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## Evidence of catalytic activation of anatase nanocrystals by vanadium oxide surface layer: Acetone and ethanol sensing properties

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## ABSTRACT

TiO<sub>2</sub> and TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> nanocrystals were prepared by coupling sol-gel and solvothermal methods, followed by heat treatment at 400 °C, after which the nanocrystal mean size was still about 5 nm. The materials were used to process chemoresistive sensors, which were tested to ethanol and acetone, with concentrations ranging from 100 to 500 ppm and from 25 to 100 ppm, respectively. The sensing data evidenced that the surface deposition of V<sub>2</sub>O<sub>5</sub> onto the anatase TiO<sub>2</sub> nanocrystals enhanced the sensor response up to almost two orders of magnitude for both gases. Moreover, the sensors behavior was completely inverted: with TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>, the highest responses were obtained at the lowest operating temperatures, contrarily to pure TiO<sub>2</sub>, which required very high operating temperatures. The comparison of the sensing data allowed concluding that the V<sub>2</sub>O<sub>5</sub> deposition effect could be interpreted as a catalytic contribution, in terms of lowered activation energies of the involved reactions and more favored gas adsorption at lower operating temperatures with respect to pure TiO<sub>2</sub>.

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## 1. Introduction

The catalytic modifications of gas sensors have been typically classified according to spill-over [1,2] and electronic sensitization mechanisms, and are related to the presence of noble metals nanoparticles dispersed in the sensing material. The addition of other metal cations into the crystal structure [3] has also been extensively investigated, with several studies encompassing a huge range of materials compositions. The field of catalysis anyway contains a huge catalog of materials architectures that could still be exploited for improving the response of chemoresistive sensors. The TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> system [4,5] is of particular interest for the following reasons: (1) it is a well-known catalyst for the oxidation of organic compounds [6,7], which is at the basis of the sensing mechanisms of many organic vapors; (2) it could be the prototype of a novel category of materials for gas sensors, where a more active surface layer boosts the response of a usually less active core material. Some studies inspired by this system have been published [8–14], but in our work we present a fully colloidal version of

the system, going beyond the classical impregnation and/or doping concepts. In particular, in this paper we present the sensing behavior of TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> nanocrystals toward two organic analytes like ethanol and acetone. We begin by showing that surface addition of V<sub>2</sub>O<sub>5</sub> remarkably improves the sensor response with respect to pure TiO<sub>2</sub>. Then, we present a systematic exploration of the sensing trends specifically aimed to show that the effect of the V<sub>2</sub>O<sub>5</sub> layer addition can be interpreted as a catalytic effect, in terms of lowered best operating temperature and simultaneously enhanced response. The results open the way for the design of whole class of novel sensing architectures.

## 2. Experimental

A detailed investigation of the synthesis process was carried out as previously described [15,16]. Briefly, TiO<sub>2</sub> amorphous nanoparticles were prepared by a sol-gel process. Then, they were crystallized by solvothermal processing in oleic acid at 250 °C, during which the vanadium precursor was added. After heat treatment at 400 °C, detailed characterization showed that the resulting nanocrystals were constituted by an anatase core covered by V<sub>2</sub>O<sub>5</sub> species and doped with V(V) ions in substitutional position with respect to Ti(IV) in the anatase lattice [16]. The mean

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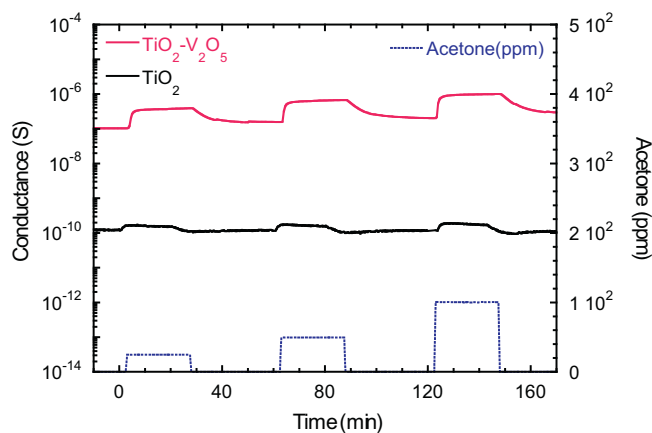


Fig. 1. Dynamic response toward concentration square pulses of acetone at a working temperature of 300 °C.

size of the nanocrystals after the heat treatment was about 5 nm. No phase separation was observed in such processing conditions, and the resulting materials were used for preparing gas-sensing devices, by depositing a mixture of the sample powder with 1,2-propanediol onto interdigitated electrodes, and subsequently annealing at 400 °C for 1 h. The gas-sensing tests were carried out using a standard configuration for resistive sensor measurement, with Pt-interdigitated electrodes and a Pt-resistive-type heater printed onto an alumina substrate. The operating temperature of the sensors was varied from room temperature to 400 °C using the platinum heating meander integrated in the alumina substrate. Preliminary investigation had shown (see supplementary information) that the TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> sensors displayed remarkable performances toward ethanol and acetone with respect to other gases like CO and methane. This result was expected due to different coordination modes of ethanol and acetone toward a surface containing V species. Hence ethanol and acetone were used as test gases, with concentrations ranging from 50 to 500 ppm and from 25 to 100 ppm, respectively, using air with 40% RH as gas carrier at 20 °C. The sensor response was defined as  $G - G_0/G_0$ , where  $G$  was the electrical conductance after equilibration with the gaseous analyte and  $G_0$  was the conductance before introduction of the gas into the test cell.

### 3. Results and discussion

The surface modification of TiO<sub>2</sub> by the V<sub>2</sub>O<sub>5</sub> layer was meant to provide a more active material capable of enhanced interaction with the gaseous analyte. Then, the electronic outcome of this reaction should be efficiently transferred to the TiO<sub>2</sub> core for having a performance improvement.

The achievement of the material architecture was not a guarantee that the planned charge transfer mechanism would be operating and efficient. While this guess was demonstrated for ethanol [16], for which further data will be discussed and analyzed in the following, our next step was to change the gaseous analyte and investigate the sensing behavior of the material. Our aim was to find a common trend between the two materials, capable of highlighting the peculiar effect of the vanadium oxide layer. In Fig. 1 an example of the dynamic response of the TiO<sub>2</sub> and TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> sensors is shown toward acetone. It can be seen that vanadium addition enhanced the conductance variation with respect to pure anatase. As expected from the reaction with n-type materials, acetone injection resulted in conductance increase (Fig. 2).

It will also be noted that vanadium addition resulted in much higher base conductance, due to the n-doping induced by the V ions

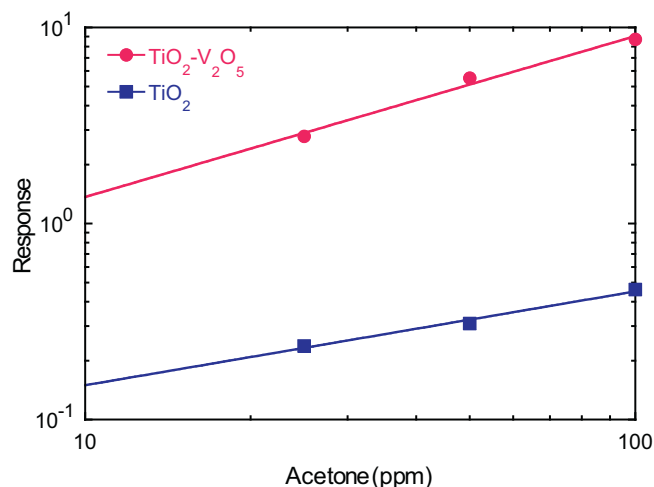


Fig. 2. Calibration curves for TiO<sub>2</sub> and TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> sensors operating at 300 °C with 40% RH toward acetone.

into the anatase lattice. The apparent improvement of the response of TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> sensor was made clearer by the calibration curves, of which an example is shown in Fig. 2, for an operating temperature of 300 °C. It can be seen that vanadium addition resulted in response improvement of almost two orders of magnitude with respect to pure anatase for all the investigated concentrations. The extrapolation of the calibration line shows that in principle the TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> sensor can detect very low gas concentrations, down to at least 10 ppm. This effect of vanadium was visible at all the operating temperatures, as shown in Fig. 3. The TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> sensor systematically showed higher response with respect to pure TiO<sub>2</sub>. Moreover, the TiO<sub>2</sub> sensor did not display an appreciable response at 200 °C, contrarily to TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> that, already at this temperature, showed an appreciable reaction with acetone. More importantly, if the whole plot is observed, the data seem to belong to the typical bell shaped curves representing sensor responses, but the TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> curve is remarkably shifted to lower temperatures (Fig. 4).

It is clear that the two sensors have completely opposite behavior and that the response of the TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub> sensor is constantly overcoming the pure TiO<sub>2</sub>. The response of pure TiO<sub>2</sub> needed very high temperatures for being activated, just when the TiO<sub>2</sub>-V<sub>2</sub>O<sub>5</sub>

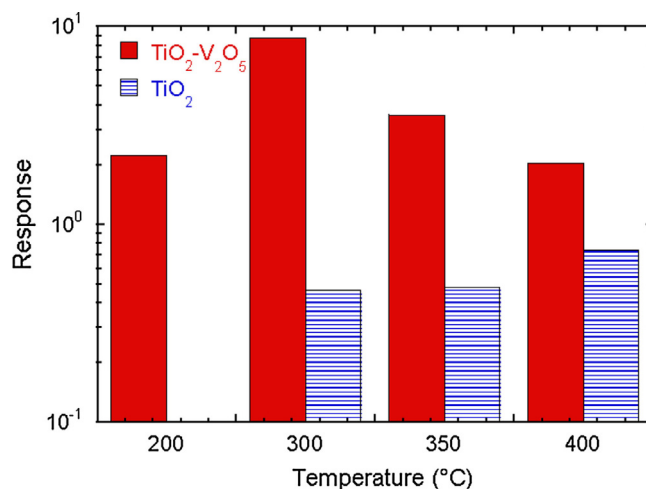


Fig. 3. Response to 100 ppm acetone as a function of the operating temperature. In fact, the shape of the response curve as a function of the temperature suggests the presence of complex and multistep reactions at the basis of the sensing process. For further evidencing this feature, the response Arrhenius plot is reported in Fig. 4.

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