When carbon meets light: synergistic effect between carbon nanomaterials and metal oxide semiconductors for photocatalytic applications

Cuando el carbón conoce la luz: efecto sinérgico entre nanomateriales de carbón y semiconductores de óxidos metálicos para aplicaciones fotocatalíticas

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Abstract

Activated carbon based materials and more recently, nanostructured carbon materials namely, fullerenes, nanotubes, nanodiamonds and graphene, have been the focus of intensive research for application in nanotechnology. In the field of photocatalysis, carbon materials have been combined with conventional semiconductors as carbon/inorganic composites seeking for synergies resulting from the coupling of both phases. This overview paper aims at exploring some important aspects that influence the photocatalytic activity of hybrid carbon/metal oxide materials such as the synthesis method, the nature and the surface chemistry of the carbon phase as well as their use immobilized in membranes or as films.

Resumen

Los materiales basados en carbón activado y más recientemente, materiales nano-estructurados de carbón, concretamente, fullerenos, nanotubos, nanodiamantes y grafeno, han sido el foco de una amplia investigación para su aplicación en nanotecnología. En el campo de la fotocatálisis, los materiales de carbón han sido combinados con semiconductores convencionales formando materiales compuestos carbón/material inorgánico con el fin de buscar sinergias del acoplamiento entre ambas fases. Este artículo de revisión tiene como objetivo explorar algunos aspectos importantes que afectan a la actividad fotocatalítica de los compuestos carbón/óxido metálico, tales como el método de síntesis, la naturaleza y la química superficial del carbón, así como su uso inmovilizado en membranas o películas.

1. Introduction

Photocatalytic technologies have been gaining increasing commercial interest worldwide mostly in the fields of environmental cleanup (water/air purification/ disinfection), architecture (self cleaning surfaces), energy (photovoltaics and solar fuels) and organic synthesis. One of the most challenging research lines in photocatalysis consists in the development of highly active catalysts for solar applications. The effectiveness of solar-driven photocatalytic processes is dictated to a great extent by the semiconductor's capability of absorbing visible light, as well as its ability to suppress the rapid combination of photo-generated electrons and holes.

Titanium dioxide (TiO_2) is the most widely used semiconductor in photocatalytic applications. Nevertheless, due to its relatively high bandgap (3.2eV corresponding to a wavelength of 388 nm), TiO_2 is marginally activated under solar irradiation, since UV light represents less than 5% of the overall solar energy reaching Earth's surface.

Carbon materials are widely employed to couple with conventional semiconductors due to properties such as large specific surface area, inertness, stability in both acid and basic media, and tunable surface chemistry. They have demonstrated to induce some beneficial effects on the photocatalytic performance of semiconductor metal oxides by creating synergies between both metal oxide and carbon phases. Generally, this effect is attributed to the decrease of the bandgap energy of the composite catalysts, to an enhancement of the adsorptive properties as well as charge separation and transportation properties.

The great diversity of carbon nanomaterials namely, fullerenes, carbon nanotubes (CNT), graphene related materials (e.g., reduced graphene oxide, –rGO, and graphene oxide, –GO) and nanodiamonds (NDs), among others, have stimulated the interest in the design of high-performance hybrid photocatalysts [1-4]. Since their discovery by Ijima [5], CNT have been the focus of various studies in catalysis due to their unique structural, electronic and mechanical properties. CNT have shown the potential to contribute to the increase of the photocatalytic activity of metal oxide semiconductors [6-9]. The high surface area, semiconducting properties and the possibility of tailoring the surface chemistry make CNT a very attractive option for producing carbon-TiO_2 photocatalysts. Recently, graphene is making a deep impact in many areas of science and technology as consequence of its unique electronic, optical, mechanical, and thermal properties. GO is an exciting precursor of graphene because oxygen-containing functional groups attached on the graphene surface can be partly removed, resulting in the partial restoration of the sp^2 hybridization of carbon [10]. The exfoliation of graphite oxide, followed by a reduction process to yield rGO, offers important advantages, namely the possibility to obtain a tailored hydrophilic surface of graphene, decorated with oxygenated functionalities, by a cost-effective approach. These surface groups can be used to facilitate the anchoring of semiconductor and metal nanoparticles, or even the assembly of macroscopic structures, which are relevant to develop highly efficient photocatalysts [11, 12]. Furthermore, the chemical reduction of GO is a promising route towards the large scale production of graphene for different applications [13]. NDs are being increasingly used for a wide range of applications due to their remarkable thermal conductivity, biocompatibility and tailored chemical properties. NDs can be obtained on a large scale at low cost by detonation of carbon-containing explosives, exhibiting a uniform distribution of particle sizes (typically 4-5 nm) together with specific surfaces areas around 250 $m^2 g^{-1}$.

In this overview paper some key aspects involved in photocatalytic processes using carbon nanomaterials/metal oxide hybrid materials will be presented namely the catalysts' synthesis route, the type of carbon and metal oxide materials, the influence of carbon materials' surface chemistry and the immobilization of such composite photocatalysts, with a special focus in the work which is being developed in our group in this field. More emphasis will be put in composite materials based on TiO_2, while some examples using ZnO will be also addressed.

2. Routes for the synthesis of carbon-metal oxide photocatalysts

The synthesis of carbon-metal oxide photocatalysts can be carried by different methods, such as mixing and/or sonication, sol-gel process, liquid phase deposition, hydrothermal and solvothermal methods [14].

The easiest technique used for coupling carbon nanomaterials with metal oxide semiconductors is by simply mixing both phases. This can be carried out by mechanical mixing of the powder materials or by suspending them in a solvent (normally water). In the first work by our group on the use of carbon materials in photocatalytic reactions, physical mixtures of different activated carbons (AC) with different surface chemistries and TiO_2 Evonik P25 (former Degussa) were successfully used for the degradation of an azo dye (solophenyl green BLE 155). The simple addition of powdered activated carbon to TiO_2 under UV irradiation induced a beneficial effect on the photocatalytic degradation of the organic dye, which has been attributed to the capacity of AC to work as a co-adsorbent and as photosensitizer since the best results were obtained with the AC sample with a more basic surface (higher electron availability). The research work was then extended to the degradation of mono-, di- and tri-azo dyes, an increase in the efficiency of the photocatalytic process being observed for the abatement of all dyes when AC was introduced in the TiO_2 slurry [15]. In another work, CNT were combined with different types of TiO_2 by a hydration-dehydration method, which consisted in mixing CNT and TiO_2 in water under sonication followed by heating at 353 K until complete evaporation of water [16, 17]. The resulting materials were used for the photocatalytic degradation of caffeine, methylene blue (MB) and several phenolic compounds. In all cases the pre-functionalization of the CNT' surface with oxygen-containing groups, such as carboxylic acids and phenols was fundamental for the enhancement of the photocatalytic activity of the hybrid materials in relation to neat TiO_2. The simple mixing and sonication method was also used to synthetize GO-TiO_2 composites but using P25 photocatalyst as TiO_2 nanoparticles [18]. The resulting composites presented narrower band gaps than that for P25 as consequence of the intimate contact between both TiO_2 and carbon phases facilitated by the formation of C–O–Ti bonds between the hydroxy groups of P25 and the oxygen-containing surface groups of GO.

The sol-gel technique is one of the most used techniques for the production of TiO_2, having many advantages over other production routes including the formation of very pure and homogeneous materials. This technique also allows the introduction of other solid phases during the TiO_2 synthesis process to form composites. It involves a hydrolysis step during which the carbon material is added, followed by the polycondensation of titanium alkoxides. The final materials are obtained after calcination for the removal of TiO_2 precursor and formation of the metal oxide. AC and CNT have been applied for the synthesis of TiO_2-based materials by an acid catalyzed sol-gel route and used for the photocatalytic degradation of azo dyes and phenolic compounds [6, 7, 9, 19-21].

Another technique used in our group for the production of carbon-TiO_2 composites is the liquid phase deposition method (LPD), which is normally followed by a thermal treatment of the obtained materials in N_2 atmosphere [3]. In particular, graphene based-TiO_2 composites were prepared using different GO contents and treatment temperatures. The photocatalytic efficiency was evaluated for the degradation of diphenhydramine (DP) pharmaceutical and methyl orange (MO) azo-dye under both near-UV/Vis and visible light irradiations [3]. The GO-TiO_2 composite with the best photocatalytic activity was that prepared with a 4.0 wt.% GO and treated at 473 K (hereafter referred as GOT). The superior performance of GOT exceeded that of the benchmark P25 photocatalyst for both DP and MO pollutants and was attributed to the optimal assembly and interfacial coupling between the GO layers and TiO_2 nanoparticles. The photocatalytic efficiency of GOT has been also tested in the degradation of other pollutants such as microcystin-LR (the most common and toxic variant of the group of microcystins) and off-odor compounds (Geosmin and 2-methylisoborneol) in water under UV-A and solar light [22], the variant microcystin-LA (MC-LA) [23], 17-beta-estradiol under simulated solar light [24], estradiol under simulated solar light [24], endocrine disruptor [25], and EU/EPA priority pollutant pesticides [26], among others. Nanodiamonds-TiO_2 composites ($ND_{ox}T$-15, containing 15.0 wt.% of NDs) were also synthesized by using the LPD method and a thermal treatment at 473 K [2, 4]. The photocatalytic activity of these materials will be presented below when discussing the effect of the surface chemistry in the activity of carbon-metal oxide materials.

3. The role of the carbon materials' surface chemistry

Carbon materials' surface groups take an important role in the way they link to metal oxide semiconductors and consequently, in the electronic and photocatalytic performance of the composite materials. Liquid-phase functionalization of CNT with nitric acid leads to the creation of large amounts of carboxylic acid and phenol groups at the surface of the CNT (referred as CNT_f); these functionalities are accountable for promoting the dispersion of TiO_2 particles in the CNT-TiO_2 composites and also contribute to the formation of C–O–Ti bonds, as in esterification reactions between the carboxylic acid groups of CNT and the hydroxy groups existent at the surface of TiO_2 [6, 16, 17]. The functional groups present at the surface of

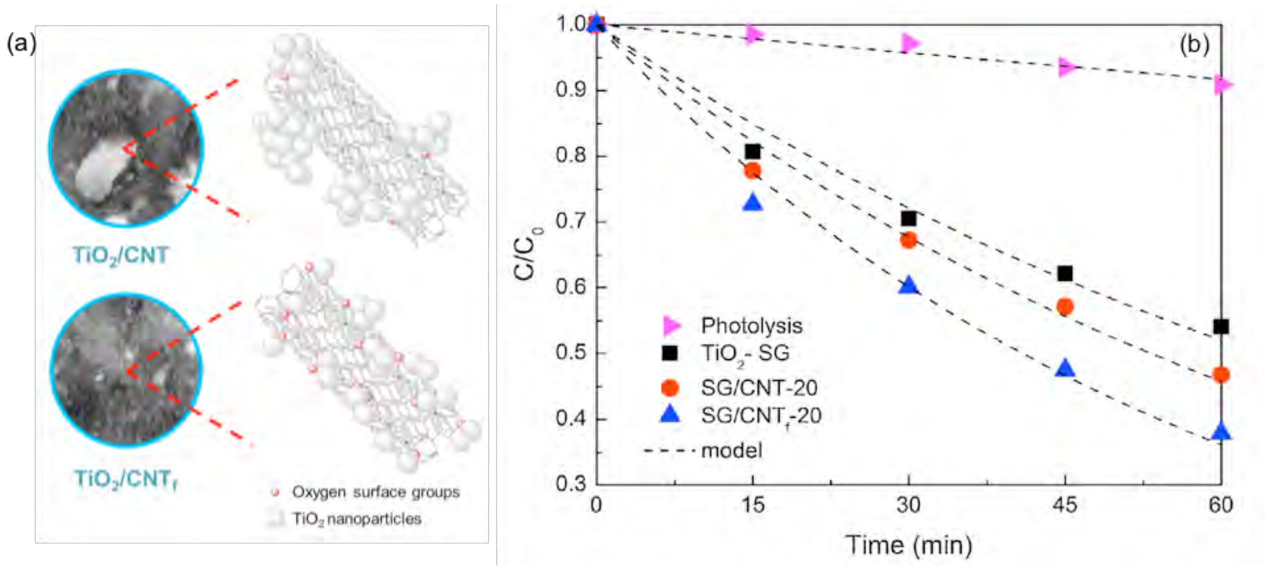

Figure 1. (a) Dispersion of TiO_2 at the surface of CNT_f and pristine CNT in composite materials prepared by SG; (b) evolution of the normalized concentration (C/C_0) of MB during photolysis and photocatalytic degradation using TiO_2, and CNT/TiO_2 composites. Figures adapted with permission from ref. [17]. Copyright 2015, Elsevier.

Figura 1. (a) Dispersión de partículas de TiO_2 sobre la superficie de CNT puros y funcionalizados en materiales compuestos preparados por el método SG; (b) evolución de la concentración normalizada (C/C_e) de MB durante la degradación por fotolisis y fotocatálisis usando TiO_2, y materiales compuestos CNT/TiO_2. Figuras adaptadas con permiso de ref. [17]. Copyright 2015, Elsevier.

CNT_f promote the anchoring of the TiO_2 particles as well as their dispersion, avoiding agglomeration and subsequently increasing the surface area of the resulting materials (Fig. 1a). It was found that for the composites prepared by sol-gel (SG) method, the introduction of CNT leads to a slight increase in the photocatalytic efficiency towards the degradation of MB under near UV to visible irradiation (Fig. 1b), which is attributed to a synergy effect due to the creation of an electronic interphase interaction between CNT and TiO_2 phases. In addition, a marked increase of the films photocatalytic activity was observed when CNT_f were used to prepare the composites as compared to pristine CNT (Fig. 1b).

The effect of CNT' surface oxygen functionalities was also explored for CNT-TiO_2 composites (loaded with Pt, acting as co-catalyst) for the photocatalytic production of H_2 from methanol and from saccharides [8]. In that case, the photocatalytic efficiency of composite materials produced by mixing and sonication of TiO_2 and oxidized (with HNO_3 10 M at boiling temperature) CNT (CNTox-TiO_2) was compared with a composite prepared by introduction of TiO_2 during the CNT' oxidation process [(CNT-TiO_2)ox]. Infrared analysis of the two materials show that in the case of (CNT-TiO_2)ox, there is a decrease in the intensity of the bands corresponding to O–H and C–O groups when compared to the spectra of CNTox-TiO_2, which suggests that TiO_2 may be attached to CNT surface groups such as phenols and carboxylic acids (Fig. 2a). Also, the bands originated from C–C and C–H, due to aromatic ring vibrations, are less intense in (CNT-TiO_2)ox compared to CNTox-TiO_2, which indicates a better dispersion of the TiO_2 particles at the surface of CNT in the (CNT-TiO_2)ox composite. This observation is in line with the higher intensity of the Ti–O band in the (CNT-TiO_2)ox composite, revealing that the TiO_2 particles are better distributed over the surface of CNT for this composite. Fig. 2b shows a schematic representation of the mechanism of photocatalytic production of H_2 from methanol using CNT-TiO_2 composites under irradiation of λ ≥ 365 nm. At these

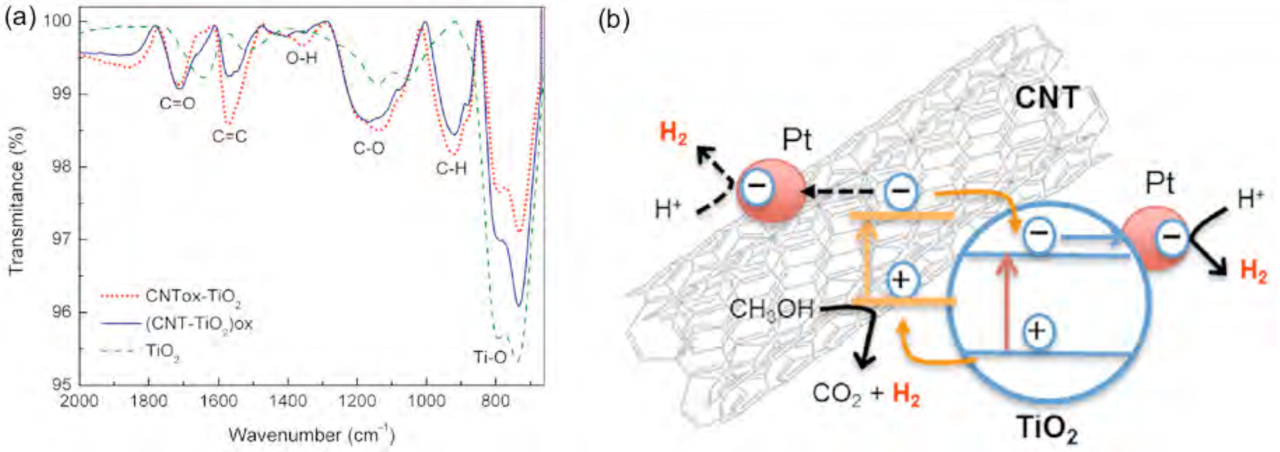

Figure 2. (a) Infrared ATR spectra of bare TiO_2, CNTox-TiO_2 and (CNT-TiO_2)ox composites; (b) schematic representation of the photocatalytic mechanism of H_2 generation from water/methanol solutions under near irradiation at λ ≥ 365 nm using Pt/(CNT-TiO_2)ox catalyst. Figures adapted with permission from ref. [8]. Copyright 2015, Elsevier.

Figura 2. (a) Espectros de infrarrojos (ATR) de TiO_2 puro, CNTox-TiO_2 y materiales compuestos (CNT-TiO_2)ox; (b) representación esquemática del mecanismo fotocatalítico de producción de H_2 a partir de disoluciones agua/metanol con irradiación λ ≥ 365 nm usando el catalizador Pt/(CNT-TiO_2)ox. Figuras adaptadas con permiso de ref. [8]. Copyright 2015, Elsevier.

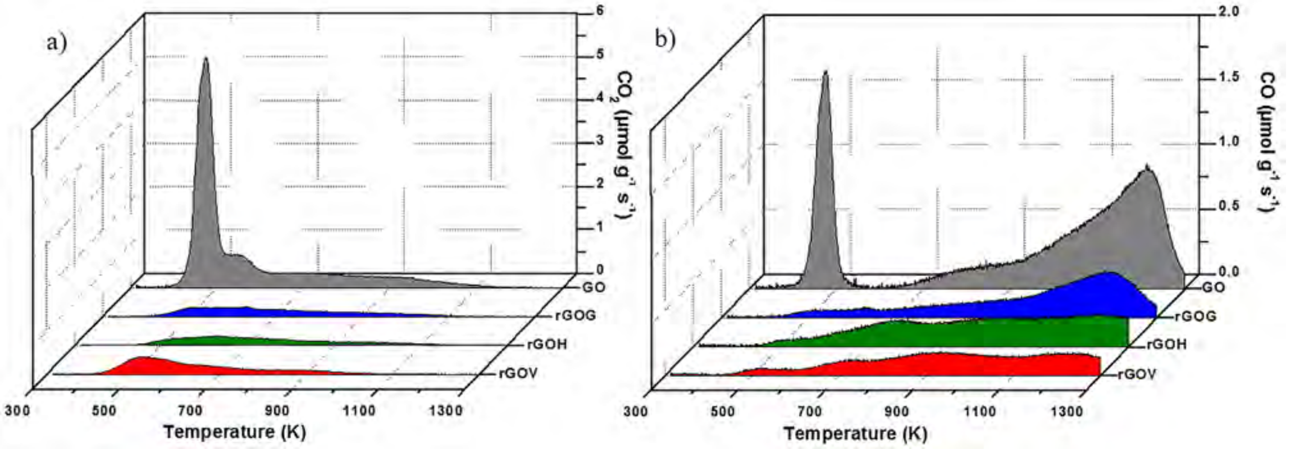

Figure 3. TPD profiles for GO and reduced samples (rGOG, rGOV and rGOH): (a) CO_2 and (b) CO release. Figures adapted with permission from ref. [27]. Copyright 2014, Elsevier.

Figura 3. Perfiles de TPD para GO y muestras reducidas (rGOG, rGOV y rGOH): formación de (a) CO_2 y (b) CO. Figuras adaptadas con permiso de ref. [27]. Copyright 2014, Elsevier.

conditions it is expected that both TiO_2 and CNT could be photo-excited. Electrons from the valence band of TiO_2 are excited to the conduction band of the semiconductor and transferred to Pt nanoparticles reducing protons and generating H_2. On the other hand, positively charged holes may migrate to the CNT phase to oxidize methanol. Simultaneously, due to the strong interphase interaction between CNT and TiO_2, photo-excited electrons in the CNT phase may migrate to the conduction band of TiO_2, increasing the availability of these species in the TiO_2 phase and therefore enhancing H_2 production. Since Pt particles could also be found in CNT, electrons may also migrate to those particles, which act as active sites for H_2 generation.

In another work [27], GO was chemically reduced using vitamin C (rGOV) and glucose (rGOG), both environmental friendly reducing agents, as well as hydrazine (rGOH), and the evolution of the graphene oxygen-containing surface groups was systematically analysed. Furthermore, the reduced GO samples (rGO)-TiO_2 composites were prepared in order to assess the effect of the nature and amounts of oxygenated groups on the photocatalytic performance of composites under near-UV/Vis and visible irradiation. The evolution of oxygen functionalities of GO, during the chemical reduction processes can be systematically analysed using different characterization techniques [27]. The UV-Vis absorption spectra of the GO suspension as well as the chemically reduced rGO suspensions can be used as a quick probe for the degree of GO reduction. After the chemical treatment with different reducing agents (rGOG, rGOV and rGOH), the absorption band at 231nm presented a red shift to ~260 nm, corresponding to deoxygenation of the GO suspensions by the reduction processes. The reduction of GO is also indicated by the colour change of the solution, i.e. from light brown to black after the reduction process. The black colour observed for the rGO dispersion has been related to the partial restoration of the π network and electronic conjugation. X-ray photoelectron spectroscopy (XPS) measurements are also a valuable technique for the determination of the oxygen functionalities. Indeed, after the chemical reduction, the contribution of the C_{1s} region associated with oxygenated species decreased for all the rGO samples, indicating considerable deoxygenation by the reduction process. The degree of deoxygenation of GO by chemical reduction was also observed in the oxygen content of the samples. The lowest O/C ratio for the rGO samples was obtained by treatments performed with glucose and vitamin C, a better reducing character being observed than that obtained with the toxic hydrazine compound.

Concerning the Raman spectra of the rGO samples, at 514.5 and 785 nm laser excitations, all samples exhibit the graphitic G band arising from the bond stretching of sp^2 carbon atoms and the dispersive, defect-activated D band together with the high frequency modes, including the 2D band, the defect activated combination mode (D+D′) and the 2G overtone that could be best resolved at 514.5 nm. Temperature programmed desorption (TPD) technique has been used to calculate the amounts of different types of oxygenated groups, which evolve as CO and CO_2. The TPD profiles for CO_2 and CO are shown in Figs. 3a and b, respectively. The high oxygen content and larger CO_2 and CO evolution, detected for the GO sample correspond to the presence of a larger amount of oxygenated groups in comparison with the rGO samples. The thermal stability of oxygenated functional groups depends on the type of group and on the surroundings to which they are bounded. The deconvolution methodology was applied considering the temperatures at which the different groups evolved as CO_2 and CO upon heating. These results showed the complex chemical composition of GO that contains mainly epoxy and hydroxyl groups on the basal planes as well as minor content of carbonyls, carboxyls, ethers, quinones, lactones, and phenols attached at vacancy and edge sites [27] (Fig. 4).

Different graphene–TiO_2 composites were prepared with the pristine GO and rGO samples by the liquid phase deposition method. The materials were tested for the photocatalytic degradation of diphenhydramine under both UV/Vis and visible light irradiation. A lower photocatalytic activity observed for the composites containing rGO, in comparison with that prepared with GO, which is attributed to the very low amount of oxygenated surface groups that leads to a weak interaction between TiO_2 and rGO during the preparation method employed. The affinity of surface hydroxyl groups on TiO_2 to undergo charge transfer interaction with carboxylic acid functional groups on GO is reported in literature [13]. These effects can be responsible for the optimal assembly and interfacial coupling between GO sheets and TiO_2 nanoparticles during the preparation of the composite (consisting of GO platelets embedded into TiO_2), as well as for the higher photocatalytic performance of the GO-TiO_2 composite.

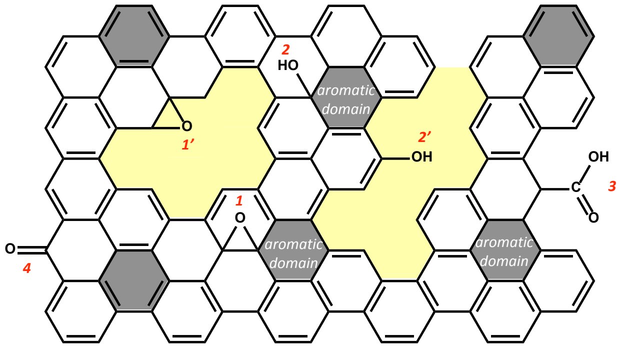

Figure 4. Schematic of oxygen-containing groups placed in the aromatic domain of GO: (1), epoxy groups located at the interior; (1'), epoxy groups located at the edge; (2), hydroxyl located at the interior; (2'), hydroxyl at the edge; (3) carboxyl and (4) carbonyl at the edge. Figure adapted with permission from ref. [27]. Copyright 2014, Elsevier.

Figura 4. Esquema de los grupos oxigenados situados en la estructura aromática de GO: (1), grupos epóxidos localizados en el interior; (1'), grupos epóxidos situados en el eje; (2), hidroxilos localizados en el interior; (2'), hidroxilos en el eje; (3) carboxílicos y (4) carbonilos en el eje. Figura adaptada con permiso de ref. [27]. Copyright 2014, Elsevier.

Concerning the NDs, the introduction of surface functional groups on the nano-sized diamond particles also plays an important role in the photocatalytic activity of the composites (Fig. 5). It is significant to refer that the oxidation treatment in air at 703 K produces not only oxygen-containing surface species but also is known to purify the nanodiamond powders (i.e. eliminating non-diamond carbon in the detonation product by a selective oxidation) [28, 29]. Therefore, the marked enhancement on the photodegradation rate for the ND_{ox}T-15 could be attributed to the significant amount of oxygen surface species on ND_{ox} (mainly carboxylic anhydrides, lactones, phenols and, to a lower extent, carbonyl/quinone groups), which are known to be beneficial for the preparation of TiO_2 nanostructured carbon composites [6, 16] and to the increased purity of the nano-sized diamond constituent after the oxidation treatment. For comparison purposes, the GO-TiO_2 composite prepared in our previous study (GOT) [3] and ND_{ox}T-15 were tested under the same conditions. The pseudo-first order rate constants were very similar for ND_{ox}T-15 ($91´10^{-3}$ min^{-1}) and GOT ($92´10^{-3}$ min^{-1}) both presenting slightly higher efficiency than P25 ($79´10^{-3}$ min^{-1}) for DP degradation.

4. The nature of carbon materials

The photocatalytic activity of GO-TiO_2 composites was compared to that obtained for other carbon-TiO_2 materials but containing CNT or fullerenes (C_{60}) and thereby, the effect of the nature of the nanostructured carbon material was studied for the photodegradation of MO and DP under both near-UV/Vis and visible light irradiation [30]. The activity of the materials depended on the nature (GO, CNT or C_{60}) and content (4 or 12wt.%) of the carbon used. Although all carbon-TiO_2 composites were more active than P25 and bare TiO_2 under Vis light irradiation, GO-TiO_2 exhibited the highest photocatalytic activity under near-UV/Vis and Vis light irradiation and thereby, it was a superior nanostructured carbon material than CNT and C_{60} to develop active composite photocatalysts.

ZnO is considered as an alternative to TiO_2 in photocatalytic applications due to its similar band gap (3.3 eV), its versatile morphology and lower cost. Since it also requires excitation in the near UV region, carbon materials have been used for increasing its activity under solar light irradiation. In a recent study by our group, ZnO synthesized by chemical vapor deposition (CVD) was combined by mixing and sonication with different carbon nanomaterials namely CNT, nanofibers (CNF), NDs, fullerene (C_{60}) and few-layers graphene (FLG)[31]. The composite materials were successfully used for phenol degradation under simulated solar light. It was found that the efficiency of the photocatalytic process depended on the nature of the carbon material used. The composites prepared from CNT (NC-CNT, AK-CNT and PYG-CNT) were less active when compared to other catalysts containing ND, fullerene, CNF and FLG, Fig. 6).

The highest photocatalytic activity was observed for the composite prepared with N-doped CNT (N-CNT). An increase of c.a. 100% in the k_{app} for phenol

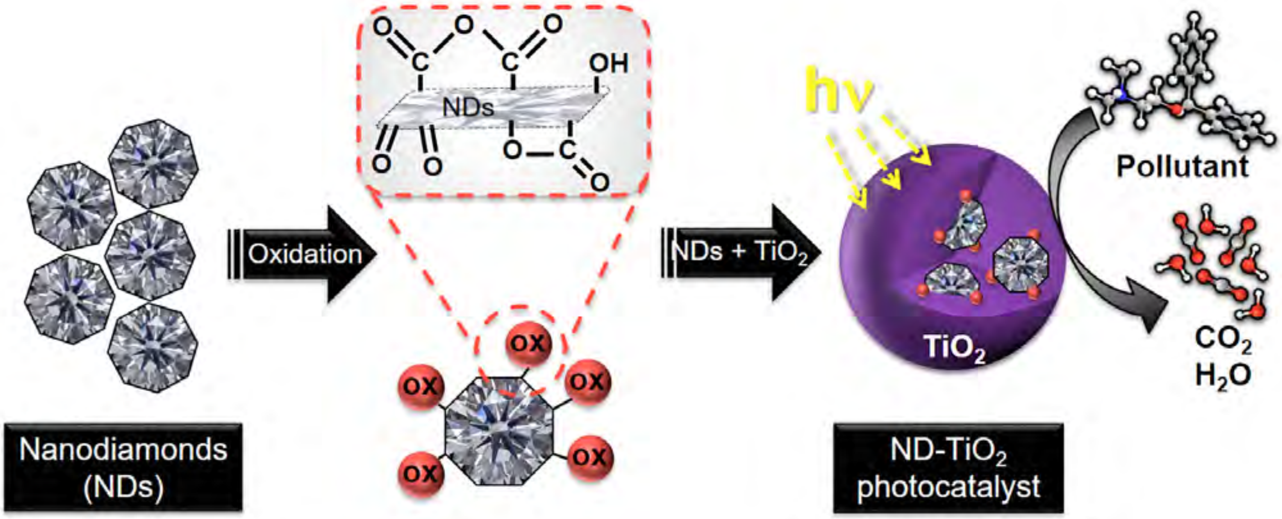

Figure 5. Schematic representation on the synthesis of ND-TiO_2 photocatalysts. Figure adapted with permission from ref. [2]. Copyright 2013, WILEY-VCH Verlag GmbH & Co.

Figura 5. Representación esquemática de la síntesis de fotocatalizadores ND-TiO_2. Figura adaptada con permiso de ref. [2]. Copyright 2013, WILEY-VCH Verlag GmbH & Co.

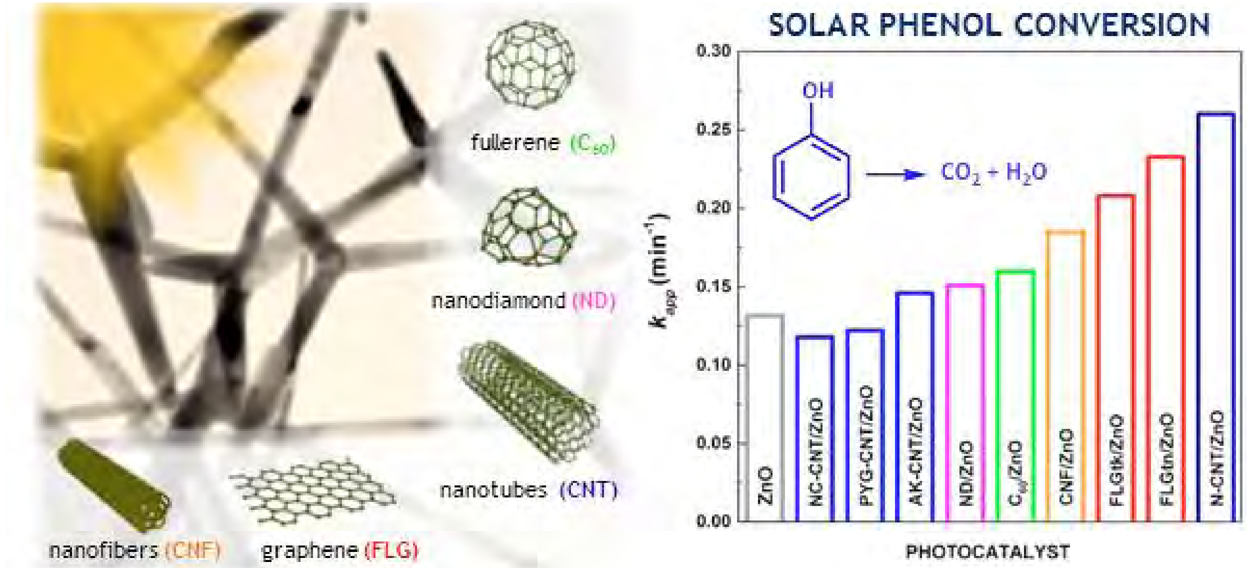

Figure 6. Apparent first order rate constants (k_{app}) for the photocatalytic reactions using ZnO and carbon/ZnO materials. Figure adapted with permission from ref. [31]. Copyright 2015 Elsevier.

Figura 6. Constantes de velocidad aparentes de primer orden (k_{app}) para las reacciones fotocatalíticas usando materiales ZnO y carbón/ZnO. Figura adaptada con permiso de [31]. Copyright 2015, Elsevier.

degradation was obtained when using N-CNT/ZnO compared to the bare material (ZnO).

For comparison purposes, composites using undoped CNT and oxidized CNT (CNT/ZnO and CNT_f/ZnO, respectively) were also prepared and tested in the degradation of phenol. As expected, the results demonstrate that CNT' functionalization promotes an increase in the efficiency of the resulting carbon/ZnO catalysts (around 10%), much lower than the effect promoted by nitrogen doping. A photocatalytic experiment using bare N-CNT was also performed and no phenol conversion was observed under these conditions, suggesting that the activity of the composite material results from cooperative interactions between the metal oxide and the carbon phase. Among the photocatalysts tested, the composite prepared using N-doped CNT as carbon phase (N-CNT/ZnO) showed the highest photocatalytic activity, which was attributed to the presence of electron rich nitrogen-containing groups on the CNT' surface. Photoluminescence analysis confirmed that N-CNT act as an effective electron scavenger for ZnO, inhibiting the recombination of photoexcited electron–hole pairs, thus improving the photoactivity.

4. Composites' immobilization

The use of photocatalysts in powder form has been associated with many drawbacks including the difficult separation of the catalyst from the treated effluent. The immobilization and deposition of the photocatalyst in supports intend to overcome the trouble of recovering the material from the treated media, as well as to improve the contact between the pollutant molecules and the photocatalyst particles. An ideal support should satisfy criteria such as to be stable during the photocatalytic process, to offer a high specific surface area and a strong adherence for the photocatalyst and to have an affinity towards pollutant molecules. In our group, several materials such as glass substrates, inorganic porous and polymer membranes, as well as fibres have been employed to immobilize highly active photocatalysts.

CNT-TiO_2 composites immobilized in glass substrates have been successfully used for the degradation of MB dyes and phenolic compounds [17, 32]. The materials were immobilized as thin films on glass slides by using the so-called doctor blade method, which can be easily employed as a fast and non-energy consuming technique for mass production of thin films with good uniformity and reproducible properties. The photoefficiency of the immobilized catalysts appeared to be related to the inherent properties of the materials and to the characteristics of the resulting films such as homogeneity, thickness, roughness and resistance to mechanical stress. Results show that in most cases, there is an increase in the photoefficiency of the hybrid materials when CNT are present in the films. For composite materials containing TiO_2 P25 and commercial TiO_2 anatase powder form Sigma Aldrich (SA), this increase in the activity for MB removal was proportional to the amount of CNT in the composite materials. The composites produced with TiO_2-SA have shown the highest efficiencies, which were attributed to both the homogeneity of the obtained films and to the photocatalytic properties of the composite materials.

In our group, the highly active GOT composite, bare TiO_2 and P25 catalysts were immobilized into three types of membranes: alginate porous hollow fibres [2], ultrafiltration (UF) mono-channel alumina monoliths [33] and flat sheet membranes [34]. The immobilization of GOT into a matrix of alginate allowed to obtain porous fibres with a rough external surface and high activity and stability in the photodegradation of DP under UV/Vis irradiation after consecutive continuous light–dark cycles [2]. In general, polymer membranes and fibres may be decomposed by the UV irradiation over long reaction times. In this context, GOT and bare TiO_2 were deposited on UF and nanofiltration (NF) alumina membranes to be tested in a hybrid photocatalysis/ultrafiltration process for the removal of typical synthetic dyes, such as MO and MB [33]. The catalytic/filtration behaviour of GOT was much better than that for the membrane with bare TiO_2, in particular under Vis light irradiation. Furthermore, the performance of the membrane with GOT was

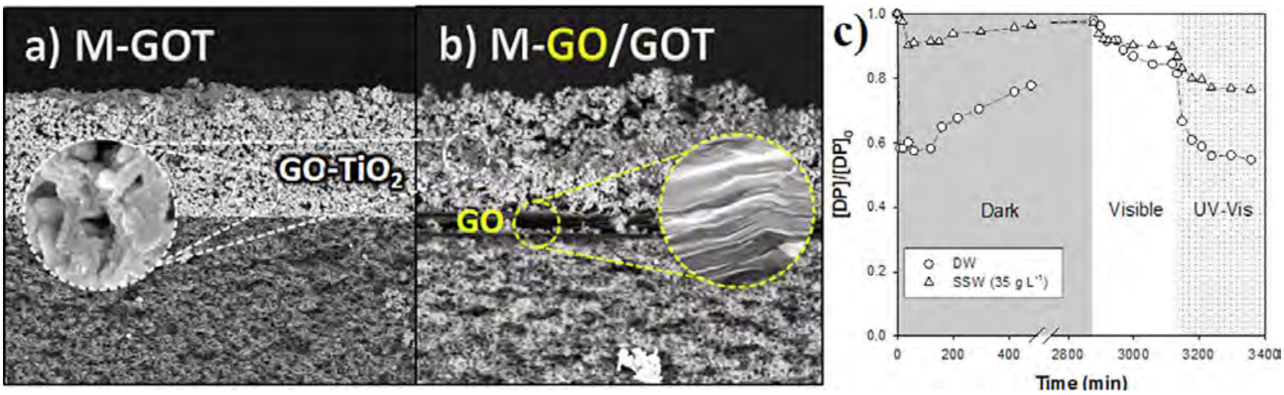

Figure 7. Cross-sectional SEM micrographs of (a) M-GOT and (b) M-GO/GOT (insets corresponds to the GOT composite or the freestanding GO membrane: M-GO, respectively); (c) DP removal in DW and SSW (35 g L^{-1}) with the M-GO/GOT membrane under dark conditions, near-UV/Vis and visible light irradiation. Figures adapted with permission from ref. [34]. Copyright 2015, Elsevier.

Figura 7. Micrografías de SEM de (a) M-GOT y (b) M-GO/GOT (las figuras pequeñas corresponden al material GOT o la membrana de GO: M-GO, respectivamente); (c) Eliminación de DP en DW y SSW (35 g L^{-1}) con una membrana M-GO/GOT en ausencia de luz, con irradiación UV cercano/Vis y luz visible. Figuras adaptadas de ref. [34]. Copyright 2015, Elsevier.

superior than that of a standard NF process in regard to the overall dye removal capacity and to the dye concentration reduction in the permeate effluent.

The deposition of photocatalysts onto flat sheet membranes was carried out by using a simple filtration method and mixed cellulose ester (MCE) membranes as supports [34]. The membranes prepared with GOT, TiO$_2$ and P25 were labelled as M-GOT, M-TiO$_2$ and M-P25, respectively. The membrane presenting the highest photocatalytic activity (M-GOT) was also modified by intercalating a freestanding GO membrane between the MCE membrane and the GOT photocatalyst layer. For that, a GO dispersion was filtered through a M-GOT membrane, and a homogeneous GO layer was obtained above the MCE membrane and the layer of GOT (labelled as M-GO/GOT, Figs. 7a and b).

The prepared membranes were compared in terms of photocatalytic activity using distilled water (DW), simulated brackish water and (SSW) seawater. The photocatalyts were homogeneously deposited without appreciable presence of cracks, holes or another defects. The M-GO/GOT membrane showed higher pollutant removal under dark conditions and good performance under visible and near-UV/Vis irradiation (Fig. 7c). However, the M-GOT membrane performed better, probably due to the higher compactness in the case of M-GO/GOT as a consequence of the synthesis conditions required for its preparation.

5. Conclusions and future perspectives

Carbon-metal oxide semiconductor materials have been widely investigated and are promising materials for photocatalytic applications. The synergic effect induced by the presence of carbon materials in the hybrid photocatalysts is mainly attributed to the decrease of electron/hole recombination, bandgap tuning and increase in the adsorptive active sites. The great morphological and electronic versatility of carbon nanomaterials offers the possibility of designing novel photocatalytically-active materials for a wide variety of applications. The full understanding of the synergies created between carbon nanomaterials and metal oxide semiconductors is crucial for the development of highly active photocatalysts. While the existence of high amounts of carbon-containing contaminants in the environment (greenhouse gases, organic water pollutants, etc) is of major concern, nanoscale carbon materials can be considered an outstanding solution towards the development of photocatalytic technologies.

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