



## Development of Hydrogen Leak Sensors for Fuel Cell Transportation

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With the aim to develop robust and reliable sensing devices for fuel cell transportation technology, a new solid state hydrogen leak sensor based on a composite of carbon nanotubes (CNTs) and platinum-doped titania nanotubes Pt-TiO<sub>2</sub>(NTs), has been reported. The thick film resistive-type sensor has been fabricated preparing first an array of Pt-TiO<sub>2</sub>(NTs) by anodic oxidation, mixing them with CNTs and finally depositing the CNTs/ Pt-TiO<sub>2</sub>(NTs) composite obtained on a ceramic substrate provided with Pt interdigitated electrodes. The electrical and hydrogen sensing characteristics of the sensor device have been investigated in the hydrogen concentration monitoring in the range 0.5-3 v/v (%) in air. The addition of CNTs and use of UV light decreased strongly the operating temperature, showing the applicability of the sensor device developed for hydrogen leak detection at near room temperature.

### 1. Introduction

Gas sensors are key components in modern electronic systems as interface with environment for recognizing, collecting, and monitoring of gas molecules. Nowadays, information from environmental detection is fundamental in many fields of science and technology especially for safety purposes, such as those concerning automobile industry, environmental and industrial process monitoring. To face the demand of real-time, compact and low cost sensing devices, several gas sensors based on different detection mechanisms have been proposed.

In this work we have investigated the behaviour of solid-state resistive sensors, which are particularly suitable to satisfy the requirements of high level of sensitivity and specificity in small and cheap packages, such as for hydrogen leak detection. The performances of these sensors can strongly be improved by the use of controlled nanoscale synthesis methods which may furnish a powerful tool to enhance the properties of sensing nano-layered materials. The development of engineered composite nanostructures have been shown to be of fundamental interest in efficient gas sensing applications, due to the possibility of optimizing sensor design by controlling their nano-surface, intrinsic channels and cavities which strongly influence sensing capabilities (Chen et al., 2011).

In the last years, a particular attention has been devoted to hydrogen detection. Hydrogen is the most promising clean fuel for the new transportation scenario based on fuel cells. In this context, detection of hydrogen leak is an important issue for safety reasons (Arndt and Simon, 2001). Indeed, hydrogen is an explosive gas (Lower Explosive Level -LEL- in ambient air is  $\sim 4$  vol. %), and safe operation of fuel cells will require inexpensive sensors to detect the presence of hydrogen leaks in air. These sensors can also find applications in the petroleum industry, chemical production, cryogenic cooling, semiconductor manufacturing processes and anywhere hydrogen is used. Inexpensive hydrogen sensors are then indispensable for the future hydrogen fuel economy.

A series of sensors based on different principles have been proposed for in-situ monitoring of hydrogen leak (Aroutiounian, 2005). Due to their simple operation, low cost of production and good performances, metal oxide semiconductor (MOS) devices have been largely investigated as hydrogen sensors. In particular, MOS sensors based on  $\text{TiO}_2$ , received special attention due to their unique performance. The addition of modifiers (e.g. noble metals) or UV irradiation to enhance the performance has been largely pursued (Epifani et al., 2008).

Earlier works also highlighted the fundamental role of the metal oxide nanostructure. Nano-structured  $\text{TiO}_2$  has attracted considerable interest due to the superior properties such as large specific surface area and high uniformity, and has been applied in the hydrogen gas sensing field. Sensitive  $\text{TiO}_2$  hydrogen sensors, relying on the resistance variations of titania nanotubes in the presence of hydrogen in nitrogen or air, have been reported (Varghese et al., 2003; Sadek et al., 2009).

Here we describe the design and operation of a solid-state hydrogen sensor based on a composite of carbon nanotubes (CNTs) and platinum-doped titania nanotubes Pt- $\text{TiO}_2$ (NTs). Carbon nanotubes have attracted increasing interests due to their unique electrical, geometrical, and mechanical properties that make them excellent materials for the fabrication of sensitive CNTs/metal oxide sensors (Balazsi et al., 2008). Moreover the addition of small quantities of CNTs to metal oxides causes a dramatic increase in the electrical conductivity of the host matrix, allowing to operate at lower temperature than with conventional sensors.

The sensing behaviour in response to  $\text{H}_2$  in the presence of UV light activation has been also investigated. Results obtained are discussed, with the final aim to help us in the development of a prototype hydrogen leak sensor.

## 2. Experimental

Titania ordered nano-arrays were synthesized by controlled anodic oxidation of Ti foils (supplied by Alfa Aesar: 0.025 mm thickness and 99.96 % purity). This method is useful to produce a dense array of  $\text{TiO}_2$  nano-tubes, which grow by organizing themselves under an applied electric field (15-60 V) in presence of a suited electrolyte (ethylene glycol with 2 vol. %  $\text{H}_2\text{O}$  and 0.3 wt. %  $\text{NH}_4\text{F}$ ) (Ampelli et al., 2008). The mechanism is essentially based on the equilibrium between two reactions: the anodic growth of an oxide layer on the Ti metal surface and the simultaneous field-aided chemical dissolution of the oxide in presence of fluoride ions. At the end of the anodization a metallic layer of Ti remains non-oxidized at the bottom of the substrate, acting as electron collector layer in many photo-electrochemical applications. After annealing at 450 °C for 3 h (heating and cooling rate of 2 °C/min) to induce crystallization in anatase phase,  $\text{TiO}_2$  nano-arrays continue to keep their morphology but assume particular electronic properties (Ampelli et al., 2011).

Pt nano-particles were deposited on  $\text{TiO}_2$  surface by a photo-reduction method.  $\text{TiO}_2/\text{Ti}$  substrate was dipped for 10 min into an aqueous solution of ethanol (50 vol.%) in presence of  $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$  as Pt precursor.  $\text{TiO}_2$  nanotubes were then irradiated by a Xe arc lamp (300 W) under a low inert gas flow, to deposit and reduce the Pt nano-particles on both the external and internal tube walls. Finally Pt- $\text{TiO}_2$ (NTs) were detached from the Ti metallic layer by sonication and reduced to powder.

CNTs/Pt- $\text{TiO}_2$ (NTs) composite was prepared by mixing functionalized CNTs (supplied by Aldrich) with Pt- $\text{TiO}_2$ (NTs). CNTs were functionalized by treatment in concentrated nitric acid (15 M) and refluxing for 18 h at 110 °C to modify their surface. The morphology of the samples prepared has been investigated by SEM and TEM.

To fabricate the sensor device, the CNTs/Pt- $\text{TiO}_2$ (NTs) composite was mixed with water in order to obtain a paste, deposited as thick film on alumina substrates equipped by platinum interdigitated

electrodes and heaters, and successively treated in air up to 400 °C. Sensing tests were performed in an home-made apparatus that allowed to operate at controlled temperature and to perform resistance measurements while varying the hydrogen concentration in the carrier stream. An Agilent 34970A multimeter data acquisition unit and a Keithley 2400 source meter were used to acquire the sensor signal while an Agilent E3632A dual-channel power supplier instrument was used to bias the 400 nm UV LED and the built-in heater of the sensor. The sensor response is given by  $[(R-R_0)/R_0] \times 100$ , where  $R_0$  is the resistance baseline in synthetic air and  $R$  the resistance recorded under different hydrogen concentrations.

### 3. Results and discussion

#### 3.1 Pt-TiO<sub>2</sub>(NTs) synthesis and characterization

It is well known that the sensitivity of TiO<sub>2</sub> nanotubes-based hydrogen sensors is dependent on the nano-tube pore size, wall thickness and length (Mor et al., 2006). Then, it is highly desirable to choose a technique of preparation which allows to “tailor” the nano-structure, in a simple and cheap way.

Among the different methods proposed to synthesize titania nanostructures, anodic oxidation of Ti foils shows several advantages: it is low costly, easy to be scaled-up to large films, suitable to synthesize ordered patterns of 1D nano-structures, but above all it allows a high grade of control on the nano-structure, simply by adjusting some synthesis parameters, such as the electrolyte type, applied voltage, pH and anodization procedure (Ampelli et al., 2010).

Figure 1 shows SEM images of TiO<sub>2</sub> sample synthesized by anodization at 50 V. A good regularity in one dimension with a nano-tube length of ~ 14 μm it can be observed. A thin layer of debris is present at the top of the surface, which can easily be removed by a short sonication treatment or mild etching, in order to free the opening of nano-tubes and voids for an effective Pt deposition. SEM mages also highlight the small wall diameter and thickness of the titania nanotubes synthesized. Smaller diameter and thin-walled nano-tubes usually lead to a large variation of electrical resistance. The small wall thickness, in fact, may result in the overlap of neighboring space charge regions, so the entire volume of the inter-tubular region may experience low resistivity. The inter-wall connecting points also play a significant role in enabling the ultra-high hydrogen sensitivity. The oxygen adsorption and its removal by hydrogen atoms, as well as chemisorption of hydrogen at these constricted points, regulates the current passing from tube to tube (Mor et al., 2006).

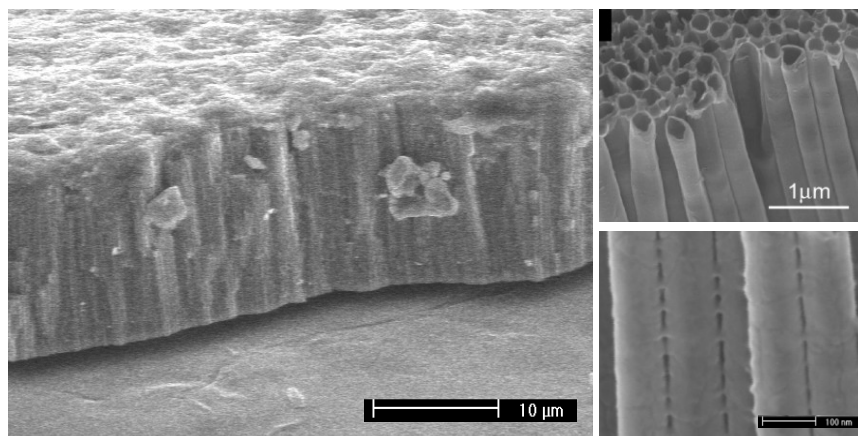


Figure 1: SEM images of TiO<sub>2</sub> 1D nano-arrays prepared by anodic oxidation at 50 V.

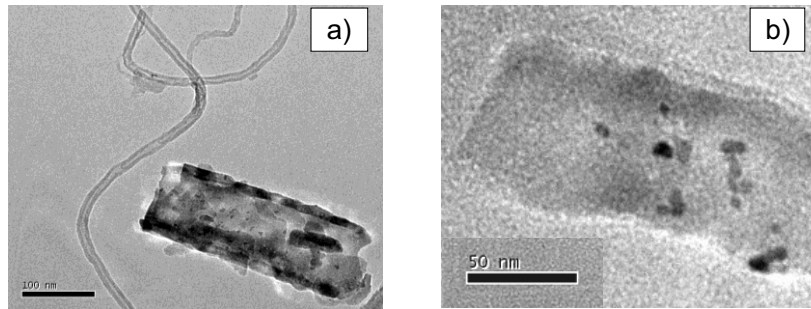


Figure 2: a) Morphology of the MWCNTs and Pt-TiO<sub>2</sub> nanotubes; b) TEM image of TiO<sub>2</sub> nanotube decorated with Pt nanoparticles.

Figure 2 reports TEM images of the Pt-TiO<sub>2</sub>(NTs), synthesized by anodization at 50 V, after detaching from the Ti metallic substrate, Pt deposition and CNTs addition, showing the morphology of CNTs and TiO<sub>2</sub> nanotubes, and Pt metal particles deposited by a photo-deposition method under gas phase conditions. This deposition technique is based on the filling up of the TiO<sub>2</sub> nano-tubes and -voids for capillarity with the Pt (IV) solution and the following reduction by UV-visible light under a low inert gas flow. The advantage of the gas phase lies in an easier control of the size of the Pt particles which are deposited on the inner and outer surface of the nanotubes, by modulating the Pt (IV) concentration within the micro-pore volume of titania.

### 3.2 Hydrogen sensing tests

The transduction mechanism for gas detection on solid-state resistive sensors is based on the variation of the electrical resistance due to target gas adsorption (Shimizu and Egashira, 1999). Therefore, by measuring the resistance changes it is possible to determine the presence and concentration of hydrogen in the environment surrounding the sensor.

Preliminary electrical tests have evidenced that the synthesized Pt-TiO<sub>2</sub>(NTs) sample has a high electrical resistance (> 10<sup>8</sup> ohm), and therefore not measurable by conventional instrumentation. Instead, the CNTs/Pt-TiO<sub>2</sub>(NTs) composite has shown a highly conductive behaviour, and its resistance can also be measured at room temperature. It is likely that mixing titania nanotubes with CNTs facilitates the electron transfer between the Pt-TiO<sub>2</sub>(NTs), due to the high conductivity of CNTs network. Moreover, the disorderly distributed CNTs may provide a better Pt-TiO<sub>2</sub>(NTs) dispersion, enhancing the availability of sensing sites. On the basis of these observations, hydrogen sensing tests were performed with the CNTs/Pt-TiO<sub>2</sub>(NTs) composite.

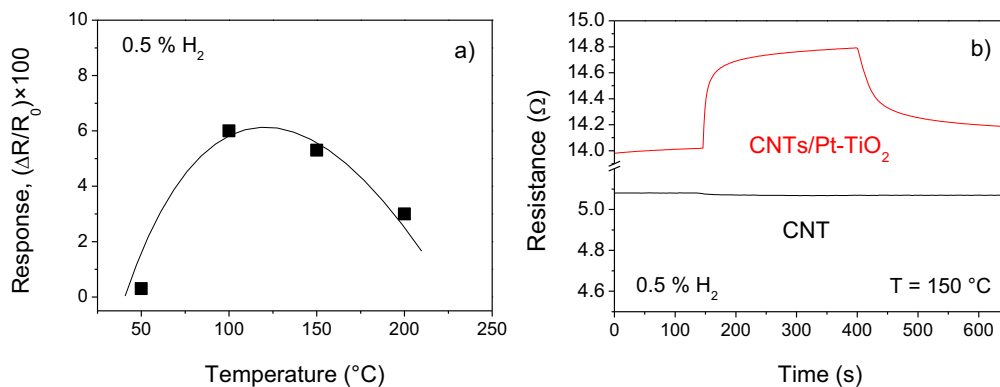


Figure 3: a) Sensor response as a function of the temperature; b) dynamic response.

Tests have shown that the device is sensitive to low hydrogen concentrations in air (0.5 – 3 v/v %), i.e. at concentrations lower than LEL for hydrogen in air, so it could be recognized as a hydrogen leak detector. In order to optimize the sensor performance, the sensor response as a function of the operating temperature, has been first investigated. Figure 3a shows a maximum in the sensor response, centred between 100 and 150 °C. In Figure 3b is reported the typical dynamic response of the sensor operating at 150 °C to a pulse of hydrogen at a concentration of 0.5 %. The sensor shows a very short response time, a critical parameter for practical applications, while the signal device requires a longer time to return to the baseline value. In the same figure is also reported a sensor based on pure CNTs. The sensor response is negligible, indicating that Pt-TiO<sub>2</sub>(NTs) are the responsible of the response of the composite sensor. This may results from two factors: firstly, a gas surface reaction enhancement due to an increment of the surface area and secondly, to a modification of the potential barrier at CNTs/Pt-TiO<sub>2</sub>(NTs) interfaces. Regarding the sensing mechanism, due to the low operating temperatures, the observed electric behaviour is not due to pathways involving the TiO<sub>2</sub> lattice, but likely it depends on the chemisorption of the spilled-over hydrogen atoms on the nano-structured surface, favoured by the Pt acting as a catalysts for hydrogen dissociation at low temperature. So, a partial charge transfer to the TiO<sub>2</sub> occurs, creating an electron accumulation layer on titania. Due to the presence of CNTs, known to have a p-type behaviour, injecting electrons in these conduction paths, decreases the holes concentration, so the resistance increases, as experimentally observed.

TiO<sub>2</sub> is a well known photocatalyst, therefore we also investigated the influence of UV illumination on the sensing characteristics of the composite sensor. Figure 4a shows the dynamic response of the sensor operating at 100 °C under UV light (400 nm). It can be observed that the sensor recovers the baseline signal faster than the sensor with no UV illumination. Experiments performed with successive hydrogen pulses (Figure 4b) confirm this characteristic. The calibration curves of the CNTs/Pt-TiO<sub>2</sub>(NTs), in both linear and log scale, are reported in Figures 4c-d.

The characteristics of this composite sensor have been compared with those of previous similar sensors reported in the literature. Varghese et al. (2003) first described room temperature hydrogen sensors based on anodic TiO<sub>2</sub> nanotube arrays, showing a change in electrical resistance upon exposure to 100 ppm hydrogen in N<sub>2</sub> of four orders of magnitude. However, the sensor was not tested in a real field application, that is in ambient air.

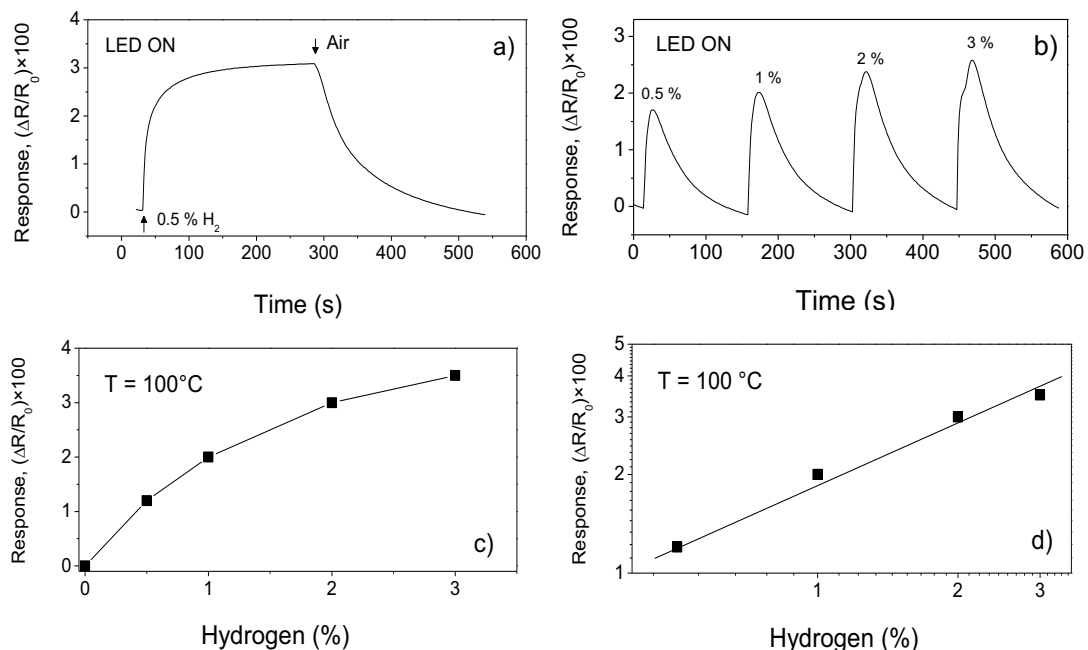


Figure 4: a, b) Dynamic response of the sensor under UV light; c, d) calibration curves.

As the presence of oxygen can affect the sensing performance, we compare the characteristics of our sensor with data reported in similar conditions. For example, Sadek et al. (2009) reported a conductometric sensor showing a response (measured as  $R/R_0$ ) for 1 %  $H_2$  of about 1.25 at 225 °C. Notwithstanding the lower sensitivity, our sensor operate at much lower temperature. This means a limited power consumption, which is a critical parameter for in-field operating instrumentation.

#### 4. Conclusion

In this paper a new solid state hydrogen leak sensor based on nano-structured ternary composite materials, has been suggested as resistive-type sensor with improved performances in terms of selectivity, response speed, and operation conditions. The sensor is characterized by an array of Pt-TiO<sub>2</sub>(NTs) fabricated by anodic oxidation, and used to prepare a highly conductive CNTs/Pt-TiO<sub>2</sub>(NTs) composite. Results of sensing tests have shown the applicability of this nanostructure for hydrogen detection at low temperatures and consequently fabrication of devices with low power consumption. This one is a crucial aspect to consider in the design of gas sensing devices, as gas sensors generally need to operate at high temperatures. Finally, this composite sensor can be considered as a promising attempt to develop a robust and reliable sensing solution over the range of technical requirements needed for fuel cells transportation technology. Studies are currently in progress and aimed to directly growth conductive TiO<sub>2</sub> nanotubes on the sensor device. On this way some important parameters of the sensing layer (thickness, nanotubes orientation) could carefully be controlled by varying the deposition parameters, and improving the reliability of the sensor.

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