SUB-ESTIOQUIOMETRIC TITANIA LAYERS PREPARED BY MOCVD FOR PHOTOCATALYSIS APPLICATIONS

I. Justícia[a], G. Garcia[a], G.A. Battiston[b], R. Gerbasi[b], A. Figueras[a] and D.Dorignac[c]

a. ICMAB/CSIC; Campus UAB, 08193 Bellaterra, Spain
b. ICIS/CNR; Corso Stati Uniti 4, 35127 Padova, Italy
c. CEMES-CNR, 29, rue Jeanne Marvig, 31055 Toulouse, France

Many researchers have proved that semiconducting TiO_2 is an excellent photocatalist which permits the degradation and finally the mineralization of stable organic pollutants such as detergents, dyes and pesticides in water (1,2). However, it requires ultraviolet (UV) radiation whose energy exceeds the band gap of 3.2 eV (λ~380 nm) of the anatase crystalline phase, hence practically ruling out the use of sunlight as an energy source for the photodegradation. Recently, theoretical calculations (3) have demonstrated that introducing oxygen vacancies in the anatase structure can induce the defect band to reach a width of 0.2 eV, and therefore to overlap with the conduction band. In this situation, the electrons in these defect states are able to hop and contribute to conduction thus enhancing photodegradation properties of the self-doped titania. These vacancy-induced band of electronic states facilitates the transport of the photocarriers to the active sites in the surface where the transfer to the target must take place for the degradation process.

In this paper, Titania films have been prepared by the MOCVD technique. The experimental parameters have been optimised in order to prepare pure anatase films of controlled thickness and surface roughness with selected oxygen stoichiometry. Films with $TiO_{1.8}$, TiO_2 and $TiO_{2.2}$ stoichiometry have been prepared by using, nitrogen, nitrogen plus 10sccm of oxygen and nitrogen plus 40 sccm of oxygen, respectively.

The calculation of the absorption coefficient of the anatase layers as a function of the wavelength pointed out that: (i) the curve of the sub-stoichiometric films is shifted to higher wavelengths indicating a decrease in the optical gap; (ii) the absorption coefficient is very much increased in the visible range. This fact is consistent with the presence of an electronic band close to the conduction band for the sub-stoichiometric material.

In table 1, we show the evolution of the methylene blue photodegradation in ppm/(cm^2 min) as a function of oxygen stoichiometry for UV and visible radiations sources. In order to ensure the effect of oxygen stoichiometry the films were selected as they showed similar surface roughness which is another factor that may influence the degradation properties. We can clearly observe that sub-stoichiometric films show higher degradation rate than stoichiometric and sup-stoichiometric films under UV radiation. A 4.5 times lower photodegradation activity when visible light is used is also observed for stoichiometric and sub-stoichiometric films. With significant values for sub-stoichiometric layers. No activity was observed under visible radiation for sup-stoichiometric layers.

In conclusion, we have demonstrated that thin films of titania with strong oxygen substoichiometry present enhanced photocatalytic properties in the visible range, which make them ideal candidates for low cost photodegradation applications. Experimental evidences show that the gap narrowing induced by the presence of oxygen vacancies is the main responsible for the enhanced optical activity in the visible range.

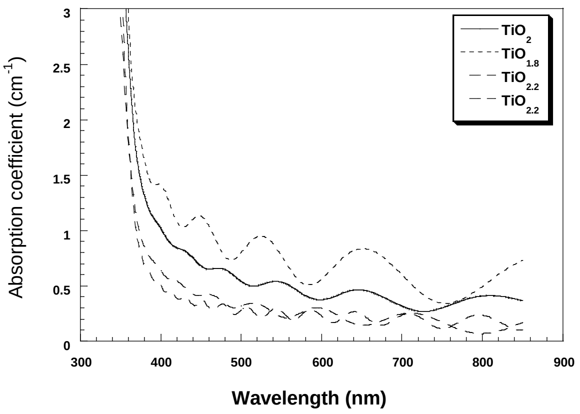

Fig.1. Evolution of the absorption coefficient as a function of wavelength for different oxygen stoichiometries of anatase films.

Degradation ($ppm/cm^2.min$)	$TiO_{1.8}$	TiO_2	$TiO_{2.2}$	$TiO_{2.2}$
UV-range	0,00309	0,00221	0,00143	0,00143
Vis-range	0,00065	0,00049	n/a	n/a
Roughness (rms)	38 nm	28 nm	22nm	25nm

Table 1: Methylene blue photodegradation rates for UV and visible radiation and for different oxygen stoichiometries.

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