

***p*-type PdO nanoparticles supported on *n*-type WO₃ nanoneedles for hydrogen sensing**

F.E. Annanouch^{1,2}, S. Roso¹, Z. Haddi^{1,3}, S. Vallejos⁴, P. Umek⁵, C. Bittencourt⁶, C. Blackman⁷, T. Vilić¹ and E Llobet^{1,*}

¹Minos-EMaS, Universitat Rovira i Virgili, Avda. Països Catalans, 26, 43007 Tarragona, Spain.

²Aix Marseille Université, CNRS, Université de Toulon, IM2NP UMR 7334, Marseille, France.

³Laboratoire des Sciences de l'Information et des Systèmes (LSIS), Aix-Marseille University, France.

⁴SIX Research Centre, Brno University of Technology, Technická 10, Brno, CZ-61600, Czech Republic.

⁵Department of Solid-State Physics, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia.

⁶Materia Nova, Univeristé de Mons, Parc Initialis - Av. N. Copernic, 1, B-7000, Mons, Belgium.

⁷Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom.

*Corresponding author e-mail: eduard.llobet@urv.cat ; Fax: +34 977 559 605.

Abstract

We report the synthesis of palladium **nanoparticle (NP)** decorated WO₃ **nanoneedles (NNs)** employing a single-step, aerosol assisted chemical vapor deposition approach. Two different Pd precursors were investigated in view of optimizing the morphology and the gas sensing performance of the resulting nanostructured films. In particular, Palladium acetylacetonate was found to be more suitable than ammonium hexachloropalladate for obtaining *n*-type WO₃ NNs uniformly decorated with well dispersed *p*-type PdO NPs. The active films could be directly deposited on the electrode area of MEMS resistive transducers. The morphology and chemical composition of the films was investigated by **scanning electron microscopy, high-resolution transmission electron microscopy**, Raman **spectroscopy** and **X-ray photoelectron spectroscopy** analysis. PdO-decorated WO₃ NNs show a response toward hydrogen that is about 680 times higher than that of bare WO₃ NNs. Finally, PdO-loaded sensors display extremely low-cross sensitivity to water vapor, which makes them remarkably immune to changes in the background humidity.

1. Introduction

Tungsten trioxide (WO₃), a transition metal oxide and *n*-type semiconductor has been employed in a wide spectrum of applications including electrochromic and photochromic devices [1,2], photocatalysis [3], and gas sensors [4]. With the development of

nanotechnology, WO_3 has been synthesized in different forms such as nanoneedles [4], nanotubes [5], and nanorods [6]. In comparison to standard polycrystalline metal oxide films, nanostructured metal oxides provide higher surface-to-volume ratio, higher level of crystallinity or the presence of quantum confinement effects, which have improved gas sensitivity [7], and long term stability [4]. The development of synthesis techniques to achieve uniform size and shape, defect-free crystal structure and homogenous stoichiometry in nanostructures metal oxides is a technological challenge. The aerosol assisted chemical vapor deposition (AACVD) has been shown a suitable method for producing tungsten oxide nanoneedles (NNs) with remarkable gas sensing properties [7]. Additionally, AACVD has been employed for co-synthesizing, in a single step, tungsten oxide NNs homogeneously decorated with metal or metal oxide nanoparticles of Pt, Au or Cu_2O [4,8-10]. It is well known that the loading of the metal oxide matrix with catalyst nanoparticles (e.g., surface functionalization of the nanostructured metal oxide) may lead to significant improvements in response, selectivity, long-term stability and cross-sensitivity to ambient moisture. In particular Pd has been widely employed as sensitizer in metal oxide films for developing hydrogen sensors [11-13]. In this paper we explore the AACVD synthesis of Pd NPs-decorated WO_3 NNs, using a single-step strategy, with two different palladium precursors (palladium(II) acetylacetonate and ammonium hexachloropalladate(IV)). Pd-decorated nanoneedles are directly grown onto MEMs based micro-hotplate transducers in view of obtaining resistive hydrogen sensors.

Scanning electron microscopy (SEM), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) have been used to determine the morphology, phase composition, and microstructure of the layers grown. Once the best precursor is identified, the hydrogen sensing properties of both bare and Pd decorated WO_3 NNs are discussed in detail. Special attention is paid to the effect of background humidity in sensor response.

2. Experimental

2.1 Transducer platforms. Micro electro mechanical systems (MEMS) based microsensor platforms employed a double side polished *p*-type (100) Si substrate with 300 μm thickness. The microfabrication steps comprised implantation, photolithography, metallization, lift-off and back side etching of the substrate to define the membranes. In one chip, four membranes with dimension of 1 mm \times 1 mm, were grown. Each membrane (see Fig.1) comprised of a POCl_3 -doped polysilicon resistive heater (16 Ω/sq , 0.47 μm thickness, and $\text{TCR} = 6.79 \times 10^{-4}/^\circ\text{C}$), silicon oxide insulator layer (800 nm thick), and platinum electrodes (0.2 μm thickness, 50 μm electrode gap). Each chip was mounted on a

standard TO-8 package [7]. During AACVD, a shadow mask was used to confine the film deposition to the electrode area.

2.2 Reactants. Palladium(II) acetylacetonate (99 %), Ammonium hexachloropalladate(IV) (99,99%), Tungsten hexacarbonyl (97 %), Methanol ($\geq 99.9\%$), Ethanol ($\geq 99.8\%$) and Acetone ($\geq 99.9\%$) were obtained from Sigma-Aldrich and were used as received without further purification.

2.3 Synthesis procedure. The synthesis was carried out in a horizontal AACVD reactor using N_2 (g) (99.96%, BOC) as a carrier gas (300 sccm). A Johnson Matthey Liquifog 2 operating at 2 MHz was used to generate the aerosol from the precursor solutions. In a previous step, MEMS microsensors substrates were cleaned with acetone, then with ethanol, dried with air and then placed inside the reactor. Pure WO_3 NNs were obtained at 500 °C, from AACVD of $W(CO)_6$ (50 mg) dissolved in a mixture of acetone (15 cm^3) and methanol (5 cm^3). One set of Pd nanoparticle decorated WO_3 NNs were synthesized at 400 °C via a single-step AACVD co-deposition route with $W(CO)_6$ (50 mg) dissolved in acetone (15 cm^3) and $[Pd(acac)_2]$ (5 mg) dissolved in methanol (5 cm^3). This sample is denoted **ac-1SD**. A second set of Pd nanoparticle decorated WO_3 NNs were synthesized at 400 °C via a single-step AACVD co-deposition route with $W(CO)_6$ (50 mg) dissolved in acetone (15 cm^3) and $(NH_4)_2PdCl_6$ (5.8 mg) dissolved in methanol (5 cm^3). This sample is denoted **am-1SD**. It is worth noting that the co-deposition with $(NH_4)_2PdCl_6$ was difficult due to the low solubility of this precursor in acetone. After deposition all samples were subjected to annealing at 500 °C for 3 h in air. Table 1 summarizes the growth conditions.

Table 1. Depositions details

Sample name	MOX precursor (mg)	Solvent (cm^3)	Metal precursor (mg)	Solvent (cm^3)	Deposition T (°C)
WO₃	$W(CO)_6$;50	A; 15 + M; 5	-----	----	500
ac-1SD	$W(CO)_6$; 50	A; 15	$Pd(acac)_2$; 5	M; 5	400
am-1SD	$W(CO)_6$; 50	A; 15 + M; 5	$(NH_4)_2PdCl_6$; 5.8	M; 5	400

Legend: A: Acetone; M: Methanol.

2.4 Material analysis tools. Scanning electron microscopy (SEM) images were taken using the FEI Quanta 600. XRD patterns were collected by Bruker, AXD D8-Discover, using Cu K- α radiation operated at 40 kV and 40 mA. Raman spectra were obtained employing a Renishaw Raman Fourier transform infrared spectrometer. High resolution transmission electron microscopy images were obtained from a JEOL JEM-2100 with a LaB_6 filament at an acceleration voltage of 200 keV. Film samples were prepared by removing the film from the glass substrate via sonication in methanol for 15 min, and then drop-casting onto an Agar Scientific 400 Cu mesh holey carbon grid. Excess

solutions were removed with filter paper. Images were recorded on a Gatan Orius charge-coupled device. XPS analysis of the films was carried out using a Thermo Scientific K α spectrometer with Al K- α radiation, a dual beam charge-compensation system, and constant pass energy of 50eV. All the XPS data were elaborated using Casa XPS v.2.3 software and binding energies were referenced with respects to C 1s peak at 284.5 eV.

2.5 Gas sensing tests. Gas-sensing tests were carried out in a Teflon/ stainless steel test chamber (2×10^{-2} dm³) under a continuous gas flow of 200 sccm. The resistance of the different samples, while exposed to the studied gases, was monitored via an Agilent-34970A multimeter. The desired concentrations of the test gases were obtained by employing calibrated gas bottles and PC-driven mass flow controllers (Bronkhost Hitech 7.03.241). Humidity measurements were performed using an Environics series 4000, which allowed us to automatically mix up to three individual gases in a balance gas (dry air, target gas, and humidified air). The sensors were exposed to the test gas for 10 min, and subsequently the chamber was purged with air for 30 min, which enabled recording response and recovery cycles. Sensor response (R) was defined as $R = R_a/R_g$, where R_a and R_g are the sensor resistances at the stationary state in air and after 10 min of exposure to the analytes, respectively.

3. Results and discussion

3.1 Morphology and composition analysis results. The different materials were grown and directly integrated onto MEMS transducers. After the annealing process, the color of all samples was white-yellow, which is indicative of the full oxidation of tungsten oxide NNs [14]. SEM imaging of WO₃ NNs revealed the formation of a layer of randomly oriented NNs, distributed homogenously over the electrode area (Fig.2.a, b). **ac-1SD** and **am-1SD** NNs had a diameter that ranged between 40 to 120 nm, and a length of approximately 8 μ m. However, an agglomeration of nanoparticles was observed on the surface of **am-1SD** samples. For bare WO₃ samples, the NNs were thicker (50–200 nm) and almost twice as long (19 μ m). This difference in morphology is likely due to the different WO₃ deposition temperature (i.e., 400°C for **ac-1SD** and **am-1SD** and 500°C for bare samples), which affects the growth rates of the materials [15].

XRD patterns (Fig.3) obtained from bare and decorated samples suggest the formation of monoclinic-phase WO₃ NNs (P21/n (14) space group, with typical cell parameters of $a=0.729$ nm, $b=0.7539$ nm, $c=0.7688$ nm, and $\beta=90.91^\circ$; ICCD card no. 72-0677). No peaks for palladium or palladium oxides were observed in the pattern, likely due to their small size (nanoscale) and/or to the relatively low amount present. This is in agreement with previously reported results on AACVD grown WO₃ NNs

decorated with Au, Pt or Cu NPs [4,8,9]. The platinum and boron nitride (BN) diffraction peaks indicated come from the electrodes and the membrane within the MEMs transducer, respectively [16]. There are no shifts in the peak positions for bare WO₃ NNs or Pd decorated WO₃ NNs, which shows that the monoclinic crystal structure of tungsten trioxide remained unchanged upon the addition of palladium.

Raman spectra of annealed films are shown in Figure 4. The spectra of **ac-1SD** and **am-1SD** films exhibited well-defined Raman bands at 272, 326, 715 and 805 cm⁻¹, characteristic of the four most intense vibrational modes of monoclinic WO₃ [17]. The bands at 272 and 326 cm⁻¹ are assigned to bending modes of the bridging oxygen (W-O-W), whereas the bands at 715 and 805 cm⁻¹ are assigned to the stretching modes (W+6-O).¹⁷ The weak band at around 949 cm⁻¹ is a typical band of W=O stretching mode for terminal oxygen atoms that are present on the surface of the NNs [18]. No peaks directly attributable to palladium or palladium oxides are observed.

Figure 4. Raman spectra of Pd/WO₃ (ac-1SD) (bottom), and Pd/WO₃ (am-1SD) (top). Labels correspond to wavenumbers and associated vibrating modes, as discussed in the main text.

In order to obtain more detailed information about the morphology and the elemental composition of the samples, HRTEM and XPS were carried out. Results obtained from pure WO₃ films are not shown because these are identical to those reported in our previous works [4,19]. Fig. 5 shows representative TEM images of the as-deposited NNs decorated with Pd nanoparticles. The results revealed the presence of well-dispersed nanoparticles along the surface of the NNs for the **ac-1SD** sample (3 -5 nm is size), consistent with results previously seen for gold and platinum NP decorated WO₃ NNs [9]. On the other hand, for **am-1SD** films the decorating nanoparticles were rather big (15 to 30 nm) and the number of particles was very small (not homogeneously distributed). This is attributed to the fact that the (NH₄)₂PdCl₆ precursor was not completely dissolved in the mixture of acetone and methanol employed. Furthermore, high-resolution TEM images show that single crystalline NNs with uniform lattice structures were obtained for all the samples synthesized. The spacing between adjacent lattice fringes is 0.378 nm, consistent with the unit cell (c=0.7688 nm) observed by XRD and with our previous results [19].

NPs were characterized by lattice fringes with interplanar spacing of 0.225 nm corresponding to the (111) plane of face-centred-cubic (fcc) palladium (ICDD card no. 00-046-1043). Thus, the presence of Pd NPs on as-deposited WO₃ NNs is confirmed.

Moreover, it is evident that the on-step method has resulted in the correct synthesis of Pd nanoparticles from Pd(acac)₂, with similar deposited Pd nanoparticle size, likely due to the good solubility of this Pd

precursor in both methanol and acetone. We note the formation of a thick amorphous layer (indicated by black arrows, see Fig. 5) surrounding the NNs of samples (ac-1SD and am-1SD), which is ascribed to the formation of carbon associated with the decomposition of the carrier solvents during the deposition process.

XPS analysis of the as-deposited and annealed films was investigated. Fig 6.a displays the W 4f spectrum recorded on the as-deposited **ac-1SD** and its fitting analysis. The components centered at 35.4 eV and 37.5 eV are associated to the $4f_{7/2}$ and W $4f_{5/2}$ spin orbit doublet respectively. These values are in good agreement with those found in the literature for W^{+6} in WO_3 stoichiometric films [20]. The weak emission located around 41 eV is originating from W $5p_{3/2}$ core level [20]. Fig 6.b spread out the W 4f XP spectrum recorded from the as-deposited **am-1SD** and its fitting analysis. To reproduce the spectrum two doublets of Voigt curves and one singlet were fitted. The doublet of the highest intensity peak, centered at 35.9 eV and 38 eV are corresponded to $4f_{7/2}$ and $4f_{5/2}$ respectively, and were generated by photoelectrons emitted from W atoms with the oxidation state +6, i.e., stoichiometric WO_3 [20]. On the other hand, the low intensity W 4f doublet found at 34 eV and 36 eV were generated by photoelectrons emitted from W atoms with the oxidation state +4 [21]. The weak emission located around 41 eV is originating from W $5p_{3/2}$ core level. After annealing, no binding energy shift was observed for **ac-1SD** and the composition of the surface remains stoichiometric (Fig 6.c). In contrast, the low intensity doublet corresponding to the W+4 oxidation state, observed from **am-1SD**, has been disappeared and the spectrum had the same features observed from **ac-1SD** film, which indicates the full oxidation of WO_3 nanoneedles.

Fig.7.a displays the 3d XPS spectra recorded from as-deposited **ac-1SD** films. This could be fitted by using two deconvoluted doublets. The more intense one with components centred at 335.3 eV and 340.5 eV is associated to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ for Pd metal respectively [22], while the low intense one at binding energy of 337.5 eV and 343.1 eV is attributed to PdO_2 [23]. After annealing at 500 °C for 3 h, the XPS spectra of the sample (Fig. 7. b), was dominated by two peaks at 337.1–342.4 eV [24], which are ascribed to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ for PdO. Hence, in annealed sample, all Pd nanoparticles were oxidized to Pd(II) (i.e., PdO). It is worth noting that for **am-1SD** the XPS signal was not observed, indicating that the amount of Pd at the sample surface is under the instrumental detection limit, in line with HRTEM results.

3.2 Gas-Sensing Response. Gas sensing tests were carried out by using dc resistance measurements. Bare and PdO decorated WO₃ NNs sensors were tested at various temperatures from 50–350 °C, in order to analyze the effect of the operating temperature on sensor response. **am-1SD** sensors performed similarly to WO₃ NNs sensors. This poor performance can be attributed to the precursor used ((NH₄)₂PdCl₆), which led to the production of small amounts of big-sized PdO NPs, irregularly distributed along the nanoneedles. As a consequence, **am-1SD** sensors were discarded and the results for bare and **ac-1SD** samples are reported and discussed only. Fig.8 displays sensor responses to 500 ppm of H₂ as a function of the operating temperature. At temperatures below 200°C, bare WO₃ NN films exhibited very low response, especially at 50 °C and 100 °C. In contrast, at temperatures exceeding 200 °C, the sensor showed good responses, their maximum ($S_R=2.21$) toward 500 ppm of hydrogen, was achieved at 250°C. Regarding the **ac-1SD** sensor, its response was increased by increasing the operating temperature, reaching the maximum ($S_R= 1500$) at 200 °C. The response and recovery times of the **ac-1SD** sensor were 2 min and 12 min, respectively (corresponding to a 90% change of the electrical resistance of the sensor). Further increasing this operating temperature resulted in a decrease in response and, also in a slight decrease in response and recovery times. Therefore, 200 °C and 250 °C are the optimal working temperatures for **ac-1SD** and pure WO₃ sensors, respectively. Conforming to these results, decoration with PdO nanoparticles promotes an increase in sensor response (S_R) and a negative shift of the optimal operating temperature, compared to pure WO₃ NNs.

Fig.9 illustrates response and recovery cycles of bare and PdO decorated WO₃ NNs, toward H₂. The nanomaterials were operated at their optimal temperature and hydrogen concentrations ranged from 40 to 500 ppm. Sensors experienced a decrease in their electrical resistance when exposed to a reducing gas such as H₂. The magnitude of resistance change considerably increases for PdO decorated WO₃ NNs. In addition, it can be noticed that the loading with PdO NPs results in an increase in the baseline resistance. PdO is a well-known *p-type* semiconductor [25], and WO₃ is an *n-type* semiconductor. Therefore, *p-n* junctions are formed at the interfaces of the PdO/WO₃ nanocomposite. A space charge layer develops at PdO/WO₃ interfaces, which decreases the free electrons in the conduction band of WO₃ NNs and, thus increases the baseline resistance of the sensor [4,26].

The calibration curves calculated from the change in resistance for bare and PdO decorated WO₃ NNs are plotted as a function of H₂ concentration are shown in Fig.10. The decoration with PdO highly enhances the sensitivity of WO₃ NNs toward H₂.

The selectivity of the different sensors toward H₂ was studied by measuring the response to different interfering gases such as NH₃, C₆H₆ and CO. As shown in Fig.11, it is clear that sensors consisting of PdO decorated WO₃ NNs exhibit significantly higher response toward H₂ than any of the other species tested. The response of the **ac-1SD** sensor (Fig.11.b) to 100 ppm of H₂ is almost 5 times higher than to NH₃ (100 ppm), 6 times higher than to C₆H₆ (200 ppm), and 29.5 times higher than to CO (200 ppm).

3.3 Hydrogen sensing mechanism. Hydrogen sensing of PdO decorated WO₃ NNs can be explained by the interplay of two mechanisms, namely electronic and chemical sensitization. Electronic sensitization occurs due to the presence of PdO NPs, which behave as *p*-type semiconductors. The PdO-WO₃ heterojunction results in electron transfer from the n-type WO₃ to the p-type PdO NPs. Charge space layers develop at the PdO-WO₃ interfaces, which narrow the conduction channel of the NNs and the electronic conductivity of WO₃ NNs is decreased. When H₂ is in contact with PdO, the hydrogen molecule dissociates into H⁺, which results in electronic charge transfer from the PdO NPs towards the WO₃ NNs, and in the relaxation of the space charge layer at the PdO/WO₃ interfaces. As a result, the electronic conductivity of WO₃ NNs is increased (this is illustrated in the upper part of Fig. 12). In chemical sensitization, PdO NPs both increase the number of oxygen species adsorbed on WO₃ NNs and favor, via a spill-over effect, the diffusion of H⁺ species onto the surface of the nanoneedles, where they react with oxygen adsorbates [27,28]. Upon reaction with oxygen surface species, trapped electrons are released and the conductivity of WO₃ NNs is increased (this is illustrated in the lower part of Fig. 12).

3.4 Humidity cross-sensitivity. The sensors were also tested in a humid background. Fig.13 displays the response and recovery of bare WO₃ NN and PdO-decorated WO₃ NN sensors, toward 500 ppm of H₂, under dry or humid (50% relative humidity (RH) at 25°C) conditions. While bare WO₃ NN sensors are heavily influenced by changes in moisture (both the baseline resistance and response are affected), PdO decorated WO₃ NN sensors show high immunity to humidity. Ma and co-workers have suggested that the electron depletion layer resulting from the *p-n* junctions present in PdO-SnO₂ may impede OH – adsorption [29]. The high immunity displayed by the **ac-1SD** sensor can be ascribed to the formation of *p-n* heterojunctions at the interfaces of the PdO-WO₃ nanohybrid material.

4. Conclusions

PdO NP decorated WO₃ NNs were grown onto MEMs based gas sensor substrates using a single-step AACVD. Unlike (NH₄)₂PdCl₆, Pd(acac)₂ was found to be suitable for the growth of well dispersed PdO nanoparticles decorating WO₃ NNs. XRD analysis showed that WO₃ NNs were monoclinic phase. HR-TEM proved the decoration of single crystalline WO₃ NNs with Pd-based NPs. XPS analysis confirmed that Pd was oxidized to PdO after the annealing process and that tungsten oxide NNs were close to stoichiometric (slightly oxygen defective). Gas sensing results revealed that the decoration with PdO NPs has highly enhanced the gas sensing performance of WO₃ NNs toward H₂ (by increasing sensor response and reducing the optimal operating temperature of the sensor). Finally, unlike bare WO₃ NN sensors, PdO-decorated WO₃ NN sensors show extremely low-cross sensitivity to ambient moisture, which make these sensors very promising for the detection of low concentrations of hydrogen in the atmosphere. These improvements are attributed to the electronic and chemical sensitization brought about by the multiple *p*-PdO/*n*-WO₃ heterojunctions present in the active films.

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Figure captions

Fig.1. SEM image of the sensing film (a); photograph of an individual microsensor platform showing the sensing-active area (b) and array of microsensors mounted on a standard TO-8 package (c).

Fig.2. SEM images of (a) Pd/WO₃ (Ac-1SD), (b) Pd/WO₃ (Am-1SD).

Fig.3. XRD patterns of undecorated and decorated WO₃ NNs deposited at MEMs based gas sensor.

Fig.4. Raman spectra of Pd/WO₃ (ac-1SD) (bottom), and Pd/WO₃ (am-1SD) (top). Labels correspond to wavenumbers and associated vibrating modes, as discussed in the main text.

Fig.5. TEM and HRTEM images of (a) ac-1SD, (b) am-1SD.

Fig 6. XPS W 4f core-level spectra of (a) as-deposited **ac-1SD**, (b) as-deposited **am-1SD** and (c) annealed samples.

Fig.7. XPS Pd 3d core-level spectra of (a) as-deposited **ac-1SD** and (b) after annealing.

Fig.8. Sensor responses to 500 ppm of hydrogen as a function of operating temperature.

Fig.9. Film resistance changes (a) pristine WO₃ film, (b) **ac-1SD**, toward various concentrations of H₂.

Fig.10. Hydrogen calibration curves for bare and PdO decorated WO₃ NN sensors.

Fig.11 Selectivity diagram of (a) pristine WO₃ NNs, (b) PdO WO₃ NNs, toward NH₃, C₆H₆ and CO.

Fig. 12 Hydrogen sensing mechanisms. Electronic sensitization (top). Chemical sensitization (bottom).

Fig. 13 Response and recovery cycles of (a) bare WO₃ NNs and (b) **ac-1SD** WO₃ NNs, toward 500 ppm of H₂, at the presence of both dry and humid (50% relative humidity (RH) at 25°C) atmospheres.