

Nanostructured carbon-TiO₂ photocatalysts for water purification: an overview

Fotocatalizadores carbón-TiO₂ para purificación de aguas: revisión

S. Morales-Torres* and L. M. Pastrana-Martínez

LCM – Laboratory of Catalysis and Materials – Associate Laboratory LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

*Corresponding author: semoto@fe.up.pt

Abstract

The outstanding properties of graphene and graphene based materials have stimulated the interest in the design of high-performance photocatalysts that might be integrated in diverse applications as water/wastewater treatment. The present work overviews some important aspects of graphene-based TiO₂ photocatalysts, such as methods of synthesis, associated photocatalytic mechanisms and applications for the photocatalytic degradation of pollutants. Graphene oxide-TiO₂ (GO-TiO₂) composites were prepared by the liquid phase deposition method and their catalytic activity was compared with that obtained by analogues prepared with carbon nanotubes and fullerenes. Finally, the immobilization of GO-TiO₂ on polymeric fibres and ceramic membranes was also assessed to aim at technological applications.

Resumen

Las extraordinarias propiedades de grafeno y sus derivados han suscitado el interés en el diseño de fotocatalizadores de alto rendimiento, que puedan ser usados en diversas aplicaciones como el tratamiento de aguas. Este trabajo trata sobre algunos aspectos importantes de fotocatalizadores basados en grafeno y TiO₂, tales como métodos de síntesis, mecanismos de reacción y aplicaciones para la degradación fotocatalítica de contaminantes. Compuestos de óxido de grafeno-TiO₂ (GO-TiO₂) fueron preparados por deposición en fase líquida y su actividad catalítica fue comparada con otros compuestos carbon-TiO₂ preparados con nanotubos de carbono y fulerenos. Finalmente, se estudió la inmovilización de GO-TiO₂ en fibras poliméricas y membranas para aplicaciones tecnológicas.

1. Introduction

Nowadays, the preservation of the environment, the search for renewable sources of energy and sustainability are probably among the most significant concerns of society. Due to wide applications in solar energy conversion and environmental remediation, the development of effective semiconductor photocatalysts has emerged as one of the most important challenges in materials science.

Titanium dioxide (TiO₂) is the most widely used photocatalyst due to its properties, such as, high stability, low cost, relatively low toxicity and excellent photocatalytic performance in comparison to other semiconductors [1]. TiO₂ is considered a key material for the complete photodegradation of hazardous organic pollutants in water and air [2, 3]. However, the practical application of TiO₂-based materials is seriously compromised by two inherent limitations, namely the low quantum yield, which is primarily impaired by the recombination of photo-generated charge carriers, and the poor light-harvesting ability

that is restricted to the UVA spectral range by the wide band gap of TiO₂ [3, 4]. In this context, typical photocatalysts can be modified in order to enhance their solar photocatalytic activity, by doping, metal particle deposition or even by their combination with other materials to produce highly photoactive composites [5].

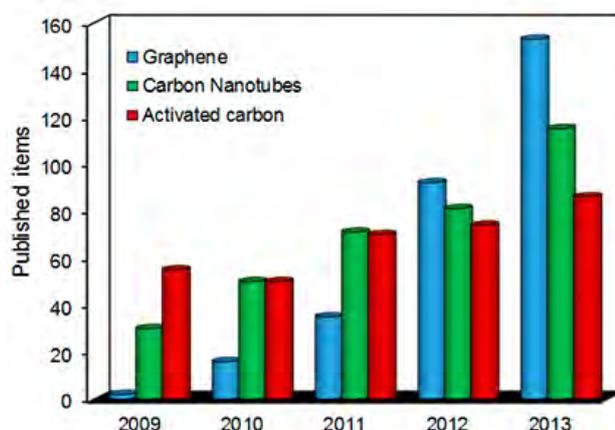


Figure 1. Published articles about graphene, carbon nanotubes or activated carbons and photocatalysis (Source used: Isi Web of Knowledge).

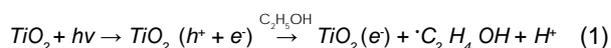
Figura 1. Artículos publicados sobre grafeno, nanotubos de carbono o carbones activados y fotocatalisis (Fuente: Isi Web of Knowledge).

Among different materials that can be selected to prepare composites with TiO₂, carbon materials offer unique advantages such as inertness, stability, in both acid and basic media, and the possibility of tuning their textural and chemical properties. Recently, nanostructured carbon materials (carbon nanotubes, fullerenes and graphene) have received increasing attention in this domain due to their unusual structural and electronic properties [6-8]. In particular, graphene has emerged as one of the most promising materials for the next generation of photocatalysts, due to its excellent mobility of charge carriers, large specific surface area, flexible structure, high transparency and good electrical and thermal conduction. In the last five years, the growing interest for graphene and graphene-based materials (e.g., reduced graphene oxide –rGO– and graphene oxide –GO–) in photocatalysis is significantly larger compared to carbon nanotubes (CNTs) or activated carbons (Figure 1). GO has demonstrated to be another promising carbon material because of its easy manipulation in aqueous solution and the presence of oxygen surface groups, which facilitate the interaction of GO sheets with a wide variety of organic and inorganic materials [9]. In addition, the possibility to obtain graphene from the reduction of GO, by using simple chemical methods, eases up its application in the synthesis of composite materials at affordable production costs and flexible scalable approaches. By the way, GO can be prepared by strong

chemical oxidation of graphite, for instance by using the method developed by Hummers and Offeman [10], followed by the sonicated-assisted exfoliation of the obtained graphite oxide. Therefore, the aims of this overview are: (i) to describe some mechanistic features of graphene-based TiO_2 composites, (ii) to compare their photocatalytic performance with other nanostructured carbon- TiO_2 composites and (iii) to provide insights on photocatalyst immobilization in polymeric fibres or ceramic membranes.

2. Fundamentals of photocatalysis with graphene-based materials

The first study about rGO- TiO_2 composites (prepared by UV-assisted photocatalytic reduction) was presented by Williams et al. [11]. They observed the reduction of GO surface groups by the acceptance of generated electrons from UV-irradiated TiO_2 suspensions and proposed a graphene-semiconductor mechanism (Figure 2), which would be subsequently confirmed for rGO-ZnO composites [12]. In the presence of ethanol, the photogenerated holes in TiO_2 structure are scavenged to yield ethoxy radicals ($\cdot\text{C}_2\text{H}_4\text{OH}$), leaving the electrons to accumulate within TiO_2 particles (Eq. 1). When GO is present, the accumulated electrons interact with the GO sheets leading to the reduction of certain surface groups, yielding rGO (Eq. 2). Therefore, a fraction of electrons is used in the reduction of GO and the other electrons are delocalized along the π basal planes of GO sheets [13].



Different reaction mechanisms have been postulated to explain the photodegradation of pollutants with graphene-based composites. Liu et al. [14] suggested that the electrons can be shuttled throughout the GO sheets and then react with adsorbed O_2 molecules to form HO^{\cdot} radicals (Figure 2), which in turn oxidize the pollutant molecules. This interpretation is in agreement with the work reported by Yu et al. [15] on CNTs and their reactivity with adsorbed O_2 to form HO^{\cdot} radicals. Accordingly, the effective charge separation could reduce the charge recombination and increase the photocatalytic activity of TiO_2 in GO- TiO_2 composites. In a subsequent publication, Liu et al. [16] studied the pathway for the photocatalytic degradation of methylene blue (MB) in aqueous solutions using rGO wrapped TiO_2 hybrid photocatalysts. They proposed that rGO acts by capturing photoinduced electrons and by adsorbing MB molecules. Therefore, the MB molecules could be oxidized by: (i) the superoxide anion radicals ($\text{O}_2^{\cdot-}$) yielded by the reaction involving dissolved O_2 and electrons accumulated in the rGO surface (Eq. 3); and/or (ii) the HO^{\cdot} radicals (Eq. 4) resulting from the photogenerated holes in TiO_2 (Figure 2).

Additionally, graphene can also act as a sensitizer, enhancing the photocatalytic efficiency under visible light irradiation [7, 8, 17, 18]. For this case, the electrons are directly transferred from graphene (or GO) to the conduction band of TiO_2 under visible light.

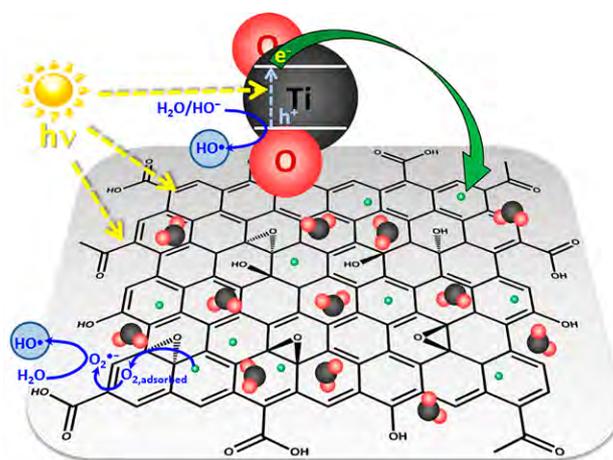


Figure 2. TiO_2 nanoparticles attached onto a GO layer and generation of HO^{\cdot} radicals from adsorbed O_2 and H_2O . Figure adapted with permission from ref. [5]. Copyright 2012, Springer.

Figure 2. Nanopartículas de TiO_2 sobre una lámina de GO y generación de radicales HO^{\cdot} a partir de O_2 adsorbido y agua. Figura adaptada con permiso de ref. [5]. Copyright 2012, Springer.

3. Graphene-based TiO_2 photocatalysts for the degradation of organic pollutants

The preparation of composites with graphene or graphene-based materials (GO or rGO) and TiO_2 (or other inorganic oxide) is commonly carried out by the following methods: simple mixing and/or sonication, sol-gel process, liquid phase deposition, hydrothermal and solvothermal methods [5]. In these methods of synthesis, graphene and GO are the most widely used graphene-based materials, since rGO may be simultaneously obtained when GO- TiO_2 composites are exposed to thermal or hydrothermal reduction treatments.

Some of the most significant applications of graphene based- TiO_2 composites are related with the detoxification and disinfection of water/wastewater. These composites present high adsorption capacity, extended light absorption range, and enhanced charge separation and transportation properties. In the literature, most of the target pollutants were dyes [14, 19, 20], although some recent exceptions include a few pharmaceuticals [7, 21], pesticides/herbicides [22], endocrine disruptors [23], bacteria [24], and cyanobacteria [25].

In our group, GO- TiO_2 composites have been synthesized by liquid phase deposition and subsequently reduced by thermal treatment in N_2 atmosphere [7, 8, 26, 27]. During thermal treatments of GO- TiO_2 composites, the partial reduction of GO occurs with simultaneous deposition of TiO_2 onto the GO. The GO content (1.2, 3.3, 4.0, 5.4, 8.0 or 12.0 wt.%) and the treatment temperature (200 °C and 350 °C) were studied and optimized, while the photocatalytic activity of the materials was evaluated for the degradation of diphenhydramine (DP) pharmaceutical and methyl orange (MO) azo-dye under both near-UV/Vis and visible light irradiation [7]. The GO- TiO_2 composites exhibited a porous structure with high surface area, the morphology depending on the GO content and concomitant variation in the distribution of the self-assembled TiO_2 nanoparticles on the GO platelets (Figure 3a). The photocatalytic efficiency of the GO- TiO_2 composites for the degradation of DP and MO pollutants, was also found to depend markedly on the GO content

(Figure 3b) and post-calcination temperature. The photocatalytic activity of the most active composite, GO-TiO₂-4 (composite treated at 200 °C with 4.0wt.% GO, shown in Figure 3a) exceeded that of the benchmark P25 photocatalyst for both DP and MO pollutants, especially under visible light, where P25 is fairly inactive (Figure 3b). This means that GO may effectively enhance the photocatalytic activity of TiO₂ in the visible range without compromising the performance under UV irradiation, a major drawback of anion-doped TiO₂ photocatalysts. The efficiency of the composite was attributed to the optimal assembly and interfacial coupling between the GO sheets and TiO₂ nanoparticles. These results, combined with the distinct quenching of the GO photoluminescence under visible and NIR laser excitation (Figure 3c), indicate that GO sheets upon binding with TiO₂ can act either as electron acceptor or electron donor (sensitizer) of TiO₂ under UV and visible light excitations, respectively [28].

In a subsequent study, GO was also used to prepare composites using the P25 photocatalyst (GOP) by a simple method of mixing and sonication [29]. The effects of the GO content and the heat-treatment temperature were evaluated. The morphology and the microporosity of GOP composites with low GO contents were comparable to those found for P25. However, the mesoporosity was larger and the pore size distribution was always shifted towards wider mesopores, because P25 nanoparticles are dispersed on both sides of GO aggregates (Figure

4a). GOP composites possessed narrower band gaps in comparison to P25 (Figure 4b). This is a consequence of the intimate contact between both TiO₂ and carbon phases, being improved by the formation of Ti-O-C bonds that are probably established between the hydroxy groups of P25 and the oxygen surface groups of GO. The surface chemistry of GOP composites varied significantly with the GO content, more acidic materials being obtained with higher GO content. The photocatalytic performance of these materials was evaluated for the photodegradation of MO under near-UV/Vis irradiation, GOP-1.4 being the most active composite among those not thermally treated (Figure 4c). Above 1.4 wt.% of GO content, the catalytic activity for the degradation and mineralization of MO decreased. The thermal treatment performed on GOP composites at 200–300 °C had a beneficial effect on the photocatalytic performance, leading to higher rate constants of photocatalytic degradation and higher mineralization. Therefore, these results demonstrate the potential of GO to blend with the benchmark P25 material and to produce more effective photocatalysts for the treatment of waste waters, in particular those polluted with dyes.

4. Are GO-TiO₂ composites different from other carbon-TiO₂ composite materials?

In spite of many studies, there are still some doubts regarding the real enhanced photocatalytic properties of GO-TiO₂ composites when compared

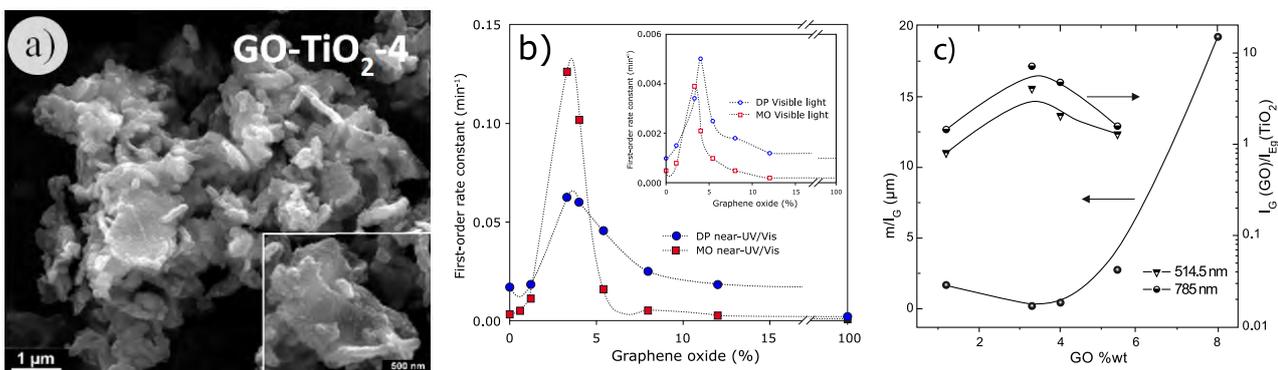


Figure 3. (a) SEM micrograph of GO-TiO₂-4. (b) Pseudo-first order reaction rate constant (k) under near-UV/Vis and visible light irradiation for DP and MO degradation. (c) Effect of the GO content on the photoluminescence of GO-TiO₂ composites. Figures adapted with permission from ref. [7]. Copyright 2012, Elsevier.

Figura 3. (a) Imagen de SEM de GO-TiO₂-4. (b) Constante de velocidad de pseudo-primer orden obtenida para la degradación de DP y MO con irradiación UV/Vis y sólo visible. (c) Efecto del contenido de GO sobre la fotoluminiscencia de compuestos GO-TiO₂. Figuras adaptadas con permiso de ref. [7]. Copyright 2012, Elsevier.

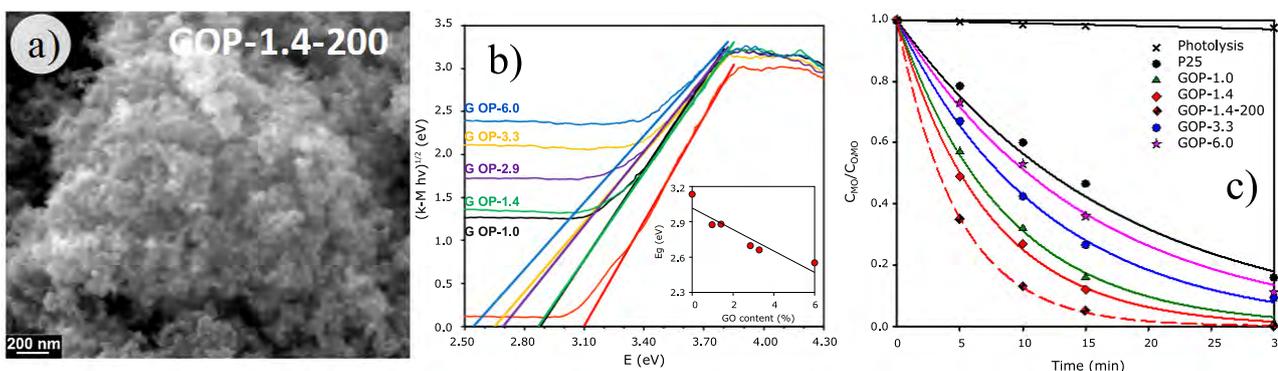


Figure 4. (a) SEM micrograph of the GOP-1.4-200 composite. (b) Plot of transformed Kubelka–Munk as a function of the energy of light (correlation between band gap energy and GO content, inset). (c) Photocatalytic degradation of MO over P25 and GOP composites under near-UV/Vis irradiation. Figures adapted with permission from ref. [29]. Copyright 2013, Elsevier.

Figura 4. (a) Imagen de SEM del compuesto GOP-1.4-200. (b) Gráfico de la función modificada de Kubelka–Munk en función de la energía de luz absorbida (correlación entre la energía de banda prohibida y el contenido de GO, gráfico interior). (c) Degradación fotocatalítica de MO con P25 y compuestos GOP con irradiación UV/Vis. Figuras adaptadas con permiso de ref. [29]. Copyright 2013, Elsevier.

with other nanostructured carbon-TiO₂ composites. In a first attempt to solve this issue, Zhang et al. [30] prepared graphene-P25 and CNT-P25 composites by the mixing/sonication method and tested in the photodegradation of MB under both UV and visible light irradiation. The tendency observed for graphene-P25 composites was also observed for CNT-P25 composites, although the graphene-P25 composites exhibited slightly higher activity than their CNT-P25 equivalents, suggesting that graphene was in essence similar to CNTs regarding the obtained photocatalytic performances. In another study, graphene-TiO₂ and CNT-TiO₂ composites were synthesized again, but using a sol-gel method [31]. In this case, the graphene-TiO₂ composite with 5 wt.% graphene showed better efficiency than its analogue CNT-TiO₂ for the photocatalytic selective oxidation of alcohols under visible light irradiation. Therefore, the preparation method plays a very important role in the photocatalytic performance of graphene-based TiO₂ composites.

To further elucidate the key role of the carbon phase on the optimization of the photocatalytic properties, our research group prepared a series of TiO₂ composites with different nanostructured carbon materials including CNTs, fullerenes (C₆₀) and GO. Composites corresponding to two different carbon contents (4 wt.% and 12 wt.%) were synthesized by the same liquid phase deposition method [7] and tested for the photodegradation of DP and MO under both near-UV/Vis and visible light irradiation [8]. Higher oxygen content and larger amounts of CO and CO₂ (determined by temperature programmed desorption) were detected for GO in comparison to the other carbon materials (CNTs and C₆₀), which were explained by the different oxidation treatments performed. The photocatalytic results suggested a synergistic effect between the carbon phase and TiO₂ particles, mainly when the composites were tested under visible light irradiation (Figure 5), where all composites were more active than the titania catalysts (bare TiO₂ and P25). The improvement on the efficiency of the photocatalytic process depended on the nature and content of the carbon used. Among all the prepared carbon-TiO₂ composites, GO-TiO₂ comprising 4 wt.% of GO (GO-TiO₂-4) exhibited the highest photocatalytic activity under near-UV/Vis and visible light irradiation, exceeding that of P25

and bare TiO₂ photocatalysts (Figure 5). Therefore, GO is a superior carbon material than CNTs and C₆₀ to develop active TiO₂-based composites. This fact was mainly attributed to the optimal self-assembly between GO and TiO₂ particles. Moreover, GO has the additional advantage that it can be produced at affordable costs in comparison with CNTs and C₆₀ materials.

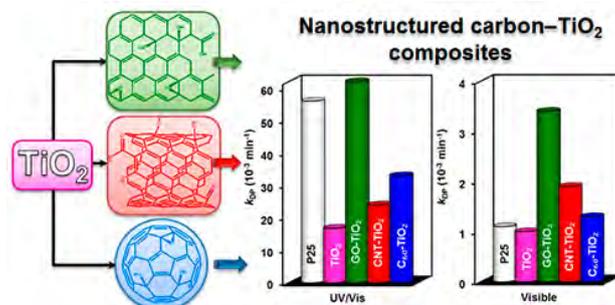


Figure 5. Pseudo-first order reaction rate constant (k) for DP degradation under near-UV/Vis and visible light irradiation, respectively. Adapted with permission from ref. [8]. Copyright 2013, Elsevier

Figura 5. Constante de velocidad de pseudo-primero orden (k) para la degradación de DP con irradiación UV/Vis y solo visible, respectivamente. Adaptado con permiso de ref. [8]. Copyright 2013, Elsevier.

5. Immobilization of GO-TiO₂ photocatalysts on fibres and membranes

Graphene-based photocatalysts are usually employed as suspended particles (slurries) in batch reactors. The immobilization of the photocatalyst into/on to filtration membranes or fibres overcomes the problem of recovering the photocatalyst from the treated media. In literature, a few works deal with the immobilization or deposition of graphene-based composites into/on to membranes. In this way, GO-TiO₂ films have already been prepared and used successfully as filtration membranes to remove hazardous dyes (MO and rhodamine B) [32]. In another work, a GO-TiO₂ membrane was developed by assembling a GO-TiO₂ microsphere composite on the surface of a polymer filtration membrane, which showed the multifunction of water filtration and photodegradation of pollutants (acid orange 7 and rhodamine B) [33]. In a subsequent study, the photocatalytic membrane was synthesized by facile deposition of TiO₂ and GO layers on a polysulfone

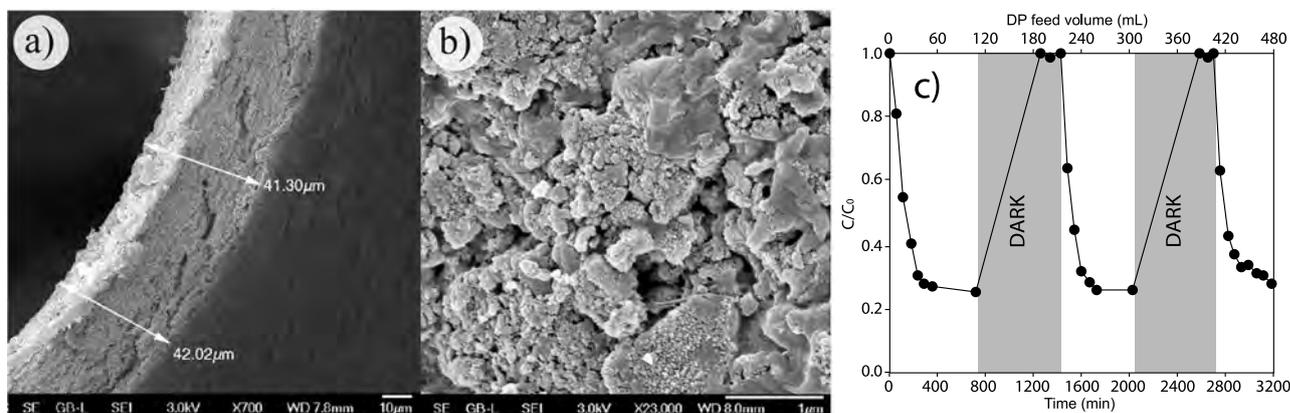


Figure 6. SEM micrographs of (a) wall thickness and (b) external surface of the GO-TiO₂-4 composite immobilized into alginate porous hollow fibres. (c) Photocatalytic degradation of DP over GO-TiO₂-4 hollow fibres in continuous mode under near-UV/Vis irradiation. Figures adapted with permission from ref. [8]. Copyright 2013, Elsevier

Figura 6. Imágenes de SEM del (a) espesor de pared y (b) de la superficie externa del compuesto GO-TiO₂-4 inmovilizado en fibras huecas porosas de alginato. (c) Degradación fotocatalítica de DP con fibras de GO-TiO₂-4 en modo continuo con irradiación UV/Vis. Figuras adaptadas con permiso de ref. [8]. Copyright 2013, Elsevier.

membrane, an increase in the membrane flux being reported as a consequence of the photo-enhanced hydrophilicity and degradation of the pollutant (MB) [34].

In collaboration with NCSR Demokritos (Athens), the highly active GO-TiO₂-4 composite (with 4 wt.% GO and treated at 200 °C) was immobilized into alginate hollow fibres by a dry/wet spinning process, as reported elsewhere [8, 35]. GO-TiO₂-4 was incorporated into the polymer matrix, and fibres with a wall thickness ca. 42 µm were prepared (Figure 6a and b). As preliminary results, the GO-TiO₂-4 hollow fibres were tested in the degradation of DP under near-UV/Vis irradiation, considerable high activity and stability being obtained in consecutive light-dark cycles of continuous reaction operation (Figure 6c).

In another recent work with NCSR Demokritos, we have also deposited the GO-TiO₂-4 composite into the pores of ultrafiltration (UF) mono-channel membranes with different pore sizes (1, 5 and 10 nm), which were tested in a hybrid photocatalysis/ultrafiltration process for the removal of dyes (MO and MB) [36]. The results obtained with cross-flow (membranes with 1 and 5 nm) and dead-end (membranes with 1 nm) filtration experiments indicated that the pore size of the monolith controlled the amount of GO-TiO₂-4 composite stabilized on the substrate and consequently, the photocatalytic efficiency of the developed membrane. The GO-TiO₂-4 membrane prepared on the UF monolith with 10 nm pore size (m-GOT-10) exhibited enhanced photocatalytic performance under visible light. This fact was attributed to the capacity of the 10 nm pores to host the composite, whereas a sparse deposition of TiO₂ was achieved in the membranes developed on the monoliths with pore sizes of 1 and 5 nm. In addition, m-GOT-10 showed a larger dye removal compared to the reference membrane prepared with bare TiO₂. Finally, the performance of the m-GOT-10 membrane in the hybrid process was compared with a standard nanofiltration process, providing firm evidence for its economic feasibility and efficiency.

6. Conclusions and future perspectives

The role of both graphene and graphene derivatives in graphene-based TiO₂ composites is commonly associated with: (i) the capture of photoinduced electrons originated from TiO₂ particles, yielding active oxygen radicals and avoiding the electron-hole recombination; (ii) the enhanced adsorption of pollutants; and (iii) the extension of light absorption to longer wavelengths.

Graphene oxide-TiO₂ composites were synthesized by liquid phase deposition, the material prepared with 4.0 wt.% GO and treated at 200 °C (GOT-TiO₂-4), being the most active photocatalyst for the degradation of diphenhydramine and methyl orange under both near-UV/Vis and visible light irradiation. The catalytic efficiency of GO-TiO₂ composites was compared with analogues prepared with carbon nanotubes and fullerenes, that prepared with GO being the most active for the degradation and mineralization of pollutants under the same experimental conditions. The GO-TiO₂-4 composite can be successfully immobilized into/on to fibres and ceramic ultrafiltration membranes, which were already tested in a hybrid filtration/photocatalysis

process, in order to combine both photocatalytic activity and separation capacity.

7. Acknowledgements

Financial support for this work was provided by projects PTDC/AAC-AMB/122312/2010 co-financed by FCT (Fundação para a Ciência e a Tecnologia) and FEDER (ERDF – European Regional Development Fund) through Programme COMPETE (FCOMP-01-0124-FEDER-019503). This work was also partially co-financed by FCT and FEDER through project PESt-C/EQB/LA0020/2013 (COMPETE), and by QREN, ON2 (North Portugal Regional Operational Programme) and FEDER through projects NORTE-07-0162-FEDER-000050, NORTE-07-0162-FEDER-000015 and NEPCAT (nr. 38900) in the National Strategic Reference Framework (NSRF). LMPM and SMT acknowledge financial support from FCT grants SFRH/BPD/88964/2012 and SFRH/BPD/74239/2010, respectively. Prof. J.L. Faria, Prof. J.L. Figueiredo and Dr. A.M.T. Silva are gratefully acknowledged for their assistance in the revision of the manuscript.

8. References

- [1] Leary R, Westwood A. Carbonaceous nanomaterials for the enhancement of TiO₂ photocatalysis. *Carbon*. 2011;49(3):741-72.
- [2] Likodimos V, Dionysiou D, Falaras P. Clean water: water detoxification using innovative photocatalysts. *Rev Environ Sci Biotechnol*. 2010;9(2):87-94.
- [3] Fujishima A, Zhang X, Tryk DA. TiO₂ photocatalysis and related surface phenomena. *Surf Sci Rep*. 2008;63(12):515-82.
- [4] Kubacka A, Fernández-García M, Colón G. Advanced Nanoarchitectures for Solar Photocatalytic Applications. *Chem Rev*. 2011;112(3):1555-614.
- [5] Morales-Torres S, Pastrana-Martínez LM, Figueiredo JL, Faria JL, Silva AMT. Design of graphene-based TiO₂ photocatalysts-a review. *Environ Sci Pol Res*. 2012;19(9):3676-87.
- [6] Marques RRN, Sampaio MJ, Carrapiço PM, Silva CG, Morales-Torres S, Dražić G, Faria JL, Silva AMT. Photocatalytic degradation of caffeine: Developing solutions for emerging pollutants. *Catal Today*. 2013;209:108-15.
- [7] Pastrana-Martínez LM, Morales-Torres S, Likodimos V, Figueiredo JL, Faria JL, Falaras P, Silva AMT. Advanced nanostructured photocatalysts based on reduced graphene oxide-TiO₂ composites for degradation of diphenhydramine pharmaceutical and methyl orange dye. *Appl Catal, B*. 2012;123-124:241-56.
- [8] Pastrana-Martínez LM, Morales-Torres S, Papageorgiou SK, Katsaros FK, Romanos GE, Figueiredo JL, Faria JL, Falaras P, Silva AMT. Photocatalytic behaviour of nanocarbon-TiO₂ composites and immobilization into hollow fibres. *Appl Catal, B*. 2013;142-143:101-11.
- [9] Dreyer DR, Park S, Bielawski CW, Ruoff RS. The chemistry of graphene oxide. *Chem Soc Rev*. 2010;39(1):228-40.
- [10] Hummers J, Offeman RE. Preparation of graphitic oxide. *JACS*. 1958;80(6):1339.
- [11] Williams G, Seger B, Kamt PV. TiO₂-graphene nanocomposites. UV-assisted photocatalytic reduction of graphene oxide. *ACS Nano*. 2008;2(7):1487-91.
- [12] Williams G, Kamat PV. Graphene-semiconductor nanocomposites: Excited-state interactions between ZnO nanoparticles and graphene oxide. *Langmuir*. 2009;25(
- [13] Lightcap IV, Kosel TH, Kamat PV. Anchoring semiconductor and metal nanoparticles on a two-dimensional catalyst mat. storing and shuttling electrons with reduced graphene oxide. *Nano Lett*. 2010;10(2):577-

83.

- ^[14] Liu J, Bai H, Wang Y, Liu Z, Zhang X, Sun DD. Self-Assembling TiO₂ Nanorods on Large Graphene Oxide Sheets at a Two-Phase Interface and Their Anti-Recombination in Photocatalytic Applications. *Adv Funct Mater.* 2010;20(23):4175-81.
- ^[15] Yu Y, Yu JC, Chan CY, Che YK, Zhao JC, Ding L, Ge WK, Wong PK. Enhancement of adsorption and photocatalytic activity of TiO₂ by using carbon nanotubes for the treatment of azo dye. *Appl Catal, B.* 2005;61(1-2):1-11.
- ^[16] Liu J, Wang Z, Liu L, Chen W. Reduced graphene oxide as capturer of dyes and electrons during photocatalysis: Surface wrapping and capture promoted efficiency. *PCCP.* 2011;13(29):13216-21.
- ^[17] Chen C, Cai W, Long M, Zhou B, Wu Y, Wu D, Feng Y. Synthesis of visible-light responsive graphene oxide/TiO₂ composites with p/n heterojunction. *ACS Nano.* 2010;4(11):6425-32.
- ^[18] Du A, Ng YH, Bell NJ, Zhu Z, Amal R, Smith SC. Hybrid Graphene/Titania Nanocomposite: Interface Charge Transfer, Hole Doping, and Sensitization for Visible Light Response. *The Journal of Physical Chemistry Letters.* 2011;2(8):894-9.
- ^[19] Nguyen-Phan TD, Pham VH, Shin EW, Pham HD, Kim S, Chung JS, Kim EJ, Hur SH. The role of graphene oxide content on the adsorption-enhanced photocatalysis of titanium dioxide/graphene oxide composites. *Chem Eng J.* 2011;170(1):226-32.
- ^[20] Zhang H, Lv X, Li Y, Wang Y, Li J. P25-graphene composite as a high performance photocatalyst. *ACS Nano.* 2010;4(1):380-6.
- ^[21] Amalraj Appavoo I, Hu J, Huang Y, Li SFY, Ong SL. Response surface modeling of Carbamazepine (CBZ) removal by Graphene-P25 nanocomposites/UVA process using central composite design. *Water Res.* 2014;57:270-9.
- ^[22] Ng YH, Lightcap IV, Goodwin K, Matsumura M, Kamat PV. To What Extent Do Graphene Scaffolds Improve the Photovoltaic and Photocatalytic Response of TiO₂ Nanostructured Films? *J Phys Chem Lett.* 2010;1(15):2222-7.
- ^[23] Maroga Mboula V, Héquet V, Andrès Y, Pastrana-Martínez LM, Doña-Rodríguez JM, Silva AMT, Falaras P. Photocatalytic degradation of endocrine disruptor compounds under simulated solar light. *Water Res.* 2013;47(12):3997-4005.
- ^[24] Liu J, Liu L, Bai H, Wang Y, Sun DD. Gram-scale production of graphene oxide-TiO₂ nanorod composites: Towards high-activity photocatalytic materials. *Appl Catal, B.* 2011;106(1-2):76-82.
- ^[25] Fotiou T, Triantis TM, Kaloudis T, Pastrana-Martínez LM, Likodimos V, Falaras P, Silva AMT, Hiskia A. Photocatalytic Degradation of Microcystin-LR and Off-Odor Compounds in Water under UV-A and Solar Light with a Nanostructured Photocatalyst Based on Reduced Graphene Oxide-TiO₂ Composite. Identification of Intermediate Products. *Ind Eng Chem Res.* 2013;52(39):13991-4000.
- ^[26] Pastrana-Martínez LM, Morales-Torres S, Kontos AG, Moustakas NG, Faria JL, Doña-Rodríguez JM, Falaras P, Silva AMT. TiO₂, surface modified TiO₂ and graphene oxide-TiO₂ photocatalysts for degradation of water pollutants under near-UV/Vis and visible light. *Chem Eng J.* 2013;224:17-23.
- ^[27] Pastrana-Martínez LM, Morales-Torres S, Likodimos V, Falaras P, Figueiredo JL, Faria JL, Silva AMT. Role of oxygen functionalities on the synthesis of photocatalytically active graphene-TiO₂ composites. *Appl Catal, B.* 2014.
- ^[28] Chatterjee D, Dasgupta S. Visible light induced photocatalytic degradation of organic pollutants. *J Photoch Photobio C.* 2005;6(2-3):186-205.
- ^[29] Morales-Torres S, Pastrana-Martínez LM, Figueiredo JL, Faria JL, Silva AMT. Graphene oxide-P25 photocatalysts for degradation of diphenhydramine pharmaceutical and methyl orange dye. *Appl Surf Sci.* 2013;275:361-8.
- ^[30] Zhang Y, Tang ZR, Fu X, Xu YJ. TiO₂-graphene nanocomposites for gas-phase photocatalytic degradation of volatile aromatic pollutant: Is TiO₂-graphene truly different from other TiO₂-carbon composite materials? *ACS Nano.* 2010;4(12):7303-14.
- ^[31] Zhang Y, Tang ZR, Fu X, Xu YJ. Engineering the unique 2D mat of graphene to achieve graphene-TiO nanocomposite for photocatalytic selective transformation: What advantage does graphene have over its forebear carbon nanotube? *ACS Nano.* 2011;5(9):7426-35.
- ^[32] Xu C, Cui A, Xu Y, Fu X. Graphene oxide-TiO₂ composite filtration membranes and their potential application for water purification. *Carbon.* 2013;62:465-71.
- ^[33] Gao P, Liu Z, Tai M, Sun DD, Ng W. Multifunctional graphene oxide-TiO₂ microsphere hierarchical membrane for clean water production. *Appl Catal, B.* 2013;138-139(0):17-25.
- ^[34] Gao Y, Hu M, Mi B. Membrane Surface Modification with TiO₂-Graphene Oxide for Enhanced Photocatalytic Performance. *Journal of Membrane Science.* 2014;455:349-56.
- ^[35] Papageorgiou SK, Katsaros FK, Favvas EP, Romanos GE, Athanasekou CP, Beltsios KG, Tziaila OI, Falaras P. Alginate fibers as photocatalyst immobilizing agents applied in hybrid photocatalytic/ultrafiltration water treatment processes. *Water Res.* 2012;46(6):1858-72.
- ^[36] Athanasekou CP, Morales-Torres S, Likodimos V, Romanos GE, Pastrana-Martínez LM, Falaras P, Faria JL, Figueiredo JL, Silva AMT. Prototype composite membranes of partially reduced graphene oxide/TiO₂ for photocatalytic ultrafiltration water treatment under visible light. *Appl Catal, B.* 2014.