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Investigating the surface state of graphene quantum dots

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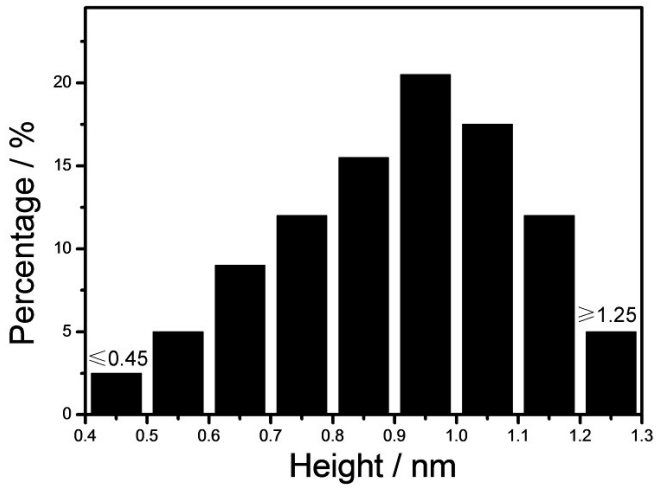


Figure S1. The height distribution of GQDs determined by AFM image.

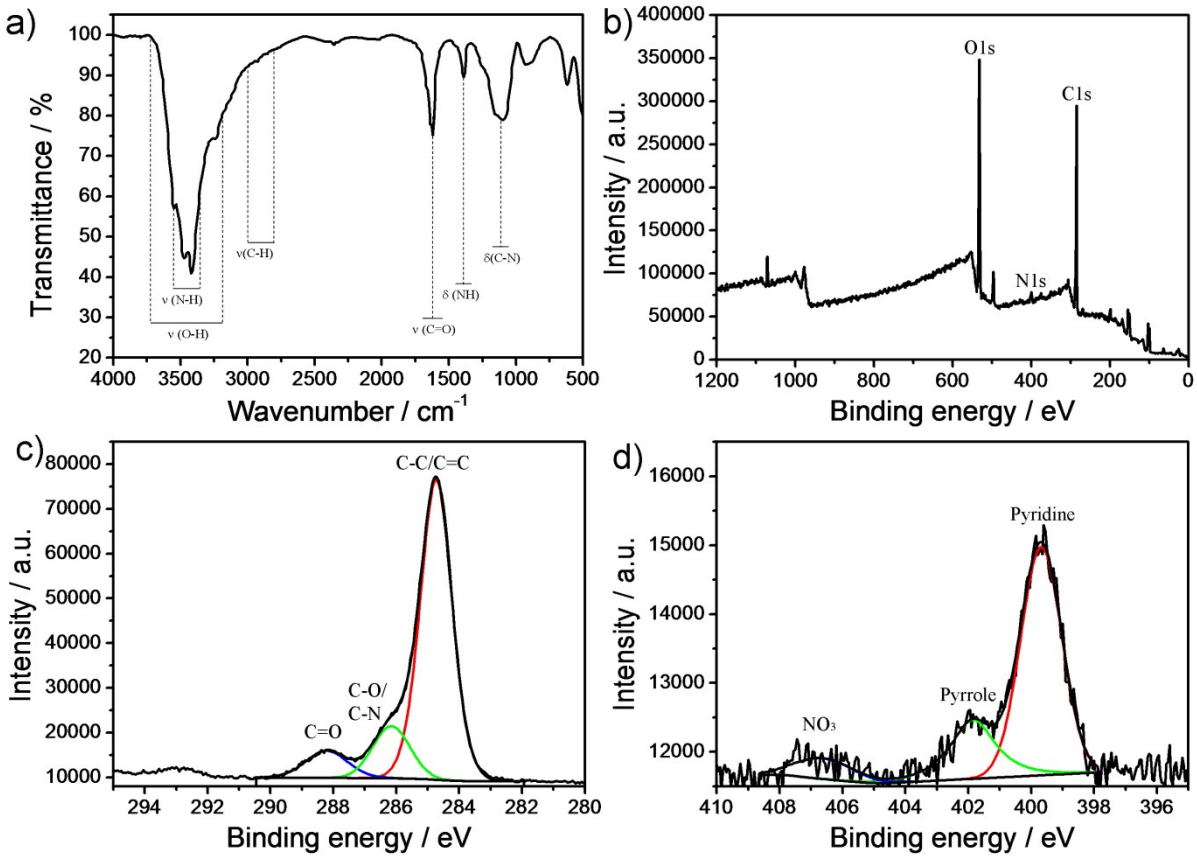


Figure S2. a) The FT-IR spectra of GQDs, b-d) XPS analysis of GQDs.

Data note:	C-C/C=C	C–O or C-N	O=C or COOH	Pyridine-like N	Pyrrole-like N	$-NO_2$ or $-NO_3$	O
Peak Binding Energy / eV	284.73	286.15	288.22	399.68	401.86	406.62	532.05
GQDs (%)	49.52	5.92	9.95	1.76	0.58	0.23	32.04

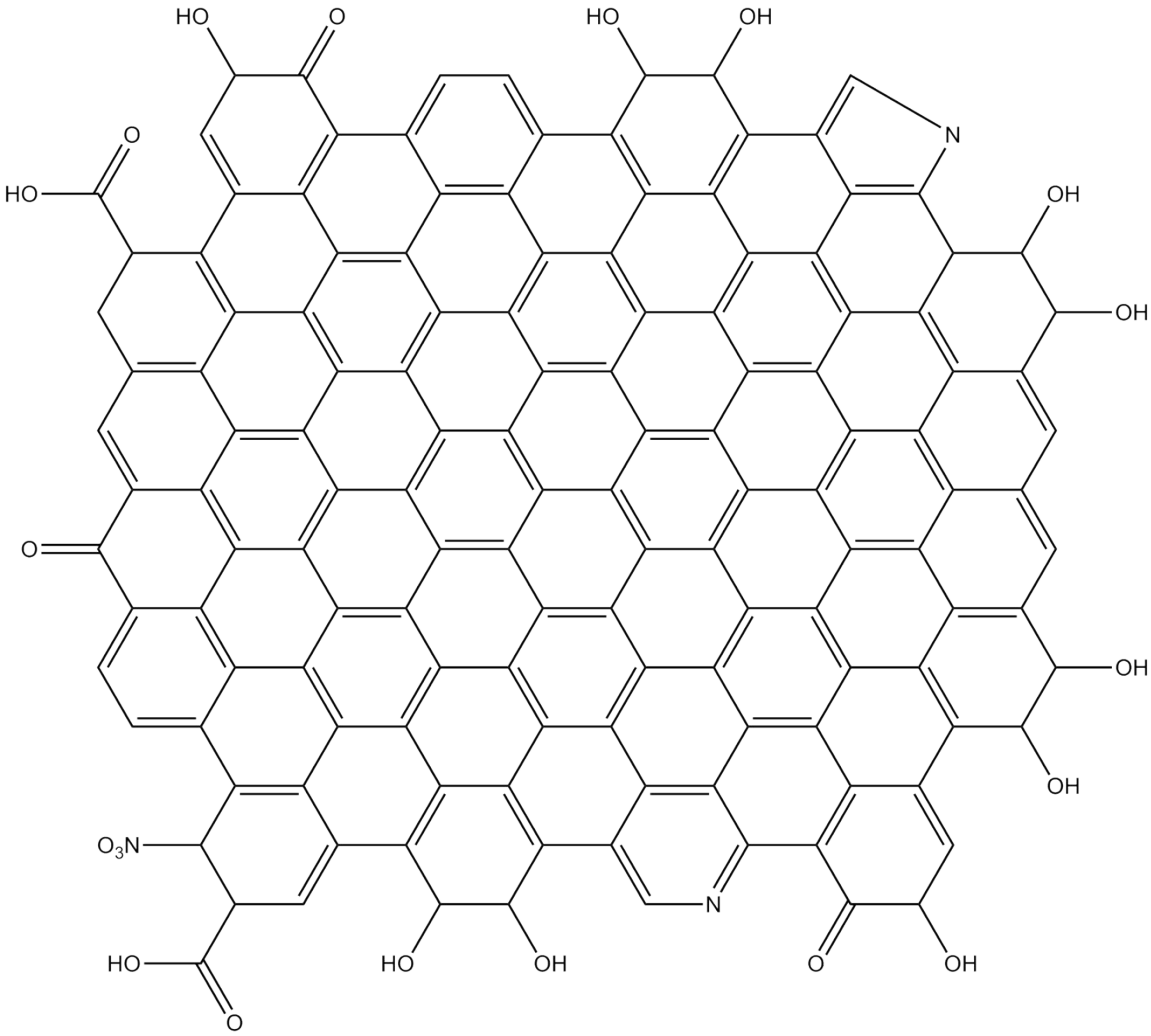


Figure S3. The possible chemical structure of GQDs. Note: the pyrrole-like and pyridine-like nitrogen were possibly endowed in the acid cutting process, the NO_3 could also be NO_2 groups.

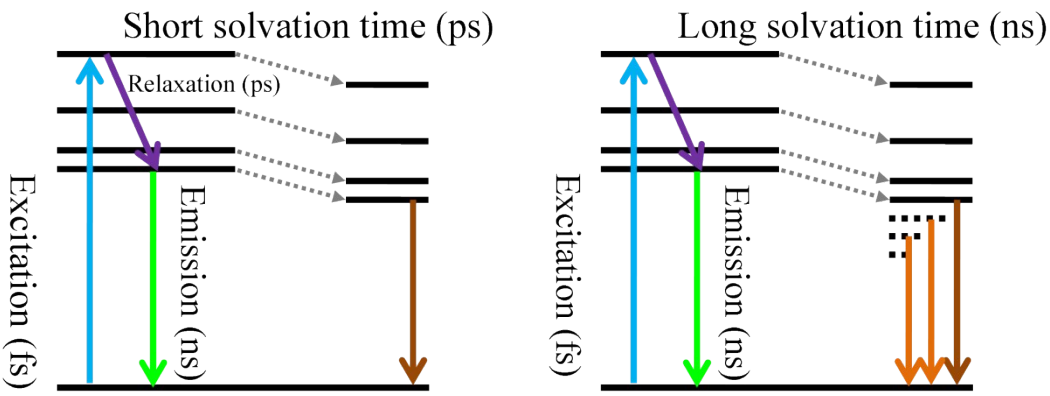


Figure S4. The solvation effect of GQDs in organic solutions (a)[1] and water (b).

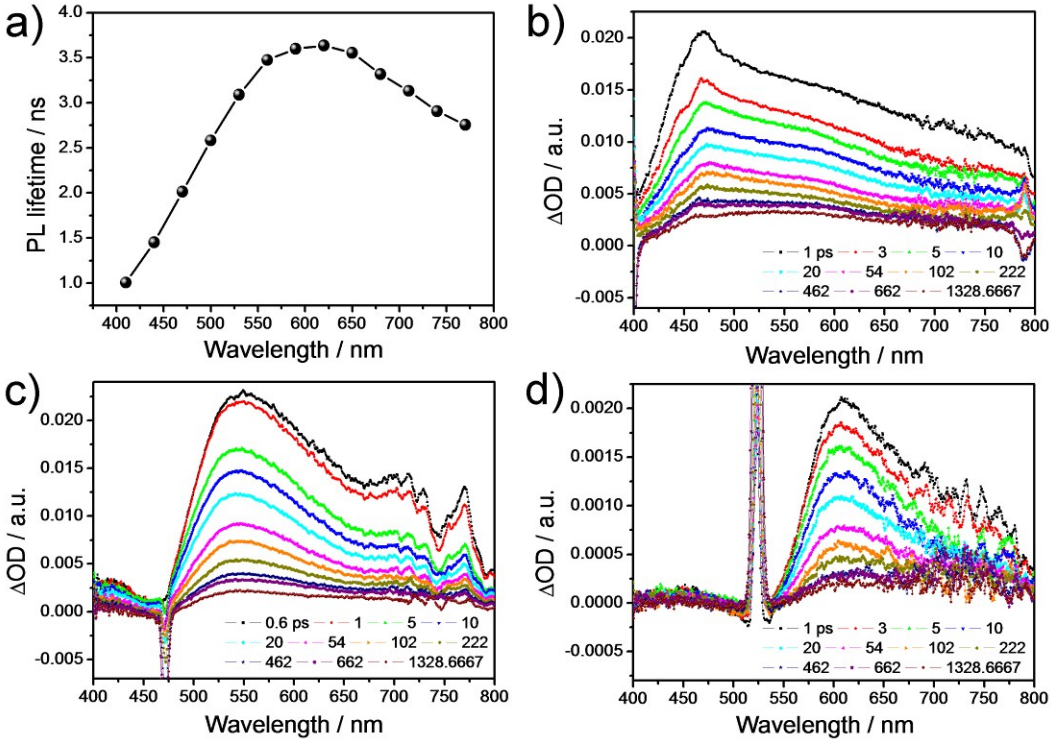


Figure S5. The excited behaviors of GQDs. a) The average PL lifetime of bare GQDs at the different probed wavelength (375 nm excitation, and the concentration of GQDs was 0.5 mg/mL). b-d) Transient spectra of GQDs at 400, 470 and 530 nm excitation, respectively.

Note: the lifetime in Figure S5a contained two nanosecond components.

Detected wavelength	τ_1 (ns)	Percent (%)	τ_2 (ns)	Percent (%)	$\tau_{average}$ (ns)
410 nm	0.55	87.26	4.12	12.74	1.004818
440 nm	0.67	81.48	4.89	18.52	1.451544
470 nm	0.72	69.43	4.95	30.57	2.013111
500 nm	0.83	61.22	5.35	38.78	2.582856
530 nm	0.96	54.48	5.64	45.52	3.090336
560 nm	1.2	52.39	5.98	47.61	3.475758
590 nm	1.2	49.27	5.93	50.73	3.599529
620 nm	1.42	51.84	6.02	48.16	3.63536
650 nm	1.48	53.79	5.97	46.21	3.554829
680 nm	1.39	55.17	5.69	44.83	3.31769
710 nm	1.38	58.79	5.63	41.21	3.131425
740 nm	1.2	59.74	5.44	40.26	2.907024
770 nm	1.15	62.92	5.48	37.08	2.755564

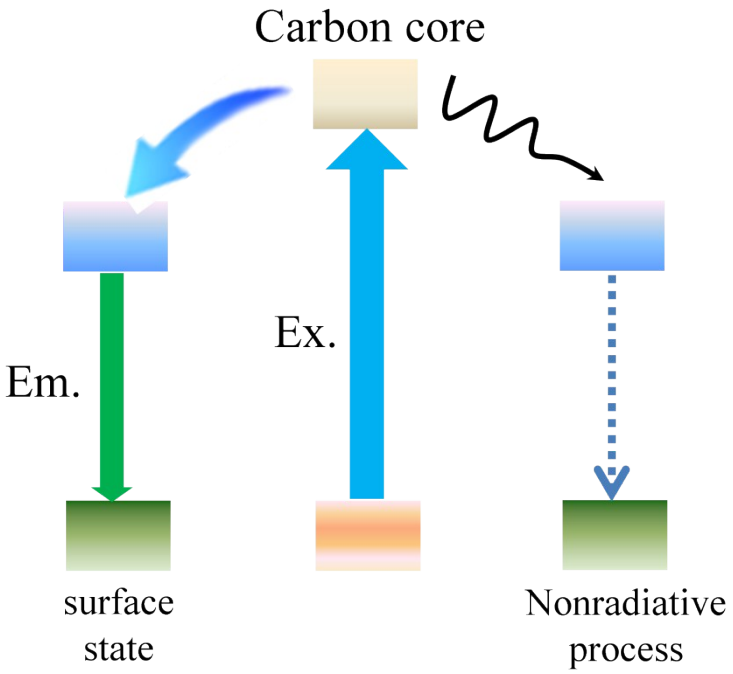


Figure S6. It was possible that the UV exposure can destroy the nonradiative structure while the percentage of the radiative process increased (shown in Fig. 3c, τ_1 was the short lifetime for the nonradiative process while the τ_2 was the long lifetime for the nonradiative process).

Table S1. The lifetime of the GQDs at 2000W UV light exposure (375 nm excitation and probed at 530 nm, the concentration of GQDs was 0.01 mg/mL).

Time of UV exposure	τ_1 (ns)	Percent (%)	τ_2 (ns)	Percent (%)	$\tau_{average}$ (ns)
0	1.35	43	5.78	57	3.8751
1	1.44	43.29	6.03	56.71	4.042989
2	1.38	38.59	6	61.41	4.217142
3	1.39	37.14	5.99	62.86	4.28156
4	1.47	40.27	6.24	59.73	4.319121
5	1.49	38.75	6.28	61.25	4.423875
7.5	1.47	34.64	6.26	65.36	4.600744
10	1.54	35.91	6.37	64.09	4.635547
15	1.64	34.82	6.51	65.18	4.814266
20	1.63	31.13	6.49	68.87	4.977082
30	1.85	31.98	6.84	68.02	5.244198
60	2.09	28.48	7.09	71.52	5.666

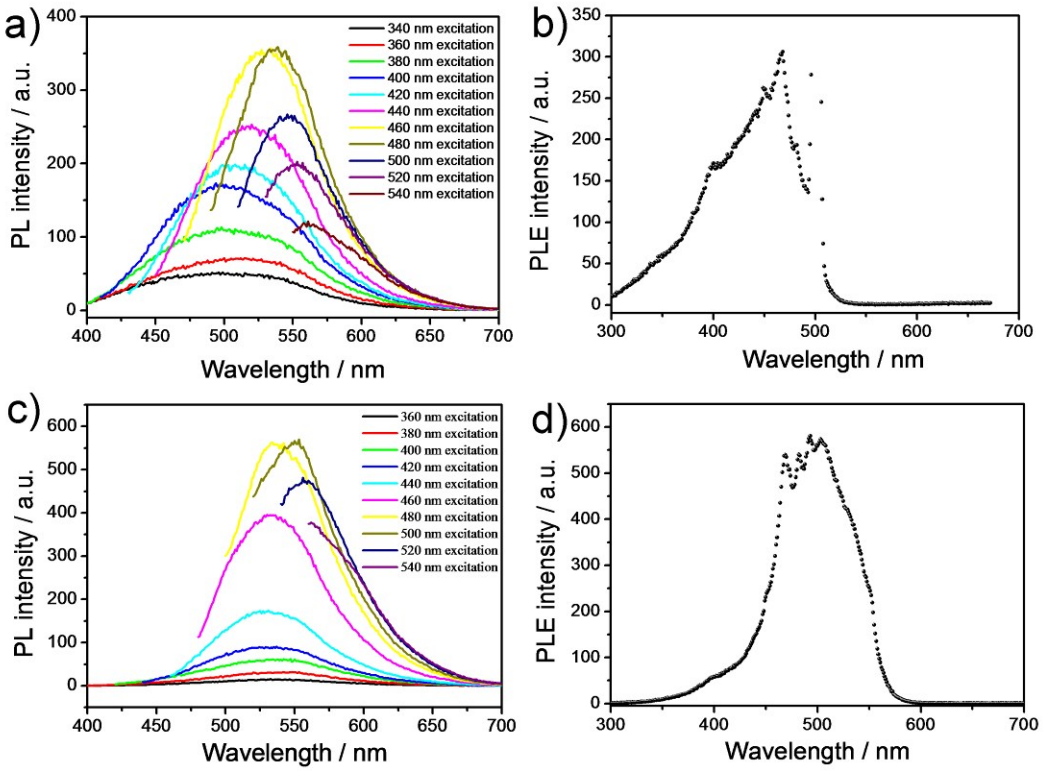
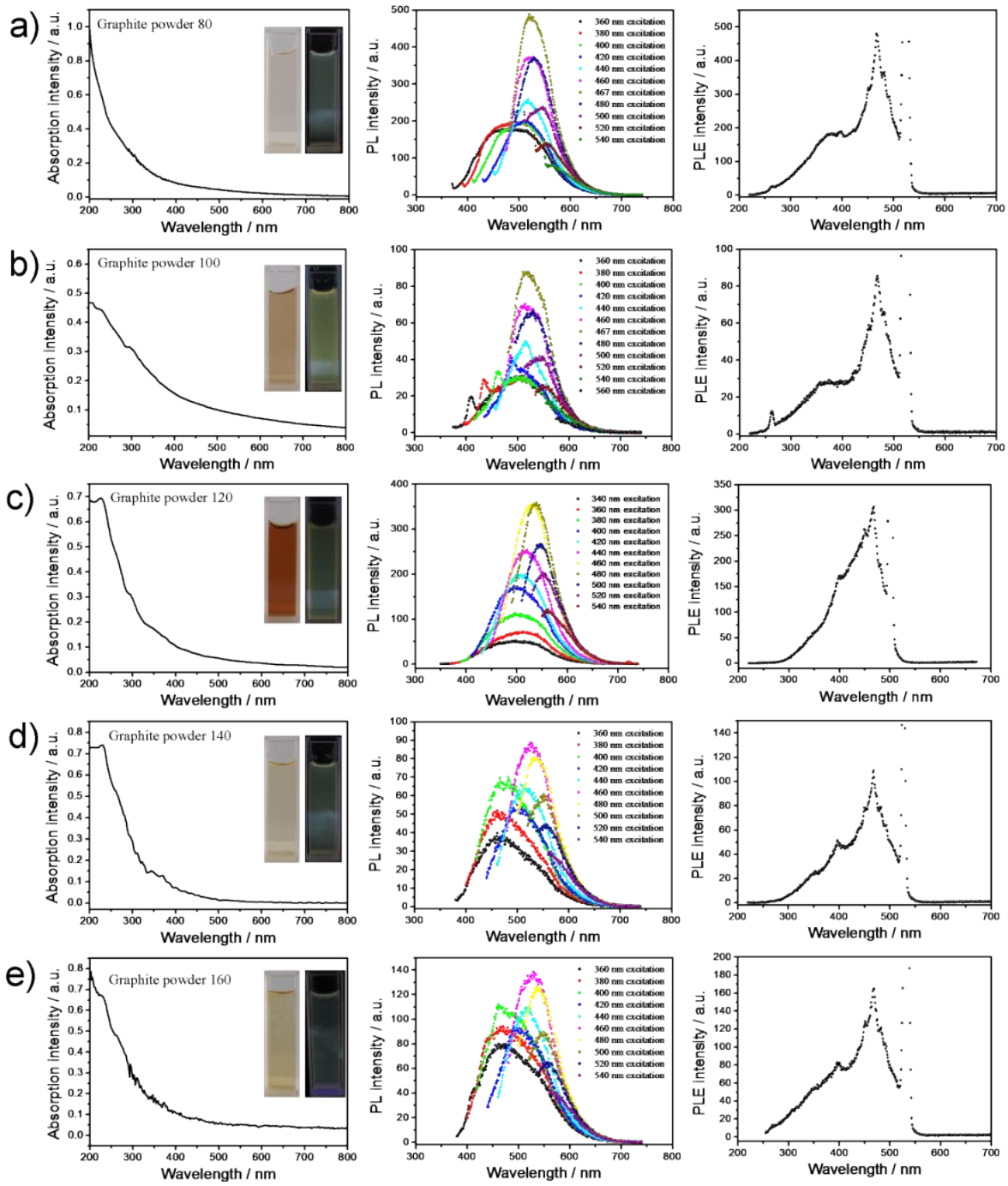


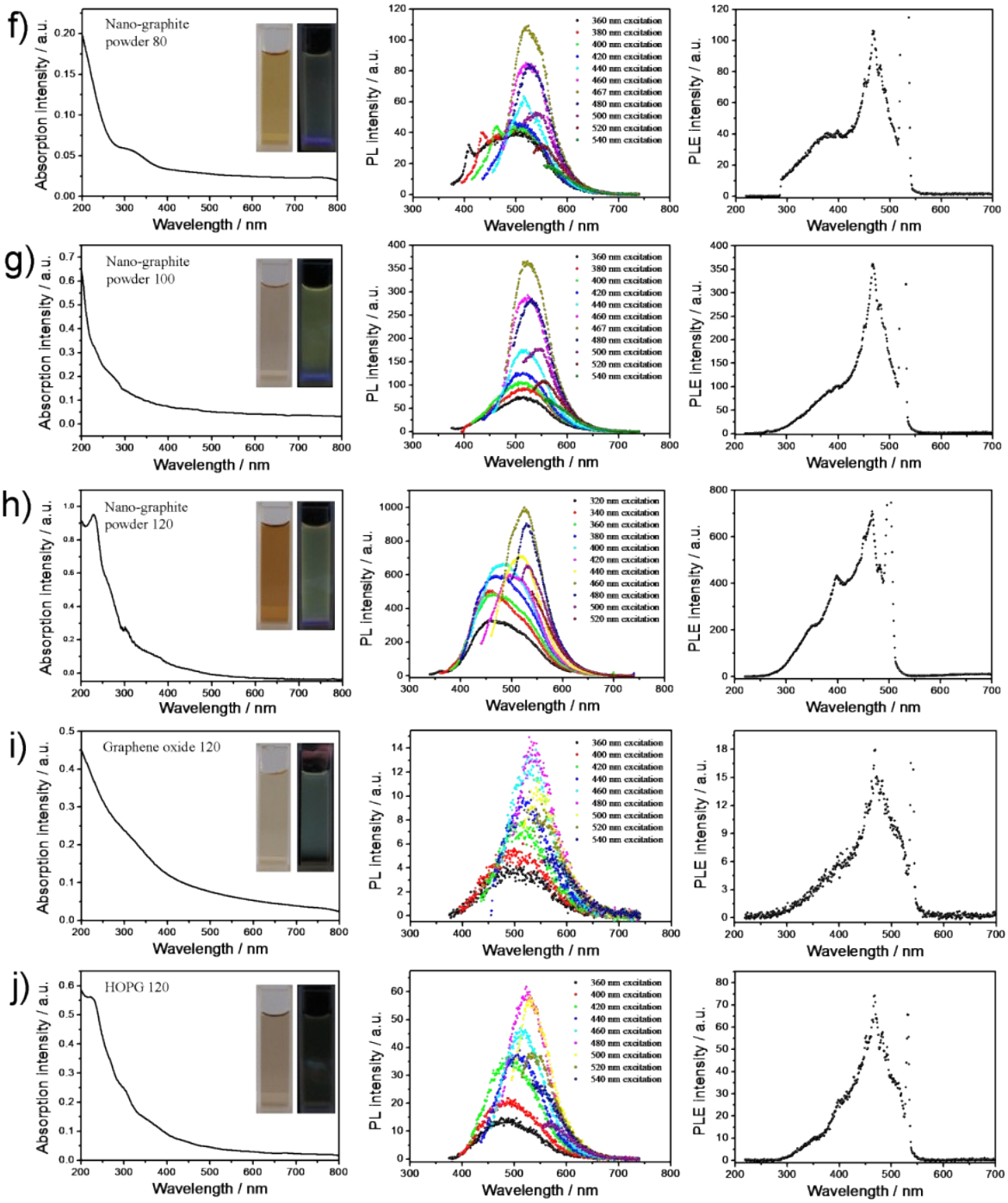
Figure S7. a-b) The excitation-dependent PL and PLE of GQDs at low concentration (0.05 mg/mL) aqueous solution. c-d) The excitation-dependent PL and PLE of GQDs at high concentration (2 mg/mL) aqueous solution.

Table S2. Other reaction conditions for GQDs.

Serial	Reaction materials	Reaction temperature / °C	Quantum yields / %	Lifetime /ns	PL peak / nm	Z-potential
1	Graphite powder	80	<1	3.58	525	-16.8
2	Graphite powder	100	<1	3.52	524	-18.5
3	Graphite powder	120	<1	3.09	535	-6.1
4	Graphite powder	140	<1	2.05	527	-13.7
5	Graphite powder	160	<1	2.49	526	-7.4
6	Nano-graphite powder	80	<1	3.54	524	-10.1
7	Nano-graphite powder	100	<1	3.26	524	-10.9
8	Nano-graphite powder	120	<1	2.86	523	-6.5
9	Graphene oxide	120	<1	2.68	535	-31.8
10	Highly oriented pyrolytic graphite	120	<1	2.64	524	-16.8
11	Single-wall carbon nanotube	120	<1	2.63	530	-15.9
12	Multi-wall carbon nanotube	120	<1	2.33	532	-19.9
13	Fullerene	120	<1	2.46	498	-15.3

Note: The reaction temperature was chosen at 120 °C. The lower temperature (80 °C and even 100 °C) lead to the incomplete reaction, while the higher temperature (140 °C and even 160 °C) resulted in the low yield of GQDs due to the over oxidation (most of the carbon resource was converted into the CO_2 and H_2O).


a)
Graphite powder 80
Absorption intensity / a.u.
Wavelength / nm
PL intensity / a.u.
360 nm excitation
380 nm excitation
400 nm excitation
420 nm excitation
440 nm excitation
460 nm excitation
467 nm excitation
480 nm excitation
500 nm excitation
520 nm excitation
540 nm excitation
PLE intensity / a.u.
b)
Graphite powder 100
560 nm excitation
c)
Graphite powder 120
340 nm excitation
d)
Graphite powder 140
e)
Graphite powder 160


f)
Nano-graphite powder 80
Absorption intensity / a.u.
Wavelength / nm
PL intensity / a.u.
360 nm excitation
380 nm excitation
400 nm excitation
420 nm excitation
440 nm excitation
460 nm excitation
467 nm excitation
480 nm excitation
500 nm excitation
520 nm excitation
540 nm excitation
PLE intensity / a.u.
g)
Nano-graphite powder 100
h)
Nano-graphite powder 120
320 nm excitation
340 nm excitation
i)
Graphene oxide 120
j)
HOPG 120

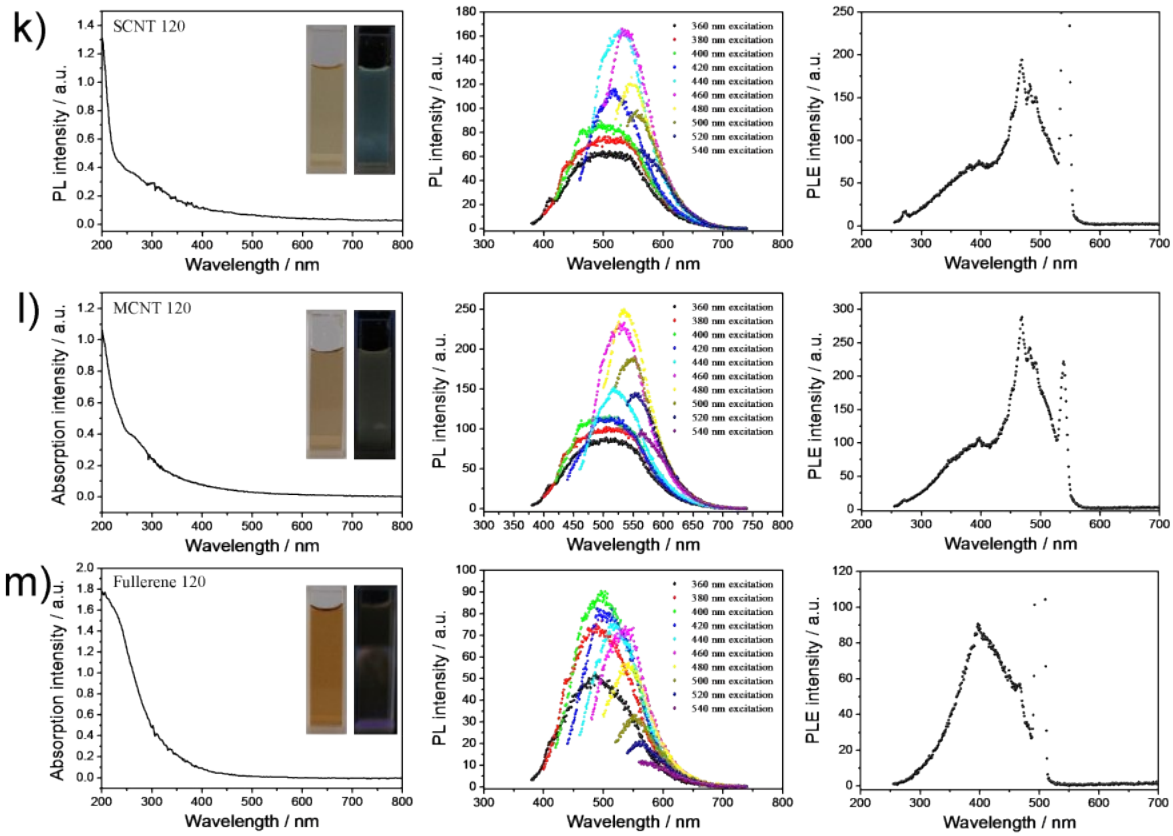
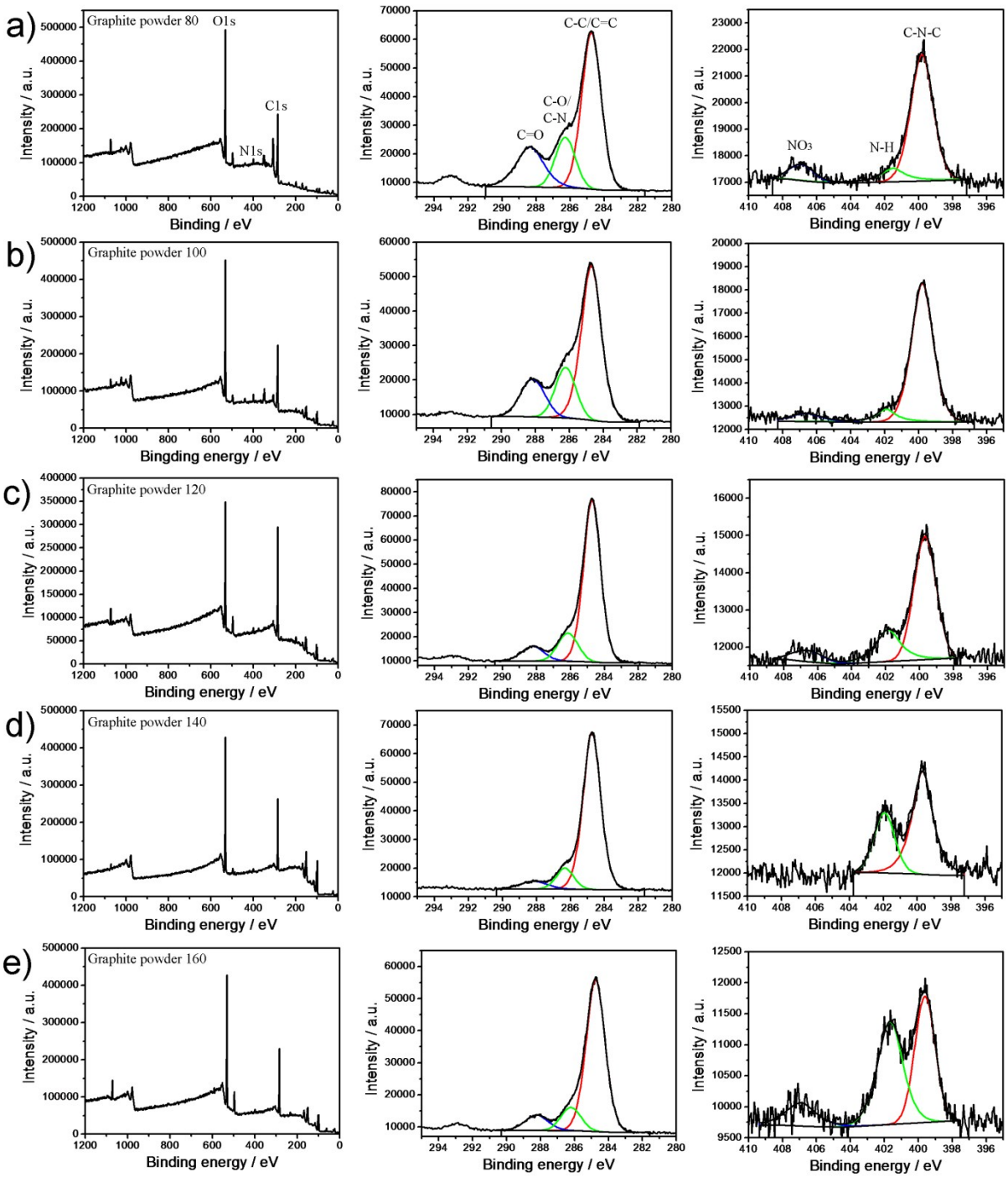
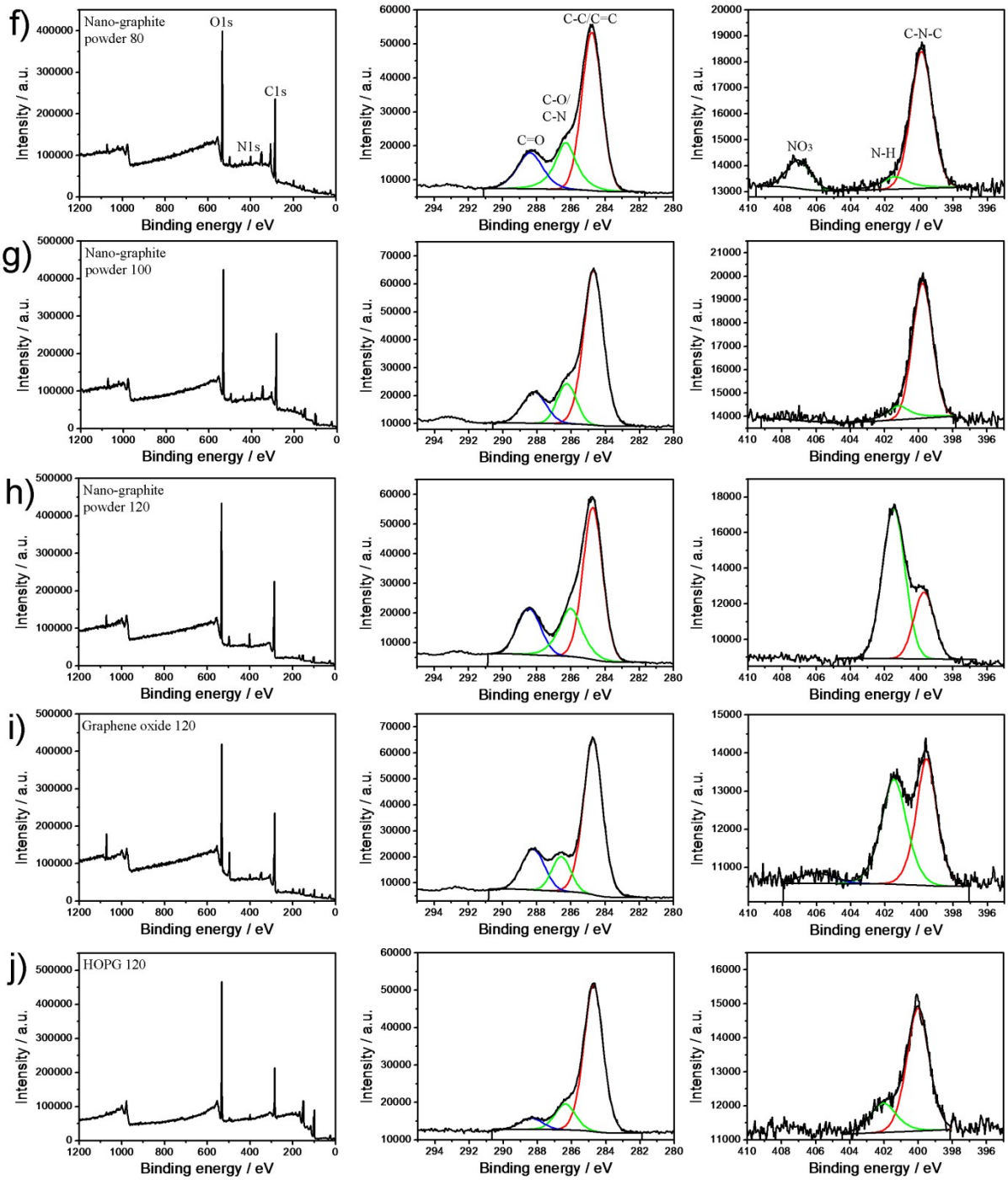


Figure S8. The absorption, PL and PLE spectra of GQDs prepared by other conditions. **Note:** The (c) was the data from Figure 2.


a)
Graphite powder 80
O1s
C1s
N1s
C-C/C=C
C-O/
C-N
C=O
C-N-C
NO3
N-H
b)
Graphite powder 100
c)
Graphite powder 120
d)
Graphite powder 140
e)
Graphite powder 160
Intensity / a.u.
Binding / eV
Bingding energy / eV
Binding energy / eV


f)
Nano-graphite powder 80
O1s
C1s
N1s
C-C/C=C
C-O/ C-N
C=O
C-N-C
NO3
N-H
g)
Nano-graphite powder 100
h)
Nano-graphite powder 120
i)
Graphene oxide 120
j)
HOPG 120
Intensity / a.u.
Binding energy / eV

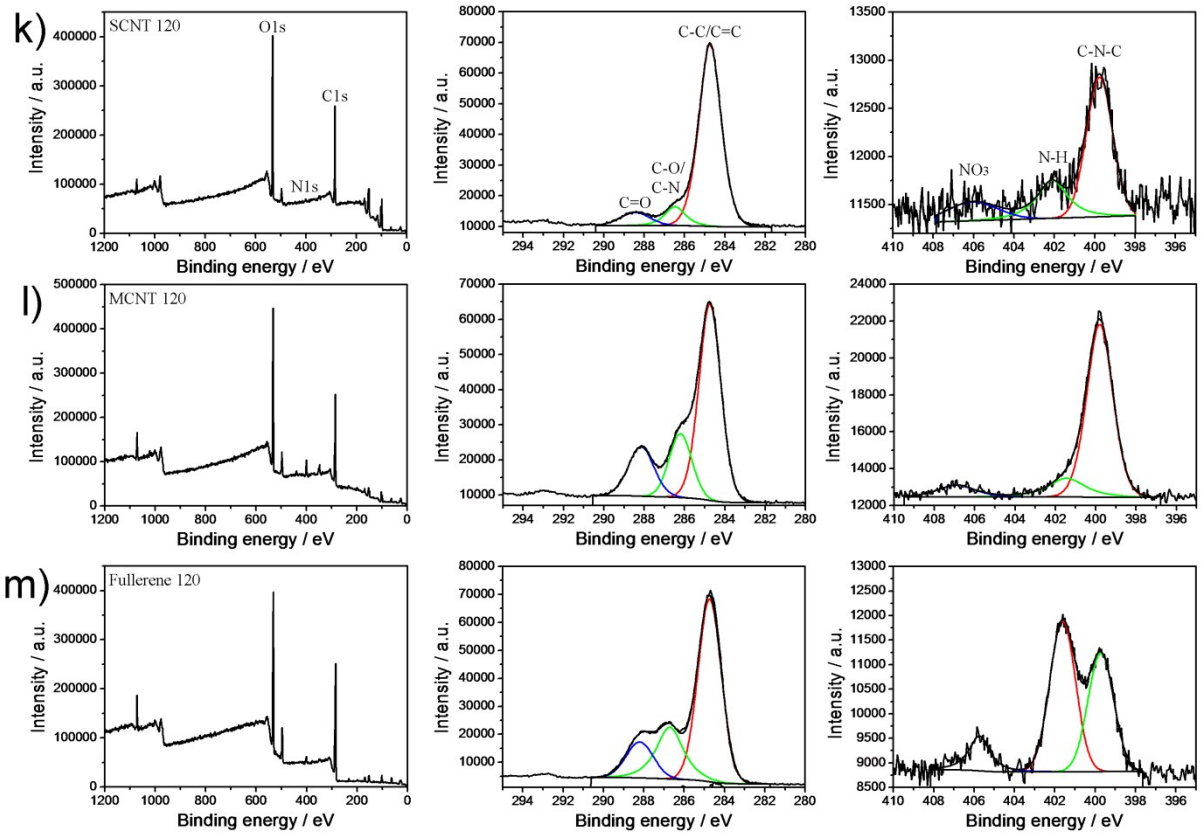


Figure S9. The XPS of GQDs prepared by other conditions.

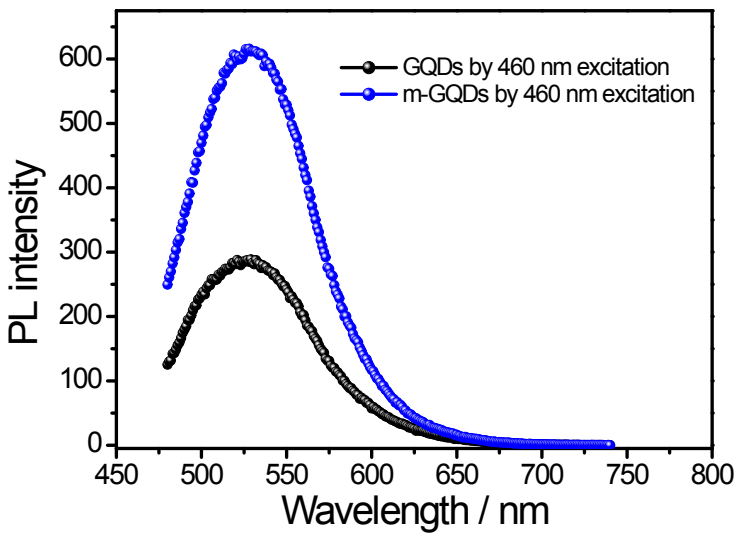


Figure **S10.** The PL of GQDs and m-GQDs aqueous solution with the same concentration (0.05 mg/mL) and 460 nm excitation. The m-GQDs possessed higher green emission than that of GQDs, because the amide was the stronger green PL center than –COOH.

Table S3. The lifetime of the m-GQDs at 375 nm excitation and probed at different wavelength sections (375 nm excitation, the concentration of m-GQDs was 0.05 mg/mL).

Detected wavelength	τ_1 (ns)	Percent (%)	τ_2 (ns)	Percent (%)	$\tau_{average}$ (ns)
410 nm	1.6	66.38	5.98	33.62	3.072556
440 nm	1.89	67.38	8.34	32.62	3.99399
470 nm	2.07	56.12	9.48	43.88	5.321508
500 nm	2.13	38.19	9.48	61.81	6.673035
530 nm	2.14	29.76	9.32	70.24	7.183232
560 nm	2.07	28.76	9.09	71.24	7.071048
590 nm	2.26	33.08	9.06	66.92	6.81056
620 nm	1.91	34.73	8.5	65.27	6.211293
650 nm	1.88	39.86	8.36	60.14	5.777072
680 nm	1.55	42.6	7.83	57.4	5.15472
710 nm	1.38	46.68	7.64	53.32	4.717832
740 nm	1.23	51.54	7.5	48.46	4.268442
770 nm	1.02	51.57	6.53	48.43	3.688493

[1] S. Zhu, L. Wang, B. Li, Y. Song, X. Zhao, G. Zhang, S. Zhang, S. Lu, J. Zhang, H. Wang, H. Sun, B. Yang, *Carbon* **2014**, *77*, 462-472.