Photooxidation reactions promoted by the photochemical activity of nanoporous carbons

Reacciones de fotooxidación basadas en materiales de carbono nanoporosos

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1. Broader context

After the early works in 1960's and 70's reporting the photochemistry of ZnO and TiO_2 electrodes and their potential application in water splitting and environmental remediation [1,2], heterogeneous photocatalysis has become a popular topic. However, the low photonic efficiency of most semiconductors is still a challenge, thus optimizing the optical features of semiconductor materials remains a largely investigated topic [3,4]. Addressing these problems calls out for a research to be conducted to enhance the performance of semiconductors or to explore the possible use of other types of materials in this kind of applications. Among different approaches, the incorporation of carbon materials in the formulation of hybrid photocatalysts seems an interesting strategy to attain high photoconversion efficiencies. First investigations in the field focused on the use of carbons as supports and additives of TiO_2, and the enhanced photocatalytic performance of carbon/TiO_2 composites has been attributed to several factors associated to visible light absorption and the porosity of the carbon support, and/or strong interfacial electronic effects [5-8]. More recently, our pioneering studies have demonstrated the self-photochemical activity of semiconductor-free nanoporous carbons [9,10], along with their ability to generate O-radical species upon irradiation [11,12]. Despite the increasing interest of the topic, there is yet a dearth in the understanding of the role of carbons in photo-assisted reactions and the underlying mechanisms leading to the conversion of light into a chemical reaction (i.e. photooxidation of pollutants). By combining catalytic, spectroscopic and photoelectrochemical tools, we herein provide an overview of the photochemical response of nanoporous carbons applied to environmental remediation.

2. The role of carbon materials on photocatalysis

Triggered by the rising interest in heterogeneous photocatalysis, numerous efforts have been made in the last decades to improve the optical properties of semiconductor materials. Among different strategies, novel hybrid materials prepared by immobilization of the photoactive semiconductor on appropriate substrates have gained increased interest due to the superior performance observed on such composites [5,8,13-17]. Despite carbons are strong light absorbing materials, they have also been extensively
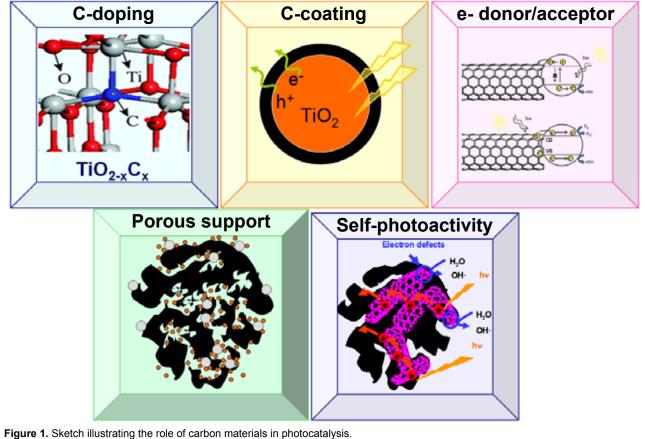

Figure 1. Sketch illustrating the role of carbon materials in photocatalysis.
Figura 1. Esquema ilustrativo del empleo de materiales de carbono en fotocatálisis.

investigated in a number of photo-assisted reactions [5-7 and references therein]. The majority of the studies deal with the use of carbon/semiconductor composites, where the carbon material acts either as a dopant or a support of the photoactive material (Fig. 1).

For instance, metallic and non-metallic doping seems a promising route to extend the optical absorption of conventional semiconductors towards the visible region, allowing the use of sunlight [18-22]. Comparatively, non-metallic doping is considered to be more effective than transition metal doping due to the high photostability and lack of photocorrosion of the resulting catalyst. Furthermore, the isomorphic incorporation of carbon atoms in the lattice of semiconductors is considered to be more effective than other non-metal heteroatoms. Most authors agree to explain this effect in terms of the redshift in the absorption properties of doped material and the modifications in the electronic band structure of the metal oxide associated to band gap narrowing and localized midgap levels [21,22].

Besides semiconductor-doping, the incorporation of nanoporous carbons as supports in hybrid carbon/semiconductor composites is another interesting alternative to prepare efficient photocatalysts. The idea, firstly introduced by Matos et al. [8], relies on the combination of the confinement of the pollutant in the porosity of the catalyst via adsorption with the photoactivity of the semiconductor. After this early work based on activated carbons, a variety of carbon sources, forms and morphologies have been explored, using from conventional (activated carbon, carbon black, graphites) to novel carbons (nanotubes, graphene), as well as different synthetic routes for the catalyst preparation (physical mixture, liquid impregnation, hydrothermal process, chemical vapor deposition) [5-7]. The increased photoconversion yields of carbon/semiconductor composites has been ascribed to the enhanced mass transfer of the adsorbed pollutant from the bulk solution to the photoactive particles through the interface between the two catalyst components, and to the interactions between the substrate and the
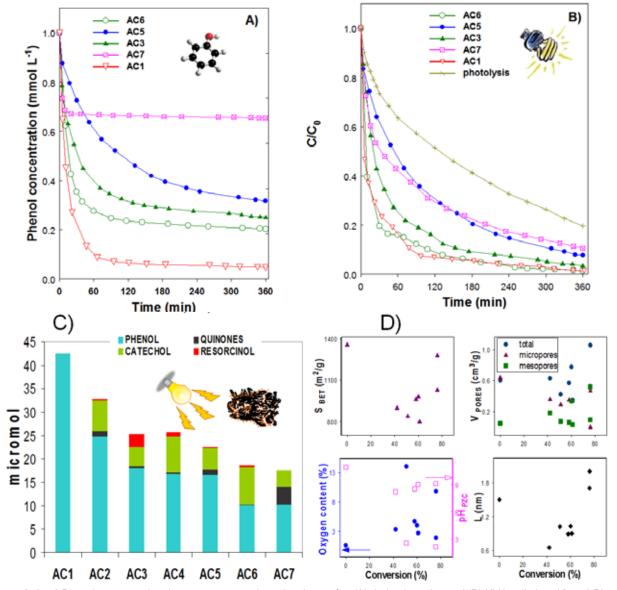

Figure 2. (top) Phenol concentration decay curves on selected carbons after (A) dark adsorption and (B) UV irradiation. (**down**) Phenol photooxidation and intermediates speciation upon irradiation of pre-loaded carbons (C) and correlation with selected characteristics of the nanoporous carbons (D).

Figura 2. (arriba) Evolución de la concentración de fenol con el tiempo en presencia de los fotocatalizadores estudiados durante (A) adsorción en oscuridad y (B) irradiación con luz UV. **(abajo)** Conversion de fenol e intermedios de oxidación tras la irradiación de los carbones pre-adsorbidos con fenol (C) y correlación de la conversión de fenol con algunas características físico-químicas de los materiales de carbono empleados (D).

immobilized catalyst [14,17]. Also, it is considered that the photocatalytic enhancement depends greatly on the nature of the carbon matrix itself, hence different mechanisms would apply for nanoporous carbons compared to nanostructured carbon nanotubes, fullerenes and graphene. Furthermore, the use of carbon/semiconductor composites overcomes the operational drawbacks associated to the use of nanosized semiconductor powders -that hinder the application in continuous flow systems due to limited recovery and reuse of the catalyst- [16].

3. Self-photoactivity of nanoporous carbons

Our recent investigations have shown the self-photochemical activity of nanoporous carbons under UV irradiation, with improved photooxidation conversions in aqueous solution compared to bare or carbon-immobilized titania [10-12,23]. Data showed that beyond the synergistic effect of carbon/ TiO_2 composites, the nanoporous carbon alone was capable of a significant level of self photo-activity under UV irradiation (Fig. 2).

Upon UV irradiation the overall rate of phenol disappearance increased remarkably for all the nanoporous carbons, particularly at the initial stage of the reaction and for those materials showing an acidic nature. The relative abundance of the degradation intermediates detected in solution was also dependent on the characteristics of the carbons, with a marked regioselectivity for the formation of catechol over quinones (as opposed to titania). Such regioselectivity is considered more advantageous for the overall reaction yield as it proceeds through a less number of subproducts. [24].

Although the self photoactivity of multiwall carbon nanotubes under visible light had been reported and attributed to the presence of structural defects and vacancies [25], amorphous nanoporous carbons had been considered merely as inert supports to enhance the photoactivity of semiconductor materials [5-8,14-17,26]. Several possible scenarios were considered to explain our findings: (1) adsorption/desorption of the photooxidation intermediates; (2) concentration effect on photolysis; (3) occurrence of carbon/light interactions and degradation of the adsorbed compounds retained in the inner porosity. Differences in conversion (rate and intermediates speciation) under dark and UV irradiation cannot be explained by the nanoconfinement of the pollutant (scenario 2) in the porosity (i.e., concentration effect on photolysis). Also, adsorption of the degradation intermediates (scenario 1) cannot account for the unbalance between the amount of compounds detected in solution and that retained in the porosity after the photocatalytic runs. To demonstrate if the UV light can somehow interact with the compounds retained inside the porosity of the carbons (scenario 3), the reaction was monitored from inside the carbonaceous matrix.

4. Photocatalytic evidences on preloaded samples

To determine the extent of phenol photodegradation (if any) inside the carbons, irradiation was performed on carbon samples pre-loaded with phenol, thereby disregarding the effects of adsorption kinetics and solution photolysis [10]. The concentration of phenol

and intermediates was exclusively detected after extraction of the carbons with solvents; data obtained for different preloaded carbons are shown in Fig. 2C. As no leaching out occurred during the irradiation, these results demonstrate that a fraction of phenol is decomposed inside the porosity of the carbons when these are illuminated.

The distribution and nature of the intermediates detected was different for the studied carbons. It is also interesting to note that for most carbons, phenol photodegradation was larger or similar than in the photolytic reaction. This is most remarkable since the incident photo flux arriving at the phenol molecules adsorbed inside the carbons porosity is expected to be smaller than that from solution. However, this singular photochemical behavior does not apply for all type of carbon adsorbents since one of the studied carbons showed negative response. No straightforward correlation has been found so far between the photochemical response of these carbons towards phenol degradation and their physicochemical and/or structural features in terms of porosity, composition and surface acidity/basicity (Fig. 2D).

These results demonstrated that a fraction of the adsorbed molecules are decomposed when certain nanoporous carbons are exposed to UV light, although it is not yet clear whether if the UV light penetrates inside the carbons porosity or if interactions occur at the external surface and are subsequently propagated through the graphene sheets. Anyhow, such carbon/photons interactions could promote the formation of charge carriers that seem to have enough redox potential to generate more reactive species (radicals) and/or directly oxidize phenol (scenario 3). To determine the occurrence of the carbon/light interactions, a deep investigation was undertaken by combining spectroscopic and photoelectrochemical tools.

5. Spectroscopic evidences

To shed light on the origin of the photochemical response of semiconductor-free nanoporous carbons and to establish the likely formation of radical species upon illumination, we have carried out spin resonance spectroscopy (ESR) studies [11,12]. The formation of paramagnetic species in solution upon irradiation of carbon suspensions was detected by a nitrone spin trapping agent (DMPO).

The ESR spectra of all the samples (Fig. 3) showed a quartet peak profile with 1:2:2:1 intensity, assigned to DMPO-OH adducts [27]. Some other adducts, identified as HDMPO-OH, DMPO-R (carbon centered radical) and DMPO-OOH, were also detected. Our results demonstrate that significant amounts of •OH and/or superoxide anion radicals are formed during the irradiation of the nanoporous carbons in the absence of semiconductor additive, likely produced from photoinduced oxidation of water. Quantification of the relative abundance of the radical species showed that the DMPO-OH concentration levels measured for certain carbons were higher than those obtained for titania, indicating a higher concentration of radical species. Among the investigated carbons, as a general rule lower ESR signals were obtained for those materials showing a rich surface chemistry. On the other hand, only for one of the studied carbons no

radicals were detected, which seemed in agreement with the lack of photoactivity observed for this material in previous works [10]. ESR patterns are a diagnostic indication of free hydroxyl radical formation in aqueous environments, and may constitute a key issue on the understanding of the photochemical response of carbon materials. Nevertheless, low ESR signals should not be considered as an indication of low photoactivity, as this technique only provides information about the formation of radicals under irradiation. Indeed, for certain materials low ESR signals corresponded to high photooxidation yields and viceversa [11,12]. This would indicate either a radical-mediated or a direct hole oxidation as dominating pathways.
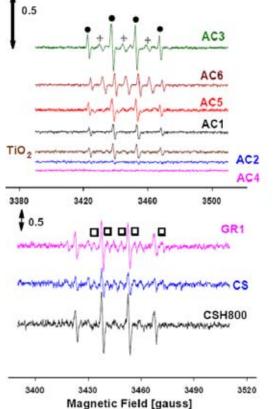
6. Photoelectrochemical evidences

Further insights on the mechanisms occurring at the carbon/semiconductor interfaces when these are exposed to light were obtained by investigating the optoelectronic and photoelectrochemical response of carbon/titania thin film electrodes of increasing carbon content ranging from 5-50 wt.% [28]. Voltammetric techniques were used to study the effect of potential bias on the photocurrent response of the different carbon/titania catalysts (Fig. 4). In the dark, the shape of the current-potential curves of the carbon/titania electrodes was similar to that of a titania electrode, with small capacitive contribution due to the non negligible porosity of the carbon matrix. The characteristic shape of n-type semiconductor was detected, with the distinctive accumulation and depletion regions (below/above -300 mV sv

SCE, respectively). Upon UV illumination, anodic photocurrents were observed in all studied electrodes when the bias potential was positive enough for an efficient hole-electron separation. As opposed to titania, no photocurrent saturation limit was observed for the carbon/titania electrodes, particularly for those with the highest carbon content.

The transient photoamperometric curves upon on-off illumination for several bias potentials (Fig. 4c) showed a similar trend. 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. Interestingly, the carbon/titania thin film electrodes showed roughly similar photocurrent values than those of TiO_2 films. Additionally, the photocurrent enhancement after phenol addition to the electrolytic solution, indicative of direct hole oxidation, 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
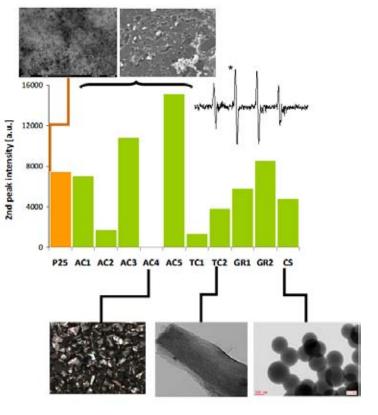
Figure 3. (left) ESR spectra of the DMPO adducts obtained after 20 minutes irradiation of aqueous suspension of semiconductor-free nanoporous carbons and TiO_2. Assignments to DMPO-OH (circles), HDMPO-OH (diamonds) and DMPO-OR (squares) adducts are indicated. **(right)** Quantification of the radical species determined from the intensity of the second line (asterisk in inset) of the ESR spectra.

Figura 3. (izquierda) Espectros de RPE de los aductos de DMPO tras 20 minutos de irradiación de suspensions acuosas de materiales de carbono y TiO_2. Las especies detectadas son: DMPO-OH (círculos), HDMPO-OH (rombos) y DMPO-OR (cuadrados). **(derecha)** Cuantificación de las especies radicalarias detectadas a partir de la integración de la intensidad del segundo pico (marcado con un asterisco) de los espectros de RPE.

important role for the photoelectrochemical response of the composites, and anticipates a potentially higher photocatalytic activity of these materials. The gathered results showed that 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 several likely mechanisms (Fig 4):

i) the smaller diffusion length of the carriers through the porous structure provided by the carbon material (favoring photohole capture and indirect oxidations).

ii) the carbon matrix can act as an acceptor of the photogenerated electrons upon UV irradiation of the titania particles; the delocalization and stabilization of the carriers within the graphene layers of the carbon additive would contribute to minimize the surface recombination.

iii) photon absorption by the carbon material itself, generating charge carriers due to direct $\pi-\pi^*$ and/or $\sigma-\pi*$ transitions, contributing to increased photocurrents.

7. Cycleability and performance under long illumination periods

Beyond establishing the origin of the photochemical behavior of activated carbons, it becomes essential to explore their performance during consecutive photodegradation runs, and determine if they fulfill the requirements of long cycle life, and good degradation efficiency. To attain this goal, we have carried out the photocatalytic degradation of phenol from solution upon 20 hours of illumination in consecutive cycles, using two nanoporous carbons with different surface chemistry [29]. The performance was also compared to commercial TiO_2 under similar illumination conditions. Given the porous nature of the carbons, the experiments incorporated a pre-adsorption step at dark conditions -before the illumination- to control the amount of pollutant adsorbed on the carbons, and hence maintaining the same phenol concentration in solution at the beginning of each cycle for the nanoporous carbons and the semiconductor [29]. Data showed that, under excess of oxygen, the overall performance of the nanoporous carbons upon cycling was comparable to that of commercial titania, with close mineralization yields in all three studied materials after six consecutive cycles. For both studied carbons, a marked accumulation of phenol degradation intermediates was observed during cycling, with preferential formation of catechol over quinones. For titanium oxide, the concentration of aromatic intermediates was lower but still the total organic carbon values showed a quite low mineralization due to the accumulation of short alkyl chain organic acids. The photocatalytic efficiency was found to depend strongly on the basic/acidic nature of the nanoporous carbons, with a somewhat lower
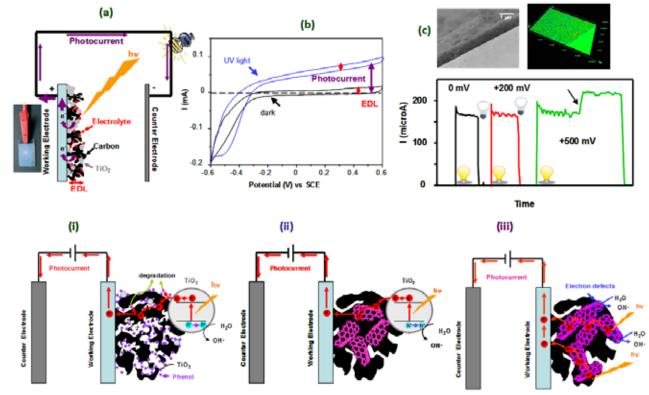

Figure 4. (top) a) Sketch of the experimental set-up used for the photoelectrochemical measurements; b) Representative potential-current curves under dark and UV light of a carbon/titania thin film electrode; c) Chronoamperometric response of the film electrodes upon on/off illumination cycles in the supporting electrolyte and in the presence of phenol (arrow) at various fixed bias potentials (vs SCE) of a carbon/titania composite. Representative images of the thin film electrodes, obtained by SEM and confocal microscope are also included. **(down)** Scheme of the mechanisms proposed for illustrating the role of carbon in the photocatalytic performance of carbon/titania interfaces: (i) diffusion length of carriers, (ii) carbon as acceptor of photogenerated electrons, (iii) photon absorption by the carbon material.

Figura 4. (arriba) a) Esquema del dispositivo experimental utilizado para las medidas fotoelectroquímicas; b) Curvas de intensidad-potencial en condiciones de oscuridad y bajo radiación UV con un electrodo C/TiO$_2$ de película fina; c) Respuesta cronoamperométrica de un electrodo C/TiO$_2$ en oscuridad/irradiación en presencia de electrolito y fenol (flecha) a varios potenciales. También se muestran imágenes de los electrodos de película fina obtenidas por SEM y microscopía confocal. **(abajo)** Esquema de los mecanismos propuestos para la interpretación de la influencia del material de carbono en la respuesta de los electrodos C/TiO$_2$: (a) difusión de los portadores de carga en la porosidad del material de carbono, (b) material de carbono como aceptor de los electrones fotogenerados en el TiO$_2$, (c) absorción de fotones por el material de carbono.

performance for the hydrophilic catalysts. Phenol conversion and mineralization rates were greatly enhanced in the presence of excess of dissolved oxygen in the solution, demonstrating the outstanding role of oxygen in the photooxidation of phenol. This was critical for the long-term performance of the hydrophilic carbon, which showed a sharp fall in phenol conversion upon cycling under oxygen depletion conditions.

8. Acknowledgements

9. References

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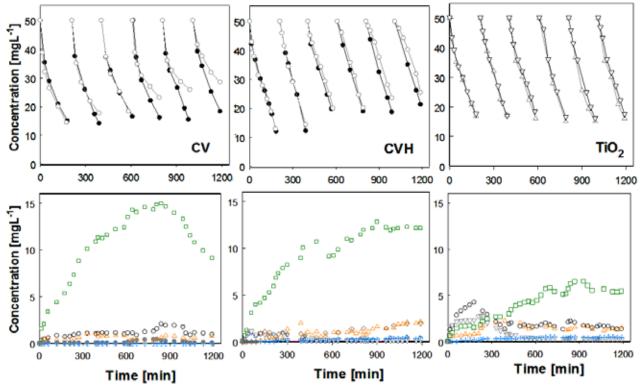

Figure 5. (top) Evolution of phenol concentration upon consecutive photocatalytic runs in the presence of nanoporous carbons and titania, under excess (solid symbols) and depleted (empty symbols) oxygen conditions. **(down)** Evolution of degradation intermediates: hydroquinone (circles); benzoquinone (down triangles); cathecol (squares); 2,4,6-trihydroxybenzene (up triangles); resorcinol (crosses); 1,3,5-trihydroxybenzene (diamonds).

Figura 5. (arriba) Evolución de la concentración de fenol durante 6 ciclos fotocatalíticos consecutivos empleando carbones activados y TiO_2 como catalizadores y en condiciones de exceso (símbolos llenos) y defecto (símbolos huecos) de oxígeno disuelto. **(abajo)** Evolución de intermedios de degradación: hidroquinona (círculos); benzoquinona (triángulos invertidos); catecol (cuadrados); 2,4,6-trihidroxibenceno (triángulos); resorcinol (cruces); 1,3,5-trihidroxibenceno (rombos).

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