Supporting Information

Rapid Synthesis of Graphene Quantum Dots using a Continuous Hydrothermal Flow Synthesis Approach

Suela Kellici,^{a*} John Acord,^b Nicholas P. Power,^c David J. Morgan,^d Paolo Coppo,^eTobias Heil^f and Basudeb Saha^a

^aSchool of Engineering, London South Bank University, 103 Borough Road, London, SE1 0AA, UK. *E-mail: kellicis@lsbu.ac.uk

^bSchool of Applied Sciences, London South Bank University, 103 Borough Road, London, SE1 0AA, UK

^c School of Life Health & Chemical Sciences, Open University, Walton Hall, Milton Keynes, MK7 6AA, UK

^dCardiff Catalysis Institute, School of Chemistry, Cardiff University, Park Place, Cardiff, CF10 3AT, UK

^eCentre for Phosphors and Display Materials, The Wolfson Centre, Brunel University, Kingston Lane, UB8 3PH, Uxbridge, UK

^fNanoinvestigation Centre at Liverpool, 1-3 Brownlow Street, Liverpool University, Liverpool, L69

Materials Synthesis

^{\dagger} GO was synthesised using a modified Hummers method from graphite.¹

^{\$}Calix[4]arene tetrasulfonic acid (SCX4) was synthesised via adaptation of previously reported methods.²</sup>

[§]CHFS experiments were conducted using a flow reactor design to that reported previously.¹ The system consists of three HPLC pumps used for the delivery of aqueous solution of reagents. Pump 1 (labelled as "P1" in Fig. 1b,) was dedicated for delivering DI water through a custom made pre-heater (labelled as "Heater" in Fig. 1b) at a flow rate of 20 mL min⁻¹. Pump 2 (P2) and 3 (P3) were used for pumping aqueous mixtures of pre-mixed SCX4 and GO solution (P2) and KOH (P3) at a flow rate of 5 mL min⁻¹. In a typical experiment, SCX4 (40 mg) was added to a pre-sonicated (30 min) aqueous solution of GO (20 mg) dispersed in DI water (40 mL), which was pumped to meet a flow of KOH (0.2 M) at a T-junction ("T" in Fig. 1b). This mixture then meet superheated water (450 °C, 24.1 MPa) inside a countercurrent mixer (Reactor in Fig. 1b), whereupon the product formation occured in a continuous matter. The aqueous suspension was cooled through a vertical cooler and the slurries were collected from the exit of the back-pressure regulator (BPR in Fig. 1b). The obtained products were filtered using a polycarbonate membrane (0.22 micron). The supernatant solutions were subjected to dialysis for 24 hrs. After dialysis, the cleaned solutions were then dried obtaining powders for further characterisation. A control reaction in the presence of 4hydroxybenzenesulfonic acid was also conducted.

* *Cellular toxicity test* - The macrophage cell line RAW 264.7 (ATCC TIB-71) was grown in fully supplemented Dulbecco's modified Eagle medium (DMEM) containing 10% foetal calf serum, 100 U mL⁻¹ penicillin and 100 μ g mL⁻¹ streptomycin. Cells were seeded in 96

well tissue-culture treated microtitre plates at a density of 5 x 10^4 cells per well and allowed to grow for 24 hrs in an incubator (37 °C, 5% CO₂) before the sample being tested was added. Samples were added to final concentrations ranging from 2 mg mL⁻¹ to 31.25 µg mL⁻¹. After 24 hrs incubation with sample, cell viability was tested using the 3-(4,5dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay. MTT dissolved in phosphate buffered saline was added to each well at a final concentration of 1 mg mL⁻¹ and the plate was returned to the incubator for 3 hrs. The media was then aspirated and 100 µL DMSO added to each well. The plate was shaken for *ca.* 10 mins at room temperature and the optical density (OD) measured at 544 nm. Cell viability was reported as a percentage value compared to untreated cells and was given by the formula: cell viability (%) = (OD_{treated}/OD_{control}) x 100%, where treated cells are those that were incubated with sample being tested and control cells were incubated under the same conditions but in the absence of any sample. Each sample was performed in triplicate and the experiments were repeated twice. Results shown are the mean values and error bars represent standard deviation.

Equipment and techniques: Freeze-drying was performed using a Heto PowderDry PL 3000. A JEOL 2010 and 2100F TEM (200 kV accelerating voltage) were used for generating images of particles. XPS measurements were performed using a Kratos Axis ultra DLD photoelectron spectrometer utilising monochromatic Alka source operating at 144 W. Samples were mounted using conductive carbon tape. Survey and narrow scans were performed at constant pass energies of 160 and 40 eV, respectively. The base pressure of the system was *ca.* 1×10^{-9} Torr rising to *ca.* 4×10^{-9} Torr under analysis of these samples. FT-IR spectra were recorded using a Nicolet Avatar 370DTGS spectrometer fitted with a Smart Orbit accessory (diamond 30000-200 cm⁻¹). A Perkin Elmer spectrometer was used for fluorescence measurements of the samples analysed at equivalent concentrations unless otherwise stated. TGA analyses were conducted on a TGA Q500 instrument under a constant flow of nitrogen at a heating rate of 10 °min⁻¹ from room temperature to 800 °C. UV-Vis data of dispersions of known concentrations were recorded using a UV-1800 Shimadzu UV-Vis instrument. Raman spectroscopy measurements were performed on a Raman microscope (XploRA Plus Raman Microscope, HORIBA Jobin Yvon) by using a 785nm laser (as this shows only a minimal fluorescence background).

The quantum yields of photoluminescence were measured using a solution of fluorescein in spectroscopic ethanol as a standard ($\Phi = 79\%$)³ with an optical density of 0.08 at the excitation wavelength (420 nm). Samples A-D were suspended in distilled water up to an optical density (A) of 0.05-0.1 at 420 nm. The suspensions were analysed in PMMA fluorescence cuvettes of 10 mm optical path. The absorption spectra were collected with a Perkin Elmer Lambda 650 C spectrophotometer and the emission spectra were collected with a Horiba Fluorolog 3 fluorimeter. The quantum yields were calculated using the equation 1.0. The refractive indexes of the solvents were sourced from the manufacturer's specifications.

$$\boldsymbol{\Phi}_{\rm S} = \frac{\rm Abs_{\rm R}}{\rm Abs_{\rm S}} \times \frac{\rm Area_{\rm S}}{\rm Area_{\rm R}} \times \frac{n_{\rm S}}{n_{\rm R}} \times \boldsymbol{\Phi}_{\rm R}$$

	Atomic %					
Sample ID	O (1s)	C(1s)	K(2p)	$\mathbf{S(2p)}^{*}$		
Control	33.85	51.08	14.55	0.51		
SCX4	22.59	72.81	0	4.61		
Sample A	28.39	57.03	11.77	2.82		
Sample B	25.94	60.15	11.9	2.01		
Sample C	30.74	48.52	12.07	3.94		
Sample D	46.36	23.86	21.34	5.94		

Table S1. XPS elemental composition of GQD and SCX4.

*Residual S(2p) as a result of the Hummers synthetic process where sulfuric acid was used.



Figure S1. TEM image of sample A (a) under a high magnification (x500K) and (b) the corresponding SEAD image.

FT-IR spectroscopy



Figure S2. FT-IR spectra of GQD.

Raman Spectroscopy



Figure S3. Raman spectra of GQD.



Figure S4. Raman spectra of GQD at selected wavenumber range.

SCX4	Sample A	Sample B	Sample C	Sample D
1116.34	1107.65	1109.04	1110.57	1112.62
1274.1	1298.95	1234.24	1209.67	1182.57
1301.69	1325.75	1293.61	1237.17	1237.17
1450.97	1464.92	1329	1287.12	1298.56
1478.23	1464.92	1439.87	1352	1352
1587.71	1586.7	1469.48	1443.16	1443.16
1607.35		1581.5	1477.43	1472.53
			1577.82	1586.3

Table S2. Raman peaks data values for GQD.

Control reaction of the GQD in the presence of 4-hydroxybenzenesulfonic acid



Figure S5. (a) TEM images of graphene quantum dots synthesised in the presence of 4hydroxybenzenesulfonic acid showing a cluster of nanoparticles and (b) corresponding photoluminescence (PL). The sample exhibited negligible quantum yield.



Figure S6. Photoluminescence (PL) data of the GQD showing tuneable excitation behaviour.

References:

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