Effect of deposition of silver on structural characteristics and photoactivity of TiO₂-based photocatalysts

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ABSTRACT

The homemade bare TiO₂ photocatalyst obtained in a previous work was modified with nanosized silver particles by liquid impregnation and photodeposition methods to obtain different noble metal loadings (0.3–1 at.%). Characterization of the synthesized photocatalysts was carried out by the BET method, XPS, TEM, SEM-EDX, XRD and diffuse reflectance measurements. Photocatalytic activity of these silver-deposited TiO₂ nanoparticles was tested by photocatalytic degradation of phenol as a reference model representing phenolic pollutants. The noble metal content on the TiO₂ surface affected the efficiency of the photocatalytic process, and the photocatalytic activity of noble metal-modified TiO₂ was considerably better than that of bare TiO₂. Phenol decomposition rate was higher with TiO₂ modified by the liquid impregnation method than with TiO₂ modified by the photodeposition method.

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1. Introduction

TiO₂ heterogeneous photocatalysis has recently been the subject of numerous investigations as it is an attractive technique for the complete destruction of undesirable contaminants both in aqueous and in gas phase [1,2] by using solar or artificial light illumination. Upon band-gap excitation of TiO₂, the photoinduced electrons and positively charged holes can respectively reduce and oxidize species adsorbed on the semiconductor particles. The high degree of recombination between photogenerated electrons and holes is a major rate-limiting factor controlling photocatalytic efficiency. Enhancement of TiO₂ photocatalytic activity is one of the most important aspects of heterogeneous photocatalysis [3]. Modification of photocatalysts with noble metals such as Pt, Au and Pd, is a procedure used to obtain more efficient photocatalysts [4–6]. Most research involving photocatalysis with noble metals is focused on the transference of electrons photoinduced by UV radiation from the conduction band of TiO₂ to the metal deposits. The positive effects of the noble metal deposits on photocatalytic activity are several [7–10]: (i) improvement of the electron–hole separation by trapping the electrons speeding up the formation of $O_2^{\bullet-}$, (ii) shift of light absorption into the visible-light range due to plasmon formation, (iii) modification of the surface adsorption properties of the photocatalysts and (iv) generation of hydroxyl radicals through the reaction with hydrogen peroxide produced by oxygen photoreduction as:

$$M + H_2O_2(ads) + H^+(aq) \rightarrow HO^\bullet + H_2O + M^+$$
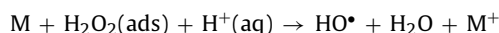
However, the amount of metal cannot be increased indefinitely. Negative effects of the presence of metal deposits on the photocatalyst surface have been described that lead to decreased photon efficiency. When metal concentration is high and, therefore, metal clusters numerous and large: (i) the negatively charged metal particles can act as recombination centers trapping holes [11], (ii) more semiconductor surface is covered by deposits decreasing the light that reaches its surface and, consequently, the number of photogenerated electron–hole pairs [12] and (iii) metal deposits can occupy the semiconductor surface active centers [13]. In the case of silver-deposited systems, the literature highlights an optimum percentage around 0.5–1.0 at.% Ag above which photoefficiency decreases.

Photocatalytic activity is not only dependent on metal type and the concentration and characteristics of the deposits, but also to a major extent on the TiO₂ base [14]. For this reason, apparently contradictory results can be found in the literature about the effects of

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a particular metal, and there are no general rules as to whether one metal is better than another or what their optimum concentrations are. The establishment of rules in photocatalysis is even more complicated since the activity will also depend on the pollutant subject to degradation [15].

In recent years, the silver ion has caught the attention of a lot of researchers due to the increased photoactivity and bactericidal effect of photocatalysts which contain it. Kondo et al. [16] reported that Ag/TiO$_2$ was more effective than bare TiO$_2$ in chloroform degradation; Sahoo et al. [17] in the degradation of C.I. Basic Violet 3; Ozkan et al. [18] in the degradation of Sirius Gelb GC dye; and Behnajady et al. [19] in the degradation of Acid Red 88 dye.

The usual methods for surface modification of TiO$_2$ with noble metals are: thermal impregnation [20] and photodeposition [11]. There is some debate as to which method leads to more efficient photocatalysts due to the lack of studies that compare them under the same conditions. It was therefore decided to use both methods in this paper to study the effect of the surface deposition of Ag on the structure and photoactivity of a homemade TiO$_2$-based photocatalyst [21]. As reference, the commercially available Degussa P25 TiO$_2$ was subjected to the same study.

2. Experimental

2.1. Equipment and methods

BET surface area and porosity measurements were carried out by N$_2$ adsorption at 77 K using a Micromeritics ASAP 2010 instrument.

Phase composition and the degree of crystallinity in the samples were determined by X-ray diffraction (XRD). XRD patterns were recorded on a Siemens D-501 diffractometer equipped with a Ni filter and graphite monochromator using Cu Kα radiation ($\lambda = 1.5418$ Å). Crystal sizes in the different phases were estimated from line broadening of the corresponding X-ray diffraction peaks by using the Scherrer equation. Peaks were fitted using the Voigt function ($R^2 > 0.995$).

Light absorption properties of the samples were studied by UV–vis spectroscopy. UV–vis spectra were recorded on a Varian Cary 100 spectrometer equipped with an integrating sphere using BaSO$_4$ as reference. Both absorbance and diffuse reflectance spectra were recorded for all samples and the Kubelka–Munk function, $F(R_\infty)$, was applied to obtain a magnitude proportional to the extinction coefficient. Band-gaps were calculated by the Kubelka–Munk function, following the method proposed by Tandon and Gupta [22].

The morphology of the samples and the dispersion and size of surface metal deposits were studied by transmission electron microscopy (TEM) using a Philips CM 200 instrument and by scanning electron microscopy (SEM) using a Jeol JSM-5400 apparatus equipped with an X-ray dispersive energy (EDX) analyzer.

Surface characterization by X-ray photoelectron spectroscopy (XPS) was conducted on a Leybold–Heraeus LHS-10 spectrometer, working with constant pass energy of 50 eV. The spectrometer main chamber was maintained at a pressure <2×10^{-9} Torr, and the machine was equipped with an EA-200 MCD hemispherical electron analyzer with a dual X-ray source of Al Kα ($h\nu$) 1486.6 eV at 120 W and 30 mA. The carbon 1s signal (284.6 eV) was used as the internal energy reference in all the measurements. Samples were outgassed in the prechamber of the instrument at 150 °C up to a pressure <2×10^{-8} Torr to remove chemisorbed water from their surfaces.

The total concentration of dissolved Ag for recyclability runs was measured by means of atomic absorption spectrophotometry (AAS – Varian SpectrAA model), with Zeeman background correction and equipped with an electrothermal atomizer.

The photocatalytic activity of the samples was evaluated in the phenol photo-oxidation reaction. Suspensions of the samples in aqueous phenol solution (50 ppm) were placed in a Pyrex immersion well photoreactor (500 mL) and illuminated for 2 h by a HPK125 W Hg lamp supplied by Philips showing main emission line at 365 nm. The photonic flow per unit area of the incident UV light (200–400 nm) on the solution was determined to be approximately 1.4×10^{15} photons cm^{-2} s^{-1} using an Ocean Optics HR2000+ spectrometer. Magnetic stirring and a constant flow of oxygen maintained the homogeneous suspension of photocatalyst in the solution. Prior to illumination, photocatalyst–substrate equilibration was ensured by stirring the suspension for 30 min in the dark. The evolution of the phenol concentration was measured by HPLC using a Discovery C18 (25 cm × 4.6 mm, 5 μm) column and an acetonitrile–water–acetic acid (40:59.6:0.4% (v/v/v)) mobile phase, with a UV detector ($\lambda = 270$ nm). Total organic carbon (TOC) was measured using a Shimadzu TOC VCSN analyzer.

2.2. Catalyst preparation

TiO$_2$ (Degussa, P25) and a homemade photocatalyst obtained by sol-gel and hydrothermal synthesis (detailed characterization of the TiO$_2$ht600 sample has been reported in a previous paper [21]) were used as initial photocatalytic materials. Silver nitrate, AgNO$_3$ (Merck) and oxalic acid (Aldrich) were used without any further purification. Two methods for the deposition of silver were used: liquid impregnation and photodeposition. The amounts of silver loaded were 0.1, 0.3, 1.0, 2.0 and 5.0 at.%. The metal loading (atomic percentage) was calculated as the ratio between moles of Ag, n_{Ag}, and the totals, n_{Ti} and n_{Ag}, $n_{Ag}/(n_{Ti} + n_{Ag})$. The photocatalysts obtained from impregnation were named xAg-iTiO$_2$ and those obtained from photodeposition xAg-pTiO$_2$, where x denominates the silver atomic percentage.

The samples from both methods were then calcined at 400 °C for 2 h. This temperature is high enough to guarantee the elimination of the nitrate from the silver precursor and, at the same time, moderate enough to avoid structural modification of the bare TiO$_2$.

2.3. Impregnation method

A modification of the impregnation method earlier described by Bickley et al. [23] was applied for the synthesis of Ag loaded TiO$_2$ photocatalytic materials. 4 g of photocatalyst was added to 1 L of MilliQ water with the appropriate amount of Ag (from AgNO$_3$). This suspension was subjected to vigorous stirring for 1 day on a stirring plate and then evaporated until dry at boiling temperature.

2.4. Photodeposition method

The method employed was a modification of the method described by Iliev et al. [24]. In an immersed reactor with stirring, 2 g of photocatalyst was dispersed into 200 mL of MilliQ water at room temperature. The dissolved oxygen was removed from the solution with nitrogen flow bubbling that was maintained for the whole process. After 30 min, the necessary silver amount was added from 1 M AgNO$_3$ solution. Oxalic acid was added as a sacrificial donor (at a molar ratio oxalic acid:silver = 25:1) and the whole volume was completed with water until 400 mL, resulting in pH <2 in all cases. The suspension was left for a further 30 min in darkness and the slurry was then irradiated with a 400 W medium pressure Hg lamp (8.1×10^{-7} einstein s^{-1} L^{-1}) placed inside a quartz tube, for about 330 min. Continuous stirring and nitrogen sparging was maintained during the whole process. The precipitate was filtered, washed with MilliQ water and then dried at 120 °C for 2 h.