

One-Dimensional Vanadium Dioxide Nanostructures for Room Temperature Hydrogen Sensors

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Abstract: In relation to hydrogen (H₂) economy in general and gas sensing in particular, an extensive set of one dimensional (1-D) nano-scaled oxide materials are being investigated as ideal candidates for potential gas sensing applications. This is correlated to their set of singular surface characteristics, shape anisotropy and readiness for integrated devices. Nanostructures of well-established gas sensing materials such as Tin Oxide (SnO₂), Zinc Oxide (ZnO), Indium (III) Oxide (In₂O₃), and Tungsten Trioxide (WO₃) have shown higher sensitivity and gas selectivity, quicker response, faster time recovery, as well as an enhanced capability to detect gases at low concentrations. While the overall sensing characteristics of these so called 1-D nanomaterials are superior, they are efficient at high temperature; generally above 200 °C. This operational impediment results in device complexities in integration that limit their technological applications, specifically in their miniaturized arrangements. Unfortunately, for room temperature applications, there is a necessity to dope the above mentioned nano-scaled oxides with noble metals such as Platinum (Pt), Palladium (Pd), Gold (Au), Ruthenium (Ru). This comes at a cost. This communication reports, for the first time, on the room temperature enhanced H₂ sensing properties of a specific phase of pure Vanadium Dioxide (VO₂) phase A in their nanobelt form. The relatively observed large H₂ room temperature sensing in this Mott type specific oxide seems to reach values as low as 14 ppm H₂ which makes it an ideal gas sensing in H₂ fuelled systems.

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Keywords: Vanadium dioxide, Room temperature, Hydrogen gas, Sensors, Depletion layer, Selectivity.

1. Introduction

Gas sensors are highly demanded for innovations towards better sensing performances, lower power consumption and more compact device structures. In this case, semi-conductors are considered the best suited materials because they present advantageous features such as simplicity in device structure, circuitry, high sensitivity, versatility and robustness.

Adsorption and/or reactions of gases generally take place in order to capture or release electrons

while a redistribution of electrons take place inside to attain the electrostatic equilibrium. In the case of small crystals, depletion extends to cover the whole material and the Poisson equation becomes dependent on the shape of the crystal [1]. Common materials used as chemoresistor gas sensors are semiconducting metal oxides generally n-type which are in use worldwide to detect traces of elements in the air. For example we have leak detection in gas pipelines, indication of petrol vapor in filling stations, or for alcohols test in exhaled air [2]. However the

well-established gas sensors polycrystalline materials such as SnO₂ [3], ZnO [4], or WO₃ [5], having shown high selectivity and sensitivity are efficient at high temperature generally above 200 °C. This results in significant power consumption, in addition to complexities in device integration, which limits their technological applications. Consequentially, there is still space and need to develop nanomaterials for gas sensors that have very good sensing performance at room temperature i.e. without the need of elevated temperatures.

In addition to standard nano-powders/thin film structures, extensive set of novel nano-scaled oxide materials such as nanowires, nanotubes, nanorods, and nanobelts based systems are being investigated as ideal candidates for gas sensing applications. This is due to their set of singular surface characteristics, shape anisotropy and readiness for integrated devices [6]. This latter component includes their large surface/volume ratio, single crystalline structure due to their preferential growth, and great availability of surface-bound chemical active sites [7].

VO₂ is well known as a semiconductor oxide which presents drastic changes of electrical and optical properties at a transition temperature $T_c \sim 68$ °C. Various vanadium oxides were studied and proved to be good candidate for sensing applications. Baik et al. [8] produced Pd nanoparticles-decorated single VO₂ nanowires and studied the sensitivity under H₂ close to the metal insulator transition temperature. Manno et al. [9] investigated the influence of the NO₂ gas on the conductance of vanadium oxides films sputtered at different concentrations of O₂. They realized that pure stoichiometric VO₂ and V₂O₅ have lowest response between 200 °C and 300 °C while V₃O₇ and V₄O₉ had the best sensitivity to 100 ppm NO₂. Hence the crystallographic phases play an important if not a critical role in gas sensing at least in such a system. Raible et al. [10] showed high sensitivity and selectivity in nanofibers of V₂O₅ based sensors capable of detecting organic amines at room temperature. They showed that the material undergoes a large downward shift in the insulator to metal transition temperature following the adsorption and incorporation of atomic hydrogen produced by the dissociative chemisorption of H₂ on Pd in VO₂.

Recently Yin et al. [11] studied the sensitivity of VO₂ (B) and VO₂ (M) in moist environment demonstrating that they exhibit good stability, fast response and good recovery detection in low relative humidity (11.5 % RH) and high relative humidity (97.2 % RH) respectively. However, and to the best of our knowledge, no report has been published on room temperature sensitivity to H₂ gas of synthesized VO₂ (A) nanostructures in general and their nanobelt form especially.

In this paper we report the successful synthesis and annealing treatment of the nanobelts vanadium dioxide and the outstanding room temperature H₂ sensor based Vanadium Dioxide-VO₂ (A) nanobelts which present limit detection below 0.17 ppm and a

characteristic Mott-Type oxide described by its ultrafast spectroscopy investigations showing the competitive phases between monoclinic and tetragonal structure.

2. Experiments and Results

VO₂ (A) nanobelts were synthesized using a hydrothermal procedure. The starting precursor V₂O₅ (2.25 g Alfa Aesar) was used as the source of vanadium and was completely hydrolysed and condensed upon addition of 50 ml of distilled water. Upon heating at 95 °C and stirring thoroughly, 3.75 ml of sulphuric acid (H₂SO₄) was added into the aqueous suspension as an acid catalyst in order to convert the metalalkoxide. Then 1.25 ml of 98 % of hydrazine hydrate was added to the solution, as a foaming agent for the creation of a three dimensional network polymer with enhancement of the stability of the colloidal by its decomposition at high temperature. Finally, we precipitated the nanoparticles by addition of a strong chemical base dilute Sodium Hydroxide NaOH and the nanoparticles were collected by filtration and washing with distilled water and ethanol. The final product was redispersed in suitable apolar solvent (water) forming stable colloidal suspensions. The hydrothermal synthesis was carried out in a Teflon-lined autoclave at ~230 °C for about 48 h. Then the content was air-cooled to room temperature followed by a filtration step of the formed precipitates. To confirm the VO₂ (A) crystallographic nature of the synthesized nano-powder, X-Rays Diffraction (XRD), High Resolution Electron Microscopy (HRTEM), as well as sensing measurements was conducted. Fig. 1 reports a typical room temperature X-ray diffraction of the filtered powder. The majority of the peaks are indexed as VO₂ (A) according to the JCPDS card referenced as 00-042-0876 with a preferential orientation along (110) and lattice parameters *a* and *c* which are 8.45000 Å and 7.68600 Å respectively and *Z*=16, with the space group of P4₂/nmc. It was demonstrated that a thermal treatment of the VO₂ (A) nanobelts irreversibly transform to the VO₂ (M) nanostructures with lattice parameters *a*= 5.75290 Å, *b*= 4.5263 Å, and *c* = 5.38250 Å with $\beta = 122.60^\circ$ [12]. See Fig. 2.

The electron transmission microscopy of the filtered synthesized powder is presented in Fig. 3. The nano-particles exhibit crystal-clear shape anisotropy: a nanobelt-like morphology. A statistical imaging study shows that they have an average size of 20-150 nm in the transverse direction and a length >20 μm with a thickness less than 10 nm. The high resolution electron microscopy analysis of the bulk of individual nanobelts indicates a significant crystallinity of the VO₂ (A) with an interspacing corresponding to the (011) reticular plane orientation.

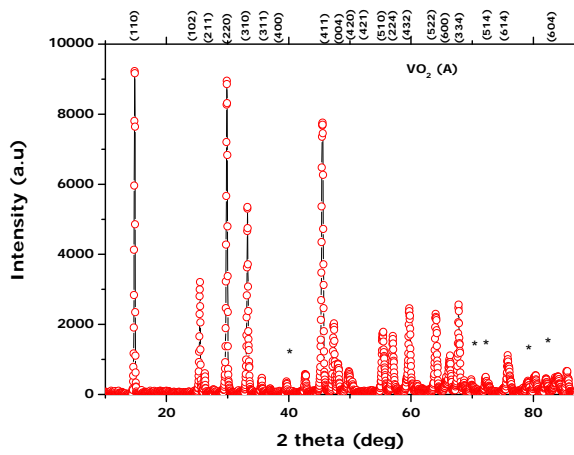


Fig. 1. XRD pattern of VO₂ (A) as-synthesized without thermal treatment with a preferential orientation along (110).

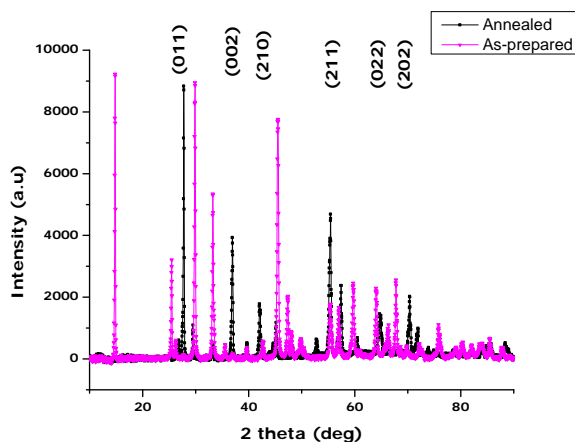


Fig. 2. Annealing treatment under Argon at 500 °C conversion of VO₂ (A) to VO₂ (M).

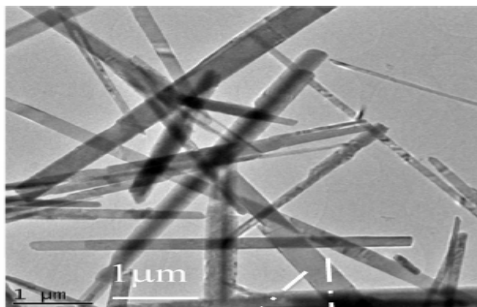


Fig. 3. Electron transmission microscopy of the filtered synthesized powder of VO₂ (A) nanobelts.

The elemental composition of the material acquired from the X-rays emitted as shown in Fig. 4 shows that the elemental composition is only constitute of vanadium atoms and oxygen with high intensity showing the nucleation of grains and crystallization of the particles. It was demonstrated that high temperature stimulates the migration of grain boundaries and causes the coalescence of more grains during the annealing process. Additionally the grain growth observed induce diffusion and

occupation of the correct site in the crystal lattice where grains with low surface energies grow larger, which contributes to increase of the surface roughness and larger microcracks corresponding to VO₂ (M) [13].

A typical characterization of VO₂ (M) crystal structure is the presence of the dimerized vanadium atoms which have alternate V-V distances of 0.2619 and 0.312 nm. Such an ability to undergo a reversible structural distortion as a function of temperature is accompanied by reversible semiconductor/insulator-to metal transition. From theoretical point of view, this phase transition has been initially interpreted in terms of Mott-Hubbard like transition [14] or electron trapping in a homopolar bond. Fig. 5 presents the description of the crystalline structure followed by XRD analysis at different temperatures showing the Mott-Hubbard phenomenon to a transition of structure at around 64.65 °C where both phases coexist. The area under the monoclinic peak decreases as the tetragonal fraction grows. The VO₂ (M) nano-crystals are entirely tetragonal at around 70 °C.

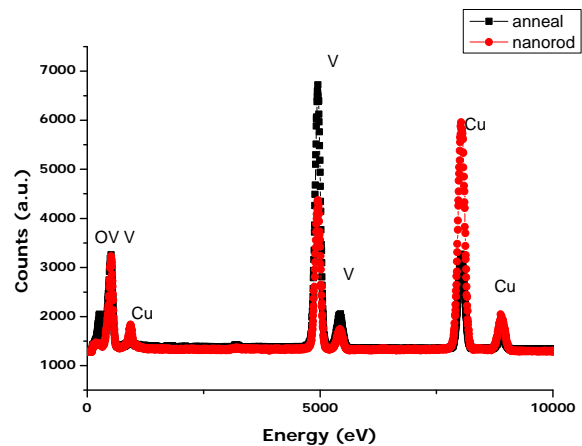


Fig. 4. EDS spectra of VO₂ nanobelts as-synthesized and annealed.

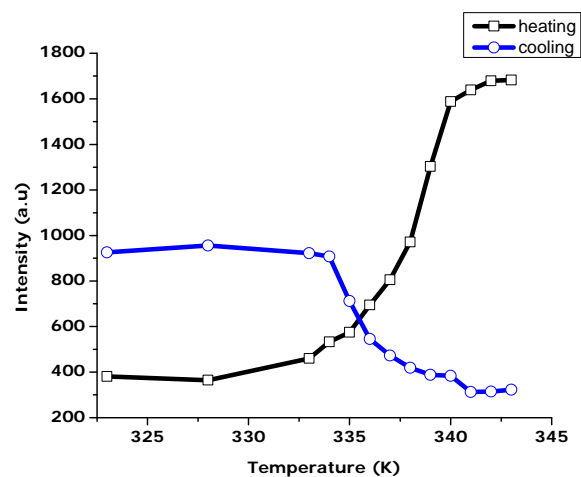


Fig. 5. Thermal evolution of the intensity of the 37.1 Bragg peak reflection with transition temperature at around 64.65 °C.

High-resolution XPS measurements were performed with a PHI 5000 Versaprobe–Scanning ESCA Microprobe spectrometer employing 100 μm 25 W 15 kV Al monochromatic x-ray beam. See Fig. 6 (a). The resolution of the instrument has been determined to be 0.1eV after 30 cycles. The specimens were nanostructures VO₂ (M) single crystals sputter for 2 min under Ar ion gun in the spectrometer vacuum of 10⁻⁷ Torr. It is well known that under typical XPS experiment, measuring conditions insulating and semiconducting samples become charged and the resulting peaks are shifted and broadened. Charging effects broadened the spectra to such an extent that no direct evidence of multiplet splitting could be obtained. The 2P_{1/2} and 2P_{3/2} peaks are separated by $\frac{3}{2} \zeta_{2p}$ where ζ_{2p} is the spin-orbit coupling constant. It was observed that the material is composed of vanadium valence V⁺⁴ and V⁺⁵ states respectively at 515.15 eV (2p_{3/2}), 522.64 (2p_{1/2}) and 516.74 (2p_{3/2}), 524.92 (2p_{1/2}) [15-16]. The simulation was done through XPS peak fit software to determine the different energy band of vanadium valence and oxygen. See Fig. 6 (b).

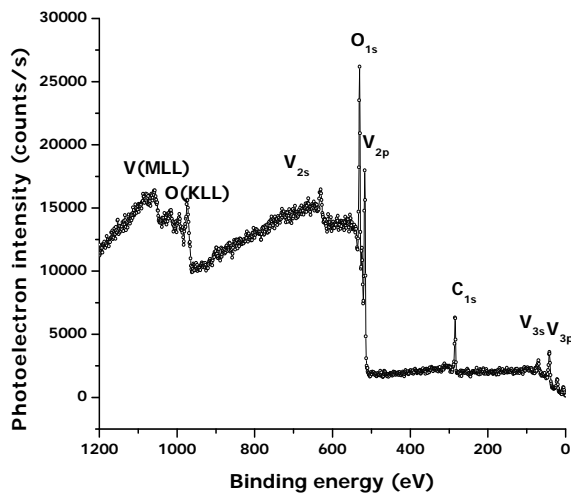


Fig 6 (a). Wide XPS scan spectra of VO₂ (M) nanocrystals.

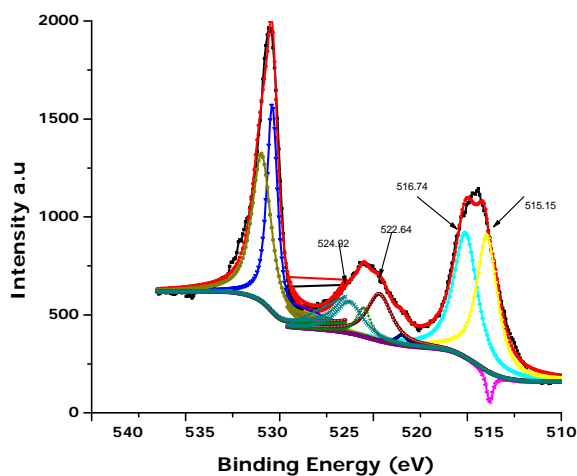


Fig. (b). Simulation analysis of the different XPS energy bands corresponding to Vanadium and Oxygen.

3. Sensing Experiments

A standard in-situ 2 contact points-based system was used. The cold pressed VO₂ (A) nanobelt pellet was squeezed between two Al electrodes and a Si substrate wafer while the whole was interfaced to a heating stage (25-300 °C). More precisely, the readings of the current and voltage during the heating and cooling stages were measured according to the set-up of Fig. 7 comprising a digital meter, an analog meter, a graphical recorder and a data logger. The isothermal responses of the pressed VO₂ (A) powders at different concentrations were measured upon injection of H₂ balanced with N₂ as a gas carrier and refluxing with pure N₂.

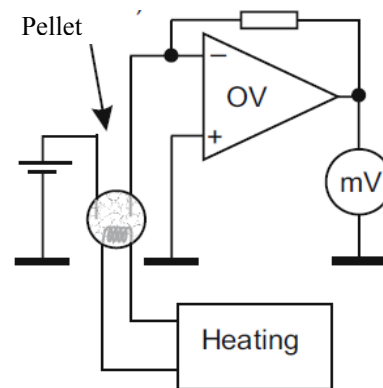


Fig. 7. Polycrystalline gas sensor with associated measuring circuit [2].

The conductometric sensing signal at different H₂ concentrations follows the pattern of any reducing gases such as methane, ethanol vapour, hydrogen sulphide and carbon monoxide. The grains of the sintered body are covered by adsorbed oxygen which removes electrons causing the formation of ionic oxygen at the surface. Consequently, the charge carrier concentration in the grain volume decreases and a potential barrier is formed at the grain boundaries (double Schottky barrier). See Fig. 8. In this case, the electric conductance of the material is decreased by the extent of oxygen adsorption. In the presence of reducing gas, the molecules interact with the adsorbed oxygen, thus decreasing the potential barrier and increasing the conductivity of the sensor. This conductance change is reversible at the working temperature (room temperature). The electrons can also be transported by tunneling through a small gap between oxide grains even when grain boundaries are not effectively formed throughout the sensing body [17]. Most of the chemoresistive sensors materials operate at high temperature, generally above 200 °C, resulting in significant power consumption, and in addition to complexities in device integration, which limits their technological applications. Consequentially, there is still space and need to develop 1-D nanomaterials for gas sensors that have very good sensing performance but at room

temperature. Upon injection of H_2 , the initial resistance is $1.2 \times 10^7 \Omega$ and for various concentrations of H_2 flow (140, 90, 50, and 14 ppm), H_2 reactions mechanism is similar to CO reduction: this mechanism describes ambient oxygen adsorbs on the surface of the grains and form negative oxygen ions with combination of intrinsic electrons from the n-type VO_2 semiconductor. See Fig. 9. This explains the presence of a strong electric field pointing outward from the oxide surface. The separation of charges into cations and anions gives strongly modulated electronic potential on the oxide surface. Hydrogen atoms are dissociatively adsorbed in opposite charges which represent different reactivities.

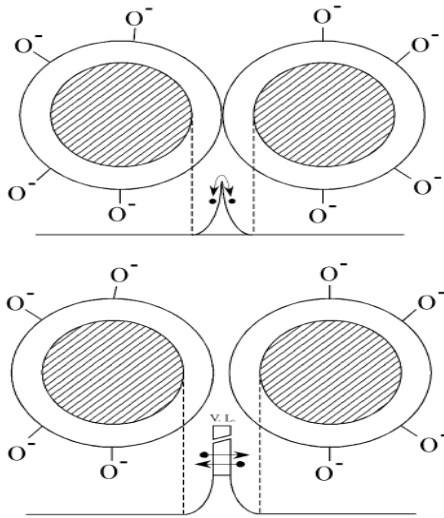


Fig. 8. Charge distribution following adsorption of oxygen at surface of n-type oxides and resulting potential distribution across grain boundary [2].

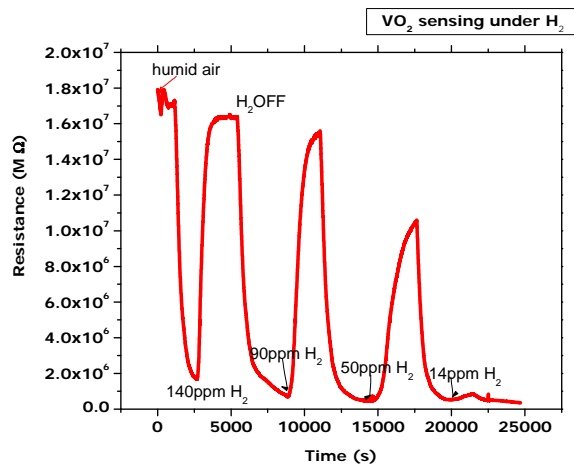
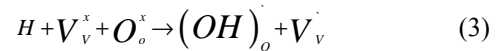
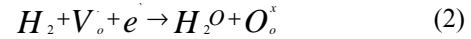
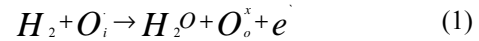


Fig. 9. Room temperature variation of the conductometric sensing signal for the considered H_2 relative concentrations i.e. 140, 90, 50, 14 ppm.

Another description to the high sensing response between H_2 and the nanobelts is the presence of

defects on the nanomaterial quantified through the lattice interspacing distance due to oxygen vacancies which act as adsorption sites for gas species. The interaction of Hydrogen with surface defects can be modeled as [18]:



where O_o^x , V_o and e^- is a neutral oxygen in an oxygen site, a positively charged vacancy and a negatively charged electron according to Kroger-Vink notation respectively. This shows that the hydrogen molecules are strongly correlated to the oxygen vacancies of the nanosensor material. In the case of vanadium dioxide, the hydrogen radicals are donor forming a direct hydrogenation of the material. The Coulombic interaction is a long range process and the surface interaction is not only dependent on the cation/anion at the vicinity of the surface but also on the ionicity of the matrix oxide of the solid solution which affects the activity energy of catalytic reactions where the rate involves the electron charge transfer between the oxide and intermediate surface.

The sensor response S of the nanobelts VO_2 powders is defined as:

$$S = \frac{|R_0 - R_g|}{R_0} \quad (4)$$

where R_0 and R_g are the resistance of the nanobelts in the absence and presence of the hydrogen gas respectively. It can be seen that the gas sensing response increases as the concentration of the injected gas increases up to 90 ppm and then decreases for higher concentrations. (See Fig. 10). One major advantage of VO_2 nanobelts is that the sensor can be used at room temperature detecting high concentrations of H_2 as well as having a detection limit below 14 ppm. Concerning the response and recovery time, the sensor exhibits approximately 850-1000 s / 450-700 s response and recovery time respectively as shown in Fig. 11 which seems to be more appreciable comparing to TiO_2 nanotubes and nanorods as reported in [19].

Finally, to shed light on the sensing selectivity of the VO_2 (A) nanobelts, further experiments were carried with other standard gases such as CO and CO_2 . Their corresponding sensing characteristics seemed to be very weak at room temperature under identical sensing conditions.

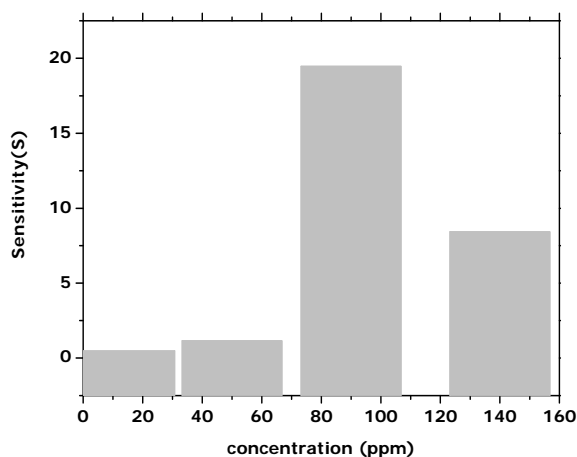


Fig. 10. Room temperature sensitivity of the nanobelts for considered H₂ relative concentrations of 140, 90, 50, 14 ppm.

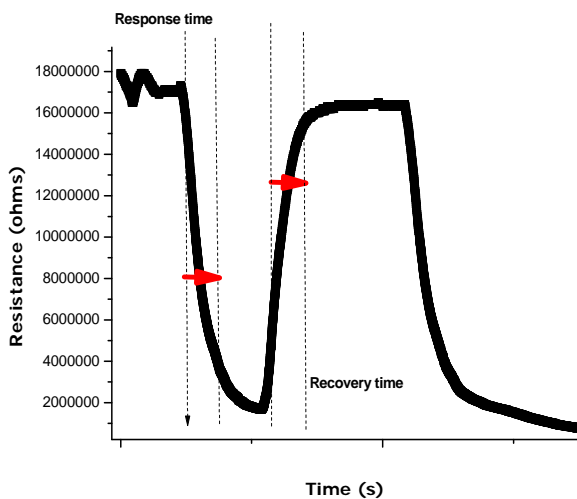


Fig. 11. Response time (90 ppm) and recovery time (140 ppm) to H₂ at room temperature for VO₂-based devices.

One cycle conductometric sensor signal for CO and CO₂ gases (200 ppm) was measured only at high temperature (170 °C). At it can be noticed, the sensing signal is at the background level. See Fig. 12. Consequentially, it could be deduced that the VO₂ (A) nanobelts present a noteworthy gas sensing selectivity towards H₂. These VO₂ nanobelts based H₂ sensor is strongly correlated to the electronic properties of the material itself (transport measurements, n-type semiconductor) as well as to its nanoscale morphology 1-D structure. What is important to note here is that the performance of the sensor material rely on the nature and the structure of the sensing material and on the nanoscale morphology of the layer and the grain size of the metal oxide.

Although this paper demonstrated the H₂ sensing efficiency of VO₂ (A) nanobelts at room temperature relatively to corresponding 1-D oxides in general,

various issues are still to be addressed. Among these, one should mention the following: the sensing properties below and above the vicinity of the semiconductor-metal transition, sensitivity to humidity at different temperature and the need to enlarge the sensor's selectivity for H₂S, NH₃, and C₂H₅OH gases. Further investigations would address all these challenges.

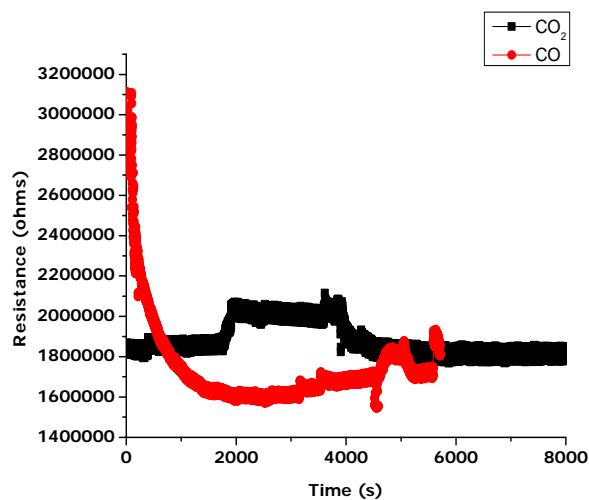


Fig. 12. Conductometric sensing signal for CO and CO₂ at threshold levels.

4. Conclusions

Metal oxide VO₂ nanobelts were successfully synthesized by hydrothermal sol-gel process. They present good sensing response and good selectivity at low temperature to H₂ gas comparing to CO and CO₂. The high sensing response is due to the large surface to volume ratio of the nanobelts and thus great active sites and surface states with chemical reducibility due to the simplicity in the device structure and adaptability to a wide variety of reductive or oxidative gases. The low power consumption should be useful for developing high performance H₂ gas sensors. To our best knowledge, this is the first report on nanobelts VO₂ hydrogen sensors.

Acknowledgements

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