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Sol–gel synthesis, characterisation and photocatalytic activity of pure, W-, Ag- and W/Ag co-doped TiO_2 nanopowders

D.M. Tobaldi [a,*], R.C. Pullar [a], A.F. Gualtieri [b], M.P. Seabra [a], J.A. Labrincha [a]

[a] Department of Materials and Ceramic Engineering/CICECO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal
[b] Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Via S. Eufemia 19, I-41100 Modena, Italy

HIGHLIGHTS

- Nano W-, Ag- and W/Ag co-doped titanias were synthesised by an aqueous sol–gel method.
- Rutile, anatase, brookite and amorphous phase were detected at 450 °C.
- Ag- and the co-doping gave the nanopowders a band gap contribution at around 2.93 eV.
- Ag- and co-doped nano-powders were photochromic.
- Powders, at 450 °C, showed noticeable photocatalytic activity under vis-light exposure.

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ABSTRACT

Tungsten, silver and tungsten/silver co-doped titania nanopowders were synthesised via an aqueous sol–gel method. The size distribution and zeta potential of the starting sols were determined via photon correlation spectroscopy (PCS). The dried gels were thermally treated at two different temperatures, and the occurrence of amorphous phase was assessed using the combined Rietveld–RIR X-ray powder diffraction method. A systematic study of the optical properties of the powders was made with diffuse reflectance spectroscopy (DRS), and the energy band gaps were calculated using the differential reflectance method; while their morphology was investigated using electron microscopy analysis (TEM). The photocatalytic activity of the samples was assessed in liquid–solid phase, under UVA-light and visible-light irradiation, monitoring the degradation of an organic dye. The influence of the phase composition, optical properties, dimensions, and specific surface area of the powders on the photocatalytic activity was thoroughly discussed.

1. Introduction

Research on semiconductor photocatalysis experienced a rapid growth in interest after the discovery, in 1972, of the so-called "Honda-Fujishima effect" [1]. This was photo-electrochemical water splitting, using a single-crystal titania electrode. As a result, in recent decades the degree of interest in semiconductor photocatalysis has grown exponentially, not only in the areas of water and air purification [2,3], but also in wastewaters treatment [4]. Semiconductors (e.g. TiO_2, ZnO, α-Fe_2O_3 or CdS) are able to act as sensitisers for light-activated redox processes because of their electronic structure: when a photon matches or exceeds the band gap energy of the semiconductor, an electron is liberated from the valence band into the conduction band, leaving a hole behind [5]. The photo-generated pair (e^-–h^+) is able to reduce and oxidise a pollutant that is adsorbed on the photocatalyst surface [6]. Amongst semiconductors, titanium dioxide (TiO_2) is indeed the most investigated photocatalytic material. TiO_2 is chemically inert and non-toxic; the reactions take place at mild operating conditions (e.g. low level of solar or artificial illumination, room temperature (RT) and atmospheric pressure); no chemical additive is necessary; the possible intermediates of the reactions are not dangerous (or at least are less dangerous than the original pollutant) [7]; volatile organic compounds (VOCs) [8,9], and even very recalcitrant and persistent pollutants can be degraded [10]. Moreover, one peculiar characteristic of titanium dioxide – simultaneous with the photocatalytic activity – is its antibacterial activity. When irradiated by light with a wavelength greater than the band-gap, TiO_2 photocatalysts can also be used to inactivate or kill bacteria that are on the photocatalyst surface, and hence to make those surfaces self-sterilising [11].

Titanium dioxide exists in a large number of polymorphs: besides the well-known and abundant rutile, anatase and brookite

* Corresponding author. Tel.: +351 234 370 041.
E-mail addresses: david.tobaldi@ua.pt, david@davidtobaldi.org (D.M. Tobaldi).

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