CDs and N-CDs preparation from xylose and xylose-enriched biomass liquors for methyl orange photocatalytic degradation

Gabriela Rodríguez-Carballo[1], Benjamín Torres-Olea[1], Ramón Moreno-Tost[1], Manuel Algarra[2], Eulogio Castro Galiano[3] and Pedro Jesús Maireles-Torres[1].

[1]Universidad de Málaga, Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Campus de Teatinos, (Unidad Asociada al ICP-CSIC), 29071 Málaga, Spain.
[2]INAMAT[2]-Institute for Advanced Materials and Mathematics. Department of Sciences. Public University of Navarre. Campus de Arrosadía. 31006 Pamplona, Spain.
[3]Department of Chemical, Environmental and Materials Engineering, Centre for Advanced Studies in Earth Sciences, Energy and Environment (CEACTEMA), University of Jaén, Jaén, 23071, Spain.

CDs are newly discovered carbon nanoparticles that present unique properties. Each nanoparticle consists of a graphitic lattice core covered by a functionalized surface composed by several polar functional groups attached[1,2]. Due to this functionalization, CDs exhibit photoinduced electronic transference, fluorescence and up-conversion photoluminescence[3]. CDs have raised increasing attention for their undemanding synthesis procedure combined with the fact that they have been proved to be non-toxic and can be modified to reach satisfactory quantum yield values. A current tendency in the obtention of CDs is the pursuit of a synthesis method that fulfils the requirements of green chemistry but keeps production costs low. Therefore, CDs obtained from green precursors coming from biomass is an emergent research topic[4,3,5,6,7]. The most frequent and best-known method for CDs production is hydrothermal or solvothermal method[7,3,2].The acidic conditions required by this method are commonly achieved using mineral acids such as HCl; nonetheless, the hydrothermal method is compatible with heterogeneous catalysis, which have been proved in this work. As a consequence of their photoluminescence and electron transfer properties, CDs can work as electron mediators, photosensitizers, as well as photocatalysts by themselves [10]. It has been proved that CDs when photo excited are outstandingly good electron donors and electron acceptors, since either electron acceptors or electron donors are able to quench the photoluminescence emitted by CDs effectively [9].
Two sources of xylose were selected for the CDs synthesis: commercial xylose and xylose contained in the liquor prepared from olive pits treatment. The preparation of CDs from commercial xylose involved a certain volume of xylose or xylose-enriched biomass solution and a certain amount of heterogeneous catalyst that were added into a Teflon-lined steel hydrothermal reactor. CDs doped with nitrogen moieties (N-CDs) were synthesized via an analogue one-step hydrothermal method.
Samples of pristine CDs and N-CDs were further characterized by means of Transmission Electron Microscopy (TEM) **(Figure 1).** Particle size varied depending mainly on the carbon feedstock, ranging from 2 nm to 6 nm for N-CDs from commercial xylose and from 15 nm to 20 nm for biomass liquors. For further confirmation of the presence of CDs, the graphitic lattice was identified in HR-TEM images and the measurement of the spacing gave out a value of 0.310 nm. Photoluminescence measurements of pristine CDs samples as expected, were lower in intensity than those of doped CDs since doping CDs generates defects in the surface that are highly emissive spots and since new N-C bonds are created with doping, there is also a contribution in the PL emission that comes from the variety of functional groups generated thanks to doping.

The obtained CDs and N-CDs were then assayed in the photocatalytic degradation of methyl orange (MO). Samples were irradiated by visible light inside photoreactor. The photoluminescent properties, being closely related to the electronic transmission phenomena occurring at the surface level in the CDs, were translated into a high photocatalytic degradation performance of methyl orange. Both doped and undoped nanoparticles provided good results in photocatalytic tests.

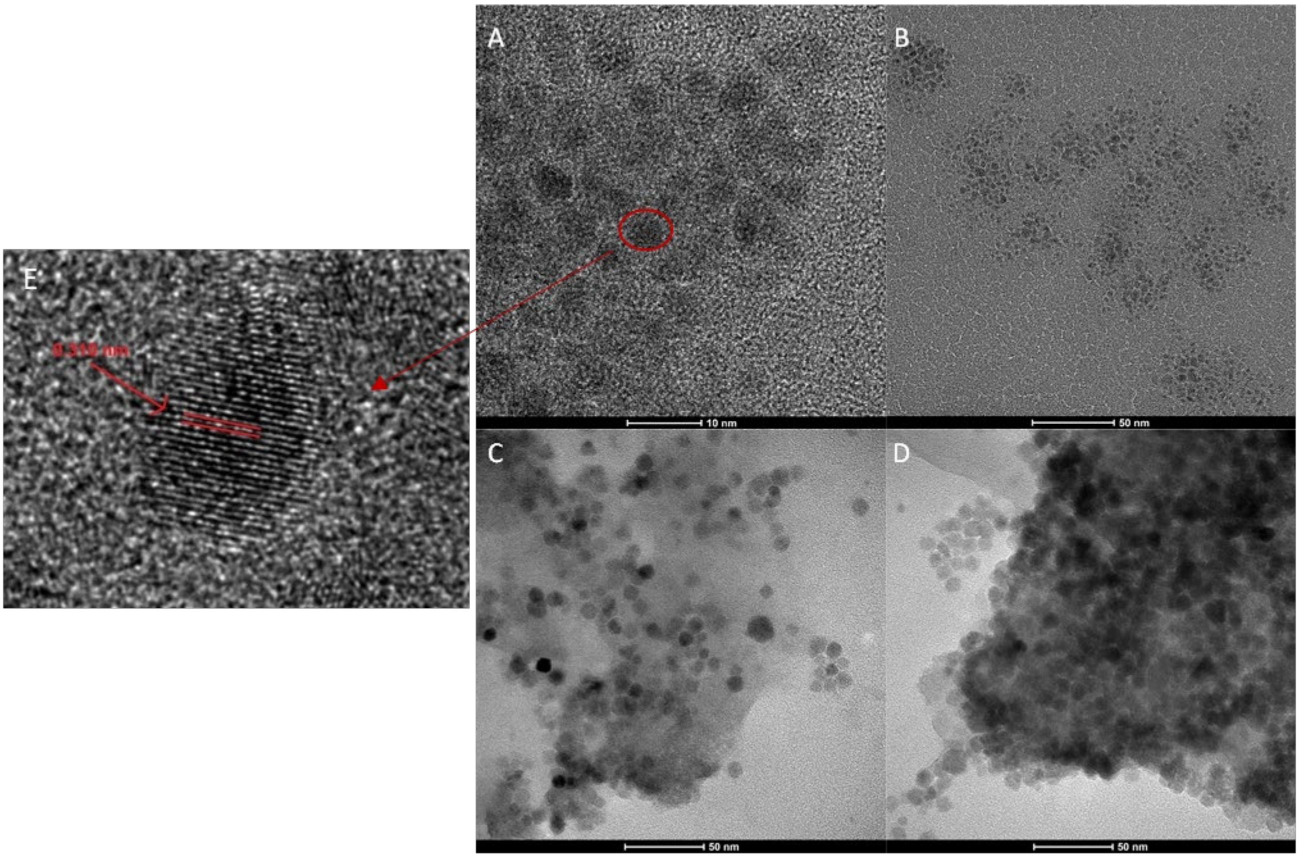

Figure 1. TEM images of **(A)** Pristine CDs from; **(B)** N-CDs from xylose; **(C)** CDs from biomass liquor; **(D)** N-CDs from biomass liquor and $NbOPO_4$ catalyst and **(E)** Graphite spacing in CDs from commercial xylose and $NbOPO_4$ catalyst.

References:

(1) Hola, K.; Zhang, Y.; Wang, Y.; Giannelis, E. P.; Zboril, R.; Rogach, A. L. Carbon dots—Emerging light emitters for bioimaging, cancer therapy and optoelectronics. *Nano Today* **2014**, *9* (5), 590–603.

(2) Zhu, L.; Shen, D.; Wu, C.; Gu, S. State-of-the-Art on the Preparation, Modification, and Application of Biomass-Derived Carbon Quantum Dots. *Ind. Eng. Chem. Res.* **2020**, *59* (51), 22017–22039.

(3) Sim L.C.; Tai J.Y.; Khor J.M.; Wong J.L.; Lee J.Y.; Leong K.H.; Saravanan, P.; Aziz, A. A. Carbon Dots Synthesized from Green Precursors with an Amplified Photoluminescence: Synthesis, Characterization, and Its Application. In *Plant Nanobionics*; Springer International Publishing, 2019; pp 1-33.

(4) Algarra, M.; Orfãos, L. dos; Alves, C. S.; Moreno-Tost, R.; Pino-González, M. S.; Jiménez-Jiménez, J.; Rodríguez-Castellón, E.; Eliche-Quesada, D.; Castro, E.; Luque, R. Sustainable Production of Carbon Nanoparticles from Olive Pit Biomass: Understanding Proton Transfer in the Excited State on Carbon Dots. *ACS Sustain. Chem. Eng.* **2019**, *7* (12), 10493–10500.

(5) El-Shabasy, R. M.; Farouk Elsadek, M.; Mohamed Ahmed, B.; Fawzy Farahat, M.; Mosleh, K. N.; Taher, M. M. Recent Developments in Carbon Quantum Dots: Properties, Fabrication Techniques, and Bio-Applications. *Processes (Basel)* **2021**, *9* (2), 388.

(6) Wu, Y.; Li, Y.; Pan, X.; Hu, C.; Zhuang, J.; Zhang, X.; Lei, B.; Liu, Y. Hemicellulose-Triggered High-Yield Synthesis of Carbon Dots from Biomass. *New J Chem* **2021**, *45* (12), 5484–5490.
(7)Rodríguez-Padrón, D.; Algarra, M.; Tarelho, L. A. C.; Frade, J.; Franco, A.; de Miguel, G.; Jiménez, J.; Rodríguez-Castellón, E.; Luque, R. Catalyzed Microwave-Assisted Preparation of Carbon Quantum Dots from Lignocellulosic Residues. *ACS Sustain. Chem. Eng.* **2018**, *6* (6), 7200–7205.
(8) Khan, M. E.; Mohammad, A.; Yoon, T. State-of-the-Art Developments in Carbon Quantum Dots (CQDs): Photo-Catalysis, Bio-Imaging, and Bio-Sensing Applications. *Chemosphere* **2022**, *302* (134815), 134815.
(9) Dhamodharan, D.; Byun, H.-S.; Varsha Shree, M.; Veeman, D.; Natrayan, L.; Stalin, B. Carbon Nanodots: Synthesis, Mechanisms for Bio-Electrical Applications. *J. Ind. Eng. Chem.* **2022**, *110*, 68–83.