



Doped sol–gel films vs. powders TiO₂: On the positive effect induced by the presence of a substrate



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ABSTRACT

SiO₂ and Ag–SiO₂ doped TiO₂ films and powders have been produced using a controlled sol–gel process. The dopant has been introduced using an alkoxy-silane-functionalized ligand, with or without complexed silver ions. The influence of dopants on physico-chemical properties of the catalysts is studied by XRD, TEM–EDX, DRUV–vis analyses in the case of powders, while GIXRD, XPS, profilometry, UV–vis absorption analyses have been used for thin films. The photocatalytic activity has been evaluated from the degradation of methylene blue under UV–A light in the presence of the different catalysts over a period of 24 h. The detailed comparison between powders and films highlights a surprising positive effect in the case of films due to the presence of the substrate. In the case of photocatalytic powders, the presence of SiO₂ or Ag–SiO₂ into the TiO₂ matrix has a detrimental effect on the photocatalytic activity while the opposite tendency is observed in the case of films, with best activities obtained with Ag–SiO₂ doping. Different factors, in particular crystallinity modification between powders and films, have been studied to explain these opposite behaviors. In the case of powders, crystallization is hindered by SiO₂ and Ag particles incorporation into the TiO₂ matrix, leading to a decrease of the photocatalytic activity. In the case of thin films, probably because of the presence of a substrate, crystallization is not influenced by the presence of SiO₂ and Ag particles. Therefore, the latter ones can fully play their role of electron traps leading to an enhanced photocatalytic activity.

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1. Introduction

Environmental pollution has become a critical issue for our society. Heterogeneous semiconductor photocatalysis is an advanced oxidation processes (AOP) which was proven to be a promising technology for the total mineralization of most organic pollutants by using natural or artificial light [1–3]. In the case of heterogeneous photocatalysis, the most frequently used semiconductor is titanium dioxide, TiO₂, due to its high oxidative potential, chemical stability, availability and its relatively low price [2,3].

TiO₂ can be used in the form of powders or films. Each has its own advantages and disadvantages. In the last decade, a lot of studies have been undertaken in order to develop efficient photocatalytic TiO₂-based powders [4–8]. However, for water cleaning applications, the use of powders is not adequate because it prevents light to diffuse efficiently in the system (slurry).

Moreover, the use of powders implies to separate the catalyst from the purified solution. Thus, in order to improve the efficiency of the process and to reduce the number of filtering operations, it is essential to develop immobilized catalysts.

Because properties of films are often difficult to evaluate, it would be tempting to use properties of the corresponding powders. However, as highlighted in the present study, such a way to proceed is dangerous because the presence of the substrate can induce major modifications leading to strong differences between powders and films properties.

In this study, the effect of the dopants to enhance the photocatalytic activity of TiO₂ is investigated in the case of both powders and films with the aim of detecting differences in behaviors. The substrate is soda-lime glass used in the glass industry. This substrate induces appearance of some interferences such as those due to sodium migration [9,10]. This can be avoided by using specific and expensive alkali-free substrates [1,11]. However, the goal of the present paper is to examine the possibility to produce photocatalytic films on widely used common glass. To examine this possible effect of shaping under powder or

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under film form on superhydrophilicity and photocatalytic activity with doping, a doping with silver nanoparticles has been chosen. The expected effect of such a doping is briefly explained below.

When TiO_2 is exposed to UV light (band gap around 3.2 eV for anatase), electrons are promoted from the valence band to the conduction band (e_{cb}^-), leading to the formation of positive holes in the valence band (h_{vb}^+). Both e_{cb}^- and h_{vb}^+ species can migrate to the surface of the catalyst and produce radical species such as $\text{O}^{2-\bullet}$ superoxides and OH^\bullet from reactions with adsorbed O_2 and H_2O . Those radicals can then react with the pollutant adsorbed on the surface of the TiO_2 particles and promote its degradation [2,12]. In order to insure a sufficient activity of the semiconductor photocatalyst, the different processes involving e_{cb}^- and h_{vb}^+ must compete effectively with the major deactivation process which corresponds to the $e_{cb}^- - h_{vb}^+$ recombination, occurring in the bulk or at the surface of the TiO_2 particles [13]. In this case, the aim of the doping is to decrease the rate of electron–hole pair recombination.

Numerous studies have been undertaken to increase the photocatalytic activity of TiO_2 by enhancing the electron–hole separation efficiency. In order to achieve this goal, deep electron traps are needed to increase the lifetime of photoexcited electrons and holes. According to literature, metallic nanoparticles, such as Au [14–17], Pd [18], Pt [19] and Ag [4,16,17,20–23], can play such a role. In the present work, silver has been chosen to be incorporated in the form of metal nanoparticles in TiO_2 . In addition to the electron trapping effect, a possible sensitization of TiO_2 to visible light due to the presence of silver [6].

A perfectly controlled sol–gel method is used to produce TiO_2 -based catalysts containing silver nanoparticles as electron trap. Generally, silver is incorporated during the sol–gel synthesis by using AgNO_3 as starting material [5,16,17,24,25]. In order to increase the probability to trap the photogenerated electrons, and thus to avoid recombination of electrons and holes, silver particles must be dispersed in the TiO_2 matrix as finely as possible and their size must be nanometric [5]. Previous works have reported that a high dispersion of metallic silver nanoparticles into a SiO_2 powder matrix can be achieved through the use of a complexing agent, as ethylenediamine, and a silver source [7,16,26–31]. By using silver acetate as silver source, it has been reported that silver ions can be complexed by the amine groups of an alkoxy silane-functionalized ligand such as *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (EDAS). Thanks to its alkoxy groups, the “ Ag^+ -EDAS” complex can therefore react with a titanium alkoxy precursor during the hydrolysis and condensation reactions. This allows anchoring Ag^+ ions onto the TiO_2 surface through the formation of Ti–O–Si chemical bonds (Fig. 1) [4,8]. After calcination, which is necessary to obtain crystalline TiO_2 , the material contains exclusively TiO_2 into which SiO_2 and silver are dispersed. The reducing atmosphere resulting from the presence of alcohol as solvent allows silver to be reduced to the metallic state during the calcination at 500 °C [4]. Because of the use of a silicon containing complex, that method implies that the final material is doped not only with silver but also with silica. This may have a beneficial effect according to several

studies mentioning a modification of photocatalytic activity in the presence of silica [5].

In the case of thin films, superhydrophilicity will be also evaluated in addition to photocatalytic activity. Indeed, both properties are based on the same underlying mechanisms. Very briefly, superhydrophilicity is induced as follows: positive holes, generated under UV illumination, can weaken bonds between oxygen and titanium resulting in the appearance of oxygen vacancies which promote adsorption of water and so the formation of -OH superficial groups [7,32]. These hydroxyl groups have a high affinity with water promoting the formation of a water film instead of a drop. Such an affinity with water is characterized by a low contact angle ($<5^\circ$) when a droplet of water is deposited at the surface of a superhydrophilic film [33]. The superhydrophilic properties of the film depend not only on film composition but also on surface properties such as roughness [9,32,34]. According to literature [32–34], introducing SiO_2 can improve superhydrophilicity. Some explanations are presented in the literature: (1) Si^{4+} , and also Ti^{4+} , can migrate during calcination, form species at the catalyst surface in favour of superhydrophilicity [32,35], (2) the formation of Ti–O–Si bonds can enhance the superhydrophilicity [32], (3) SiO_2 induces the creation of Lewis acid sites and thus promotes the OH adsorption at the catalyst surface [34].

With the aim of producing “easy-to-clean” surfaces, the combination of photocatalytic activity allowing the degradation of adsorbed pollutants, with superhydrophilicity inducing the formation of a water film which easily flows at the surface of the TiO_2 -based film, should provide a way to reach such a property for an adequately coated substrate.

The concomitant hydrolysis and condensation of the alkoxy silane-functionalized silver complex with titanium alkoxyde, that is their cogelation, has been adapted to produce SiO_2 doped and Ag– SiO_2 co-doped TiO_2 catalysts presenting enhanced photocatalytic activity and superhydrophilicity. The photocatalytic activity has been evaluated by monitoring the degradation of methylene blue under UV-A light in the presence of either powders or films over a period of 24 h. The photoinduced superhydrophilicity of the TiO_2 thin films and its evolution over time has been studied by measuring the contact angle at different times.

2. Experimental

2.1. Preparation of TiO_2 sols

Three types of sols have been prepared: pure TiO_2 sol, TiO_2 sol prepared using *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (EDAS) in order to obtain SiO_2 doped catalysts (named SiO_2 - TiO_2 in the following sections), and finally, TiO_2 sol prepared using EDAS complexing silver in order to obtain Ag– SiO_2 - TiO_2 catalysts (named Ag– SiO_2 - TiO_2 in the following sections).

Each sol has been prepared according to the procedure described in Fig. 2. That procedure is based on the synthesis reported by Braconnier et al. [4]. It has been however adapted to produce stable colloidal suspensions of pure and doped TiO_2

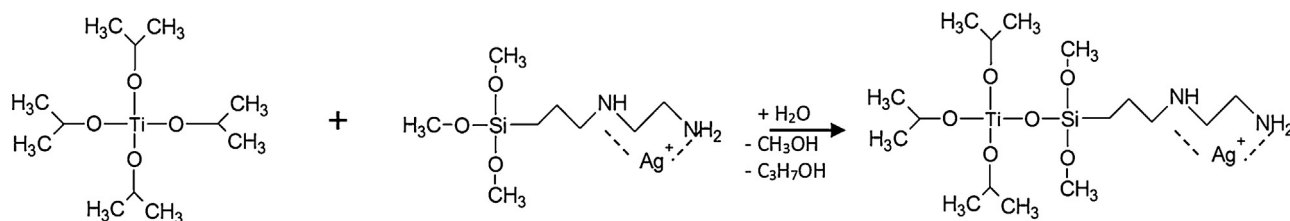


Fig. 1. Reaction between titanium isopropoxide (TTIP) and *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (EDAS) complexing Ag^+ in presence of water.

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