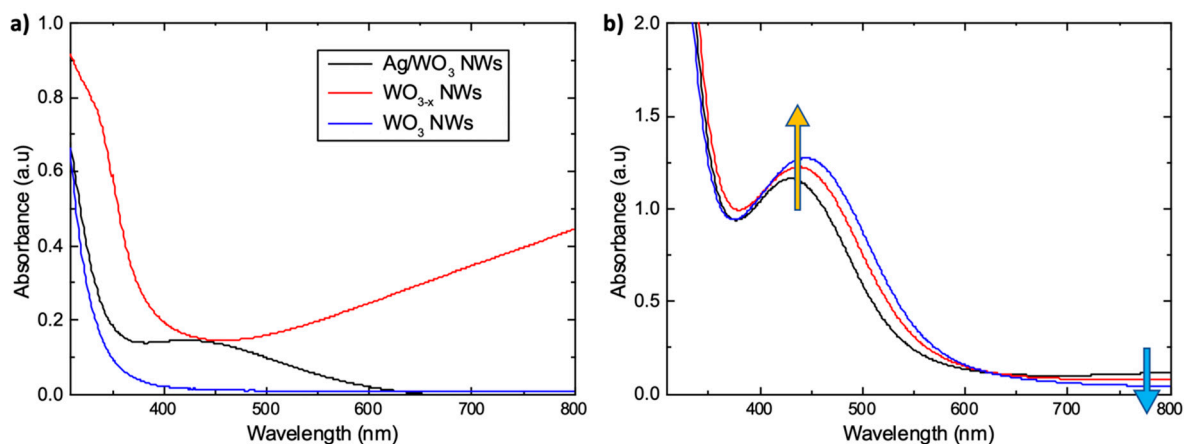


Figure 2. UV-visible absorption spectra for the three forms of tungsten oxide NWs (a) and evolution of the absorption spectra with silver growth for Ag/WO₃ NWs (b).

Gas-sensing performances were then studied using these materials. UV-light assisted detection was used as it greatly enhances the detection of gas with metal oxides in general [4] and more specifically in the case of WO_3 [10]. The mechanism involves the conversion of NO_2 molecules from NO_2 to NO under light wavelength below 420 nm, as shown also with ab initio calculations [11]. This leads to the resistance increase observed on Figure 3 when the NO_2 gas is introduced in the chamber. The best amplitude and time responses were obtained at 130 °C. At this temperature, as seen on Figure 3a, the DC electrical measurements using the reduced form WO_{3-x} NWs is weak and not stable. However, the oxidized WO_3 NWs show still weak but much more stable response (Figure 3b). This material could detect NO_2 even at concentration as low as 0.2 ppm. Importantly, sensitivity was increased by two orders of magnitude when using the Ag/WO_3 NWs. Indeed, these Ag/WO_3 NWs present higher response to NO_2 than WO_3 NWs even for NO_2 concentrations as low as 0.2 ppm (Figure 3c). A recovery time improvement is also observed.

Additionally, the UV-ozone post treatment of the sensing layer appears to be critical for the high sensitivity. In the case of Ag/WO_3 NWs, a comparison of the sensing properties was done on layers being exposed or not to this post-treatment. Responses of the sensors at 130 °C under UV light in the presence of 2 ppm of NO_2 revealed that an increase of $R(NO_2)/R(\text{dry air})$ from 7.2 to 472 in average was obtained thanks to this post-treatment (Figure 3d). This is related to the use of surfactants, namely oleylamine, to redisperse the NWs in toluene and that needs to be removed from the NWs surface before use. The UV-ozone treatment is efficient for this purpose and mandatory before any use.

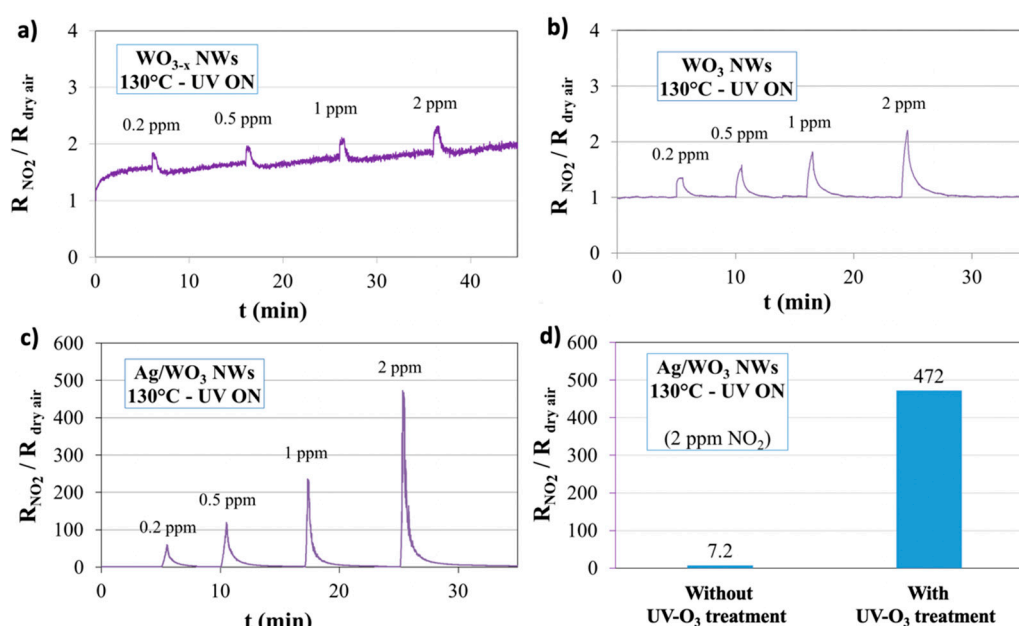


Figure 3. Sensor responses at 130 °C under UV illumination for WO_{3-x} NWs (a), WO_3 NWs (b) and Ag/WO_3 NWs (c). Comparison of the sensor responses for Ag/WO_3 NWs with or without the UV-O₃ post-treatment (d).

4. Conclusions

In this study, ultrathin WO_{3-x} NWs were used for their ability to reduce silver in order to realize Ag/WO_3 nanocomposites formed by silver islands grown on the WO_3 NWs surface. Homogeneous nucleation of silver nanocrystals was avoided, allowing only a controlled heterogeneous growth on the NWs surface. UV-light assisted gas-sensing performances were performed and showed an increase in sensitivity by two orders of magnitude when using the Ag/WO_3 NWs. This study provides an interesting approach to fabricate nitrogen dioxide sensors on conformable substrate with significant properties for applications in environmental monitoring devices.

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Conflicts of Interest: The authors declare no conflict of interest.

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