

# BLACK TITANIAS FOR PHOTOCATALYSIS, SOLAR CELLS AND ENVIRONMENTAL APPLICATIONS

**P** PATENTED TECHNOLOGY

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## ABSTRACT

The Molecular Nanotechnology Lab (NANOMOL) of the University of Alicante (Spain) and the Organometallic Molecular Materials Research Group from the University of La Rioja (Spain) have developed a new synthetic approach for the synthesis of black titanias with outstanding photocatalytic activity under visible light. This novel procedure is simple (one-pot synthesis), versatile and cheap (mild conditions, without the concurrence of surfactants, calcinations or high temperature steps) thereby saving cost in materials and energy.

The technology has been developed and successfully tested at the laboratory getting black titanias with excellent photocatalytic activity both in the ultraviolet, and what is more interesting, in the whole visible range, and good thermal and hydrothermal stability. These materials find application in very different areas such as the degradation of organic pollutants, DeNO<sub>x</sub> processes or as an alternative to the Grätzel solar cells.

The technology is protected by a Spanish patent application and the group is looking materials producing companies interested in acquiring the technology for commercial purposes, or to establish partnerships for the development and industrial scale, or companies interested on testing the materials for photocatalysis, solar cells or environmental applications.

## INTRODUCTION

Titanium dioxide, also known as titania, is one of the most widely used semiconductors photocatalysts in water/air purification, hydrogen production from water splitting, pollutants elimination (VO<sub>x</sub> and NO<sub>x</sub>) and high-efficiency dye-sensitized solar cells (DSC). Titania has many advantages: it is cheap, abundant, non-toxic, chemically stable, and biocompatible, and is widely used in health care products as well as in paints. However, TiO<sub>2</sub> overall efficiency for solar-driven photocatalysis is very limited, because of its large band gap (3.2 eV for anatase phase) which corresponds to the UV light range (380 nm anatase phase) which accounts for less than 5% of the total solar irradiation. Therefore, significant efforts are being conducted to reduce its band gap to the 400-900 nm spectral range (visible and near-IR), but the results are so far from the market requirements.

So, there is an urgent need for a new and disruptive technology based on a simple and cheap synthesis methodology which will allow for the engineering of the band gap of semiconductors to fully utilize the visible light range, giving these promising photoactive materials a commercial opportunity.

We have developed a new synthesis approach to reduce the band gap of titania materials by using an environmentally friendly one-pot method (no surfactant, using only water and a minimum quantity of ethanol as solvents and mild conditions) that allows the incorporation of different functionalities (organic compounds, dyes, metal complexes...) in the structure of titania. Hybrid materials have anatase structure and BET areas of c.a. 300 m<sup>2</sup>/g.

By using this approach, we have produced a highly active and stable photoactive black titania, with a remarkable reduction of its band gap (from 3.20 eV to 2.74 eV), being able to absorb in the whole visible range (Fig. 1).

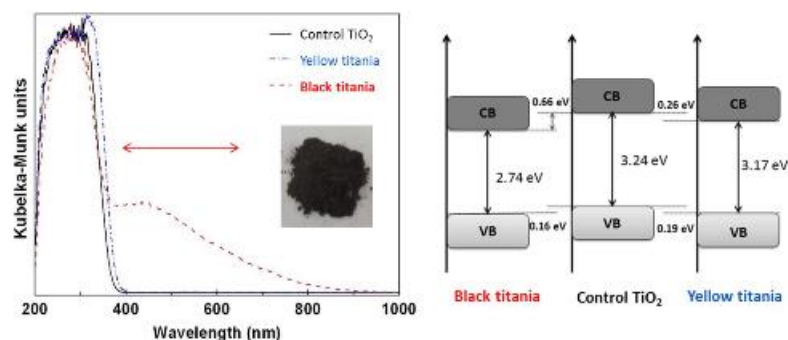


Fig 1. DRUV spectra (up) and schematic illustration of the density of states, DOS, (bottom) of black titania (in red) in comparison with the control titania (in black) and with one yellow titania also synthesized by our groups (in blue)

The black titania exhibited enhanced photocatalytic activity under UV and visible light in the Rhodamine 6G degradation reaction under both UV and visible irradiation (TOC measurements confirmed degradation towards CO<sub>2</sub>), Fig. 2, left. Recycling tests under the same conditions prove the stability of this hybrid titania (Fig. 2, right). This new photocatalyst has been recently tested indicating very good NO<sub>x</sub> degradation values with high selectivity towards nitrates when tested in a road. This material constitutes the only example on the use of polymetallic titanium alkoxides as organotitania precursors for the synthesis of stable and visible-light active titanias.

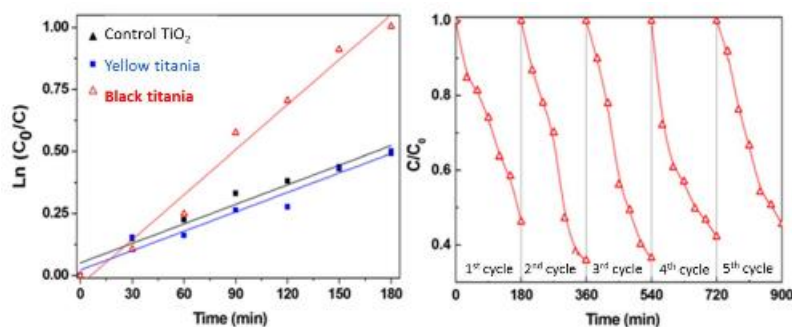


Fig 2. Photocatalytic activity and recycling tests under the same conditions in the degradation reaction of an aqueous solution of R6G (5\*10<sup>-5</sup> M) under visible (400 W) irradiation

The technological potential of these hybrid titanias covers areas ranging from photocatalytic splitting of water for hydrogen production or purification of water/air to dye-sensitized solar cells or materials for example, for self-cleaning applications.

## TECHNOLOGY ADVANTAGES AND INNOVATIVE ASPECTS

### ADVANTAGES OF THE DEVELOPED TECHNOLOGY

- The proposed synthetic method is very simple, versatile and can be carried out at low temperature and pressure, avoiding the use of hazard conditions, such as hydrogen or ammonia at high temperatures, with the consequent saving.
- Our black titania is able use the whole UV and visible range of solar radiation showing a really high photocatalytic activity and thermal stability with an increase of only 0.6% in the production cost in comparison with control titania.
- Crystal disruptors are incorporated into the bulk of the semiconductor which greatly protects them (avoiding the problems associated to the stability of the dye) and improves the electronic transference of the charge-transfer dye.
- Band gap control is carried out by crystal engineering instead of the traditional band gap engineering based on chemical methods (i.e. doping and hydrogenation) diminishing the charge-recombination probability.

### INNOVATIVE ASPECTS OF THE TECHNOLOGY

- The titania is black, and then absorb in the whole visible range (band gap 2.74 eV) and maintains its photocatalytic activity at least after 5 cycles reaction with an efficiency of 95 %.

- The synthesis process is simple, inexpensive and versatile (a wide variety of functional compounds can be incorporated in the structure of the titania lattice avoiding blocking the mesoporosity and maintaining the anatase structure).
- Excellent thermal and hydrothermal stability. The functionality is incorporated into the structure of the titania being protected thereby.

#### CURRENT STATE OF DEVELOPMENT

The technology has been developed and successfully tested at the laboratory. The results of the different tests have demonstrated the effectiveness of the synthesis process and the good properties of the obtained functionalized titanias. This technology is available for demonstration – field tested.

#### MARKET APPLICATIONS

- Photocatalysis. Companies producing photocatalytic materials.
- Solar panels. Companies producing materials for solar panels for the enhancement of its efficiency.
- Materials degradation of contaminants in soil, water or asphalt.

#### COLLABORATION SOUGHT

Companies interested in acquiring this technology for commercial exploitation by:

- Agreements patent license to use, manufacture or commercialization of the technology.
- Partnerships for development and industrial scale and technology for application in various sectors.

#### INTELLECTUAL PROPERTY RIGHTS

This technology is protected by patent application.

- Title: "In-situ functionalized mesoporous titania. Methods of Making and Use"
- Application number: 201300536
- Date of application: 06/05/2013

Also, a PCT application has been filed for international extension.

#### MARKET APPLICATION (4)

Construction and Architecture  
Pollution and Environmental Impact  
Materials and Nanotechnology  
Chemical Technology