Films of brookite TiO_2 nanorods/nanoparticles deposited by MAPLE as NO_2 gas sensors

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The ability to reveal trace amount of NO_2 is of primary importance for detecting explosives, such as EGDN, TNT, PETN, RDX, at concentrations on the order of 50 ppm and 30 ppb, while the detection limit for TNT and nitroglycerin should reach as low as 1 ppm and 1 ppb, respectively. Oxide semiconductors are well recognized materials to be used as resistive gas sensors, as they exhibit resistance variations induced by the presence of ambient gases. However, in order to increase the sensitivity and the selectivity of sensors, new active materials and structuring strategies are requested. This is why innovative sensors based on nanoparticles, nanorods and nanotubes are being extensively studied. The matrix-assisted pulsed laser evaporation (MAPLE) is a laser-based technique that has recently been developed for the deposition of organic and biological materials. Moreover, it is very promising for the deposition of colloidal nanoparticles to fabricate thin active films for sensing applications. In the MAPLE technique the material of interest (polymer, biological material or colloidal nanoparticles/nanorods) is diluted/suspended in a volatile solvent, at a concentration of up to a few weight percents, and frozen at the liquid nitrogen temperature, forming the target to be laser-irradiated. The laser radiation is mainly absorbed by the solvent, which vaporizes entangling the solute particles and promotes their deposition on suitable substrates. The MAPLE technique, as a derivative of the pulsed laser deposition (PLD) method, can successfully be used for the deposition of materials onto plastic and other thermolable substrates, as well as on rough and flexible supports at room temperature.

Size-tunable brookite (orthorhombic) TiO_2 nanorods, covered with an oleate/oleyl amine capping layer, were synthesized by a colloidal nonhydrolytic sol-gel route based on surfactant-assisted aminolysis of titanium oleate complexes at 280 C under air-free conditions. After the synthesis and the extraction/purification procedures, the nanocrystals were suspended in toluene at a concentration of 0.016 wt %. The solution was first treated in an ultrasonic bath for 10 minutes to prevent aggregation, after which it was frozen at the liquid nitrogen temperature and mounted into a vacuum chamber on a target holder, while being cooled with liquid nitrogen to maintain a low and constant temperature (-160 C). The vacuum chamber was evacuated down to 5×10^{-4} Pa. The frozen solution was then irradiated with a KrF (λ=248 nm, τ=20 ns) excimer laser at the repetition rate of 10 Hz. The laser beam was attenuated and focused (with a rectangular spot of 0.075 cm^2) to obtain an energy density of 350 mJ/cm^2 on the target. The target was placed in front of the substrate at a distance of 40 mm and rotated at the frequency of 3 Hz to allow uniform erosion. 6000 laser pulses were used to deposit a single film. The films were deposited on $< 100 >$ Si substrates, silica slabs and carbon coated Cu grids to perform the different characterizations. Films very adherent to their substrates were deposited, as demonstrated by scotch tests. The morphological and structural properties of the nanostructured films were investigated by scanning (SEM) and transmission (TEM) electron microscopy. UV-Vis transmittance and reflectance spectra of films deposited on silica substrates were recorded at room temperature by a spectrophotometer equipped with an integrating sphere.

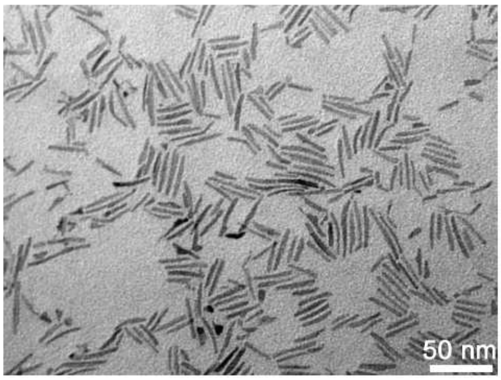

Figure 1. Representative BF TEM image of the TiO_2 nanorods.

The TiO_2 nanorod layer to be used as a sensor was deposited onto an Al_2O_3 substrate equipped

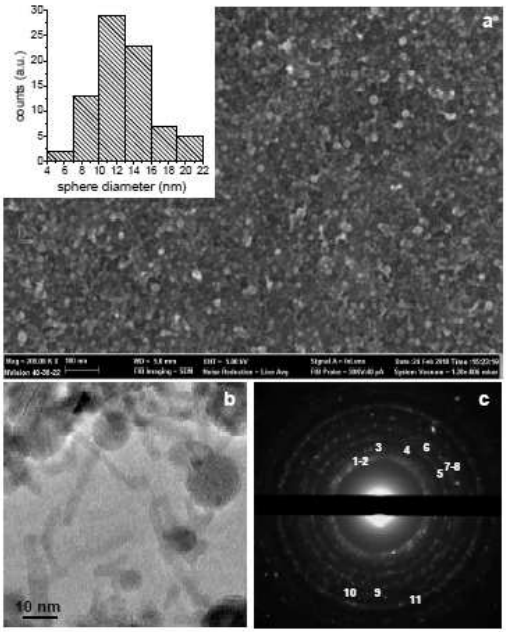

Figure 2. High-resolution SEM image of the nanostructured TiO_2 film deposited onto a Si substrate (a) along with the histogram of the diameter distribution of the spherical structures in the film (inset). BF TEM image (b) and SAED pattern (c) of the film deposited on carbon-coated Cu grids.

Exp. data					Theor. data
				Broockite	Rutile
label	d(A)	d(A)	hkl	d	hkl
1	3.54	3.50	210		
2	3.28			3.25	110
3	2.86	2.89	211		
4	2.68	2.72	020		
5	2.47	2.47	102	2.49	101
6	2.30	2.29	400	2.30	200
7	2.16	2.13	221		
8	2.07	2.07	212	2.05	210
9	1.87	1.89	321		
		1.85	312		
10	1.78	1.75	420		
11	1.67	1.68	230	1.69	211

Table 1
Experimental and theoretical lattice spacings corresponding to the diffraction rings in the SAED pattern of fig. 2 (c)

with Pt interdigitated contacts and a Pt heater on the backside. A total flow of 100 sccm was fixed during the measurements. We have exploited anisotropic brookite TiO_2 nanocrystals as building blocks for thin films suitable for gas-sensing purposes. A representative BF TEM image of brookite TiO_2 nanorods used by us is shown in Fig. 1. The diameter and length dimensions are in 3 - 4 nm × 20 - 50 nm intervals. A high-resolution SEM image of a typical TiO_2 MAPLE-deposited film onto a Si substrate starting from a toluene solution of TiO_2 nanorods is presented in Fig. 2a. The image evidences the simultaneous presence of rod-like and spherical nanostructures. The spherical structures have an average diameter of 134 nm, with a broad size distribution, as shown in the inset of Fig. 2a. Examples of nanorods and spheres are more clearly visible at higher magnification in the TEM image of Fig. 2b, which displays an area of TiO_2 films deposited by MAPLE onto the carbon film of a TEM grid. They have an average length of about 25 nm and a diameter of 3 nm. The SAED pattern demonstrates a prevalence of the brookite phase (Fig. 2c). Nevertheless, the presence of rutile phase can also be admitted due to the presence of a diffraction maximum, corresponding to a lattice spacing of 0.325 nm, which is not compatible with the brookite phase.

Table 1 reports the indexing of the diffraction pattern and compares the experimental interplanar spacings with the theoretical values belonging to the rutile and brookite phases. the average volume of the nano-spheres is approximately double with respect to that of the nanorods. The unexpected observation of TiO_2 spheres suggests occurrence of a laser-induced process, which induces a melting/coalescence of the nanorods, driving their transformation into most thermodynamically stable spherical shapes. A decrease of the actual melting temperature has been already reported for low-dimensional solids, compared to their corresponding bulk materials. Therefore, although the laser fluence used in this work was quite low (350 mJ/cm^2) and the fusion temperature of bulk TiO_2 is very high (1850^o C), lower thermal loss rates could be associated with the nanorods due to their nanometer-scale dimensions, which could in turn cause them to increase in temperature. Such combined effects can reliably explain the observed modification of the TiO_2 nanorod morphology in terms of laser-induced heating effects.

The total transmittance and the specular reflectance UV-Vis spectra of the MAPLE-deposited films are shown in Fig. 3. High optical transparency can be noted over a wide wavelength range (300 nm- 1500 nm). The visible interference effects are due to the small film thickness (150 nm). The steep profile of the transmittance spectrum with a sharp cut off at around 350 nm (3.5 eV) suggests a quite high value of the band gap for TiO_2 in agreement with theoretical and ex-

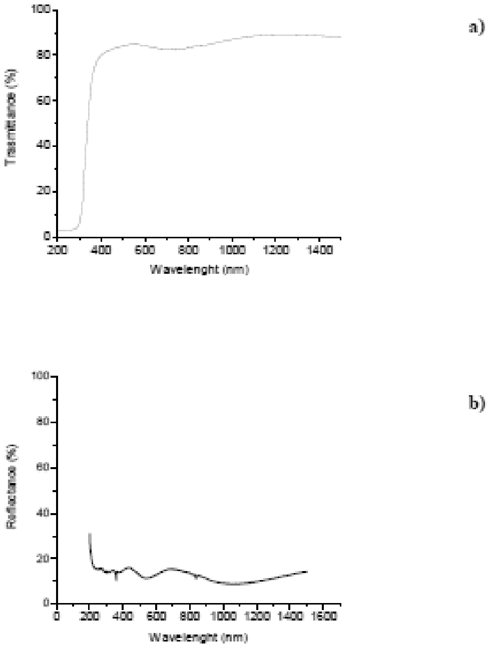

Figure 3. Total transmittance (a) and the specular reflectance (b) UVvis spectra of the MAPLE - deposited TiO_2 nanorod films.

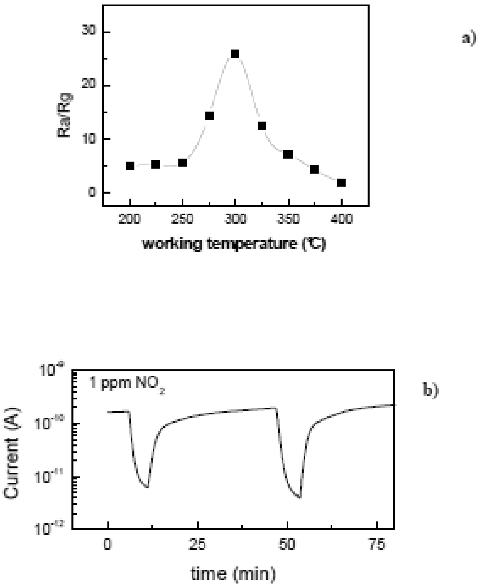

Figure 4. (a) Sensor response for different working temperatures under 1 ppm NO_2 exposure; (b) typical dynamic response to the NO_2 presence/absence at the working temperature of 300 C.

perimental works, which report for the brookite phase higher band gap values with respect to the other two TiO_2 phases, anatase and rutile. The MAPLE-deposited TiO_2 brookite films with complex morphology and high surface to volume ratio have revealed very promising performances for sensing applications. The sensor response to 1 ppm of NO_2 in dry air for different working temperatures is given in Fig. 4a. The gas response of the sensor is calculated as Ra/Rg, where Rg is the current of sensor in the target gas and Ra is the current value in dry air. The TiO_2 nanorod-based thin films were subjected to several cycles of 1 ppm of NO_2 exposure in dry air, separated by a recovering flux of dry air.

A typical dynamic response curve recorded at the working temperature of 300 C (at which the sensor response was the highest) is shown in Fig. 4b, where quite stable and reversible sensing signals can be appreciated. From the dynamic response curves, response and recovery times of about 2 min and 13 min have been estimated, respectively. Further tests are in progress to optimize the performances of the sensing material to detect lower that 1 ppm NO_2 gas concentrations, as required for detection of explosives and, at the same time, to analyze the sensitivity and reduce the response and recovery times. Studies are in progress also to analyze the response of this material towards reducing gases like CO, in order to investigate its selectivity in the presence of interfering gases. To this purpose, preliminary measurements have put in evidence typical reducing behavior, since the conductivity of the thin sensing layer increased in the presence of 50 ppm of CO gas mixed in dry-air. Moreover, measurements to investigate the possible beneficial effects of light illumination in a wavelength region close to the absorption edge of TiO_2 have been performed. An increased sensor response and dynamics of interactions were interestingly achieved.