Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Graphene quantum dots from fishbone carbon nanofibers

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S1. MATERIALS AND METHODS

Fishbone carbon nanofibers synthesis

CNF were synthetized via catalytic decomposition of CH_4:CO_2 mixtures in a rotary bed reactor (set-up characteristics are summarized elsewhere[1]). A Ni/Al_2O_3 catalysts (Ni:Al molar composition: 2:1) prepared by the fusion method as described in previous works of our research group,[2,3] was used for carbon nanofibers growth and led to the formation of solid (with or without a narrow hollow core) fishbone carbon nanofibers. CNF were obtained in a 180 min run with a feed of 150 l h^{-1} of 50 % of CH_4 and 50 % of CO_2 at 600 ºC and with a weight hourly space velocity of 30 l g_{cat}^{-1} h^{-1}. Raw CNF included metal particles (from the remaining catalyst) as Ni and Al_2O_3 accounted for 12 wt. %. More details about the CNF properties and process conditions can be found elsewhere [4].

Obtention and separation of graphene oxide-based suspensions

As-prepared fishbone CNF were subjected to a modified Hummers method[5-9] followed by ultrasonic exfoliation. In a typical synthesis, 1.5 g of CNF, 1.5 g of $NaNO_3$ (purity ≥ 99.0 %), and 69 ml of H_2SO_4 (96 %) were stirred together in an ice bath. $KMnO_4$ was slowly added to the mixture under vigorous stirring with an oxidation ratio (OR) of $KMnO_4$ to CNF equals to 10 (wt./wt.; mass of CNF excluding the catalyst content), previously optimized in a previous work using MWCNT.[9] After addition of $KMnO_4$, temperature was kept below 20 ºC during mixing and then the solution was stirred at 30±5 ºC for 2 hours and at room temperature overnight. After oxidation, a brownish thick paste was formed. Then, 120 ml of deionized water was slowly added while maintaining the temperature below 70 ºC. Subsequently, the solution was stirred for 60 min and was diluted with 300 ml of deionized water.13 ml of H_2O_2 (33 %) were added dropwise, turning the solution colour to yellowish brown. Resulting material exfoliation was carried out for 120 min by sonication. Product was washed by centrifugation with HCl (10 %) and deionized water until neutral pH. The clean precipitate was dispersed in deionized water and separated in differentiated fractions by DDC in a fixed-angle centrifuge. Centrifugation was carried out in 1 hour cycles for successive decreasing rates by step (14800, 9500, 7000, 4500 and 2000 rpm), using the redispersed precipitate collected from the previous faster-rate step and separating supernatants in order of increasing particle sizes. After centrifugation, fractions with a concentration between 0.1 and 0.6 mg ml^{-1} were obtained. Finally, fractions were reduced in suspension by the hydrothermal reduction method (HR),[10] in which 30 ml of sample was introduced into an autoclave at 180 °C for 6 h.

Characterization techniques

XRD patterns of raw CNF and dried fractions were acquired in a Bruker D8 Advance Series 2 diffractometer. The angle range scanned was 4º-55º using a counting step of 0.02º and a counting time per step of 4 s. XRD data were fitted using the structure analysis software TOPAS (Bruker AXS) including subtraction of a Chebyshev polynomial background and peak deconvolution by fitting to a split pseudo-Voigt functions. The graphite peak fit gave information on structural parameters such as interlayer spacing, d_{002}, or mean crystallite size along c axis (transverse to the graphene planes), L_c, which are used in this study to estimate the exfoliation degree and the average number of graphene layers, n. The mean interlayer spacing was evaluated from the position of the (002) peak applying Bragg's Law,[11] while the mean crystallite size was calculated using the Scherrer formula, with a values of $K = 0.89$.[11] From these, n was calculated as $(L_c/d_{002})+1$.[9]

XPS analyses were carried out with an ESCAPlus OMICROM system equipped with a hemispherical electron energy analyser. The spectrometer was operated at 15 kV and 10 mA, using a non-monochromatic MgKα X-ray source ($h\nu = 1253.6$ eV) and under vacuum (< 5×10^{-9} Torr). Analyser pass energy of 50 eV was used for survey scans and 20 eV for scans of C1s region. For calibration purposes, the C1s binding energy of the graphitic peak (BE) was referenced at 284.5 eV. A survey scan (1 sweep/200 ms dwell) was acquired between 1200 eV and 0 eV. The CASA XPS data processing software allowed smoothing, Shirley type background subtraction, peak fitting and quantification.

Morphological appearance and topography of CNF and products were performed by TEM and AFM. **TEM** images were taken on a Tecnai F30 (FEI) microscope, equipped with a cannon of 300 KeV and a maximum resolution of 1.5 Å. Tapping-mode **AFM** images were taken using a Multimode 8 scanning probing microscopy (Veeco-Bruker). AFM sample was prepared by depositing solution as obtained ($0.3\ \mathrm{mg \cdot ml^{-1}}$) onto a freshly cleaved mica surface and dried in desiccator overnight. Image processing and particles analysis including height profiles and surface area determination were performed with Gwyddion software.

Optical properties of GO- and rGO-based suspensions were characterized at ambient conditions in 10 mm pathlength quartz cuvettes using a UV-VIS spectrophotometer (Shimadzu UV-2401PC) and a spectrofluorometer (FluoroMax-P, HORIBA Jobin Yvon). The PL quantum yield (PLQY) of suspensions of GOQD and rGOQD was estimated by the method described by Williams *et al.*[12] using quinine sulphate as standard ($\Phi_r = 0.54$) according to the equation:

$$\Phi = \Phi_r \cdot \frac{I}{A} \cdot \frac{A_r}{I_r} \cdot \frac{n^2}{n_r^2}$$

Where the Φ is the PLQY, I is the integrated PL emission intensity (excited at 355 nm for GOQD and quinine sulphate, and at 330 nm for GQD), n is the refractive index (1.33 for GOQD and GQD in aqueous suspension and for quinine sulphate in 0.1 (M)

H_2SO_4), and A is the absorbance value at the excitation wavelength of 355 nm and 330 nm for GOQD and GQD, respectively. The subscript “r” refers to the standards.

Additionally, an Olympus FV10-i Oil Type confocal fluorescence microscope was used to obtain fluorescence microscopy images, with excitation wavelength at 473 nm.

S2. SUPLEMENTARY FIGURES

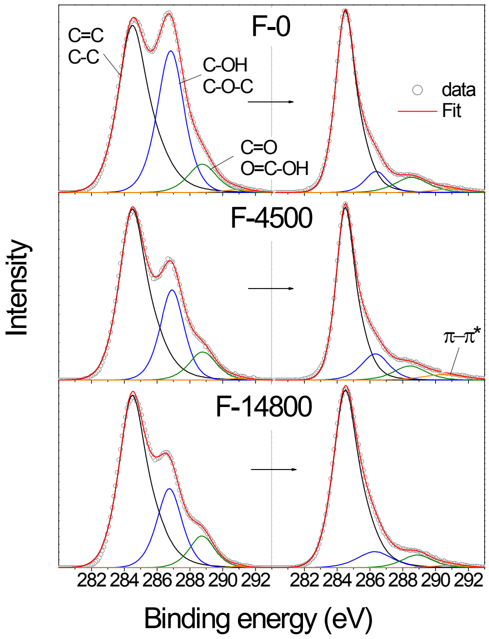

Fig. S1 Deconvoluted C1s spectra of some fractions before (left) and after hydrothermal reduction (right).

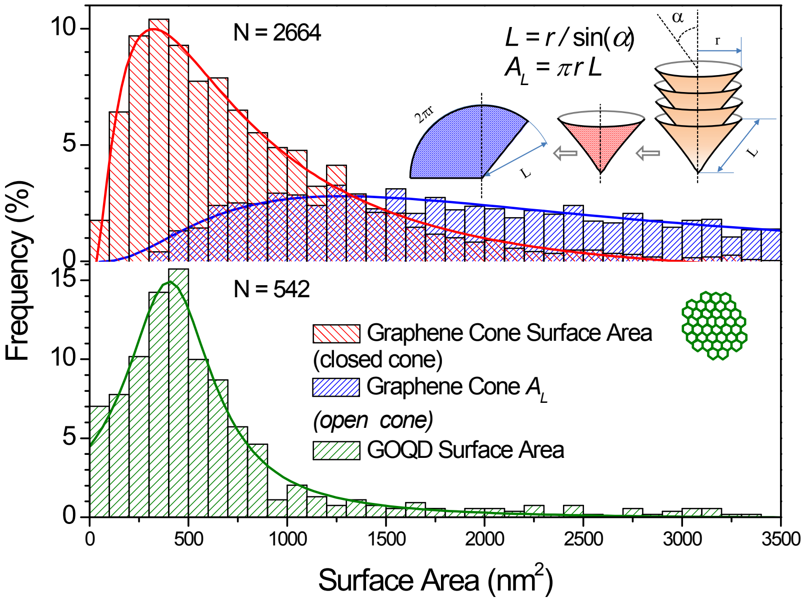

Fig. S2 CNF cone lateral area (estimated using diameters and α angles of CNF observed by TEM) and GOQD surface area log-normal distributions; e) representation and calculation of the lateral area of an open graphene cone in a CNF structure.

The theoretical lateral area (A_L) of a graphene cone in CNF both open and unopened were estimated from TEM image measurements of diameters and α angles of CNF, according to the equations: $A_L = \pi r L$ and $A = r L \cos(\alpha)$, respectively.

Table S1 Surface areas and equivalent diameters of the normal distributions of Fig. S2.

	Graphene cone (closed)	*Graphene cone (open)*	*GOQD*
N	2664	2664	542
Mean Surface Area (nm^2)	862	3120	703
Std. Error (nm^2)	15	53	33
Equivalent Diameter (nm)	33	63	30
Median Surface Area (nm^2)	660	2435	482
Equivalent Diameter (nm)	29	56	25
5 % Trimmed Mean (nm^2)	795	2887	632
Equivalent Diameter (nm)	32	61	28

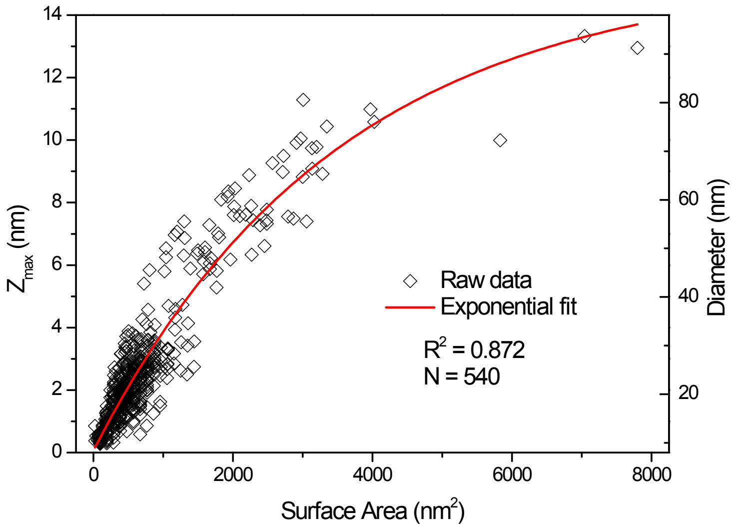

Fig. S3 Exponential function fitting between surface area and height (or equivalent diameter) for GOQD measured by AFM.

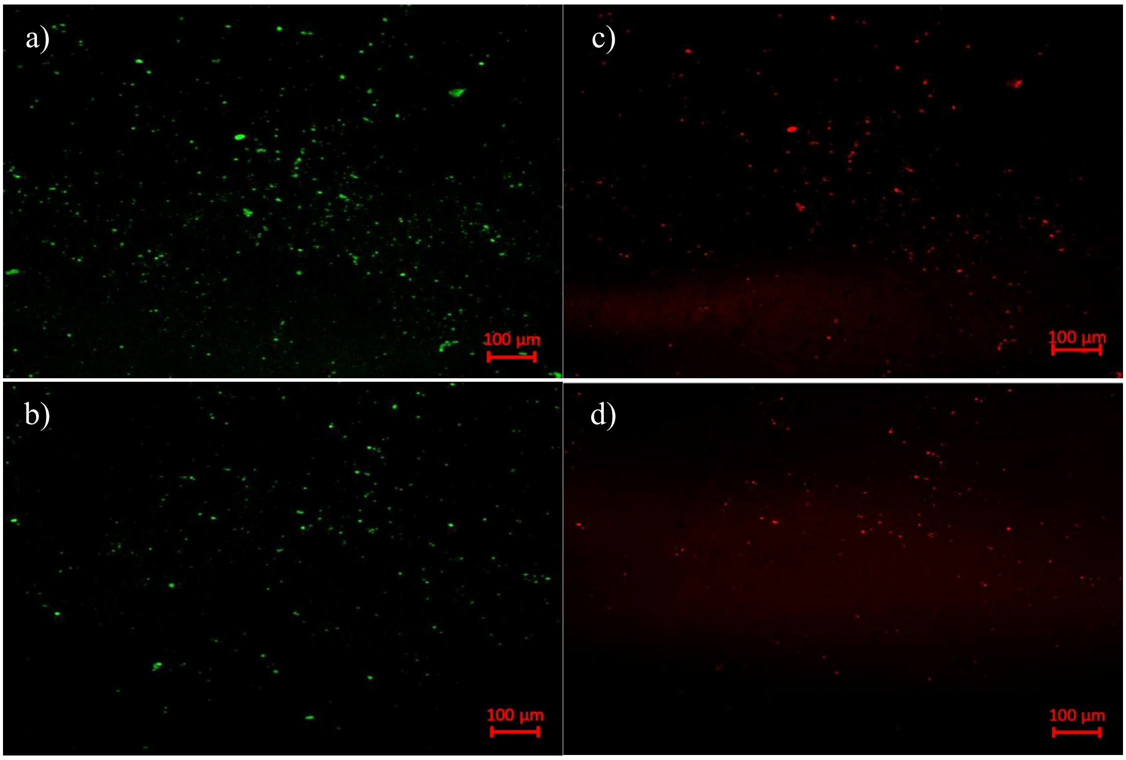

Fig. S4 Confocal fluorescence microscopy images of the GOQD at the excitation wavelength of 473 nm collecting the fluorescence between (a-b) 490 and 590 nm; and (c-d) 570 and 670 nm.

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