

A comparison of the photocatalytic activity between commercial and synthesized mesoporous and nanocrystalline titanium dioxide for 4-nitrophenol degradation: Effect of phase composition, particle size, and addition of carbon nanotubes

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ABSTRACT

The photodegradation of 4-nitrophenol in aqueous solution was studied by using titania-based photocatalysts, in particular standard commercial titania samples (anatase and rutile, Hunstmann; P25 and Aeroxide VP P90, Evonik) and a mesoporous and nanocrystalline titania synthesized under hydrothermal conditions. A comparison between the commercial products and our preparations made evident a different particle size and phase composition. Moreover, in order to investigate a possible synergism between TiO₂ and carbon nanotubes (CNTs), further two samples were purposely synthesized by adding to the reaction mixture used for the catalyst preparation a small amount of single-walled or multi-walled carbon nanotubes (SWCNTs and MWCNTs). Among the investigated solids, the nanocrystalline titania resulted to be the most active photocatalysts. The less active solids were rutile and mesoporous titania. The addition of a small amount of MWCNTs further increased the photoactivity of the nanocrystalline titania.

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1. Introduction

The presence in wastewater of nitrogen-containing organic compounds, and, in particular, some phenol derivatives, is of particular concern due to their heavy toxicity which remarkably affects the ecosystems via the contamination of surface and ground water supplies, this causing very serious problems all along the food chain and on the human health. Therefore, the removal of nitrogen-organic compounds from the wastewater is a matter of great concern and the photodegradation still remains one of the most attractive methods to accomplish that. The use of titania as active photocatalyst for the photodegradation of nitrogen-containing compounds is well established and several reviews were published on this and related subjects [1–7]. The photodegradation of organic compounds usually occurs through highly reactive radicals as O₂•⁻, HO₂•, OH• that are generated from

the reaction of molecular oxygen or water molecules, adsorbed on the titania surface, with the photogenerated electrons and holes resulting from the interaction of the light with the TiO₂-based photocatalyst. These reactive radicals initiate redox reactions with the adsorbed organic compounds until their complete mineralization.

In spite of the interest and continuous growth of literature data on the TiO₂-based photocatalysts, the major issues concerning the photoactivity of the titania polymorphs are still under debate and a number of hypotheses have been proposed to explain the high catalytic efficiency of anatase [1–7]. They include: (i) special surface active sites whose formation is favoured by the crystal structure of anatase; (ii) the presence on anatase powder of differently oriented facets particles; (iii) the higher specific surface of anatase powder particles; (iv) a difference in the band gap of bulk anatase (3.2 eV) relative to bulk rutile (3.0 eV); and (v) differences in the photoexcited electrons–holes lifetime.

The specific function and influence of each one of the structural and electronic features of titania polymorphs is difficult to be identified separately since the relevant parameters are often correlated.

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In the present contribution, we compared the photocatalytic activity for the degradation of 4-nitrophenol (4-NP) in aqueous solution of standard commercial TiO₂ samples (Evonik: P25, and Aeroxide VP P90; Huntsman: anatase and rutile) with that of some mesoporous and nanocrystalline titania samples synthesized in our laboratory under hydrothermal conditions. The results of this study may be of interest in developing new photocatalysts based on porphyrine sensitizers supported on titania to increase and extend the photoactivity from UV to visible region of the solar spectra [8,9].

In order to confirm the synergism between TiO₂ and carbon nanotubes (CNTs) [10], the mesoporous and nanocrystalline samples were synthesized adding to the reaction mixtures used for the photocatalyst preparation a small amount of single-walled or multi-walled carbon nanotubes (SWCNTs and MWCNTs). This seemed to be an interesting point to explore since spontaneous formation of Schottky-type rectifying junctions TiO₂-CNTs were previously reported to improve the charge transport toward the anode of dye-sensitized solar cells with respect to the charge recombination phenomena [11]. Indeed the improved performance of thermal reduced graphene oxide-P25 composite photocatalyst for the photodegradation of methyl orange dye reported by Morales-Torres et al. [12] was also attributed to the good contact between the TiO₂ and the carbon phases.

2. Experimental

2.1. Materials

Evonik P25, Aeroxide VP-P90 and Huntsman (rutile and anatase) were the commercial titania samples used in this study. Mesoporous titania nanosized samples were prepared by using TiOSO₄·H₂O as precursor and cetyltrimethylammonium bromide

(CTAB) as a surfactant-directing and pore-forming agent [13]. These samples were labeled as 'TiO₂-CTAB'. The samples TiO₂-CTAB-1 and TiO₂-CTAB-2-C have the same CTAB:Ti:H₂O = 1:11:833 molar ratio whereas the sample TiO₂-CTAB-3 was prepared using a molar ratio of CTAB:Ti:H₂O = 1:0.27:20. The synthesis procedure consisted in the following steps (the reactants amount reported refer to the TiO₂-CTAB-1 sample). 29.5 g (0.166 mol) of TiOSO₄·H₂O (Alfa Aesar) were dissolved in 92 mL distilled water after 1 h sonication and then a solution containing 5.47 g (0.015 mol) of CTAB (Alfa Aesar) in 133 mL of distilled water, preliminarily stirred for 12 h at room temperature (RT), was added to it. The resulting mixture was kept under stirring at RT for 13 h, poured in a Teflon lined stainless steel autoclave (V=275 mL) and kept at 100 °C for 72 h for the hydrothermal treatment. The resulting solid was separated by centrifugation, washed 3 times first with distilled water and then with ethanol (RPE, Carlo Erba) and finally dried at RT for 3 days. The surfactant was removed from the solid upon stirring its suspension in a mixture of water (150 mL) and ethanol (500 mL) containing NaCl (20 g). The residual solid material was separated by centrifugation, dried overnight in air at 120 °C and then calcinated in air at 400 °C for 6 h. TiO₂ samples containing carbon nanotubes were prepared by adding a small amount of SWCNTs to the TiOSO₄·H₂O solution. In particular, 3.3 mg of SWCNTs were added per 30 g of TiOSO₄·H₂O. SWCNTs were purchased by Cheap Tubes (Battleboro, Vermont, USA).

The nanocrystalline titania photocatalyst, labeled as TiO₂-1, was prepared starting from the precursor Ti(OPrⁱ)₄, acetic acid (glacial, AcOH) and water (molar ratio 1:1:80) in absence of the surfactant-directing agent [14]. The experimental procedure for the synthesis of this samples follows: 28.3 g (0.0995 mol) of Ti(OPrⁱ)₄ (Vertec, +97%) was added to 5.78 g (0.0960 mol) glacial acetic acid (99.8 wt%, RPE, Carlo Erba) and the mixture was kept under stirring at RT for

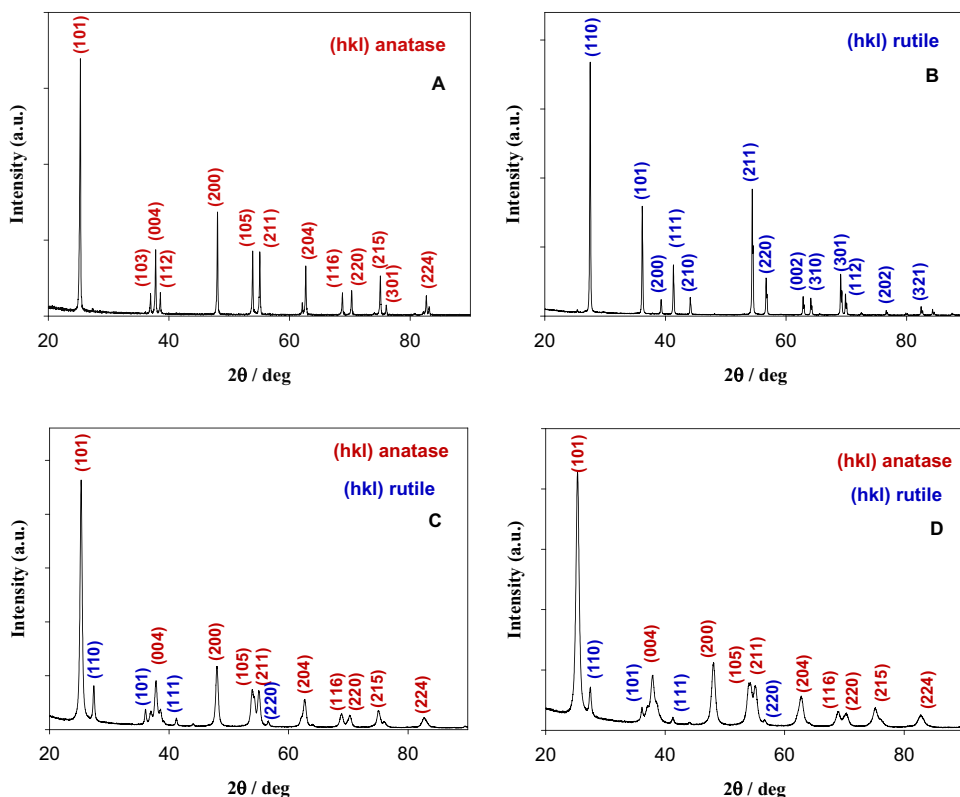


Fig. 1. X-ray diffraction patterns (Cu K α radiation) of commercial titania samples: (A) Huntsman anatase; (B) Huntsman rutile; (C) Evonik P25; (D) Evonik Aeroxide VP P90.

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