Journal of Photochemistry and Photobiology A: Chemistry 329 (2016) 189–202

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Full length article

Towards a large scale aqueous sol-gel synthesis of doped TiO_2: Study of various metallic dopings for the photocatalytic degradation of *p*-nitrophenol

Julien G. Mahy[a,*], Stéphanie D. Lambert[a], Géraldine L.-M. Léonard[a], Anthony Zubiaur[a], Pierre-Yves Olu[b], Abdelfattah Mahmoud[c], Frederic Boschini[c], Benoît Heinrichs[a]

[a] *Nanomaterials, Catalysis & Electrochemistry, Department of Chemical Engineering, University of Liège, B6a, Quartier Agora, Allée du six Août 11, 4000 Liège, Belgium*
[b] *Materials and Chemical Engineering, Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan*
[c] *LCIS/GREENMAT, Institute of Chemistry B6a, University of Liège, Allée de la Chimie 3, 4000 Liège, Belgium*

ARTICLE INFO

Article history:
Received 4 April 2016
Received in revised form 20 June 2016
Accepted 30 June 2016
Available online 1 July 2016

Keywords:
Doped aqueous TiO_2
Photocatalysis
Up-scaled synthesis
p-Nitrophenol degradation
Sol-gel process

ABSTRACT

In this paper, an easy aqueous sol-gel synthesis developed previously by Mahy et al. [1] is adapted to produce highly active TiO_2 catalysts doped with Fe^{3+}, Ag^{+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, Mn^{2+}, and Co^{2+} ions and Pt metallic nanoparticles. Samples are characterized by inductively coupled plasma–atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), Mössbauer spectroscopy, transmission electron microscopy (TEM), nitrogen adsorption–desorption measurements and diffuse reflectance spectroscopy measurements. Results show that the samples are composed of anatase-brookite TiO_2 nanoparticles with a spherical shape and mean diameter of around 5–8 nm and a surface area of between about 150 – 250 $m^2 g^{-1}$. In each doped sample, the dopant is present in the form added during the synthesis, given that the sample has not undergone any particular treatment. Photoactivity tests show improvement in catalyst activity for Fe^{3+}, Ag^{+}, Cu^{2+}, Zn^{2+}, and Al^{3+} ion and Pt metallic nanoparticle dopants, while a decrease of activity is obtained for Cr^{3+}, Mn^{2+} and Co^{2+} ion dopants. For some dopants, the activity of TiO_2 doped with metallic ions and synthesized from the aqueous sol-gel process is equal or superior to the activity of the commercial photocatalyst Degussa P25. Some mechanisms are proposed to explain these modifications of activity with doping. Furthermore, cost comparison at laboratory scale showed that Zn and Cu nitrate salt dopings are clearly less expensive for a halogen light (UV/visible) or low energy light enhanced catalyst and may be considered for industrial applications. Using this method, a large scale Zn-doped TiO_2 photocatalyst is synthesized with properties homologous to the lab-scale product. Results show that the aqueous sol-gel synthesis developed previously can be easily adapted for doping in order to produce an up-scalable synthesis.

1. Introduction

Environmental pollution is a major concern in our society and numerous researches are undertaken to treat water, air, and soil pollution. Pollutants can be aromatic compounds, pesticides, chlorinated compounds, heavy metals, or petroleum hydrocarbons. Among the different methods developed to reduce pollution, photocatalysis is a way to degrade organic pollutants [2].

This phenomenon consists of a set of oxidation-reduction (redox) reactions between organic compounds (pollutants) and active species formed from a photocatalyst. This method requires illumination of the catalyst to generate the first active species [3,4].

The most widely used photocatalyst is TiO_2 [5–7], which is a non-toxic and cheap semiconductor sensitive to UV radiation [8]. The amount of energy required to activate the TiO_2 is high in view of the width of the band gap (3.2 eV → 388 nm, for anatase phase) and, in the case of illumination by natural light, only the most energetic light (UV wavelengths) will be used for activation, which corresponds to 5–8% of the solar spectrum [9]. When TiO_2 is illuminated by sufficiently energetic light, electrons (e^-) are promoted from the valence band to the conduction band leading to

---

* Corresponding author.
E-mail address: julien.mahy@ulg.ac.be (J.G. Mahy).

http://dx.doi.org/10.1016/j.jphotochem.2016.06.029
1010-6030/© 2016 Elsevier B.V. All rights reserved.

the formation of positive holes (h^+) in the valence band. When these photo-generated e^- and h^+ are at the surface of the catalyst, they produce radical species, $O_2^{-\bullet}$ (superoxide) and $^\bullet OH$, from reactions with adsorbed O_2 and H_2O. These radicals react with the pollutant adsorbed on the surface of TiO_2 and induce pollutant degradation [1,4,5].

For several years, sol-gel synthesis has proven to be effective for the synthesis of TiO_2 in the form of powders or films with control of the nanostructure and surface properties [8,10–15]. The sol-gel process is called "soft chemistry" because reactions occur at low temperature and low pressure. The titanium precursor undergoes two main reactions: hydrolysis and condensation (Eqs. (1) and (2)) [16].

$$\text{Ti-(OR)}_4 + H_2O \rightarrow \text{(OR)}_3\text{-Ti-OH} + \text{ROH} \quad (1)$$

$$\text{(OR)}_3\text{-Ti-OH} + \text{HO-Ti-(OR)}_3 \rightarrow \text{(OR)}_3\text{-Ti-O-Ti-(OR)}_3 + H_2O \quad (2)$$

By controlling the rate of these reactions, a liquid sol or a solid gel is obtained. In order to obtain TiO_2 by sol-gel processes, two paths can be considered depending on the solvent used: non-aqueous and aqueous.

In a non-aqueous process, the sol-gel synthesis is conducted in an organic solvent able to complex the titanium precursor (Ti-$(OR)_4$) to control its reactivity. A stoichiometric amount of water is added to avoid precipitation [10,14,17,18]. The material then undergoes a drying and calcination step to remove residual organic molecules and to crystallize amorphous TiO_2 in anatase or rutile phases [19].

In an aqueous process, water is the solvent and is present in large excess. In this synthesis, peptizing agents are used to form small TiO_2-anatase nanoparticles at low temperature ($<100\,°C$) [9,20–24]. The main advantages of this route are that water is used as the solvent and anatase phase is obtained at low temperatures. This method is thus well suited for industrialization [1].

In a previous work [1], a global process has been developed to produce pure TiO_2 films deposited on steel at a large scale, in order to get an easy-to-clean surface [1]. For this work, the large scale process implies an easy aqueous sol-gel process for the synthesis of the TiO_2 sol. A synthesis has been simplified from [22] to make the extrapolation towards an industrial scale easier, and a pure TiO_2 sol is synthesized with this method up to volumes of 5 L. However, pure TiO_2 is not so useful for applications where only visible light is available. Thus, it is necessary to adapt this industrializable TiO_2 sol-gel aqueous synthesis [1] to enhance its photocatalytic properties by adding small amounts of dopant, but to keep the simplicity of the synthesis protocol. To improve the photocatalytic properties of TiO_2, several researches were conducted to extend TiO_2 activity in the visible light range by introducing metallic nanoparticles [11], metal ions [9,25–27] or combining TiO_2 with other semi-conductors [3]. These types of doping can enlarge the wavelength range absorbed by TiO_2 or enhance the electron-hole separation efficiency [28–30]. Some elements have shown their potential efficiency for photocatalytic enhancement of TiO_2 materials and/or photocatalytic properties in visible light. These elements are Fe [27,31–36], Ni [9,37,38], Ru [37], Ag [39–41], Cu [9,27,38], Zn [42], W [27,43], Cr [27,31,38,44], Al [45,46], Mn [38,47,48], Co [27,37,38], V [27,49–51], Nb [49], Zr [50,52,53] and Pt [54–58].

The aim of the present work is to validate a new doped experimental procedure at the laboratory scale and to select a type of dopant with optimal production costs and improved photocatalytic activity for a possible industrial scale-up of this synthesis. To reach this goal, the previously developed TiO_2 sol-gel aqueous synthesis [1] is doped with Fe^{3+}, Ag^+, Cu^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, Mn^{2+}, and Co^{2+} ions and platinum (Pt) metallic nanoparticles. The synthesis was adapted to produce the doped TiO_2. In the first part of this study the material formation, the resultant phases, the nature of the doping, the influence of doping and the catalyst textures are discussed. Samples were characterized by inductively coupled plasma–atomic emission spectroscopy (ICP-AES), X-ray diffraction (XRD), Mössbauer spectroscopy, transmission electron microscopy (TEM), nitrogen adsorption–desorption measurements and diffuse reflectance spectroscopy measurements. In the second part of this study, the photocatalytic activity of samples are tested for the degradation of *p*-nitrophenol (PNP, $C_6H_5NO_3$) under UV/visible light or low energy light to show the influence of dopants on the photoactivity. For a large scale synthesis, the best dopants have been identified based on their cost and the observed improvement of catalyst properties. From this, the best catalyst for cost and photoactivity has been synthesized at a larger scale in a pilot reactor (5 L) and has been characterized to check that the textural and photocatalytic properties are similar to the photocatalyst synthesized at the laboratory scale. The reference water pollutant used here is *p*-nitrophenol (PNP). This chemical is used in industry to produce pesticides, herbicides and insecticides, which can cause methemoglobinaemia, and eye and skin irritation upon contact [12].

2. Materials and methods

2.1. Sample preparation

2.1.1. Pure TiO_2 powder synthesis

A pure TiO_2 sol is synthesized by using titanium (IV) tetraisopropoxide (TTIP > 97%, Sigma-Aldrich), nitric acid (HNO_3, 65%, Merck), isopropanol (IsoP, 99.5%, Acros) and distilled water as starting materials [22]. Firstly, 250 mL of distilled water is acidified by HNO_3 to a pH equal to 1. Then, 35 mL of TTIP is added to 15 mL of IsoP, and the mixture is stirred at room temperature for 30 min. The TTIP + IsoP mixture is added to the acidified water under vigorous stirring. The liquid stays under stirring for 4 h at 80 °C. After this time, a light blue transparent liquid sol is obtained. Then, the sol is dried under an ambient air flow to obtain a xerogel which is crushed to form a white-yellow powder [1]. The powder is dried at 100 °C for 1 h. Pure TiO_2 samples are denoted as "TiO_2".

2.1.2. Doped TiO_2 powder synthesis

The TiO_2 catalyst is doped with 8 different transition metal ions (Fe^{3+}, Ag^+, Cu^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, Mn^{2+}, Co^{2+}) from the corresponding nitrate salts, and by platinum metallic nanoparticles (Pt).

For the transition metal ion doped TiO_2, the synthesis steps are identical to the pure TiO_2 synthesis except that the nitrate salt corresponding to the dopant is added to the distilled water before adding HNO_3.

For the platinum metallic nanoparticle doped TiO_2, a platinum colloid solution is prepared according to an adaptation of the Turkevich method [59], where sodium citrate is used as (i) a reducing agent of the Pt precursor salt and (ii) a capping agent of the metallic Pt colloidal nanoparticles. The precise experimental procedure for the synthesis of the Pt colloid solution used in the present work is specified in [60]. 250 mL of this colloid is acidified by HNO_3 to a pH equal to 1. Then, 35 mL of TTIP is added to 15 mL of IsoP, the mixture is stirred at room temperature for 30 min. The end of the protocol is the same as for pure TiO_2.

As for pure TiO_2, doped TiO_2 catalysts are dried under ambient air and crushed to obtain powder. The powders are dried at 100 °C for 1 h. Doped TiO_2 samples are denoted as "TiO_2/MX", with M the symbol of the metallic dopant and X the molar percentage of