

Titanium dioxide modified with transition metals and rare earth elements: Phase composition, optical properties, and photocatalytic activity

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Abstract

A series of titania–transition metal and titania–rare earth element mixtures, with the stoichiometry $Ti_{1-x}M_xO_2$, where $M=Ce, Eu, La, Nb, W, Y$, and x ranging from 0 to 0.05 atoms per formula unit, were prepared via solid-state reaction of the precursor oxides. The products of the synthesis were thermally treated in air and two maximum temperatures (900 and 1000 °C) were reached.

The addition of transition metal and rare earth ions to the TiO_2 structure modified the anatase-to-rutile phase transition temperature, depending on the valence state of the ions added. Transition metals entered the titania structure, but essentially no solid solution between the rare earth elements and TiO_2 was detected.

The photocatalytic activity of the powders was assessed in liquid–solid and gas–solid phases, under UVA and visible-light irradiation, monitoring the degradation of an organic dye and isopropanol, respectively. The results were explained by taking into account the relative amounts of anatase and rutile in the samples, the specific surface area of the powders, and their optical properties.

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1. Introduction

Titanium dioxide (TiO_2) is a very common material used in everyday life applications. In recent decades, TiO_2 rose as the most popular material for photocatalytic applications—outdoor and indoor air purification [1–3] or decontamination of polluted waters [4]. Photocatalysis is the phenomenon in which a substance, the photocatalyst, modifies the rate of a reaction, via the action of light having a suitable wavelength; semiconductors are such substances [5,6]. When a semiconductor is irradiated with photons having energy higher than or equal to its energy band gap (E_g), an electron (e^-) is able to migrate from the valence band to the conduction band, leaving a hole (h^+) behind. Such a photo-generated couple (e^-h^+) is able to reduce and/or oxidise a pollutant adsorbed on the photocatalyst surface [7]. TiO_2 – mainly in

its anatase and rutile crystallographic polymorphs – is one of the most appreciated semiconductor photocatalysts. The positive features of heterogeneous photocatalysis with it, are: the reactions take place at mild operating conditions (low level of solar or artificial illumination, room temperature (RT), and atmospheric pressure); no chemical additive is necessary; the likely intermediates of the reactions are not dangerous or, at least, less dangerous than the original pollutant [8]; even very recalcitrant and persistent pollutants may be degraded [9]. Moreover, TiO_2 is also a relatively low-cost product, as well as non toxic.

Being a wide band gap semiconductor material ($E_g=3.2$ and 3.0 eV for anatase and rutile, respectively), the photocatalytic reaction of TiO_2 is activated by UVA light, although titania is transparent for most of the visible radiation region. This means that the photocatalytic reaction is exploited by only 3–5% of the solar spectrum. A number of attempts have been made to overcome this negative aspect. One of the routes followed, with the aim

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of extending the spectral response of pure titania to visible-light, was modifying its electronic structure by the insertion of non-metal atoms [10–14], transition metal (TM) ions [15,16], or rare earth elements (REE) [17,18]. The addition of dopants – such as anions, TMs, or REEs – into the TiO₂ lattice should produce a narrowing of the band gap, or an introduction of mid-states in the titania band gap, resulting in an absorption toward the visible region of the spectrum [14]. The non-metal doping often had a detrimental effect on the photocatalytic activity of TiO₂ under UVA exposure, because of an enhancement of charge recombination [19]; moreover, anion-doped titania also showed a low thermal and chemical stability [20]. Therefore, the use of suitable dopants (at a suitable concentration) such as TM or REE ions, should improve the photocatalytic performances of TiO₂, when thermally treated at high temperatures.

The present work deals with an investigation of TiO₂ modified with TMs (Nb₂O₅ and WO₃) and REEs (CeO₂, Eu₂O₃, La₂O₃, and Y₂O₃). The modification that TMs and REEs would exert on titania – anatase-to-rutile phase transition (ART) temperature, morphology, microstructure, and optical properties – were taken into account, in order to fully describe the modified titania powders, and their photocatalytic activity under UVA, and visible-light irradiation. Furthermore, the TiO₂–TM and TiO₂–REE mixtures were fired at high temperature (900 and 1000 °C), with the purpose of checking whether the photocatalytic activity was retained at such temperatures. Consequently, the studied mixtures may be employed on the surface of materials that need treatments at high temperature, so as to give them an innovative surface functionalisation [21,22].

2. Experimental

2.1. Sample preparation

The powders were prepared via solid-state reaction of the two crystalline end-members, according to this stoichiometry: Ti_{1-x}M_xO₂ where M = Ce, Eu, La, Nb, W, and Y. For the REE addition (CeO₂, Eu₂O₃, La₂O₃, and Y₂O₃) $x = 0, 0.01$ and 0.025 atoms per formula unit (apfu), whilst for TM addition (Nb₂O₅ and WO₃), x was equal to $0, 0.01, 0.025,$ and 0.05 apfu. Aeroxide P25 TiO₂ powder was used as the titania source (hereafter designated as D), while reagent-grade CeO₂, Eu₂O₃, La₂O₃, Nb₂O₅, WO₃, and Y₂O₃ (all supplied by Aldrich) were used as TM and REE precursors. Powders were admixed and wet ground in a rotary ball mill (30 min with deionised water and zirconia sintered balls). Mixtures were dried in an oven (105 °C overnight), ground in an agate mortar, and then calcined; the firing was performed in an electric oven with static air atmosphere, the heating rate was 200 °C h⁻¹, and two maximum temperatures were reached (900 and 1000 °C), with a soaking time at the maximum temperature of 4 h, followed by natural cooling. TiO₂ samples, used as

reference, were referred to as the first initial of the commercial powder used, followed by a number indicative of the maximum firing temperature reached (i.e. D-900 for Aeroxide P25 TiO₂ powder fired at 900 °C); in case of TiO₂–TM or TiO₂–REE mixtures, the symbol of the chemical element followed by the amount of apfu inserted was used (i.e. sample with 0.01 apfu of Europium added to Aeroxide's titania, and calcined at 900 °C, is referred to as: Eu0.01-900).

2.2. Sample characterisation

The phase composition of the starting titania powders, as well as of the TiO₂–TM and TiO₂–REE mixtures, was obtained via X-ray diffraction, using a Rigaku Geigerflex (JP); the patterns were collected in the 15–80° 2θ range (0.02° 2θ s⁻¹ step-scan and 5 s/ step). The anatase/rutile relative amounts in the titania reference powders, as well as in the modified samples that were composed only of anatase and rutile, were calculated using the Spurr–Myers procedure [23]. Instead, a semi-quantitative estimate of the likely amount of anatase/rutile ratio, as well as the secondary phases – in the TiO₂–TM and TiO₂–REE mixtures – was achieved by adopting the generalised RIR method [24]. In both cases, we assumed the absence of amorphous phase in the examined powders.

The morphology of the samples was investigated by SEM (Hitachi SU-70, JP), equipped with an energy dispersive X-ray spectroscopy (EDS) attachment (Bruker AXS, DE). Optical spectra of the samples – and subsequently, the E_g – were acquired on a Shimadzu UV 3100 (JP), in the UV–Vis range (200–800 nm), with 0.02 nm step-size, and using BaSO₄ as reference. The diffuse reflectance was converted into the absorption coefficient α , using the Kubelka–Munk function [25]:

$$\alpha \approx \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \equiv F(R_\infty) \quad (1)$$

The E_g of the powders was calculated using the differential reflectance method: plotting the first derivative of reflectance versus the wavelength λ (dR/d λ), the maximum value of such plot corresponds to the band gap of the semiconductor material [26]. The specific surface area (SSA) of the prepared samples was evaluated by the Brunauer–Emmett–Teller method (BET) (Micromeritics Gemini 2380, US) using N₂ as the adsorbate gas.

2.3. Evaluation of photocatalytic activity

The photocatalytic activity of the prepared powders was evaluated both in liquid–solid phase and in gas–solid phase, the former monitoring the degradation of an organic dye – methylene blue (MB) – via a spectrometer (Shimadzu UV 3100, JP), the latter monitoring the degradation of isopropanol, and the subsequent formation of acetone, by FT–IR spectroscopy.

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