Nanostructured TiO$_2$ Layers for Photovoltaic and Gas Sensing Applications

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Abstract

Titanium dioxide (TiO$_2$) has been an important material for decades, combining numerous attractive properties in terms of economy (low price, large availability) or ecology (non-toxic), as well as broad physical and chemical possibilities. In the last few years, the development of nanotechnologies offered new opportunities, not only in an academic perspective but also with a view to many applications with particular reference to the environment. This chapter focuses on the many ways that allow to tailor and organize TiO$_2$ crystallites at the nanometre scale to make the most of this amazing material in the field of photovoltaics and gas sensing.

Keywords: titanium dioxide, solar cell, gas sensing, nanotube, anodization

1. Introduction

Titanium dioxide (TiO$_2$), also known as titania, has attracted a great deal of interest over the past decades because of its ability to create electron-hole pairs when absorbing light in an adequate wavelength range, taking into account that the valence and conduction bands are separated by a ca. 3.2 eV gap. Such a charge separation capacity makes TiO$_2$ a very convenient material for photovoltaic (see Section 2) and photocatalytic applications. Basically, once an electron is excited by absorption of a photon of sufficient energy, either of the following phenomena can occur: the electron-hole pair dissociates and both charge carriers migrate toward opposite electrodes...
generating a voltage that constitutes the photovoltaic effect or both charge carriers act like very active reagents in many chemical reactions what constitutes a photocatalytic effect (Figure 1).

Another interesting characteristic of crystalline TiO\textsubscript{2} is the variation of its semiconductivity because of charge transfer induced by the chemisorption of gaseous molecules onto the solid surface, making this material also very interesting for gas sensing applications (see Section 3).

The photocatalysis field has already a very rich literature, hence it is not discussed in this chapter, despite its extreme importance, to focus on photovoltaic and gas sensing applications.

TiO\textsubscript{2} may crystallize in different allotropic structures, mainly anatase, rutile and brookite. Anatase is generally considered to have the best properties for the above-mentioned applications. It is metastable (or “kinetically stable”) up to 550°C. Above this temperature, it transforms into the equilibrium rutile allotrope though anatase nanocrystallites (about 10 nm in size) appear to be metastable over a wider temperature range.

Figure 1. Schematization of either photocatalytic or photovoltaic effect following photon absorption by TiO\textsubscript{2}. 

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Of course, the manufacturing and optimization of a TiO$_2$ layer will be conducted in different ways depending on the intended application, but there is an important parameter that must be maximized in any case, which is the specific surface area. Therefore, such layers will always consist of nanocrystallites or nanostructures.

From a practical point of view, TiO$_2$ is also cheap, thermally and chemically stable and nontoxic (food additive E171, stated Kosher and Halal). However, in 2006, the International Agency for Research on Cancer (IARC) classified the titanium dioxide as possibly carcinogenic for humans.

2. TiO$_2$ for dye sensitized solar cells

2.1. Generalities and operating principle of a DSSC

In 1991, Professor Michael Grätzel from the École Polytechnique Fédérale de Lausanne (EPFL) published an article [1] describing the functioning of a new type of solar cell (called of the third generation) based on the use of a TiO$_2$ layer sensitized with a dye (dye-sensitized solar cell [DSSC]). This cell differs from the massive (single crystal or polycrystalline) silicon cells based on a $p$-$n$ junction that allows an easy dissociation of the electron-hole pairs generated following photons absorption by the silicon itself (first-generation cells) or from other solar cells also based on a $p$-$n$ junction but using thin layers of various semiconductor materials such as CdS-CdTe or CdS-CuInSe$_2$ (second-generation cells) [2].

Probably to increase their eco-attractiveness, DSSCs are now often presented as biomimetic devices inspired by photosynthesis though the comparison seems rather misleading if one looks closely. Indeed, when chlorophyll absorbs a photon, an electron-hole pair is created, which established the energy quantum needed for the photosynthetic reaction to occur. This electron-hole pair has to diffuse randomly over a long distance (and therefore with a high recombination probability) along the chlorophyll molecule antenna until it reaches the heme-like porphyrin group, which is the chemical reaction locus. Of course, neither voltage nor electrical current is produced. The role of the dye in a DSSC is completely different and is discussed thoroughly below.

Like in any solar cell, the photogenerated electron-hole pairs must readily dissociate. This is the reason why each type of solar cell is made up of two media of different conduction modes, which prevents the charge carriers once separated to recombine (too easily) so that a voltage can be generated. The TiO$_2$ layer is an electron conductor, and the electrolytic solution acts as an ionic conductor (Figure 2). An electric current is generated when the dye molecules anchored onto the surface of the TiO$_2$ nanoparticles absorb the incoming photons and inject the photoexcited electrons into the TiO$_2$ layer.
The function of the ionic redox couple (traditionally $I_3^−/I^−$) in solution is to reduce the oxidized dye molecules back to their ground state to enable continuous electron production, a process in which the reduced form of the redox couple ($I^−$) gets oxidized itself. The electrons are collected from the TiO$_2$ (photoanode) and transferred through an external circuit to the counter-electrode (cathode) where they complete the operating cycle of the cell by reducing the oxidized redox species ($I_3^−$) back to its original state.

Kinetic aspects are of utmost importance: electron injection from the dye into the TiO$_2$ conduction band must be much faster than the dye relaxation, electron transport into the TiO$_2$ must be faster than electron trapping or recombination and the reduction of the dye by the reduced ion in solution must not be a rate-limiting step (Figure 3).

Figure 2. Functional scheme of a DSSC (thermodynamic point of view).
Figure 3. Functional scheme of a DSSC (kinetic point of view).

Nevertheless, since TiO$_2$ has a wide band gap (3.2 eV), only the most energetic photons ($\lambda < 400$ nm, i.e., about 5% of the total amount of photons) are able to induce a charge separation, thereby leading to a very poor conversion efficiency if TiO$_2$ was used alone. The dye, thus, allows to harvest photons on a wider wavelength range (up to 920 nm, for instance) [3] so as to raise the photocurrent, and therefore the efficiency of the cell. So, unlike the cells of first and second generations, the vast majority of electron-hole pairs are not generated by the material (here TiO$_2$) itself, but following the dye excitation. As outlined above, a very large specific surface area is therefore needed to increase the amount of dye molecules chemically grafted onto the TiO$_2$ surface.

Each component of the cell has undergone many developments since 1991 [4]:

- **The electrodes**: both electrodes must obviously be conducting but at least one must be transparent, and it is best to choose the TiO$_2$ photoanode to be exposed directly to the light so as to avoid great absorption of photons by the counter electrode (cathode) and the
electrolytic solution. So the TiO$_2$ layer should always be deposited onto a transparent conducting oxide (TCO) like an indium-tin oxide (ITO) coating onto a glass substrate. Nowadays, the classical ITO is progressively replaced by FTO (fluorine-doped tin oxide), which presents a lower sheet resistance, a better thermal resistance and avoids the use of indium whose long-term availability is uncertain. The ultimate goal would be to use flexible electrodes (conductive polymer films), but their low long-term stability, especially when exposed to UV-light, is a drawback;

- **The redox couple**: the Nernst potential of the mediator must be little less negative than the dye HOMO potential (Figure 2) so that the reduction of the oxidized molecule is thermodynamically promoted, but some other redox couples may be used (Co$^{3+}$/Co$^{2+}$, for instance) instead of the classical (I$^{-}$/I$_3^-$);

- **The solvent**: the role of the solvent is obviously to solubilize the redox species and let them cycle between the cathode and the dye molecules, but liquid solvents (ethylene glycol, for instance) may have some drawbacks (dye desorption, leakage, etc.). Therefore, the aim is now to replace the liquid electrolytic solution by a solid-hole transport material (HTM) such as P3HT and Spiro-OMeTAD. Unfortunately, using a HTM instead of a liquid electrolyte leads to lower cell performance mainly because of low hole mobility;

- **The dye**: of course, the dye has a key role in the conversion process. It must (1) have a high photon absorption efficiency (or IPCE [incident photon to current conversion efficiency]) on a wide wavelength range, (2) be densely chemisorbed onto the TiO$_2$ surface, (3) be chemically stable for a long time (even if it spends a part of its “life” in an oxidized state), (4) have a LUMO whose potential is a little less negative than the bottom of the TiO$_2$ conduction band (Figure 2) and (5) have a convenient gap between the HOMO and the LUMO (taking into account that a wide gap will lead to a higher voltage but a lower current and vice-versa if the gap is narrower). One possible perspective would be to use block copolymers acting as HTM, the part of which chemisorbed onto the TiO$_2$ also acting as a dye (work in progress).

Nevertheless, the rest of this section focuses on the TiO$_2$ layer. The first prototypes were using TiO$_2$ nanoparticles (10–20 nm) in liquid suspensions and deposited by some simple processes such as the “doctor blade” technique. Sometime later, the dip-coating and the sol-gel techniques starting from a titanium alkoxide aqueous solution were combined to produce well-controlled TiO$_2$ layers made up of anatase nanocrystallites after thermal treatment. Nevertheless, these deposits were completely disorganized and of rather poor conductivity because of high contact resistance at the grain boundaries. This electrical resistance favored the electrons recombination leading to great loss of efficiency. An improvement was brought by combining the templating techniques to the previous ones (Figure 4): surfactant molecules were used to organize the TiO$_2$ layer and, therefore, to create higher conductivity channels inside the layer (Figure 5). However, this process was still not sufficient and the conductivity of the TiO$_2$ layer remained one of the main weak spots of DSSC.
Figure 4. Scheme of the dip-coating + sol-gel + templating technique.

Figure 5. TiO$_2$ layer constituted by nanocrystallites obtained by the dip-coating + sol-gel + templating technique (with kind permission of the GREENMAT-LCIS Department, ULg, Belgium).
The last step is currently to produce “one-dimensional” (1-D) crystallites in the form of TiO$_2$ nanotube array (TNA or TiO$_2$ – NTA) \[5\] (Figure 6). Such a structure combines good specific surface area and high conductivity. It can be obtained by anodization of metallic titanium in well-defined experimental conditions that are discussed later.

2.2. Techniques and recent developments

2.2.1. Overview

Anodization is the oxidation of a metal, forced by a potential difference willingly induced between an anode (the metal to oxidize) and a cathode (classically Pt), in an electrolytic bath. The positive potential set at the anode induces the metal oxidation, whereas the cathode reaction is water reduction that leads to hydrogen evolution.

Anodization can lead to either dense or porous structures, depending on the anodization conditions (especially the bath composition). Nanotubular structures are well-known for anodized aluminum oxide, but anodization also makes it possible to elaborate nanostructured layers of several metal oxides (WO$_3$, Fe$_x$O$_y$, ZrO$_2$, etc.) \[6\], including TiO$_2$. The obtained structure depends on numerous parameters such as applied potential, bath composition, temperature and anodization time. Therefore, a good knowledge of the impact of these parameters allows a precise morphological control of the anodized layer.

As explained before, nanotubular structures are of particular interest in various fields, including photovoltaics. To obtain those porous nanostructures, anodization has to be carried out in a medium with the ability to dissolve the formed oxide. For titanium, fluoride ions are the most efficient, forming a TiF$_6^{2-}$ complex. Initially, aqueous solutions of HF or fluoride salts were used, but because of the high reactivity of these compounds with TiO$_2$, only small nanotube lengths were achieved. Anodization in organic electrolytes has then been investigated to get longer nanotubes and smoother aspect of the layers. In this case, a small amount of water (at least 0.18% \[7\]) is added as a source of oxygen. Classical organic solvents such as glycerol, dimethyl sulfoxide or ethylene glycol have been used to produce nanotube layers of dozens (even hundreds) of micrometres on a Ti foil.

The formation mechanism of these nanotubes is quite well known and has been described on several occasions \[6, 8\]. Focusing on the electrochemical reactions, it can be summarized as follows: at the anode, the main reaction is the oxidation of titanium:

$$ Ti \rightarrow Ti^{4+} + 4 e^- \quad (1) $$

This oxidation leads to the formation of titanium dioxide, by a hydrated intermediate:

$$ Ti^{4+} + 4 OH^- \rightarrow Ti(OH)_4 \quad (2) $$
Equation (2) shows that titanium oxidation goes with a decreasing pH, which favours the formation of nanotubes by increasing the dissolution rate at the bottom of the tubes. It is worth noting the presence of a side reaction of oxygen evolution taking place at the anode, which can impact the quality of the structure (especially for the anodization of thin films, as shown below):

\[
2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4e^-
\]  

At the cathode, the reaction is water reduction, with hydrogen evolution:

\[
4 \text{H}^+ + 4 e^- \rightarrow 2 \text{H}_2
\]

And the overall equation is:

\[
\text{Ti} + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2 \text{H}_2
\]

To get a porous structure, a compound that can chemically dissolve the formed titanium dioxide is needed. This is achieved by fluoride ions forming a complex:

\[
\text{TiO}_2 + 6 \text{F}^- + 4 \text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2 \text{H}_2\text{O}
\]

It is the competition between reactions (3) and (7), that is, between the electrochemical formation of the oxide and its chemical dissolution by the fluorides that mostly determine the structure of the anodized layer. The anodized TiO_2 is generally amorphous, and this is detrimental to the charge transport properties of the nanotubular layer. Therefore, a thermal treatment around 450°C is commonly used to crystallize it into anatase (the most suited TiO_2 polymorph for photovoltaics).

### 2.2.2. Anodization parameters

The first important parameter to consider is the bath composition. As said previously, it mainly consists of an organic solvent with usually 1–5 wt% of water as a source of oxygen and 0.1–5 wt% of fluorides from NH₄F or HF.

The anodization process is mostly carried out in potentiostatic mode because the control of the morphological properties is easier than in galvanostatic mode [9]. The applied voltage has an important impact on the nanotube diameter. Several studies have shown a linear relationship...
between the tube diameter and the applied voltage in the 10 to 60 V range [10, 11], allowing to tune the nanotube diameter from approximately 20 nm (10 V) to 120 nm (60 V).

In organic electrolytes, the nanotube length increases with the anodization duration, as the chemical dissolution is much lower than the electrochemical growth of the tubes. Therefore, nanotubes of several hundreds of micrometres can be achieved on Ti foil by a very long anodization time [12]. However, very long nanotubes are not especially suited for photovoltaic applications because the electron diffusion length in dye-sensitized solar cells is commonly a few micrometres. Longer nanotubes only increases charge recombination and finally decreases the cell efficiency.

The anodization temperature is another key parameter in the anodization process. In the case of titanium anodization, most studies are carried out at room temperature (20–25°C). On the one hand, a higher temperature obviously increases the kinetics of the reactions (which means a higher growth rate), but this is not the only effect. It also favours water oxidation (side reaction) and an increase of the tube diameter, which is disadvantageous. On the other hand, a low temperature anodization provokes an important increase of the wall thickness of the nanotubes and, consequently, reduces the porosity of the structure (and hence the specific surface area). This is also undesirable as a high specific surface area is required for the dye to adsorb and get high efficiency DSSCs. The structures obtained at 5, 20 and 30°C are shown in Figure 6.

![Figure 6. TNAs obtained by anodization at 40 V in a bath at 5°C (top left), 20°C (top right) and 30°C (bottom).](image-url)
2.2.3. Anodizing a TiO$_2$ thin film

In order to get a transparent photoelectrode made of TNA on a conducting substrate, a Ti thin film is sputtered onto a FTO glass substrate. This film is then anodized to fully convert the dense titanium into titania nanotubes. The need for an adherent, homogeneous and dense film requires the use of magnetron (or sometimes rf) sputtering, since a simple evaporation leads to insufficient adherence and a delamination of the Ti film during anodization [13]. Some studies have pointed out that substrate preheating allows a better adherence of the film, therefore this kind of thin film is often deposited with a substrate preheated around 400°C [14, 15]. Another method is to apply a bias, so the growing Ti film is hit by more energetic ions [16]. Using these methods, several micrometres thick Ti layers can be obtained on FTO glass.

When anodization is performed on a thin Ti film on a transparent substrate to make a transparent electrode, the nanotube length is no longer linked to the anodization duration but to the thickness of the Ti film, as the anodization is carried out until the complete metal oxidation and hence the full transparency of the film are obtained. It is worth noting that the expansion factor (the ratio between the TNA film thickness and the initial Ti film thickness) varies from 1.3 to 2.5 approximately, depending on the anodization parameters (especially the applied voltage).

Another specificity of anodizing thin films on FTO glass is the role of the substrate. In this case, the anodization is carried out until the full oxidation of the Ti film is achieved, which means that there can be interactions between the electrolyte and the substrate at the end of the anodization process. The main problem is the side reaction of water oxidation (Equation (4)) taking place at the substrate–electrolyte interface, evolving oxygen. This reaction is known as a side reaction even on Ti foils but remains secondary compared with the oxidation of Ti. In this case, at the substrate–electrolyte interface, it is the only reaction and it can lead to a sufficiently intense bubbling to destruct the TNA film and provoke local delamination, even at low anodization potentials.

Knowing this side reaction is not a problem on Ti foils or on isolating substrates (such as conventional glass), there are mainly two ways to address the delamination problem. The first one is to stop anodization as soon as any contact between the substrate and the electrolyte is detected (bubbles appears), thus leaving a few nanometres of non-oxidized Ti that are oxidized during the thermal treatment of crystallization. The second is to prevent any contact between the FTO glass and the electrolyte by adding a compact underlayer of TiO$_2$ on which oxygen evolution is less favoured than on a highly conducting substrate such as FTO, but that is conducting enough to transport the electrons in the solar cell. Consequently, the thickness of that underlayer is chosen similar to the thickness of conventional blocking layers in DSSCs (50–100 nm). This compact underlayer is deposited by reactive sputtering just before the metallic Ti deposition, the transition between TiO$_2$ and Ti being triggered by switching off the oxygen admission in the vacuum chamber. The process of anodization of thin films with and without an underlayer is shown in Figure 7.
2.2.4. Impact of a TiO$_2$ underlayer

A first impact of sputtering a compact TiO$_2$ underlayer is a better adherence of the film, allowing to sputter the Ti without preheating the substrate. This is a significant gain of productivity, probably by ensuring a higher chemical affinity between the metallic Ti and the substrate. Another impact is on the regularity of the nanostructure. Indeed, from a microscopic point of view, the introduction of this underlayer has little impact on the nanotubes morphology. However, from a macroscopic point of view, it induces considerable improvements of homogeneity (reducing edge effects, for example). This is especially important for samples of larger size and as pointed out earlier, it prevents delamination, allowing a complete anodization at different applied potentials. SEM cross-sectional view of nanotubes on FTO glass with a TiO$_2$ underlayer is shown in Figure 8a and top views at different potentials of anodization (with tube diameters from 30 to 60 nm) are shown in Figure 8b, 8c and 8d.

![Diagram of Sputtering and Anodization](Figure7.png)

**Figure 7.** Schematized process to elaborate TNAs on conducting glass with and without underlayer.

![SEM views of TNAs](Figure8.png)

**Figure 8.** SEM views of TNAs: (top left) cross-sectional, (top right and bottom) top views at 20, 30 and 40 V, respectively.
Another important parameter for a photoelectrode is its transparency, as any absorption by the defects in the TiO$_2$ is parasitic and will not be converted in electricity (recombination). The transmittance of the photoelectrodes based on TNAs are shown in Figure 9 and compared with classical photoelectrodes with the same TiO$_2$ thickness (about 1 μm). If the transmittance of commercial nanoparticles is the highest (around 80% in average in the 450–850 nm range), it is worth noting the great difference between the TNA elaborated with and without an underlayer (73–75% and 63–68% in average, respectively). The lower transmittance observed without an underlayer indicates that the residual Ti left to avoid delamination at the end of the anodization process is not completely oxidized by the thermal treatment or it creates other absorbing defects. A complete oxidation by anodization is therefore encouraged, and this can only be done with an underlayer to prevent delamination. Moreover, this oxidation by the thermal treatment is known for creating a resistive layer under the nanotubes (especially on Ti foils). A complete anodization allows avoiding this resistive layer, and therefore an improvement in the electron transport properties can be observed for the samples with a TiO$_2$ underlayer.

Figure 9. Transmittance of the photoelectrodes based on TNAs.

3. TiO$_2$ for gas sensing

3.1. Overview and principles

TiO$_2$ is a member of the large family of the semiconducting metal oxides used for chemical gas sensors applications [17, 18]. The detection principle is based on the conductivity change of
those materials when they are in contact with certain gases. When a gas is adsorbed onto the surface, and if the interaction is strong enough (meaning chemisorption), an electron transfer between the semiconductor and the adsorbed species takes place resulting in an increase (decrease) of the charge carrier concentration in the semiconductor and as a consequence an increase (decrease) of the conductivity. As there is an equilibrium between the gas concentration in the atmosphere and the adsorbed quantity, a direct relation is expected between the conductivity change and the gas concentration. This phenomenon can be observed with organic or inorganic semiconductors.

The general scheme of such a sensor is presented in Figure 10.

**Figure 10.** Scheme of a semiconductor sensor.

The sensor acts just like a variable resistance and is often called chemoresistive sensor or chemoresistor.

As the detection principle deals with chemisorption and surface reactions with the gas, an activation energy is generally needed. Otherwise, the response to the gas and the recovery are too slow or even no response is observed. That is why a heating element is usually added on the substrate (very often in the form of a coil).

Historically, the effect of gases on semiconductors was discovered by Brattain and Bardeen. Already in 1953, they observed that Ge samples modified their resistance, depending on the atmosphere they were in contact with [19]. Later in the 1960s, Seiyama [20], using a zinc oxide (ZnO) thin film, was able to demonstrate that gas sensing is possible with simple electrical devices. He studied a simple chemoresistive device sensitive to propane based on ZnO thin films, operating at 485°C. Taguchi [21] fabricated and patented the first chemoresistive gas sensor device for practical applications using tin dioxide (SnO₂) as the sensitive material. This led to the foundation of the company Figaro Inc whose first main product was alarms for
explosive gases. This paved the way to intense researches to extend the principle to numerous applications of the semiconductor gas sensors.

Because of their simplicity, low cost, small size and ability to be integrated into electronic devices, chemical sensors have been the object of an extensive work as they have a big potential in all kinds of applications: industrial emission control, household security, vehicle emission control and environmental monitoring, agricultural, biomedical, and so on [22–27].

Although organic materials are potentially very attractive because they can be more easily modified than inorganic materials and thereby their performances “tailored”, they encountered considerably less success than the inorganic semiconductors, especially metal oxides. The main reasons are the bad long-term stability, and it is often impossible to use them at temperatures at which gas–solid interactions proceed rapidly and reversibly.

The detection mechanism for metal oxide is represented in Figure 11 [18–28].

Figure 11. Detection mechanism for metal oxide sensors.

Taking the example of an n-type semiconductor, in air, oxygen will be adsorbed at the surface of the oxide. An electron transfer occurs from the oxide to the oxygen leading to the formation of oxygen ions O$_2^-$, O$^-$ or O$^{2-}$. The nature of the ion depends on the temperature. The consequence is that the surface of the crystals is depleted, a potential barrier appears and the conductivity is decreased. Very often, the sensitive films are constituted of grains in contact
and the potential barrier will modulate the transfer of electrons between the grains and so the overall conductivity.

So for $n$-type semiconductors, the global conductance can be expressed as follows [29, 30]:

$$G = k \cdot \sigma_b \cdot \exp \left( \frac{-e \cdot V_s}{k_b \cdot T} \right)$$

with

- $G$, conductance of the sensitive layer;
- $k$, geometrical factor (including thickness of the sensitive layer, length, width of the electrodes);
- $\sigma_b$, bulk conductivity;
- $V_s$, potential at the surface.

This formula is established assuming the electron transfer limitation by the surface potential. Adsorption of the gases can modify this potential leading to conductivity changes. For instance, reduction of the oxygen pressure in the atmosphere means reduction of the adsorbed oxygen surface concentration leading to an increase of the conductivity.

In general, for $n$-type semiconductors, the contact with reducing gases (CO, H$_2$, CH$_4$, etc.) will increase the conductivity. Indeed, reducing gases can react with adsorbed oxygen, thereby releasing the trapped electrons that increase the charge carrier concentration. For oxidizing gases (NO$_2$, Cl$_2$, O$_3$, etc.), their adsorption will cause an increase of the barrier because of the trapping of electrons. For $p$-type semiconductors, the effects are opposite.

The nature of the oxide is a key factor for the choice of the sensitive layer for a given gas but the defects at the surface of the material play an important role as they are adsorption centres for gases. So the control of the surface is a major concern for gas sensing.

The most studied metal oxides for gas sensing as $n$-type semiconductors are SnO$_2$, ZnO, In$_2$O$_3$, WO$_3$ and TiO$_2$, whereas NiO, Cr$_2$O$_3$ and CuO are the most studied as $p$-type semiconductors.

The main drawbacks of these sensors remain the lack of selectivity because of the fact that the interaction between the semiconductor and the target gas is not always specific, and the need to heat the sensitive layer to rather high temperatures leading to increased power consumption. The current developments strive to reduce these drawbacks by studying a lot of other materials and by exploiting the opportunities provided by the new nanoscale technologies. Nanoscience, enabling controllable manipulation of matter at the molecular level, has become a precious tool for innovations in materials processing. A smaller size and so lower power consumption, greater sensitivity and better selectivity are expected. For instance, it is quite clear that grain-size reduction at nanometric scale can enhance the detection properties of metal oxides gas sensors.
Adding suitable promoters (metal particles, foreign metal oxide, ions, etc.) on the metal oxide layer is a common way of enhancing the sensing characteristics of metal oxide gas sensors [31, 32]. For instance, Pt promotes the gas-sensing reaction by the spill-over mechanism (massively exploited for heterogeneous catalysis). Pt clusters catalyse the dissociation of the gases, favouring the reactions with the adsorbed oxygen species. Figure 12 shows the mechanism with hydrogen. The result is an increase of the sensitivity to hydrogen and a lowering of the working temperature.

TiO$_2$ is particularly attractive for gas sensors because of its cross-sensitivity to humidity lower than other metal oxides [33]. Among the other applications, TiO$_2$ has been largely investigated as a sensing layer in resistive oxygen gas sensors operating at medium-high temperatures for automotive air/fuel ratio (A/F) control. The first titania gas sensors were developed in the late 1970s and early 1980s. The first application was the detection of the stoichiometric A/F ratio for engines [34]. Indeed, the sensor resistance was increased by orders of magnitude around the stoichiometric A/F, making it a very useful device for these applications. It was a competitor to the classical Lambda probe based on a solid state electrochemical cell.

Depending on the application of interest and availability of fabrication methods, different surface morphology and configurations of the metal oxides have been achieved, including single crystals, thin films, thick films and one dimensional (1-D) nanostructures [35–37]. Among all these, following the same trend as for photovoltaics, 1-D nanostructures have recently attracted much attention because of their potential applications in gas sensors [38]. 1-D nanostructures are particularly suited to this application because of their high surface-to-volume ratio as well as their good chemical and thermal stabilities [39, 40]. This chapter focuses on these materials and in particular, TiO$_2$. 

Figure 12. Spill over mechanism with hydrogen enhancing the oxidation rate.
3.2. Techniques and recent developments

The purpose is not to perform a comprehensive research survey in this chapter. There are already many excellent review articles on the topic of chemoresistive gas sensors [17, 41–45], but the aim is to give an overview of the use of nanostructured TiO$_2$ in the gas sensing field.

The development of fabrication methods for producing 1-D nanostructures has been the object of an intense research in the field of nanoscience and nanotechnology [37, 44, 46]. Several metal oxides such as ZnO, SnO$_2$, TiO$_2$, In$_2$O$_3$, WO$_3$, AgVO$_3$, CdO, MoO$_3$, CuO, TeO$_2$ and Fe$_2$O$_3$ have been investigated for gas sensing. However, according to our findings [47], 1-D structures are not always preferable for all gases. Several routes (chemical or physical) have been investigated for 1-D metal-oxide nanostructures for gas sensing applications. Arafat et al. [36] give a good summary of these routes. The most important ones are explained in this chapter focusing on TiO$_2$.

The sensor’s response to a given gas can be enhanced by the modification of both surface states and bulk properties of the 1-D metal-oxide nanostructures. These modifications can be achieved by either depositing nanoparticles on the nanostructure’s surface or coating and doping with impurities or even cover them with organic molecules [48, 49]. Sensors utilizing these types of surface and bulk property modifications showed higher sensitivity compared with unmodified systems. The functionalization can be performed in a second step after the synthesis of the 1-D structures or in one step during their formation.

Another trend is to use organized nanostructures as porous templates for the deposition of a sensitive material. This was done for instance with polypyrrole on TiO$_2$ for NH$_3$ detection [50] and was studied in our lab for the fabrication of molecularly imprinted polymers (MIP) based on polypyrrole electropolymerized in TiO$_2$ nanotubes for aldehydes detection.

3.3. Growth of TiO$_2$ nanostructures

The synthesis methods of 1-D TiO$_2$ nanostructures can be divided into two groups: solid-state etching and wet processing routes. The solid-state etching process includes nanocarving by H$_2$ gas, UV lithography and dry plasma etching [51, 52]. The wet processing route is, by far, more popular as it does not need complex equipment. The wet processing route includes hydrothermal synthesis, electrospinning and anodization.

Different surface morphologies such as nanotube arrays, branched nanotubes, coated nanotubes, nanoparticle added nanotubes, nanobelts, nanofibres and nanowires of TiO$_2$ can be obtained, depending on the synthesis method and the process parameters. Generally, the process ends with an annealing phase to define and stabilize the crystal structure. Depending on the starting materials and process conditions, the crystal structure of TiO$_2$ nanostructures varies from anatase, rutile and brookite to lepidocrocite.

The morphology of the nanostructures can be altered by combining two different processes. As an example, branched nanotubes can be obtained by the combination of anodization and hydrothermal processes [53].
As an example of wet processing route to obtain pure TiO$_2$, let us cite Rout et al. [54] describing TiO$_2$ nanowires obtained by hydrothermal process using TiCl$_3$ solution in HCl and saturated NaCl. The mixture was put in a Teflon-lined autoclave and heated at 200°C for 2 hours. After washing with water and alcohol and drying in vacuum, 1-D nanostructures with diameters of 20–80 nm and lengths of 100–800 nm were obtained. The crystal structure was found to be rutile.

A one-step functionalization and synthesis method of TiO$_2$ nanotubes by hydrothermal processing covered with Pd and Pt nanoparticles was detailed by Han et al. [48]. In this case, commercial anatase TiO$_2$ powder and PdCl$_2$ or H$_2$PtCl$_6$ were dispersed in an aqueous solution of NaOH and charged into a Teflon-lined autoclave at 150°C for 12 hours. The precipitates were separated by filtration, washed with dilute HCl and water and finally dried at 120°C, yielding Pd-Pt-TiO$_2$. The resulting nanotubes were 100 nm in diameter with a lepidocrocite-type phase.

A two-step method is illustrated by Hu et al. [55] with Ag clusters on TiO$_2$ nanobelts. The nanobelts were prepared via an alkaline hydrothermal process using commercial TiO$_2$ powders, NaOH, HCl and deionized water. The obtained H$_2$Ti$_3$O$_7$ nanobelts were annealed at 600°C for 1 hour to obtain crystalline TiO$_2$ nanobelts. The surface of the TiO$_2$ nanobelts was coarsened by adding H$_2$SO$_4$ into H$_2$Ti$_3$O$_7$ aqueous solution under magnetic stirring followed by heating at 100°C for 12 hours. The obtained phase of TiO$_2$ nanobelt was anatase. For the preparation of Ag nanoparticle-TiO$_2$ nanobelts, the as-prepared TiO$_2$ nanobelts obtained by hydrothermal route were dispersed into AgNO$_3$ and ethanol solution. Taking advantage of a photoreduction process, the solution was illuminated with a 20 W ultraviolet lamp under magnetic agitation.

Electrospinning was exploited by Landau et al. [56] to synthesize TiO$_2$ nanofibres. Biao et al. [49] describe a method to prepare Cu-doped TiO$_2$ nanofibres by electrospinning in one step.

A very elegant method that is used for both gas sensing and photovoltaics is anodization as described earlier (see Section 2.2).

Varghese et al. [57] used a platinum foil as a cathode and titanium foil as an anode at an anodization potential of 12 V and 20 V between the electrodes. The electrolyte consisted of 0.5% hydrofluoric acid in water. The samples were then annealed at 500°C in pure oxygen for 6 hours. The nanotubes were approximately 400 nm in length with a 46–76 nm diameter. A barrier layer with a thickness of 50 nm was formed in between the nanotubes and foil. Nanotubes fabricated using 20 V had an average pore diameter of 76 nm with a wall thickness of 27 nm, while samples anodized at 12 V had an average pore diameter of 46 nm with a wall thickness 17 nm. Anatase concentrated on the walls of the nanotubes and rutile in the barrier layer [58].

Lu et al. [59] also synthesized TiO$_2$ nanotube arrays by anodization of a titanium foil in a NH$_4$F and (NH$_4$)$_2$SO$_4$ aqueous solution. The titanium foil was used as an anode under a constant potential of 20 V (for 2 hours at room temperature) and the cathode was a platinum foil too. The as-prepared amorphous TiO$_2$ nanotube arrays were annealed at 450°C in air for 2 hours to obtain anatase phase. The resulting nanostructure had an outer and inner diameter of 150 nm and 110 nm, respectively, with length of approximately 2.3 μm. As usual, the
nanotube dimensions could be varied in the anodization process by changing both the pH of the electrolyte and the electrode voltage [60]. Paulose et al. [60] prepared nanotube arrays by anodization of titanium foils in an aqueous solution containing sodium hydrogen sulfate monohydrate, potassium fluoride and sodium citrate tribasic dihydrate. It was seen that the pore diameter depended on the anodization voltage, whereas the nanotube length depended on both the electrolyte pH and anodization voltage. Hu et al. [53] also synthesized TiO\textsubscript{2} nanotube arrays by the anodization approach. A titanium foil was cleaned by soap, acetone and isopropanol and used as an anode. The cathode was a platinum foil. The anodization solution contained NH\textsubscript{4}F and dimethyl sulfoxide. The anodization was conducted at a 45 V constant potential for 9 hours. The obtained amorphous TiO\textsubscript{2} nanotube arrays were annealed at 400°C for 1.5 hours. The resulting nanotubes were 350 nm in diameter and 3.5 μm in length with a wall thickness of 10 nm. The branched TiO\textsubscript{2} nanotubes were obtained through a modification process on TiO\textsubscript{2} nanotubes array by hydrothermal methods [53]. The as-prepared TiO\textsubscript{2} nanotube arrays were immersed in a solution containing HCl with constant stirring at 25°C for 15 minutes. Titanium (IV) isopropoxide was dropped into the solution under constant stirring for 1 hour, and then the beaker was sealed and heated at 95°C for 9 hours with slight stirring. After the reaction, the reactant was cooled to room temperature and washed with ethanol and distilled water. The as-prepared branched TiO\textsubscript{2} nanotube arrays were annealed in a muffle furnace at 400°C for 2 hours. It was observed that TiO\textsubscript{2} nanocrystal nucleus formed on the rough surfaces of the TiO\textsubscript{2} nanotubes with special bamboo structures with a larger and rougher surface area. Similarly, P25 (a commercial photocatalyst from Degussa, Germany) coated TiO\textsubscript{2} nanotube arrays were synthesized by the hydrothermal approach on the uncoated TiO\textsubscript{2} nanotube arrays [53]. In this process P25 was added to distilled water and then mixed vigorously by magnetic stirring and ultrasonicing, followed by transferring into a Teflon-lined autoclave. The treatment at 80–120°C for 12 hours was carried out to coat P25 on the TiO\textsubscript{2} nanotube arrays. After washing with distilled water, the P25 coated TiO\textsubscript{2} nanotube arrays were annealed at 400°C for 2 hours in air.

3.4. Sensing performance of TiO\textsubscript{2} 1-D nanostructures

The sensitivity of nanowire arrays on silica fabricated by Francioso et al. [52] according to a solid-state process was studied for ethanol sensing. It was seen that the sensitivity of the sensor (defined as the ratio $I_{\text{EtOH}}/I_{\text{air}}$) was approximately 50 at 550°C for 2% ethanol. Comparing these results with the response of TiO\textsubscript{2} thin film, the nanowire array showed higher sensitivity towards ethanol. The response is less than 10 in the case of TiO\textsubscript{2} thin film for the same concentration.

Gönüllü et al. [61] studied the impact of doping the surface of TiO\textsubscript{2} nanotubes. TNA for NO\textsubscript{2} detection at high temperature were obtained by anodization. They showed the cross-sensitivity with CO was almost cancelled after doping compared with pure TiO\textsubscript{2} nanotubes.

Hu et al. [55] synthesized four types of TiO\textsubscript{2} nanobelts (TiO\textsubscript{2} untreated nanobelts, TiO\textsubscript{2} surface-coarsened nanobelts, Ag nanoparticles-TiO\textsubscript{2} untreated nanobelts and Ag nanoparticles-TiO\textsubscript{2} surface-coarsened nanobelts) for the detection of ethanol vapour according to the above-
mentioned hydrothermal process. The best performance is obtained for Ag nanoparticles-TiO$_2$ surface-coarsened nanobelts. The response (defined as the ratio $R_{\text{gas}}/R_{\text{air}}$) was about 100 at 200°C for 500 ppm ethanol. The optimum working temperature was in the range of 200–250°C. The response and recovery for ethanol were very short (a few seconds).

Landau et al. [56] measured the sensitivity of TiO$_2$ nanofibres obtained by electrospinning towards NO$_2$ gas. These nanofibres showed a good sensitivity at low concentrations of CO and NO$_2$ in air. The sensor was more sensitive at 300°C than at 400°C (sensitivity to 250 ppb NO$_2$ (defined as the ratio $R_{\text{gas}}/R_{\text{air}}$) was 74.3 at 300°C and 3.3 at 400°C).

Biao et al. [49] compared the sensitivity of Cu-doped and undoped TiO$_2$ nanofibres also by electrospinning for CO detection. It was observed that Cu-doped TiO$_2$ nanofibres showed much higher sensitivity compared with pure TiO$_2$ nanofibres. The sensitivity of Cu-doped TiO$_2$ nanofibres was approximately 21, which is 17 times larger than pure TiO$_2$ at 300°C for 100 ppm CO (temperature of maximum sensitivity). The response and recovery times are 4 and 8 seconds, respectively. Moreover, the Cu-doped TiO$_2$ presented a higher selectivity towards CH$_4$, CH$_3$OH, C$_2$H$_5$OH, H$_2$ and NO.

Lu et al. [59] synthesized an amorphous TiO$_2$ nanotube array for the detection of O$_2$ using the anodization process. The sensitivity of amorphous TNA approximately increased with increasing temperature, but exhibited non-reproducible behaviour with a very poor recovery above 180°C. However, at 100°C, high sensitivity, excellent recovery and a linear relationship with oxygen concentration was observed. Other metal-oxide sensors such as Ga$_2$O$_3$ thin film (∼1.5) [62], nanoscale TiO$_2$ thick film (∼1.5) [63] and SrTiO$_3$ thick film (∼6.5) [64] showed lower responses towards oxygen at 100°C. Crystalline TiO$_2$ is highly advantageous for H$_2$, CO, NO$_2$ and CH$_4$ detection [65–67] but for oxygen, crystalline TiO$_2$ exhibits a very poor recovery [57, 59]. That is why, as for photovoltaics, TiO$_2$ is usually annealed in air or oxygen atmosphere at high temperature to form a crystalline structure more favourable for gas sensing.

TNA on Ti foil obtained by the anodization process described by Varghese et al. [57] were tested for H$_2$ sensing. They were able to detect H$_2$ at temperatures as low as 180°C. The sensitivity of TiO$_2$ nanotubes increased with increasing temperature showing a variation of three orders in magnitude of resistance to 0.1% of H$_2$ at 400°C. As always, the response time decreased with increasing temperature. At 290°C the response time was typically 3 min. The sensors showed high selectivity to H$_2$ compared with CO, CO$_2$ and NH$_3$. TiO$_2$ nanotubes with a smaller pore diameter (46 nm) had higher sensitivity than larger pore diameters (76 nm) towards H$_2$ gas. The high sensitivity of the nanotubes to H$_2$ was due to the highly active surface states on the nanotube walls, high surface area of the nanotube architecture and the ordered geometry of the tube-to-tube electrical connections. Han et al. [48] showed that Pt and Pd nanoparticles on TiO$_2$ nanotubes had a response almost twice that of pure TiO$_2$ nanoparticles or nanotubes. As usual, the sensitivity goes through a maximum at 25°C. The rate of reaction on the catalytic surface is probably the fastest at this temperature, resulting to a large change of conductivity. This also suggests that the higher response of Pt and Pd nanoparticle-TiO$_2$ is due to the higher number of adsorption sites or the catalytic surface area. Another possible reason for the enhanced response of Pt and Pd nanoparticle-TiO$_2$ nanotubes is due to increased
adsorption of hydrogen on the TiO$_2$ nanotube surface that facilitates the hydrogen oxidation reaction by the Pd and Pt catalysts.

Comparing the sensitivity of anatase and rutile nanostructures, it was stated that anatase shows high sensitivity towards reducing gases such as H$_2$ and CO [68–70]. The reason would be that the diffusing hydrogen atoms go to the interstitial sites [70, 71] and as the c/a (lattice parameters along c-axis and a-axis) ratio of anatase is almost four times that of rutile, anatase lattice accommodates hydrogen more easily and hence has a higher sensitivity to hydrogen.

3.5. TiO$_2$ used as a porous template

TiO$_2$ can also be used as a porous support for the deposition of an organic sensitive layer as described by Wang et al. [50] for the case of ammonia detection with polypyrrole. Polypyrrole (PPy) is a well-known organic semiconductor that was studied for gas detection, in particular NH$_3$ and VOC. The problem with PPy films is that they are rather non-porous leading to low surface-to-volume ratio and low sensitivity.

To increase this surface-to-volume ratio, Wang et al. [50] proposed to synthesize PPy on a very porous TiO$_2$/ZnO nanofibre network (diameter of the fibres ~100 nm). The nanofibres were obtained by electrospinning. The TiO$_2$/ZnO nanofibre network was dipped into a FeCl$_3$ alcoholic solution for 30 minutes. After drying, it was exposed to saturated pyrrole vapours at room temperature for 5 hours, resulting in a thin PPy covering the nanofibres. The obtained material showed a good sensitivity for NH$_3$ in the ppm concentration range although the response time was still long (15 minutes).

TiO$_2$ nanotube arrays can be used as a sacrificial template for the preparation of nanowires or nanotubes materials. This is inspired by the new trends in photovoltaic applications of TNA.

In the example detailed below, it was done with polypyrrole for formaldehyde detection. The sensitive polymer is a molecularly imprinted polymer (MIP) based on the polymerization of a mixture of pyrrole and polypyrrole-3-carboxylic acid. Formaldehyde, the target gas, is used as the template for the formation of the MIP. The formation of MIP films by electropolymerization is simple but leads to low porosity films that show a weak sensitivity to formaldehyde. To increase the specific surface area of the polypyrrole, it was synthesized by electrodeposition in an anodized TiO$_2$ matrix. After getting rid of the TNA by dissolution in NH$_4$F solution, porous polypyrrole is obtained with high specific surface area.

The anodization was performed on Ti foils cleaned with isopropanol and treated with 1M nitric acid for 30 minutes. The foil was used as the anode and a platinum electrode as the cathode in an electrochemical bath filled with 500 mL ethylene glycol, 10 mL water and 1.7 g NH$_4$F. A 40 V voltage is applied for 4 hours. After washing with water and drying, the foil is annealed in air at 475°C for 2 hours. Regularly spaced nanotubes with diameter 80–90 nm and wall thickness 7–9 nm were obtained (Figure 13).
Figure 13. TiO$_2$ nanotubes used for the synthesis of polypyrrole based MIP.

The obtained anodized Ti is then used as anode for the electrodeposition of the conducting polymer.

The electropolymerization is carried out as follows:

Working electrode: TNA

Counter electrode: Platinum

Reference electrode: Ag/AgCl

Composition of the bath: 50 mL acetonitrile | 0.614 g NaClO$_4$ | 0.17 g sodium dodecylsulfate (SDS) | 0.335 g pyrrole | 55 mg pyrrole-3 carboxylic acid | 10 mL formaldehyde solution (37% in water).

Deposition mode: pulsed 1000 cycles 2 V pulses for 0.1 second | −0.3 V for 0.04 seconds.

By so doing, the nanotubes are covered with the polymer, as shown in Figure 14.

Figure 14. Growth of the polymer in the TiO$_2$ nanotubes.

After dissolution of the TiO$_2$ matrix, the porous polymer is obtained (Figure 15).
Figure 15. Obtained sensitive polymer after removal of the TiO$_2$ matrix.

The crushed polymer is deposited by drop coating on a polyimide substrate fitted with interdigitated silver electrodes (electrode width 100 μm, spacing 100 μm, length 20 mm and 20 fingers).

Figure 16 shows the evolution of the resistance of the sensitive polymer after exposure to formaldehyde in humid air (60% at 22°C).

Figure 16. Evolution of the resistance of the porous MIP film when exposed to formaldehyde in humid air.

The same substrate fitted with a continuous film deposited by electropolymerization in the same conditions gives a response three times lower.

4. Conclusion

As can be seen in this chapter, the potentialities of TiO$_2$ and, in particular, the 1-D nanostructures are very attractive. Due to its unique combination of chemical, electronic and optical
properties, TiO₂ has become one of the major components in the third generation of solar cells and various possible variations (doping, hydrothermal synthesis, hybrid materials, etc.) expand the horizon. On the other hand, the applications of TiO₂ in gas detection are numerous and the interest for this material is growing. One can expect a lot of developments with TiO₂ as sensitive material for chemoresistors, leading to better performances in terms of sensitivity, selectivity and durability.

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