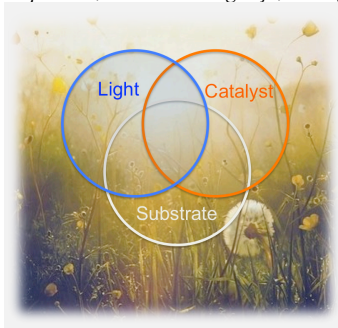


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When dealing with chemical wastewater treatments one depends on the addition of auxiliary oxidants, which may include molecular oxygen, ozone, and hydrogen peroxide, working on their own, or activated by means of a catalyst or photocatalyst. Typical solutions are the thermal processes at elevated temperatures and pressures. Alternatively, it is possible to use heterogeneous photocatalysis at room temperature and atmospheric pressure. With the development of new carbon allotropes a whole range of advanced oxidation processes, traditionally based on the action of the HO<sup>•</sup> radical, can be explored using carbon materials as common denominator.

### Introduction

Typical solutions for chemical wastewater treatments use auxiliary oxidants, which may include molecular oxygen, ozone, and hydrogen peroxide. Chemical treatments are by nature definitive processes, since they can lead to complete mineralization of the existing pollutants. However, this is seldom the case, when looking for a rational solution from the socio-economical point of view. In the case of industrial effluents, special treatments are often required, even when only a partial oxidative degradation is targeted, due to the complex nature of the pollutants.

Thermal processes at elevated temperatures and pressures are still very popular in spite of their environmental and energetic costs. Heterogeneous photocatalysis at ambient conditions is rapidly gaining importance. Somewhere between these two limits lies the catalytic wet peroxide oxidation (CWPO) a thermal approach with mild conditions where the main role of the catalyst is to promote H<sub>2</sub>O<sub>2</sub> decomposition through the formation of hydroxyl radicals (HO<sup>•</sup>) with high oxidizing potential, effective in the destruction of a huge range of pollutants. All these AOP, traditionally based on the action of the HO<sup>•</sup> radical, can be explored using carbon materials as common denominator.

The present work will cover different types of approach on fabrication of nanostructured photocatalysts. The focus will be on pure carbon materials with nanometric dimensionality, nevertheless some attention will be paid to metal oxides, in order to explore the hybrids or the composite materials consisting of the two phases – carbon and metal oxide. Their use will be

illustrated by some potential applications under development in our group.

Heterogeneous photocatalysis has emerged as a very important tool in the development of sustainable technologies for energy production, chemical synthesis and water and air treatment. There is no way of circumvent the importance of TiO<sub>2</sub>, the most widely used photocatalyst, essentially because of its indisputable performance in general case photocatalytic applications, due to its robustness and low toxicity – the later should not be confused with hazardousness since the long lasting effects of nano-sized titania particles in human health is still under discussion. Of course that the uncontrolled release of such particles can be avoid if the photocatalyst is stably supported in a given material, which can be more easily handled. Recent cases studied at our group involve the degradation of emergent pollutants such as caffeine [1] and the use of TiO<sub>2</sub> coatings for chemical engineering applications [2].

Nevertheless, the current utilisation of TiO<sub>2</sub> in many applications, the interest on finding alternative materials presenting efficiencies similar or even higher is a growing filed of research.

Before dealing with the photochemical properties of carbons, we will revisit ZnO, which has a bandgap similar to TiO<sub>2</sub> (3.2 eV) and recently caught the attention as an interesting material for photocatalytic applications. The morphology of ZnO particles can be controlled by varying the synthesis technique, process conditions, precursors, pH of the system or concentration of the reactants. A wide variety of shapes are possible, such as nanospheres, nanowires, nanotubes, nanorings and

nanotetrapods. It will be described the preparation of ZnO nanostructured materials with different morphologies including nanowires, nanorods and flower-like structures by hydrothermal and solid-state processes. The performance of these materials when used as powders, or immobilized as films, will be demonstrated for the photocatalytic degradation of phenolic compounds in water.

In previous works, the use of carbon materials without any supported phases for CWPO was established. Activated carbons and activated carbon xerogels were used as catalysts for the degradation of organic pollutants in aqueous solutions [3,4]. Commercial multi-wall carbon nanotubes (CNT), without any supported phase were used in the removal of 2-nitrophenol (2-NP) from aqueous solutions [5]. 2-NP is representative of non-biodegradable phenols often found in industrial effluents, including wastewater from pharmaceutical, petrochemical, metallurgical, textile, rubber, and plastic industries, refineries, fungicides, and even from municipal landfill leachate. Although the relation of this thermally activated process to photochemical activation may not seem obvious there are several common points to explore: they are both oxidative in nature, they may include the participation of HO<sup>•</sup>, in many instances they deal with the conversion of related organic pollutants, and they are both heterogeneous catalytic engineered processes. In fact the same materials used as catalysts or supports can be activated either photochemically or thermally.

Until recently the properties of carbons as photocatalysts have been neglected. If some allotropes of carbon can be considered as semiconductors or not, is still a matter of current discussion. At any rate, to elucidate the key role of the carbon phases on the optimization of the photocatalytic properties, a series of TiO<sub>2</sub> nanocomposites with structured carbon materials including CNT, C60 and graphene oxide (GO) will be presented. Composites corresponding to two different carbon contents (4 wt.% and 12 wt.%) were synthesized by the liquid phase deposition method [6] and tested (for the degradation of model water pollutants) in photocatalytic experiments under both near-UV/Vis and visible light irradiation, and in the form of powder slurries.

Looking towards novel technological applications, a matrix of alginate porous hollow fibres can be used to immobilize the most active composite and to test its photocatalytic performance [7]. Other examples can be provided showing the photochemical and photocatalytic

capabilities of carbon materials.

## Methods

The photocatalytic experiments were performed in a glass reactor filled with a given amount of the organic substrate. The loading of suspended catalyst was set typically at 1 g L<sup>-1</sup>. The solution was magnetically stirred and continuously purged with airflow.

The photocatalytic degradation of the organic substrate was also performed under simulated solar light (500 W m<sup>-2</sup> of irradiation power). Samples were withdrawn regularly and analysed by chromatographic methods.

The efficiency of the synthesized materials was compared with TiO<sub>2</sub> P25, the benchmark in photocatalytic applications.

## Carbon-TiO<sub>2</sub> as photocatalyst

For the preparation of nanostructured carbon-TiO<sub>2</sub> composites different amounts of oxidized CNT and C60 were dispersed in distilled water and sonicated for 30 min to obtain a homogeneous suspension. Then, nanostructured carbon-TiO<sub>2</sub> composites were synthesized with these dispersions by the liquid phase deposition method (LPD) at room temperature.

In the preparation of GO-TiO<sub>2</sub> fibers the composite was added to an aqueous solution of sodium alginate under dynamic stirring. When the homogenization was complete, alginate fibers (containing the composite) were prepared by a dry/wet spinning process. The resulting hydrogel hollow fibers were converted to alcogel via successive immersion in a series of ethanol-water solutions of increasing alcohol concentration (10%, 30%, 50%, 70%, 90%, and 100%) for 1 h, for complete solvent exchange, and the alcohol was evaporated under air at room temperature.

The photocatalytic efficiencies of the nanostructured carbon catalysts were evaluated for the degradation of diphenhydramine (DP) and methyl orange (MO) at room temperature (25 °C) under near-UV/Vis and visible light irradiation. A Heraeus TQ 150 medium-pressure mercury vapour lamp was held in a quartz immersion tube located inside a DURAN® glass water-cooling jacket that was used to control the operating temperature, resulting in near-UV/Vis irradiation ( $\lambda > 350$  nm).

For visible light experiments a cut-off long pass filter was used ( $\lambda > 430$  nm). The composite fibers are quite active in the photodegradation of both DP and MO pollutants, especially under visible light, where P25 (Degussa/Evonik) is practically inactive. The pathways for photocatalytic degradation were investigated by isolating the main oxidative routes of the photodegradation

process. It is found that reactive species such as hydroxyl ( $\text{OH}^\cdot$ ) and possible others ( $\text{O}_2^{\bullet-}$  or  $\text{HOO}^\cdot$ ) radicals (or even  $^1\text{O}_2$ ) participate in the photocatalytic mechanism under near-UV/Vis irradiation, but the role of photogenerated holes on the mechanism can't be ignored.

### ZnO nanostructured photocatalysts

ZnO materials were synthesized by different hydrothermal and solid-state thermal procedures. ZnO rods (ZnO-r) and ZnO wires (ZnO-w) were produced by a room temperature hydrothermal process. ZnO with a flower-like structure (ZnO-f) was obtained through a high-pressure (autoclave) hydrothermal route starting from  $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$  and hexamethylenetetramine (1:4 molar ratio). Finally, by a solid-state thermal route at  $600^\circ\text{C}$  starting from zinc acetate precursor ZnO-t was produced.

As expected, materials with different morphologies were obtained when varying the synthesis method and preparation conditions of ZnO. SEM images show that ZnO-t is mainly composed of 1-D rod-like particles. The particle diameter is about 50 nm with length about 250 nm; also, some spherical-like particles with diameter about 100 nm are present.

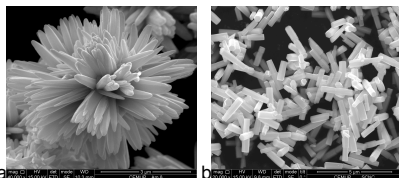


Figure 1. SEM images of ZnO-f (a) and ZnO-r (b).

ZnO-f (Fig. 1a) mainly consists of pencil-like rods radiated from the center vividly resembling natural flowers in shape. ZnO-r (Fig. 1b) is made of individual rods with more than  $1\ \mu\text{m}$  length and

hexagon-shaped tops with around 250 nm of radial size, while ZnO-w is constituted by nanowires with about 50 nm in diameter and 700 nm in length (image not shown). Regardless the preparation conditions used, XRD analysis of the synthesized materials revealed the presence of hexagonal wurzite crystal structure. The specific surface area of all the materials was lower than  $10\ \text{m}^2\ \text{g}^{-1}$ .

In photocatalytic runs ZnO-f revealed very low activity, removing only 13% of the initial PH content after 60 min of irradiation. ZnO-r and ZnO-w presented similar efficiencies, resulting in 43% conversion. Although able to promote PH degradation, ZnO-f, ZnO-r and ZnO-w didn't produce any effect on the abatement of total organic carbon (TOC) content, *i.e.*, there are stable reaction intermediates being formed. On the other hand, the photocatalytic reaction using ZnO-t resulted in 97% and 49% of PH and TOC removal, respectively. In fact, in terms of kinetics of PH removal, the photocatalytic activity of ZnO-t was very similar to that obtained with  $\text{TiO}_2\text{-P25}$ , the main difference being related with the capacity for TOC mineralization (around 90% for  $\text{TiO}_2\text{-P25}$ )

### Conclusions

Heterogeneous photocatalysis is a very efficient tool for water treatment provided the adequate photocatalyst is used.

Carbon nanotubes and graphene oxide present a set of specific structural and electronic properties, when combined with titanium dioxide ( $\text{TiO}_2$ ) semiconductor phases produce efficient photocatalysts.

In addition nanostructured carbon allotropes can be used on their own as heterogeneous catalysts for photochemical processes.

### Acknowledgements

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