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ORIGINAL PAPER

Characterization of TiO₂ Nanoparticles in Langmuir-Blodgett Films

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Abstract In this work we have synthesized TiO₂ nanoparticles, using either a sol–gel base catalysed process in the interior of CTAB reversed micelles (TiO₂ CTAB sol), or the neutralization of a TiO₂/H₂SO₄ solution in the interior of AOT reversed micelles. From the absorption and emission data of the TiO₂ nanoparticles it is possible to conclude that in the sol–gel route there remains alkoxide groups in the structure, originating transitions lower than the energy gap of TiO₂ semiconductor. These transitions disappear in the neutralization procedure, where the alkoxide groups are absent in the structure. We have assigned the observed indirect and direct optical transitions according to the anatase band structure. TiO₂ Langmuir-Blodgett (LB) films were prepared either by direct deposition of titanium *isopropoxide* or by deposition of the TiO₂ CTAB sol. These films showed photoluminescence, which was attributed to band-gap emission and to surface recombination of defect states.

Keywords TiO₂ · Nanoparticles · Band gap · Photoluminescence

Introduction

Photodegradation catalysed by TiO₂ particles is becoming an important technological method for treatment of water, air and solid wastes from industries and household [1–3]. The use of wide band-gap semiconductors, especially titania, as

photocatalysts for water cleaning is an attractive method, because the catalyst is non-toxic and has low cost. In particular, the elimination of colour in waste water from textile industries involves the removal of very low quantities of organic pollutants (0.01% w/w). The overall efficiency of the photodegradation system is an important issue and nanoparticulated TiO₂ proved to be more efficient than bulk TiO₂ [4]. There is some controversy in the existence of quantum-size effects for this indirect semiconductor [5–8]. Also, TiO₂ deposited in thin films offers several technological advantages over dispersed TiO₂ powders because there is no need of recovering the particles by filtration. This step would be a major difficulty when using nanoparticles of TiO₂ in the 1–10 nm size range.

In this work, we have prepared TiO₂ films by the Langmuir-Blodgett (LB) technique, using either the deposition of a TiO₂ alkoxide resulting in a 2D sol–gel process [9], or the deposition of TiO₂ nanoparticles obtained from sol–gel process within the cavities of CTAB w/o microemulsions [10]. Also, in order to eliminate the presence of residual alkoxide groups in the TiO₂ nanoparticles, we have tried a different method, where a reversed micelle containing an acidified solution of TiO₂ is neutralized by collision with a reversed micelle containing a sodium hydroxide solution.

Experimental

Materials and methods

TiO₂ sols

TiO₂ particles were prepared by slow hydrolysis of titanium *isopropoxide* in alkaline media [10], using CTAB reversed micelles as the templating environment. In these

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conditions, the surface of the growing TiO₂ particles is negatively charged. This fact either causes the particles to bind to the positive surface of CTAB micelles, or attracts CTAB molecules to its surface. Both processes result in the control of the particles growth and determine their dimensions. The resulting particles are hydrophobic as bounded CTAB molecules point outwards. The TiO₂ particles were extracted from the CTAB sol by adding acetyl acetone (ACAC) as a surface capping agent, followed by water and sonication. The aqueous phase was removed and the process was repeated three times. The remaining solution was dried and dispersed in pH = 4 buffer.

Another way of obtaining a sol of TiO₂ particles in reversed micelles from titanium isopropoxide was, first, to completely hydrolyse the alkoxide with a strong acid solution (H₂SO₄ 0.1 M). In the resulting solution, titanium exists as oxosulfate complexes. This acid titanium solution was then added to AOT in isooctane (0.1 M) resulting in a water content of $\omega_0 = 2.5$ ($\omega_0 = [\text{H}_2\text{O}]/[\text{AOT}]$). This reversed micelle solution was neutralized by adding AOT reversed micelles containing NaOH at 0.1 M concentration at the same ω_0 . The collision of different reversed micelles results in neutralization of the titanium acid solution with the formation of TiO₂ particles in the micelles interior.

TiO₂ Langmuir-Blodgett films

The solution of TiO₂ in CTAB reversed micelles was spread on the surface of the aqueous subphase in a Langmuir-Blodgett trough (KSV Minitrough). To facilitate the spreading process, 20% v/v of hexane was added to the TiO₂ sol [10]. Compression/expansion cycles were performed until an equilibrium isotherm was obtained, followed by dipping of a glass substrate at a constant surface pressure of 9 mN/m. Prior to dipping the glass, slides were washed with ethanol and water (Milli-Q grade). After each compression, excess CTAB molecules are expelled to the bulk of the subphase. As a consequence, in the next compression isotherm, the surface pressure starts to rise at lower surface area values. When an equilibrium isotherm is obtained, the substrate is immersed in the subphase. Simultaneously, the barriers of the LB equipment are moved in order to keep a constant surface tension. Considering that the floating monolayer adsorbs on the substrate surface, the surface tension is kept constant by the compression movement of the barriers, in order to reduce the surface area and keep the monolayer concentration constant. The observed reduction of subphase surface area upon immersion of the substrate gives a clear indication that TiO₂ monolayer is transferred to the substrate, as reported by Kotov *et al.* [10]. Using the observed variation of surface area, an estimate of 4.12×10^{-8} mol of titanium in the film can be obtained. This estimate assumes that the floating monolayer is uniform and also that the surface reduction

during the LB film deposition originates only from coating of the substrate area with the same monolayer. A further confirmation of the success of the TiO₂ LB deposition comes from the experimental observation that the obtained films sensitize the photodegradation of phenol, upon irradiation with 365 nm light (results not shown).

An alternative TiO₂ film preparation procedure involves the direct spreading of the titanium alkoxide in the surface of an aqueous subphase in which the hydrolysis process is very slow [9]. This is accomplished by addition of acetic acid and acetyl acetone (ACAC) to the aqueous subphase. The titanium alkoxide monolayer is then transferred to a glass substrate at a constant surface pressure of 14 mN/m by the LB technique. The hydrolysis of the titanium alkoxide is supposed to occur on the glass surface through a 2D sol-gel process [9], either with the air humidity or while the substrate is immersed in the aqueous subphase during the LB film deposition. Using the variation of the surface area resulting from film deposition, an estimate of 1.31×10^{-6} mol of titanium in the film can be obtained.

Fluorescence and absorption measurements

Steady state fluorescence measurements were performed using a Spex Fluorolog 2 spectrofluorimeter. The absorption measurements were performed in a Shimadzu 3101 UVPC UV-Vis-NIR spectrophotometer.

Results and discussion

In Fig. 1 the absorption spectra of TiO₂ sols from CTAB and AOT reversed micelles are shown. The spectrum of the extracted and water dispersed TiO₂ particles was corrected in order to eliminate the dispersion caused by remaining organic solvent and by agglomerated and precipitated TiO₂ particles.

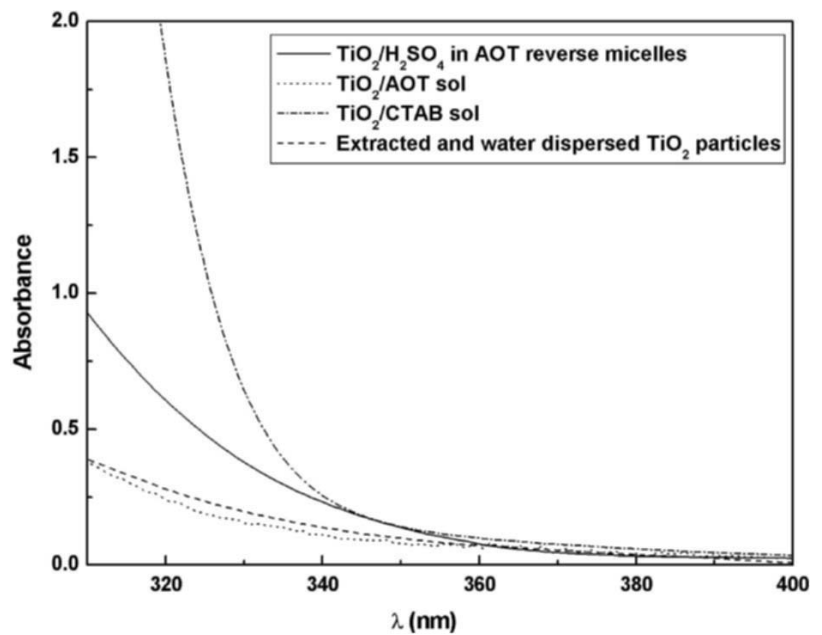
TiO₂ is an indirect semiconductor. The following relation is valid for indirect electronic transitions [11]:

$$\alpha = \begin{cases} B_i(h\nu - E_g)^2/h\nu, & h\nu > E_g \\ 0, & h\nu < E_g \end{cases} \quad (1)$$

where $\alpha = 2.303A/b$ is the absorption coefficient, b is the optical path length and E_g is the transition energy. Plots of $\sqrt{A h\nu}$ as a function of $h\nu$ should be linear. In the case of direct transitions, the linearity should be present in the plot of $(A h\nu)^2$ as a function of $h\nu$, as the relation between the transition probability and energy is given by:

$$\alpha = \begin{cases} B_d(h\nu - E)^{1/2}/h\nu, & h\nu > E \\ 0, & h\nu < E \end{cases} \quad (2)$$

Fig. 1 Absorption spectra of TiO_2 sols



In Figs. 2 and 3, these plots are shown for indirect and direct transitions. The obtained energy values, along with the assigned transitions from the band structure of TiO_2 (Scheme 1), are given in Tables I and II. These assignments were made using the theoretical calculations of Daude *et al.* [12] and using a similar absorption spectra analysis to that of Serpone *et al.* [7].

For TiO_2 particles covered with stearic acid, the band gap was measured as 2.25 eV [13]. Thus, we can assign the band at 2.8 eV to the presence of residual *isopropoxide* groups in the CTAB sol of TiO_2 . Upon extraction and dispersion in water, the disappearance of this band is observed. One possible explanation is the removal, by hydrolysis, of the remaining

isopropoxide groups mostly in the particles surface. As a general trend, the transitions occur at higher energies upon extraction and water dispersion of the particles. This fact can again be explained by the removal of residual organic groups in the TiO_2 particles.

The band gap, E_g , of TiO_2 is 3.19 eV in the anatase form and 3.0 eV for the rutile polymorph. As anatase is the most usual TiO_2 form obtained from the sol–gel process [14,15], the transition $\Gamma_3 \rightarrow X_{1b}$ [7] that occurs at 3.26 eV corresponds to the E_g value of the particles prepared in this work.

For CdS semiconductor nanoparticles there exists a clear correlation between the band gap and the particle size [16], with the occurrence of a blue shift when size decreases. This

Fig. 2 Determination of indirect transition energies

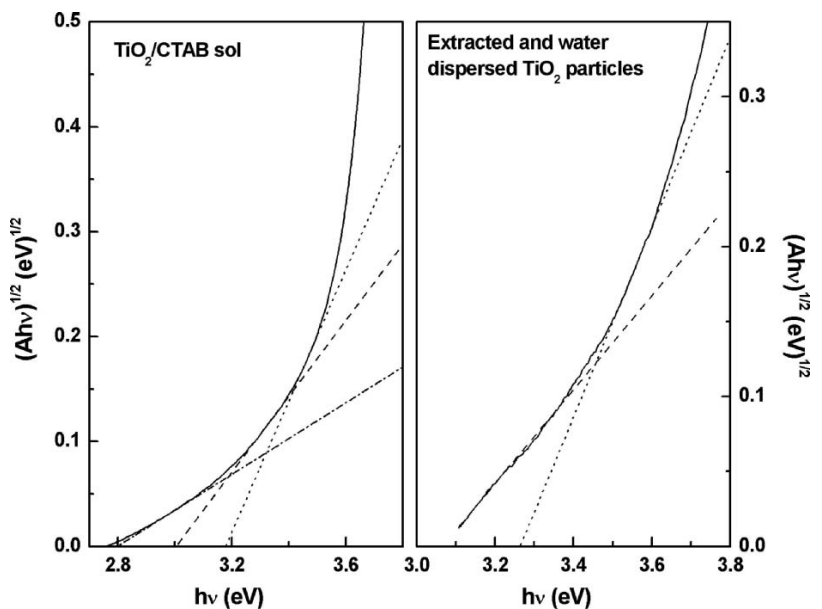
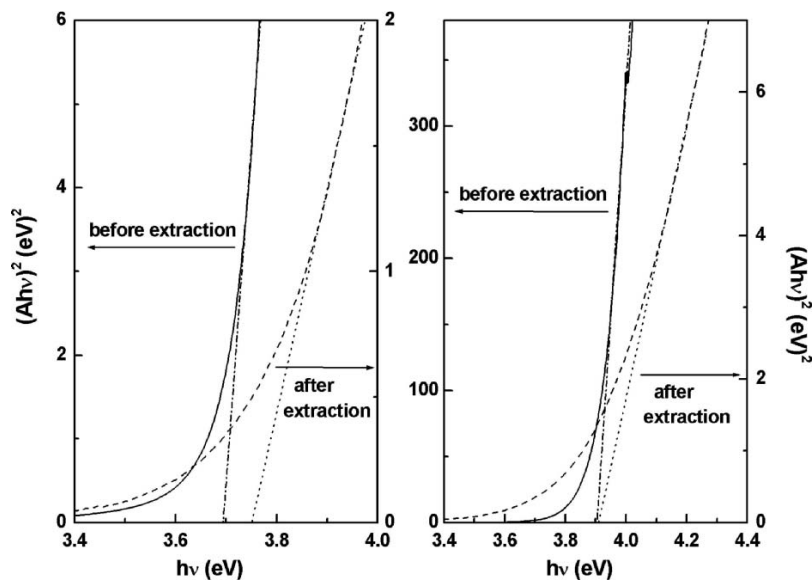


Fig. 3 Determination of direct transition energies



is known as the quantum-size effect. As for TiO_2 there is some controversy on the existence of quantum-size effects [5–8], the slight blue shift observed for the band gap of the prepared nanoparticles will not be considered. Nevertheless, Scolan *et al.* [17] have shown that, using an acid catalysed sol–gel process with surface deactivation by ACAC, it is possible to prepare controlled size TiO_2 nanoparticles, with diameter in the range 1–5 nm. Using this experimental protocol, Monticone *et al.* [5] concluded that, for particle size between 1.5 and 3 nm, the E_g value remains constant at ~ 3.2 eV, the spectral shape not being maintained. Another aspect is that the higher length of the unit tetragonal cell of anatase is 9.52 \AA . In small size particles (~ 1 nm diameter), most metallic centers are at the surface interacting with organic molecules (ACAC). Thus, TiO_2 “particles” in the sub-nm size range are better described as titanium ox-

oorganocomplexes. Measurements of dynamic light scattering of TiO_2 dispersions prepared with a similar protocol to that used in this work showed that the particles diameter is 4 nm [14]. Therefore, the radius of the particles prepared in this work is expected to be approximately 2 nm.

In order to confirm that the observed low energy transitions are due to residual *isopropoxy* groups, we attempted to prepare reversed micelle templated nanoparticles by neutralization of titanium acid solution, in which the titanium *isopropoxide* is fully hydrolysed into titanium oxosulfate complexes and *isopropyl* alcohol. Upon neutralization, the spectrum shifts 50 nm to the blue and becomes similar to that obtained for the CTAB sol (see Fig. 1). Using the procedure corresponding to Eq. (1), we obtain an estimate of 3.15 eV for the lowest indirect transition and an absence of the 2.8 eV transition observed for the CTAB TiO_2 sol.

Scheme 1 TiO_2 anatase band structure (adapted from reference [7])

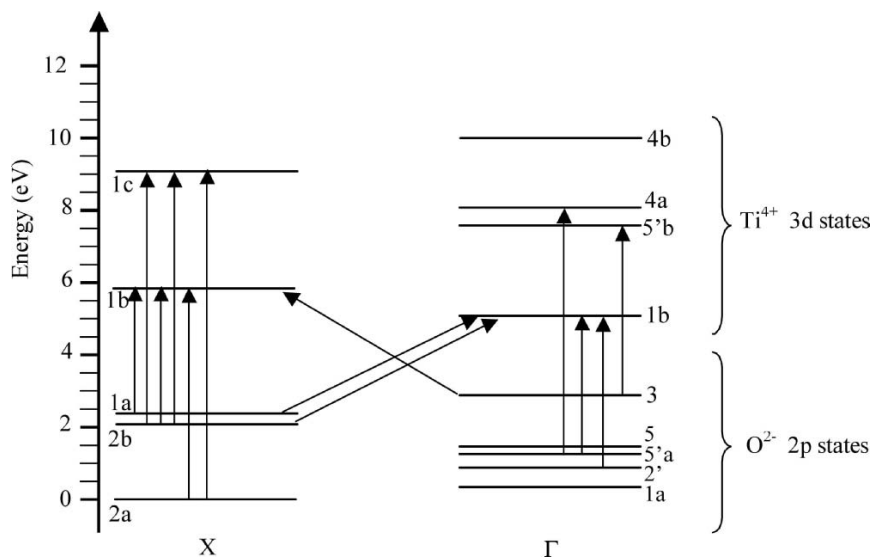


Table 1 Indirect transition energies (eV) and assigned electronic band transitions

Experimental <i>E</i>	Transition	Energy
Before extraction		
2.80	?	?
3.00	X _{1a} →Γ _{1b}	2.91
	X _{2b} →Γ _{1b}	3.05
3.18	Γ ₃ →X _{1b}	3.19
After extraction and water dispersion		
3.07	X _{1a} →Γ _{1b}	2.91
	X _{2b} →Γ _{1b}	3.05
3.26	Γ ₃ →X _{1b}	3.19

Table 2 Direct transition energies (eV) and assigned electronic band transitions

Experimental <i>E</i>	Transition	Energy
Before extraction		
3.69	X _{1a} →X _{1b}	3.61–3.68
3.90	Γ _{5'a} →Γ _{1b}	4.03–4.04
After extraction and water dispersion		
3.75	X _{1a} →X _{1b}	3.61–3.68
3.91	Γ _{5'a} →Γ _{1b}	4.03–4.04

Usually, TiO₂ shows a very weak photoluminescence [18]. This happens because indirect transitions in semiconductors must occur with simultaneous interaction between photons and lattice phonons [11]. As a result, the transition probabilities in emission, as well as in absorption, are very low. This explains why it has been very difficult to observe band-edge emission from TiO₂ particles [18,19]. Band gap (*E_g*) excitation in vacuum originates a broad emission band centered at ~2.3 eV (~500 nm). Its intensity is strongly dependent on the presence of other molecules with electron accepting or donating properties [19], and it seems that the photogenerated hole is not directly involved. Thus, the photoluminescence seems to be determined mainly by surface states.

In Fig. 4, the emission spectra of TiO₂ particles in CTAB sol and in the prepared two LB films are shown, together with a global analysis fit, using a sum of three Gaussian

functions.

$$I_F = A[f_1 e^{-((\lambda-\lambda_1)/\sigma_1)^2} + f_2 e^{-((\lambda-\lambda_2)/\sigma_2)^2} + f_3 e^{-((\lambda-\lambda_3)/\sigma_3)^2}] + I_b \tag{3}$$

In the fitting procedure, the three maximum intensity wavelengths were common to all emission spectra. In the case of the 2D sol-gel film, only two Gaussian functions were needed, with an additional background intensity (*I_b*). Table III presents the results of the global fit to the photoluminescence data.

The excitation wavelength used (3.25 eV) is nearby the band gap of TiO₂. Thus, only transitions originating from the X_{1b} state are possible. The emission band observed at 2.95 eV can correspond either to the band edge emission (X_{1b}→Γ₃) shifted to lower energy due to solvent relaxation, or to the degenerate bands (Γ_{1b}→X_{2b}/X_{2a}). The emission bands centered at 462.1 nm (2.69 eV) and 498.8 nm (2.49 eV) can only correspond to transitions from/to states within the band gap. These states originate from surface or lattice defects. The majority of published work [7, 20–23] indicates

Fig. 4 Photoluminescence of TiO₂ Langmuir-Blodgett films and TiO₂ CTAB sol

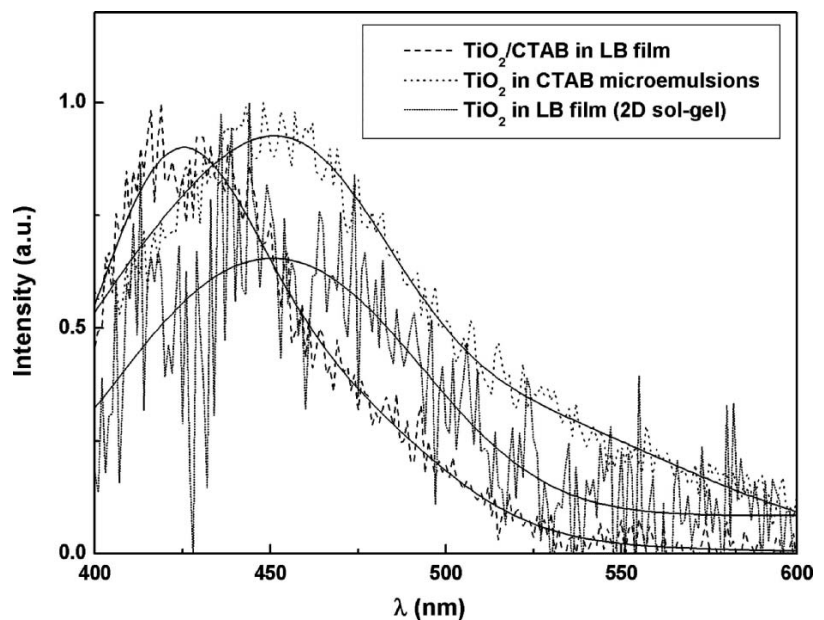


Table 3 Fluorescence parameters obtained from global fit to TiO₂ photoluminescence data

Sample	(a)	(b)	(c)
$\lambda_1 = 420.8 \text{ nm}$ (2.95 eV)			
f_1	0.682	0.416	0.292
σ_1 (nm)	33	48.6	36.6
$\lambda_2 = 462.1 \text{ nm}$ (2.69 eV)			
f_2	0.300	0.296	0.708
σ_2 (nm)	45.6	35.8	47.9
$\lambda_3 = 498.8 \text{ nm}$ (2.49 eV)			
f_3	0.0180	0.287	0
σ_3 (nm)	95.3	88.0	—
I_b	—	—	0.0848

Note: Sample (a): TiO₂ Langmuir-Blodgett film obtained from CTAB sol. Sample (b): TiO₂ in CTAB sol. Sample (c): TiO₂ Langmuir-Blodgett film obtained from the 2D sol-gel process.

that these states correspond to the absence of oxygen atoms (V_O) and are 0.5–0.8 eV below the conduction band [21, 23]. The radiative recombination could occur either with the photogenerated holes (in the “bulk”) or with surface holes ($\{\text{Ti}^{\text{IV}}\text{-O}^{2-}\text{-Ti}^{\text{IV}}\}\text{-O}^\bullet$). Serpone *et al.* [24] estimated an average migration time for electrons and holes of 0.05 ps for 2.1 nm particles. Thus, the luminescence observed at lower energies (2.69 and 2.49 eV bands) originates from the surface states and these are also the electronic states that are important in the photocatalytic effect of the TiO₂ particles.

Comparing the emission from the CTAB sol with that of the corresponding LB film, we conclude that, upon deposition, the weight of the emission from defect states decreases. This indicates that some residual *isopropoxide* groups are eliminated during the LB deposition procedure. We can also observe that the emission from the TiO₂ 2D sol-gel film is much lower than that obtained from the deposition of the CTAB TiO₂ sol, although the quantity of TiO₂ deposited is much higher.

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