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Short communication

Room temperature hydrogen sensors based on metal decorated WO_3 nanowires

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ABSTRACT

The emerging hydrogen economy has created a demand for the development of improved hydrogen sensors operating at room temperature. In this work, we present hydrogen detectors based on metal decorated WO_3 nanowires that were able to detect 1000 ppm of H_2, even at room temperature (30 °C), with relatively short recovery time and high sensitivity. The nanowires were synthesized by a hydrothermal process and decorated with PdO and PtO_x nanoparticles by decomposition of $Pd(acac)_2$ and $Pt(acac)_2$ precursors. The gas responses were tested for H_2, NO, H_2S and CO analyte gases in an air buffer at 150, 200 and 250 °C (H_2 also at 30, 70 and 130 °C).

1. Introduction

Commercial hydrogen gas sensors are already utilized in hydrogen powered transport, fire alarms, process and flue gas analyzers, and leakage detectors. Such devices must meet strict specifications related to performance, lifetime, reliability and cost. Sensing of hydrogen is based on a number of different physical/chemical phenomena related to, e.g. the change in thermal/electrical conductivity, work function, mechanical properties but even optical/acoustic methods may be applied [1–5].

In resistive gas sensing devices, such as the ones discussed in this work, gaseous analytes are causing local polarization in the solid (i.e. redistributing the local charge carriers) upon adsorption [6]. The change of the local electrical field is screened by the carriers, and will vanish after some distance, called the Debye length [7]. If the diameter or thickness of the particles, wires or films is sufficiently low, the adsorbed molecules are influencing the whole volume of the solid thus inducing significant change in the electrical transport behavior [6]. Accordingly, smaller particles suggest better gas sensing. However, one should also take into account the increasing number of contacts and the superposition of the corresponding contact resistances between the nanoparticles in the percolation path [6]. Therefore, there is an optimal size for the particles. In order to maximize the gas sensor response, at least one dimension of the sensing particles should be about twice the Debye length $L_D = [\varepsilon_0 \varepsilon_r k_B T/(q^2 n)]^{1/2}$, where ε_0 is the vacuum permittivity, ε_r is the dielectric permittivity, k_B is the Boltzmann constant, T is the temperature, q is the elementary charge and n is the carrier concentration [8]. The carrier concentration is dependent on the type and the crystal structure of the material as well as on the concentration of defects and impurities present in the lattice. Carrier concentration in tungsten oxides has been evaluated to be from 10^{23} to 10^{25} m^{-3} [9–13] with a corresponding DC dielectric permittivity of ~20 [14]. Based on these values, the optimum crystal size $2L_D$ is between 4 and 40 nm (at 500 K), which is similar to the conclusion of a previous study [15].

Tungsten oxide nanowires were first prepared about 10 years ago [16] and since then have been considered as promising functional materials for catalytic/sensing [17–22], photocatalytic [23], electrocatalytic [24], electrochomic [25], gasochromic [26] and field-emission devices [27]. Due to the unique properties caused by the large surface area/volume ratio, synthesis methods of one dimensional tungsten oxide structures have been studied extensively. Solvo-/hydrothermal [28,29], sol–gel [22], template-assisted [30], electrospinning [17], and various physical [31–35] and chemical vapor deposition [36] methods have been presented.

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In this work, the gas sensing characteristics of hydrothermally processed WO_3 nanowires decorated with PdO or PtO_x nanoparticles are discussed. Most of the work is focused on evaluating the sensitivity of the prepared sensors: $S = (G - G_0)/(G_0 c) \times 100\%$, where G and G_0 are the conductance of the sensor before and after gas exposure, respectively, and c is the gas concentration. Gas sensors based on nanowire networks are expected to deliver higher stability over devices with nanoparticles of a similar diameter. The more pronounced tendency for sintering of nanoparticles at elevated operating temperatures is favoring the use of nanowires [37]. In addition, nanowires enable percolation between the metal electrodes with fewer contacts than in the case of nanoparticles. Durability over bulk Pd/Pt based sensors is also expected due to the lack of continuous Pd/Pt films that crack under repeated hydrogen exposures. The prepared nanowires have relatively small crystallites to optimize the responses to gas exposures. Also short response and recovery times are expected due to short diffusion paths of gases to the surfaces of loosely packed nanowires. The prepared sensors were observed to compete [19] and even outperform previously studied tungsten oxide nanowire sensors decorated with Pd or Pt in terms of sensitivity to hydrogen at room temperature [20,21].

2. Experimental

Pristine tungsten oxide nanowires were synthesized by the hydrothermal method described elsewhere [38,39]. In brief, sodium-tungstate (2.5 g) and sodium-sulfate (3.0 g) were dissolved in distilled water (80 ml), then hydrochloric acid (4.5 ml, 3 M) was added drop-wise under continuous stirring. After 10 min of stirring the mixture was transferred into a Teflon-lined stainless steel autoclave and was kept at 180 °C for 48 h. The product (i.e. WO_3 nanowires) was collected by centrifugation, washed with distilled water and ethanol, and finally dried at 60 °C in air. To decorate the surface with PdO or PtO_x nanoparticles, 28.6 mg $Pd(acac)_2$ or 20.2 mg $Pt(acac)_2$ was dissolved in 100 ml acetone followed by dispersion of 1.0 g of the prepared WO_3 by 3 h of ultrasonic agitation and 6 h of magnetic stirring. The solvent was evaporated at 80 °C in an N_2 atmosphere, while stirring the mixture. The product was annealed at 300 °C in air for 2 h. 3.2 ± 0.1 mg of the obtained WO_3, WO_3–PdO and WO_3–PtO_x nanowires were dispersed in deionized water of 1.0 ± 0.1 ml by ultrasonic agitation (5 min). Five droplets of the dispersions were drop cast (~3 μl of each) over the Pt electrode fingers of the Si/SiO_2 substrates while keeping the substrate temperature at 90 °C to allow for quick drying. Each droplet was dried before depositing the subsequent one. As a result, a dense, light gray film of the nanowires formed over and between the electrodes. Before inserting into the gas chamber, the prepared devices were allowed to dry overnight at room temperature.

The microstructure of the samples was studied by energy filtered transmission electron microscopy (EFTEM, Leo 912 Omega) and field-emission scanning electron microscopy (FESEM, Zeiss ULTRA plus). The crystal structure was examined by X-ray diffraction (XRD, Siemens D5000, Cu Kα radiation). The analysis of the chemical composition and the oxidation states was carried out by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, monochromated Al Kα source, analysis area of 0.3 mm × 0.7 mm, applying a charge neutralizer).

Gas response measurements were performed in a Linkam THMS600 heating and freezing stage connected to an Agilent 3458A multimeter and a pre-mixing gas blender controlled by a computer. The sensitivities of the prepared gas sensors were studied in the following order for NO, H_2, CO, and CH_4 (at 150, 200 and 250 °C) and finally for H_2 (at 30, 70 and 130 °C) analytes in a dry synthetic air buffer at 5 V of constant bias. Before each gas measurement, a 2-h temperature pulse of 250 °C in synthetic air was applied to clean the sensors' surfaces. Sensors were heated and cooled at 10 °C/min during the gas measurements. Note: In this paper, 30 °C is considered as the room temperature, because it can be easily kept constant in our measurement setup. The real room temperature is fluctuating and cannot be maintained without additional cooling.

3. Results and discussion

Particles of size 4.9 ± 2.1 nm (PdO) and 2.5 ± 1.9 nm (PtO_x) were formed on the surface of the WO_3 nanowires after the decomposition of their acetylacetonate precursors (Fig. 1). At least partly due to their smaller diameter, PtO_x nanoparticles were observed to

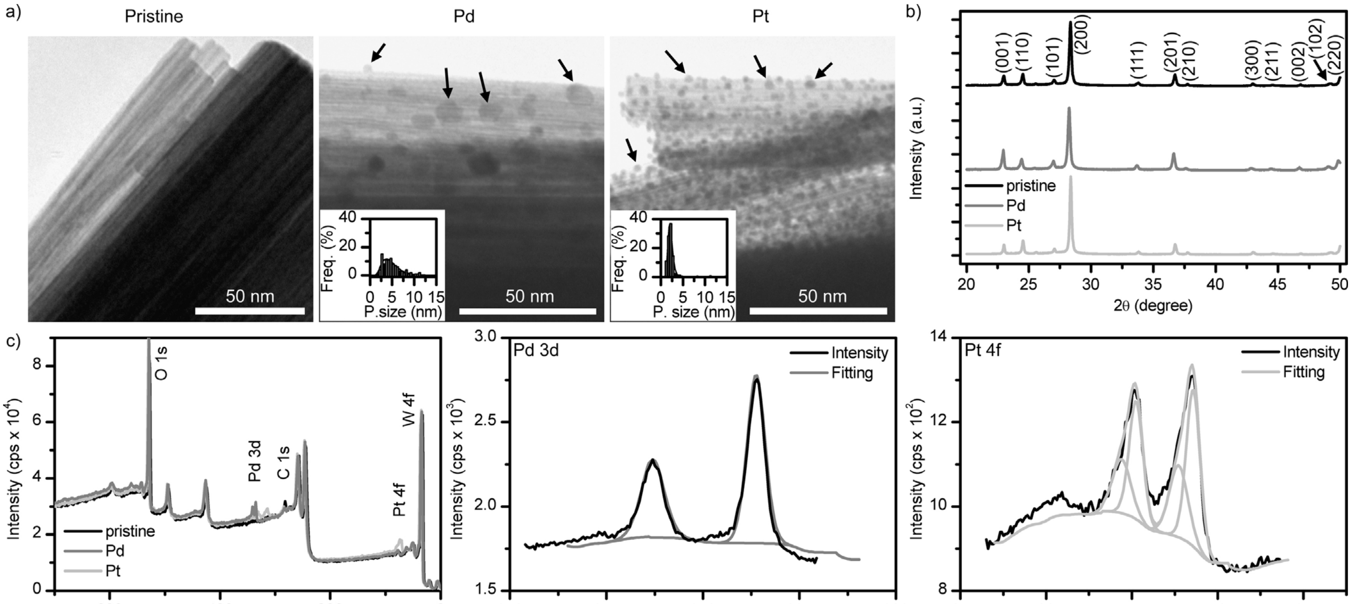

Fig. 1. (a) EFTEM images of pristine, PdO and PtO_x decorated WO_3 nanowires used for active sensing layers in the gas sensors. Insets show the corresponding size distribution diagrams of the decorating nanoparticles. (b) XRD patterns and (c) X-ray photoelectron spectra of pristine and decorated WO_3 nanowires.

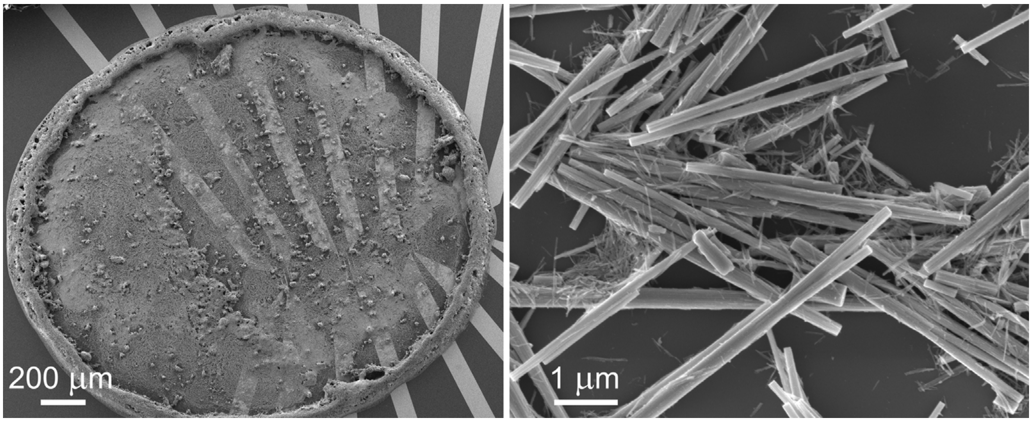

Fig. 2. Field emission scanning electron images of drop cast WO_3 nanowires on Si/SiO_2 substrate with Pt-electrodes. The inset shows the microstructure of the nanowire network in the middle of the droplet.

cover the surface of the WO_3 nanowires more uniformly than the PdO nanoparticles.

Based on XRD analysis, the nanowires are hexagonal WO_3 with an average crystal diameter of 38 ± 5 nm as calculated from the broadening of (1 1 0), (1 0 1), (2 0 0), (2 0 1) and (1 1 1) reflections. Almost identical XRD patterns were obtained for the pristine and the metal decorated samples (Fig. 1b), i.e. the analysis failed to uncover the reduced, or the oxide phases of the decorating particles (could be caused by their small size, low concentration and/or amorphous structure).

Results of X-ray photoelectron spectroscopy (Fig. 1c) indicate the nanoparticles in the Pd-modified sample are PdO rather than metallic Pd (binding energy of Pd $3d_{5/2}$ peak at 337.3 eV). In the case of the Pt modified WO_3, both the metallic and oxide phases are present (Pt $4f_{7/2}$ peak positions at 71.4 and 72.3 eV).

The prepared gas sensors are based on modulation of the resistance of the WO_3 nanowires that fill the gaps and percolate between the Pt electrodes. Dried WO_3 nanowire droplets have a thick outer border caused by a common coffee ring effect [40,41], while in the middle section, a tangled but thinner layer of the nanowires forms (Fig. 2). Based on FESEM and EFTEM micrographs, the diameter of the nanowires has relatively large variation from ~20 to ~200 nm. Relating this to the XRD peak broadening results, we concluded that in the dried powders, not only individual crystallites but also bundles of nanowires are present.

At all temperatures and concentrations, the response of the pristine nanowires to hydrogen was relatively low compared to the decorated samples (Fig. 3), while the response of all samples to NO, CO and CH_4 was moderate (see supplementary material). At the optimal operation temperature of the PdO and the PtO_x decorated nanowire based sensors, the sensitivity values after 5 min of 1000 ppm H_2 exposure are as high as 140 ± 70%/ppm (at 200 °C) and 24 ± 5%/ppm (at 250 °C) respectively, as seen in Fig. 5. For the pristine nanowires, this figure is 0.3 ± 0.3%/ppm (at 250 °C), which is consistent with the results in our earlier article on nanoparticle based sensors [42]. The high response of the PdO and the PtO_x decorated sensors is related to the partial reduction of the particles and the dissociation of H_2 on metal nanoparticles followed by a spill-over onto the WO_3 surface [43]. The supposed surface reduction of the PdO and the PtO_x nanoparticles, along with the initial pulses of H_2, seems to be supported by the lower sensitivity of the devices upon the very first injections of 10 ppm H_2 compared to the subsequent 10 ppm H_2 pulses.

Since the sensor response toward H_2 was still very large, even at 150 °C, we have performed further measurements at 30, 70 and 130 °C to see whether the devices could be used without external

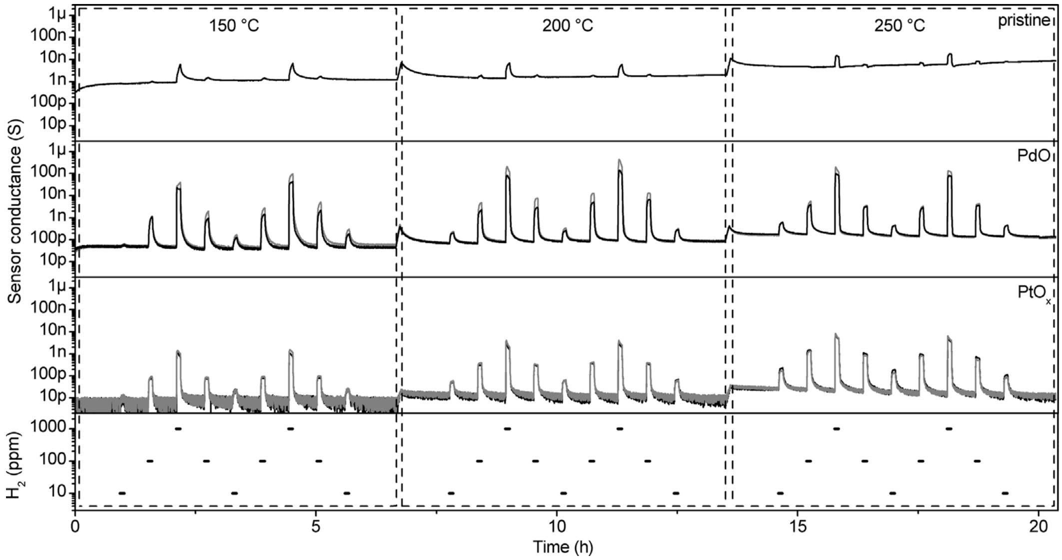

Fig. 3. The conductance of the sensors as a function of hydrogen concentration at 150, 200, and 250 °C. The black and gray curves represent two identically prepared gas sensing devices. Please note the curves are partially overlapping thus the otherwise similar noise levels are not clearly visible for the black curves.

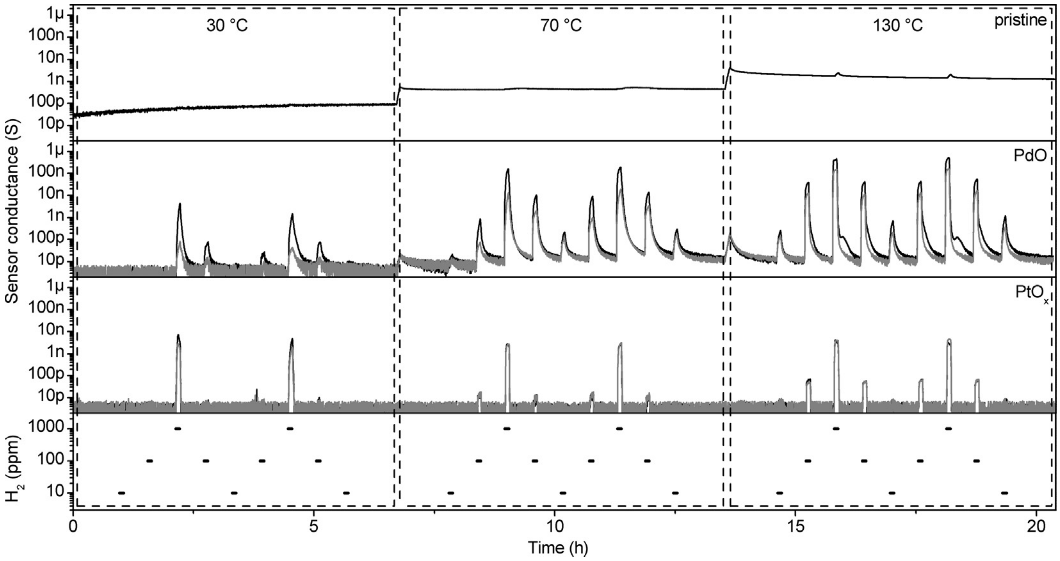

Fig. 4. The conductance of the sensors as a function of hydrogen concentration at 30, 70, and 130 °C. The black and gray curves represent two identically prepared gas sensing devices. Please note the curves are partially overlapping thus the otherwise similar noise levels are not clearly visible for the black curves.

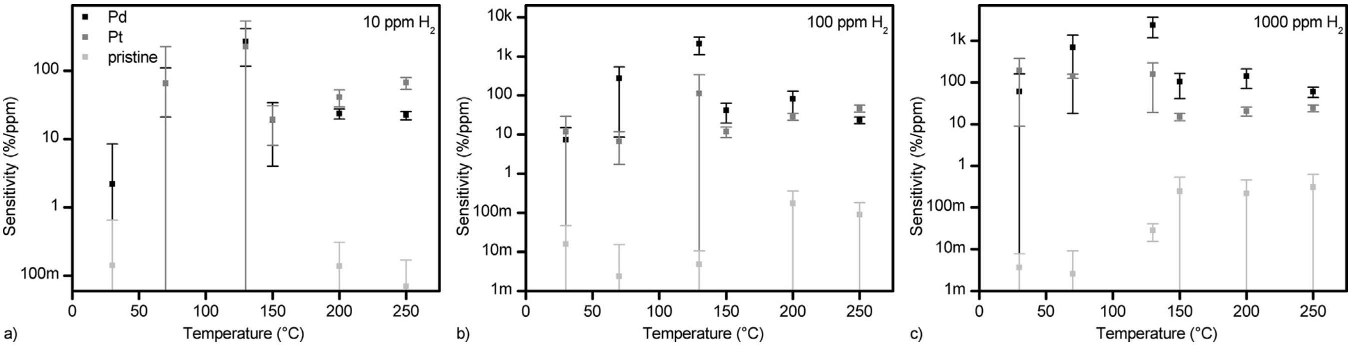

Fig. 5. The sensitivity of the sensors as a function of temperature at (a) 10 ppm, (b) 100 ppm, and (c) 1000 ppm concentrations. These values are calculated after 5 min of gas exposure. It should be noted that the conductance is further increasing, even after 1 h of gas exposure, as seen in Fig. B1 of the supplementary material.

heating. Although the pristine WO_3 nanowires failed to detect H_2 at room temperature (30 °C), both the PdO and the PtO_x decorated samples showed excellent response for 1000 ppm H_2 (Fig. 4) compared to sol–gel processed WO_3/Pd [44] or WO_3/Pt [45] thin film hydrogen sensors reported by other groups. Whilst a significant response caused by the H_2 gas was seen, the conductance did not stabilize even during very long, (up to 1 h), gas pulses at 30 and 70 °C (Fig. B1). The conductance was increasing almost linearly as a function of time during the gas exposure. As concluded earlier for porous WO_3 films [46] hydrogen molecules dissociate to hydrogen atoms that spill-over to WO_3 surface and bind to surface oxygen of the lattice thus forming water molecules. Desorption of these water molecules remove oxygen and hence create oxygen vacancies, which diffuse to the interior of the crystal. Accordingly, the slow response time of our sensors (similar to gasochromic coloration of WO_3 described in Ref. [46]) is explained by the slow diffusion of oxygen vacancies and also slow desorption of water from the tungsten oxide surface. The recovery time constant of the Pt and Pd decorated samples was observed to be less than 10 and 15 min, respectively, at 30 °C.

Even though, many of the nanowires used in this work (Figs. 1 and 2) appear to have larger diameter (20–200 nm) than the optimum (4–40 nm) for resistive gas sensing applications, the sensors show an extraordinary increase of conductance upon exposure to H_2. One reason can be a good percolation of thin nanowires (i.e. those that are ideal) between the electrodes. In a random network of thin (ideal) and thick (less ideal) nanowires, the change of conductance in the thicker nanowires is not expected to influence the gas sensitivity as much as the thin nanowires provided these latter ones are percolated. On the other hand, according to the EFTEM micrographs (Fig. 1), the larger nanowires seem to be consisting of smaller crystals, which could possibly also contribute to the large conductivity modulation caused by H_2.

4. Conclusions

Hexagonal tungsten oxide nanowires decorated with PdO or PtO_x nanoparticles proved to be excellent materials for detecting H_2 gas with very high sensitivity and good selectivity in contrast to the NO, CO and CH_4 analytes. Both decoration types resulted in very similar sensor performances. The conductance of the decorated nanowire sensor devices was found to increase with up to five orders of magnitude when exposed to 1000 ppm of H_2 in air, even at room temperature. Both types of decorated sensors had long response times (conductance is almost a linear function of time), though the recovery slopes could be fitted well with exponential decay curves of a ~10 min time constant. The overall power consumption of the devices is very low. Without the presence of H_2, there is practically no current through the device and therefore the power consumption is almost zero. When H_2 molecules are present, the peak power consumption at 30 °C is $P = U^2S = (5\,V)^2 \times 10\,\mu S = 250\,\mu W$. Accordingly, the device could be operated reasonably well from an ordinary battery-type power source, and thus the decorated WO_3 nanowires reported here are attractive materials for gas sensing elements in a number of different devices, such as portable low power consumption hydrogen leakage detectors, autonomous sensor assemblies and in fire alarms.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2013.05.082.

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Biographies

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