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Preparation of Sm-loaded brookite TiO_2 photocatalysts

A. Di Paola [a,*], M. Bellardita [a], G. Marcì [a], L. Palmisano [a], F. Parrino [a], R. Amadelli [b]

[a] "Schiavello-Grillone" Photocatalysis Group, Dipartimento di Ingegneria Elettrica, Elettronica e delle Telecomunicazioni, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy
[b] Dipartimento di Chimica and ISOFCNR, Università degli Studi di Ferrara, Via Luigi Borsari 46, 44100 Ferrara, Italy

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ABSTRACT

Pure and Sm-loaded brookite nanoparticles and thin films were prepared using $TiCl_4$ as precursor of TiO_2. The samples were characterized by X-ray diffraction (XRD), specific surface area (SSA) determination, diffuse reflectance spectroscopy (DRS) and photoluminescence (PL) measurements. The photocatalytic activity of the powders was investigated by employing the photodegradation of 4-nitrophenol in a liquid–solid system whilst the photoreactivity of the films was tested by evaluating the rate of degradation of 2-propanol in a gas–solid system. Loading with Sm resulted in a significant improvement of the photoreactivity of brookite and the beneficial effect was attributed to an increased separation efficiency of the photogenerated electron–hole pairs. The content of samarium was an important factor affecting the photocatalytic activity. The optimum amount of samarium was 1% for the powders and 0.1% for the films. There is a relationship between PL spectra and photoactivity, namely, the lower the PL intensity, the higher the photocatalytic activity.

1. Introduction

Titanium dioxide is the most widely studied photocatalyst for the oxidative degradation of organic pollutants present in wastewater effluents or in air [1–3]. TiO_2 has many attractive characteristics such as chemical stability, non toxicity and low cost [4] but its photocatalytic efficiency is limited by a high rate of recombination of the photogenerated electron–hole pairs.

The main crystalline modifications of TiO_2 are rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). All three crystalline structures consist of deformed TiO_6 octahedra connected differently by corners and edges [5]. Anatase and rutile are the forms more frequently studied because pure brookite is rather difficult to be prepared.

Pure brookite was prevalently prepared from titanium(IV) compounds via hydrothermal treatments at high temperatures [6–11]. Brookite nanoparticles were synthesized in mild conditions of temperature and pressure [12–14] or by employing titanium(III) compounds as TiO_2 precursors [15–17]. Only a few papers have concerned with the preparation of brookite films [18–21].

The photoactivity of TiO_2 can be improved by surface functionalization [22–24] or by doping with metallic and non-metallic species. Many controversial results are reported in the literature because the photoactivity of the resulting catalysts depends both on the dopant and the substrate to be photodegraded. Choi et al. [25] studied the effect of 21 different metal ion dopants both for the oxidation of $CHCl_3$ and for the reduction of CCl_4. The results showed that some metal ions increased the photoactivity of TiO_2 whilst others were detrimental. The photooxidation of various aliphatic and aromatic organic compounds revealed that the methanoic acid degradation was enhanced by the presence of cobalt ions whilst the sample doped with W was the most efficient for the mineralization of benzoic acid and 4-nitrophenol [26]. An explanation was proposed by taking into account the nature of the reacting molecules and the acid–base and electronic properties of the photocatalysts.

Recently, lanthanide-doped TiO_2 samples have received an increasing attention for their enhanced photocatalytic properties [27–43]. The increase in activity was attributed to a higher adsorption and reduction of the electron–hole recombination. Ranjit et al. [27] prepared a series of lanthanide ions doped TiO_2 ($Ln^{3+} = Eu^{3+}$, Pr^{3+}, Yb^{3+}) which revealed a substantially enhanced activity for the photodegradation of p-nitrobenzoic acid, p-chlorophenoxyacetic acid, aniline, salycilic acid and trans-cinnamic acid. Various lanthanide ions with different 4f electronic configurations were studied as dopants of TiO_2 for the degradation of phenol [28], 2-mercaptobenzothiazole [29], nitrite [30] and various dyes [31–41]. All lanthanide-doped samples exhibited an improvement of photoactivity with respect to undoped TiO_2. The introduction of lanthanide ions extended the optical absorption of the doped samples to longer wavelengths enhancing the photocatalytic activity under UV or visible light illumination [36–42].

Sm-doped TiO_2 is an attractive material for its spectroscopic properties [43–45] and good photocatalytic performances [30–39]. The photoactivity of the TiO_2 samples doped with samarium ions

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[*] Corresponding author. Tel.: +39 091 238 63729.
E-mail address: agatino.dipaola@unipa.it (A. Di Paola).

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has been generally compared to that of other lanthanide-doped TiO_2 materials [30–36] and some researchers [30,34–39] have studied the effect of the samarium content on the photocatalytic activity of TiO_2. Anatase is the crystallized phase usually doped with lanthanide ions and only few works have concerned a mixture of anatase and rutile doped with samarium [37,38]. To the best of our knowledge no studies on the photocatalytic activity of brookite samples containing samarium have ever been published either in liquid–solid or in gas–solid systems.

In this study we report on the synthesis of Sm-loaded brookite powders and films obtained by a sol–gel method. The preparation method is very simple and does not require the use of expensive thermal or hydrothermal treatments. The photodegradation of 4-nitrophenol (4-NP) was used to evaluate the reactivity of the powders whilst the films were tested for the photodegradation of 2-propanol. The effect of the content of samarium on the photocatalytic efficiency was also studied.

2. Experimental

2.1. Preparation of the samples

2.1.1. Powders

15 mL of $TiCl_4$ (Fluka 98%) was added dropwise to a solution containing 630 mL of demineralized water and 240 mL of concentrated hydrochloric acid. The hydrolysis reaction was highly exothermic and released fumes of HCl. The solution obtained after continuous stirring was heated in a closed bottle and aged at 100 °C in an oven for 48 h. The resultant precipitate contained a mixture of brookite and rutile. Pure brookite nanoparticles were separated by peptization by removing many times the surnatant and adding water to restore the initial solution volume. After a few washings, a dispersion of brookite particles formed whilst the rutile phase remained as precipitate [46]. The dispersion was recovered and the washing treatment was repeated till the liquid on the solid rutile became transparent. All dispersions containing the brookite particles were collected and dried under vacuum at 55 °C.

Samarium loading was accomplished by adding Sm_2O_3 (Aldrich 99.9%) to the solution obtained by dissolution of $TiCl_4$. The following code was used for the loaded samples: B(*x*%Sm), where *x*% indicates the nominal percentage of metal with respect to total amount of TiO_2.

2.1.2. Films

Bare TiO_2 films were prepared by immersing microscopy glasses (75 mm × 25 mm × 1 mm) in the brookite dispersion obtained by peptization of the mixture of brookite and rutile. The withdrawal speed was 60 mm/min. After each coating the films were first dried at room temperature for 15 min and then calcined at 400 °C for 2 h. The treatment was repeated 10 times. The samarium loaded films were prepared as above described for bare TiO_2 but in the presence of Sm_2O_3.

2.2. Characterizations of the samples

XRD patterns of the powders were recorded at room temperature by a Philips powder diffractometer using the CuKα radiation and 2θ scan rate of 2°/min. The diffractograms of the films were obtained by a D8 Bruker X-ray diffractometer with a 2θ scan rate of 0.01°/s and an incident angle of 0.5°. The specific surface areas of the powders were determined in a Flow Sorb 2300 apparatus (Micromeritics) using the single-point BET method. Visible-ultraviolet spectra were obtained by diffuse reflectance spectroscopy by using a Shimadzu UV-2401 PC instrument. $BaSO_4$ was the reference sample and the spectra were recorded in the range 200–800 nm. Photoluminescence spectra were recorded at room temperature with a Jobin Yvon Spex Fluoromax II spectrofluorimeter equipped with a Hamamatsu R3896 photomultiplier.

To determine the adsorption behavior of the Sm-loaded samples, 0.06 g of powder was added to 100 mL of a 20 mg L^{-1} aqueous solution of 4-nitrophenol. The suspension was stirred for 3 h in the dark to ensure the equilibration of the substrate over the catalyst surface and the amount of adsorbed 4-nitrophenol was calculated by comparing the concentration before and after stirring. The catalyst was separated from the solution by filtration through a 0.1 μm Teflon membrane (Whatman). Some drops of a 1 M NaOH solution were added before filtration to obtain agglomeration of the particles. The quantitative determination of 4-NP was performed by measuring its absorption at 315 nm with a spectrophotometer Shimadzu UV-2401 PC.

2.3. Photoreactivity experiments

A Pyrex batch photoreactor of cylindrical shape containing 0.5 L of aqueous suspension was used. A 125 W medium pressure Hg lamp (Helios Italquartz, Italy) was immersed within the photoreactor and the photon flux emitted by the lamp was $\Phi_i = 13.5\,\text{mW}\,\text{cm}^{-2}$. O_2 was continuously bubbled for ca. 0.5 h before switching on the lamp and throughout the occurrence of the photoreactivity experiments. The temperature inside the reactor was ca. 30 °C. The amount of catalyst was 0.6 g L^{-1} and the initial 4-nitrophenol (BDH) concentration was 20 mg L^{-1}. Samples of 5 mL were withdrawn at fixed intervals of time with a syringe, and the catalyst was separated from the solution by filtration through 0.1 μm Teflon membranes (Whatman).

The photoreactivity of the films was evaluated in a cylindrical Pyrex batch photoreactor ($V = 0.9\,\text{dm}^3$) where two juxtaposed coated glasses were placed. The films were irradiated from the top by a 500 W medium pressure Hg lamp. The irradiance at the film surface was 1.3 mW cm^{-2}. A water filter was interposed between the lamp and the photoreactor to cut the infrared radiation. O_2 was fluxed in the reactor for ca. 0.5 h before turning off the inlet and outlet valves. Subsequently, 2-propanol was injected into the reactor and the lamp was switched on. 0.5 mL of the mixture was withdrawn at different irradiation times using a gas-tight syringe. 2-Propanol and propanone concentrations were measured by a GC-17A Shimadzu gas chromatograph equipped with a HP-1 column and a flame ionization detector. CO_2 was detected by a HP 6890 Series GC System equipped with a packed column GC 60/80 Carboxen-1000.

3. Results and discussion

3.1. Characterization of the samples

X-ray measurements confirmed that the solids separated after selective peptization of the precipitate obtained by thermolysis of the $TiCl_4$ solution at 100 °C for 48 h contained only single-phase rutile or brookite [46]. The identity of the brookite polymorph was also verified by Raman spectroscopy. All peaks of the Raman spectrum of the as-prepared brookite powder were consistent with those of natural brookite crystals [47].

No peaks related to other TiO_2 phases such as anatase or rutile were observed in the diffractograms of the brookite samples loaded with various samarium contents. The peaks were rather broad, characteristic of partially crystalline powders with nanosized structure. The lack of appreciable diffraction peaks due to samarium oxide indicates a high degree of dispersion of the loaded metal onto the support, probably because the preparation temperature of the samples was too low to enable the formation of a “bulk” oxide. The Raman spectra of the loaded samples were similar to