Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

Ultrasonic-Assisted Synthesis of Leather-Derived Luminescent Graphene Quantum Dots: Catalytic Reduction and Switch on-off Probe for Nitro-Explosives

Shamsa Kanwal^{a,b,c}, Shanaz Jahan^c, Farukh Mansoor*a



Figure S1: TEM images of GOS oxidative cleavage (a), shortening of GOS sheets (b), production of GONFs (c) and GOQDs (d) during the synthesis of GQDs.



Figure S2: UV-visible (a) and PL spectra (b) of GQDs under nitric acid oxidation at successive ultrasonic time intervals (5-50 min).



Figure S3: PL spectra of GQDs (70 μ L to 5 ml H₂O) at different excitation wavelengths from 270 nm to 420 nm (a); The representative PL spectra of GQDs before and after 24 h exposure to UV-lamp at 360 nm wavelength (b).



Figure S4: Raman spectra of GQDs



Figure S5: FTIR spectra of GQDs



Figure S6: Effect of NaCl concentration on PL intensity of GQDs GQDs+NaCl after 30 mins GQDs+NaCl after 24 h



Figure S7: FTIR spectra I of pure PNP; and II of PNP-GQDs mixture under 360 nm UV irradiation for 2 h.



Figure S8b: H¹-NMR for PNP-NaBH₄-GQDs in deionized water.



Figure S8c: H¹-NMR for PNP-GQDs (under UV-illumination for 2 hours) in deionized water.



Figure S9a: H¹-NMR for pure TNP in deionized water.



Figure S9b: H¹-NMR for TNP-GQDs (under UV illumination for 2 h) in deionized water.



Figure S10: Photocatalytic reduction of PNP, DNP and TNP in the presence of interfering species. The concentration of fluorene, HA, TNT, pyrene, Hg^{2+} , Cd^{2+} and Pb^{2+} was 10 nM and for 2, 4 DCP, PCB-28, PCB-52, PCB-153 was 50 nM. Whereas, 100 nM concentration was used for, Cu^{2+} and Ni^{2+} .

	Amount/Concentration	Absorbance	PL
Reaction parameters			
	(mg or N)	I/270 nm	I/420 nm
	-		
	3 mg	0.188	200
	6 mg	0.339	600
Cranhite course concentration	0	1.972	075
Graphite source concentration	9 mg	1.8/2	8/3
	12 mg	0.392	420
	0.25N	1.112	130
	0.5N	1.442	770
~			
Concentration of HNO ₃	1N	1.875	874
	2) I	1 101	000
	2N	1.101	800

Table S1: Specified UV-Vis and PL peak intensities/wavelength with different carbonized source and HNO₃ concentration (20 min ultrasonication).

Table S2: FTIR peak assignments/intensities of few specific functional groups of graphitic products with respect to ultrasonication reaction time (RT) and their related band gaps (eV).

FTIR peaks & Related band gap (eV)	Peak intensity @5RT/30°C	Peak intensity @10RT/40°C	Peak intensity @15RT/50°C	Peak intensity @20RT/60°C	Peak intensity @25RT/70°C	Peak intensity @40RT/90°C
Carbonyl (C=O) at 1709 cm ⁻¹	-	89%T	88%T	86%T	84%T	-
Epoxy (C-O- C) at 1042 cm ⁻¹	98%T	94%T	92%T	91%T	89%T	-
Related band gap (eV)	0.82 eV	0.87 eV	0.90 eV	0.96 eV	1.00 eV	1.04 eV

Table S3: FTIR peak characterization of some assigned groups before and after addition of 5 nM catalyst GQDs into 2 mL of 1 µM PNP.

S. No.	FTIR Assigned Peaks	Spectral Data I	Spectral Data II		
	PNP				
1.	NO ₂ rocking vibration at 535 cm ⁻¹ \checkmark		-		
	NO ₂ scissoring at 629 cm ⁻¹ \checkmark		-		
	NO ₂ wagging at 755 cm ⁻¹	~	-		
	PNP+GQDs				
2.	Symmetric N-H stretch at 3236 cm ⁻¹	-	~		
	Asymmetric N-H stretch at 3410 cm ⁻¹	-	~		
	N–H bending vibration at 1662cm ⁻¹	-	~		

Table S4: Linear ranges, LODs and regression equations for detection of nitrophenols on PL quenching of GQDs.

Type of nitrophenols	Ype of nitrophenols Linear detectable Concentration range		Regression equation, coefficient (I	
PNP	10-550 nM	10 pM	I= 914.97+(-1.038) C, 0.995	
DNP	20-310 nM	65 pM	I= 975.30+(-1.9502) C, 0.995	
TNP	10-500 nM	80 pM	I= 943.03+(-1.261) C, 0.996	

Samples	Nitrophenols detected nM, RSD, n=3	Samples Spiked ^a nM	Nitrophenols measured nM, RSD, n=3	Recoveries
Soil Sample 1	320.3±1.1 TNP	400 TNP	359.6±1.4 TNP	99.73%
Soil Sample 2	47.3± 2.3 TNP	52 TNP	49.3±2.1 TNP	98.6%
Industrial Water 1	90.3±1.7 PNP	100 PNP	95.4±1.9 PNP	101.3%
Industrial Water 2	120±2.1 PNP	135 PNP	127.4±3.1 PNP	99.7%

Table S5: Determination of PNP and TNP in industrial water and in soil samples, respectively.

^a1 mL of spiked solution was added to 1 mL of sample volume.