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TITANIA NANOSTRUCTURES PREPARATION FOR GAS SENSOR APPLICATIONS*

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ABSTRACT

The preparation and structural characterization of titanium oxide nanowires as functional materials for the development of chemical sensors is presented in this work. The new types of materials for sensorics, aspects of material preparation relevant for gas sensing applications is presented .The functional characterization is focused on the detection of alcohols. Titanium oxide thin films prepared by solvotermalthermal method in highly alkaline conditions and the performance of 1D nanostructure is compared with mesoporous thin film prepared by sol-gel method.

KEYWORDS: TiO_2, conductometric gas sensor, nanostructures, mesoporous materials

1. Introduction

Many fields of nanotechnology are based on physical and chemical interactions, involving nanoparticles of particular size and shape. In order to use the nanomaterials as sensors it is fundamental to understand the aspects involved in the synthesis and also in interaction mechanism during the sensing act. The ability to systematically manipulate the size and shape of metal oxide nanoparticles is a major scientific breakthrough in opening new ways for production of materials capable of sensing.

It has been known that the electrical resistance of the semiconductor material (like TiO_2, which is n-type) is sensitive to the presence of gases at elevated temperatures (200-600˚C). As an example, reducing gases (CO, H_2, CH_4, etc.) lead to an increase of the conductivity, whereas the effect of oxidizing gases (O_3, etc.) is vice versa.

The model most frequently mentioned in the literature is based on the fact that oxygen atoms absorbed or adsorbed at the surface form negative ions resulting in a decrease in the surface conductivity. Three different types of ionic species have been observed on the surface in addition to adsorbed O_2 molecules: O_2^-, O^-, and O^{2-}, which are desorbed at characteristic temperatures [1]. The presence of a reactive gas (oxidant or reducer) in the atmosphere, its adsorption at the surface and its reaction with the oxygen atoms will result in a decrease or an increase in surface electrons and, hence, in the conductivity. Typically, the value measured is the resistance of the semiconductors, *Rs:*

$$R_S = KC_S^{-\alpha} \qquad (1)$$

where C_s is the concentration of gas in air, *K* the sensitivity coefficient, and α is the dimensional power exponent between 0 and 1. In most cases however, the value given is the sensitivity value, that is, the ability of a sensor to detect a given concentration of a test gas (analyte), is usually estimated as the ratio of the metal oxide electrical resistance (conductivity) ($S = R_{gas}/R_{air}$, or R_{air}/R_{gas}) measured in air and in an atmosphere containing the target gas.

A typical sensor element (Fig. 1) comprises the following parts:

- *Sensitive layer* deposited over a
- *Substrate* (glass, Si, SiO_2, ceramics) provided

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- *Electrodes* (Pt, Pd, Au, etc.) for the measurement of the electrical characteristics. The device is generally heated by its own
- *Heater*; this one is separated from the *sensing layer* and the *electrodes* by an electrical insulating layer [2].

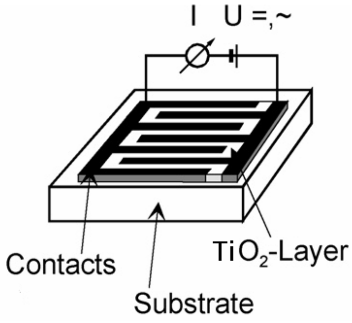

Fig. 1. *Representation of a sensor element.*

Conductometric (resistive) metal oxide sensors comprise a significant part of the gas sensor component market. While many different approaches to gas detection are available, metal oxide sensors remain a widely used choice for a range of gas species. These devices offer low cost, high sensitivity, fast response and relative simplicity. Also, these sensors possessed a number of unwanted characteristics, such as high cross-sensitivity, sensitivity to humidity and long-term drift. In order to improve their performance a series of various metal-oxide semiconductors have been tested such as: SnO_2, ZnO, TiO_2, WO_3 etc.

It was settled that the sensor characteristics can be changed by varying the crystal structure, dopants, preparation technology, operation temperature, etc. Nonetheless, highly specific metal-oxide sensors were still not available. In recent years, the interest of researchers to gas-sensitive materials has grown substantially due to the progress in nanotechnology. This interest is primarily related to the promising electronic properties of nanomaterials, their size dependence and ability to control the material structure by new experimental techniques. More and more materials and devices are produced every year with the use of nanotechnology. This paper discusses several synthetic strategies for preparation of nanostructured materials for gas sensor applications.

2. Nanostructured materials obtained used for new generation sensors

Up to now a large number of publications reported the capability of nanosized TiO_2 to detect gas molecules of organic compounds (alcohol, methanol, n-propanol, acetone, benzene) [3-6], oxidants (NO_2, CO, O_2) [7–10], and reductants (H_2, NH_3) [11–13] have been reported for nanosized TiO_2.

The metal oxide film can take a number of forms, generally determined by the deposition method.

Films deposited using chemical vapor deposition or sputtering tend to be thin and compact. Films deposited by casting of sol–gels and colloidal dispersions, tend to be thicker and porous with nanostuctured features.

2.1. Porous nanostructured materials obtained by sol–gel methods

Sol-gel processing is a low temperature, high versatile synthesis route that is particularly suitable for the deposition of thin nanostructured films from a liquid phase. It is efficacious way to control the dimensions of the grains. By reducing the particles sizes, the conduction of the sample may be controlled either by the grain boundaries, necks, or by the grains. The latter case is the most desirable, since it allows achieving the highest resistance change.

In the synthesis, the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides, undergo hydrolyze followed by condensation and polymerization reactions. Complete polymerization and loss of solvent leads to a solid gel phase [14]. In case of titania, as precursors can also be used titanium halides.

Several factors are known to affect the hydrolysis reaction:

(a) the nature of the precursor;
(b) the nature of the solvent;
(c) the concentration of each species in the solvent;
(d) the temperature;
(e) the water to precursor molar ratio;
(f) the presence of acid or base catalysts.

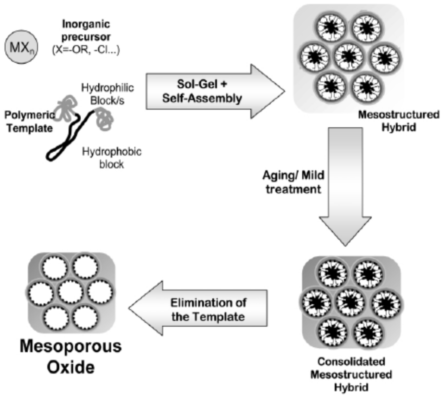

Fig. 2. *Schematic view of the steps leading from a solution to a mesoporous oxide network [21].*

The properties of sol-gel materials can be enhanced by increasing their surface area by making them porous materials. In such material the volume of the layer is accessible to the gases and therefore the active surface is much higher than the geometric area and the sensor response is higher. Thus, mesoporous TiO_2, fabricated using a self-assembly of a surfactant (Fig. 2) exhibit higher sensor performance than corresponding metal-oxide materials, having lower specific surface area.

Depending on the required pore size, block copolymers, latex spheres, water-in-oil emulsions, polystyrene particles, colloidal crystals, and bioskeletons have been used as templates [15-18]. The most commonly used organic templates were amphiphilic poly (alkylene oxide) block copolymers, such as $HO(CH_2CH_2O)_{20}$-$(CH_2CH(CH_3)O)_{70}$ $(CH_2CH_2O)_{20}H$ (called Pluronic P-123) and $HO(CH_2CH_2O)_{106}(CH_2CH(CH_3)O)_{70}$-$(CH_2CH_2O)_{106}H$ (called Pluronic F-127). Carbon nanotubes [19] and mesoporous SBA-15 [20] have also been used as the skeleton for mesoporous TiO_2. A disadvantage of using a template is that the dominant length scale of the resulting porous structure is fixed by the template size.

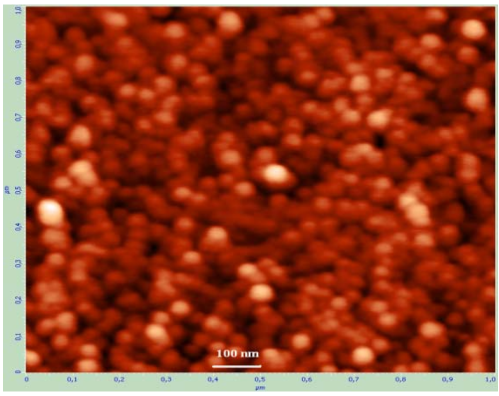

Fig. 3. *AFM image of TiO_2 thin mesoporous film [25].*

Recently, Sanchez and co-workers showed the formation of highly organized mesoporous titania thin films [21-24]. Our group obtained TiO_2 mesoporous thin film (Fig. 3) with average roughness 0.9969 nm, grains 27-40 nm, and average pores’ diameter 17 nm [25].

M.M. Yusuf and coworkers [26] prepared a porous anatase film by the surfactant-templeting method having the porosity of about 64% and grain size of 30 nm. The grains are columnar as a result of surfactant micelles shape before annealing process.

Yu et al. prepared three-dimensional and thermally stable mesoporous TiO_2 without the use of any surfactants [27]. Briefly, monodispersed TiO_2 nanoparticles were formed initially by ultrasound-assisted hydrolysis of acetic acid modified titanium isopropoxide. Mesoporous spherical or globular particles were then produced by controlled condensation and agglomeration of these sol nanoparticles under high-intensity ultrasound radiation.

The mesoporous TiO_2 had a wormhole-like structure consisting of TiO_2 nanoparticles and a lack of long-range order [27].

2.2. Porous doped nanostructured materials

The application of nanotechnology in preparation of gas sensors is not limited by production of nanostructured semiconducting thin films only. It is known that by dispersing a low concentration of metallic nanoparticles (such as Pd, Pt, Nb, La, Cu, W, Cr, Sn, etc.) on the TiO_2 grains, the sensitivity and selectivity can be improved [28-33]. Carney et al. found that sensors based on SnO_2-TiO_2 with higher surface areas were more sensitive to H_2 [34]. Devi et al. found that ordered mesoporous TiO_2 exhibited higher H_2 and CO sensitivities than sensors made from common TiO_2 powders due to increased surface area, and the sensitivity could be further improved by loading the sensor with 0.5 mol % Nb2O5 [35].It has been observed that TiO_2 doped with Nb and Pt sensors have a good performance in detecting ethanol vapor [36-40], while Cu- or Co- doped TiO_2 nanoparticles were good candidates for CO sensing [41].

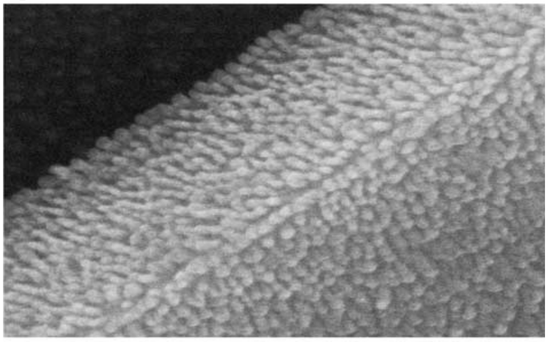

Fig. 4. *SEM image of TiO_2 film [26].*

Also, one of the most popular nanomaterials nowadays, carbon nanotube (CNT), was used as dopant to improve the gas detection. It was found that CNTs can be added to TiO_2 substrate to form alcohols-sensitive material. The doping increases the sensitivity in comparison with pure TiO_2 sensor. Hybrid SWCNTs/Nb-Pt co-doped TiO_2 thin films were prepared by the sol–gel spin-coating process [42]. The SWCNTs were well embedded in the TiO_2 matrix and did not affect the morphology of the TiO_2 thin film and the particle size. Experimental results revealed that the responses to ethanol of Nb–Pt co-doped TiO_2 sensors with SWNCTs inclusion increase by factors of 2–5, compared to that of the sensor without SWCNTs. Moreover, all hybrid sensors can operate with high sensitivity and stability at relatively low operating temperature (<335 ˚C).

Titania (usually in the rutile phase) is widely used bulk conductivity sensors for oxygen [43-44]. The detection mechanism implies the diffusion of oxygen ions in the bulk of the material, at high temperatures (700–1000 ˚C).

For anatase titania, oxygen detection can be associated to a surface reaction, which takes place at lower temperatures (400–500 ˚C). Llobet et al. [45] achieved at significantly lower operating temperature (350 ˚C), a response more than four times higher than the one found for titania not containing carbon nanotubes.

Pt addition in TiO_2 promoted the structural transformation of the starting anatase phase to rutile, with a more enhanced effect with increasing the Pt concentration. H_2 gas-sensing tests evidenced that the anatase phase was much more sensitive than the rutile one. The presence of Pt further enhanced the gas-sensing properties, lowering the optimum sensor operation temperature to about 330 ˚C [46].

In our work [25] we obtained an Nb doped TiO_2 mesoporous thin film with average roughness of 0,594704 nm, grain size: 19-26 nm and pore diameter: 16 nm (Fig. 5).

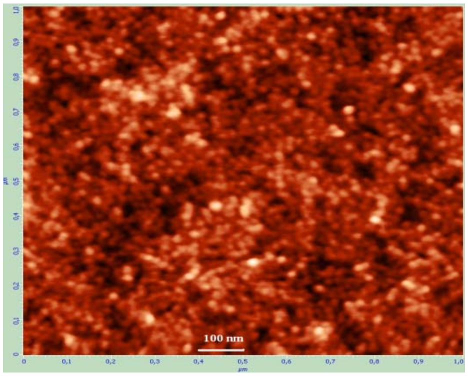

Fig. 5. *Nb (1wt.%)-TiO_2 mesoporous thin film [25].*

2.3. 1D nanostructured materials for new generation of gas-sensors

Nowadays, most of the commercial metal-oxide gas sensors are manufactured using the screen-printing method on small and thin ceramic substrates. The power consumption of this kind of sensor can be as high as 1 W, which makes it impossible to use in battery-driven devices. Also they face problems with thermal isolation between sensor element and housing. These shortcomings promote the development of substrate technology and strong research in sensitive layer preparation. Concerning the substrate issue, one way to solve it is the integration of sensing layer in standard microelectronic processing.

At present, the efforts are focused on the sensing layer. This layer can be compact or porous, depending on the preparation technique used. Typically, porous layers possess higher active surface than the geometric one. The most common sensor preparation techniques are presented in Table 1.

Table 1. *Deposition techniques used for the preparation of metal oxides [49]*

Paste/slurry deposition	CVD	PVD	
		Sputtering	Evaporation
Screen-printing	Thermal	Sputtering	Molecular beam epitaxy
Drop deposition	Plasma activated	Reactive sputtering	Thermal evaporation
Dip coating	Laser induced	Cathode sputtering	Reactive evaporation
Spray deposition	Electroless plating	With bias voltage	Ion plating
			Reactive ion plating
			Arc evaporation
			Laser evaporation

Nanotechnology provided the new tools to control the microstructure of sensitive layer, allowing to obtain materials with narrow grain size distribution, this meaning a greater stability in time. The studies of thin films of TiO_2 have shown the strong increase of sensitivity with the reduction of the oxide particle size to nanometer scale. Systematic analysis of grain size dependence of TiO_2 sensitivity was reported in literature. [47-48]

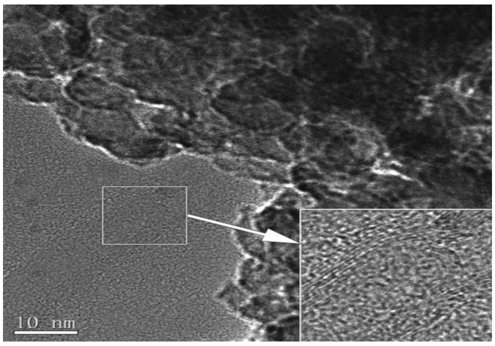

Fig. 6. *Nb (3wt.%), CNT(0.002wt.%) -codoped TiO_2 [45].*

New promising methods are based on deposition of metal on a substrate followed by oxidation. Controlling the oxidation parameters the stoichiometry of the oxide can be varied. After annealing, the particles can be oxidized (totally or partly) to form the highly porous sensitive layer.

Among these techniques there are Rheotaxial Growth and Thermal Oxidation (RGTO), Low Temperature Physical Vapor Deposition (LTPVD) and sputtering-oxidation method.

Other methods, based on modified sol–gel, solvothermal method and CVD techniques are also used to improve the gas sensor performance of nanostructured metal-oxide materials.

2.3.1. One-dimensional metal oxide structures

Semiconducting one-dimension metal oxide structures with well defined geometry and perfect crystallinity represent a material family for systematic experimental study and theoretical understanding of the gas-sensing mechanisms in semiconducting metal oxides. In analyzing the opportunities of one-dimensional structures of various types for their practical application in gas sensors, nano-belts (nano-ribbons) probably could be the most promising one-dimensional structure to exploit for gas-sensing applications. Nano-belts are thin and plain belt-type structures with rectangular cross-section. At present, nano-belts have been obtained for nearly all oxides used in gas sensors. There is considerable data pertaining to the synthesis of nano-belts for SnO_2, TiO_2, In_2O_3, ZnO, Ga_2O_3, etc.. Typical nano-belts have widths of 20–300 nm, and lengths from several mm to hundreds, or even some thousands of mm.

The typical width-to-thickness ratio for nano-belts ranges from 5 to 10 and for nanowires (or nanorods) this ratio equals 2–5. Synthesis of 1D nanostructures could be done through various methods. Nano-belts, for example, have structural homogeneity and crystallographic perfection. It is well known that crystallographic defects may destroy quantum-size effects. It is necessary to emphasize that that suitable geometry (see Fig. 7), high homogeneity of the structure, and long length are important advantages of nano-belts for mass manufacturing of gas sensors.

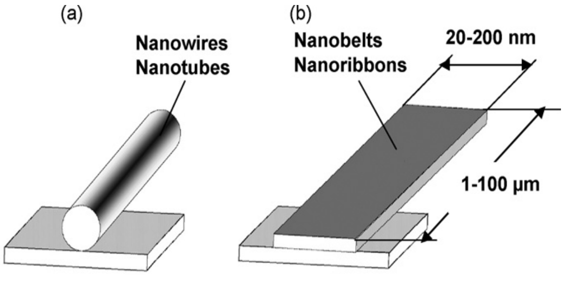

Fig. 7. *Nanowires (a) and nano-belts (b) position on bonding pad and typical sizes of nano-belts used in gas sensor design.*

It is necessary to note that many parameters used for characterizing polycrystalline materials aimed for gas sensor design lose meaning for one-dimensional structures, because they are single crystalline materials.

These parameters include the following: film thickness, porosity, grain size, grain network, grain boundary, agglomeration, and texturing, i.e. all the parameters that it is considered to influence the metal oxide sensor response. The main structural and morphologic parameters that characterize one-dimensional structures would become geometric sizes, characterizing the profile of one-dimensional structures, and crystallographic planes, framing these one-dimensional structures. At that, the minimal distance between faceting planes in one-dimensional structures would play in gas-sensing effects the same role as grain size plays in polycrystalline material. It should be noted that one-dimensional structures have better crystallinity (i.e. less concentration of point defects), and thus possibly a lower concentration of free charge carriers, in comparison with polycrystalline materials. On the other hand, in one-dimensional gas sensors the role of contacts increases because of their small area and therefore greater specific resistance.

With regard to the sensors on the base of nanowire arrays, there are the same regulations for them as for the ones on the base of the usual nanoparticle films. Impedance spectroscopy studies have showed that the gas-sensing mechanism for sensors on the base of networked nanowire thin films involves changes in both the nanowire and the inter-nanowire boundary resistances [49].

For gas sensor design the thin films, containing nanowires in a highly networked fashion, are promising. A study, carried in [49] has shown that the sensors on the base of those films had a behavior, similar to that of single nanowire devices without much post-processing effort. According to Ref. [50] this is possible only when the individual nanowires within the gas-sensing matrix are bonded to each other and form two- and three-dimensional networks of nanowires.

Solvothermal method involves a reaction of a hot solution within or on the surface of a substance, proceeds in a sealed pressure vessel (autoclave) at temperatures above the boiling point of the solvent.

Fig. 8. *The general scheme for 1D TiO_2 nanostructures synthesis.*

Solvothermal synthesis is a ‘‘soft solution chemical processing’’ which provides an easy route to prepare a well crystalline oxide under the moderate reaction condition, i.e. low temperature and short reaction time (Fig. 8).

When the solvent is water, the method is called hydrothermal. The solvothermal method normally has better control than hydrothermal methods of the size and shape distributions and the crystallinity of the TiO_2 nanoparticles.

The hydrothermal method has been widely used to prepare TiO_2 nanotubes since it was introduced by Kasuga et al. [51] in 1998, also is very simple and inexpensive. Over the years, they carried out many research on 1D titania, for example supported nanowires [52]. Grimes et al. conducted a series of excellent studies on sensing using TiO_2 nanotubes [53-58]. They found that TiO_2 nanotubes were excellent room-temperature hydrogen sensors not only with a high sensitivity but also with ability to self-clean photo actively after environmental contamination.

Many other groups have synthesized and investigated the properties of 1D TiO_2 nanomaterials for different applications [59-63]. Lee and coworkers [59] developed a low temperature synthesis of TiO_2 nanowires directly synthesized on fluorine-doped tin oxide ($F:SnO_2$ or FTO)-coated soda-lime glass substrates (Fig.9). They use successfully these nanowires in photovoltaic cells.

Figure 10 shows rutile nanorods obtained through a combined sol-gel and solvothermal method. C. Su and co.[60] demonstrated that these particles have a good photocatalytic activity and , modifying the synthesis parameters can be obtained particles with different shapes and properties.

The solvothermal method can be associated with different techniques. Porous single-crystalline TiO_2 nanorods have been prepared though a solution aggregation-based growth process followed by the calcination treatment.

The morphology of the resulting nanorods can be tuned with different surfactants [64] or by changing the solvent compositions [65]. TiO_2 nanorods with narrow size distributions can also be developed with the solvothermal method. For example, in a typical synthesis from Kim et al. [66], TTIP was dissolved in anhydrous toluene with OA as a surfactant and kept at 250℃ for 20 h in an autoclave without stirring.

Long dumbbell-shaped nanorods were formed when a sufficient amount of TTIP or surfactant was added to the solution, due to the oriented growth of particles along the [001] axis.

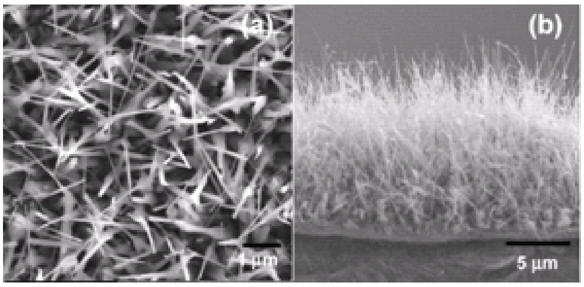

Fig. 9. *Images of TiO_2 nanowires (a) (top view) and (b) cross-sectional SEM [52].*

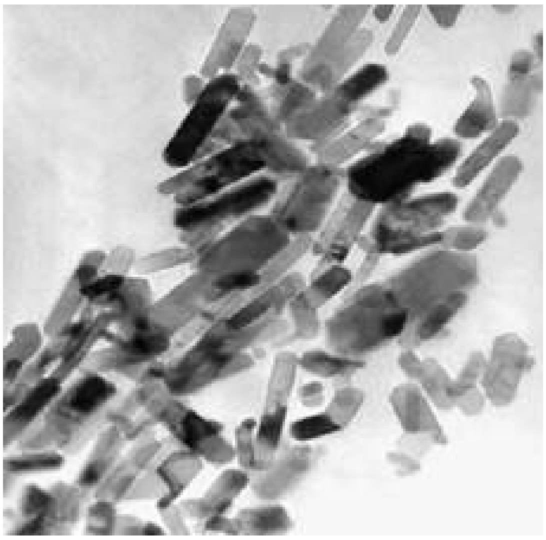

Fig. 10. *The TEM micrographs of TiO_2 nanorods [60].*

The average particle size was smaller and the size distribution was narrower than is the case for particles synthesized without surfactant.

The crystalline phase, diameter, and length of these nanorods are largely influenced by the precursor/surfactant/solvent weight ratio.

The diameter and length of these nanorods were in the ranges of 3-5 nm and 18-25 nm, respectively.

Concerning the 3D → 2D → 1D formation mechanism various hypotheses have been proposed. In case of TiO_2 nanotubes, Wang and co-workers [67] stated that the raw TiO_2 was first transformed into lamellar structures and then bent and rolled to form the nanotubes and the two-dimensional lamellar TiO_2 was essential.

Also, the doping of 1D nanostructures with ions was used to improve their sensitivity. Proton-exchange was carried out by suspending the TiO_2 nanotubes (Fig. 11) [68] in the corresponding aqueous solutions of the metal (Cu^{2+}, Co^{2+} and Ca^{2+}) nitrate or chloride at room temperature].

The exchange reactions were demonstrated to be an option for chemically modifying TiO_2 nanotubes. Additionally, the analysis of the products of thermal decomposition allowed to get information about the composition and structure of the nanotubes.

Despite the fact that the doping technique has been used for a long time in commercial and industrial sensors, the working principle of additive-modified metal-oxide materials is still not well understood.

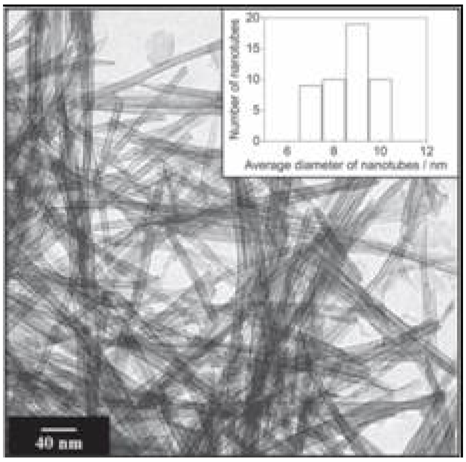

Fig. 11. *TEM image of titanium oxide nanotubes. The inset is a distribution of the average external diameter [68].*

In the chemical scheme the reaction takes place at the oxide surface. The role of the additive nanoparticles is considered within a spillover process, increasing the metal-oxide surface coverage of the gas involved in the sensing scheme. In the electronic mechanism the reaction involves the additive atoms and the oxide material has to transduce the electrochemical changes into a detectable output signal. Moreover, the introduction of additives can create new donor or acceptor levels, or influence the grain size and growth mechanism.

3. Conclusions and future prospects

The optimization of the structural parameters of metal oxides, such as grain size, porosity, texture, faceting, grain network, etc., is an important factor for improving gas-sensing characteristics of conductometric type sensors. For example, it was shown that grain size and porosity control are the best ways for the improvement of metal oxide sensor response to oxidizing gases.

For reducing gas detection the requirements are more ambiguous and depend on both the sensor material and the nature of the detected gas.

Nanotechnology is very promising for the preparation of clean, structurally pure perfectly ordered materials for the new gas sensors generation. Beside this, it helps researchers to understand the sensing mechanism at atomistic level, which undoubtedly will promote fast progress in this field.

New nanomaterials that appear today, such as highly ordered arrays of metal/semiconductor core–shell nanoparticles, may be soon used in gas sensor applications. At the same time, the creation of new materials for gas sensor applications is necessary to solve a number of basic problems of nanochemistry. Among them we consider the following ones as the most important:

a) Management of the size, structure and stability of metal, semiconductor and hybrid nanomaterials by controlled conditions of synthesis, in particular, with the use of low temperature synthesis.

b) Understanding of kinetics and thermodynamics of self organization processes, which take place at the surface of nanoparticles, and extension of the working temperature interval.

c) Determination of the influence of shape of nanoparticles, particularly for nanowires and nanotubes of different materials, on their chemiresistive properties.

The solution of these tasks in combination with the search of new nanosystems will allow the preparation of new sensor materials. The nanotechnology opens the new possibilities for the production of gas-sensitive materials of new types and also allows controlling the structure of conventional semiconducting metal-oxide materials on nanoscale level.

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