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Antimicrobial activity of Fe–TiO_2 thin film photocatalysts

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ABSTRACT

Fe–TiO_2 sol–gel thin film photocatalysts were prepared by the spin-coating method. Precursory Fe–TiO_2 films, containing 3 and 5 wt.% Fe, were thermally treated at 400 and 800 °C; the dominant crystalline phases of TiO_2 were anatase and rutile, respectively. The thin films were characterized by X-ray diffraction, UV–vis spectroscopy, and scanning electron microscopy. The antimicrobial photocatalytic activity over colonies of *Escherichia coli* bacteria, deposited on the thin films and induced by the incidence of visible radiation was evaluated by the plate counting method. The thin film containing 5 wt.% Fe and treated at 800 °C had a microcrystalline texture and could eliminate *E. coli* bacteria completely after 60 min. In these materials the active phases are both anatase and rutile.

1. Introduction

Surface chemistry investigation has been significantly increasing as it is shown by the numerous studies that have been recently performed about this topic. Many studies in surface chemistry deal with activated materials and, indeed, the thermal activation of surface processes on diverse substrates is currently a driving force behind a myriad of technological applications.

Electronic excitation is another source of surface activation, which can be induced by absorption of electromagnetic radiation. The electronic activation of surface species has become the first step for developing a new surface chemistry on various materials. Exploration concerning the electronic activation of surface processes is now a very actively and recurring research front line and, in the future, it will grow significantly in interest with respect to sunlight employment for producing electricity and to create and apply new photocatalytic surfaces [1].

Because of its outstanding properties and applications, titanium dioxide (TiO_2) is up to date the most important semiconductor for photochemically decomposing environmental pollutants in order to diminish the harmful effects of these compounds in air or water. TiO_2 is a non-toxic material and is capable to oxidize several compounds under UV irradiation. Many studies about the photodecomposition of pollutants by this metal oxide are currently under way and the preparation of highly effective photocatalysts that are activated by UV radiation has already been pursued [2]. The semiconducting and insulating properties that these solid materials possess are mostly due to the convenient value of their energy band gap (Eg); nevertheless, only a few semiconductors are suitable for photoactivation since Eg for insulators is too large to allow absorption of visible light. Eg is then a very important parameter given that it enables excited electrons to remain in a high energy level for a relatively long period of time thus allowing a fine exploitation of the material properties [3].

Under UV photoexcitation, valence electrons absorb energy thus generating electron hole pairs ($e^- - h^+$) in the valence and conduction bands. Each $e^- - h^+$ pair can diffuse and recombined among themselves in the TiO_2 bulk volume or surface. These $e^- - h^+$ entities have both strong reducing and oxidizing activities and can react with water and oxygen to yield active species, such as hydroxyl radicals ($^\bullet OH$) and superoxide anions (O_2^-). Electron–holes, $^\bullet OH$, and O_2^- are extremely reactive after contacting organic compounds. The oxidation of bacterial cell components, such as lipids and DNA, by these species can produce cell death [4].

The control of dangerous emissions to the environment and the degradation of pollutants are important topics that should be taken into account when trying to reduce the affectations produced by pollution. For the elimination of microorganisms or organic pollutants, several methods such as biological digestion and chemical oxidation are now widely applied. Nevertheless, these methods are not very effective, thus it is important to develop new materials and novel technologies for allowing an improvement of the

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performance regarding the processes of environmental decontamination [5–7].

Photocatalysis together with the development of effective photocatalytic materials are excellent alternatives for eliminating pollutants in air and water. The degradation mechanism can be activated with UV and visible radiation without generating secondary residual products [8,9].

Thin films are an important option for the treatment of water and air, these materials can eliminate pathogen agents (bacteria, viruses, and other microorganisms) as well as dangerous organic compounds hence leading to their total mineralization [10–14].

The aim of this study is to investigate the antibacterial activity under visible-light irradiation of Fe-doped TiO_2 thin films loaded with 3 and 5 wt.% of Fe; these films, deposited on sodium glass by the spin-coating method, are a fine alternative for the *Escherichia coli* (*E. coli*) water disinfection treatment. The Eg value of these thin films was determined from the UV–vis spectra of these materials. The thin film having 5 wt.% of Fe reached the lowest Eg, as well as a microcrystalline domain texture that was suitable for fine bacterial adherence to the surface. The photocatalytic reaction, induced by visible radiation, and the detection of viable and unviable *E. coli* bacteria were studied. Bacterial concentrations were determined by the standard method of counting the microbe number that was grown on a plate.

2. Experimental

2.1. Synthesis

Fe–TiO_2 thin films were prepared by the spin-coating method, using a burnished Na glass substrate that was treated with concentrated HF in order to improve the adhesion between them. The material to be deposited on the sodium glass substrate was previously synthesized as follows: a volume of 39 mL of ethanol was placed in a glass reactor and subjected to magnetic agitation; afterward, 39 mL of titanium ethoxide, $Ti(OC_2H_5)_4$, and an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ were dropwise added to obtain materials with either 3 or 5 wt.% Fe on TiO_2. The reactant system was adjusted to pH 3 through the addition of diluted HCl, while kept under stirring until all hydrolysis and condensation reactions were accomplished [15]. Subsequently, the resultant gel was filtered, washed with deionized water, and dried at 100 °C. The powder samples obtained this way were labeled as: Fe–TiO_2 3 and Fe–TiO_2 5. When these materials were thermally treated at 400 °C an asterisk was added (i.e. Fe–TiO_2 3* and Fe–TiO_2 5*); similarly, two asterisks were added to the labels of the samples treated at 800 °C (i.e. Fe–TiO_2 3** and Fe–TiO_2 5**). The procedure selected to deposit thin films on glass substrates was the spin-coating method. This was made via a SEVE SC-1000 commercial device. The film formation conditions were chosen as follows: 45 °C, a temperature measured in situ by means of an IR sensor thermometer, and a spinning speed of 700 rpm. On top of a burnished sodium glass substrate, 1 mL of a TiO_2 colloidal suspension was deposited dropwise in order to form a thin film over the glass. After some solvent evaporation, the film was annealed at 400 °C in order to improve its adherence to the glass substrate. The colloidal TiO_2 suspension was prepared as follows: a certain amount of photocatalyst powder that was previously synthesized by the sol–gel procedure was kept under stirring and refluxed at 70 °C, in a 50/50 (v/v) mixture of ethanol and water at pH 10 during 48 h. The suspension thus obtained was used to form the thin film on the glass substrate by repeating twelve times the deposition procedure (one deposition after another) described above.

The resultant thin film samples were labeled, depending on the annealing temperature to which the powder photocatalyst was subjected as: F Fe–TiO_2 3*, F Fe–TiO_2 3**, F Fe–TiO_2 5*, F Fe–TiO_2 5**; the * symbol means a temperature of 400 °C and the ** symbol represents a temperature of 800 °C (in the text it is already stated that the digits 3 and 5 represent the wt.% Fe in the samples).

The average film porosity could be determined by measuring the film apparent density in the following way. The substrate is weighed before the deposition of the film, and then the film and substrate are weighed together. From the values of the film thickness and weight, the apparent density can be calculated. Nevertheless, in the present work, the average-size bacteria, i.e. the rod-shaped *E. coli* is about 0.5 μm in diameter and 2 μm in length; these dimensions easily surpass any actual pore diameter that could be present in the film. Therefore, in this case, bacteria are more likely to remain on the external film surface than to penetrate in its interior and therefore porosity of the film plays no major role.

2.2. Characterization

2.2.1. X-ray diffraction

The X-ray diffraction patterns (XRD) of the Fe–TiO_2 thin film specimens were obtained with a Siemens D500 diffractometer coupled to a Cu anode tube with. The desired Cu-K_α ($\lambda = 1.5406$ Å) radiation was selected by using a diffraction beam monochromator [16].

To study the microcrystalline coating characteristics of the TiO_2 film deposited on glass substrates, the grazing incidence X-ray diffraction (GIXRD) technique was used [17,18]. In this GIXRD technique, the angle of incidence of the X-ray beam with respect to the sample surface is kept fixed at a low value while changing the 2Θ diffraction angle. This procedure allows an enhancement of the diffracted signal coming from the thin film, thus revealing detailed information about sample microstructure; the Bragg reflection width increases due to microstructural features, microcrystal distribution, microcrystal shape, and shrinking of the crystallite sizes.

2.2.2. UV–vis spectroscopy

The UV–vis spectra were obtained via a Cary 100 UV–vis spectrophotometer. From these spectra, the energy band gap (Eg) was calculated.

2.2.3. Scanning electron microscopy (SEM)

Images of the films were obtained with a DSM-940 Carl Zeiss scanning electron microscope, with 30 kW of acceleration voltage and a resolution of 6 nm. The materials were previously coated with gold, using a SCD050 Baltec device. The SEM image magnification was set at 5000×.

2.2.4. Photocatalytic activity

The photocatalytic activity of the Fe–TiO_2 thin films was evaluated in liquid medium inside a stirred photoreactor containing a Luria–Bertani (LB) bacteria culture medium. The photoreactor consisted of a Pyrex glass beaker of 250 mL. The thin film photocatalyst and the liquid culture medium were put inside the beaker and then stirred during the microbial degradation process. The radiation source was a Kr UVP Pen Ray 90-0014-01 lamp that was immersed in the beaker; the radiation emitted by the krypton lamp corresponded to the visible interval of the electromagnetic spectrum. To avoid any kind of interference radiation, coming from other sources, measurements were made in a black walls container. Bacterial photodegradation was carried out at 37 °C, under atmospheric pressure, while dry air was bubbled constantly (1 mL/min) during 1 h.

The photocatalyst film was a square thin layer of 5 cm × 5 cm, with an average thickness of 718 nm that was evaluated by oscillation interferometry [Smith D.L. Thin film deposition Principles & Practice] while applying the Uv–vis spectroscopic procedure