ON THE NATURE OF CARBON NANODOTS PHOTOLUMINESCENCE FROM OLIVE WASTES

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A great structural diversity of carbon nanodots (CNDs) have been obtained in the last ten years by a variety of methods, carbon sources, additives and/or passivating agents, and operation parameters. Not unexpectedly, many properties diverge owing to disparate structural features. The photoluminescence (PL) is one of them. A vast literature is already available on this topic, with findings that are somehow apparently contradictory. At least three possible origins of PL in CNDs have been identified: i) quantum confinement effects associated with the sp^2 domains of the carbon core; ii) surface states lying in the edges of sp^2 carbogenic core; iii) molecular states originating from molecular species embedded or covalently linked to the carbon matrix.

We have investigated the temperature-dependent PL of CNDs derived from olive mill wastewater. The highly emissive (Φ_F ~ 0.4) nanodots exhibit a main (slightly asymmetric) emission band peaking at ~ 410 nm (λ_{exc} = 340 nm) which decreases linearly as the temperature raises from 0ºC to 80ºC, owing to an increased population of non-radiative channel traps activated on temperature rising. The PL spectra, fitted by two Gaussian functions at each evaluated temperature, reveal the presence of two main emitting components in line with the PL excitation spectra (two bands centred at 242 nm and 336 nm, monitored at the emission maximum) which do not change their position upon an increase in temperature. The high energy PL band (H) at 400 nm with an fwhm of 50.1 nm may be ascribed to π-π* core transitions while the broader (fwhm = 75.3 nm) lower energy band (L) found at 434 nm may be a result of mixed n-π* and π-π* transitions (ratio L/H = 1.38). Both bands show a very slight (*ca.* 2-3 nm) increase of bandwidth and only a small red shift gap of the bands (14 and 15 meV, respectively) upon heating, an effect that is similar to that observed in metallic quantum dots (QD) and divergent from that in semiconductor QD. Under conditions where the formation of larger regions of carbogenic cores are favoured (*e.g.* 300ºC), the ratio of bands above assigned to core and surface states increased (L/H = 0.83), and a concomitant reduction of quantum efficiency is observed, further pointing to the origins of PL in these CNDs. Emission from molecular states may be ruled out given the PL excitation-dependency of CNDs.

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