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Rhodium as Efficient Additive for Boosting Acetone Sensing by TiO$_2$ nanocrystals. Beyond the Classical View of Noble Metal Additives

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Abstract

Anatase TiO_2 nanocrystals were prepared by solvothermal synthesis and modified by *in-situ* generated Rh nanoparticles, with a starting nominal Rh:Ti atomic concentration of 0.01 and 0.05. After heat-treatment at 400 °C the TiO_2 host was still in the anatase crystallographic phase, embedding Rh nanoparticles homogeneously distributed and whose surface had been oxidized to Rh_2O_3, as established by X-ray diffraction, Transmission Electron Microscopy and X-ray Photoelectron spectroscopy. Moreover, Rh seemed also homogeneously distributed in elemental form or as Rh_2O_3 nanoclusters. The acetone sensing properties of the resulting materials were enhanced by Rh addition, featuring a response increase of one order of magnitude at the best operating temperature of 300 °C. Moreover, Rh addition enlarged the detection range down to 10 ppm whereas pure TiO_2 was not able of giving an appreciable response already at a concentration as high as 50 ppm. From the sensing data, the enhancement of the sensor response was attributed to the finely dispersed Rh species and not to the oxidized Rh nanocrystals.

Keywords: TiO_2 nanocrystals, acetone sensing, rhodium, noble metal additives, solvothermal synthesis.

Introduction

Already for a long time noble metal additives have been used as performance promoters of chemoresistive, metal oxide based gas sensors [1-3]. Such effect is classically [4] attributed to spillover of adsorbed species onto the oxide semiconductor support or Fermi level control. Indeed, loading with noble metals has been exploited already in the early commercial gas sensors fabricated by Figaro Engineering Inc. , where Pd was traditionally added to the oxide host. Along with Pd, even Pt has been often employed as additive [5, 6]. Much less attention has been paid to another noble metal group element such as rhodium. Only few examples are known of Rh addition to Ga_2O_3 [7], SnO_2 [8, 9], In_2O_3 [10], WO_3 [11]. Interestingly, it has been recently pointed out [12, 13] that the effectiveness of Rh addition is due to Fermi level control upon contact of SnO_2, In_2O_3 and WO_3 host with Rh nanoparticles oxidized to Rh_2O_3. To date, there are no studies on the effect of Rh addition to TiO_2 with the exception of a single paper about the response to oxygen [14]. This combination is, however, interesting since the sensing performance of anatase TiO_2 is known to benefit from noble metal loading [15-19]. TiO_2 is, therefore, a suitable host for investigating and understanding how sensing is positively affected by the Rh additive. This paper demonstrates the beneficial effect of Rh addition to the sensing properties of TiO_2 nanocrystals. The Rh additive was present in several different structures, large rhodium nanoparticles in which only the surface is oxidized and small homogeneously dispersed Rh species. On this basis, the actual importance of electronic sensitization by Rh_2O_3 was discussed in comparison with the possible effect of other Rh species present on the TiO_2 host, such as elemental Rh and/or Rh_2O_3 nanoclusters. application-aimed but is serves to show how the effects of noble metal additives should be investigated when dealing with such complex systems.

Experimental

Pure TiO_2 nanocrystals were prepared by first precipitating 4 mL of TiO_2 sol in 10 mL of *n*-dodecylamine (DA, 98%, Sigma-Aldrich), followed by heating for 1 h at 100 °C in a glass vial. The TiO_2 sol was prepared by solvolysis of 1.5 g $TiCl_4$ in 10 mL of methanol, followed, after cooling, by the addition of 2.4 mL of water. The precipitate obtained in DA was extracted by methanol and washed two times in acetone, then redispersed in 12 mL of oleic acid (90%, Sigma-Aldrich). The resulting suspension was transferred to a borosilicate glass vial and treated for 2h at 250 °C into a steel autoclave (45 mL). After cooling, and without any purification, the prescribed amount of $Rh(acac)_3$, dissolved in 1 mL of chloroform, was added, followed by another heating step in the same autoclave at 250 °C for 1h. Two nominal Rh concentrations were considered, equal to 1% and 5% atomic concentration with respect to Ti. In the following, such samples will be indicated as TiO_2-1Rh and TiO_2-5Rh, respectively. The final product was extracted by methanol, washed 3 times with acetone and then dried at 90 °C in air, after which a black powder was obtained. Heat-treatment of the samples at 400 °C for 1 h was carried out in a muffle furnace at a rate of 5 °C/min, after placing them into a glazed porcelain crucible. After the heat-treatment, a black powder was again obtained.

X-ray diffraction (XRD) patterns were recorded on a PANalytical Empyrean diffractometer. Cu K-α radiation was obtained with a Cu anode operated at 45 kV/40 mA and a graphite monochromator. A programmable divergence slit was used to illuminate a 10x10 mm^2 area of the sample surface. Rietveld refinement of the patterns was carried out by the MAUD software [20].

The X-ray photoelectron spectroscopy (XPS) analyses were carried in an Escalab MkII (VG Scientific, East Grinstead, UK) electronic spectrometer equipped with unmonochromatized Al/Mg source and a 5-channeltrons detector. The samples were pressed on the grated Au

foil (99.99%) fixed on the standard Escalab holder stubs. Large area XPS measurements were performed at 20 eV pass energy. The binding energy (BE) scale was calibrated by measuring the reference peak of $Au4f_{7/2}$ (84.0 ± 0.1 eV) from the supporting foil. Experimental data were processed by using the software Avantage v.5 (Thermo Fisher Scientific).

High-resolution TEM (HRTEM) and scanning TEM (STEM) studies were carried out using a field emission gun FEI Tecnai F20 microscope at 200 kV with a point-to-point resolution of 0.19 nm. High angle annular dark-field (HAADF) STEM was combined with electron energy loss spectroscopy (EELS) in the Tecnai microscope by using a GATAN QUANTUM filter.

The sensing devices were processed onto alumina substrates (2x2 mm^2) provided with Ti/Pt electrodes and heaters. A paste was prepared by mixing the as-prepared samples with 1,2-propanediol. Heat-treatment of the paste at 400 °C was carried out in the device itself, by using the integrated heaters. The gas-sensing tests were carried out in flow-through mode with dry air as gas carrier [21]. The desired gas concentration was obtained by mixing with mass flow controllers the target gas with dry air. The response of the devices was defined as $|G_{gas}-G_0|/G_0$, where G_0 was the sensor baseline electrical conductance in dry synthetic air and G_{gas} indicated the sensor electrical conductance after dynamic equilibration with the target gas. The sensor signal readout was carried out with a picoammeter (Keithley, 6485). A fixed voltage (1V) was applied to the sensors.

Results and Discussion

A. General considerations on the synthesis procedure. Structure and composition of the samples

Two main issues were considered in the synthesis design, the choice of the Rh precursor and the addition procedure to the TiO_2 host material. Previous work [22] on noble metal

precursors had shown that metal acetylacetonates are a preferred choice with respect to ordinary salts, due to more controlled decomposition and nanoparticle growth and dispersion into the oxide host. Rhodium was no exception, since $RhCl_3$ effectively resulted into the formation of Rh nanoparticles but also in vigorous reaction into the autoclave, with the suspension splashed all over the autoclave walls. For reacting $Rh(acac)_3$ with the TiO_2 suspension, its addition was also attempted without any preliminary solvothermal treatment of pure TiO_2. Nevertheless, as shown in the Supporting Information (Figure S1), a few unidentified peaks appeared in the related XRD pattern, which did not occur with the finally chosen procedure described in the Experimental. After clarifying these issues, the crystal structure and chemical composition of the materials was investigated. **Figure 1** shows the comparison between the XRD patterns of the as-prepared and heat-treated samples. The reflections of anatase TiO_2 are clearly present in the patterns, with obvious narrowing after heat-treatment due to grain growth. It can be seen that the signal of elemental Rh only appears for the TiO_2-5Rh sample, while for the TiO_2-1Rh sample the effective Rh presence was ensured by XPS (see Supporting Information, Figure S2).
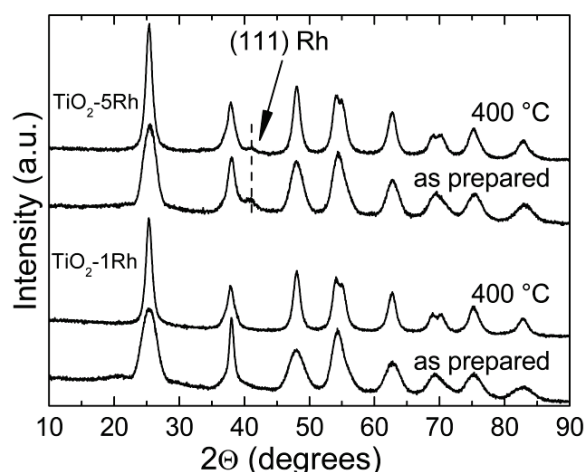

Figure 1: XRD patterns of the indicated samples. Only the (111) Rh reflection is marked, all the other reflection belonging to anatase TiO_2.

There is no evidence of Rh_2O_3 reflections and the Rh peak intensity after heat-treatment at 400 °C decreased with respect to the as-prepared sample. In the Supporting Information the Rietveld refinement results are shown of both the as-prepared and heat-treated TiO_2-5Rh samples (Figures S3 and S4). The TiO_2 lattice parameters were in full agreement with the values reported for anatase. Moreover, the TiO_2 crystal domain size increased from 6.5 to 11.4 nm after the heat-treatment at 400 °C, while the Rh grain size increased from 2.4 to about 8.2 nm. Despite the low Rh concentration made the quantitative determination highly uncertain, further refinement by the diffractometer proprietary software confirmed the obtained trends. The Rietveld analysis also provided the Rh weight %, which decreased from 0.683 to 0.155% after the heat-treatment, in agreement with the qualitative evaluation of the XRD patterns. The actual atomic concentration of nanocrystalline Rh with respect to Ti was therefore calculated as 0.12 %. Also shown in the Supporting Information is the refinement of the XRD patterns of pure TiO_2 heat-treated at 400 °C. The obtained TiO_2 size of 7.8 nm was even lower than in the TiO_2-5Rh sample, which could also be due to artifacts of the Rietveld refinement or also indicative of Rh catalytic effect on the removal/decomposition of oleic acid ligands. Anyway even simple calculation of the grain size by Scherrer's equation provided similar results, despite they were more comparable (6.3 nm for pure TiO_2, 7.7 nm for TiO_2-5Rh). What was important from these size determinations was that any sensing difference between pure and Rh-TiO_2 could not be ascribed to any size effect.

XPS spectra recorded for the 400 °C TiO_2-5Rh sample are shown in Figure 2. The related quantification results are reported in Table 1.

Table 1: Elemental quantification of the TiO$_2$-5Rh sample after heat-treatment at 400 °C.

Peak	BE, eV	FWHM, eV	Atomic %	Chemical State
C1s A	285.0	2.1	11.1	aliphatic
C1s B	286.8	2.1	2.8	C-O
C1s C	289.3	2.1	1.0	carboxyl
O1s A	530.4	1.9	50.9	oxide
O1s B	532.2	1.9	8.1	OH$^-$
Rh3d	308.3	2.2	0.2	Rh$_2$O$_3$
Ti2p	459.1	1.9	25.9	TiO$_2$
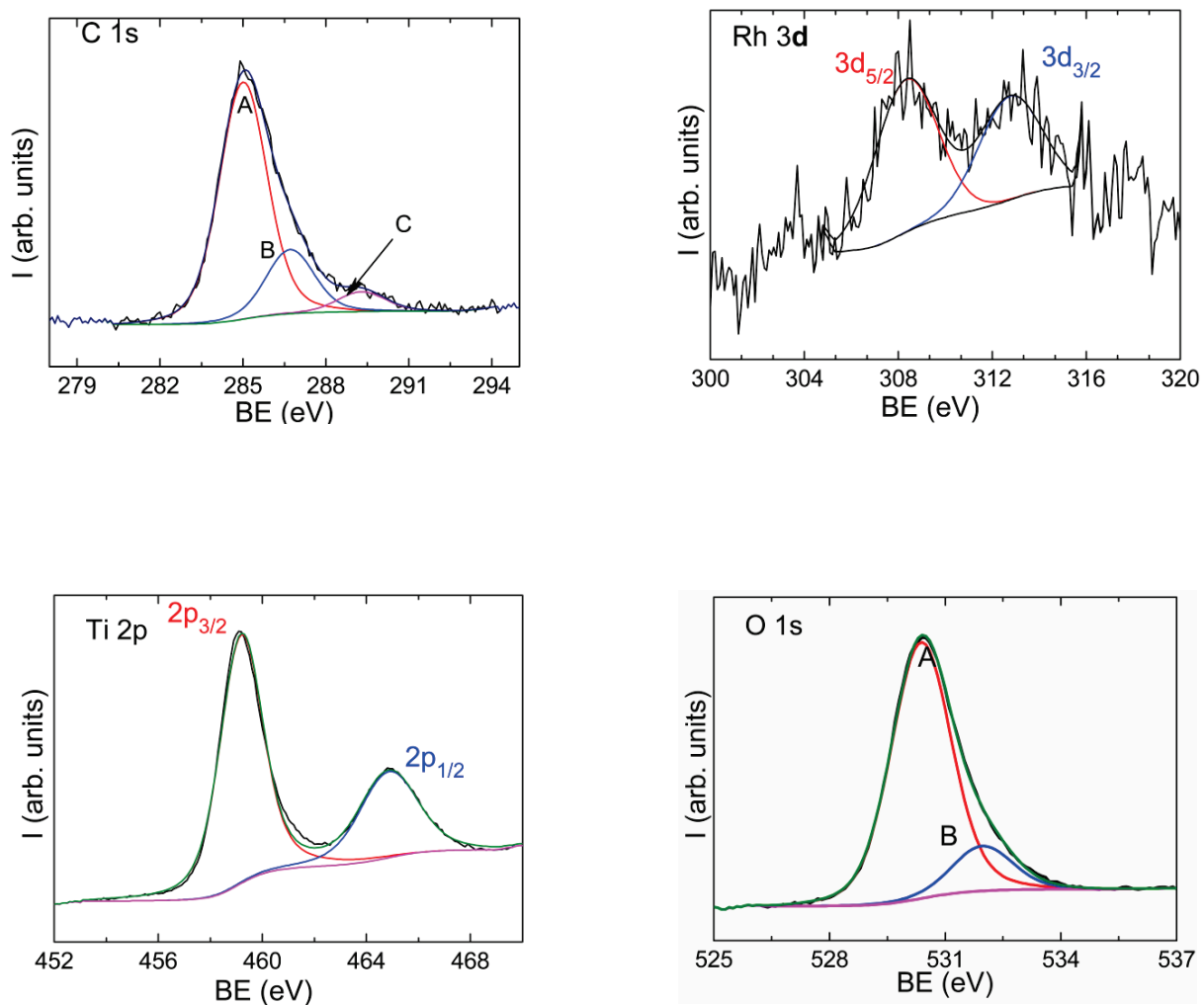
Figure 2: XPS spectra of the main peaks for the TiO$_2$-5Rh sample heat-treated at 400 °C.

No chlorine (possible residual of $TiCl_4$) was detected but a negligible concentration of carboxylic carbon (possible fingerprint of oleic acid residuals) was present. The O 1s signal was composed only of the expected hydroxyl and oxide components. The 0.77 % Rh:Ti concentration ratio was lower than the nominal 5% value, consequently to the loss of Rh during the purification step. The supernatant recovered after centrifugation was indeed deep brown colored, indicating that a part of Rh had not been retained in the TiO_2 matrix. Another sample was prepared and analyzed, and the same Rh concentration was detected. Instead, XPS detection of Rh in the TiO_2-1Rh samples was very hard (see Figure S2), so in the rest of the work any consideration will be referred to the TiO_2-5Rh samples and devices. It is interesting that only Rh(III) was consistently detected in all of the analyzed samples, indicating bonding with oxygen as in Rh_2O_3.

No Rh nanocrystals could be singled out in the TEM images, many of which were analyzed, as shown in the Supporting Information (Figure S5). As an example, Figure 3 shows a collection of HRTEM images from the 400 °C TiO_2-5Rh sample. The treatment removed the oleic acid capping, resulting in the observed aggregation of nanocrystals. Nevertheless, it was still possible to confirm a typical size around 10 nm, in agreement with the previously reported result of the Rietveld refinement. The inset shows a magnification of the remarked region and the related power spectrum. The analyzed nanoparticles, like many others investigated in the sample, displayed lattice parameters typical of anatase TiO_2, in full agreement with the XRD data. Once again, there was no evidence of Rh incorporation into the TiO_2 lattice.
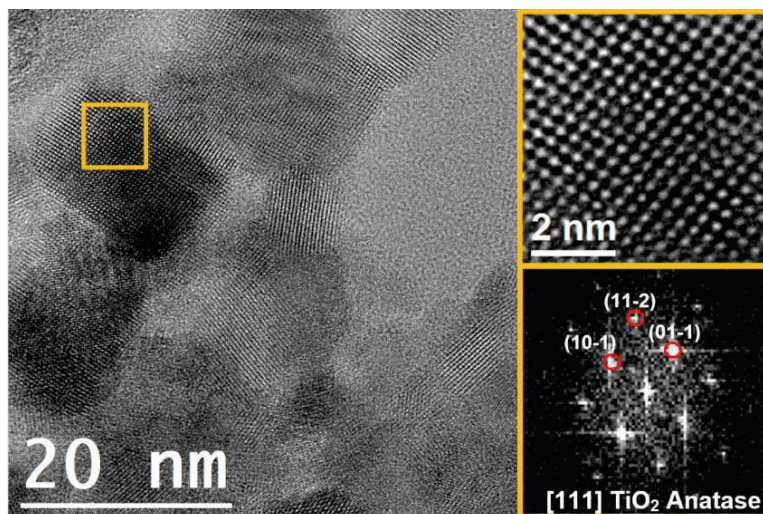
Figure 3: HRTEM micrograph of the 400 °C TiO$_2$-5Rh sample, detail of the orange squared region and its corresponding power spectrum.

More interesting is the observation of the EELS mapping shown in Figure 4. It is evident that the Rh distribution follows quite closely that of Ti and of O.

Summarizing:

i) the XRD results in **Figure 1** only showed the reflections of Rh nanocrystals.

ii) In XPS spectra only Rh (III) was detected. The XPS Rh : Ti atomic concentration was 0.77 %, larger than that obtained from XRD (0.12%). Therefore Rh in form of nanocrystals was only a small fraction of the overall Rh content.

iii) EELS showed homogeneous Rh distribution but it was not possible to detect Rh nanocrystals in many analyzed images.
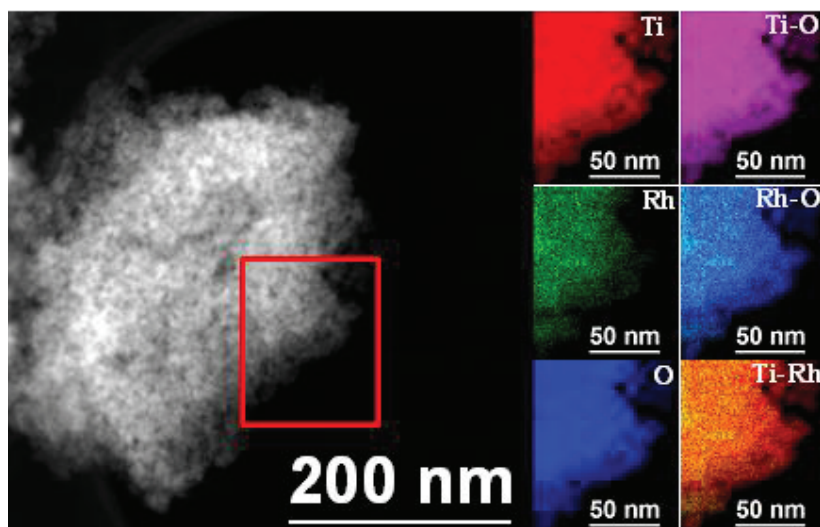
Figure 4: EELS chemical composition maps obtained from the red squared area of the STEM micrograph for the 400 °C TiO$_2$-5Rh sample. Individual Ti L$_{2,3}$-edges at 456 eV (red), O K-edge at 532 eV (blue) and Rh M$_{4,5}$-edges at 307 eV (green) as well as the composite (Ti-O, Rh-O and Ti-Rh) elemental maps are shown.

For putting together all of these results, it was concluded that in the 400 °C TiO$_2$-5Rh sample there were two Rh species:

i) a prevalent distribution of oxidized Rh species dispersed homogeneously, most probably small species comprising a few Rh atoms, not detectable by TEM; in the following these species will be referred to as "Rh oxide nanoclusters" despite this nomenclature may be not completely appropriate. For instance it is not excluded that single Rh cations may be incorporated into the surface lattice of anatase.

ii) a few Rh nanocrystals, with a size comparable to the TiO$_2$ host, and whose surface was oxidized to Rh(III) to such an extent that the XPS probe did not get to the Rh core, which was instead detected by XRD. In the following these species will be referred to as "surface oxidized nanocrystals".

The resulting compositional and structural status of the samples made very complex to ascertain how Rh may influence the gas-sensing properties. Fortunately, as discussed in the

following section, comparison with recent literature results allowed proposing some working hypotheses.

B. Gas-sensing properties

Figure 5 shows the comparison between the dynamic response curves to acetone of pure TiO_2 and the 400 °C TiO_2-5Rh sample at an operating temperature of 300 °C (the data for other temperatures are shown in the Supporting Information, Figure S6). The response improvement when Rh was added to TiO_2 is obvious. The same holds for ethanol response, as shown in the Supporting Information (Figure S8). It can also be noted that TiO_2 poorly reacts to acetone concentration changes.
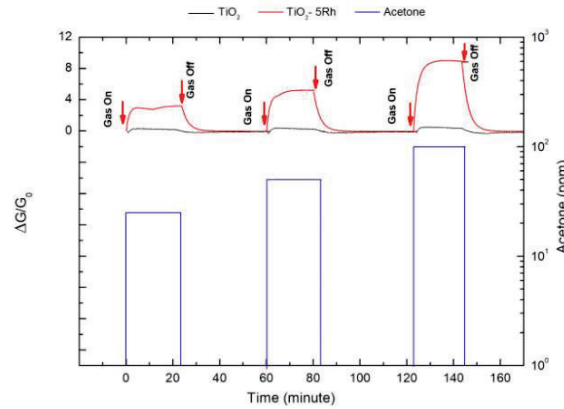

Figure 5: Dynamic response curves to acetone at 300 °C of TiO_2 and TiO_2-5Rh devices.

The calibration data in Figure 6 show that the acetone response is enhanced by almost one order of magnitude for all the tested concentrations. The best operating temperature was 300 °C, as demonstrated in Figure 7. The response data for the various acetone concentrations followed the typical volcano curve. The sensing data as such clearly demonstrated the beneficial effect of Rh addition, and in this sense the results discussed until now are in line with the well-established effect of noble metals on gas-sensing properties. On the other hand, it has been recently pointed out [12] that Rh (oxidized to

Rh$_2$O$_3$) may also have a detrimental effect on acetone and NO$_2$ sensing properties of In$_2$O$_3$, SnO$_2$ and WO$_3$, while the response of WO$_3$ to CO and ethanol was improved.
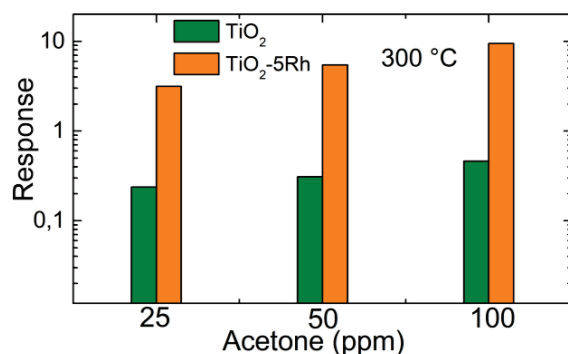

Figure 6: acetone calibration curves of TiO$_2$ and TiO$_2$-5Rh devices at an operating temperature of 300 °C.

In the present case, response improvement was observed (also for ethanol, see Supporting Information, Figure S9). It was concluded that it must be due to a combined effect by the various Rh species. In which way would such species interact with the support to provide response improvement?
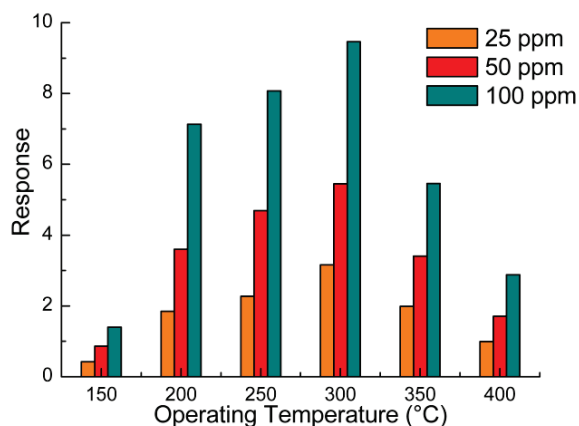

Figure 7: comparison between the TiO$_2$-5Rh acetone responses at various operating temperatures. The typical volcano behavior can be observed.

For investigating this point, conductance measurements were carried out in increasing concentrations of oxygen in nitrogen. The results are shown in Figure 8. There are some

striking differences between the two series of samples. First of all the TiO_2-5Rh sensor showed much lower conductance than pure TiO_2 in analogous conditions, suggesting that Rh species resulted in charge extraction from TiO_2. More importantly, the TiO_2-5Rh series is much less sensitive to changes in the oxygen concentration, above all at temperatures from 200 to 400 °C, when oxygen ionosorption becomes more and more important, resulting in conductance decrease. This result suggested that electronic control was carried out by Rh species onto the sensing properties, so detection of acetone (and ethanol and other analytes, see the Supporting Information) is favored by charge restoring from such species to the TiO_2 lattice upon interaction with the gases. This conclusion would seem contradictory with ref. 12 since acetone response in the present case has been enhanced by Rh addition. But: in the present work, the Rh surface oxidized nanocrystals are not present in high concentration, as explained above.
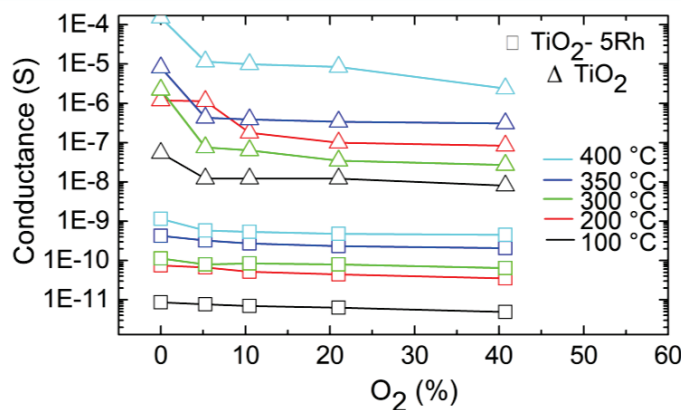

Figure 8: Conductance values of the indicated devices measured as a function of the oxygen concentration and operating temperature in dry nitrogen.

Second, since only their surface is oxidized, quite a different situation from ref. 10 must be considered. Third, the size of Rh surface oxidized nanocrystals and TiO_2 nanocrystals is comparable, which is a different situation from the classical view of Fermi level pinning. Even more importantly, Rh is largely present as oxide nanoclusters, as evidenced above in

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the discussion of the EELS data. Moreover, the ex situ characterization of the materials did not allow establishing the actual oxidation state of Rh in operando conditions. Finally, it was excluded that extensive doping of TiO_2 had occurred, as elaborated in detail in the Supporting Information.

For putting together all these facts, it was concluded that the sensor response is still dominated by exchange of charges with the TiO_2 support, also occurring by Rh oxide nanoclusters. For such species, the exchange of charges would be the analogue of Fermi level control, despite the Fermi level cannot be defined for such non-bulk, non-crystalline species [6]. Why even acetone response is enhanced, not only that to ethanol, is not clearly attributable to a specific Rh additive species. In fact, analyzing the various contributions to the response does not appear as straightforwardly feasible. In ref. 6 the authors defined the presence of PtO_x nanoclusters, which could also be evidenced by TEM as flat structures attached to the surface of SnO_2 support. In the present work, the hypothesized presence of few-atoms RhO_x species, still defined as nanoclusters, ultimately raises the level of difficulty when analyzing the noble metal effect onto the sensing properties of a given oxide support. The last sentence is meant as the main indication to future workers in the field: are tiny, dispersed species ("nanoclusters") present when using noble metal additives in the processing of gas sensors? In this case, how to deal with such species? While it is tempting to treat their effect analogously to the classical promotion mechanisms, their size and structure fundamentally hinders such approach. As we have seen above, the difficulty in defining a Fermi level for them hinders the electronic sensitization mechanism to be immediately applied. But also in the case of spillover it would be difficult to suppose a steady reservoir of adsorbed analyte species without any concurrent interaction with sensing semiconductor.

Conclusions

It is possible to homogeneously add Rh to anatase TiO_2 nanocrystals by suitably controlling the Rh precursor and the overall processing route. The heat treatment temperature can determine a complex distribution of Rh species, where aside surface oxidized Rh nanocrystals a distribution of Rh oxide nanoclusters exists. From the analysis of the sensing tests and comparison with literature reports, it has emerged that this distribution of Rh oxide nanoclusters can be responsible for remarkable enhancement of the sensor response with respect to pure TiO_2. It is necessary then, when establishing the effect of noble metal additives, to determine in fine detail the effective speciation of the noble metal. As a consequence, the classical concepts of electronic sensitization and spillover must be cautiously used and possibly rethought.

Competing interests statement

The authors have no competing interests to declare.

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Supplementary Material

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Author Biographies

Mauro Epifani obtained the PhD degree in Physics in 2000 from the University of Lecce, with a thesis on the chemical preparation of metal and metal oxide nanostructures and their optical and electrical characterization. Since then, his research interests include the preparation, processing and characterization of metal and semiconductor colloids, metal oxide thin films and powders, hybrid organic-inorganic materials for gas sensing, water remediation and energy. Since the end of 2001 he is a researcher at the Italian National Council of Researches (CNR).

Saulius Kaciulis received his PhD in 1983 at the University of Vilnius in Lithuania. At present time, he is a senior researcher at the Institute for the Study of Nanostructured Materials of the CNR of Italy. His primary research activities are focused on the surface analysis of innovative materials, such as thin films for thermionic converters and gas sensing, 2D carbon materials, anticorrosion coatings, biocompatible materials, etc. Co-author of over 200 scientific papers.

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