



The role of Pt addition on the photocatalytic activity of TiO₂ nanoparticles: The limit between doping and metallization

Adriane V. Rosario, Ernesto C. Pereira*

Laboratório Interdisciplinar de Eletroquímica e Cerâmica, Centro Multidisciplinar para o Desenvolvimento de Materiais Cerâmicos, Departamento de Química, Universidade Federal de São Carlos, P.O. Box 676, 13565-905 São Carlos, SP, Brazil



ARTICLE INFO

Article history:

Received 23 January 2013

Received in revised form 15 June 2013

Accepted 12 July 2013

Available online 8 August 2013

Keywords:

TiO₂

Photocatalysis

Polymeric precursor method

Pechini method

Pt doping

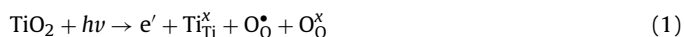
ABSTRACT

Platinum-loaded titanium oxide nanoparticles, Pt-TiO₂, were prepared using the polymeric precursor method with titanium isopropoxide as metal precursor. Platinum ions were added to the titanium precursor solution with Pt/Ti molar ratios between 0.005 and 10 mol%. The characterization of the physical properties was carried out by BET-surface area, transmission electron microscopy (TEM) and X-ray diffraction (XRD) with Rietveld quantitative analysis. The XRD patterns indicated that Pt doping occurred only for samples containing less than 1.0 mol% of platinum, and a small amount of rutile phase was observed after doping. For 1.0 mol% or higher Pt concentration a metallic Pt phase was detected. On the other hand, TEM analysis showed that the doping/metallization limit is still lower. Samples with nominal Pt concentration of 0.1 mol% presented signal of Pt metal particles. The photocatalytic activities of the samples were studied using methyl orange (MO) as model compound under UV illumination. In all Pt-TiO₂ samples the photocatalytic activity was found to increase in comparison with pure TiO₂ samples, either by the doping mechanism (at a low Pt concentration level), or by charge transfer mechanism in the interface metal/oxide (at a high Pt concentration level). The increase in Pt content, up to 0.2 mol% of Pt, was found to enhance the photocatalytic activity of TiO₂ towards the decomposition of MO. At even higher concentrations, platinum no longer acted as a dopant: instead, metallic Pt particles decorated the oxide surface. Doped and metallized samples had similar photocatalytic activity.

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1. Introduction

Photocatalytic reactions based on semiconductors, as TiO₂, are initiated by light absorption, in this case in the UV range. UV radiation absorption leads to the excitation of electrons (e⁻) from the valence band (VB) to the conduction band (CB), producing positive charge carriers, holes (h⁺), in the valence band, as reproduced in Equation 1 according to Kröger–Vink notation (e⁻ and h⁺ are represented by a negative e' and a positive defect O_O^x, respectively):



Both charge carriers, e⁻ and h⁺, migrate to the TiO₂ surface acting as reduction or oxidation sites, respectively. However, the use of TiO₂ as photocatalyst has important challenges, once the quantum efficiencies of photo-induced processes are very low. This occurs due to photocatalytic reaction rates are not fast enough to compete with the charge carrier recombination. As a consequence, in the last years, most of the published papers directed their attention

towards the synthesis of TiO₂ with improved properties. It is well established that the activity of TiO₂ depends on its surface and bulk properties in addition to, of course, the nature of the substrate to be degraded. In this sense, during the last decade different methods for producing TiO₂ have been employed, such as chemical vapour deposition (CVD) [1–3], metal organic chemical vapour deposition (MOCVD) [4,5], sputtering [6–8], pyrolysis [9,10], sol–gel processes [11–14], anodic oxidation [15–20], and hydrothermal synthesis [21,22].

Moreover, different strategies have been used to improve TiO₂ photocatalytic activity such as deposition over other materials, dye sensitization, doping and metallization. Among these strategies, doping and metallization are the main used procedures. It has been reported that doping with different transition metal ions can lead to an enhancement in the photocatalytic activity of TiO₂ as this process extends the sample's light absorption to the visible region. Different chemical elements have been proposed to dope TiO₂, either metals, such as Fe, W, Nb, or non-metals, such as N, C and S. The latter case, non-metals are used to replace oxygen atoms in the lattice. This effect has been reviewed by Carp et al. [23] and Rehman et al. [24]. However, the explanation of the results about photocatalytic efficiency variation is still controversial. Different structural and morphological changes depend on the preparation

* Corresponding author. Tel.: +55 16 33615215; fax: +55 16 33615215.

E-mail addresses: ernesto@ufscar.br, ernestopereira51@gmail.com (E.C. Pereira).

method and dopant concentration, resulting in positive or negative influences on the photocatalytic properties. Indeed, doping ions can also change the life time of the charge carriers, since they act as trapping sites, promoting the e^-/h^+ recombination.

In the metallization case, TiO_2 photocatalysts are modified with nanoparticles of noble metals such as Ag, Au, and Pt deposited on the particles surface [25–31]. In this case, it is proposed that the metal/ TiO_2 heterojunction influences the charge transfer process over the semiconductor particles. The difference between the work function of the metal islands and the Fermi level of TiO_2 results in the formation of a Schottky barrier between these components. With irradiation, the electrons in the conduction band flow from TiO_2 particles to the metal, increasing the charge separation and, consequently, decreasing the e^-/h^+ recombination. Additionally, electrons trapped on the metal surface can also act as reduction centres for adsorbed species. Usually, photodeposition has been used to decorate TiO_2 particles [29–31].

In the last years, Pt-modified TiO_2 are being investigated mainly under visible light irradiation [32–35], and although there are several studies regarding Pt-coated TiO_2 catalysts, Pt-doped TiO_2 samples have not been deeply studied. Currently, platinum is one of the most applied metals to enhance the photocatalytic properties of TiO_2 . However, it is important to stress out that there is some confusion in the literature due the incorrect use of the term “doping”. In most of the cases, TiO_2 decorated with Pt nanoparticles are called “doped systems”. In fact, such term can only be employed if Pt ions are incorporated into the oxide matrix, replacing Ti^{4+} ions, or eventually, in interstitial sites. In this sense, Kim et al. [36] studying Pt_{ion} -doped TiO_2 at doping levels ranging from 0.2 to 2.0 at%, observed noticeable differences in the photocatalytic properties when these samples are compared to Pt-metal-loaded TiO_2 . Choi et al. [35] prepared TiO_2 samples doped with 13 different metal ions, among them Pt^{2+} and Pt^{4+} . The authors confirmed the substitution of Ti^{4+} by Pt ions through elemental composition analysis by energy dispersive X-ray spectroscopy and observed significant enhanced visible-light photoactivity for decomposition of methylene blue, iodide and phenol.

In this context, this paper presents a systematic study of the effect of Pt-loading composition on photocatalytic properties. We have used the polymeric precursor method as an alternative synthesis route with the purpose of evaluating the effect of Pt content variation. This experimental procedure enables not only to control the concentration of Pt, working with very low doping levels, but also, permits the obtainment of samples decorated with Pt-metal maintaining the characteristics of oxide preparation. Thus, in this one-step synthesis, the effects observed on the photocatalytic properties of TiO_2 can be directly related only to the addition of platinum, eliminating other preparation variable effects. Finally, we corroborate this with evidence about the correlation between doping and photoactivity enhancement, which depends on the solubility limit of platinum metal ions in the TiO_2 matrix.

2. Experimental

2.1. Sample preparation

Pt-doped TiO_2 powders were prepared according to the process shown in Fig. 1, using citric acid (Synth p.a.), ethylene glycol (Mallinckrodt) and as metal precursors, titanium IV isopropoxide (Alfa Aesar) and hexachloroplatinum acid (Sigma–Aldrich). The precursor solutions were prepared by dissolving titanium IV isopropoxide and hexachloroplatinum acid in ethylene glycol under vigorous stirring at 70 °C. After this, the citric acid was added while stirring and heat were maintained until the complete dissolution of the citric acid. Precursor solutions were prepared in the following

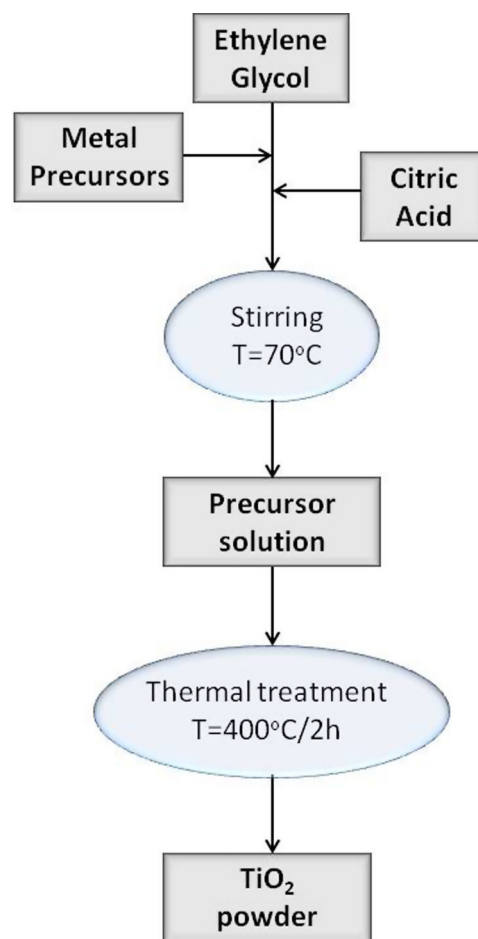


Fig. 1. Schematic representation of the preparation process of the Pt- TiO_2 powders.

rate: titanium IV isopropoxide: citric acid: ethylene glycol 1:8:32, which was loaded with different Pt ions concentrations; between 0.005% and 10 mol%. Subsequently, the precursor solutions were submitted to thermal treatment at 400 °C for 2 h to promote the elimination of organic part and oxidation of the metal. Fine powders were obtained by grinding TiO_2 samples after calcination.

2.2. Photocatalytic experiments

The experiments were performed in a box photoreactor equipped with six UV lamps of $\lambda = 253.7$ nm (Phillips – 15 W). The experiments were conducted in an open glass vessel surrounded by a water circulating jacket to maintain the thermostated temperature at 20 °C. The substrate was a 6×10^{-5} mol L⁻¹ methyl orange (MO) aqueous solution at pH = 3. This compound has a maximum absorption at 508 nm. For each photocatalytic run, 50 mg of TiO_2 powder was added to 50 mL of MO solution. The suspension was maintained under stirring and in the dark for 30 min (for the dye adsorption on the oxide particles surface). After this, the irradiation was started and solution aliquots were collected every 10 min. The samples were immediately centrifuged to separate the TiO_2 and the analysis of MO concentration in the reaction products was carried out by spectrophotometry using a UV–vis–NIR spectrophotometer (Cary model 5G). Previously, a calibration plot based on the Lambert–Beer law was established, relating the absorbance to the concentration. The maximum absorbance of the MO solution was used to determine the concentration of the collected aliquots.

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