Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Synthesis of N, F and S Co-Doped Graphene Quantum Dots

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1. Synthesis of CNTs by CVD method:

Materials: MWCNT arrays of average diameter 50-80 nm were synthesized by the CVD technique.[1] The synthetic details of CVD grown MWCNTs have been given in the supporting information along with a field emission - SEM image (**Figure S1**, supporting information). 1-methyl-1-propylpiperidiniumbis(trifluoro-methylsulfonyl) imide, (IL) (99% Sigma Aldrich, Figure 1) and an Emerson microwave (1100 W output power) were used.

Materials Characterization: Transmission electron microscopy (TEM) images of GQDs were taken using a Make-FEI TEM (Model-TECNAI G^2 20, Voltage-200 kV, Wave length- 0.0024 nm). GQDs were dispersed in DMF and the UV-Vis absorption spectra were obtained using a (Varian, Cary 5000) UV-VIS-NIR Spectrophotometer. Raman spectroscopy was carried out using (Renishaw make) a laser of wavelength 632.8 nm. Photoluminescence studies were carried out using Fluorescence Spectrophotometer (make Varian). XRD was carried out using powder X-ray Diffractometer by Bruker with Al Kα (1.54 Å) x-ray as an excitation source and IR spectrum was recorded using a BRUKER TENSOR 27 FT-IR Spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out using PHI-5000C ESCA system. SEM imaging was carried out by a FEI Quanta 400 FEG scanning electron microscope.

CNTs were synthesized using liquid chemical vapor deposition (CVD) technique at 900^{o}C in argon/hydrogen atmosphere. Benzene and ferrocene were used as precursor. The quartz tube was preheated to 900^{o}C in argon atmosphere and then precursor solution was injected in the quartz tube at a flow rate of 12ml/hr in argon and hydrogen ambience of 800 SCCM and 200 SCCM respectively. CNTs were formed in the hot zone of quartz tube. We have collected these CNTs after cooling in argon ambience. These CNTs were annealed in air at 360^0C for 3 hrs to remove other carbonaceous impurities. **Figure S1** represents a SEM image of the synthesized CNTs on silicon wafer.

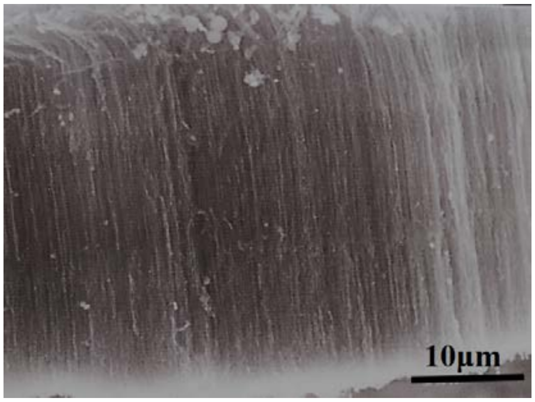

Figure S1: SEM image of CNTs

2. Photoluminescence Quantum Yield (QY) calculation:

Quinine sulfate in 0.1 N sulfuric acid (QY 0.54) was chosen as a standard. For the experiment both the solutions (sample and standard) were taken in very dilute concentration to avoid molecular interactions. 375 nm excitation maxima was fixed for both the standard and sample. Slit width was taken 2.5 nm. At 375 nm both of them showed maximum emission intensity. Same dilute solution was used for PL measurements. **Figure S 2** (a) represents the corresponding UV-VIS absorption and the Fig S 2 (b) shows the PL of standard solution and our co doped GQD sample. And the **Figure S 2** (c) shows the PL of undoped GQDs.QY was calculated using following formula

$$ø = ø_r . (I/I_r) .(A_r/A) . (n^2/n_r^2)$$

where ø = quantum yield, I is the integrated emission intensity, n is the refractive index of the solvent (dimethyl formamide, DMF = 1.43, water = 1.33), A is the optical density. The subscript "r" refers to the reference standard with known quantum yield. Table S 1 contains all the required data for the QY calculation. We can see from table of PLQY that the doped GQDs show an enhanced QY (70%) compared to undoped one (13%).

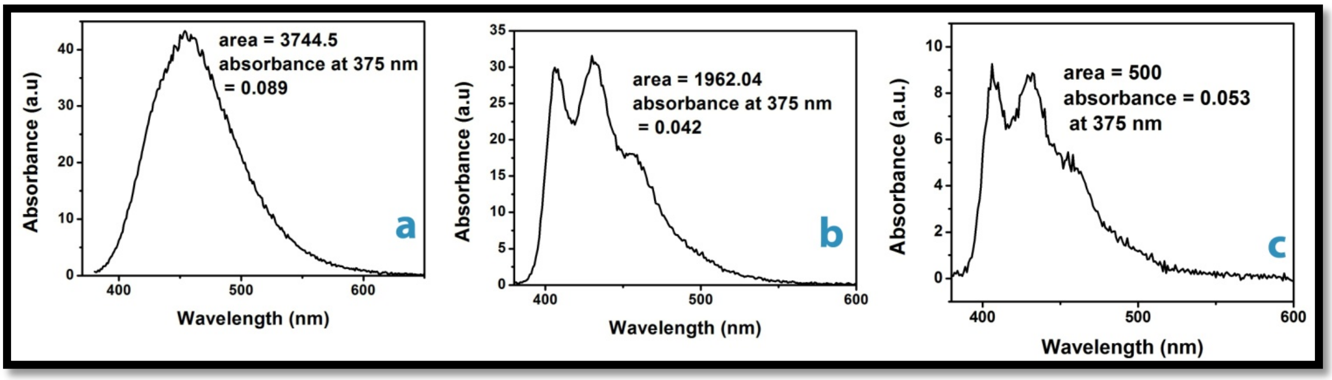

Figure S2 : (a) PL of Quinine sulfate (standard) in 0.1 N sulfuric acid at 0.089 absorption maxima at 375 nm wavelength in UV-Vis. (b) PL of co-doped GQDs in DMF at 0.042 absorption maxima at 375 nm wavelength in UV-Vis. (c) PL of GQDs (without doping) in DMF at 0.053 absorption maxima at 375 nm wavelength in UV-Vis.

Table S1: QY calculation data (slit width used = 2.5 nm)

Name of the sample	Integrated emission intensity (I)	A at 375 nm	Refractive Index (n)	Quantum yield(ø) (%)
Co-doped GQDs	1962.04	0.042	1.43	70
Quinine sulfate	3744.5	0.089	1.33	54
Without doping GQDs (synthesized by oxidation method)	500	0.053	1.43	13

3. Thermo gravimetric analysis (TGA) :

Thermal analysis has been carried out to judge the purity of the sample. **Figure S3** shows the TGA plot of the material in nitrogen atmosphere in a temperature range of 0-800 ^{o}C. By this experiment a weight loss percentage can be obtained with temperature. *Hsieh et al.*, have shown how heating rate can affect the weight loss onset temperature.[2] They have shown that weight loss onset temperature increases for MWCNTs with the increase in heating rate as well as concentration of acid treatment. They found the weight loss onset temperature of as grown MWCNTs is 551°C for 2°C/min and for acid treated MWCNTs is 597°C for 15N acid (HNO_3). They have carried out the TGA in presence of oxygen atmosphere.Whereas in our case a heating rate is 10°C/min has been used. It shows a nominal ~ 4 % weight loss at a temperature of 82.20°C. This could be due to the adsorbed water loss from the lattice. It shows a ~ 10 % weight loss at 352°C which could probably due to decomposition of sulfone groups which can be seen in the IR spectrum of the material **Figure 3** (d). Onset weight loss temperature has been observed here is at 570°C.

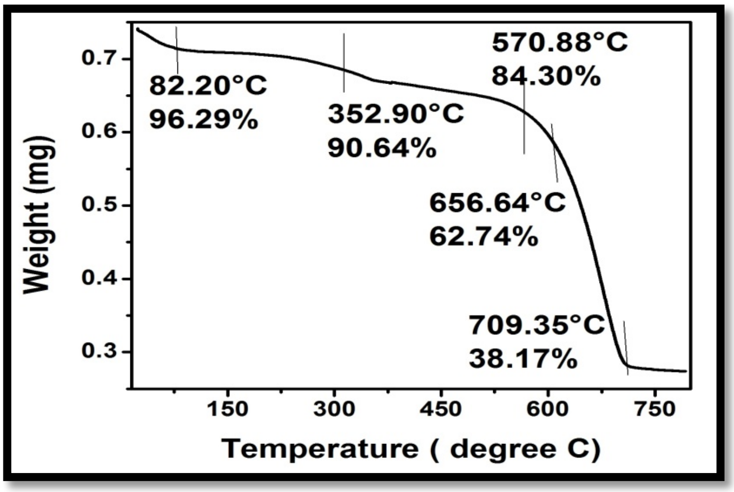

Figure S3 : Thermogravimeric analysis of co-doped GQDs from 0°C to 800°C in nitrogen atmosphere

Table S2: Different synthesis method with their various parameters :

Methods	Starting material	Size (nm)	Height (nm)	Color	Yield (%)	Quantum yield	Reference
Acidic oxidation	GO	~3	1.45	Blue			3
	Carbon black	15	0.5	Green	44.5		4
	Carbon fibers	1-4	0.4-2	Blue, Green,			5

	Coal			Yellow			
		2.30±0.78	1.5-3	Yellow, Green, Blue	20		6
Hydrothermal	GO	5-13	1-2	Blue	5	6.9	7
	GO	1.5-5	1.5-1.9	Green			8
Amino-Hydrothermal	GO	2.5	1.13	Blue to Yellow			9
Solvothermal	GO	3-5	0.95	Green		11.4	10
Microwave	GO	2-7	0.5-2	Green, Blue		8	11
	Graphite	2-8	0.7-3	Blue to Green	70±5	9	12
Ultrasonic Chemistry	Graphene	3-5		Blue		3.4	13
Electrochemistry	Graphene	3-5	1-2	Green			14
	Graphite rods	5-10	<0.5	Yellow		14	15
	MWCNTs	3±0.3	1-2	Green		5.1-6.3	16
		5±0.3	3	Green			16
		8.2±0.3	5	Green			16
		23±2		Green			16
Photo-Fenton	GO	40	1.2	Blue	45		17

Reaction							
Oxygen plasma etching	Graphene	11±4.3	4.5				18
K intercalation	MWCNTs	~20	<1	Blue	22.96	6.53	19
	Graphite flakes	~20	0.9	Blue	9.9		19
Stepwise solution Chemistry	Organic precursors	~ 2.5-5		Red			20, 21
Precursor pyrolysis	Glucose	1.65-2.1	3.2	DUV, blue			22
	Citric acid	~15	0.5-2	Blue		9	23
Catalyzed cage -opening	C_{60}	2.7-10			15-30		24
Pyrolysis and Exfoliation	Unsubstituted HBC	~60	2-3	Blue			25
Thermal plasma jet	Ethylene gas, carbon tubes	10-19	< 1			13.5	26
Hydrothermal Cutting (Boron doped GQDS)	Boron doped graphene	2-4	0.5-0.8	Blue			27

Electrolysis (Sulfur doped GQDs)	Graphite	2-4	0.7	Blue to Green		10.6	28
Electrochemical method (N doped GQDs)	Graphene and Tetrabutyl ammonium perchlorate	2-5	1-2.5	Blue			29
Hydrothermal (N doped GQDs)	Citric acid	1.8-3.8	0.5-2	Blue		94	30
Hydrothermal (S, N co-doped GQDs)	Citric acid, Urea	2.69± 0.42	0.5-2	Yellow Green		71-78	31
Hydrothermal (S, N co-doped GQDs)	Oxidized graphene, ammonia, powder S	2.4-5.35		Blue		18.6	32
Hydrothermal	Pyrene	2.4-4.8	0.9-1.9	Yellow, Blue, Green, Cyan	63		33
(Hydroxyl functionalized						23	33

GQDs)							
(Amine functionalized GQDs)						7	[33]
(-NH-NH_2 functionalized GQDs)						26	[33]
Acidic oxidation (Amino functionalized GQDs)	GO, ammonia	5-7		Blue, Green, Cyan			[34]
Microwave (S, N, and F co-doped GQDs)	MWCNTs	~ 2	1	Green	~ 85	70	This work

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