



TiO₂ modifications by hydrothermal treatment and doping to improve its photocatalytic behaviour under visible light

P. Esparza^{a,*}, T. Hernández^b, M.E. Borges^b, M.C. Álvarez-Galván^c, J.C. Ruiz-Morales^a, J.L.G. Fierro^c

^a *Inorganic Chemistry Department, University of La Laguna, Avda. Astrofísico Fco. Sánchez s/n, La Laguna, Tenerife, Canary Island 38200, Spain*

^b *Chemical Engineering Department, University of La Laguna, Avda. Astrofísico Fco. Sánchez s/n, La Laguna, Tenerife, Canary Island 38200, Spain*

^c *Institute of Catalysis and Petroleum Chemistry, CSIC, C/Marie Curie 2, Cantoblanco, Madrid 28049, Spain*

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ABSTRACT

Heterogeneous photocatalysis based on TiO₂ materials is an interesting method for the treatment of polluted water because it allows degradation of a wide variety of organic contaminant compounds. The performance of TiO₂ based photocatalysts was studied by aqueous solutions of methylene blue (MB) as a model contaminant compound by using 50 mg L⁻¹ as initial water contaminant concentration in order to compare the photocatalytic behaviour of TiO₂ Degussa P25 and some synthesized photocatalysts by hydrothermal treatment (nanostructured TiO₂ and metal-doped nanostructured TiO₂ photocatalysts: nanostructured Co-TiO₂, nanostructured Fe-TiO₂ and nanostructured Mn-TiO₂) under UV and visible light irradiation. Photocatalytic materials characterization was carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen adsorption-desorption, mercury porosimetry, XPS and diffuse reflectance UV-vis spectra. An improvement of the photocatalytic activity has been observed when nanostructured and doped photocatalysts were used under visible light irradiation, concluding that the hydrothermal treatment produces a nanostructuring of commercial titania by the formation of nanoparticles, which results in a large decrease of average crystallite size of undoped and doped titania, and in an important increase of BET specific area and total pore area.

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1. Introduction

Nowadays heterogeneous photocatalysis is one of the most important Advanced Oxidation Technologies (AOT). It is based on the oxidation of polluting compounds, which can be found in air or water by means of an oxidation reaction occurring on a semiconductor catalytic surface activated by light in a specific wavelength range.

Heterogeneous photocatalysis using TiO₂ is an interesting method for the treatment of wastewater because it allows degradation of a wide variety of organic compounds.

TiO₂ is the most investigated system particularly due to its properties: good chemical stability, non-toxicity, abundance and inexpensive [1–3]. Among the common TiO₂ crystalline forms, anatase and rutile have been investigated extensively as photocatalysts and anatase has been reported to be more active as a photocatalyst than rutile [4,5]. However, TiO₂ shows a large band gap energy (3.2 eV for anatase – 3.0 eV for rutile) in order to act as a photocatalyst. This fact implies that TiO₂ only can be activated by

UV light [6–8], therefore limiting the use of sunlight as an energy source for heterogeneous photoreaction, because sunlight is composed of less than 5% ultraviolet light. Therefore, it is necessary to develop photocatalysts that could be activated under visible light irradiation in order to use sunlight as an energy source [9].

In order to enhance the photoreactivity of TiO₂ bulk, by providing a broader range of wavelengths suitable for band gap excitation and an inhibition of electron-hole recombination, the properties of the TiO₂ particles have been modified by selective doping with different cations such as Fe, Cr, V, Mo and other trivalent, tetravalent and pentavalent cations. It has been found to produce a beneficial or detrimental effect on photoreactivity of titania depending on the molecule to be removed and the dopant used [10].

Several studies have been carried out with the aim to investigate the effect of doping titania photocatalysts with different transition metals under visible light irradiation [11–13]. In these studies, photocatalysts have been prepared mainly by two different methods: sol-gel method and hydrothermal method. The hydrothermal method is widely applied because it is a simple and an efficient method to obtain titania nanotubes and to prepare doped photocatalysts under mild temperature and pressure conditions [14].

On the other hand, this method could lead to the formation of very small particles (i.e. Q-size particles), with different photochemical characteristics. The advantages of these nanoparticles

* Corresponding author. Tel.: +34 922 315426.

E-mail address: pesparza@ull.es (P. Esparza).

are related with respect macroparticles such as those found in commercial TiO₂ (Degussa P25) derived from the following factors: (i) these small particles with diameters between 1 and 10 nm exhibit characteristics between molecular and bulk semiconductors, (ii) the blue shifts of the band gap in UV absorption enhance the redox potentials of the photogenerated electrons and holes, and (iii) the high surface, area/volume ratio leads to improved effectiveness for surface-limited reactions [15].

2. Materials and methods

2.1. Photocatalyst preparation

Photocatalysts were prepared by hydrothermal method. Commercial TiO₂ (Degussa P25) was used as a source of titania. Doped catalysts (with Co²⁺, Fe³⁺ or Mn²⁺ as doping cations) were prepared using Co(NO₃)₂·6H₂O; Fe(NO₃)₃·9H₂O and MnSO₄·H₂O salts, respectively, as precursors of dopants and adding the dopant metal in an metal/titanium atomic ratio M/Ti=0.02. NaOH solution 1 M was added to a suspension of titania and metal salt solutions in a Teflon autoclave which was backed up by a stainless steel pressurized vessel. The same procedure was applied for the hydrothermal treatment of titania but in absence of any metal salt. The autoclave was heated at 140 °C for 22 h in an oven. Afterwards, the solid was washed with HCl solution 0.1 M and distilled water until a pH of 7 was achieved. Finally, the solid was dried at 140 °C for 22 h in an oven.

2.2. Photocatalyst characterization

Photocatalysts were structurally characterized by X-ray diffraction (XRD). The microstructure was examined using by transmission electron microscopy (TEM) (JEOL 2011) operating at 200 kV. The equipment used an Oxford Link detector to perform energy-dispersive X-ray spectroscopy analysis. Samples for TEM observation were prepared by dispersion of a very fine ground powder in acetone and then deposited onto a perforated carbon film supported on a Cu grid. The textural properties of the samples were evaluated by nitrogen adsorption-desorption (for micro and mesopores characterization) and mercury porosimetry (for meso and macropores characterization). The specific area of the samples was calculated by the BET method from the nitrogen adsorption-desorption isotherms (−196 °C), recorded with a Micromeritics ASAP 2100 apparatus. Prior to adsorption the samples were degassed at 150 °C under vacuum ($P < 3 \times 10^{-5}$ mbar) for 4 h. Mercury porosimetry data were recorded with an Autopore 4 mercury porosimeter, Micromeritics. Before the analysis, the samples were degassed at 180 °C.

The chemical composition in the surface of the photocatalyst samples was determined by XPS. The X-ray photoelectron spectra of solids were recorded on a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser and an Mg K α ($h\nu = 1253.6$ eV) X-ray source was used. The samples were placed in a copper holder mounted on a sample-rod in the pre-treatment chamber of the spectrometer. The samples were degassed at 10^{-5} mbar before being transferred to the analysis chamber. The base pressure in the analysis chamber was kept below 7×10^{-9} mbar during data acquisition. The binding energies (BE) were referenced to the C 1s peak of contamination at a binding energy of 284.8 eV to account for charging effects. The areas of the peaks were computed after fitting of the experimental spectra to Gaussian/Lorentzian curves and removal of the background (Shirley function). Surface atomic ratios were calculated from the peak area ratios normalized by the corresponding atomic sensitivity factors [16].

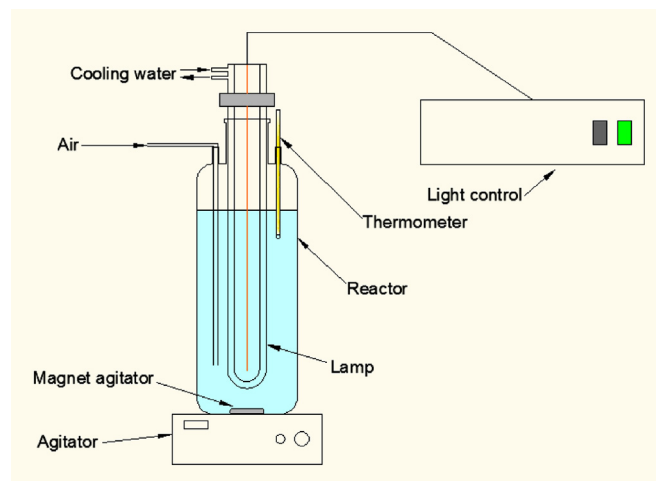


Fig. 1. Diagram of the reactor employed in photocatalytic experiments.

The UV–vis spectra of the materials were recorded with a UV–vis spectrometer equipped with a Varian Cary 3 UV–vis spectrometer equipped with an integration sphere. The spectra were recorded in diffuse reflectance mode and transformed by the instrument software to equivalent absorption Kubelka–Munk units.

2.3. Photocatalytic activity

The performance of the photocatalysts was evaluated by its capacity for removing methylene blue (MB) from an aqueous solution (a typical textile dye used as model contaminant in water compound). The photocatalytic oxidation reaction was carried out in a stirred photoreactor with a capacity of 650 mL with UV Hg-lamp (Heraeus TQ-150, 150 W) or visible Xe-lamp (Hamamatsu L2274, 150 W) placed inside the photoreactor (Fig. 1). In this reactor, the temperature was kept constant at 20 °C, the aqueous solution of MB (50 mg L^{−1}, initial concentration) and 0.5 g L^{−1} of the photocatalyst were introduced as a suspension into the reactor and aliquots were taken at different times during 2 h duration (experimental time) in order to follow the temporal evolution of MB concentration. The photocatalytic activity of the catalysts was evaluated and compared upon irradiation with either UV or visible light in separate experiments. In both cases photolysis experiment (in absence of solids) produced a MB conversion less than 5%. Photocatalytic activity tests were carried out with five photocatalytic materials: TiO₂ Degussa P25 (a commercial photocatalyst with high photocatalytic activity), nanostructured TiO₂ (prepared by means of above commented hydrothermal method without adding the dopant metal in a Teflon container) and nanostructured Co–TiO₂, Fe–TiO₂ and Mn–TiO₂ (prepared by means of hydrothermal method adding the dopant metal, in a Teflon container).

3. Results and discussion

3.1. Photocatalyst characterization

The morphology of the photocatalyst samples was revealed by TEM (Fig. 2). The TEM images of TiO₂ Degussa P25 (Fig. 2a) show isolated crystallites. The synthesized photocatalysts: nanostructured-TiO₂ (Fig. 2b), Co–TiO₂ (Fig. 2c), Fe–TiO₂ (Fig. 2d) and Mn–TiO₂ (Fig. 2e) exhibit a nanostructured morphology with the presence of large amount of nanotubes and nanosheets. Consequently, it is conceivable that the formation of these nanoparticles is achieved by the hydrothermal treatment at low temperature.

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