Tuning the Surface Chemistry of Nanoporous Carbons for Enhanced Nanoconfined Photochemical Activity

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We showed the effect of surface oxidation on the conversion of light into a chemical reaction in the confined pore space of nanoporous carbons. The photoactivity of carbons is caused by the combination of high porosity and the presence of photoreactive sites that favor the splitting of the exciton inside the pores, which boosts its efficient use in chemical reactions. The incorporation of O-containing groups in the carbon matrix decreased the photoconversion inside the pores, although values were higher than those attained in solution. This is attributed to the lower stabilization of the exciton through the delocalization within the conjugated sp² network of the basal planes because of the electron-withdrawing effect of the O-containing groups. The photochemical conversion of light inside the pores is very sensitive to the acidic/basic nature of the O-containing groups of the carbon matrix, and can be enhanced by balancing the surface composition, porosity, and electronic mobility.

Introduction

The conversion of light energy has been long explored in environmental chemistry for the degradation of pollutants as the excitation of electronic molecular states may induce chemical bond breaking. Indeed, after the studies in 1977 that reported the performance of zinc and titanium oxides to decompose cyanides in solution,^[1] the interest in the development of advanced oxidation processes based on semiconductor photocatalysis for the degradation of pollutants in air and water has increased.^[2]

Triggered by the low photonic efficiency of most semiconductors, the optimization of the optical features of photoactive materials remains a widely investigated topic.^[3] Aside from transition metal oxides and sulfides as photocatalysts, hybrid materials prepared by their immobilization on appropriate substrates have been investigated extensively.^[4] Although carbons are strong light-absorbing materials, their incorporation in hybrid carbon/semiconductor composites is an interesting strategy to attain high photoconversion efficiencies in the degradation of a variety of pollutants.^[5] The first investigations in this field focused on the use of carbons as inert additives to

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This publication is part of a Special Issue on Carbon in the Catalysis Community. Once the full issue has been assembled, a link to its Table of Contents will appear here. TiO_2 , and the enhanced performance of carbon/titania photocatalysts was attributed to i) the porosity of the inert porous carbon support or ii) strong interfacial electronic effects in the case of carbon additives with a high electronic mobility (i.e., carbon nanotubes, graphenes).^[5]

Our recent research has demonstrated the photochemical activity of semiconductor-free nanoporous carbons under different irradiation conditions,^[6] showing their ability to photogenerate radical oxygen species (ROS) in aqueous environments.^[7] This has opened new perspectives in the field of applied photochemistry based on carbon materials that covers environmental remediation, water splitting, enhanced adsorption/oxidation, and photoluminescence.^[8]

In spite of increasing interest in this field, there is still a multitude of fundamental questions that are worth investigating to understand the underlying mechanisms that govern the conversion of light into a chemical reaction to exploit the potential applications of light-responsive carbons in different fields.

With the aim to shed light on this topic, we herein provide an overview on the effect of the surface composition of nanoporous carbons on the photochemical reactions hosted inside the nanopores. By combining catalytic, spectroscopic, and photoelectrochemical tools, we show the dependence of the photochemical response in the confined pore space with the surface functionalization of the carbon matrix, and we chose the photo-oxidation of phenol as a model reaction.

Results and Discussion

The elucidation of the mechanism of the photochemical reactions that occur in the constrained pore space of nanoporous solids is a complex task because of the simultaneous coexistence of various processes inherent to high-energy irradiation sources and porous materials: direct and indirect photo-oxida-



tion/reduction, reactions on the catalyst surface and adsorption and diffusion phenomena that lead to changes in the reaction rate and reactant concentration. To disregard these contributions, we have developed a strategy that allowed us to isolate and evaluate the efficiency of the photochemical reaction inside the pore voids of a catalyst.^[6] The approach consisted of the introduction of a target compound inside the pore structure (adsorbed) before illumination. After irradiation, the compounds still retained inside the pores are extracted into an appropriate solvent and analyzed to determine the yield of the photochemical reaction that takes place inside the pores of the material (Figure 1a). As no desorption occurs during the irradiation of the preadsorbed catalysts, the extent of the photochemical reaction provides direct evidence on the existence and fate of the host-light interactions in the confined pore space. Our previous studies have validated this experimental approach of monitoring the reaction from inside the pores for the photo-oxidation of phenol in aqueous solution using nanoporous carbons.^[6]

With the aim to explore the effect of the functionalization of the carbon matrix on the photochemical activity, we prepared



Figure 1. a) Scheme of the experimental procedure designed to evaluate the photochemical yield inside the nanoporous structure of the carbon materials; b) phenol conversion and c) intermediates formed during the photocatalytic reaction in the presence of activated carbons B, BOH, and BO. Data that correspond to direct photolysis are included for comparison.

 Table 1. Main physicochemical and textural properties of the nanoporous carbons studied.

Sample	В	BOH	BO	
$S_{BET} [m^2 g^{-1}]$	1033	1045	989	
$V_{\rm total}^{[a]} [{\rm cm}^3 {\rm g}^{-1}]$	0.52	0.52	0.50	
$V_{\rm micro}^{[b]} [\rm cm^{3} g^{-1}]$	0.32	0.32	0.31	
$V_{\rm meso}^{[b]} [\rm cm^3 g^{-1}]$	0.09	0.08	0.07	
pH _{PZC}	8.9	5.7	3.3	
O [wt%] ^[c]	2.1	6.4	7.5	
CO [µmol g ⁻¹] ^[d]	491	1903	1945	
$CO_2 [\mu mol g^{-1}]^{[d]}$	167	238	647	
[a] Evaluated at a relative pressure of 0.99. [b] Evaluated from DFT meth- ods. [c] On a dry basis. [d] From TPD-MS measurements.				

a series of oxidized materials by mild wet oxidation. It is important to highlight that the surface modification did not change the textural parameters of the pristine carbon (Table 1, see further characterization details in Figures S1–S5 in the Supporting Information) in terms of pore volume or surface area. This is critical as the photochemical experiments were designed to control the amount adsorbed and the confinement state inside the pores of the carbons.

The incorporation of O-containing groups on nanoporous carbons decreases the uptake of phenol, although it does not alter the adsorption mechanism, which is governed by dispersive interactions between the pore walls and the phenol molecules.^[9] To overcome these differences in the adsorption capacity of the carbons upon oxidation, the amount of phenol preadsorbed before irradiation was fixed and kept below the saturation limit. This allows the formation of a single adsorption layer in the pores (phenol molecules are adsorbed predominantly in an edge-wide orientation in which the aromatic ring is parallel to the pore walls and the hydroxyl moiety projects toward the solution),^[9] and we assume that the confinement of phenol is the same for all the samples. Hence, the differences in the photochemical performance should be caused by the nature and fate of the carbon-light interactions in the pore space.

The evolution of phenol conversion and the intermediates detected in the extracts upon irradiation of the preadsorbed carbons by using a low-pressure Hg lamp is shown in Figure 1. Data that correspond to direct photolysis (absence of catalyst) are included for comparison. The three tested materials led to very similar phenol conversions. Furthermore, the superior photo-oxidation performance of the carbons over the photolytic reaction confirmed that the light conversion is boosted in the nanoconfined pore space. The effect is already very pronounced at short irradiation times, and for instance, after 150 min of irradiation the conversion of phenol is approximately eight times higher inside the porous network of sample B than in the absence of catalyst. This is remarkable if we consider that the carbon matrix absorbs a large fraction of the incident irradiation and the actual fraction of light responsible for the photochemical conversion of phenol inside the pores is expected to be much lower than that in solution.

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The amount of intermediates detected inside the nanopores is also larger than that in solution (Figure 1 c), which seems reasonable if we consider that the phenol conversion is higher. Interestingly, although the amount of intermediates decreases with time for the carbons, there is a clear accumulation of subproducts of the photolytic reaction. An important difference can be seen in the speciation of the intermediates (Figure 1 b); catechol is the predominant intermediate in all cases, although its concentration is higher if phenol is decomposed inside the nanopore space. This finding is significant as the regioselective degradation of phenol in the *ortho* position is considered more advantageous than conversion via quinones⁽¹⁰⁾ as the mechanism involves a lower number of intermediates. This confirms that the uncatalyzed photodegradation is less efficient than photo-oxidation inside the pores of the carbons.

As for the effect of surface chemistry, the better performance of the pristine carbon than that of the oxidized counterparts indicates the negative impact of the oxidation on the photochemical conversion of phenol. The abundance of degradation subproducts followed the trend: BO > BOH > B. This means that the incorporation of O-containing functionalities does not only reduce the conversion of phenol itself, but also the subsequent oxidation of the intermediates. Hence, the overall phenol photo-oxidation is more efficient on the parent carbon.

To gain further insight into the effect of the surface chemistry of the carbons in the photochemical conversion of light in the confined pore space, we calculated the photochemical quantum yield (ϕ), defined by IUPAC as the ratio between the amount reacted ΔN [mol], per mole of photons absorbed ($I_A\Delta t$),^[11] from the slope of the correlation between the moles of degraded compounds per incident photon flux versus the irradiation time (Figure 2) with Equation (1):

$$\Delta N = \phi I_{\mathsf{A}} \Delta t \tag{1}$$

in which I_A is the photon flux absorbed by the sample evaluated from the product of the incident photon flux I_o , which is de-



Figure 2. Correlation of the amount [mol] reacted per incident photon flux with the irradiation time for the nanoporous carbons and the photolytic reaction. The points represent experimental values, and the lines are guides for the eye.

termined by actinometry and the integrated absorption fraction over the wavelength range used in the experiments (see details in the Supporting Information).

If the photochemical reaction occurs inside the nanopores, it becomes very complex to evaluate the actual photon flux that reaches the molecules adsorbed in the pores because of the contributions of light scattering by the particles suspended in solution and the strong light absorption by the carbon matrix itself. For comparison, we calculated an apparent or pseudophotochemical quantum yield (ϕ_{ps}) for the carbons by assuming that all emitted photons eventually reach the fraction adsorbed inside the pores. Although this is a simplistic approximation, it allows a straightforward comparison of this family of nanoporous carbons as all the experiments were recorded under similar conditions (in terms of carbon matrix, catalyst loading, and particle size). Besides, the actual photon flux would be smaller because of the above-mentioned side reactions that consume photons, hence even if ϕ_{ps} cannot be strictly considered as a quantum yield, it accounts for the minimum limit of the actual quantum yield value. Importantly, it provides a more accurate viewpoint of the overall photochemical reaction that occurs inside the pores of the carbons by considering the intermediates formed in the course of the reaction.

The dependence of the number of moles reacted per photon flux with the irradiation time is shown in Figure 2. The profile of direct photolysis in solution followed the expected linear pattern with the irradiation time, with a quantum yield of 12 mmol/Einstein, in agreement with reported values.^[12]

Interesting features are revealed if the photochemical reaction is performed inside the pores of the carbons. As opposed to the uncatalyzed reaction, the dependence of $\phi_{\rm ps}$ with time shows two different regimes. Below 30 min of irradiation, the number of moles reacted is very high for the nanoporous carbons with $\phi_{\rm ps}$ values close to unity, whereas at longer times, a second less steep linear region is observed and the $\phi_{\rm ps}$ values decrease by an order of magnitude (but they are still larger than that in solution). This indicates that the photochemical reaction inside the nanopores is very fast at short irradiation times and leads gradually to steady conversion values over time.

With regard to surface chemistry, ϕ_{ps} values followed the trend B > BOH > BO. Given the similar textural properties of the carbons (Table 1), differences in the photochemical response must be discussed in terms of the surface functionalization of the carbon matrix. The dependence of phenol conversion and ϕ_{ps} values with selected parameters of the nanoporous carbons characteristic of the degree of surface functionalization (oxygen content, surface pH, nature of O-containing groups) is shown in Figure 3. Data show that the incorporation of oxygen groups of an acidic nature is the most determinant parameter in the decrease of the photochemical activity. This is supported by correlations with the amounts of gases (CO and CO₂) quantified from the thermodesorbed species by temperature-programmed desorption (TPD) followed by MS.

As seen, the amount of CO_2 -evolving groups (attributed to carboxylic acids and anhydrides of an acidic nature) is approximately three times higher in BO than in BOH, whereas both

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Figure 3. Effect of surface functionalization on phenol conversion (plots a and b) and ϕ_{ps} values (plots c–f) for the nanoporous carbons calculated for the first (plots c and d) and second (plots e and f) regime of the correlation of the moles reacted per incident photon flux with the irradiation time (see Figure 2).

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hole oxidation and/or radical mediated mechanisms) with electron donors present in the reaction medium if splitting is favored.^[14,15]

If we take this into consideration, the decrease in the photochemical conversion of the functionalized carbons can be associated with several factors that would affect either their optical features (because of the creation of structural defects or changes in the sp²/sp³ hybridization state of carbon atoms derived from the incorporation of the O-containing groups)[6d, 15] or the stabilization of the photogenerated carriers through delocalization within the conjugated sp² network of the basal planes.

Several scenarios are possible; the first is that the holes might react directly with the adsorbed phenol molecules. This seems plausible as the reaction occurs inside the pores and the splitting of the carriers would be favored by the immediate reaction with the adsorbed molecules. This explains the higher conversion values in the tight nanopore confinement compared to that in solution. However, as the carbons display similar textural features, this cannot account for the differences between the car-

carbons displayed similar amounts of CO-releasing groups (mainly phenolic and quinone-type groups).^[13] Thus, the higher performance of BOH than BO is because of its increased surface hydrophobicity (Table 1, Figure 3). If we analyze data by considering the number of moles reacted (Figure 3 c-f) and not just phenol conversion (Figure 3 a-b), a similar trend is observed. In this case, the dependence of the chemical features of the carbons follows a polynomial pattern, which indicates a more sensitive response of the light conversion yield to small changes in the surface acidity of the nanoporous carbons.

According to literature reports, the light absorption features of amorphous nanoporous carbons depend on the density of electronic states (DOS; mainly sp²/sp³ hybridization of the carbon atoms), and in the UV range are dominated by π - π * and σ - π * transitions that involve free zig-zag sites and carbine-like sites.^[14] Under sunlight irradiation, some other transitions that involve the activation of chromophoric groups on the carbon surface have been proposed.^[15] These electronic transitions generate carriers (holes and electrons) that can participate in charge transfer reactions (which either involve direct

bons themselves, which must be attributed to the fate of the charge carriers in the pores.

Another possibility is the stabilization of the holes through the oxidation of water molecules coconfined in the nanopore space and the effect of the surface functionalization on the exciton splitting. This was supported by EPR spectroscopy, which allowed the detection of radical species upon the illumination of aqueous suspensions of the carbons using a nitrone spintrapping agent, 5,5-dimethylpyrroline-*N*-oxide (DMPO; Figure 4).

Similar EPR spectra were obtained for all the carbons, in which the characteristic quartet peak profile with a 1:2:2:1 intensity (g=2.006, $a_N=ab_H=14.8$ G hyperfine splitting constants) of the DMPO-OH adduct was attributed to the presence of hydroxyl and superoxide radicals.^[16] The quantification of the relative abundance of the ROS showed lower concentrations in the functionalized carbons. Interestingly, similar amounts of radicals were detected for BO and BOH, which indicates the importance of the acidic/basic nature of the O-containing groups that decorate the carbon surface (Table 1) in





Figure 4. a) Typical EPR spectrum of the DMPO adducts obtained after 20 min of irradiation of aqueous suspensions of the nanoporous carbons. b) Quantification of the radical species that correspond to DMPO-OH adducts determined from the intensity of the second line (marked by a star) in the profiles.

the formation of radicals. Indeed, the amount of ROS correlates well with the CO-evolving groups of a basic nature (Figure S6), whereas the strongly acidic groups (CO₂-evolving) seem to inhibit the formation of radicals. The strong electron withdrawal effect of carboxylic acid and anhydride groups on the π -electron density of the carbon basal planes would increase the surface recombination of the carriers, which would result in the formation of fewer radicals. Notably, low-intensity EPR signals should not be considered as an indication of low photochemical activity; EPR spectroscopy only provides information about the formation of radicals, whereas the reaction may proceed by other mechanisms (e.g., direct hole transfer).^[9] Thus, the lower-intensity EPR signals for the oxidized carbons indicate that the radical-mediated mechanism might not be the dominant mechanism.

Further insights into the fate of the photogenerated carriers were obtained by exploring the photo-electrochemical response of the carbons. The transient photocurrent response of the photoanodes after on/off illumination at various potentials is shown in Figure 5. Dark currents at the applied potentials were allowed to equilibrate before irradiation to stabilize the large capacitive contributions of the nanoporous carbon electrodes. The background photocurrent generated by the illumination of the bare Ti foil used as the current collector is shown for comparison.

A remarkable photocurrent was generated if the electrodes were illuminated and the bias potential was positive enough



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Figure 5. a) Transient photocurrent densities vs. bias potential of the nanoporous carbons. b) Example of the chronoamperometric response of photoelectrodes built on carbon B that show a square-shaped profile and the cathodic/anodic shoots in the transient photocurrent response.

for efficient exciton separation. Furthermore, the potential onset of the photocurrent for the carbon anodes is approximately +0.8 V vs. Ag/AgCl, which is clearly lower than the value for the Ti collector.

The transient photocurrent response presents a squareshaped profile if the light is switched on (Figure 5b) with a prompt initial increase followed by a smooth decrease until a steady-state regime is achieved; the photocurrent reverts to the original values if the illumination is turned off. In the aqueous electrolyte in which water molecules are the only hole scavengers, the anodic photocurrent corresponds to water oxidation, which is corroborated by measuring the O₂ concentration in the electrolyte, whereas the photogenerated electrons migrate to the substrate through the electrode film. The photocurrent response was stable and reproducible during repeated on/off cycles of illumination.

In some electrodes the initial anodic increase upon illumination was preceded by a cathodic undershoot (Figure 5 b), whereas the steady-state regime was followed by an anodic overshoot if the illumination was turned off. Anodic and cathodic current shoots are frequently reported for semiconductor materials and attributed to surface recombination processes of the photogenerated charges or photocorrosion phenomena.^[17] In our materials the cathodic undershoot is most likely attributed to either the reduction of trace amounts of dissolved O_2 that remains in the pores of the carbons that could not be removed by N_2 bubbling (photocurrent disappears in subsequent cycles) and/or the reduction of photogenerated 'OH radicals (according to the reaction $OH+1e^{-}\leftrightarrow OH^{-}$) as evidenced by the EPR spectra (Figure 4).

The presence of undershoots can be used as an indicator for insufficient mass transport and poorly efficient reaction. This is expected if we consider the low electron mobility of the studied nanoporous carbons (BO, BOH, and BO have a DC conductivity of \approx 0.5, 0.2, and 0.02 mS cm⁻¹, respectively).

At 1 V and above, the photocurrent density increased considerably for all the carbons because of the more efficient photoassisted oxygen evolution reaction if higher potential values are applied (extensive bubbling was seen on the electrode surface, not observed in the dark or during the irradiation of the bare collector).

All the carbons showed the same potential onset for the photocurrent detection, although current densities decreased for the functionalized materials. This contrasts with our previous work in which we studied the photo-electrochemical oxidation of water using visible light and highly functionalized carbon photoanodes.^[15] The ability to oxidize water was linked to the presence of S- and N-containing groups that work as chromophores and leave reactive vacancies that are able to accept electrons from oxygen in water molecules upon light excitation. The role of the sulfur and nitrogen species was supported by the lack of activity detected on a commercial nanoporous carbon free of these heteroatoms.

The fact that the nanoporous carbons studied herein do not have S- and N-containing groups but display photochemical activity gives a new perspective to the origin of this behavior and on the role of the surface chemistry. Firstly, the porosity of these nanoporous carbons is more developed than that studied previously (Table 1, Figures S3 and S4), with larger pore volumes adapted for the adsorption of water and phenol (by dispersive forces).^[9, 18] Besides porosity, hydrogen bonding with the surface groups that exist in the pores could be expected to promote the surface wetting and hence increase the photoelectrochemical oxidation of water inside the pores. Conversely, oxidation caused a reduced hydrophobicity of the carbons (Table 1). It seems that beyond surface wetting, the carbon materials must have photoactive sites inside the pores at which carbon-light-water and/or carbon-light-phenol interactions can take place.

The photoactivity of these carbons is certainly not linked to the presence of chromophoric surface groups, our previous studies also disregarded the contribution of metal impurities,^[7] but to the generation of carriers in the reactive sites. Such reactive sites in carbons are located at the edges of the basal planes, either associated with surface functionalities or to free edges sites linked to various configurations (carbyne-like and carbene-type).^[19] The free sites are also responsible for the reactivity of carbons to incorporate heteroatoms to give rise to stable surface functionalities.^[19] If we consider this, the reduced photoactivity of the oxidized carbons would be linked to a lower density of free reactive sites (at which the O-containing groups are most likely incorporated).

Additionally, because of the presence of O-containing groups and their high electron-withdrawing effect on the π electron density of the basal planes, oxidation of the carbons

affects the stabilization/splitting of the exciton by charge propagation through the carbon matrix, which results in higher surface recombination (i.e., lower photocurrents). Further support for the superior electron mobility in the pristine carbon is provided by its high DC conductivity.

The stability of the carbon photoanodes after the on/off illumination cycles was also explored; the materials proved to be quite resistant to illumination (Figures S7 and S8) but became oxidized if the bias potential was higher than 0.8 V vs. Ag/AgCl because of the effect of the oxygen released during water oxidation. The TPD-MS analysis of the used photoanodes evidenced the oxidation and decrease in surface hydrophobicity, whereas the appearance of new humps in the cyclic voltammograms showed the loss of conductivity caused by these changes in the surface chemistry.

Finally it should be highlighted that current densities up to 0.70 mA cm⁻² were recorded for the highest potentials on sample B. Although these are low values compared to data in the literature for the photo-electrochemical splitting of water,^[20] they are remarkable if we consider the nature of the carbon photoanodes (metal-free and amorphous nanoporous carbons) and the low overpotential for the photo-electrochemical oxidation of water.

Conclusions

Our results show that the conversion of light inside the porous network of nanoporous carbons depends on the porosity, surface functionalization, and presence of photoreactive sites that lead to the photogeneration of charge carriers that can be used effectively in chemical reactions. The presence of a welldeveloped porosity is essential to obtain a high conversion in the constrained pore space, which distinguishes low-cost nanoporous carbons from graphene, carbon nanotubes, and other nanostructured carbon materials.

With regard to functionalization, the decoration of the carbon surface with O-containing groups caused a decrease in the photo-oxidation of phenol inside the pores; however, conversions were still higher in the confined pore space of the functionalized carbons than in solution.

Besides the density of surface groups, the yield of the light conversion is very sensitive to small changes in the acidic/basic strength of the oxygen groups, particularly to the presence of acidic groups (CO₂-releasing groups). The number of moles reacted increased with the surface hydrophobicity, as inferred by the superior performance of the carbons that show either low functionalization or mainly phenolic and quinone-type groups. This behavior is linked to the lower ability of the acidic carbons to stabilize/promote the splitting of the photogenerated exciton through the delocalization within the conjugated sp² network of the basal planes because of the high electron-withdrawing effect of O-donating groups. This was corroborated by the lower amount of oxygen radical species and lower photocurrent densities measured in the functionalized carbons.

As a result of the versatility of nanoporous carbons and abundance of precursors (which allow simple and cost-effective synthetic methods), it is highly feasible to champion nano-



porous carbons as sustainable metal-free photoanode/cathode materials for different applications (e.g., photo-electrochemical water splitting for hydrogen and oxygen evolution, pollutant photo-oxidation). The future challenge is in the further enhancement of the photochemical activity by balancing the surface composition (by the incorporation of adequate photosensitizer groups), porosity, reactivity, and change-carrier mobility (increasing conductive graphene-like units). Work focused on the optimization of the nanoporous carbon layout in a controlled way to achieve stable carbon photoelectrodes with higher efficiency is ongoing.

Experimental Section

Materials

A nanoporous carbon obtained from the CO₂ activation of bituminous coal was selected for this study (sample B). The pristine carbon was submitted to several treatments to modify its composition to explore the effect of the surface chemistry on the photochemical response. The incorporation of oxygen was performed by mild wet oxidation. Sample B (≈ 1 g) was put in contact with a saturated solution of ammonium persulfate in H₂SO₄ (10 mL; 4 N) at RT and left to stir overnight. After oxidation, the carbon was collected by filtration, washed with distilled water until a constant pH was obtained, and dried at 110 °C overnight (sample BO). Subsequently, a portion of this carbon was submitted to a thermal treatment at 400 °C for 30 min under a flow of N₂ (50 mL min⁻¹) to partially remove the incorporated functionalities (sample BOH).

Characterization

The textural properties of the samples were determined by N₂ adsorption at -196 °C (Micromeritics, ASAP 2010). Before the experiments, samples were outgassed at 120 °C overnight to constant vacuum (10⁻⁴ Torr). The main textural parameters such as specific surface area, S_{BET}, pore volume, and distribution of pore sizes were evaluated from the N₂ adsorption isotherms. The carbon materials were further characterized by elemental analysis (LECO CHNS-932 and LECO VTF-900 automatic analyzers). A custom-made device for TPD-MS was used to evaluate the surface chemistry of the activated carbons. The samples were heated in a fused-silica reactor up to 900 °C at a heating rate of 10 °C min⁻¹. The analysis was performed under high-vacuum conditions (below 10⁻⁵ mbar) and the gas phase was monitored continuously by MS. The acidic/basic character of the nanoporous carbons was determined by the measurement of the pH of point of zero charge (pH_{PZC}) by a modification of the mass-titration method by Noh and Schwarz.^[21]

Phenol photo-oxidation

A low-pressure mercury lamp (6 W, which emitted at 250, 401, 433, and 542 nm) was used as the irradiation source. The incident photon flux of the lamp ($\approx 3.3 \times 10^{-9}$ Einstein s⁻¹) was measured by ferrioxalate actinometry^[11] and used to normalize the photochemical conversions. Suspensions of the carbons in a phenol solution were allowed to equilibrate until all the phenol was completely removed and the suspensions were irradiated for different times. The solution was filtered and analyzed by reversed-phase HPLC (C₁₈ column, water/methanol 95:5). The carbons were further extracted with ethanol, and the alcoholic solution was also analyzed by

HPLC. Extraction yields were determined for each pure compound on each carbon material. The corresponding blank of direct phenol photolysis was performed under similar conditions for comparison. All the measurements were performed at least in duplicate (the standard deviation was lower than 5%), and average values are presented.

Photo-electrochemical measurements

A standard three-electrode cell equipped with an optically flat quartz window on the side, the nanoporous carbon photoanode as the working electrode, a graphite rod as the counter electrode, and a saturated Ag/AgCl reference electrode was used. For the preparation of the electrodes, a slurry of the nanoporous carbon and polyvinylidene fluoride (90:10) in N-methyl-2-pyrrolidone was coated onto a 1 cm² Ti foil collector and dried at 120 °C before usage. A Xe lamp, which emitted between 200 and 600 nm (150 W), was used as the irradiation source to amplify the signal of the carbon electrodes. A potentiostat (Biologic) was used to evaluate the electrochemical behavior. The transient photocurrents were obtained under a constant bias potential between 0 and +1.5 V vs. Ag/AgCl under on/off illumination. Dark current equilibrium at the applied potential was allowed before irradiation. The photoanodes were suspended in an aqueous solution of 0.1 м Na₂SO₄ (20 mL) and purged with N₂ before illumination (the dissolved O₂ concentration in the electrolyte was measured by using a sensor). The electrochemical behavior of the electrodes was also explored by cyclic voltammetry at a potential sweep of 20 mV s⁻¹ before and after light exposure.

Spin-trapping EPR measurements

The formation of paramagnetic species in solution during the irradiation of the carbon suspensions was detected by a nitrone spin trapping agent, DMPO. This compound is able to form spin adducts with hydroxyl and superoxide radicals, which creates more stable nitrone radicals that are detected easily by EPR spectroscopy in aqueous solution. The carbon sample ($\approx 0.5 \text{ g L}^{-1}$) was suspended in HClO₄ buffer (pH 3, 5 mL), and the appropriate volume of DMPO was added to the suspension to reach a final concentration of 18 mм. Samples were introduced into quartz capillary tubes and irradiated for 5, 10, 20, and 60 min (Philips TL K40W/05 lamp, with a broad emission peak centered at 365 nm). EPR spectra were recorded immediately from the solution (after the solids were removed by filtration) at RT by using a Bruker ESP 300E X band spectrometer with the following spectral parameters: receiver gain 10⁵; modulation amplitude 0.52 G; modulation frequency 100 kHz, microwave frequency 9.69 GHz; microwave power 5.024 mW; conversion time 40.96 ms; center field 3450 G; sweep width 120 G. The intensity of the second line in the spectrum was used for the quantification of the signals.

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