Nanoporous Carbon

DOI: 10.1002/ange.201400887

Visible-Light Photochemical Activity of Nanoporous Carbons under Monochromatic Light**

*Leticia F. Velasco, Joao C. Lima, and Conchi Ania**

Abstract: *By using monochromatic light the ability of semiconductor-free nanoporous carbons to convert the low-energy photons from the visible spectrum into chemical reactions (i.e. phenol photooxidation) is demonstrated. Data shows that the onset wavelength of the photochemical activity can be tuned by surface functionalization, with enhanced visible-light conversion upon introducing N-containing groups.*

After the early works in the 1960s and 1970s reporting on the photochemistry of ZnO and TiO_2 electrodes, and their potential application in water splitting and environmental remediation,[1] heterogeneous photocatalysis has become a popular topic. However, the low photonic efficiency of most semiconductors is still a challenge, and calls for research to be conducted on exploring novel materials.[2] The use of carbon materials as additives and supports to semiconductors has been long explored and many studies have shown that adding a carbonaceous phase in the catalyst provides superior performance.[3] Our recent investigations[4,5] have also proved the photoactivity of semiconductor-free carbon under UV light and their ability to photogenerate O radicals. The occurrence of carbon–light interactions has been reported,[4–6] but the origin and the mechanisms of the photoinduced reactions initiated upon illumination of carbon materials still remain uncertain.

With the aim of shedding some light on this issue, the goal of this work was to explore the wavelength dependence of the photochemical response of semiconductor-free nanoporous carbon. The novelty of our approach is the use of monochromatic light to critically determine the wavelength onset of the photochemical activity of nanoporous carbons (Figure 1). In particular we evaluated this activity in terms of phenol photooxidation conversion, a well-known reaction described in the literature. Although photochemical applications of carbon nanostructures (graphene, nanotubes, graphite oxide) has gained considerable attention,[3] few studies deal with nanoporous carbon. Furthermore, most of them use polychromatic light and disregard the contribution of UV light to solar irradiation (ca. 4–10%), thus making it difficult to determine if the reported effect is actually a visible-light conversion.[7]

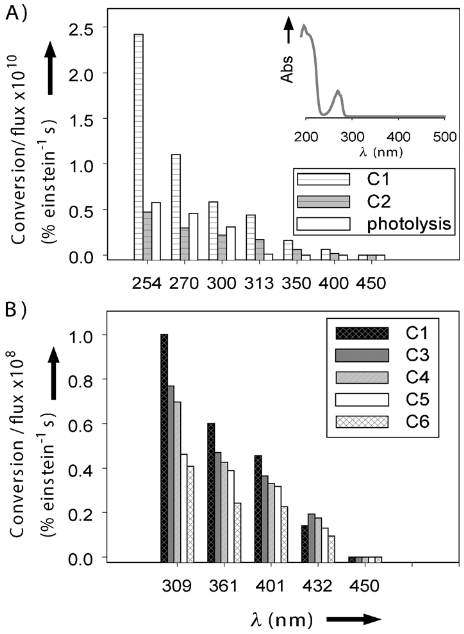

Figure 1. Phenol conversion per incident flux under monochromatic light provided by A) a Xe lamp (150 W) and B) a high pressure Hg lamp (125 W). Inset in (A): UV/Vis spectrum of a phenol solution.

To attain this goal, experiments were designed to suppress secondary reactions (i.e., direct photolysis and adsorption) by irradiating aqueous suspensions of the nanoporous carbons preloaded with phenol. This methodology was developed in our previous work[4] as a way to avoid adsorption/desorption and solution photolysis during the assays, and thus allow assignment of the extent of phenol photodegradation exclusively to the carbon–light interactions.

Figure 1 shows the normalized conversion values of selected nanoporous carbons by using monochromatic light. To stress the importance of the wavelength dependence on the photochemical response, data of direct phenol photolysis (absence of photocatalyst) is also shown. Two different lamps were used to explore the role of the irradiation source (see details about the emission spectral lines in Figure S1 in the Supporting Information). The expected low photonic efficiency of the phenol photooxidation reaction under visible light is evidenced by the decreasing pattern of phenol conversion at high wavelengths. Other differences became

---

[*] Dr. L. F. Velasco, Dr. C. Ania
Department of Chemical Processes in Energy and Environment
Instituto Nacional del Carbon (INCAR, CSIC)
C/Francisco Pintado Fe 26, 33011 Oviedo (Spain)
E-mail: conchi.ania@incar.csic.es

Dr. J. C. Lima
Departamento de Química, REQUIMTE/CQFB
Faculdade de Ciências e Tecnologia
Universidade Nova de Lisboa, Lisboa (Portugal)

[**] This work was partially supported by the Spanish MINECO (grants CTM2008/01956 and CTM2011/23378) and Fondos Feder (PCTI Asturias, grant PC10-02).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201400887.

evident when analyzing the data. Even though the high conversion values under UV irradiation have been previously reported using monochromatic light,[4] we herein show the wavelength dependence under monochromatic light and the performance of the isolated wavelengths of each lamp.

Phenol photolysis was negligible at wavelengths above $\lambda = 300$ nm, as was expected based on the light absorption features of the phenol solutions (inset Figure 1 A). Below $\lambda = 300$ nm, conversions were higher for the nanoporous carbons at all wavelengths. This conversion is remarkable considering that nanoporous carbons are strong light-absorption materials. More importantly, whereas the onset wavelength for phenol photolysis was above $\lambda = 300$ nm, most of the nanoporous carbons showed important photochemical activity when illuminated at $\lambda = 400$ and 432 nm. This data becomes direct evidence of the ability of nanoporous carbons to convert low energy photons from visible light irradiation into a chemical reaction: phenol photooxidation from solution. Another outstanding finding is that the onset wavelength for the photooxidation reaction for the nanoporous carbons was $\lambda = 432$ nm, which corresponds to an over 100 nm redshift compared to direct photolysis. The effect became more remarkable under higher photon fluxes (Figure 1 B).

With the exception of sample C7, which shows no photoactivity, all the studied carbon samples showed outstanding phenol conversions at $\lambda = 432$ nm, thus corresponding to photochemical activity under visible light. The lack of photoactivity of carbon C7, regardless of the wavelength, is in agreement with its performance under polychromatic light (see Figure S2),[4] and corroborates the finding that the ability to convert light into chemical reactions is not an intrinsic property of all carbon materials. Interestingly, none of the studied carbon samples seemed to be photoactive at $\lambda = 450$ nm, regardless the irradiation source. We attribute this effect to the low photon flux of both lamps at this wavelength (Figure S1), rather than to the inactivity of carbon materials above $\lambda = 450$ nm. Indeed, further studies need to be done at higher wavelengths to clarify this issue.

To gain additional insight into the role of the carbon composition on their photoactivity at different wavelengths, sample C1, which showed among the highest photochemical response, was chemically modified to introduce oxygen and nitrogen groups. As seen in Figure 2, the chemical functionalization barely modified the photooxidation yields, with the phenol conversions following the trend: undoped $\approx$ N doped $>$ O doped carbon C1. However, interesting features are revealed for the wavelength dependence of the photochemical response of the chemically modified samples. Whereas the oxidized carbon showed a similar wavelength dependence to that of C1, N doping provoked an outstanding redshift in the light absorption features, as seen by the increased conversion at $\lambda = 545$ nm. We attribute these differences to the likely changes in the density of electronic states (DOS) of the nanoporous carbon upon functionalization. It is generally accepted that the DOS in amorphous carbon is composed of bands formed by σ and π states, wherein the energy spread of states depends upon the sp^2/sp^3 content.[6,8] The size of the sp^2 clusters, and the ordering and distortions of π states control the optical band gap. In the visible/near UV band, the light absorption features of carbon materials are dominated by direct π–π^* transitions,[6,8,9] although transitions arising from intermediate hybridization states (mixed s/p character) or distorted sites are also allowed.

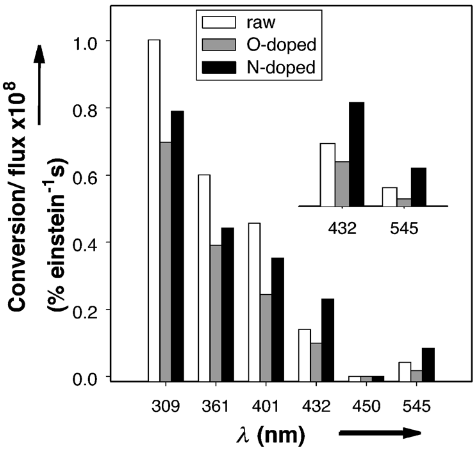

Figure 2. Effect of surface functionalization on phenol conversion values per incident flux upon illumination at different wavelengths using monochromatic light provided by a Hg lamp (125 W).

Chemical functionalization has a strong effect on the band gap that is associated with the sp^2/sp^3 rehybridization of the carbon atoms, and the creation of defects and midgap states, below the conduction band edge, which affect the location of the Fermi level.[8]

For O groups, the observed fall in phenol photooxidation conversion can be attributed to the electron-withdrawing effect of O-containing groups, which could affect the stabilization of the photogenerated carriers, by delocalization within the carbon basal planes, and the creation of distorted sites in the DOS. The effect would be similar to that reported for other carbon nanostructures, where the negative impact of oxidation was explained to result from the modifications in the sp^2/sp^3 content (carbon atoms with sp^3 hybridization increase after oxidation; see Table S5) and the medium-range order.[11] Although the effect of carbon oxidation on photocatalytic applications is still rather unclear,[5,12] we herein report that the onset of the photochemical activity remained unchanged after the incorporation of O functionalities.

In contrast, N doping caused an enhanced light absorption in the visible range, as seen in the increased conversion at $\lambda = 432$ and 545 nm, compared to the undoped C1 carbon. XPS analysis revealed that nitrogen was inserted mostly in the form of quaternary nitrogen and pyridine-type groups, with an increase in the sp^2/sp^3 ratio (see Figure S3 and Table S5). According to Ref. [8] the adequate N doping of carbon distorts the DOS, thus introducing midgap states below the conduction band edge. Such midgap states would explain the light absorption at high wavelengths in the N-doped carbon, compared to the undoped sample. Another effect of N doping is to favor interlayer bonding, thus producing higher electron mobility, as opposed to that of O doping.[8]

Upon irradiation of carbons direct π–π^* transitions occur, thus generating carriers (holes or electrons) which can participate in charge-transfer reactions with electron donors present in the reaction.[6,8,13] Similar optical properties have been reported for luminescent carbon nanotubes and nanoparticles in aqueous solutions, where intense absorption transmission is reported at $\lambda = 230$ and 320 nm.[9,10] The first one is associated with the strong π–π^* transition, whereas that at $\lambda = 320$ nm has been assigned to the σ–π^* transitions involving free zig-zag sites and carbene-like sites.[9,10] We have detected light absorption at energies below 2 eV, which could correspond to the σ–π^* transitions according to computational calculations.[14] Thus, the assignment of these transitions to the light absorption features, herein observed for nanoporous carbons above $\lambda = 400$ nm, seems reasonable.

Since the use of carbon nanostructures in photochemical applications has recently gained considerable attention, we believe these results are most outstanding as they provide direct experimental evidence of the photochemical activity of semiconductor-free carbon materials under visible light, as well as the dependence of this photochemical behavior on the wavelength of the irradiation source. This data offers an interesting opportunity to explore the light absorption features of carbon materials in the fields of solar energy conversion and environmental remediation.

Experimental Section

Materials: A series of nanoporous carbons obtained from different precursors was selected for this study. Selected physicochemical characteristics are compiled in the Supporting Information (see Table S1).

Surface functionalization: The incorporation of oxygen was carried out by mild wet oxidation. About 1 g of sample was put in contact with 10 mL of a saturated solution of ammonium persulfate in 4 N H_2SO_4 at room temperature and left stirring overnight. After oxidation, the carbon was filtered out, washed with distilled water until constant pH, and dried at 110 °C overnight. The N-doped carbon was prepared by dispersing 0.1 g of carbon in a 0.3 M urea solution and stirring for 24 h. After filtration, the material was heated at 800 °C under inert atmosphere.

Irradiation set-up: A Xe lamp (150 W) and a high pressure Hg lamp (125 W) were used to irradiate the samples, and a monochromator (Oriel, 1 nm resolution) was used to provide monochromatic light. The photon flux arriving at each wavelength was measured through ferrioxalate actinometry.[15] All phenol conversions were normalized versus the incident flux at each wavelength.

Phenol photooxidation: Suspensions of the carbons in a phenol solution are allowed to equilibrate until all phenol is completely removed and then irradiated for 60 min (see Scheme S1). The solution is filtered out and analyzed by reverse-phase HPLC (C18 column, water/methanol 95:5). The carbon material was further extracted with ethanol and the alcoholic solution is also analyzed by HPLC.[5] Extraction yields are previously determined for each pure compound on each carbon material. Direct phenol photolysis was also performed for comparison. All the measurements were done in duplicate and the standard deviation was lower than 5 %.

Received: January 27, 2014

Keywords: nanoporous carbon · photochemistry · surface functionalization · visible light

[1] a) T. I. Barry, F. S. Stone, *Proc. R. Soc. Lond. A* **1960**, *255*, 124–144; b) F. Romero-Rossi, F. S. Stone, Actes *2nd Congr. Intern. Catalyse* Paris, Tome II **1960**, pp. 1481–1497; c) R. I. Bickley, G. Munuera, F. S. Stone, *J. Catal.* **1973**, *31*, 398–407; d) A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38.

[2] a) J. M. Herrmann, *Appl. Catal. B* **2010**, *99*, 461–468; b) M. A. Henderson, *Surf. Sci. Rep.* **2011**, *66*, 185–297.

[3] a) R. Leary, A. Westwood, *Carbon* **2011**, *49*, 741–772; b) J. L. Faria, W. Wang, *Carbon Materials for Catalysis* (Eds.: P. Serp, J. L. Figueiredo), Wiley, New York, **2009**, Chap. 13, pp. 481–506; c) C. O. Ania, L. F. Velasco, T. Valdes-Solis, *Novel Carbon Adsorbents* (Ed.: J. M. D. Tascon), Elsevier, London, **2012**, Chap. 17, pp. 521–547.

[4] a) L. F. Velasco, I. M. Fonseca, J. B. Parra, J. C. Lima, C. O. Ania, *Carbon* **2012**, *50*, 249–258; b) L. F. Velasco, J. B. Parra, C. O. Ania, *Appl. Surf. Sci.* **2010**, *256*, 5254–5258.

[5] a) L. F. Velasco, V. Maurino, E. Laurenti, I. M. Fonseca, J. C. Lima, C. O. Ania, *Appl. Catal. A* **2013**, *452*, 1–8; b) L. F. Velasco, V. Maurino, E. Laurenti, C. O. Ania, *Appl. Catal. A* **2013**, *453*, 310–315.

[6] a) A. D. Modestov, J. Gun, O. Lev, *Surf. Sci.* **1998**, *417*, 311–322; b) A. D. Modestov, J. Gun, O. Lev, *J. Electroanal. Chem.* **1999**, *476*, 118–131.

[7] a) T. J. Bandosz, J. Matos, M. Seredych, M. S. Z. Islam, R. Alfano, *Appl. Catal. A* **2012**, *445*, 159–165; b) M. Seredych, L. Messali, T. J. Bandosz, *Carbon* **2013**, *62*, 356–364.

[8] a) J. Robertson, *J. Phys. Rev. Lett.* **1992**, *68*, 220–223; b) C. Oppedisano, A. Tagliaferro, *Appl. Phys. Lett.* **1999**, *75*, 3650–3652; c) J. Robertson, *Mater. Sci. Eng. R Reports* **2002**, *37*, 129–281; d) M-L. Theye, V. Paret, *Carbon* **2002**, *40*, 1153–1166; e) I. Velo-Gala, J. J. López-Peñalver, M. Sánchez-Polo, J. Ribera-Utrilla, *Appl. Catal. B* **2013**, *142–143*, 694–704.

[9] a) D. Pan, J. Zhang, Z. Li, M. Wu, *Adv. Mater.* **2010**, *22*, 734–738; b) D. Pan, J. Zhang, Z. Li, C. Wu, X. Yan, M. Wu, *Chem. Commun.* **2010**, *46*, 3681–3683.

[10] L. Bao, Z.-L. Zhang, Z.-Q. Tian, L. Zhang, C. Liu, Y. Lin, B. Qi, D.-W. Pang, *Adv. Mater.* **2011**, *23*, 5801–5806.

[11] a) Y. Zhu, X. Li, Q. Cai, Z, Sun, G. Casillas, M. J. Yacaman, R. Verduzco, J. M. Tour, *J. Am. Chem. Soc.* **2012**, *134*, 11774–11780; b) H. Soleymanabadi, J. Kakemam, *Phys. E* **2013**, *54*, 115–117.

[12] a) J. Matos, J.-M. Chovelon, T. Cordero, C. Ferronato, *Open Environ. Eng. J.* **2009**, *2*, 21–29; b) R. Ocampo-Pérez, M. Sánchez-Polo, J. Rivera-Utrilla, R. Leyva-Ramos, *Appl. Catal. B* **2011**, *104*, 177–184.

[13] a) V. V. Strelko, V. S. Kuts, P. A. Thrower, *Carbon* **2000**, *38*, 1499–1524; b) Y. Zhao, R. Nakamura, K. Kamiya, S. Nakanishi, K. Hashimoto, *Nat. Commun.* **2013**, *4*, 2390; c) D. Jana, C.-L. Sun, L.-C. Chen, K.-H. Chen, *Prog. Mater. Sci.* **2013**, *58*, 565–635.

[14] L. R. Radovic, B. Bockrath, *J. Am. Chem. Soc.* **2005**, *127*, 5917–5927.

[15] H. K. Kuhn, S. E. Braslavsky, R. Schmidt, *Pure Appl. Chem.* **2004**, *76*, 2105–2146.