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Nanograined anatase titania-based optochemical gas detection

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New Journal of Physics **10** (2008) 053030 (10pp)

Received 12 March 2008

Published 22 May 2008

Online at <http://www.njp.org/>

doi:10.1088/1367-2630/10/5/053030

Abstract. Optochemical sensing properties of thick films of titanium dioxide (titania) in anatase phase have been studied and compared with tin dioxide cassiterite. Anatase titania exhibits a large photoluminescence response to nitrogen dioxide, which acts as a luminescence enhancer. Intrinsic surface phenomena rather than bulk defectivity are proposed to account for the behaviour and the experimental results are fitted with the Langmuir model. Good operational performances working at room temperature are achieved.

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1. Introduction

Within the last few years, extensive technological efforts have been made to develop sensitive and inexpensive chemical gas species detectors. Among these, technology based on semiconductor metal oxides (MOX) has been very profitably exploited for such purposes. The synthesis of nanostructures has allowed one to get MOX structures (nanograins, nanobelts, nanowires to cite some of the most common) possessing huge surface-to-volume ratios, making them extremely sensitive to changes of their surrounding environment [1]–[4]. Low cost deposition and synthesis techniques allow one to obtain MOX structures characterized by small sizes and high robustness. MOX-based sensors show significant variations of electrical conductivity even in response to traces of gases [5]. The main disadvantage of such sensors is their need for a high working temperature, which leads to power wastage. Recently, it has been proposed to resort to other properties of such materials, in particular to monitor their optical response to environmental changes [6]. Such an analysis offers the advantage of being less sensitive to electromagnetic noises and the potential selectivity given by the complex vectorial nature of the electromagnetic radiation by exploiting the different degrees of freedom (intensity, wavelength and polarization) [6]. By monitoring variation of the photoluminescence (PL) response of nanostructured MOX, sensitive gas detection has been achieved, even working at room temperature [7].

Titanium dioxide (titania) is a wide band-gap semiconductor with a wide range of applications. In industry, it is used as white pigment and an opacifer in paints and cosmetics. It is widely used as a photocatalytic element [8], for photocatalysed electrolysis of water [9], solar energy conversion [10], oxidation of organic pollutants [11], photocatalytic antibacterial disinfection [12] and as a biocompatible interface for medical implants [13]. TiO_2 has, moreover, found applications in air purification, self-cleaning surfaces and transparent superhydrophilic coatings [14]. These different functions depend critically on the surface properties of the oxide [15]. Titania has, moreover, been profitably used as an electrochemical detector [16]. A very comprehensive review of the surface properties of titania can be found in [17].

Titania can crystallize in three forms: anatase, rutile (both tetragonal) and brookite (orthorhombic), the last one exhibiting no significant chemical and catalytic activities and so

is not usually considered. In the following we will focus our attention on the anatase, as it is the most chemically and catalytically active form [8].

In the present work, the use of nanograined anatase TiO_2 as an optochemical gas detector is proposed. It strongly reacts to the presence of nitrogen dioxide, as its PL intensity is greatly enhanced by the chemical agent presence. The observed behaviour suits well the framework of the Langmuir adsorption model. Moreover, anatase sensoristic performances in comparison to a well-known material such as SnO_2 will be analysed and its better performing optochemical sensing ability will be highlighted.

2. Experimental details

2.1. Sample preparation

Both titania and tin dioxide powders were synthesized via the sol-gel route involving metal organic compounds, with general formula $\text{M}(\text{OR})_x$ (R = alkyl group). SnO_2 was synthesized using $\text{Sn}(\text{II})$ -alkoxide dissolved in *n*-butanol and hydrolysed by an acidic solution whose pH was 0.8. By means of calcination, carried out at 550°C for 2 h, the hydroxyl-precursor was decomposed into pure and partially crystalline cassiterite (rutile-like structure), as confirmed by XRD analysis.

The titania powders were prepared, according to the procedure described in [18], starting from a hydro-alcoholic solution of $\text{Ti}(\text{IV})$ -alkoxide with extremely high $\text{Ti}/\text{H}_2\text{O}$ ratio. The thermal decomposition of the precursor at 400°C for 2 h yields pure anatase TiO_2 .

The obtained powders were deposited in the form of thick films through a screen-printing technique onto silicon substrates. Both titania and tin dioxide films were fired at 650°C for 1 h, obtaining layers with very similar morphology and grain sizes ranging from 30 to about 60 nm. In figure 1, the SEM viewgraphs of the obtained samples are reported.

2.2. Setup

PL analysis was performed by exciting the samples through the UV spectral line (325 nm and 3.8 eV) of an He–Cd laser. The emitted spectra were analysed through a monochromator (equipped with a $600\text{ grooves mm}^{-1}$ grating blazed at 500 nm) coupled with a Peltier-cooled CCD camera. The sample was placed at fixed room temperature within a chamber with quartz windows for optical access; the chamber atmosphere could be controlled through a mass flow control system which provided calibrated mixing of different gaseous species, in particular nitrogen dioxide diluted in synthetic dry air. During the whole experiment, the gas flux was kept constant at 0.3 l min^{-1} in order to avoid turbulences within the test chamber atmosphere. PL measurements were carried out by exposing the samples to the pump light just for a few seconds required to perform the spectral acquisition; this precaution was taken in order to avoid the onset of light-induced catalytic reactions [8].

3. Experimental results and discussion

3.1. Origin of the observed PL spectra

As observed in figure 2, the PL spectra emitted from the two phases are different: anatase has a broad PL spectrum in the visible range centred at about 2.3 eV, while rutile emission consists of

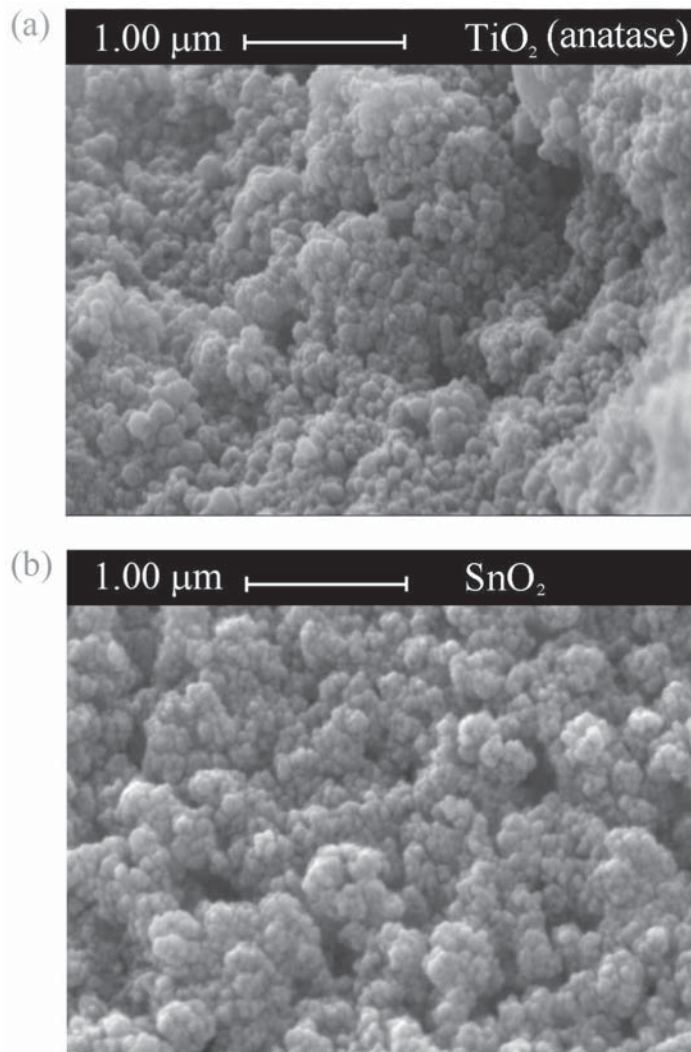


Figure 1. (a) Titania and (b) tin dioxide film fired at 650 °C for 1 h.

a narrow spectrum in the near infrared range (NIR) centred at about 1.25 eV. Differences in the emission spectra have to be searched in the structural analogies and differences between the two phases. Both polymorphs of TiO₂ are built by a chain of coordinated TiO₆ octahedra, but they differ by the distortion of each octahedron and by the assembly pattern of the octahedral chains. In rutile, each TiO₆ octahedron is connected to ten neighbouring ones sharing a corner or an edge. In anatase, the coordination of the TiO₆ octahedra is less compact and each octahedron is coordinated only with eight neighbouring ones. The different packing within the unit cell and the different coordination amongst contiguous octahedra has a deep implication on the nature of their emission mechanisms [19, 20]. As a matter of fact, the emission in the two polymorphs is ascribed to excitons with opposite nature, i.e. self-trapped excitons (STE) in anatase against free excitons in rutile. STE, often also called *charge-transfer* excitons, occur in titanates whose structures are built on a network of TiO₆ octahedral units [21]. They result from the interaction of conduction-band electrons located on Ti 3d states with holes built on oxygen 2p states. The exciton can be localized on a TiO₆ octahedral site if the transfer of the exciton from one site to neighbouring is not energetically favoured; this depends, beside other factors,

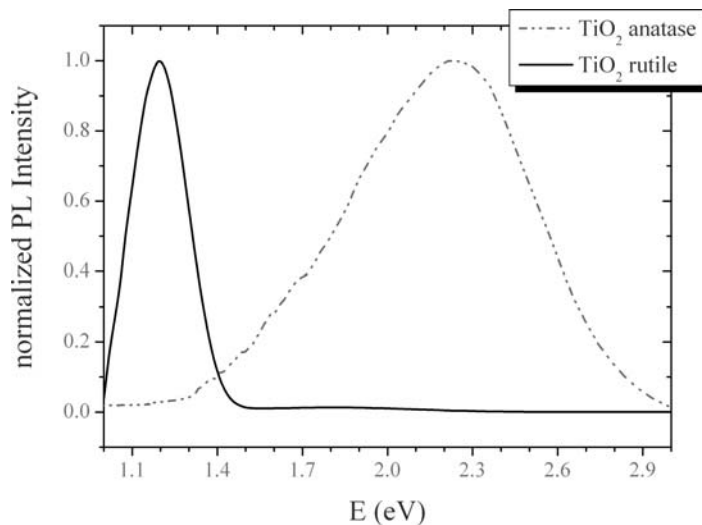


Figure 2. PL emission spectra from rutile titania (full line) and from anatase titania (dashed line).

on how compactly the TiO_6 units are condensed into the crystalline structure. In rutile, each TiO_6 octahedron is connected to ten neighbours, while in anatase it is connected only to eight; the intersite transfer of excitons is thus more probable in rutile than in anatase. Moreover, taking into account the lower octahedra coordination, the lower symmetry and the longer bond lengths of anatase, it appears clear why excitons undergo self-trapping in anatase. Free-exciton emission is not commonly observed in rutile samples although lines of weak intensity are reported to be observed in highly purified rutile crystals [22]. The NIR emission observed in rutile samples has been ascribed to the ionization of oxygen vacancies [23]. Therefore, it is possible to ascribe a more intrinsic character to the PL of anatase than to that of rutile, which is directly linked to its defectivity.

3.2. Interaction with nitrogen dioxide

After the introduction (figure 3(a)) of nitrogen dioxide—which is a typical polluting chemical agent used in sensoristic experiments—within the chamber atmosphere, a variation of the intensity of the anatase PL spectrum is observed: a net enhancement of the PL intensity occurs by increasing the concentration of nitrogen dioxide. In figure 4, PL maxima (i.e. the peak values of the PL spectral distribution at 2.3 eV) versus gas concentration are reported. Apart from the increase of intensity, the anatase PL signal does not undergo any other significant spectral modification, keeping unaltered the value of the peak position and the width of the spectral distribution (figure 3(b)), suggesting that the adsorption event results in an increase of the number of radiative recombination events. The acquisitions were taken at room temperature. When the gas was removed from the chamber, the initial intensity of the PL spectra was recovered within a few minutes, ensuring a good reversibility.

The very peculiarity of the anatase response to NO_2 appears clear by comparing it with the reaction of other materials to the presence of the same chemical species. For example, the effect of the interaction between tin dioxide [7] or meso- and nanoporous silica [24] and nitrogen dioxide is a net reduction of the PL intensity—often called quenching of the PL signal.

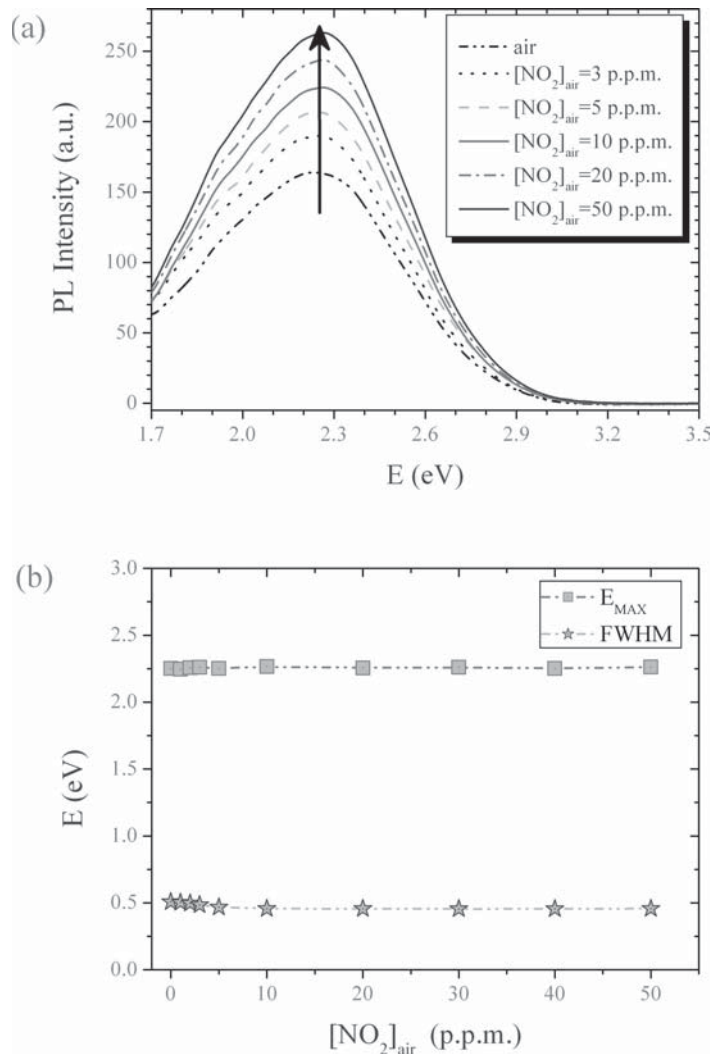


Figure 3. (a) Anatase PL emission spectra for different nitrogen dioxide concentrations and (b) energy position of the maxima (squares) and full width at half-maximum (stars) of the PL spectral distribution versus nitrogen dioxide concentration.

Such a behaviour is explained by considering a model in which the source of the PL emission—called *emitting centres* and whose origin has still to be fully clarified, although studies involving annealing treatments suggest [25] that their origin is strictly related to the oxygen vacancies—is just turned off as a consequence of the adsorption of a gas molecule, often thus referred to as a quencher. One can say that the capture of an electron from NO_2 —that in virtue of its oxidizing nature acts as an electron acceptor—switches an emitting centre off [4].

The anatase PL signal, in contrast, is enhanced by the presence of nitrogen dioxide which acts as an enhancer of the PL signal rather than as a quencher. There are no emitting centres that are switched off. Such a peculiar behaviour resembles the different origin of the PL emission mechanism occurring in anatase. As reported by Tang [20], defectivity and impurities appear to play a small role since the same luminescence spectrum is observed in anatase crystals with various dopants, in anatase thin films and in samples exposed to radiation damage. The highest

luminescence response has been found in the purest samples. Although further studies on this subject are mandatory and no conclusion on the origin of such a behaviour can be drawn, we might suppose that a mechanism similar to those proposed by Tang [26] in his work on the electric sensing ability of anatase titania to different chemical species comes into play, whose effect results in tuning the presence of electrons in the conduction band (which is composed mainly of the Ti 3d states). Moreover, electron mobilities are relatively high in anatase with respect to those in rutile and any charge carriers donated from surface reactions efficiently populate the conduction band.

Thus, in anatase, the result of the adsorption events is a variation of the number of electrons in the conduction band and a consequent increase of the probability of STE radiative emission.

A further support to the fact that the anatase PL origin relates to the electron mobility and is strongly influenced by surface properties and modifications comes from depositing some Pt drops on the titania surface [27]. The Schottky barrier formed at the Pt/titania surface acts as an efficient electron trap. It is observed that the anatase PL signal vanishes once Pt has been deposited on its surface and electrons have been trapped by the Schottky barrier. On the contrary, PL emission from rutile samples—whose origin is related to the ionization of oxygen vacancies—is completely unaffected by the Pt deposition.

3.3. The Langmuir adsorption mechanism and comparison with tin dioxide

Regarding the behaviour of the PL intensity, when the atmosphere undergoes some chemical changes, it is possible to show that, under very simple assumptions, the PL intensity in the presence and in the absence of adsorbed gas molecules can be written as [28]:

$$I(c) = I_0(1 + k\vartheta(c)), \quad (1)$$

where $I(c)$ means the PL intensity in the presence of some adsorbed chemical agent whose concentration is indicated as c , I_0 is the PL intensity without adsorbed gas molecules, k is the constant and $\vartheta(c)$ is the surface coverage of the sample, i.e. the surface density of gas molecules actually adsorbed normalized by the density of adsorption sites. In order to relate the surface coverage $\vartheta(c)$ to the gas concentration, which is the parameter that can be experimentally tuned, one can resort to a simple statistical model—the Langmuir model [29]—that starts from very realistic assumptions (just an adsorbed layer of non-interacting atoms) and states that:

$$\vartheta(c) = \frac{bc}{1 + bc}, \quad (2)$$

where b is a constant depending on the free energy of desorption of the adsorbed gas molecule from the material surface. The dashed line in figure 4 represents the best fit of our experimental data with (1) and (2). It can be seen that there is good agreement between the model and the experimental data. The b value obtained from the fit is: $b_{\text{TiO}_2} = (0.10 \pm 0.01) \text{ ppm}^{-1}$.

In order to test the anatase response to nitrogen dioxide, we plotted the relative variation of the PL signal versus surface coverage and compared it with the signal emitted by a SnO₂ nanograined sample obtained with the same preparation procedure. The b value obtained for this latter sample is: $b_{\text{SnO}_2} = (2.0 \pm 0.3) \text{ ppm}^{-1}$. To allow a direct comparison, we took the absolute value of the relative intensity variation. In the case of tin dioxide, in fact, nitrogen dioxide acts as a PL quencher resulting in an opposite trend with respect to that shown in figure 4. As can be seen in figure 5, under the same coverage conditions, the anatase sample has a stronger variation of the PL signal than the tin dioxide one, providing strong evidence of the higher response of anatase as a nitrogen dioxide detector.

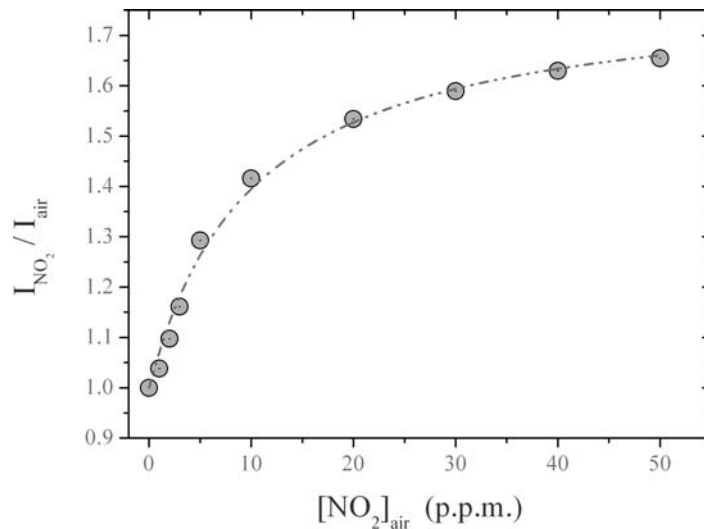


Figure 4. Intensity of the PL emission versus gas concentration. The dashed line represents the fitting of the data after the Langmuir models ((1) and (2)).

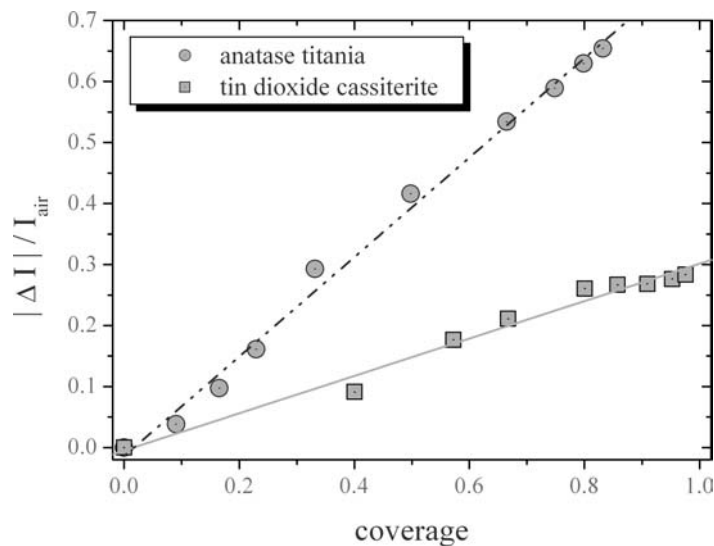


Figure 5. Relative variation of the PL intensity versus surface coverage for anatase TiO₂ (circles) and cassiterite SnO₂ (squares). The absolute value of the intensity variation is taken in order to make a direct comparison between the two relative responses.

4. Conclusions

In conclusion, we have studied the PL behaviour of nanograin anatase samples under exposure to a nitrogen dioxide atmosphere. Anatase PL emission has an *intrinsic* character (due to STE emission) rather than being related to the material defectivity, in contrast to what happens for other materials. For instance, oxygen vacancies are believed to lead the light emission mechanisms in nanostructured tin dioxide. The differences in the origin of the light emission

mechanisms are also reflected in the different kinds of responses to the external chemical agent. As a matter of fact, the action of the gas results in the quenching of the tin dioxide PL while enhancing the anatase one. The relative response of the PL signal to the chemical agent presence scales linearly with the nanograin surface coverage and can be conveniently modelled as following the Langmuir adsorption mechanism. A comparison with the relative response versus surface coverage between anatase and tin dioxide samples has been made, showing the higher response of the anatase sample with respect to the tin dioxide one. Such remarkable properties, together with the fact that the system works at room temperature and presents good reversibility, suggest the use of anatase as a sensitive candidate for gas detecting purposes.

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