Carbon mediated photoinduced reactions as a key factor in the photocatalytic performance of C/TiO₂

Marta Haro, Leticia F. Velasco, Conchi O. Ania*

Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain

Abstract

We have explored the photoelectrochemical behavior of carbon/titania composites, aiming at understanding the mechanisms of the photoinduced processes occurring in such hybrid photocatalysts that lead to enhanced photocatalytic efficiencies of the pristine semiconductor for the photodegradation of refractory pollutants in water. In a first step, spectrometric techniques have been applied to investigate the structural and optical properties of the carbon/semiconductor composites compared to the intrinsic characteristics of the unsupported semiconductor. The second approach consisted in the preparation of thin film electrodes to explore the photoinduced reactions occurring at the interface under UV light and bias potential. The gathered results provided experimental evidence on the carbon-mediated photoinduced reactions, distinguishing different mechanisms: i) the carbon matrix acts as a charge trapping network that modifies the fate of the photogenerated charge carriers (avoiding recombination and thus enhancing the photocatalytic efficiency); ii) illumination of the carbon additive renders photogenerated carriers due to π - π^* transitions, capable of participating in charge transfer reactions with electron donors present in the reaction medium. Our results point out that beyond the beneficial effect of the porosity of the support, the carbon matrix does play an important role in the photo-induced reactions of carbon-supported photocatalysts.

Broader context

The use of light energy is particularly useful for the degradation of refractory pollutants, since the excitation of electronic molecular states at energies provided by light may induce chemical bond breaking. Consequently, heterogeneous photocatalysis based on semiconductors is becoming one of the most promising green chemistry technologies in the environmental remediation arena. However major cornerstones of photocatalytic processes that prevent their large scale implementation are related to the photoelectrochemical properties of the semiconductor (low visible light activity, high recombination of photogenerated species, etc.). Coupling carbon materials as additives to semiconductor has long proved to be an attractive strategy to improve the photocatalytic efficiency of carbon/semiconductor composites on the photodegradation of a variety of recalcitrant pollutants, albeit the exact role of the carbon phase on the enhanced performance of the composites has not yet been fully understood. Aiming at understanding the mechanisms of the photoinduced processes occurring in such hybrid photocatalysts, we have investigated the photoelectrochemical response of carbon/titania thin film electrodes under UV light, and their efficiency for the photo-oxidation of phenol. Our findings show the key role of the carbon matrix on the photoinduced reactions occurring at the carbon/semiconductor interface, beyond the reported beneficial effect of porous supports.

* - corresponding author, E-mail: conchi.ania@incar.csic.es (CO Ania); Tel. +34 985 118846; Fax +34 985297662

Introduction

The use of light energy has been long explored by scientists due to its potential applications in many areas such as light harvesting for solar energy storage and conversion (solar cells and hydrogen production in water splitting), carbon dioxide remediation, self-cleaning surfaces, and air purification and wastewater remediation, among most representatives [1-3]. In environmental chemistry, photochemical reactions are particularly useful for the degradation of refractory pollutants since the excitation of electronic molecular states at energies provided by light -typically corresponding to the UV region- may induce chemical bond breaking.

Heterogeneous photocatalysis based on the use of semiconductor catalysts is becoming one of the most promising green chemistry technologies. Indeed, after the pioneering studies in 1977 reporting the performance of semiconductor powders to decompose cyanides in solutions [4], the interest of photocatalysis for environmental applications has largely increased and nowadays it has become one of the most popular and promising Advanced Oxidation Process (AOP) for the degradation of recalcitrant pollutants in air, water and wastewater [1-3, 5-7].

The success of semiconductor photocatalysis as an efficient environmental remediation tool is mainly related to the choice of titanium oxide as photo-active material [8], although other transition metal oxides and sulfides (e.g. ZnO, CdS, WO₃) have also been investigated [3, 4, 9]. The mechanism of light absorption in a wide band gap n-type semiconductor is based on the photogeneration of electron/hole pairs (e^-/h^+) leading to a series of chain oxidative-reduction reactions. These photogenerated charge carriers can recombine radiatively (photoluminescence) or non-radiatively (dissipating the energy as heat), or migrate to the surface and get scavenged by electron donors present at the interface. The competition between the recombination of the e^-/h^+ pairs and their ability to migrate to the gas or liquid-solid interface leading to subsequent chemical events -eventually involving other reactive species- usually determine the overall efficiency of the photocatalytic process [10]. Major drawbacks are also related to the low semiconductor activity under visible light, high recombination rate of photogenerated electron-hole pairs, and technological limitations associated to the separation (filtration), recovery and reutilization of the typically fine semiconductor powders -an important challenge that prevents the large scale implementation of photocatalytic processes- [2,3].

Numerous efforts have been made in the last decades to improve the photocatalytic activity of semiconductors. Aside from tuning their nanostructure and chemical composition, hybrid catalysts prepared by immobilization of the photoactive semiconductor on appropriate substrates have been explored due to significantly improved performance observed on such composites [11-16]. Among them, the potential role of carbon materials as additives and supports for the immobilization of semiconductors has recently attracted considerable attention because of the high efficiencies reported for carbon/semiconductor composites on the photodegradation of a variety of pollutants both in liquid and gas phase [14, 15 and references there in].

The enhanced photocatalytic response of carbon/TiO₂ composites has not yet been fully understood, although it seems generally accepted that it strongly depends on the characteristics (composition and structure) of the carbon material itself. In this regard, extensive work has been carried out on a variety of carbon sources, forms and morphologies [14-19], and different mechanisms have been postulated to describe the effect of porous carbons compared to other forms of nanostructured carbons (such as carbon nanotubes, fullerenes and graphene). All of them are generally attributed to either single or collective factors associated to: i) enhanced visible light absorption of the composites; ii) synergistic effects based on the confinement of the target pollutant on the porosity of the carbon material; iii) strong interfacial electronic effects on the carbon support, and iv) more recently the self-photochemical activity of certain carbon materials under UV light [14-23].

Despite the increasing interest of the topic, neither the exact role of carbon on the photochemical behavior of carbon/semiconductor, nor the mechanisms occurring at the carbon/semiconductor interfaces have yet been clarified; most plausible hypothesis remain yet rather speculative. Bearing this in mind, the objective of this work was to provide experimental evidence on the role of carbon as additive to semiconductor photocatalysts, aiming at understanding the mechanisms of the photoinduced processes occurring at the carbon/semiconductor interface when exposed to UV irradiation. For this purpose, we have investigated the photoelectrochemical response of carbon/titania thin film electrodes of increasing carbon content, and compared to that obtained for bare titania under similar illumination conditions. Special attention has been paid to explore the correlation between the opto-electronic and photoelectrochemical properties of both photocatalysts components and the photocatalytic activity of the carbon/semiconductor films. The gathered results provided experimental evidence on the carbon-mediated photoinduced reactions, and their positive impact on the enhanced photocatalytic activity of the carbon/titania catalysts towards the degradation of a recalcitrant pollutant (i.e., phenol) in solution.

Experimental

Materials

The carbon additive employed in the preparation of the carbon/semiconductor composites was an activated carbon obtained by steam activation of bituminous coal. A detailed physicochemical and structural characterization of this activated carbon has been reported elsewhere [24]. The choice of this material was based on previous studies, where the beneficial synergistic effect of this porous carbon on the enhancement of the photocatalytic activity of titanium oxide was demonstrated [20, 21]. As semiconductor and reference photocatalyst, commercially available TiO₂ powders (P25 from Degussa, Evonik) were used. Further characterization details on both precursors used for the synthesis of the composites is provided in the Supporting Information (Fig. S1 and S2).

Synthesis of the electrodes

For the fabrication of the thin film electrodes, about 200 mg of the catalysts (either bare titania or carbon:titania composites) were dispersed in 2.5 mL of N,N-dimethylformamide and sonicated in an iced bath for 2 minutes; 200 microL of this dispersion were spread by a syringe onto an indium tin oxide (ITO) conductive glass substrate (sheet resistivity 15-25 Ω /sq) and spin-coated at 2500 rpm. The films were dried at 100 °C overnight and subsequently annealed in a muffle furnace at 300 °C for 30 min in air (heating rate 5 °C/min). The annealing temperature for the electrodes preparation was carefully chosen to avoid modifications in the carbon substrate (ca. oxidation or pore clogging due to the solvent). The carbon/titania composites will be labeled as TiAC_x where *x* stands for the amount of carbon additive incorporated to the composite expressed as wt.%. A series of composites containing 5, 10, 25 and 50 wt.% carbon were prepared.

Physicochemical, textural and structural characterization of the electrodes

Textural characterization was carried out by measuring the N₂ adsorption isotherms at -196 °C in an automatic apparatus (Micrometrics ASAP 2020). Before the experiments, the samples were outgassed under primary vacuum at 120 °C overnight. The isotherms were used to calculate specific surface area S_{BET} , total pore volume V_{T} , and micro- and mesopore volumes using the DFT method. SEM/EDX analyses were performed with a FE-SEM apparatus (QuantaSEM, FEI). The morphology of the electrodes, as well as the dispersion of the individual components in the composite was directly observed (no metallic coating was required). Thickness measurements were determined by confocal optical microscopy, in a Leica microscope (DMI 5000M). X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance instrument operating at 40kV and 40 mA and using CuK α ($\lambda = 0.15406$ nm) radiation. Diffraction data were collected by step scanning with a step size of 0.02° 2 θ and a scan step time of 5 s. UV-Vis diffuse reflectance spectra were recorded on a Shimadzu spectrometer equipped with an integrating sphere and using BaSO₄ as a blank reference.

Photoelectrochemical measurements

The photo-electrochemical behavior of the catalysts was investigated in a standard three electrodes system using a quartz cell. In our experiments, the temperature of the reaction vessel was carefully controlled using a thermostatic bath and the solution remained at room temperature within + 2°C, for which extreme temperature variations do not seem to apply. The thin films deposited onto the ITO substrates were used as working electrodes, and a saturated calomel (SCE) and platinum wire were used as reference and counter electrodes, respectively. The UV irradiation source was provided by a high pressure mercury lamp (light intensity 50 mW/cm²) provided with a double-walled quartz jacket cooled by flowing water to prevent overheating of the suspension due to the irradiation. The prepared electrodes were immersed in a 20 mL solution containing 0.1 M Na₂SO₄ (pH 6) as inert electrolyte, placed in front of the irradiation source and allowed to equilibrate for ca. 1 hour before recording any

measurements. The photo-electrochemical response of the thin film electrodes upon on and off illumination was recorded on an electrochemical workstation (Biologic VMP3) applying a linear potential sweep from -600 to +600 mV vs SCE at a scan rate of 20 mV/s. The transient photocurrent response of the electrodes at a fixed bias potential was also recorded for several times to evaluate the electron transfer mechanism and reproducibility of the prepared electrodes. Spikes of a concentrated phenol solution (ca. 20 microL, 10 g/L) were added to the electrolytic solution to evaluate the photoelectrochemical response of the thin film electrodes in the presence of an electron donor, and their ability towards the photocatalytic degradation of this aromatic compound.

Results and discussion

Characterization of the catalysts

Spin coating deposition of the catalysts suspensions (titania or carbon/titania mixtures) on ITO substrates followed by annealing at 300 °C resulted in the immobilization of ca. 0.6-0.8 mg cm⁻² of catalyst particles on the conductive support. The surface morphology of the films deposited onto the ITO substrates was examined by scanning electron microscopy. Micrographs in Fig. 1A show quite uniform film coverage, with titania nanoparticles evenly distributed throughout the ITO surface. Examination at higher magnification (Fig. 1B) revealed that the TiO₂ film consisted of agglomerated particles with irregular sizes and average diameters below 40 nm, which is consistent with the average particle diameter of the titania particles used. When the carbon material was added to the mixture the film coverage was still quite uniform (Fig. 1C-E), although some grains or islands of variable size were occasionally seen on the surface (Fig. 2). These globular structures appeared randomly distributed on the substrate and they seemed to be more abundant as the carbon content in the composite was raised (Fig. 2 and Fig. S3 in the Supporting Information). The good dispersion of the carbon particles within the semiconductor particles was also corroborated through the SEM mapping of the film electrodes; the dark red dots in the micrographs shown in Fig. 1F depict the dispersion of the carbon phase within the titania matrix. The uniform coverage of the films showing interconnected particles anticipates good electron transport properties, which is an important parameter for the performance of the electrode.

The confocal microscope images also allowed the estimation of the thickness of the films at the interface of a clean layer. The profiles obtained for different optical sections were rather homogenous, which is in good agreement with SEM images; average thickness ranged between 1-2.5 microns for all the prepared electrodes, regardless the carbon content. This illustrates that the casting procedure allowed a fine control in the colloidal mixtures that guaranteed an efficient coverage of the substrate. This is most significant since the thickness of the electrodes has an important effect on the photoelectrochemical performance and photocatalytic activity of semiconductor thin films [25-27]. Moreover the thin film electrodes, with geometric areas of 1.5 x 1 cm, were mechanically stable and transparent, exhibiting ca. 70 % of visible light transmittance regardless the carbon content.

Further characterization of the electrodes by XRD indicated that the crystallinity of the titania particles did not change by the casting processing, which was expected based on the mild annealing temperature applied during the preparation of the electrode films. Although better results (in terms of film mechanically stability and titania crystallinity) have been reported for higher calcination temperatures [28], the presence of carbon additive in the composites imposes the use of lower calcination temperatures to avoid losses coming from the burning out the carbon phase.

The optical properties of the TiO₂ and carbon/titania composites were also explored by UV-Vis diffuse reflectance spectroscopy (Fig. 3A). The spectrum of bare titania nanoparticles presented the characteristic absorption sharp edge of the anatase form of TiO₂ (predominant phase) in the UV region rising above 400 nm. Comparatively, the carbon/titania composites showed a broad background absorption in the visible light region due to the introduction of black body properties characteristic of the carbon additive. The band gap absorption onsets of the composites at the edge of the UV-vis region showed a slight red-shift (tens of nm) with the carbon content; this observation became more evident for the composites with 25 and 50 wt.% carbon. The relationship between the band gap and the absorption coefficient was obtained from the Tauc equation [29]:

$$h\nu\alpha(\nu) = A (h\nu - E_g)^n$$

where A is the optical constant, α is the absorption coefficient, E_g is the band-gap of allowed transitions (eV), h is Planck's constant, ν is the frequency of the light, and n is a number characterizing the transition process ($n = \frac{1}{2}$ for TiO₂) [30].

The spectral shift upon incorporation of increasing amounts of carbon became more evident in the Tauc plots shown in Fig. 3B; and it has to be attributed to the overlapping of the corresponding spectra of carbon and titania, where UV and visible light absorption are respectively suppressed and increased with the carbon content due to the light absorption capacity of the carbon matrix itself [17, 31]. Although calculation of the band gap is quite well established for semiconductors, the estimation of this parameter becomes difficult when a carbon material is introduced in the composite since the values obtained are very sensitive to the region selected for fitting. Anyway, the red-shift is clearly observed, indicating that the corresponding band gaps for the carbon/titania composites are smaller than the value determined for TiO₂ (i.e. 3.16 eV). In short, the carbon as additive to titania nanoparticles allowed the narrowing of the optical band gap, and hence improved the visible light harvesting properties of the composites; this would be expected to lead to modifications of the fundamental process of electron/hole pairs photogeneration formation during irradiation.

Photo-electrochemical response

The electronic properties of titania and carbon/titania composites were investigated in aqueous solutions containing 0.1 M Na₂SO₄ as supporting electrolyte. The systems were initially investigated at open-circuit conditions upon immersion of the electrodes in the electrolyte solution both in dark and UV conditions (Fig. 4). In the dark at open circuit, immersion of the titania electrode in the electrolyte

brings about the formation of a depletion layer at the electrolyte/semiconductor interface, arisen from the charge flow between both phases until the equilibrium is reached. This interfacial charge-transfer process causes an excess of positive charges in the space charge layer on the semiconductor -in the form of immobilized ionized donors- and an excess of negative charges in the electrolyte [32-34]. To counteract the charge flow, a potential ($V_{oc\ dark}$) appears at the semiconductor/electrolyte junction that represents the energy barrier for the interfacial electron transfer and in the case of the titania electrode accounted for +50 mV vs SCE. As long as the semiconductor-electrolyte interface is not perturbed by an external (bias) potential, no net charge flow will occur.

For the carbon/titania electrodes, the interfacial equilibration between the two phases needed a longer time, which is attributed to the increasing porosity of the composites upon incorporation of the carbon additive (Table 1). Additionally, the incorporation of the carbon matrix modified the charge-transfer equilibrium at the depletion layer, as inferred by the gradual shift in the $V_{oc\ dark}$ values towards more positive values with raising the carbon content in the electrodes (Fig. 4).

This anodic shift (a few tens of mV) indicates that the semiconductor becomes more positively charged, and suggests that the carbon matrix favors the withdrawal of electrons from the semiconductor, likely through the stabilization within the π electron density of the graphene sheets in the carbon material. Positive potentials at open circuit (rest potential) have also been reported upon immersion of carbon electrodes in aqueous electrolytes, a parameter that seems to be strongly linked to the nature of the carbon material [35].

When the electrodes were illuminated under UV light, electron-hole (e^-/h^+) pairs were formed at the space charge region; the photogenerated holes are driven towards the solid/electrolyte surface and the electrons are injected in the conduction band of the semiconductor and from there to the external circuit; such increase in the electrons population in the conduction band provokes a potential drop ($V_{oc\ UV}$), that in the case of titania accounted for -470 mV vs SCE, compared to +50 mV vs SCE at dark conditions (Fig. 4). It is interesting to note that the incorporation of carbon to the electrodes gradually shifted the $V_{oc\ UV}$ to more positive potentials (Fig. 4), as already observed in the dark. Since the conduction band of the carbon material is expected to be more positive [36] than that of titania [36], a charge equilibration between the two systems is expected upon irradiation. When the electrodes were short circuited right after UV illumination, the TiO_2 electrode immediately adopted the $V_{oc\ dark}$ value, whereas for the carbon/titania composites a more gradual and slow recovery of the potential was observed; we attribute this to the slow diffusion in the porosity of the composites.

It has to be pointed out that no temperature changes were detected in the photoelectrochemical cell upon irradiation of the electrodes, for which no modification of temperature-dependent parameters of photocatalytic and electrochemical reactions (i.e., variations on the electrode potentials or the semiconductor optical properties) are expected, since these have only been reported for extreme conditions with respect to room temperature (i.e., above 80°C) [36,37].

The anodic shift of $V_{oc\ UV}$ of the carbon/titania composites points out that the carbon acts as an acceptor of the photogenerated electrons, lowering the electrons population in the conduction band of the semiconductor. A similar behavior has been reported for carbon nanotubes [38] and graphene [39], and explained in terms of their ability to accept electrons and undergo charge equilibration based on their electronic conductivity and charge mobility. In our case the finding is most significant since the carbon additive chosen (i.e., activated carbon) has a turbostratic structure, and thus a much lower electronic conductivity compared to carbon nanotubes or graphene. Also, the lower cost of traditional activated carbons compared to other carbon nanostructures offers an interesting perspective for the large scale implementation of heterogeneous photocatalysis based on more efficient (high conversions) and sustainable (low cost carbons, which also can be produced from green precursors) photocatalysts.

Voltammetry in Na_2SO_4 solution was also employed to study the effect of potential bias on the photocurrent response of the different catalysts. In the dark, the characteristic shape of photocurrent-potential curves of n-type semiconductor was obtained for the TiO_2 electrode, with two distinctive regions depending on the applied potential (Fig. 5). Below -300 mV vs SCE, the cathodic current corresponds to the flux of excess electrons in the accumulation region; above this potential value, the voltammograms showed a flat signal corresponding to the depletion region where electrons can no longer flow and the electrode behaves like a diode. In the case of the carbon/titania composites, tiny net currents were measured in the whole potential range at dark conditions, due to the capacitive contribution upon the formation of the electrical double layer in the porosity of the electrodes. Hence the expected trend of high capacities currents with increasing the surface area of the composites - provided by the carbon- was observed.

Upon UV illumination, anodic photocurrents were observed in all studied electrodes when the bias potential was positive enough for an efficient hole-electron separation. Under these conditions, minority and majority carriers are driven to opposite directions by the imposed electric field across the depletion layer; the electrons are transferred through the bulk semiconductor to the counter electrode to the external circuit, while the holes generated at the interface are accumulated or react with any suitable electron donor present in the electrolyte [34]. In the inert supporting electrolyte, the magnitude of the photocurrent is related to water oxidation by the photoholes (through the formation of $\bullet\text{OH}$ radicals), whereas in the presence of organic pollutants the holes may also be captured by the pollutant causing direct photo-oxidation (degradation) reactions.

For all the thin film electrodes a linear dependence was obtained for the plot of the square of photocurrent vs the bias potential in the raising part of the photovoltammograms; this demonstrates that the prepared film electrodes are thick enough to form a depletion layer where the photogenerated charge carriers are separated. Consequently the anodic photocurrent is controlled either by the migration of the majority carriers or the holes capture (recombination is not dominant) [41,42].

For the TiO_2 film electrode, the photocurrent increased with the potential bias reaching a saturation limiting value above 0 mV vs SCE, which is characteristic of systems where the overall photocatalytic process is governed by a photohole capture regime [33, 42]. When phenol was incorporated to the solution the photocurrent increased, although still a saturation limit was attained above ca. 0 mV vs SCE; this confirms the direct hole-mediated phenol oxidation reaction at the TiO_2 thin film electrode. Thus, while the holes are captured by the scavenger, the constant photocurrent flow in the outer circuit is maintained due to the electrons diffusion to the platinum counter-electrode.

The shape of the current-potential curves of the carbon/titania electrodes was similar to those of titania (Fig. 5), although no photocurrent saturation limit was observed, particularly for the composites with the highest carbon content (TiAC25 and TiAC50). Interestingly, the photocurrent values generated upon illumination of the carbon/titania electrodes were similar to those obtained for the TiO_2 films. Although this effect is partially due to the capacitive contribution of the electrical double layer formed in the porous composites, the evaluation of the photocurrent–time response at fixed potentials disregarding the capacitive current contribution of porous electrodes showed a similar trend (Fig. 6). This is most outstanding as the semiconductor content in the electrodes is reduced as the carbon additive in the composite was raised, and variations in the thickness of the film electrodes were too small to account for this observation.

The transient photoamperometric curves upon on-off illumination for several bias potentials (ca. 0, +200 and +500 mV vs SCE) showed the typical fingerprint of a n-type semiconductor for all the systems. On switching-on the light, an initial sharp current spike is followed by a steady-state regime, which retracted to original values almost instantaneously once the illumination was turned off. In the absence of hole scavengers other than water, this photocurrent corresponds to water oxidation. The photocurrent response was rapid and reproducible during repeated on/off cycles of illumination, for which the initial current decay is attributed to fast recombination processes rather than to photocorrosion of the electrodes. As above-mentioned, all the film electrodes showed roughly similar photocurrent values (counteracting the capacitive contribution) regardless their composition (see Fig. 6); additionally, the photocurrent enhancement after phenol addition to the electrolytic solution, indicative of a direct hole scavenger process, was clearly observed for all the thin film electrodes.

The high photocurrents measured in the composites are related to a higher density of photogenerated electrons recovered at the back contact of the electrical circuit likely as a result of an efficient charge carrier separation; this indicates that the incorporation of the carbon additive plays an important role for the photoelectrochemical response of the composites, and anticipates a potentially higher photocatalytic activity of these materials.

Such enhanced separation of the photogenerated charge carriers in the presence of the carbon additive could be explained by different factors. First of all, the diffusion length of the minority carriers in porous electrodes is smaller (see scheme of Fig. 7A); this is expected to reduce recombination as the carriers can easily reach the surface; secondly, the three-dimensional conjugated π structure of the

carbon could act as an acceptor of the photogenerated electrons that would be rapidly stabilized by delocalization within the carbon basal planes (graphene sheets). These electrons could be either injected from the conduction band of titania or directly injected to the graphene sheets upon UV irradiation of the composites. Although increased electron migration has already been reported for carbon nanostructures with high charge carrier mobility (such as nanotubes and graphenes), we herein demonstrate that carbon materials with a turbostratic structure (i.e. activated carbons) can also lead to the same behavior (Fig 7B).

The most interesting feature of the photovoltammograms in Fig. 5 was the distinctive shape observed for the carbon/titania electrodes, particularly for sample TiAC25 and TiAC50, characterized by a marked change in the slope of the photocurrent-potential plots at potential values higher than 50-100 mV vs SCE. The effect was more remarkable when phenol was added to the electrolytic solution (Fig. 5). It should be mentioned that no electrochemical oxidation of phenol took place for the electrodes in the dark between -600 and +600 mV vs SCE in the supporting electrolyte solution. This singularity in the photoelectrochemical response was only observed for the carbon/titania film electrodes upon irradiation, thus it seems reasonable to link it to a specific role of the carbon matrix exposed to UV light.

To understand the change in the slope of the photocurrent-voltage curves of the carbon/semiconductor electrodes, different aspects must be considered. On the first hand, the increase in photocurrent at higher bias potentials could arise from the release of the photoelectrons trapped in the carbon graphene sheets (injected from the semiconductor TiO_2) due to the role of the carbon matrix as electron acceptor, as mentioned above. However, as photocurrents of the composites were similar (not lower) than those of titania -despite the gradual reduction in the semiconductor content-, this effect does not seem to be dominant.

On the other hand, the change in the slope of the photocurrent-potential curves of the carbon/titania composites (Fig. 5) suggests the occurrence of another redox process, which could be linked to direct π - π^* transitions arising during the absorption of photons by the carbon matrix, in a similar mechanism as that proposed in the literature for graphite and glassy carbon (Fig 7 C) [37, 43]. This seems most plausible given that activated carbons can be considered as assemblies of defective graphene layers in a turbostratic structure (where carbon atoms show sp^2/sp^3 -hybridization) [44]. These transitions would create an unstable defective electron state at the carbon, thus undergoing rapid recombination reactions unless the bias potential is high enough. Consequently, more positive potentials are needed to drive these charge carriers to the electrode/electrolyte interface, escaping recombination and therefore inducing photocurrents (Fig. 5). Once separated, these charge carriers can participate in charge transfer reactions such as water photooxidation, generation of radical species, charging of surface redox groups, or other redox reactions involving the carbon matrix itself and/or reactions of intermediates producing an increased photocurrent. Indeed, photoreduction of dissolved O_2 at irradiated highly oriented pyrolytic graphites has been reported [43], and most recently the photooxidation of phenol at

irradiated activated carbons [21]. Furthermore, a thorough characterization of the carbon support after exposure to UV irradiation has shown that this material is resistant to oxidation despite the formation of hydroxyl radicals during illumination of the composites.

These carbon-mediated photoinduced reactions explain the photochemical response of activated carbons under UV light recently reported in our earlier investigations, accounting for the enhanced photocatalytic efficiency of carbon/semiconductor photocatalysts towards phenol photooxidation [20, 21, 45]. Indeed, the use of the studied activated carbon as titania additive has led to higher mineralization yields compared to the unsupported semiconductor. These results indicate that beyond the already reported beneficial effects of carbons as additives, mainly related to the porosity and the modification in the photocatalytic degradation pathway of phenol [14, 19, 20, 31], the carbon matrix also plays an important role in the photoinduced reactions occurring at herein studied carbon/titania composites.

As mentioned above, no modification of the photoelectrochemical cell temperature was observed upon illumination of the electrodes. Moreover, although a local slight temperature increase in the electrodes by direct heating of the composites due to intensive light absorption (particularly when immobilized on the ITO substrate) cannot be disregarded, this would not affect at the role observed for the carbon matrix discussed in terms of charge transfer reactions at the porous carbon/titania interface. Such local temperature increase would favor the recombination of the e^-/h^+ pairs, thus lowering the photoelectrochemical efficiencies measured experimentally.

All these results demonstrate the key role of carbon in the photocatalytic performance of hybrid carbon/semiconductor composites. The carbon matrix would not only hinder the e^-/h^+ recombination, as a result of an improved dynamics of carrier transportation across the carbon graphitic sheets and/or an improved efficiency of the carrier-intercepting surface reactions at the electrode interface. The carbon also contributes to trap the photogenerated electrons -which can be easily propagated through the graphene sheets-, as well as the contribution of the photocurrent generated due to direct $\pi-\pi^*$ transitions during irradiation of the carbon matrix. Although more efforts are needed to further comprehend the photocatalytic mechanism applying for other carbon materials, we believe this work marks a starting point for further research in this field.

4. CONCLUSIONS

Coupling of a semiconductor oxide and a carbon additive has largely shown to be an interesting strategy to enhance the photocatalytic response of the semiconductor, leading to better efficiencies in the environmental remediation arena. This study demonstrates that the synergistic effect between carbon and TiO_2 particles can be ascribed to the different photoelectrochemical behavior of the carbon/titania electrodes when exposed to UV light. The incorporation of the porous carbon matrix to

the titania film electrodes favors the probability of charge transfer reactions at the porous carbon/titania interface by different mechanisms:

- i) the smaller diffusion length of the carriers through the porous structure provided by the carbon material, as a result of which photohole capture and indirect oxidation reactions are favored, leading to increased photocatalytic oxidation yields.
- ii) the carbon matrix can act as an acceptor of the photogenerated electrons upon UV irradiation of the titania particles; the charge carriers separation through delocalization and stabilization within the graphene layers of the carbon additive contributes to minimize the recombination.
- iii) photon absorption by the carbon material itself generates charge carriers due to unstable electronic states (direct π - π^* transitions), which contribute to increased photocurrents and thus participate in charge transfer reactions at the electrode surface.

All these carbon-mediated reactions account for the enhanced photocatalytic yields reported for carbon/semiconductor hybrid photocatalysts. We believe this provides new perspectives and very useful information from the viewpoint of the design of low-cost and more efficient photocatalysts for environmental remediation.

ACKNOWLEDGMENTS

The authors thank the financial support of the Spanish MINECO and FICYT (grants CTM2008/01956, CTM2011/02338 and PC10-002). LFV and MH thank CSIC for JAE-Pre and JAE-Doc contracts.

REFERENCES

1. R. P. Wayne, in *Principles and applications of photochemistry*, Oxford Science Publications, Oxford University Press, USA, 2nd edn., 1988.
2. D. F. Ollis and H. Al-Ekabi, in *Photocatalytic purification and treatment of water and air*, ed. D. F. Ollis and H. Al-Ekabi, Elsevier, London, 1993.
3. E. Pelizzetti and N. Serpone, in *Photocatalysis: fundamental and applications*, ed. E. Pelizzetti and N. Serpone, Wiley-Interscience, New York, 1989.
4. S. N. Frank and A. J. Bard, *J. Phys. Chem.*, 1977, **81**, 1484.
5. M. Battzill, *Energy Environ. Sci.*, 2011, **4**, 3275.
6. S. Parsons, in *Advanced Oxidation Processes for Water and Wastewater Treatment*, ed. S. Parsons, IWA Publishing, London, 2004.
7. M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69.
8. A.L. Linsebigler, L. Guangquan, J.T. Yate, *Chem. Rev.*, 1995, **95**, 735.
9. M. D. Hernandez-Alonso, F. Fresno, S. Suarez and J. M. Coronado, *Energy Environ. Sci.*, 2009, **2**, 1231.
10. N., Serpone, D., Lawless, R., Khairutdinov and E. J. Pelizzetti, *J. Phys. Chem.*, 1995, **99**, 16655.
11. X.Hu, G. Li and J. C. Yu, *Langmuir*, 2009, **26**, 3031.
12. M.A. Henderson, *Surf. Sci. Reports*, 2011, **66**, 185.
13. A. Fernández, G. Lassaletta, V. M., Jiménez, A. Justo, A. R. González-Elipe, J. M. Herrmann, H. Tahiri and Y. Ait-Ichou, *Appl. Catal. B Environ.*, 1995, **7**, 49.
14. R. Leary and A. Westwood, *Carbon*, 2011, **49**, 741.

15. J. L. Faria and W. Wang, in *Carbon materials in photocatalysis*, ed. P. Serp and J. L. Figueiredo, Wiley & Sons, New Jersey, 2009, ch. 13, pp. 481-506.
16. A. M. Balu, B. Baruwati, E. Serrano, J. Cot, J. Garcia-Martinez, R. S. Varma and R. Luque, *Green Chem.*, 2011, **13**, 2750.
17. J. Matos, A. García, L. Zhao and M. M. Titirici, *Appl. Catal. A: General*, 2010, **390**, 175.
18. C. H. Kim, B.-H. Kim and K. S. Yang, *Carbon*, 2012, **50**, 2474.
19. J. Matos, J. Laine and J.-M. Herrmann, *J. Catal.*, 2001, **200**, 10.
20. L. F. Velasco, J. B. Parra and C. O. Ania, *Appl. Surf. Sci.*, 2010, **256**, 5254.
21. L. F. Velasco, I. M. Fonseca, J. B. Parra, J. C. Lima and C. O. Ania, *Carbon*, 2012, **50**, 249.
22. R. Ocampo-Perez, M. Sanchez-Polo, J. Rivera-Utrilla and R. Leyva-Ramos, *Appl. Catal. B-Environ.*, 2011, **104**, 177.
23. J. Matos and J. M. Herrmann, *Appl. Catal. B-Environ.*, 1998, **18**, 281.
24. C. O. Ania, B. Cabal B, C. Pevida, A. Arenillas, J. B. Parra, F. Rubiera and J. J. Pis, *Water Research*, 2007, **14**, 330.
25. Z. Yi, C. Guofeng, W. Ma and W. Wei, *Prog. Org. Coat.*, 2008, **61**, 321.
26. J. Yu, X. Zhao and Q. Zhao, *J. Mater. Sci. Lett.*, 2000, **19**, 1015.
27. S.-C. Jung, S.-J. Kim, N. Imaishi and Y.-I. Cho, *Appl. Catal. B-Environ.*, 2005, **55**, 253.
28. C. Kim, J. T. Kim, K. S. Kim, S. Jeong, H. Y. Kim and Y. S. Han *Electrochim. Acta*, 2009, **54**, 5715.
29. J. Tauc, *Phys. Stat. Sol.*, 1966, **15**, 627.
30. R. López and R. Gómez, *J. Sol.-Gel Sci. Technol.*, 2012, **61**, 1.
31. J. Araña, J. M. Doña-Rodríguez, E. Tello Rendón, C. Garriga i Caboa, O. González-Díaz, J. A. Herrera-Melián, J. Pérez-Peña, G. Colón and J. A. Navío, *Appl. Catal. B-Environ.*, 2003, **44**, 153.
32. A. J. Bard, *J. Photochem.*, 1979, **10**, 59.
33. A. Hagfeldt, M. Grätzel, *Chem. Rev.*, 1995, **95**, 49.
34. A. J. Bard and Stratmann M, in *Semiconductor Electrodes and Photoelectrochemistry*, Encyclopedia of Electrochemistry, vol. 6, ed. S. Licht, Wiley-VCH, Weinheim, 2002.
35. M. Nakamura, M. Nakanishi and K. Yamamoto, *J. Power Sources*, 1996, **60**, 225.
36. J. Herrmann, *J. Photochem. Photobiol. A Chem*, 2010, **216**, 85.
37. M.A. Buttle and D.S. Ginley, *J. Mater. Sci.*, 1980, **15**, 1.
38. A.D. Modestov, J. Gun and O. Lev, *Surf. Sci.*, 1998, **417**, 311.
39. P. Brown, K. Takechi and P. V. Kamat, *J. Phys. Chem. C*, 2008, **112**, 4776.
40. E. Gao, W. Wang, M. Shang and J. Xu, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2887.
41. L. M. Peter, *Chem. Rev.*, 1990, **90**, 753.
42. R. Beranek, *Adv. Phys. Chem.*, 2011, **2011**, ID 786759.
43. A.D. Modestov, J. Gun and O. Lev, *J. Electroanal. Chem.*, 1999, **476**, 118.
44. *Activated Carbon*, ed. H. Marsh and F. R. Reinoso, Elsevier, 1st edn, 2006, ch. 1, pp. 1-22.
45. L. F. Velasco, J. B. Parra and C. O. Ania, *Ads. Sci. Technol.*, 2010, **28**, 727.

Figure 1. SEM images of the thin film electrodes of titania and the carbon/titania composites at different magnifications: (A,B) titania; (C,D) TiAC10; (E) example of the film thickness. EDX mapping showing the distribution of the titania (blue) and carbon (red bright spots) phases in sample TiAC10 is also shown (F).

Figure 2. Representative images obtained at the confocal optical microscope of the film electrodes. Dark areas indicate the presence of thicker regions (islands) upon incorporation of the carbon additive.

Figure 3. (A) UV-Vis diffuse reflectance spectra and (B) Tauc representation of bare titania and carbon/titania mixtures.

Figure 4. Evolution of the open circuit potential (V_{oc}) under dark and UV irradiation of the thin film electrodes. Solid and empty arrows indicate the starting and ending points of the illumination, respectively (all profiles follow similar patterns).

Figure 5. Potential-current characteristics of the dark (stars) and irradiated film electrodes in the supporting electrolyte (triangles) and after incorporation of phenol (squares). Plot (A) represents a comparative of anodic currents for all the electrodes in the presence of phenol (the arrow indicates the carbon increase in the composites).

Figure 6. Chronoamperometric response of the film electrodes upon on/off illumination cycles in the supporting electrolyte and in the presence of phenol at fixed bias potential of ca. + 500 mV vs SCE. (A) titania, (B) TiAC25 as representative of the carbon/titania composites.

Figure 7. Scheme of the mechanisms proposed for illustrating the role of carbon on the photocatalytic performance of carbon/titania interfaces: I) diffusion length of carriers through the porous carbon matrix, II) carbon matrix as acceptor of photogenerated electrons, III) photon absorption by the carbon material.

Table 1. Main physicochemical characteristics of the investigated photocatalysts obtained from N₂ adsorption at -196 °C.

	TiO ₂	TiAC5	TiAC10	TiAC25	TiAC50
S_{BET} [m² g⁻¹]	57	103	154	297	548
V_{TOTAL} [cm³ g⁻¹]^a	0.09	0.15	0.18	0.23	0.34
V_{MICROPORES} [cm³ g⁻¹]^b	0.01	0.01	0.03	0.07	0.15
V_{MESOPORES} [cm³ g⁻¹]^b	0.08	0.12	0.14	0.09	0.08
^a <i>evaluated at p/po 0.95</i>					
^b <i>evaluated from DFT method</i>					

Supporting Information

Carbon mediated photoinduced reactions as a key factor in the photocatalytic performance of C/TiO₂

Marta Haro, Leticia F. Velasco, Conchi O. Ania*

Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain

E-mail: conchi.ania@incar.csic.es

Figure S1. TEM (top right) and SEM images of the materials (activated carbon and TiO₂) used for the preparation of the composites.

Figure S2. XPS data of the activated carbon used as support. A) wide-scan; B) C1s and C) O1s signals, showing deconvolution of main components.

Figure S3. Images obtained at the confocal optical microscope of the film electrodes. Dark areas indicate the presence of thicker regions (islands) upon incorporation of the carbon additive.