Shifting to the red the absorption edge in TiO_2 films: a photoacoustic study

F. Gordillo-Delgado[*,º], K. Villa-Gómez
Laboratorio de Optoelectrónica, Universidad del Quindío
Apdo. Postal 2639 Armenia, Colombia.

E. Marín
[*] *Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del I.P.N, Unidad Legaria*
Calz. Legaria 694. Col. Irrigación México D.F, México 11500.
(Recibido: 4 de enero de 2010; Aceptado: 22 de febrero de 2011)

When Titanium dioxide in contact with a polluted water sample is irradiated with ultraviolet light, electron-hole pairs can be generated, which can react with oxygen and water producing free radicals that can degrade the pollutants, changing them into harmless compounds for the environment. The ultraviolet component of the solar radiation is around 7%. Therefore, it is convenient to modify the TiO_2 films crystalline structure for obtaining photocatalytical processes with visible light. In this work we report on the growth of TiO_2 thin films by the Sol-gel technique considering the incorporation of $AgNO_3$ in the initial solution containing the precursor. The concentration of the $AgNO_3$ saline solution was changed between 5 and 30% to control the grain size of the grown TiO_2 nanocrystals, impregnating 6 layers over glass slide substrates and using a sintering temperature of 600 °C. The obtained films were characterized structurally by means of X-ray diffraction. The shift in the forbidden energy bandwidth value to the red part of the optical absorption spectrum was evidenced by Photoacoustic Spectroscopy. The photocatalytic activity was tested on a solution of methylene blue using also the Photoacoustic technique.

Keywords: Titanium dioxide; Thin films; Sol-gel; Photocatalysis; Photoacoustic

1. Introduction

Heterogeneous photocatalysis has become an alternative method for air and water purification as a very efficient process for removing organic pollutants in the environment. This catalytic effect has shown a high potential in applications related to gas and liquid phase pollution control processes, and renewable hydrogen production [1, 2]. One of the most common photocatalyst is titanium dioxide (TiO_2), a wide-gap, cheap, reusable, nontoxic, photocorrosion resistant, and high oxidant power semiconductor. However, the efficient use of sunlight for photocatalysis with this material needs that the photoexcitation energy threshold become lower than the corresponding to the bulk material. One way to do that is by doping the TiO_2 with transition metals and non-metallic impurities [3].

The photocatalytic efficiency evaluation has been frequently measured by spectrophotometric methods using the methylene blue (MB) blanching as a function of time when this is placed in contact with the photocatalyzer radiated with light. However, this technique does not allow observing gases generation in the process and it is affected by light dispersion problems.

In this work, in-situ evaluation of the photocatalytic effect of TiO_2 films was done using the Photoacoustic (PA) Technique. This technique is based in measuring the pressure changes in a thin layer of gas adjacent to a body radiated with intensity modulated light, which are due to heating by non-radiative de-excitation process [4]. This effect can be detected as sound with a microphone placed inside a cell that also encloses the sample. If in addition, the sample presents photochemical activity, the production of gases contributes to the PA signal too. Then, when PA measurements are resolved in time it is possible to study, for instance, the photocatalytic activity.

2. Experimental

The TiO_2 films were grown by the sol-gel technique using titanium tetraisopropoxide as alcoxide precursor and nitride acid as catalytic acid. Silver was incorporated from an $AgNO_3$ dissolution, with concentration changing from 5 to

Table 1. Size grain (S) and band gap energy (E_g) estimated for TiO_2 films using Scherrer equation and indirect transitions model (equation (1)), respectively.

Sample	**S** (nm)	$\mathbf{E_g}$ (eV)
Ag 5%	18	2,3
Ag 10%	23	2,1
Ag 15%	24	2,0
Ag 20%	25	2,0
Ag 25%	29	2.0
Ag 30%	30	2.0

ºfgordillo@uniquindio.edu.co