

Reseña Tesis. Photochemical response of nanoporous carbons. Role as catalysts, photoelectrodes and additives to semiconductors

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OBJECTIVES AND NOVELTY

Research related to light energy conversion and storage continues to be a topic at the forefront of technology that is attracting the attention of scientists; particularly, solar light receives a high consideration due to its readily availability. Numerous approaches have been established to improve the photocatalytic activity of semiconductors (photocatalysts) limited by their low photonic efficiency under solar light focus on the development of new materials with improved harvesting features across the visible region (organic metal halides, perovskites, transition metal oxides and sulphides, nonnoble metalbased catalysts). Extensive work has also been carried out on the use of carbon materials for this purpose, employing different forms of carbons as additives to semiconductors for enhancing the spectral response in the UV and visible light range. Enhancement of the photocatalytic response of such carbon/semiconductor composites has been traditionally attributed to either the strong interfacial electronic effects provided by the carbon matrix, and/or improved mass transfer effects when nanoporous carbons are used as nonphotoactive supports [1,2].

However, in 2010, studies carried out in ADPOR research group reported for the first time the experimental evidence on the self-photochemical activity of nanoporous carbons under UV-Vis irradiation in the absence of semiconductors [3,4]. Despite the interest raised by the topic, elucidating the origin of such behaviour is a complex, challenging and fascinating task in which there is still a large number of questions that remain unanswered on this topic. Knowledge of the underlying mechanisms governing the photochemical properties of nanoporous carbons would allow to understand and to integrate this phenomenon in various fields of application. Indeed, the photochemical activity of these costeffective nanoporous carbons (as catalysts, additives or electrodes) offers a plethora of possibilities in several applications such as environmental remediation and energy conversion. To throw some light on this issue, the main goal of this thesis was to study and to analyse several photoassisted processes (phenol photooxidation and water photoelectrochemical oxidation) based on the use of nanoporous carbons as photocatalysts and photoanodes, so as to clarify the exact role of the carbon materials as well as the origin of their intrinsic photochemical activity and the mechanisms of actuation.

RESULTS

The first part of the thesis was devoted to explore

the combined effect of nanoconfinement and surface functionalisation of the photochemical activity of nanoporous carbons towards phenol photooxidation. For this purpose, an activated carbon (sample F) was selected as starting material, that is a highly microporous carbon with high surface area and pores of narrow dimensions as well as a low chemical functionalisation. Hence, various series of carbon materials were synthesised showing gradually increasing pore size (samples F, F1 and F4, obtained by smooth physical activation under CO₂) and different surface chemistry due to the incorporation of S-containing groups (F-S, F1-S and F4-S samples). The photocatalytic runs were especially designed to avoid secondary reactions during illumination of nanoporous carbons, which are mainly associated to their porous nature and the high intensity of irradiation sources. Briefly, the procedure consisted on the preadsorption of phenol on the porosity of the carbons, and hence irradiating the loaded carbons dispersed in water. After irradiation, both phases (solution and carbon) were analysed to determine the compounds still retained inside the carbon porosity after light exposure and to obtain the extent of the photochemical reaction that takes place inside the nanoporosity of the material [4,5,6].

Figure 1A displays the normalised photochemical conversion (per photon flux) of phenol inside the confined nanopore space of the materials upon selected wavelengths. For the six studied samples, photochemical conversion dependence on wavelength followed a U-shaped pattern, with more efficient conversion at low (269 nm) and high (500 nm) wavelengths, corresponding to energy photons in UV and visible light, respectively, and all the carbons showed a minimum of conversion at 400 nm. This suggests the presence of various photoactive sites in the carbons, which would be activated under different illumination conditions (incident photon energy). As for the effect of sulphur, higher phenol conversions were obtained for the S-containing carbons at all wavelengths, with respect to the pristine materials, being this fact more remarkable at 269 and 500 nm, thus demonstrating the role of sulphur in the exploitation of both UV and visible light.

The differences in the photochemical response observed for carbons must be discussed in terms of confinement state of phenol retained inside the nanopores and the distinct surface chemistry of materials. For unmodified carbons (samples F, F1 and F4), a gradual activation mainly affects in the carbons pore size, hence lower conversions for F1 and F4 compared to those for F carbon are then attributed to

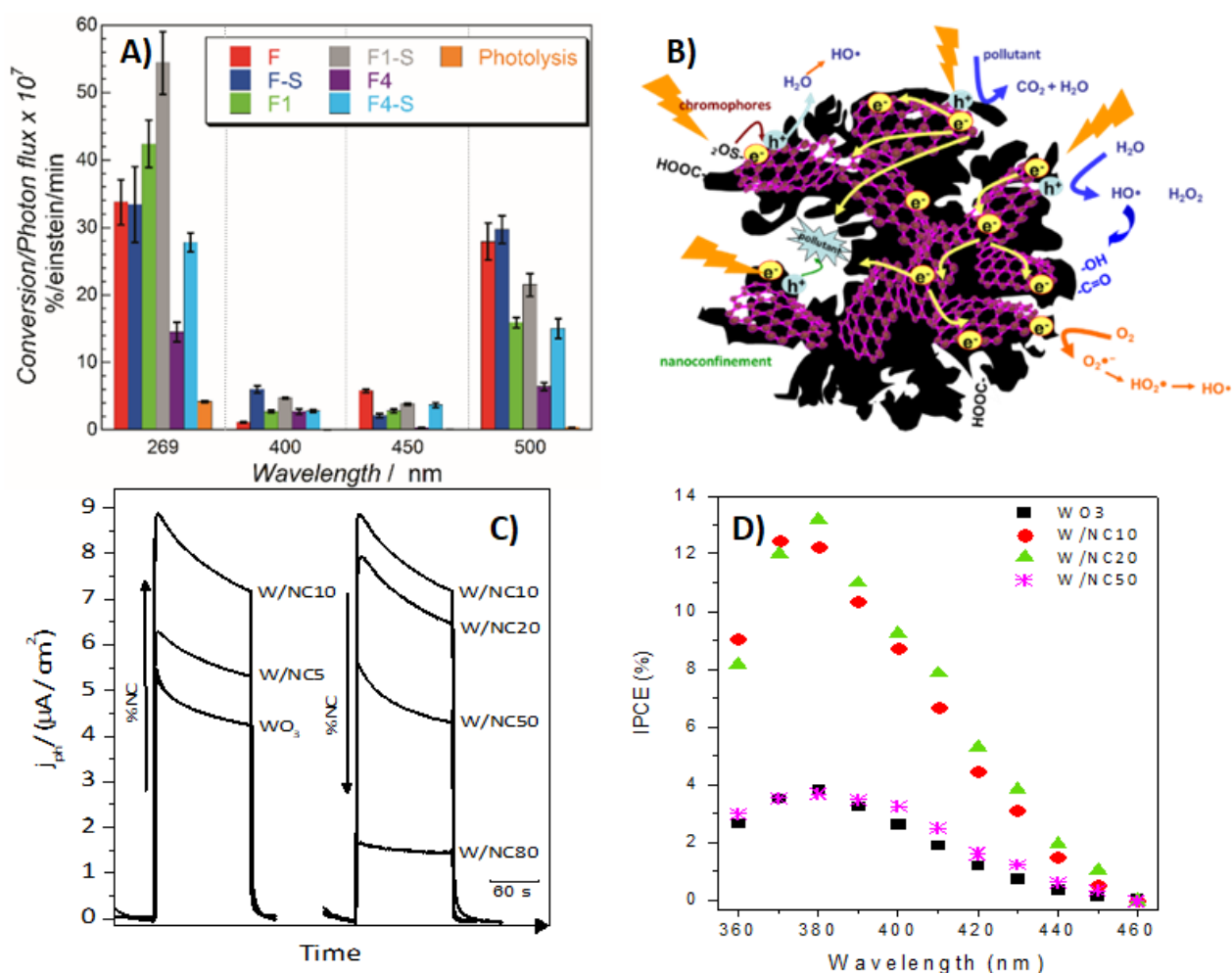


Figure 1. **A)** Normalised phenol conversions at different wavelengths for the studied nanoporous carbons. **B)** Schematic representation of the mechanism proposed for the exciton formation and fate upon irradiation of a nanoporous carbon. **C)** Transient photocurrent responses at 0.6 V vs Ag/AgCl under illumination using a 371 nm LED of the studied electrodes (W/NCx, where W refers to WO₃ and x indicates the weight percentage of NC) and **D)** dependence of IPCE (Incident Photon to Current Efficiency) values with illumination source wavelength.

the weaker adsorption of phenol molecules in large pores, thus decreasing the probability of splitting the photogenerated exciton by a fast charge transfer with electron donors and/or hole scavengers [5]. In the case of the S-functionalised carbons, fast charge transfer is favoured, as the presence of heteroatoms is known to lower the energy difference between the electronic levels of the carbons; additionally, S- and O- containing groups can act as chromophores, photogenerating excitons that also participate in the observed photochemical reactions [6]. Figure 1B summarizes the different mechanisms that take place upon illumination of a nanoporous carbon particle [4]. The role of a carbon material when used as additive to a semiconductor was also investigated with the main objective to understand the mechanisms governing the effect of the incorporation of a nanoporous carbon (sample NC) to an n-type semiconductor (WO₃) used as photoanode for the photoelectrochemical oxidation of water [7]. In this respect, Figure 1C shows a direct comparison of photocurrent transients obtained for all electrodes under illumination. As seen, a sharp increase in the photocurrent responses is registered upon addition of small quantities of carbon. For the electrodes with carbon content of 50 wt.% and below, the recorded photocurrent values

are higher than those of the bare semiconductor. This is most remarkable considering that the amount of semiconductor is gradually reduced as the amount of carbon additive increases, which proves that these hybrid electrodes are more photoactive than bare WO₃. The fall in carrier generation due to a decreasing amount of WO₃ in the electrodes is overcompensated by an improvement in the diffusion length of the carriers brought about by the carbon additive. To investigate the wavelength dependence of the photochemical response of the electrodes, the photoelectrochemical response of the anodes was recorded using various wavelengths (Figure 1D). In the case of WO₃, the maximum conversion was recorded at about 370-400 nm and similar profiles were obtained for W/NC photoanodes. Previous studies have shown that this nanoporous carbon is photoactive towards the oxidation of phenol in a different spectral range, showing a poor conversion efficiencies at ca. 400 nm [4], which suggests that different mechanisms apply for these reactions (phenol and water photooxidation). As already observed at 371 nm (Figure 1C), higher photocurrents were obtained for all W/NC electrodes, confirming that the effect of the carbon additive applies for a wide wavelength range.

CONCLUSIONS

In the last decade, the use of nanoporous carbons in photochemical reactions, covering their role as additives to semiconductors and as photocatalysts themselves has opened up new opportunities for these materials in various disciplines related to light harvesting and applied photochemistry in nanoconfined systems. Porosity is a critical parameter since pores could act as nanoreactors and surface composition of the materials is also important as it might affect the electron acceptor capacity of the carbon matrix. By tailoring the carbon material, in terms of pore size as a function of the molecular dimensions of the target compound and chemical surface functionalisation, it is possible to boost the exploitation of light towards a chemical reaction. Some progress is yet to be done towards the understanding of the fundamentals of the photochemical and photophysical properties of nanoporous carbons and the light/carbon/molecule interactions at a nanoscale level, as the key for integrating photochemical reactions based on semiconductor free nanoporous carbons in a wide panel of technological processes.

RELATED PUBLICATIONS

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Full thesis can be download from:
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