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Surface chemistry of TiO_2 nanoparticles: influence on electrical and gas sensing properties

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Abstract

The modification of the surface chemistry of semiconducting nanoparticles is often required for optimising their performance. For example, surface modifications of semiconductor-based sensors can be envisaged to tailor the device selectivity. However, surface chemical modifications should deteriorate neither the bulk characteristics nor the electrical properties of the material. This becomes critical for nanoparticles due to their high surface-to-bulk ratio. In this work, surface modifications of titanium oxide nanoparticles by grafting hexamethyldisilazane (HMDS) are monitored in situ by Fourier transform infrared spectroscopy. The HMDS grafting decreases the density of the hydroxyl groups at the titanium oxide surface and, therefore modifies the surface affinity to water molecules. The consequences of these surface modifications on the gas sensing properties of the nanomaterial are discussed. In particular, it is shown how moisture adsorption subsequently alters these new grafted chemical species, resulting in a decrease of the cross-sensitivity to humidity. The variations of the infrared background absorption versus gas exposures are demonstrated to follow a λ^2 dependence in agreement with the Drude–Zener theory, thus indicating that they are essentially due to the free carrier absorption. Therefore, the variations of the infrared absorption versus gas exposures can be directly correlated to the electrical conductivity variations.

Keywords: Electrical conductivity; FTIR spectroscopy; Gas sensors; Surface chemistry; Titanium oxide

1. Introduction and motivation

Titanium oxide (TiO_2) is a very large volume chemical product and one of the leading inorganics at more than 3.5 million metric tons consumed per year worldwide, representing an annual global market of several billions of €. The majority of TiO_2 produced worldwide goes into paints, coatings, plastics and paper industries.

But, TiO_2 is also a semiconductor with photocatalytic properties that scientists are still investigating to take full advantage of this non-toxic and extremely stable material. Indeed, the surface chemistry of TiO_2 is rather complex and quite dependent on the synthesis method and on the crystalline state.[1]

Titanium oxide nanosized powders are now widely produced on an industrial basis and the average grain size of commercialised nanopowders usually varies in the 10–30 nm range. This has stimulated a growing interest from scientists working in the booming field of nanomaterials and nanotechnology.

In this paper, we focus on a high-added-value application of TiO_2 nanoparticles, namely chemical gas sensors. The main purpose of this work is to study the electrical properties of TiO_2 nanoparticles in relation with their surface chemistry in order to improve the sensitivity to CO detection in humid environment. It is indeed well known that the major drawback of semiconductor-based sensors is their sensitivity to humidity which makes the sensor response unreliable in atmospheres with variable relative humidity levels. The hydroxyl groups present at the surface of all metal oxides appear to be partly responsible for the variations of the sensor sensitivity in presence of humidity but the chemical reactions which can possibly occur at the sensor surface are not clearly understood.[2] In order to obtain a better understanding of the role of these hydroxyl groups, the surface of the TiO_2 nanoparticles has been functionalized by grafting hexamethyldisilazane.

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These chemical modifications of the TiO_2 surface lead to a decrease of the density of the surface hydroxyl groups. The consequences of these surface chemistry changes on the sensor response in a humid environment have been analyzed.

Changes in the surface chemistry simultaneously with their consequences on the sensitivity to gases are monitored in situ by Fourier transform infrared (FTIR) spectroscopy.

2. Experimental

The TiO_2 nanopowder (n-TiO_2) used for this study is a commercial product (P25, Degussa-France). The specific surface area measured by the supplier is 50 ± 20 m^2 g^{-1} and the estimated primary particle size is 21 nm. The material is a mixture of anatase (70%) and rutile (30%) phases. For the infrared analyses, 50 mg of nanopowder are slightly pressed into a 20 mm-diameter pellet on a stainless grid (Gantois, France). This grid which has been checked to be inert towards TiO_2 and any other chemicals, allows an homogeneous thermal distribution while ensuring a robust sample.

All the gases have been provided by Air Products and are 99% pure at a minimum. Hexamethyldisilazane (HMDS) from Fluka (Germany) is 99.5% pure while water is bi-distilled and de-ionized.

The infrared spectra are recorded from 5000 to 450 cm^{-1} with a 4 cm^{-1} resolution by using a Fourier transform infrared spectrometer (Perkin Elmer, Spectrum 2000) equipped with a MCT cryodetector. The FTIR experiments are run in situ thanks to a vacuum cell specially designed to fit in the sample compartment of the spectrometer.[3] A small furnace inside the cell allows heat treatments of the sample from room temperature up to 773 K. Controlled pressures of gases or liquid vapours can be introduced in the cell through a valve system.

The experimental procedure to identify the surface chemical groups, to functionalize the nanoparticle surface and to monitor the surface reactions has been described elsewhere.[3,4]

3. Surface functionalization of TiO_2 nanoparticles

Like all metal oxides, the surface of TiO_2 nanoparticles presents hydroxyl (OH) groups originating from the surface hydrolysis as soon as the material is in contact with moisture or regular atmosphere.[1] At room temperature, water molecules are adsorbed on the surface mainly through hydrogen bonds. A thermal treatment under dynamic vacuum (referred to as *activation*) usually removes all hydrogen-bonded water molecules leaving the surface OH groups free to interact with whatever surrounding molecules.[3]

In the present case, the activated surface of the TiO_2 nanoparticles has been subjected to HMDS liquid vapour and the chemical reaction leading to the surface functionalization is expected to take place as follows:[5]

$$2\ \text{Ti-OH} + \left[\text{Si(CH}_3)_3\right]\text{NH}\left[\text{Si(CH}_3)_3\right]$$

$$\rightarrow\ 2\ \text{Ti-O-Si(CH}_3)_3 + \text{NH}_3$$

In previous works,[6] we have shown that, under HMDS liquid vapour, the surface OH groups are replaced with new $Si(CH_3)_3$ groups bonded to the TiO_2 surface. Ammonia is formed and rapidly adsorbed on Lewis acid surface sites. It is worth noting that ammonia is a reducing gas and therefore the HMDS grafting is a reducing process. A thermal desorption eliminates coordinated NH_3 but the original OH groups are not restored, thus showing that the TiO_2 surface is irreversibly modified by HMDS.

Fig. 1 shows the 4000–2000 cm^{-1} region of the spectra of n-TiO_2 after activation at 673 K (spectrum 1a) and after HMDS grafting followed by a thermal desorption at the same temperature (spectrum 1b). After activation, the main absorption bands correspond to the ν(OH) stretching vibrations of the OH surface groups. After HMDS grafting, the ν(OH) bands have almost completely disappeared whereas new bands can be observed in the 3000 cm^{-1} region. These new bands are assigned to the ν(CH_3) stretching vibrations of $Si(CH_3)_3$ trimethylsilyl groups,[6] thus indicating that the HMDS

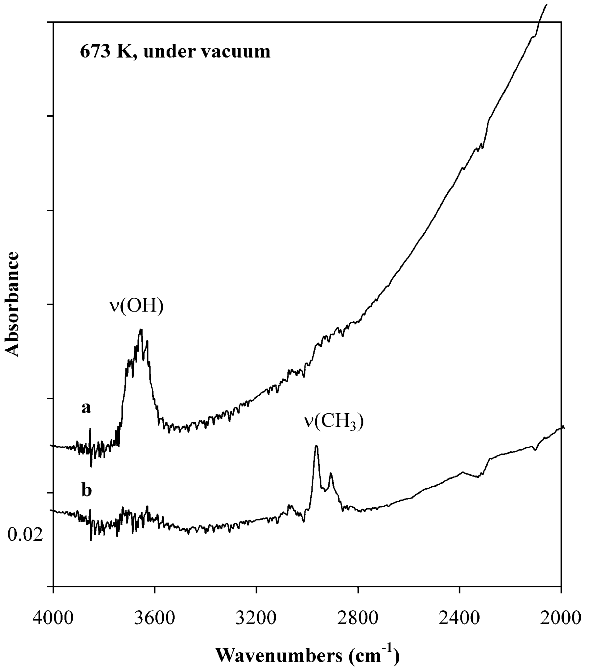

Fig. 1. FTIR spectra of pure n-TiO_2 (a) and HMDS-grafted n-TiO_2 (b) at 673 K under dynamic vacuum (10^{-2} mbar). (The spectra have been shifted for clarity sake.).

grafting has proceeded successfully according to the above reaction.

To check the effects of humidity on the new grafted trimethylsilyl groups, the HMDS-grafted n-TiO_2 sample has been placed in contact with regular atmosphere at 673 K. Fig. 2 compares the infrared spectra of pure and HMDS-grafted n-TiO_2 under air in the 4000–2000 cm^{-1} region. On the spectrum of the pure sample (spectrum 2a), only bands due to isolated or perturbed OH groups are visible. A comparison of the spectra of the grafted sample before (Fig. 1b) and after (Fig. 2b) atmosphere addition shows that two main bands above 3600 cm^{-1} appear to the detriment of the $\nu(CH_3)$ bands. One of these new bands indicates the partial recovery of the original OH groups whereas the relatively narrow band at 3738 cm^{-1} is assigned to the ν(OH) vibration in silanol (Si–OH) groups.[1,7] These silanol groups are formed by reaction of water molecules with the grafted trimethylsilyl groups.[8] It is obvious that the formation of SiOH groups on the n-TiO_2 surface modifies the surface reactivity of the nanoparticles. Indeed, it is known that most of the OH groups linked to titanium atoms at the TiO_2 surface show strong Brønsted acid characteristics[1,7] whereas all the OH groups linked to silicon atoms should be similar to the OH groups at the silica surface which present no or very low Brønsted acidity.[1]

4. Sensing properties of non-grafted and HMDS-grafted n-TiO_2 samples

On a n-type semiconductor, such as TiO_2, the adsorption of CO at relatively high temperature produces an increase of the electrical conductivity. It is generally agreed that CO reacts with ionosorbed oxygen species to form CO_2 releasing electrons in the conduction band:[9,10]

$$2\ CO + O_2^- \rightarrow 2\ CO_2 + e^-$$

$$CO + O^- \rightarrow CO_2 + e^-$$

The effects of these reactions on the infrared spectrum are twofold:

- The absorption bands corresponding to gaseous CO_2 are observed;
- The background absorption level of the spectrum increases due to the increase of the free carrier density.[11,12]

Indeed, as demonstrated by Harrick,[11] a very broad band is observed in the infrared spectrum if the free carrier density is altered in the semiconductor space-charge region. This broad band is quite characteristic of the free carrier absorption. Most theories predict a λ^2 dependence for this absorption (λ being the infrared wavelength) although variations often occur.[11–13]

Therefore, in addition to the surface reactions and to the creation of new chemical species, we have followed the variations of the background infrared absorption when the non-grafted and HMDS-grafted n-TiO_2 samples are subjected to CO in absence or in presence of humidity. The addition of 9 mbar of pure CO on both non-grafted and HMDS-grafted samples leads to the formation of a very small amount of CO_2 (Fig. 3) but the oxidation of CO into CO_2 is enhanced by the presence of humidity (Fig. 4). We note the formation of silanol groups on the grafted n-TiO_2 under the $[CO + H_2O]$ mixture as previously discussed (Fig. 4b).

The modulation of the electronic population in the space-charge region of the n-TiO_2 particles by varying the gaseous environment leads to a modulation of the infrared energy transmitted by the sample.[11] We have indeed proved in earlier works[8,14–16] that the variations of the infrared energy transmitted by the semiconductor sample versus gas exposures can be directly compared to the response of the real sensor obtained from standard electrical measurements. Under a reducing gas, such as CO, the transmitted infrared energy decreases due to the increase of the free carrier density leading to a higher absorption over the infrared range.

As examples, Figs. 5 and 6 show the variations of the infrared energy transmitted by the non-grafted and the HMDS-grafted n-TiO_2 samples under additions of CO mixed with water vapour. The total pressure of the gaseous mixture is kept constant ($p[H_2O] + p[CO] =$

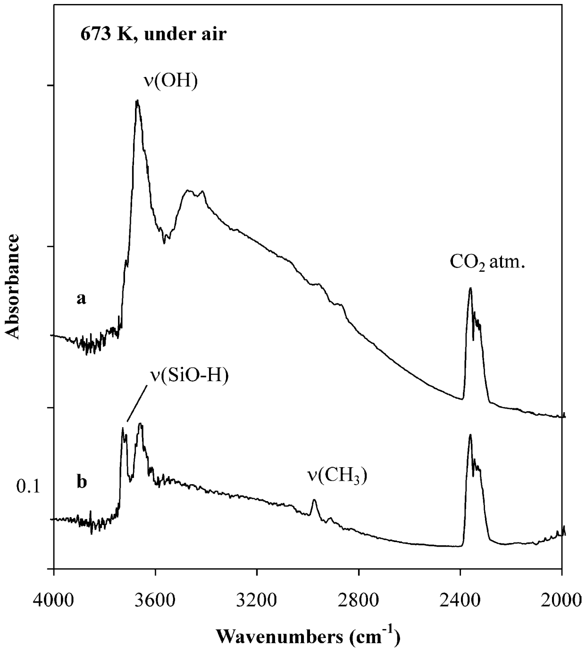

Fig. 2. FTIR spectra of pure n-TiO_2 (a) and HMDS-grafted n-TiO_2 (b) at 673 K under air (atmospheric pressure). (The spectra have been shifted for clarity sake.)

10 mbar) and the pressure ratio is varied ($p[H_2O]/p[CO] = n/8$, with n varying from 0 to 8). The transmitted infrared energy is measured 2 and 10 min after addition of the gaseous mixture. Then, after a 10-min contact, the gaseous mixture is evacuated before the addition of a new dose of gases. In Fig. 5, we can observe that the electrical conductivity of the non-grafted sample increases during the first 2 min, thus giving some indication that CO is first detected. But, after 2 min, an oxidizing effect becomes preponderant and at the end of the 10-min contact, the sample is slightly oxidized. The same effect is observed whatever the relative humidity ratio and the overall effect of the "gas addition-evacuation" cycles is an oxidation. This

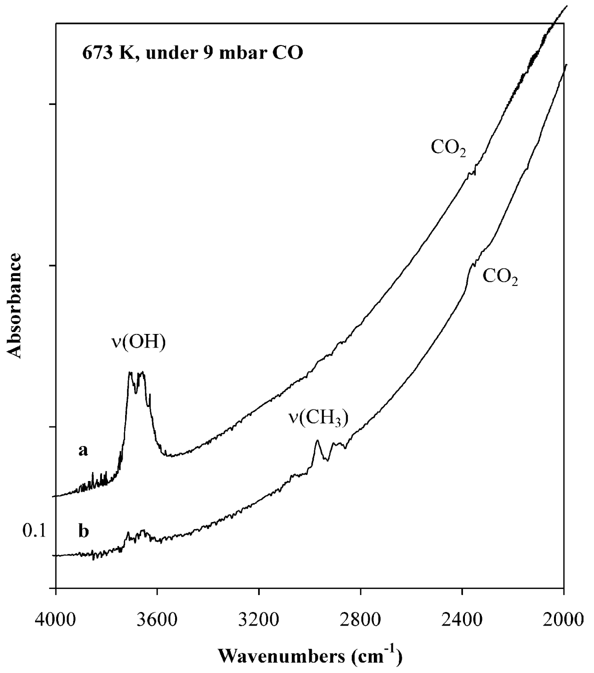

Fig. 3. FTIR spectra of pure n-TiO_2 (a) and HMDS-grafted n-TiO_2 (b) at 673 K under 9 mbar of CO. (The spectra have been shifted for clarity sake.)

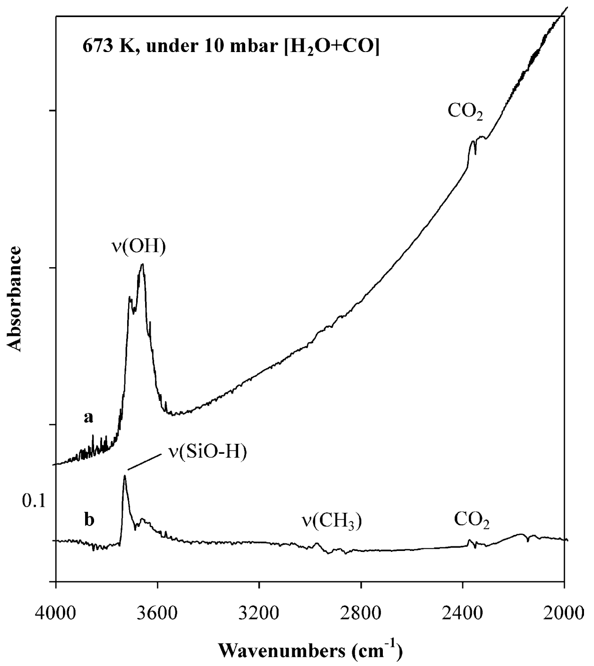

Fig. 4. FTIR spectra of pure n-TiO_2 (a) and HMDS-grafted n-TiO_2 (b) at 673 K under 10 mbar of [$CO + H_2O$] (9 mbar CO and 1 mbar H_2O). (The spectra have been shifted for clarity sake.)

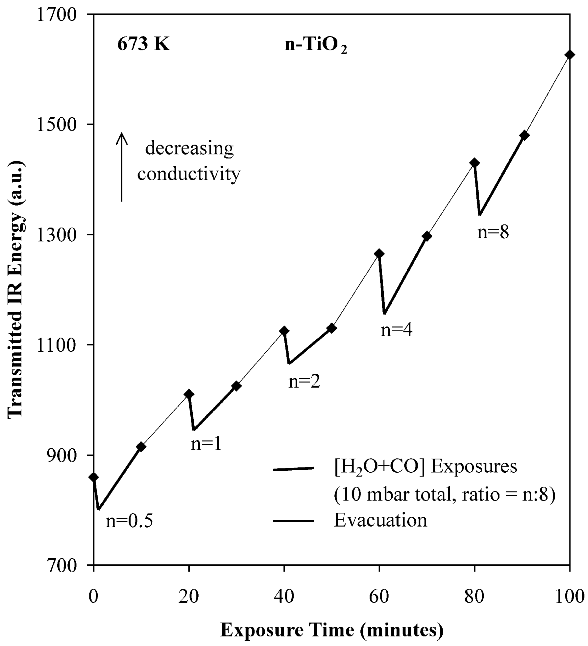

Fig. 5. Infrared energy transmitted by the n-TiO_2 sample versus [$CO + H_2O$] exposures.

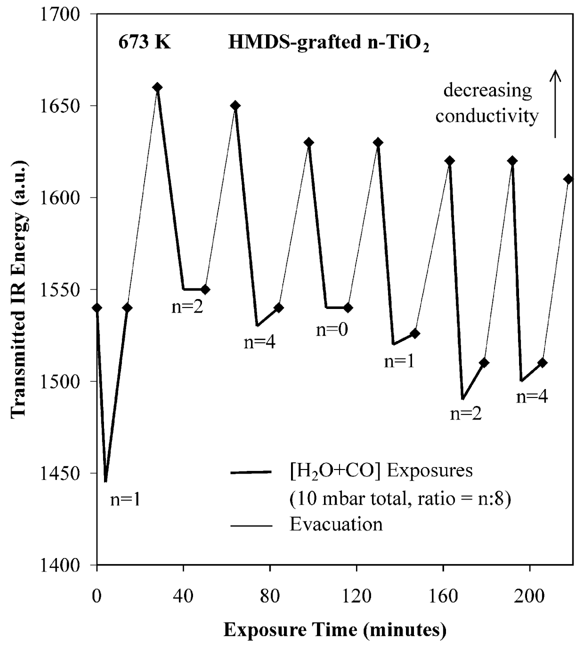

Fig. 6. Infrared energy transmitted by the HMDS-grafted n-TiO_2 sample versus [$CO + H_2O$] exposures.

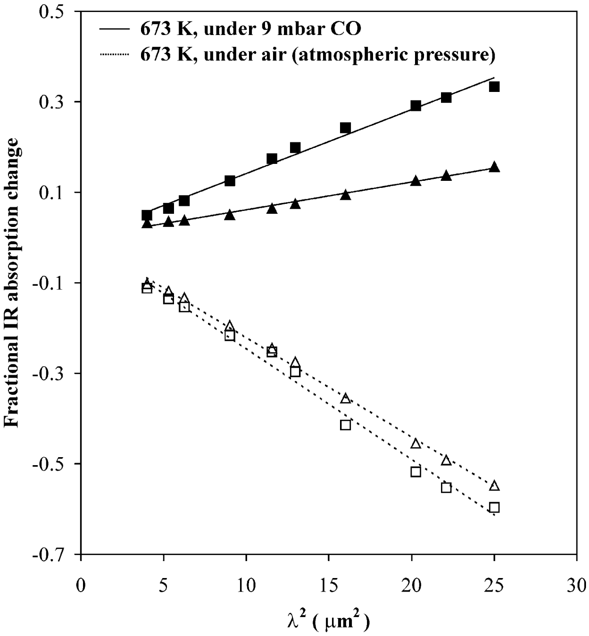

Fig. 7. Fractional infrared absorption changes versus λ^2 upon CO and air exposures: ■ n-TiO$_2$; ▲ HMDS-grafted n-TiO$_2$.

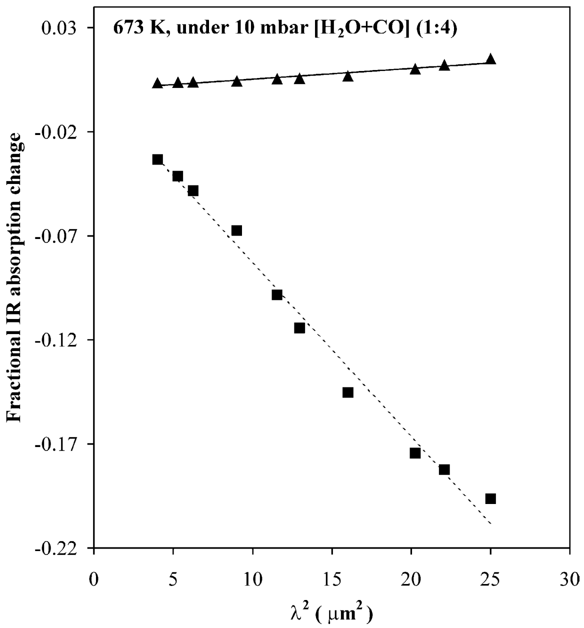

Fig. 8. Fractional infrared absorption changes versus λ^2 upon [CO + H$_2$O] exposures: ■ n-TiO$_2$; ▲ HMDS-grafted n-TiO$_2$.

behaviour is drastically different from that observed under pure CO and indicates that humidity has a strong adverse effect on the electrical response to CO.

On the contrary, no qualitative change of the response can be noted in the case of the HMDS-grafted sample (Fig. 6). The sample is reduced by CO and the amplitude of the response to CO appears to be fairly reproducible whatever the humidity content. The different electrical behaviour noted under the first dose of gas, either pure CO or CO mixed with water vapour, has tentatively been explained by a rearrangement of the electronic structure of the titanium oxide surface after the reducing effect of the HMDS grafting.[8]

As explained above, the free carriers are expected to give rise to a broad λ^2 absorption band in agreement with the Drude–Zener theory.[17] The fractional infrared absorption changes are plotted versus λ^2 in Fig. 7 in the 5000–2000 cm^{-1} range (2–5 μm) for several gaseous environments. For both non-grafted and HMDS-grafted titanium oxide, we observe positive variations of the absorption under reducing adsorbates, namely CO, whereas negative changes corresponding to oxidation are observed under air adsorption. These curves show a good agreement with the theoretical λ^2 dependence, thus indicating a free carrier absorption.

Fig. 8 shows the fractional infrared absorption changes versus λ^2 under a mixture of CO and water vapour. Unlike the previous case of pure CO, a negative curve is observed for non-grafted titanium oxide, thus indicating an oxidation under the gaseous mixture of CO and water vapour. This corresponds to the response curve of the nanoparticles (Fig. 5) and shows the very strong adverse effect of humidity on the response of titanium oxide towards CO. On the contrary, a positive curve is obtained for the HMDS-grafted sample, thus confirming that the response to CO of the HMDS-grafted sample is qualitatively non affected by water adsorption. Therefore, by grafting HMDS on the surface of the titanium oxide nanoparticles, the cross-sensitivity to humidity has been decreased.

5. Conclusion

Fourier transform infrared spectroscopy appears to be a very valuable tool for fundamental studies of semiconductor nanosized particles. Indeed, this technique makes it possible to simultaneously:

- study the chemical reactions at the nanoparticles surface;
- monitor in situ the surface functionalization;
- check the stability of the surface modification under various environments;
- access electrical phenomena taking place at the nanoparticles surface and inside the bulk without contact perturbation.

Our preliminary results show that the modification of the n-TiO$_2$ surface by grafting hexamethyldisilazane, which leads to a decrease of the density of the surface hydroxyl groups, has beneficial effects on the cross-sensitivity to humidity without jeopardizing the sensitivity to carbon monoxide.

Acknowledgements

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