Conclusiones Finales

Estudio de fotocatálisis heterogénea

1. En la primera publicación se han realizado nuevas aportaciones al campo de la *fotocatálisis heterogénea* a través del estudio de la degradación fotocatalítica de cuatro compuestos orgánicos (fenol, guayacol, 2-clorofenol y catecol) que se encuentran normalmente en las aguas residuales de la industria papelera. La irradiación con luz UV de soluciones acuosas aireadas de estos compuestos, en presencia de TiO_2 en suspensión, da lugar a la completa eliminación de la materia orgánica. Este proceso es posible bajo condiciones de reacción suaves, a una temperatura de 25ºC y a presión atmosférica y es menos eficiente para soluciones altamente alcalinas.

2. La degradación fotocatalítica de los cuatro compuestos orgánicos estudiados obedece una cinética de Langmuir-Hinshelwood con constantes de velocidad decrecientes en el orden: guayacol > 2-clorofenol ≅ fenol > catecol, que es el mismo orden obtenido para la estabilidad de los complejos σ estimada teóricamente a partir de la reacción homogénea entre los anillos aromáticos y el radical $OH^{\cdot}$, excepto para el catecol, probablemente debido a su fuerte adsorción sobre el fotocatalizador.

3. Se han detectado intermedios altamente hidroxilados tras la irradiación de las soluciones fenólicas correspondiente en presencia de TiO_2. También se ha detectado la formación de intermedios que poseen dos núcleos aromáticos, que se habrían formado a través del acoplamiento directo de dos radicales fenoxi.

4. Estudios de degradación por fotocatálisis heterogénea de mezclas de los cuatro compuestos orgánicos han permitido la degradación

completa de todos ellos. Al proceso de degradación se le ha aplicado el modelo de Langmuir-Hinshelwood competitivo, que tiene en cuenta la competición entre las diferentes moléculas orgánicas por los lugares de reacción de la superficie del catalizador.

Métodos de preparación de películas de TiO_2

5. Se han desarrollado tres métodos de preparación de películas de TiO_2 a baja temperatura, presión atmosférica y utilizando disolventes acuosos en lugar de los habituales disolventes orgánicos. Se trata de una aportación al desarrollo de nuevos procesos sintéticos de bajo coste y de interés ambiental.

6. Cada uno de los métodos da lugar a películas de TiO_2 de muy diferentes características, en cuanto a tamaño de partícula, grosor del depósito, cristalinidad y propiedades fotocatalíticas. En la Tabla 12 se resumen las características de las películas obtenidas mediante los tres procesos. Se obtienen en todos los casos películas bien adheridas.

Tabla 12. — Resumen de las características de las películas de TiO_2 preparadas en la presente tesis doctoral.

	Grosor película	Tamaño de cristal (nm)	Estructura cristalina	Temperatura del proceso (°C)	Actividad fotocatalítica
Publicación 2 (proceso de drenaje)	~2 nm/proceso	7-11, largo 3-6, ancho	anatasa	60°C	sí
Publicación 3 (drenaje+microondas)	< 550 nm	50-100	anatasa	≤ 100°C	no
Publicación 4 (electrodeposición)	1,5-13,5 µm**	21 (partículas de DP25)	anatasa +amorfo	25°C	sí

** A potencial constante de 3,50V. Tiempo de deposición 10-90 min.

A parte de los datos que se encuentran en la Tabla 12, conviene comentar los siguientes aspectos de cada una de los trabajos:

7. ***Publicación 2***:
    - Se ha depositado TiO_2 nanocristalino sobre diferentes substratos (vidrio, vidrio recubierto de ITO y Si) a partir de un coloide de TiO_2 anatasa estabilizado con TBAOH, mediante un proceso de drenaje (*drain-coating*).
    - La preparación del coloide de TiO_2 anatasa se realiza a baja temperatura, comprendida entre 25ºC y la temperatura de ebullición del agua, a presión atmosférica y utilizando como disolventes EtOH y H_2O.
    - Las películas obtenidas no precisan un tratamiento térmico posterior a la deposición ni para eliminar la materia orgánica (pues su contenido es muy bajo) ni para inducir la cristalinidad del material depositado, puesto que el material de partida, el coloide de TiO_2, ya es cristalino.

8. ***Publicación 3***:
    - Se ha depositado TiO_2 anatasa sobre diferentes substratos (vidrio y Si) mediante la combinación de dos procesos diferentes: ***1)*** la deposición por drenaje de nanocristales de TiO_2, a partir de una solución coloidal acuosa y ***2)*** la deposición de TiO_2 inducida por la irradiación con microondas de un precursor de TiO_2 soluble en agua.
    - Es posible controlar el tamaño de grano y el grosor de las películas mediante la potencia y el tiempo de la radiación microondas aplicada.
    - Se obtienen películas de TiO_2 cristalinas sin necesidad de un proceso posterior de calcinación. Tampoco es necesario el proceso térmico para eliminar substancias orgánicas procedentes de los

productos de partida, pues las películas no presentan un contenido detectable de las mismas.

- Las películas de TiO_2 obtenidas no muestran actividad fotocatalítica, lo cual no es un inconveniente para su uso en aplicaciones como, por ejemplo, ópticas o aislantes.

9. ***Publicación 4***:
   - En este trabajo se combinan los procesos de electrodeposición catódica y deposición electroforética para preparar películas de TiO_2 porosas sobre Al. Es posible controlar la cantidad de material depositado sobre el substrato mediante el potencial y el tiempo de electrodeposición utilizados.
   - No es necesario un tratamiento térmico posterior de las películas obtenidas para obtener un depósito cristalino, ya que parte del depósito consiste en partículas cristalinas de TiO_2 DP25 depositadas electroforéticamente. Tampoco es necesario un tratamiento térmico para compactar las películas o mejorar su adherencia al substrato, ya que junto con las partículas de TiO_2 DP25 se codeposita una matriz de TiO_2 amorfo con esta finalidad.
   - La actividad fotocatalítica de las muestras indica que las partículas de TiO_2 no están completamente ocluidas por la matriz de TiO_2 amorfo.

Apéndice

Apéndice 1

Otras publicaciones relacionadas con el trabajo de esta tesis doctoral, en las que se ha colaborado durante la elaboración de la misma son:

1. ***Preparation of anatase powders from fluoride-complexed titanium (IV) aqueous solutions using microwave irradiation***, J.A. Ayllón, A.M. Peiró, L. Saadoun, E. Vigil, X. Domènech, J. Peral, *Journal of Materials Chemistry* **10** (2000) 1911-1914.

2. ***TiO_2 layers grown from flowing precursor solutions using microwave heating***, E. Vigil, J.A. Ayllón, A.M. Peiró, R. Rodríguez-Clemente, X. Domènech, J. Peral, *Langmuir* **17** (2001) 891-896.

Puede encontrarse una copia de estas publicaciones en las páginas 185 y 189, respectivamente. Cabe mencionar que ninguna de ellas forma parte de otra tesis doctoral. Ambas tratan sobre la preparación de TiO_2 a partir de precursores solubles en agua a los que se aplica radiación microondas para lograr su precipitación en forma de TiO_2 cristalino.

En el caso de la primera publicación, se utilizó como precursor una solución acuosa de Ti (IV) complejado con fluoruros en presencia de H_3BO_3, que es la misma especie descrita en la Publicación 3 que conforma esta tesis doctoral. En el presente caso, sin embargo, la técnica no se utilizó para obtener películas de TiO_2 sino para obtener este material en forma de polvo. Era posible controlar el tamaño de cristal y el nivel de aglomeración del polvo mediante la variación de la concentración de las especies químicas involucradas y el tiempo de irradiación con microondas. Los materiales obtenidos no presentaban actividad fotocatalítica, posiblemente debido a su considerable contenido de fluoruros (en el rango de 2-5%).

La segunda publicación trata sobre la preparación de películas de TiO_2 sobre vidrio recubierto de ITO mediante el método de deposición desde la fase líquida asistido por microondas. En este trabajo se recirculó la disolución del precursor de TiO_2 de manera continua hacia el interior de la cavidad del horno microondas, de manera que no se permitía que aumentara la temperatura de la disolución (como ocurría en la Publicación 3 y la (1) del Apéndice). De esta manera, se observaba formación de TiO_2 sobre la superficie del vidrio recubierto del ITO, pero no en la disolución. Se utilizaron dos precursores de TiO_2 distintos: (1) una solución acuosa de Ti (IV) complejado con fluoruros en presencia de H_3BO_3 y (2) una solución acuosa de sulfato de titanilo en medio ácido.

Se obtuvieron películas de TiO_2 transparentes y muy bien adheridas. El interés del trabajo consiste en que: (1) es un método simple, (2) tiene lugar a bajas temperaturas (menores a 100ºC), (3) las películas se forman en tiempos relativamente cortos, (3) es posible el controlar el grosor de las películas mediante la potencia MW y/o el tiempo de irradiación y (4) la solución de precursor puede ser reutilizada porque la nucleación ocurre sobre el vidrio recubierto de ITO, pero no en la disolución. Las películas obtenidas a partir del precursor complejado con fluoruros estaban formadas por cristales de TiO_2 anatasa, mientras que las obtenidas a partir de sulfato de titanilo presentaban un carácter amorfo.

La colaboración en ambos trabajos fue muy útil para conocer la técnica de deposición desde la fase líquida asistida por microondas y sirvió de base para la posterior elaboración del trabajo presentado en la Publicación 3 que conforma esta tesis doctoral.

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Preparation of anatase powders from fluorine-complexed titanium(IV) aqueous solution using microwave irradiation

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The microwave radiation activated precipitation of titanium dioxide from homogeneous aqueous solutions of titanium–fluoro complexes and boric acid has been carried out in batch reactors. Crystalline anatase powders with narrow monodisperse size distribution have been obtained in a short time, at low temperature and atmospheric pressure. Microwave power, irradiation time and precursor concentration determine the properties of the obtained materials, *i.e.* crystal size, powder aggregate morphology and BET surface area. The obtained materials do not show photocatalytic activity, probably due to a considerable fluoride content that is in the range of 2–5%.

Introduction

The preparation of fine anatase particles of uniform size and specific shape is an important area of research, crucial to application in fields as diverse as catalysis, wet solar cells and ceramic synthesis. Many different strategies have been essayed in order to control the growth of titania particles, using different precursors and additives. The precursor hydrolysis kinetics is the principal factor determining the growth of titania particles. As this reaction is normally very fast for the usual TiO_2 precursors, titanium alkoxides and titanium tetrachloride, the use of different precursors or the addition of ligands to retard hydrolysis and then allow controlled growth is a current topic of research. Ligands present in the reaction medium could also favour the precipitation of one of the titanium dioxide phases: either rutile or anatase.

The production of titanium dioxide through the ligand exchange (hydrolysis) reaction between ammonium hexafluoro titanate and boric acid or aluminium metal as fluoride scavengers has been widely studied.[1–3] This reaction is used to produce titania thin films onto different substrates by a liquid-phase deposition (LPD) process. In this process, some material precipitates in the bulk of the solution, thus titania powder is simultaneously obtained, which has also been characterised.[1] In a similar area of research, our group has studied a new method for the deposition of TiO_2 thin films on conducting glass by using microwave irradiation as the heating source to promote oxide formation from homogeneous aqueous solutions of different precursors.[4,5] Microwave processing offers many new possibilities that are currently being examined.[6–9] In particular, microwave assisted precipitation of particles from water solution is a recent issue in industrial crystallisation. The rationale of this technique is the use of the solvent as the coupling agent for microwaves leading to homogeneous heating of the solution. In this way, heat-enhanced processes such as hydrolysis, ligand substitution, polymerisation, *etc.*, are favoured, eventually leading to precipitation of solids such as oxides, carbonates, phosphates and many others.[10–15] The microwave irradiation of homogeneous aqueous solutions of titanium–fluoro complexes and boric acid has used in our laboratory for the preparation of TiO_2 thin films.[5] In this paper the characteristics of nanosized powders of titanium oxide produced by the same process are described.

Experimental

Experiments were carried out in a Microwave furnace Maxidigest MX 350 (Prolabo) operating at 2.45 GHz. The instrument consists of a 250 cm^3 Pyrex reactor immersed into a resonant cavity, and equipped with a condenser. A programmer allows the control of the operating power and irradiation time. The fluorine-complexed titanium(IV) solution was prepared from titanium tetraisopropoxide (TIP), HF and NH_4F. TIP (10.0 ml, 0.034 mol) was dissolved in 50 ml of ethanol to which aqueous HF (6.0 ml 40% aqueous solution, 0.136 mol) was added. A solution of NH_4F (2.52 g, 0.068 mol) in water (100 ml) was also added subsequently. In order to evaporate the alcohols, the clear solution thus obtained was heated in an open vessel until its volume was reduced to *ca.* 30 ml. The residue was diluted with water to the volume required in order to obtain the desired final concentration. The precursor aqueous solution was freshly prepared by mixing equal volumes of the former solution and boric acid solution. In each run, 80 ml of solution were exposed to microwave radiation for different times. The specific conditions for the synthesis of each sample are summarised in Table 1. At the end of the experiments, solids were centrifuged, washed three times with distilled water and dried at 60 °C. The size distribution of the freshly obtained precipitates was analysed using a Malvern Zetasizer 3. The powder was analysed by X-ray diffraction with a Rigaku Rotaflex RU-200 B instrument using Cu-Kα (1.5418 Å) radiation, and characterised by transmission electron microscopy (TEM) using a JEOL JEM 1210 microscope. Measurements of BET surface area were performed using N_2 adsorption–desorption isotherms on a Micromeritics ASAP 2000. Each sample was heated overnight at 533 K under vacuum before measurements. For UV–Vis measurements, the powder was suspended in water using an ultrasound bath and the spectrum was recorded over the wavelength range 200–800 nm using a Varian Cary UV-V spectrophotometer. TiO_2

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Table 1 Experimental conditions

Sample	[Ti] ($\times 10^{-3}$ M)	[H_3BO_3] ($\times 10^{-3}$ M)	Microwave power/W	Heating time/h
TiO_2-A	17	34	60	2.0
TiO_2-B	17	34	60	0.50
TiO_2-C	68	136	60	0.50
TiO_2-D	17	34	30	0.50
TiO_2-E	17	34	30	0.33

fluoride content was measured with an ion selective electrode after melting the sample with a CaO–NaOH mixture and dissolving the resulting mixture with dilute HCl.

The photocatalytic oxidation of phenol in aqueous suspensions of TiO_2 under UV-illumination was studied as a test experiment, in order to determine the activity of the titania powders obtained. The concentration of TiO_2 in suspension was 1.5 g L^{-1}. A 1.0×10^{-3} mol dm^{-3} phenol solution was employed as a target. Experiments were conducted in a thermostatic cylindrical Pyrex cell of 130 cm^3 capacity. All experiments were carried out at 25.0 ± 0.1 °C. The pH of the phenol solution was adjusted to 3.0 with dilute $HClO_4$. The reaction mixture inside the cell was maintained in suspension by magnetic stirring and air was bubbled into the suspension throughout the experiment. A 125 W Philips HPK medium pressure mercury vapour lamp was used as a light source. The TOC (total organic carbon) of initial and irradiated samples were determined with a Shimadzu TOC 5000 total organic carbon analyser.

Results and discussion

In the titania precursor solution employed in the present work, titanium(IV) is strongly complexed by fluoride anions. However, an equilibrium exchange between water and the fluoro ligands takes place.[16] Therefore, in the presence of a fluoride scavenger like H_3BO_3, the equilibrium is displaced towards the hydrolysis reaction, leading to the formation of titanium dioxide.[3,17] The global reaction is very slow at ambient temperature. However, at higher temperatures the process is accelerated. Microwave radiation was used as the heating source in the experiments described here. The influence of microwave irradiation time and power has been investigated in four sets of experiments.

A quantitative yield of TiO_2 precipitate was observed in the preparation of TiO_2-A. For TiO_2-B the yield was 78%, only 39% for TiO_2-D and less than 20% for TiO_2-E. The yield was also quantitative for TiO_2-C, after only half an hour of irradiation. This means that increasing the precursor concentration provides a higher density of crystallisation nuclei that favours complete precipitation.

A good correlation between the size of the TiO_2 agglomerates precipitated from the most diluted precursor solutions and the time of heating was observed, the largest agglomerates corresponding to the more severe conditions (Fig. 1). TiO_2-C is not included in the figure because it is composed of larger agglomerates, which are difficult to maintain in suspension.

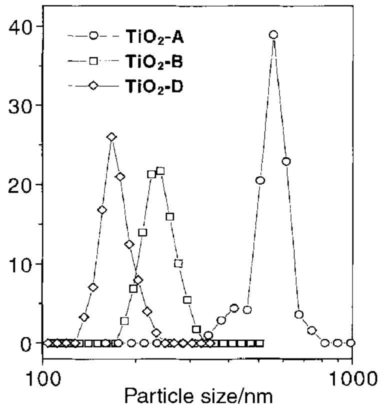

Fig. 1 Mass distribution per aggregate size of the freshly obtained precipitates for TiO_2-D (i), TiO_2-B (ii) and TiO_2-A (iii) samples.

The XRD pattern for all the samples was essentially that of anatase (see Fig. 2). Traces of rutile and $TiOF_2$ were observed for the samples obtained after the shortest irradiation time (peaks at $2\theta = 23.4°$, $TiOF_2$, and 27.4° rutile, indicated by arrows in Fig. 2). The presence of $TiOF_2$ traces in the precipitates obtained with the shortest reaction time is reasonable, since the existence of this species in titanium–fluoro complexes in aqueous solution has been described.[18] On the other hand, anatase formation is in accordance with the fact that the transformation of anatase into the thermodynamically stable rutile is inhibited by the addition of strongly titanium complexing ions, such as sulfate, phosphate or fluoride. Strongly complexing ligands hinder the condensation of TiO_6 octahedra at opposite edges to form linear chains of rutile, while growth of the spiral chains of TiO_6 octahedra constituting anatase is still possible.[19]

The peaks present different relative intensities than those of the anatase patron (which correspond to complete random order) in the XRD patterns of all samples. For example, the relative intensity of the peak corresponding to the (004) plane at 37.8° is notably increased while that of (112) plane at 38.6° is very weak (see Table 2). This fact suggests that the differential adsorption of fluoride anions on the faces of titania crystallites determines a preferential growth. It should also be noticed that the peaks are very well defined, with a small half-width, usually only attainable after annealing TiO_2 materials at temperatures well above those attained in our experimental procedure, in which the temperature increase is limited by the solution boiling point. It has been suggested that fluoride anions induce an increase in the anatase crystallinity.[20] On the other hand, peaks in the XRD pattern of the TiO_2-C sample are wider than those of the TiO_2-B sample (Fig. 3), suggesting that an increase in precursor concentration gives smaller crystallites, as we can

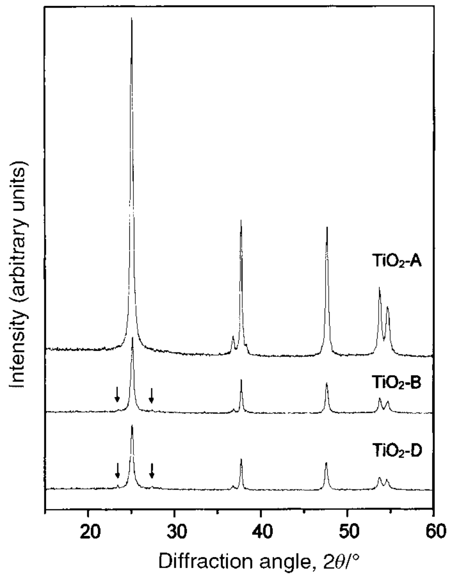

Fig. 2 XRD spectra corresponding to TiO_2 powders obtained from the same precursor solution and different microwave power and time conditions. The arrows point out minor peaks corresponding to $TiOF_2$ (left) and rutile (right) phases.

Table 2 Powder XRD data: relative peak intensity comparison between anatase patron and sample TiO_2-A

hkl	I_{rel} (patron)	I_{rel} (TiO_2-A)
101	100	100
103	10	6
004	20	42
112	10	4
200	35	42
105	20	21
211	20	16

expect considering the surely higher density of crystal growth nuclei.

TEM observations show that TiO_2-A powder consists of crystallites with elongated ellipsoid shapes mainly grouped in flower-like arrangements. Similar morphologies are observed for samples TiO_2-B and TiO_2-D (Fig. 4). A great difference is observed in the sample obtained from a higher precursor concentration, TiO_2-C. For this sample, large agglomerates are observed that seem to be made from the heavy aggregation of smaller crystallites.

BET surface area (S_{BET}) measurements give $S_{BET} = 30\ m^2\ g^{-1}$ for TiO_2-A, and $85\ m^2\ g^{-1}$ for TiO_2-B, showing that an increase in the heating time leads to a decrease in the surface area. An S_{BET} value of $140\ m^2\ g^{-1}$ was observed for sample TiO_2-C, indicating that this material is porous. Changes in sample texture observed by TEM are related to different shapes on the nitrogen adsorption–desorption isotherm (Fig. 5).

Fig. 6 shows the UV–Vis spectra obtained from the light transmitted through suspensions of TiO_2 powders with a 1 cm optical path length, prepared as in ref. 21. The concentrations of each sample are practically the same and are given in the figure caption. In ref. 21, the light scattering and light absorption spectral dependences of different TiO_2 powder suspensions are obtained from experimental transmission spectra. The log(1/*T*) dependence of the experimentally obtained spectra show a good correspondence in the high energy range with computed absorption spectra, due to the predominance of absorption over scattering in this range. Absorption spectra corresponding to Degussa P-25 show the best well-defined absorption edge because of the abrupt increase in the absorption. This is not so for the rest of the TiO_2 powders studied. This can be explained because the absorption edge is a consequence of the band structure and this depends on the atoms order in the solid. Therefore, Degussa P-25 shows a higher crystallinity than the rest of the powders in ref. 21. Comparing results in Fig. 6 with those of ref. 21, it can be said that the degree of crystallinity of TiO_2 obtained with microwave heating over two hours almost equals that of Degussa P-25. The absorption edge is less defined for spectra corresponding to only 30 min of microwave heating. It can be observed that in this last case, the precursor solution is still present in some amount and this causes the absorption to increase abruptly around 220 nm.

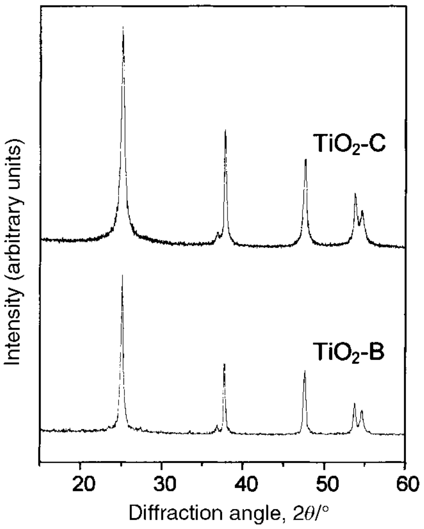

Fig. 3 XRD spectra corresponding to TiO_2 powders obtained after 30 min of 60 W microwave irradiation with the two different precursor solutions employed.

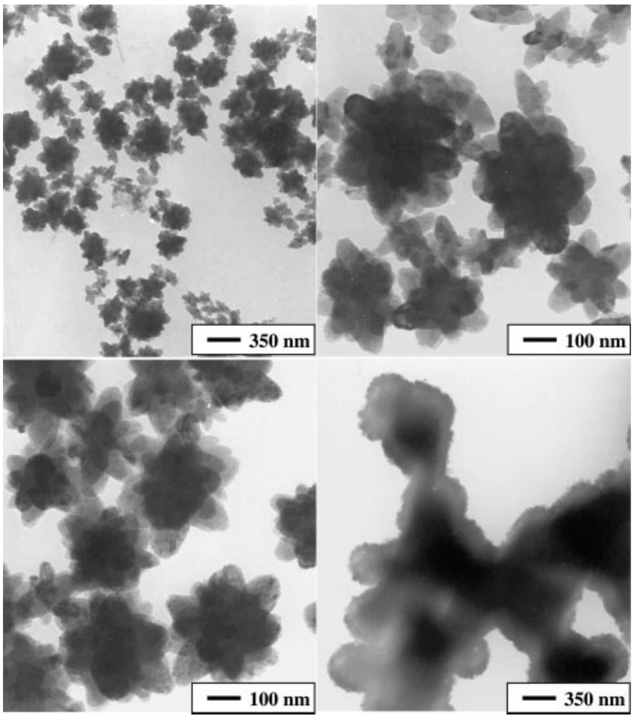

Fig. 4 TEM photographs of (top) TiO_2-A, (bottom left) TiO_2-B and (bottom right) TiO_2-C.

Elemental analysis of the different samples shows that they contain amounts of fluoride that follow particular trends. The mass percent of fluoride slightly decreases when the microwave irradiation time increases: TiO_2-B contains 3.9% F, while TiO_2-A contains 3.5% F. The most concentrated precursor solution gives the sample with more F^- content: sample TiO_2-C retains 4.4% F. Annealing reduces the fluoride content but complete removal of the halogen is never observed. For example, the sample TiO_2-A retains 2.2% F after annealing at 573 K for 2 h. This fact suggests that, although part of the fluoride anions that were adsorbed on the oxide surface could be easily removed, a significant amount must be included in the bulk of the oxide, where complete removal is difficult. Fluoride anions may substitute oxygen in the TiO_2 structure, being incorporated to some extent into the anatase lattice.[19] Nevertheless, the amounts of fluoride are lower than those reported from the same precursor in LPD experiments at lower temperature.

Deki *et al.* have reported the photocatalytic activity of anatase samples (films and powder) produced from a similar precursor.[1] Their samples are less crystalline and contain a higher amount of fluoride (7.2% fluoride in the as-synthesised sample), but despite this fact, they are photoactive in the degradation of acetaldehyde in the gas phase. We have essayed thoroughly the photocatalytic activity of our TiO_2 samples front phenol, an experiment that has been proposed as standard,[22] but no significant TOC reduction was observed. Most probably the content of fluoride is the origin of the lack of photocatalytic activity for our titania samples. Under the same experimental conditions, TiO_2 Degussa P-25 allows the complete mineralization of phenol in 6.5 h. Further informa-

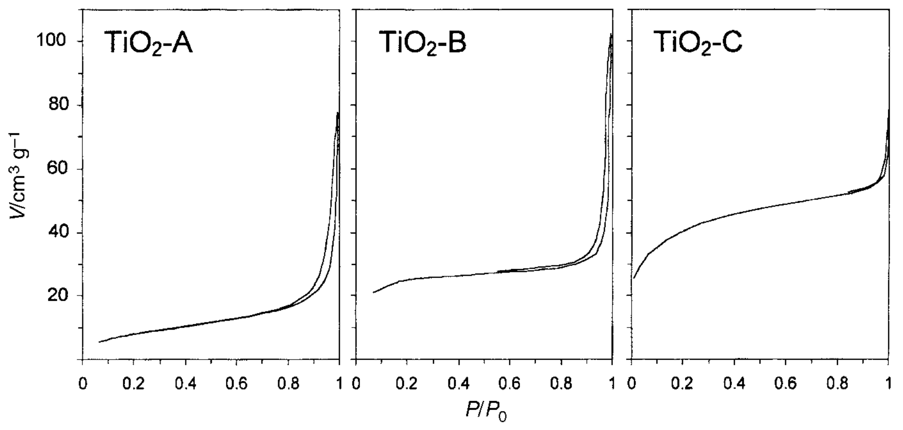

Fig. 5 N_2 gas adsorption–desorption isotherms for samples TiO_2-A, TiO_2-B and TiO_2-C. The N_2 volume is at standard temperature and pressure (STP) and P/P_o is the relative partial pressure of N_2 in equilibrium with the sample at 77 K.

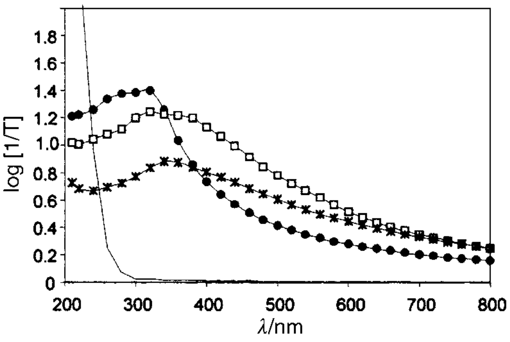

Fig. 6 Spectra obtained from the spectral measurement of light transmitted through a suspension of TiO_2 with a 1.0 cm optical path length. The concentration for both Degussa P-25 (●) and TiO_2-B (*) is 0.042 mg ml^{-1}. For TiO_2-A (□), the concentration is 0.047 mg ml^{-1}. Absorption corresponding to the precursor solution is also shown for comparison (solid line).

tion about titania doped with fluoride is given in the references. Positive effects have been found for low fluoride content. The photoactivity of TiO_2 films, obtained by a sol–gel procedure, was significantly enhanced by addition of a small amount of ammonium fluoride into the sol–gel precursor.[20] The optimum amount of F was 0.06%, a percentage far lower than those found in our samples. An improvement in the photoelectrochemical response of rutile single crystal electrodes doped with fluoride ions, in the order of 0.01%, has also been observed.[23] On the other hand, negative effects of fluoride in the photoactivity of titania have also been reported. Fluorides strongly adsorb to the TiO_2 surface and interfere with adsorption of organic substrates.[19,24] The photocatalytic activity of TiO_2 is decreased after surface fluorination with fluoromethane.[25]

Conclusions

Microwave irradiation of aqueous solutions of titanium–fluoro complexes containing boric acid as fluoride scavenger allows the synthesis of highly crystalline anatase TiO_2 powders at very low temperatures, under atmospheric pressure and in a short period of time without annealing. The crystal size and agglomeration level of the TiO_2 powders obtained can be controlled by modifying the concentration of the chemical species involved and the time of microwave irradiation. For a 0.034 M precursor concentration, the most appropriate irradiation time was two hours in order to obtain maximum yield and high crystallinity. For shorter irradiation times, yields were lower, crystallinity decreased and the fluoride content in the materials was higher, though less than previously reported.[1] Our materials did not show photocatalytic activity, contrary to previous reports.[1] We believe that this is possibly due to their contamination with fluoride anions from the precursor.

Acknowledgements

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TiO_2 Layers Grown from Flowing Precursor Solutions Using Microwave Heating

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TiO_2 films have been deposited on indium tin oxide covered glass. These substrates are immersed in a flowing aqueous solution containing a soluble titania precursor. TiO_2 growth is activated by microwave (MW) radiation heating. This method produces transparent and well-adhered films at low temperatures (lower than 100 °C) and short times. Flowing the precursor solutions allows growth of titania films on the substrate and avoids titania powder precipitation in the solution. It is demonstrated that thickness and crystallinity are controlled through MW power, process time, and precursor choice.

Introduction

Interest in some very prospective applications of nanostructured TiO_2 has given rise to a considerable number of reports concerning different techniques for obtaining nanostructured thin films of this semiconductor.[1−11] Well-packed films completely covering the substrate surface are necessary for certain applications.[12,13] Good adherence is also very desirable. We have previously reported on the use of microwaves (MW) for obtaining TiO_2 thin films using two different precursor solutions.[14,15] Quiescent solutions were used in both cases. The obtained films were well-adhered and transparent. Their crystalline structure was anatase, and they showed different degrees of crystallinity depending on the precursor solution and technological parameters used. As far as we know, microwave heating had not been used for growing thin films previously to these reports. In these previous papers where quiescent solutions were used,[14,15] we argue about the possible role that MW could be playing, different from traditional heating. Two mechanisms were considered in ref 15: direct growth of TiO_2 on the surface and nucleation in the solution that later adheres to the growing layer surface. For the first mechanism, we considered it plausible that growth is favored by the MW interaction with the conduction electrons[16,17] of the conducting layer on the glass substrate. The acquired electron energy given up to lattice vibrations could be thought of as a localized heating of the conducting layer. This would favor the growth of TiO_2 on the substrate even before the solution acquires the necessary temperature for the formation and nucleation of TiO_2, and it probably adds up to the possible role of the substrate acting as seed for nucleation.

In the present report, the conducting substrate, ITO glass (indium tin oxide covered glass), has been immersed in a flowing precursor solution, seeking to form TiO_2 only on the conducting glass and not in the solution, because the flowing solution is not allowed to heat up as in previous experiments using quiescent solutions.[14−15] This would demonstrate that the ITO layer enhances the growth of TiO_2 on its surface because of an activating effect. On the other hand, the proposed growth technique is of technological importance. This is due to (a) the characteristics of the grown layers (good adherence and transparency), (b) the simplicity of the technique, (c) the possibility of controlling the layer thickness with MW heating time, (d) the low temperatures needed, and (e) the possibility of reusing the precursor solution. In this paper, we describe for the first time the deposition and the characteristics of thin TiO_2 films that have been deposited from two different flowing precursor solutions using MW heating.

Experimental Description

The experimental setup is shown schematically in Figure 1. The flow speed, heating time intervals, and MW heating were adjusted so that the solution temperature was below 50 °C for all experiments in order to prevent the nucleation of TiO_2 in the precursor solution. Because the precursor solutions used were transparent and colorless, haziness was immediately visible when nucleation in the solution reached a significant concentration.

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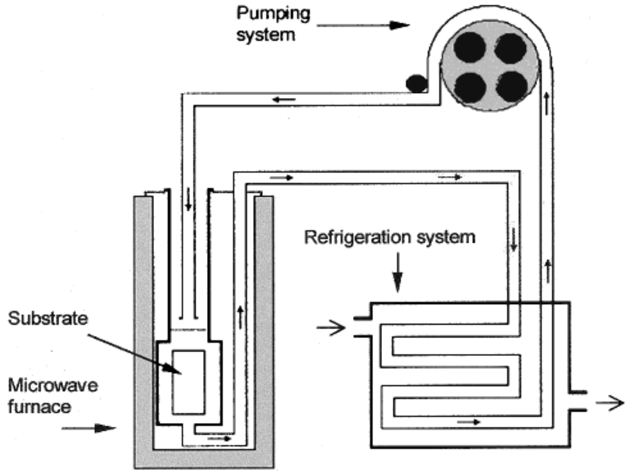

Figure 1. Experimental setup.

Table 1. Conditions Used for the Different Deposition Experiments

sample	precursor solution[a]	MW power (W)	heating time (min)
S-10-10	S	30	10
S-10-20	S	30	20
S-10-30	S	30	30
S-10-40	S	30	40
S-10-60	S	30	60
S-40-2	S	120	2
S-40-4	S	120	4
S-40-5	S	120	5
S-40-16	S	120	16
S-40-20	S	120	20
F-40-5	F	120	5
F-40-10	F	120	10
F-40-20	F	120	20
F-40-24	F	120	24

[a] Solution S is a homogeneous aqueous solution composed of $[TiOSO_4] = 5 \times 10^{-3}$ M and $[H_2SO_4] = 2.5 \times 10^{-3}$ M. Solution F consists of equal volumes of a fluorine-complexed titanium(IV) solution ($[Ti] = 3.4 \times 10^{-2}$ M) and a 6.8×10^{-2} M boric acid solution. [4]

If the external cooling (see Figure 1) was not efficient enough to prevent formation of TiO_2 in the solution, growth experiments were conducted by interrupting the MW power cyclically so as to give time for the solution to cool during the MW-off period. This occurred in experiments with higher MW power and/or relatively longer heating times. A recirculating flow of 2−3 mL/s was used. The amount of circulating precursor solution was 35 mL; therefore, in the time intervals used (see Table 1) there were around 10−100 recirculating cycles of the precursor solution.

A Maxidigest MX 350 (Prolabo) microwave furnace operating at 2.45 GHz and 300 W maximum power was used.

The resistivity of the ITO glass substrate was 10 Ω\□. Pieces with a 15 × 7 mm area were cut. They were thoroughly cleaned and sonicated with organic solvents before each experiment. The substrate immersed in the precursor solution was sonicated for 3 min before each deposition process.

Two different precursor solutions were tried. Solution S was a homogeneous aqueous solution composed of $[TiOSO_4] = 5 \times 10^{-3}$ M and $[H_2SO_4] = 2.5 \times 10^{-3}$ M.[14] Precursor solution F was freshly prepared by mixing equal volumes of a fluorine-complexed titanium(IV) solution ($[Ti] = 3.4 \times 10^{-2}$ M) and a 6.8×10^{-2} M boric acid solution prepared as described in ref 15. Conditions used for the different experiments performed appear in Table 1. Deposition experiments using only 10% of the total microwave power (30 W) were successful with solution S but not with solution F.

Layer growth was easily noticed because of the color change of the reflected light that is due to different deposited thicknesses and thin-film light interference. The obtained samples were very transparent. No whitish appearance due to light scattering was observed as in ref 15. This was expected because this haziness must be due to TiO_2 formed in the solution that later adheres to the growing film.[15]

To investigate their microcrystalline structure and surface characteristics, films from different regimes were gold-covered and examined with scanning electron microscopy (SEM). Also, optical absorption and transmittance spectra were obtained using a HP8453 spectrometer. Transmittance spectra were used to analyze relative film thickness behavior from the spectral difference of consecutive maxima shown. Wavelength values corresponding to spectrum maxima were found using numerical differentiation of the spectra. Absorption spectral shape was used to investigate the gap energy that depends on the internal Bloch potential, in other words, on the way in which atoms are ordered in the crystalline phase. To further study atom ordering, X-ray diffraction experiments were performed with each of the different samples. Cu Kα radiation ($\lambda = 0.154\,056$ nm) was used for all X-ray experiments.

Results and Discussion

As can be observed in Table 1, three types of processes were used and for each the heating time was changed from sample to sample. Two processes used titanyl sulfate as the precursor solution, and the difference between them was the MW heating power used. The third one used the fluorine-complexed titanium(IV) solution, and the MW heating power was equal to the highest one used (120 W) with the other precursor solution. When using this precursor, it was not possible to obtain films with the lowest MW heating power used (30 W).

In Figure 2, SEM images corresponding to these three different types of technological process are shown. Parts a and b of Figure 2 correspond to processes in which titanyl sulfate as the precursor and 10% of the maximum heating power were used. The sample shown in Figure 2a had the shortest heating time for this type of process (10 min), and the sample shown in Figure 2b had the longest one (60 min). These images show that the smallest particles seen are approximately 10 nm in both cases. They tend to join together and form islands, but each island is an agglomeration of these smaller particles. They do not form a larger crystal; frontiers are visible. The difference between the sample heated for 10 min and the one heated for 60 min appears in the separation between islands, that grows smaller with time, rendering a better covering of the substrate surface.

In Figure 2c,d, samples obtained with short (2 min) and long (16 min) heating times are shown corresponding to the second type of technological process. That is, titanyl sulfate was also used as precursor solution but the heating power used was 4 times larger than in the first case. The aspects previously mentioned for comparison between parts a and b of Figure 2 also apply to the comparison between parts c and d of Figure 2. When comparing these two processes with different MW heating powers (30W and 120 W), it must be noted that equivalent surface coverage is obtained with a shorter heating time when MW power is increased, but the nanostructure character is very similar for both. Parts e and f of Figure 2 show samples corresponding to the third type of process in which the fluorine-complexed titanium(IV) solution was used as the precursor. Figure 2e, with the shorter heating time, does not differ much from parts a and c of Figure 2, which also correspond to shorter heating times in the two previous process types. Nonetheless, the difference between Figure 2f and the rest is remarkable. The smaller particles assemble in rounded grains. Parts a and b of Figure 3 also show the difference between the layer F-40-20 obtained using the fluorine-complexed titanium(IV) solution and sample S-40-16 obtained with similar MW

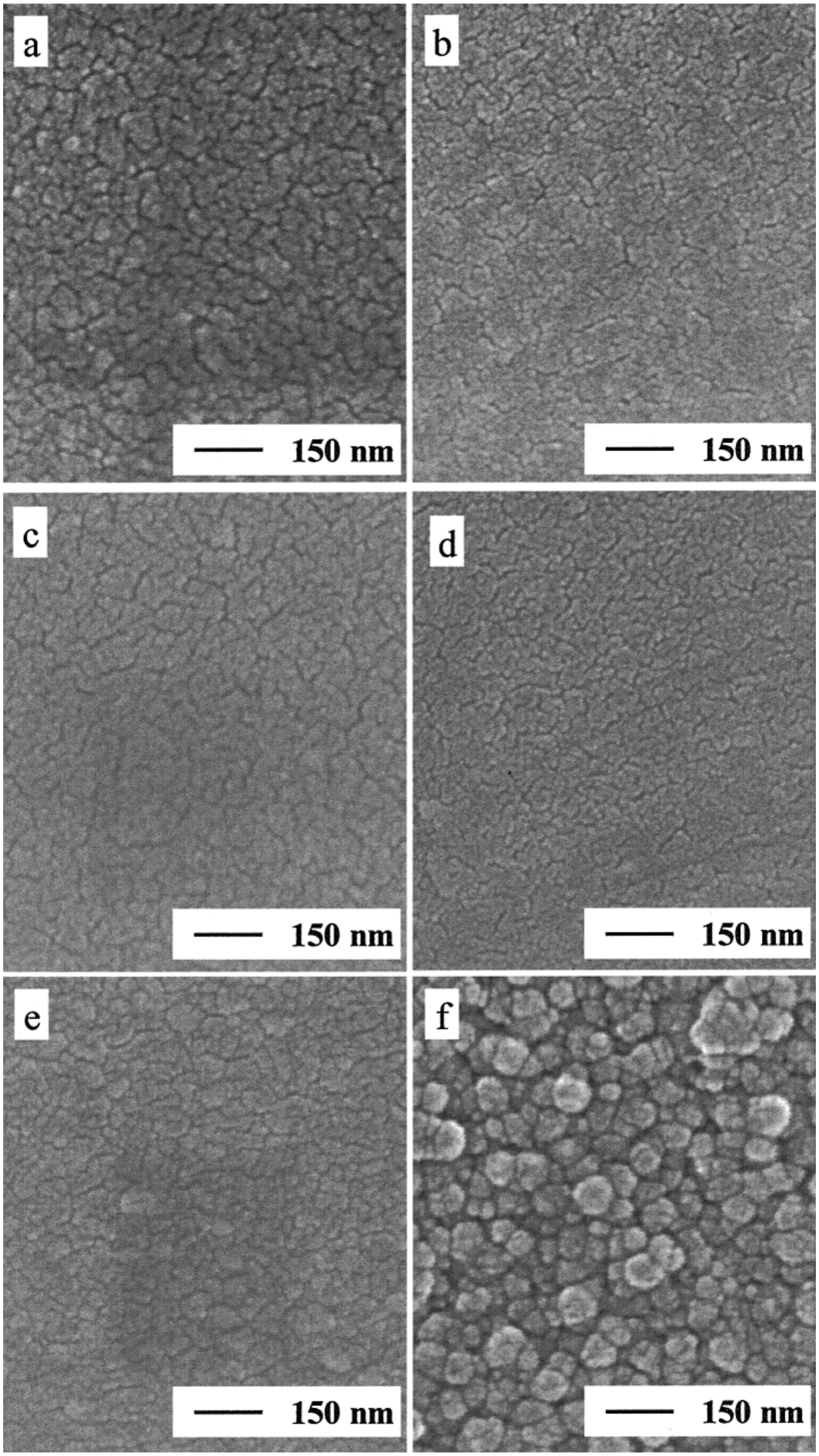

Figure 2. SEM images of TiO_2 films obtained under different regimes: samples S-10-10 (a), S-10-60 (b), S-40-2 (c), S-40-16 (d), F-40-5 (e), and F-40-24 (f).

heating power and time but using titanyl sulfate as the precursor. As observed, even for this smaller magnification the difference is quite remarkable. This fluorine-complexed titanium(IV) solution used also in ref 15 rendered layers with very good crystallinity even without thermal post-treatment, which was not the case for layers reported in ref 15 using the other precursor solution.

To further study crystallinity, X-ray diffraction experiments were performed. Figure 4 shows diffraction spectra corresponding to the ITO glass used as substrate (a), sample F-40-24 (b), and sample S-40-16 without heat treatment (c). This sample was heat-treated for 2 h at 450 °C, and the corresponding spectrum is also shown in Figure 4d. Relative intensities for the diffraction peaks corre-

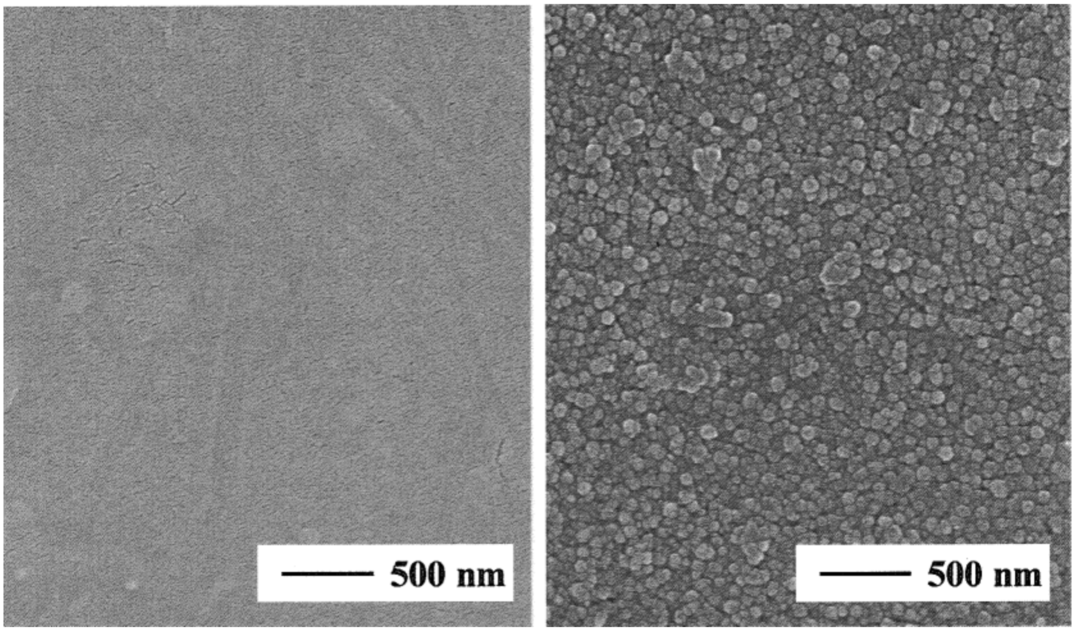

Figure 3. SEM images of samples S-40-16 (left) and F-40-24 (right).

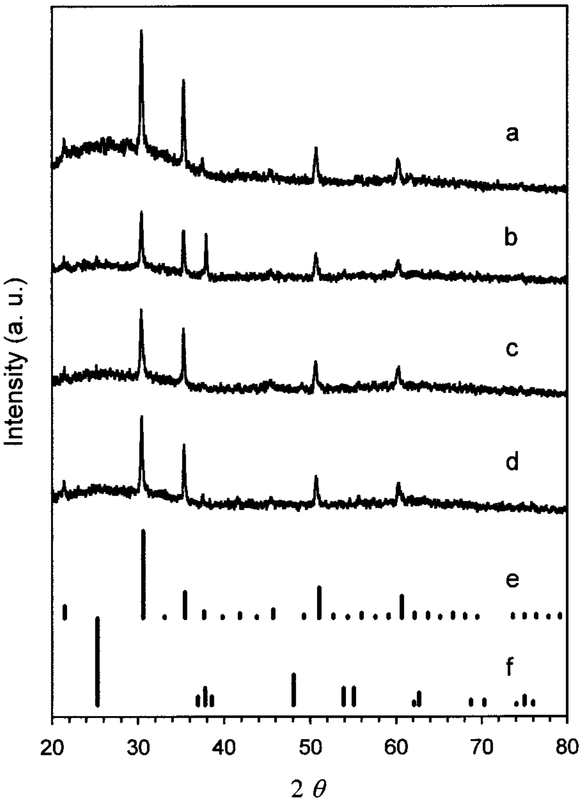

Figure 4. XRD patterns corresponding to ITO covered glass used as substrate (a), sample F-40-24 (b), sample S-40-16 (c), and sample S-40-16 after heat treatment (d). Also shown are the relative intensities of diffraction peaks for randomly oriented crystals of In_2O_3 (e) and TiO_2 anatase (f), from JCPDS reference data.

sponding to JCPDS reference data of In_2O_3 (pattern 6-416) and the TiO_2 anatase phase (pattern 21-1272) are also shown in parts e and f of Figure 4, respectively.

Comparison of parts a and b of Figure 4 shows the appearance of a narrow peak at $2\theta = 37.8°$ ($d = 2.37$ Å) which corresponds to the crystal plane (004) of the anatase structure. In Figure 4f, one can observe that the (101) line is the dominant one for randomly oriented crystals, but in the film studied in Figure 4b this line is not differentiated from the random noise. Therefore, from the higher intensity of the (004) peak in Figure 4b, it can be said that there is a preferential direction for crystal growth. The high degree of crystallinity obtained with the fluorine-complexed titanium(IV) precursor solution must be pointed out. This is evident from the half-width of the (004) peak. In Figure 4c, no peaks other than those corresponding to the ITO layer are visible; that is, an as-grown film with one of the larger thicknesses, that was obtained using titanyl sulfate as precursor solution and the highest MW heating power, does not present the crystallinity of the sample shown in Figure 4b. Even after heat treatment of this film, S-40-16, a peak at $2\theta = 37.8°$ ($d = 2.37$ Å) corresponding to plane (004) of the anatase structure is hardly visible (see Figure 4d); neither is the clear peak (101). The anatase (004) peak is very close to the small (411) peak at $2\theta = 37.7°$ of the ITO structure (see Figure 4a,e). From the relative intensities between this hardly visible peak in Figure 4d and the peaks at $2\theta = 30.6°$ and $2\theta = 35.5°$ of the ITO structure, it cannot be ascertained that there is an extra contribution to the diffraction intensity present in Figure 4d from the TiO_2 layer. Apparently, films obtained with the fluorine-complexed titanium(IV) precursor solution tend to crystallize in the anatase structure as the film thickness grows, whereas those obtained with the titanyl sulfate solution have an amorphous character. This result agrees with the previous SEM images shown in Figures 2 and 3.

Parts a−c of Figure 5 show transmission spectra corresponding to some of the samples obtained using the two different precursor solutions, titanyl sulfate and fluorine-complexed titanium(IV). Interference maxima were visible in all samples measured. The transmittance spectra of all samples obtained using titanyl sulfate as the precursor solution showed at least two maxima. In this case, it was possible to measure the spectral difference between adjacent maxima. This difference must be related to the thickness of the deposited TiO_2 film because the thickness of the ITO layer is constant for all samples. The previous statement assumes that there is no change in interference order, which should be the case according to the spectral position of the maxima in Figure 5. In Figure 6, these differences have been plotted. From the behavior

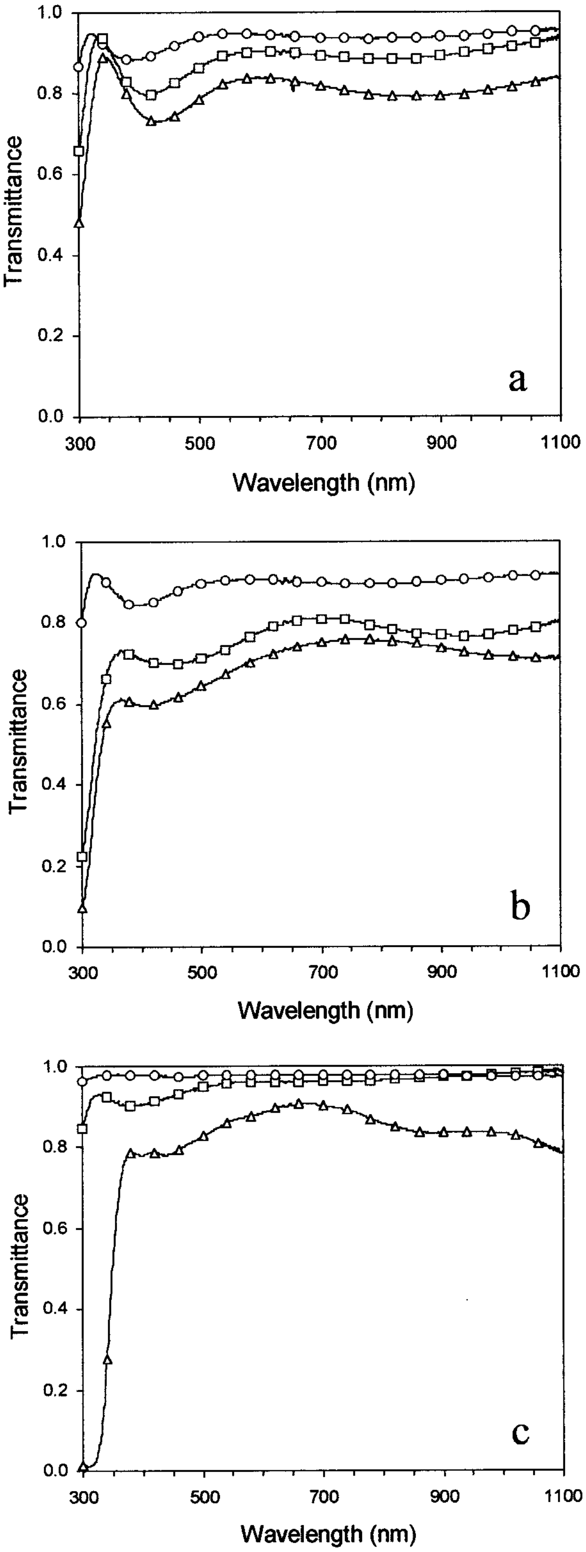

Figure 5. Transmission spectra: (a) samples S-10-20 (○), S-10-30 (□), and S-10-60 (△); (b) samples S-40-2 (○), S-40-4 (□), and S-40-20 (△); (c) samples F-40-5 (○), F-40-10 (□), and F-40-20 (△).

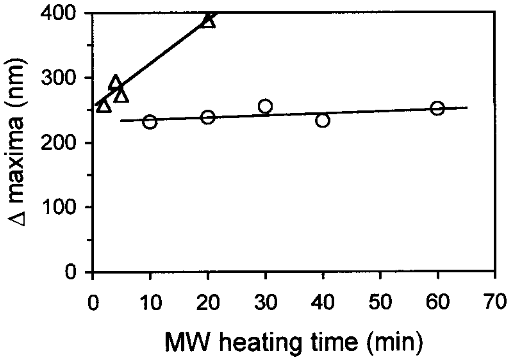

Figure 6. Spectral difference between adjacent maxima of the transmission spectra obtained from solution S: (△) MW power of 120 W and (○) MW power of 30 W.

of this spectral difference, it is clear that the thickness of the samples increases with MW heating power. An increase with heating time is also evident for samples obtained with the higher MW power. Using the data shown in Figure 6, the straight lines that best fit the shown data were calculated, and they are also shown. According to the behavior of samples obtained with higher microwave power and the small slope of the best-fitted straight line corresponding to samples obtained with the lower MW power in Figure 6, one can expect that thickness does increase but very slowly in this case. The thickness differences obtained for the lower MW power with heating time are smaller, and therefore it is more difficult to establish these differences experimentally. The dependence on MW heating time and power is important for the control of sample thickness in future applications of this new technique. In the previous experiments reported in refs 14 and 15, nucleation of TiO_2 in the liquid depleted the precursor solution and consequently limited the layer thickness of the grown sample. Therefore, besides being able to reuse the precursor solution, the use of precursor flow makes it easier to control the thickness of the growing film with time and/or MW heating power. Through a comparison of the values of transmittance in Figure 5b,c, it can be said that the thickness of sample S-40-20 is greater than that of sample F-40-20. Therefore, the titanyl sulfate precursor solution favors TiO_2 deposition more than the fluorine-complexed titanium(IV) precursor solution. On the other hand, as noticed before from X-ray experiments, the fluorine-complexed titanium(IV) precursor solution favors crystallinity, contrary to the titanyl sulfate precursor solution. It can be concluded that the titanyl sulfate precursor solution is more efficient in promoting TiO_2 deposition but less effective in producing high crystallinity.

The absorption coefficient spectral dependence was assumed to be given by (1) in the spectral range above 3.75 eV where the absorption coefficient α for anatase is greater than 2×10^5 cm^{-1}.[18,19] In this case, light transmission is mostly determined by absorption and reflection can be neglected. Therefore, the spectral dependence of the absorption coefficient is given by the spectral dependence of the absorbance, A:

$$\alpha(h\nu) \sim A(h\nu) = \log(1/T) \qquad (1)$$

The value of the gap energy for indirect gap semiconductors, such as anatase, can be obtained from

$$\alpha(h\nu) \sim (h\nu - E_g)^2/(h\nu) \qquad (2)$$

Taking into consideration expression 1, spectra have been processed in order to obtain the energy band-gap from expression 2.

In Figure 7, the corresponding spectral dependencies of $(\alpha(h\nu)\, h\nu)^{1/2}$ in arbitrary units have been plotted to find

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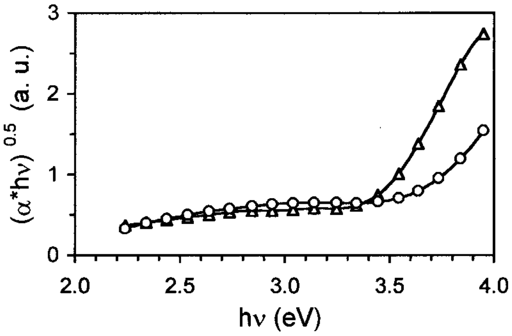

Figure 7. Spectral dependence of $(\alpha(h\nu)\ h\nu)^{1/2}$ in arbitrary units for the S-40-20 (○) and F-40-20 (△) samples.

the value of E_g for two of the samples with higher thickness values, each grown with a different precursor. For these thicker samples, the values of E_g obtained are the closest to reported values for anatase that are around 3.2 eV.[20] The best agreement exists for the sample grown using the fluorine-complexed titanium(IV) precursor solution. For samples with smaller thicknesses, the values of E_g obtained following this procedure are over 3.3 eV and as high as 3.7 eV. Values higher than 3.2 eV have been reported before.[21−23] We think that, at least in our case, this results from the disordered nature of these samples, as shown in X-ray experiments. The E_g results are in agreement not only with the previous X-ray analysis (Figure 4) but also with the SEM images (Figure 2).

Conclusions

TiO_2 layers have been grown on top of ITO conducting layers using microwave heating and a flowing precursor solution for the first time. The samples obtained had a high transparency and were well adhered. The following advantages have been found for the method described: it is very simple, it uses low temperatures (less than 100 °C), layers grow in a relatively short time, thickness control is possible through MW power and/or time, and the precursor solution can be reused because nucleation occurs on the sample but not in the solution.

SEM images of the samples obtained with two different precursor solutions, fluorine-complexed titanium(IV) and titanyl sulfate, show that all samples are nanostructured. The morphology observed for most of them is very similar; only the surface coverage increases with time and power. The morphology obtained using the fluorine-complexed titanium(IV) precursor solution and a heating time of 20 min or more is an exception (see Figure 2f). In this case, smaller nanoparticles assemble in rounded grains. X-ray diffraction of this sample shows a very well defined anatase structure, whereas the rest show an amorphous character. It is concluded that the fluorine-complexed titanium(IV) precursor solution favors crystallization in the anatase structure more than the titanyl sulfate precursor solution. Nonetheless, the failure to grow films with the fluorine-complexed titanium(IV) precursor solution using only 30 W and the relative sample thicknesses inferred from transmittance spectra characteristics indicate that, given equal MW power and growth time, thicker films are obtained with the titanyl sulfate precursor solution. Gap energy was analyzed using the absorbance spectral dependence. A value of 3.2 eV corresponding to the anatase structure was found for thicker samples, but those with smaller thicknesses showed higher energy gap values because of their disordered nature.

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Apéndice 2

En este Apéndice se recogen brevemente algunos datos sobre un último trabajo realizado en esta tesis doctoral que, por limitaciones de tiempo, está pendiente de publicación.

Como ya se ha visto en el Capítulo 4, apartado 3, es posible utilizar la radiación microondas para asistir la deposición de películas finas de TiO_2 sobre vidrio conductor. En el trabajo que se recoge en este Apéndice se amplia el uso de esta técnica a la deposición de ZnO sobre vidrio conductor.

El interés de la preparación de películas de ZnO se encuentra en sus múltiples propiedades, que permiten su uso en aplicaciones tan diversas como en sensores luminiscentes, sensores amperométricos, sensores fotoconductores, celdas solares sensibilizadas[Keis,K.1999][Tsubomura,H.1976] e incluso como catalizadores en reacciones de fotocatálisis heterogénea.[Neppolian,B.1999][Poulios,I.1998][Yeber,M.C.2000]

Se han utilizado gran variedad de técnicas en la preparación de películas de ZnO. Al igual que en el caso de las películas de TiO_2, página 58, se han utilizado métodos físicos *(sputtering,*[Exarhos,G.J.1995] *pulsed laser deposition,* [Exarhos,G.J.1995][Prasad,S.V.2000] *pyrosol deposition,*[Smith,A.2000] etc.) y químicos (electro-deposición catódica,[Gal,D.2000] deposición electroforética,[Hossein-Babaei,F.2000] *sol-gel dip-coating,*[Ignjatovic,N.1998] *sol-gel spin-coating,*[Meulenkamp,E.A.1999][Natsume,Y.2000] etc.).

El desarrollo de una técnica basada en el uso de radiación microondas como fuente de energía que induce la precipitación del ZnO sobre el substrato tiene varias ventajas, como son la simplicidad de la técnica y que el proceso de deposición tiene lugar a baja temperatura (siendo la temperatura máxima alcanzada en el proceso la de ebullición del disolvente, que es H_2O en el presente estudio). Los tiempos de deposición son inferiores a 30 minutos, por lo que el consumo de energía también es bajo. Por último, bajo estas condiciones de deposición relativamente suaves, es posible obtener depósitos cristalinos de ZnO.

El proceso desarrollado se inicia sumergiendo el substrato deseado, en este caso vidrio recubierto de SnO_2:F y vidrio recubierto de ITO (óxido de Sn e In), en una solución acuosa del precursor de ZnO (nitrato o acetato de Zn) y de un complejante orgánico (urea, hexametilentetraamina (HMTA) o ácido etilen-diamintetraacético (EDTA)). A continuación, se aplica radiación microondas al conjunto y tiene lugar la hidrólisis del precursor de ZnO y la deposición de ZnO sobre el substrato. Es bien conocida la hidrólisis de la urea al aumentar la temperatura, dando lugar a medio básico. El equipo y metodología utilizados son los mismos que se han descrito anteriormente, en la Publicación 3, para la obtención de películas de TiO_2.

Mediante el proceso descrito, se obtuvieron películas cristalinas de ZnO (wurtzita), fuertemente adheridas al substrato. El grado de recubrimiento del substrato depende las siguientes variables experimentales:

1) La potencia de la radiación microondas: mayor potencia implica mayor recubrimiento;
2) El tiempo de reacción: tiempos más largos implican mayor recubrimiento;
3) La relación molar del precursor de ZnO y el complejante: existe una relación molar óptima, que da lugar a mayor recubrimiento, para una potencia y tiempo fijos;
4) La concentración inicial de los reactivos: mayor concentración implica mayor recubrimiento;
5) el substrato utilizado: se ha observado mayor deposición sobre vidrio recubierto de ITO que sobre vidrio recubierto de SnO_2:F, siendo el primero el más conductor.

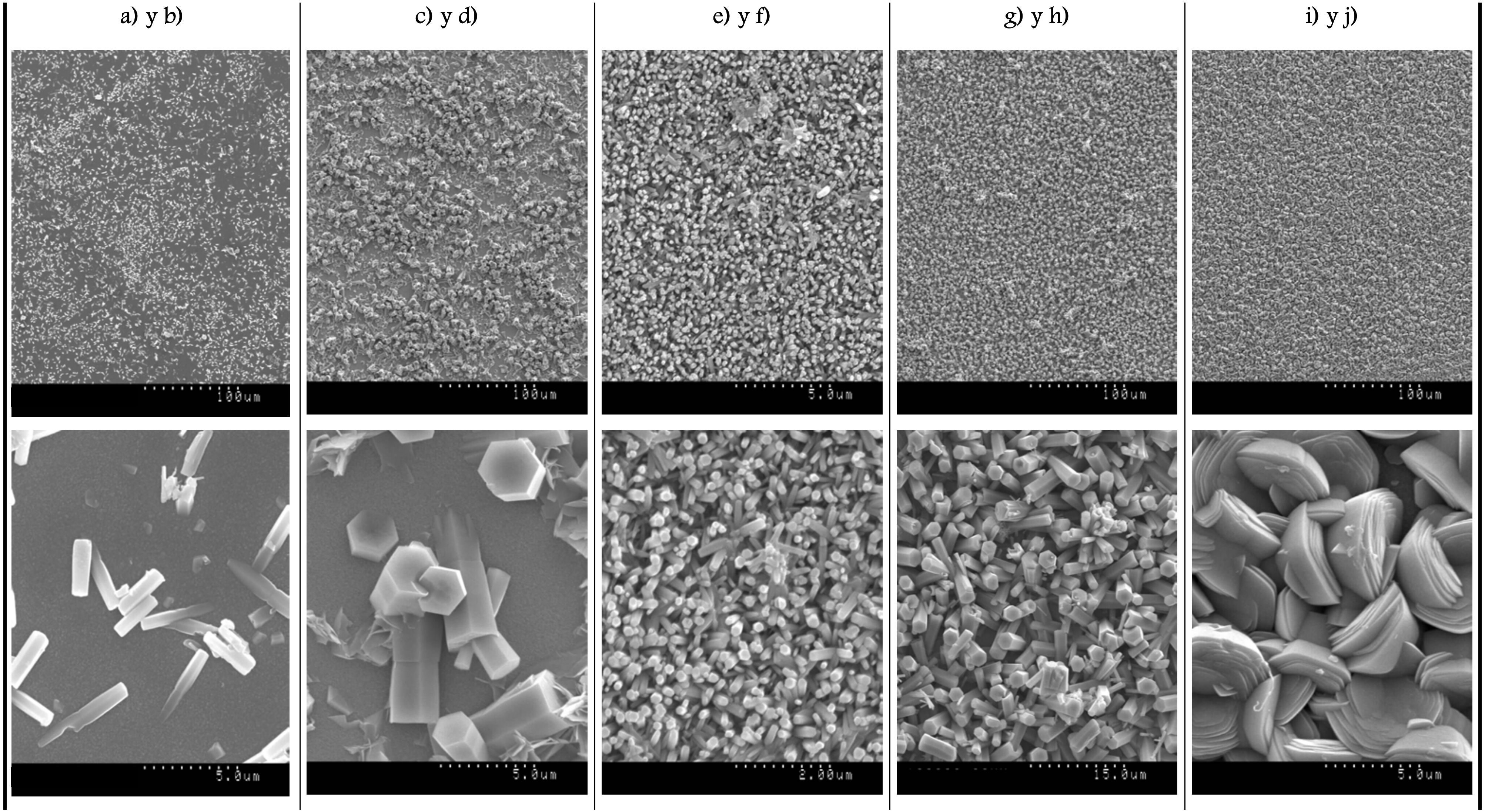
Asimismo, también es posible modular la morfología de los cristales de ZnO según la naturaleza del precursor de ZnO y del complejante. El tamaño de los cristales depende de la potencia y del tiempo de deposición utilizados. Estas películas mostraron fotoluminiscencia. Su uso en reacciones de fotocatálisis heterogénea para la degradación de compuestos orgánicos en agua se prevé en un futuro próximo.

Por último, en la Figura 17 se muestran algunos ejemplos de películas de ZnO obtenidas mediante el proceso descrito. Las imágenes están agrupadas por parejas, correspondiendo ambas a la misma película, con diferente grado de magnificación. Las condiciones experimentales en las que fueron obtenidas estas películas se indican en la Tabla 13.

Tabla 13. Condiciones experimentales de obtención de películas de ZnO mediante irradiación de los precursores acuosos con microondas. Substrato: vidrio recubierto de SnO_2:F

Película	[$Zn(NO_3)_2$] (M)	[$ZnAc_2$] (M)	[urea] (M)	[HMTA] (M)	[EDTA] (M)	Tiempo (min)	Potencia radiación (W)
a) - b)	0,068	---	0,272	---	---	20	105
c) - d)	---	0,068	0,408	---	---	20	105
e) – f)	0,068	---	---	0,068	---	12	150
g) - h)	---	0,050	---	0,05	---	30	60
i) - j)*	---	0,047	0,256	---	0,006	8	150

* Proceso de irradiación repetido cuatro veces consecutivas sobre el mismo substrato.


a) y b)
c) y d)
e) y f)
g) y h)
i) y j)
100um
100um
5.0um
100um
100um
5.0um
5.0um
2.00um
15.0um
5.0um

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