

A microwave-hydrothermal synthesis of graphene quantum dots (GQDs) with strongly blue-photoluminescence

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Abstract (Arial 10)

Research in photoluminescent nanomaterials is of great interest because of their many applications. It is now widely known that graphene materials can emit light in the visible range, when they are excited at different wavelengths, just in case they are reduced at 3D nanometer scale. In these “zero dimensional” carbon nanodots (C-dots) or graphene quantum dots (GQDs), an energy GAP is induced, its value being dependant on both size and surface traps [1]. Compared with semiconductor QDs, GQDs exhibit nonblinking fluorescence, excellent water solubility, are cheaply produced, are more environmental friendly and could be much safer for biological use [2-4].

Of particular interest and significance is the finding that GQDs can exhibit photoluminescence (PL) emission in the near-infrared (NIR). It should be noted that NIR PL emission of GQDs is particularly significant and useful for in vivo bionanotechnology because of the transparency of body tissues in the NIR region [5].

Samples were prepared from commercial grade, low density ultra-thin graphite (UTG) purchased from Avanzare S.L. (La Rioja, Spain) previously heat-treated at 600°C under nitrogen flux for two hours. Adequate amount of powder was dispersed in MQ water for a concentration of 1mg/ml assisted by high power ultrasounds for 30 minutes. Dispersions were hydrothermally processed with 4 ml of ammonia in a Teflon reactor placed inside an Ethos 1600 microwave oven at 220°C for different time intervals reaching a steady pressure of 20 bar. Solutions were filtered with a 0.1 µm membrane and the resulting yellowish solution was kept at 50°C overnight. Finally, samples were dialysed by a 1000 MWCO membrane.

UV-vis absorption spectra of the samples (Fig. 2) show a peak at 215-220 nm (5.8-5.6 eV) that is blue-shifted in comparison to that of graphene sheet (270 nm, 4.6 eV). This peak is expected to shift toward higher energies as GQDs size reduces, which is consistent with the quantum confinement effect.

Raman spectra present two characteristic vibrations at ≈ 1350 and ≈ 1575 cm^{-1} (Fig. 1), which can be related to the defect band (D band) and the graphite band (G band), respectively [6]. The G band is attributed to the vibration of sp^2 -bonded carbon atoms in a 2D hexagonal lattice, while the D band is associated with vibrations of carbon atoms with dangling bonds in plane terminations of the disordered graphite and is related to the presence of defects and disorder in the nanostructures of carbon materials. The peak frequency of the D band is almost irrespective of nanoparticle size, whilst the G band shows clear size dependence.

TEM and AFM measurements show a nanoparticle narrow size distribution with a mean size of 8.4 nm with an average depth of 2 nm (Fig. 4).

Photoluminescence (PL) leads to a broad emission peak that is red-shifted when the excitation wavelength changes to higher values with a decreasing of the PL intensity (Fig. 2). This dependence of the emission wavelength and intensity on the excitation energy is a common phenomenon in GQDs. These GQDs exhibit Quantum Yields (QYs) up to 3.5%. The upconverted PL property of the samples was also investigated under excitation wavelengths in the range 700–900 nm (Fig. 4).

XPS measurements reveal the presence of functional groups (-O-H, -C-H, -C-O-C and -C=O) located at the surface of the GQDs. These functional groups act as a self-passivation layer on the GQDs surfaces that may facilitate the solubility of GQDs in water as well as the efficient PL properties.

Time resolved photoluminescence (TRPL) decays were monitored using a 337nm pulsed laser as excitation source. Each decay curve fits a single-exponential function obtaining a lifetime of 4.2 ns consistent with reported values [7].

In conclusion, these GQDS, prepared by a microwave–hydrothermal method, possess higher QYs and longest lifetime than those previously reported [8], making them very suitable for optoelectronic and biological applications.

References

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Figures

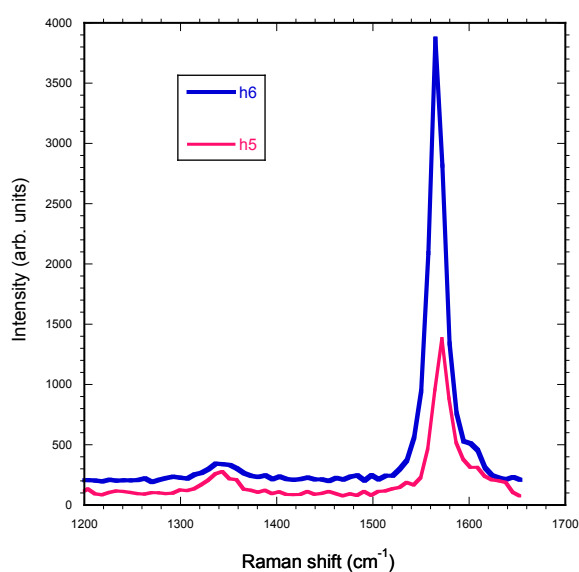


Fig. 1

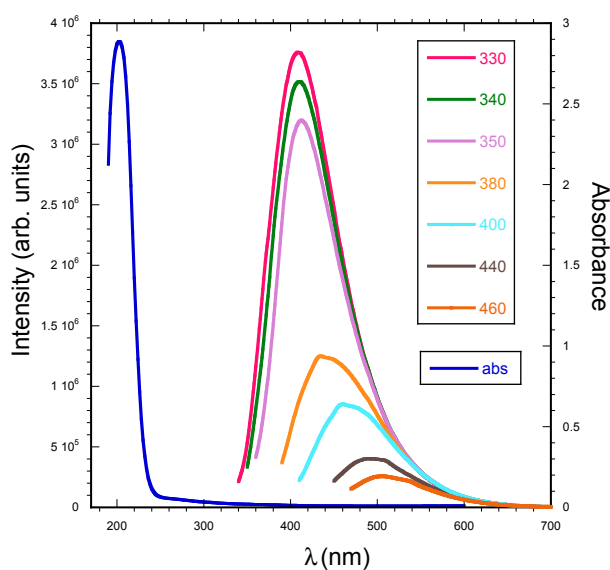


Fig. 2

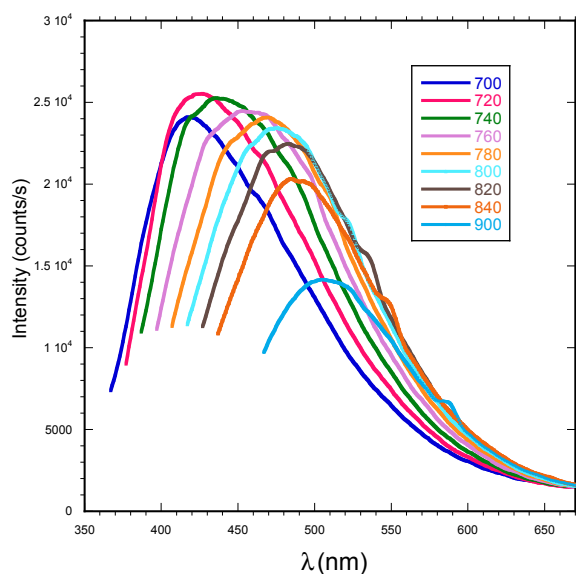


Fig. 3

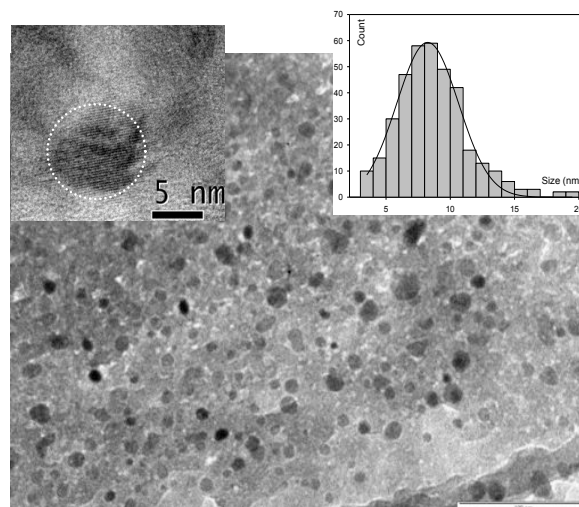


Fig. 4