

Bright nanoparticles for an even brighter future: efficient production of luminescent carbon nanodots from olive mill wastewater

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Carbon nanodots (CNDs) are a very recent class of spherical-shaped nanosized carbon materials possessing average typical diameters < 10 nm. Since the very first reports on carbon dots,^{1,2} a variety of methods (top-down and bottom-up strategies), carbon sources and passivating agents, have dealt with their synthesis.³ The bottom-up approach, encompassing the use of pyrolytic/solvothermal processes, is more amenable for large-scale production and can cope with a large diversity of carbon precursors, either from natural or synthetic sources, typically endowed with acid, alcohol and amine functionalities.⁴ Some of the interesting CNDs properties include tunable photoluminescence, outstanding photostability and negligible cytotoxicity. These unique properties have prompted their intense and widespread use in several fields, such as fluorescent bioimaging and nanomedicine, chemo/biosensing, photocatalysis and optoelectronics.⁴

Olive oil is obtained from the fruit of the olive tree (*Olea europaea* L.) by batch press and continuous centrifugation processes. Large amounts (200-1600 L) of olive mill wastewater (OMWW) may be produced per tonne of processed olives, depending on the process. The main organic constituents of OMWW are sugars, pectins, phenols/polyphenols, tannins and lipids. OMWW exhibits phytotoxicity and antimicrobial activity, usually attributed to its phenolic content, leading to very low biodegradability parameters and serious environmental concerns for its uncontrolled disposal.

Following sustainable and expedite hydrothermal processes, we have been able to synthesize highly luminescent CNDs directly from OMWW. The as-prepared CNDs were obtained in excellent yields under a variety of conditions. In order to maximize the quantum yield of the as-synthesized carbon nanoparticles, several operation variables (*viz.* reaction temperature, reactor dwell time and amount/nature of organic additives) were investigated. Certain processing-structure-property correlations have been established and will be presented in this communication, along with the photophysical properties (UV-Vis, excitation and fluorescence emission), surface analysis (FTIR, ¹H/¹³C NMR), microanalysis, and morphology (TEM) of selected CNDs.

Under specific synthetic conditions, and without any further purification procedure, the as-synthesized CNDs are deep blue emitters ($\lambda_{em\ max} \sim 410\ nm$; $\lambda_{exc} = 340\ nm$) reaching notable quantum efficiencies ($\phi_f = 0.3-0.4$), an extremely high photostability (upon being continuously irradiated at 340 nm), and a pH-responsive luminescence (pH 1-12).

Such luminescent properties of CNDs, allied to the carbon source affordability, their easy synthesis, and excellent dispersion behaviour in aqueous solutions and polar protic and non-protic organic solvents, render them with unique capabilities to be used in several important domains such as bioimaging tools, in sensory analysis, and as organocatalysts and/or nanocomposites components in photocatalysis.

Acknowledgments: We thank Instituto Politécnico de Lisboa (Project NANOLIVE/IDI&CA/2016) and Fundação para a Ciência e a Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior (UID/QUI/00616/2013) for financial support.

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