



# Photocatalytic activity of TiO<sub>2</sub>-WO<sub>3</sub> mixed oxides in relation to electron transfer efficiency



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## ABSTRACT

Aiming at producing photocatalysts with minimized photoproduced electron – hole pairs recombination, a series of titanium – tungsten mixed oxides has been prepared, by coupling TiO<sub>2</sub> with different amounts of WO<sub>3</sub>, according to an alkaline-catalyzed sol-gel method followed by an incipient wetting procedure. The photocatalysts were characterized by surface and bulk techniques and tested in both an oxidation and a reduction photocatalytic reaction, *i.e.* in formic acid (FA) mineralization and in Cr(VI) reduction. Tungsten was mainly present as hexagonal WO<sub>3</sub> on the TiO<sub>2</sub> surface, though a fraction of W migrates into the TiO<sub>2</sub> lattice substituting Ti atoms, as evidenced by XRPD analysis. Different photoactivity scales were found in the two test reactions, both occurring in the same pH range under similar substrate-photocatalyst electrostatic interactions. In fact, photoexcited electrons transferred from the conduction band (CB) of TiO<sub>2</sub> to the CB of coupled WO<sub>3</sub>, being energetically unable to reduce O<sub>2</sub> molecules, easily recombine with photoproduced holes, with a consequent photoactivity decrease in FA photo-mineralization with increasing W/Ti ratio. On the contrary, coupling TiO<sub>2</sub> with small WO<sub>3</sub> amounts (0.2–1.0 mol%) is beneficial in the removal of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anions. These species, being characterized by a redox potential more positive than the CB edge of WO<sub>3</sub>, may efficiently accept the electrons trapped in WO<sub>3</sub> domains, converting into less toxic Cr(III) species. Thus, WO<sub>3</sub> surface domains effectively promote photoproduced charge separation by efficiently trapping CB electrons; increased photocatalytic efficiency depends on the redox potential of the electron acceptor species directly (or indirectly) involved in the photocatalytic process.

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## 1. Introduction

Many strategies have been employed in the last decade in order to minimize a crucial drawback of TiO<sub>2</sub> use as photocatalytic material, *i.e.* the fast and undesired recombination of photoproduced electron – hole pairs, strongly limiting the overall efficiency of photocatalytic processes occurring on the oxide surface [1,2]. In particular, besides the well-established effects in photogenerated electron-hole separation induced by surface noble metal (Au, Pt) nanoparticles able to capture conduction band electrons [3,4], the idea of coupling TiO<sub>2</sub> with another metal oxide with suitable band gap and edge positions can be pursued as a possible route to enhance photoproduced charge separation [5,6]. In fact, by coupling TiO<sub>2</sub> with a metal oxide having the conduction band (CB)

lower in energy than the CB of TiO<sub>2</sub>, photopromoted electrons may transfer from the CB of TiO<sub>2</sub> to that of the other metal oxide, while photogenerated holes remain trapped within the TiO<sub>2</sub> particles, with consequent increased electron-hole separation. Among the possible semiconductor metal oxides, crystalline WO<sub>3</sub> has a suitable CB energy which enables electrons photopromoted in the CB of TiO<sub>2</sub> to transfer into the CB of WO<sub>3</sub> [5].

TiO<sub>2</sub>/WO<sub>3</sub> nanocomposites, prepared by different techniques, including sol-gel [7–9], impregnation [10,11], hydrothermal reaction [12], ball milling [13], flame spray synthesis [14], and in different forms [15–17] were mainly used in the photocatalytic degradation of organic pollutants also under possible visible light activation [7,15]. Unfortunately, most of these studies employed dyes as degradation substrates [7–9,11,12,14,16], which makes the interpretation of the photoactivity results rather controversial, due to the possible dye-sensitized path parallel to photocatalyst activation, charge separation and charge transfer at the photocatalyst surface [18].

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In general, the increased photocatalytic activity observed upon tungsten addition to TiO<sub>2</sub> was ascribed to increased charge separation efficiency [19], though other effects also need to be invoked, such as the increased surface acidity consequent to WO<sub>3</sub> introduction, which may alter the surface charge and thus the substrate adsorption equilibria [10,14], and the increased surface area of the W-modified material, consequent to the stabilized anatase phase upon doping TiO<sub>2</sub> with W and leading to increased absorption capacity of the doped materials [8,11].

In the present work we systematically investigate the effects on photoactivity induced by modifying TiO<sub>2</sub> with different amounts of WO<sub>3</sub> in TiO<sub>2</sub>-WO<sub>3</sub> mixed oxides. This study follows a previous investigation on the same mixed oxides [20] prepared by sol-gel synthesis starting from alkoxide solutions of the two metals, which left open the question if the superior performance of these mixed oxide photocatalysts should be ascribed to the presence of separate domains of the two oxides, or simply be a consequence of W-doping of TiO<sub>2</sub>. For this reason, in the present work the photocatalytic materials were prepared starting from pure titania, followed by its surface modification by different amounts of WO<sub>3</sub>. The so obtained mixed oxides photocatalysts were tested in both an oxidation and a reduction photocatalytic reaction, *i.e.* in formic acid (FA) mineralization and in Cr(VI) reduction. The fact that both reactions occur in aqueous suspension at pH 3.7 starting from negatively charged substrates makes the comparison between the photoactivity of the TiO<sub>2</sub>-WO<sub>3</sub> photocatalysts much easier, any effect related to different pH conditions being avoided.

In fact, the pH of aqueous suspensions may strongly affect the charging process of -OH groups exposed on the photocatalyst surface which may act as specific adsorption sites for the photocatalytically transformed species. Indeed, the here chosen test compounds (*i.e.* formate and dichromate anions) are both negatively charged, so they have similar affinity for the investigated photocatalysts surface in the same pH range.

Formic acid (FA) is an excellent photodegradation substrate to preliminarily check photoactivity because it does not absorb in the UV-vis region and it undergoes direct photomineralization without forming any stable intermediate species, which simplifies the interpretation of kinetic results. Though not being a pollutant, FA can be envisaged as a model substrate of the oxidative degradation of organic species mainly occurring through direct interaction with the holes photoproduced in the semiconductor photocatalyst system.

On the other hand, Cr(VI) ions, which are notoriously toxic and carcinogenic, are generally released in effluents by various industrial activities (*e.g.* electroplating, leather tanning, textile production, steel fabrication). The development of materials able to efficiently promote their photocatalytic reduction has great importance in the scenario of photocatalysis as innovative and clean technology for industrial wastewaters decontamination.

## 2. Experimental

### 2.1. Photocatalysts preparation

Amorphous TiO<sub>2</sub>, labeled as P, was synthesized according to an alkaline-catalyzed sol-gel method, as follows. Titanium isopropoxide (40 mL) was mixed with 2-propanol (50 mL) and the so obtained solution was vigorously stirred for 15 min. Then 250 mL of a 15 mM aqueous KOH solution were added dropwise to the titanium-containing solution. Hydrolysis occurred immediately. After stirring for 90 min at room temperature, the obtained white slurry was centrifuged, washed twice with freshly distilled water, dried in air at 80 °C for 24 h and finally ball-milled for 5 min at 10 Hz.

The series of TiO<sub>2</sub>-WO<sub>3</sub> mixed oxides was prepared by an incipient wetting procedure, as follows. An aqueous solution (3 mL) containing the proper amount of ammonium *meta*-tungstate hydrate, (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·xH<sub>2</sub>O, was added dropwise to 1.5 g of P, in order to obtain W/Ti nominal percent molar ratios in the 0.2–3.0 range. The slurry was mildly stirred for 24 h, then dried in air at 120 °C for 24 h and ball-milled for 5 min at 10 Hz. The resulting powder was annealed in air at 450 °C for 24 h, with an initial heating ramp of 7 °C min<sup>-1</sup>.

The so obtained samples were labeled as T.W(X), with X referring to the nominal W/Ti percent molar ratio. Samples prepared with W/Ti = 5.0% were mainly used for XRPD characterization. They were calcined either at 450 °C or at 600 °C for 24 h and labeled as Ti.W(5) and Ti.W(5).600, respectively. Moreover reference TiO<sub>2</sub> samples, labeled as T and T.600, were prepared by following exactly the same synthetic route in the absence of any W precursor, followed by thermal treatment at 450 °C or 600 °C for 24 h, respectively. Finally a bare WO<sub>3</sub> powder, labeled as W, was obtained by annealing a batch of solid ammonium *meta*-tungstate hydrate at 450 °C for 24 h.

All chemicals employed in the synthesis of the materials and in the preparation of the solutions were purchased from Aldrich. Water purified by a Milli-Q water system (Millipore) was used throughout.

### 2.2. Photocatalysts characterization

The BET specific surface area (SSA) of the materials was measured by N<sub>2</sub> adsorption/desorption at liquid nitrogen temperature in a Micromeritics Tristar II 3020 V1.03 apparatus, after out-gassing at 300 °C for 1 h under N<sub>2</sub> stream. Diffuse reflectance (DR) spectra of the photocatalyst powders were recorded with a Jasco V-670 spectrophotometer equipped with a PIN-757 integrating sphere, using barium sulphate as reference, and then converted into absorption (A) spectra (A = 1 - R).

X-ray photoelectron spectroscopy (XPS) data were collected in a multi-technique ultra-high-vacuum (UHV) chamber (base pressure: 1.0 × 10<sup>-9</sup> mbar) equipped with a VG MKII ESCALAB electron analyzer (5 channeltrons). XPS spectra were collected at room temperature in normal emission using a non monochromatized Mg anode X-ray source (hν = 1253.6 eV). The calibration of the binding energy (BE) scale was determined using the Ti 2p<sub>3/2</sub> maximum as reference. Powder samples were suspended in bi-distilled water and drop-casted on high-purity copper foils. After drying in air, the obtained films were introduced into the UHV chamber and outgassed overnight. The charging observed during measurements was corrected by aligning the Ti 2p<sub>3/2</sub> core-level peak signal to 459.0 eV.

Energy dispersive X-ray (EDX) spectroscopy experiments, performed using a Zeiss Leo 1430 Scanning Electron Microscope equipped with an Energy Dispersive Spectroscopic (EDS) microanalysis probe from Oxford instruments, provided information on the composition of the photocatalysts, in terms of atomic percent amounts.

X-ray powder diffraction (XRPD) patterns were recorded at the ID22 beamline of the ESRF (European Synchrotron Radiation Facility, Grenoble) at room temperature with an incident wavelength λ = 0.31992 Å, up to 2θ = 50°. The powdered samples were packed into 1.0 mm in diameter kapton capillaries and were spun during data collection. The patterns were analyzed employing the Rietveld refinement, as implemented in the GSAS software [21]. Patterns were corrected for anomalous scattering and for absorption through the Lobanov formula [22], after direct determination of the packing fraction of the powder into the capillary. The distribution of W ions within the anatase phase was determined by refining the atomic Ti/W occupation factor of the 4b site (0, ¼, 3/8)

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