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# Optical properties of in situ doped and undoped titania nanocatalysts and doped titania sol–gel nanofilms

A. Ferreira da Silva [a,*], I. Pepe [a], James L. Gole [b], S.A. Tomás [c], R. Palomino [d],
W.M. de Azevedo [e], E.F. da Silva Jr.[f], R. Ahuja [g], C. Persson [h]

[a] *Instituto de Fisica, Universidade Federal da Bahia, Campus Ondina, 40 210-340 Salvador, BA, Brazil*
[b] *Schools of Physics and Mechanical Engineering, Georgia Institute of Technology Atlanta, GA 30332-0430,USA*
[c] *Departamento de Física, CINVESTAV-IPN, AP 14-740, México D.F. 07300, Mexico*
[d] *Facultad de Ciencias Físico-Matemáticas, BUAP, AP 1152, Puebla, Mexico*
[e] *Departamento de Quimica Fundamental, Universidade Federal de Pernambuco, Cidade Universitaria, 50670-901 Recife, PE, Brazil*
[f] *Departamento de Fisica, Universidade Federal de Pernambuco, Cidade Universitaria, 50670-901 Recife, PE, Brazil*
[g] *Department of Physics, Uppsala University,SE-751 21 Uppsala, Sweden*
[h] *Department of Materials Science and Engineering, Royal Institute of Technology SE-100 44 Stockholm, Sweden*

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## Abstract

In this paper we present spectroscopic properties of doped and undoped titanium dioxide ($TiO_2$) as nanofilms prepared by the sol–gel process with rhodamine 6G doping and studied by photoacoustic absorption, excitation and emission spectroscopy. The absorption spectra of $TiO_2$ thin films doped with rhodamine 6G at very low concentration during their preparation show two absorption bands, one at 2.3 eV attributed to molecular dimmer formation, which is responsible for the fluorescence quenching of the sample and the other at 3.0 eV attributed to $TiO_2$ absorption, which subsequently yields a strong emission band at 600 nm. The electronic band structure and optical properties of the rutile phase of $TiO_2$ are calculated employing a fully relativistic, full-potential, linearized, augmented plane-wave (FPLAPW) method within the local density approximation (LDA). Comparison of this calculation with experimental data for $TiO_2$ films prepared for undoped sol–gels and by sputtering is performed.

## 1. Introduction

$TiO_2$ is a promising oxide for the fabrication of thin dielectric films used in dynamic random access memory (DRAM), storage capacitors and as gate dielectrics for metal-oxide-semiconductor field effect transistors (MOSFET) [1]. $TiO_2$ nanoparticles might serve as an excellent source for the photocatalytic decomposition of organic pollutants in water. Currently, however, the highly efficient use of $TiO_2$ in photocatalysis applications is prevented by its wide bandgap (3.2 eV), which responds to only a small fraction of the sun's energy spectrum. Thus, one of the goals to improve the performance of $TiO_2$ is to increase its optical activity by shifting the onset of its response from the UV to the visible region [2,3]. Here we will present spectroscopic properties of doped and undoped $TiO_2$ as nanofilms prepared by the sol–gel process, including rhodamine 6G doping during film preparation, studied by photoacoustic absorption, excitation and emission spectroscopy. The absorption spectra of $TiO_2$ thin films doped with, for example, rhodamine 6G at very low concentration show two absorption bands, one at 2.3 eV attributed to molecular dimmer formation, which is responsible for the fluorescence quenching of the sample and the other at 3.0 eV attributed to $TiO_2$ absorption. The optical absorption and band gap energy for the rutile phase of titanium dioxide are calculated employing a fully relativistic, full-potential linearized augmented plane-wave (FPLAPW) method [4] within the local density approximation (LDA). The LDA is improved by

* Corresponding author. Tel.: +55 71 3263 6647; fax: +55 71 3263 6606.
  *E-mail address:* ferreira@venus.fis.ufba.br (A.F. da Silva).

an on-site Coulomb self-interaction correction (SIC) potential as represented by the LDA + U$^{SiC}$ approach [5]. These calculations are presented and compared with the experimental data [6] for TiO$_2$ as films prepared by the sol–gel and sputtering techniques and the results discussed.

## 2. Experimental

Titania films were deposited on Corning glass substrates by the sol–gel method. The precursor solution consisted of 1 mol of titanium isopropoxide (TIPO, 99.9%, Aldrich) mixed with 2 mol of acetic acid (Aldrich) and 2 mol of isopropanol (Baker) at room temperature. For R6G-doped TiO$_2$ films, rhodamine 6G (Aldrich) was separately dissolved in a mixture of 2 mol of water, 2 mol of acetic acid and 2 mol of isopropanol. Both solutions were then mixed together under vigorous agitation. With this procedure it was possible to obtain titania sols doped in situ with rhodamine 6G at different molar concentrations. Further details of the sol–gel method are found in [7]. The preparation process of the thin films prepared by DC magnetron sputtering is described elsewhere [8]. Transmission spectroscopy was performed with a spectrophotometer consisting of a halogen lamp as the light source. The wavelength of the beam can be varied from 850 to 300 nm corresponding to photon energies from about 1.5 to 4.0 eV as the light is detected by a photomultiplier tube (PTM) (EMI 9558). The fluorescence and emission analyses were performed using a Jobin Yvon Monochromator Model U-1000, where the samples were excited with a 100 W Xe lamp, and the signal was detected by a photomultiplier (RCA C31034-02) and processed by the Jobin Yvon spectralink data acquisition system.

## 3. Theoretical calculations

To obtain the absorption coefficient we calculated first the dielectric functions $\varepsilon_2(\omega)$ and $\varepsilon_1(\omega)$ [6]. The dielectric function was calculated in the momentum representation, which requires matrix elements of the momentum, $p$, between occupied and unoccupied eigenstates. Specifically, the imaginary part of the dielectric function, $\varepsilon_2(\omega) = \mathrm{Im}[\varepsilon(q = 0,\omega)]$, was calculated as

$$\varepsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{knn'\sigma} \langle kn\sigma | \hat{p}_i | kn'\sigma \rangle \langle kn'\sigma | \hat{p}_j | kn\sigma \rangle$$
$$\times f_{kn}(1 - f_{kn'})\delta(E_{kn'} - E_{kn} - \hbar\omega). \tag{1}$$

The imaginary part of the dielectric function, $\varepsilon_2(\omega)$, in the long wavelength limit, has been obtained directly from the electronic structure, using the joint density-of-states and the optical matrix overlap [6]. In Eq. (1), $e$ is the electron charge, $m$ its mass, $\Omega$ the crystal volume and $f_{kn}$ is the Fermi distribution. Moreover, $|kn\sigma\rangle$ is the crystal wave function corresponding to the $n$th eigenvalue $e_{kn}$ with crystal momentum $k$ and spin $\sigma$. The summation over the Brillouin zone in Eq. (1) has been calculated using the tetrahedral interpolation with a $k$-mesh consisting of about 450 uniformly distributed $k$-points. The matrix

elements, eigenvalues and eigenvectors are calculated in the irreducible part of the Brillouin-zone. Finally, the real part of the dielectric function, $\varepsilon_1(\omega)$, is obtained from $\varepsilon_2(\omega)$ using the Kramers-Kronig transformation

$$\varepsilon_1(\omega) \equiv Re(\varepsilon(q = 0, \omega))$$
$$= 1 + \frac{1}{\pi}\int_0^\infty d\omega' \varepsilon_2(\omega')\left(\frac{1}{\omega' - \omega} + \frac{1}{\omega' + \omega}\right) \tag{2}$$

The absorption coefficient, $\alpha(\omega)$, is obtained directly from the relation [6]

$$\alpha(\omega) = \frac{\omega}{c}\left(-2\varepsilon_1(\omega) + 2\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}\right)^{1/2} \tag{3}$$

where $c$ is the velocity of light.

The LDA + U$^{SIC}$ potential describes accurately the electronic band-edge structure of rutile TiO$_2$. The calculated fundamental band-gap energy $E_g(\mathrm{LDA} + \mathrm{U}^{SIC}) = 2.97$ eV is similar to the previous room temperature measured value of 3.0 eV [6].

## 4. Results

In Fig. 1 we show typical absorption spectra of TiO$_2$ sol–gel films doped with rhodamine 6G 0.1% [curve (rd)]: absorption bands just over 2.3 eV and at 2.5 eV are attributed to rhodamine 6G, and a band above 3.0 eV corresponds to TiO$_2$ absorption. A shift of these bands occurs due to the rhodamine doping concentrations. For the sake of comparison and to establish similarities, Fig. 1 also presents the experimental absorption spectra for amorphous sol–gel TiO$_2$ [curve (ap)], rutile TiO$_2$ prepared by sputtering [curve (ru)], and the theoretical results of our calculations [curve (te)]. The calculated fundamental band-gap energy $E_g = 2.97$ eV agrees with the value measured at room temperature, 3.0 eV.

The electronic structure of TiO$_2$ is calculated and shown in Fig. 2. The conduction band edge of TiO$_2$ consistes of several
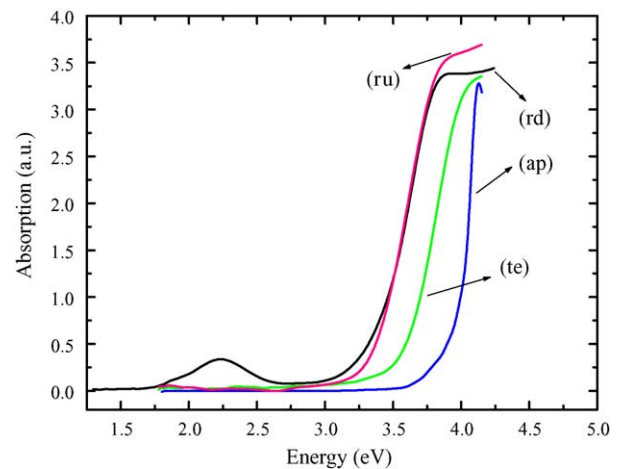


Fig. 1. Absorption spectra of TiO$_2$ sol–gel films dip-coated as a function of rhodamine 6G concentration 0.1% (rd). The experimental result for amorphous sol–gel TiO$_2$ is written as (ap). Rutile sputtering is represented by (ru) and theoretical results by (te).
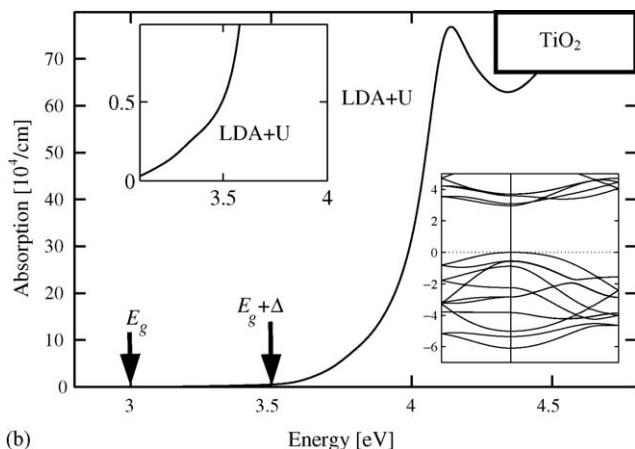
Fig. 2. Absorption coefficient $a(w)$ and electronic structure of rutile TiO$_2$.

close lying bands. The many conduction bands and their flat energy dispersion improve the optical absorption in TiO$_2$. The strong onset at $E_g + 0.5 \approx 3.5$ eV is due to absorption associated with the direct transitions near the $\Gamma$-point involving higher lying conduction bands and lower lying valence bands, as depicted in the inset of Fig. 2.

At low R6G concentration, only two absorption bands appear, one broad absorption band at 2.3 eV with an weakly defined shoulder at 2.5 eV attributed to rhodamine 6G and the second above 3.0 eV attributed to TiO$_2$ absorption. The measured excitation spectra indicate that besides the efficient excitation bands for R6G at 2.3 eV, two new bands appear: one at 3.0 eV and the second at 3.4 eV. This second band appears to be excited as efficiently as the absorption band at 2.3 eV. We suggest therefore that an efficient energy transfer may result due to the overlap of the TiO$_2$ conduction band and molecular R6G excited states. These states yield a strong fluorescence emission band at 600 nm when excited at this energy. This feature was confirmed by evaluating the fluorescence spectra of TiO$_2$ sol–gel films as a function of rhodamine 6G concentration (not shown here).

## 5. Summary

We have established a route to produce high quality TiO$_2$ sol–gel generated samples doped with R6G dyes. Different from other processes, which result in the adsorption of the organic molecule onto TiO$_2$, where the particle is already formed, the sol–gel method allows organic molecules to interact quite strongly with the TiO$_2$ particles in the formation process to produce quite large aggregates. The spectroscopic properties attributed to the samples in this form indicate that the material may have potential to be applied in catalytic processes as we have been able to extend its energy absorption band edge into the visible region. The fluorescence results appear to suggest that an efficient energy transfer to the conduction band of TiO$_2$ from the excited states of the R6G dye occurs. The results for undoped TiO$_2$ are compared to experimental data obtained from the rutile material prepared by sputtering as well as to theoretical calculations. The absorption measurements compared to the theory indicate a similar behavior.

## References

[1] K. Kim, C.G. Hwang, J.G. Lee, IEEE Trans. Electron. Devices 45 (1998) 598.
[2] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269.
[3] J.L. Gole, J. Stout, C. Burda, Y. Lou, X. Chen, J. Phys. Chem. 108B (2004) 1230.
[4] P. Blaha, et al., WIEN95, Technical University of Vienna, 1995 [Improved and updated Unix version of the original copyrighted WIEN-code, which was published by P. Blaha, et al., Comput. Phys. Commun. 59 (1990) 399].
[5] C. Persson, A. Ferreira da Silva, Appl. Phys. Lett. 86 (2005) 231912.
[6] A. Ferreira da Silva, I. Pepe, C. Persson, J. Souza de Almeida, C. Moysés Araújo, R. Ahuja, B. Johansson, C.Y. An, J.H. Guo, Phys. Scr. T109 (2004) 180.
[7] S.A. Tomás, S. Stolik, R. Palomino, R. Lozada, C. Persson, I. Pepe, A. Ferreira da Silva, J. Appl. Phys. 98 (2005) 073516;
R. Palomino-Merino, A. Conde-Gallardo, M. García-Rocha, I. Hernández-Calderón, V. Castaño, R. Rodríguez, Thin Solid Films 401 (2001) 118.
[8] T. Lindgren, J.M. Mwabora, E. Avendaño, J. Jonsson, A. Hoel, C.-G. Granqvist, S.-E. Lindquist, J. Phys. Chem. B107 (2003) 5709.