Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Electrochemical Synthesis of Nitrogen-doped Carbon Dot Inks and Evaluation of their Use for Anti-Counterfeiting Applications

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XPS characterization of N-CDs

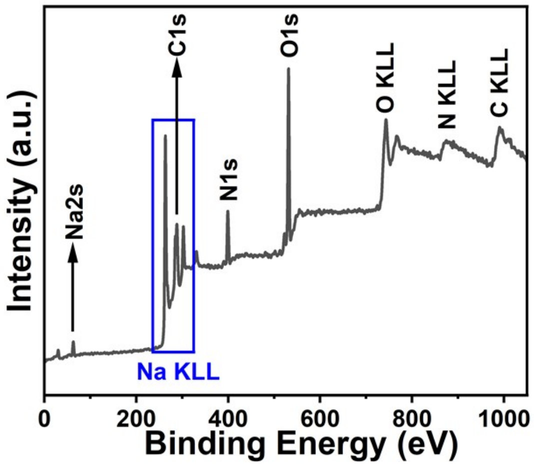


Figure S1. XPS spectrum of N-CDs

The atomic percentages of carbon, nitrogen, and oxygen, as presented in Table S1, were calculated from the intensities (peak area) of the XPS peaks, weighted with the corresponding Relative Sensitivity Factors (RSF) and considering the analyzer's transmission characteristics.

Table S1. Atomic percentages of carbon (C), oxygen (O), sodium (Na), and nitrogen (N) in the sample.

	C	O	N
Sample (%)	44.9	22.2	12.7

Table S2. Atomic concentrations (%) of the different kinds of C, N, and O.

		Sample (%)
C 1s	C-C sp^2	44.3
	C-C sp^3	5.1
	C-O(H), C≡N	11.8
	C=O	29.6
	COOH	9.1
N 1s	Pyridinic-like N	41.0
	Amine-like N	59.0
O 1s	C=O	84.0
	C-O(H)	16.0

Optical characterization of N-CDs as prepared

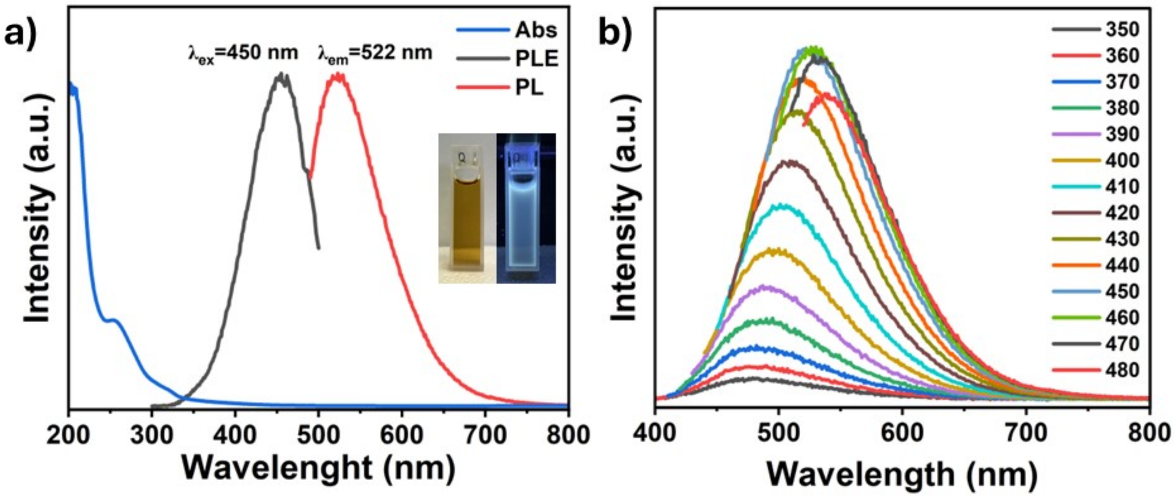


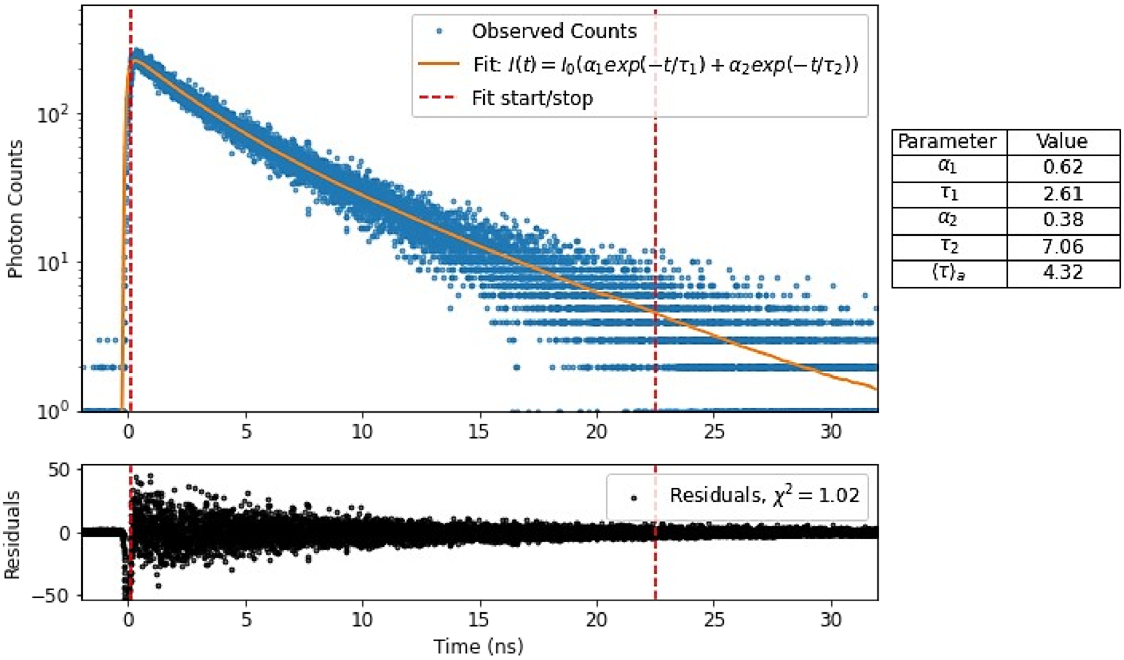
Figure S2. (a) UV-vis absorption, PL excitation and emission spectra of N-CDs as-synthesized. The insets show the optical images of N-CDs aqueous solution under daylight (left) and under UV light (365 nm). (b) Fluorescence spectra of N-CDs at different excitation wavelengths.

Lifetime measurements

Table S3. Details of α and τ *for each of the three measurements taken.*

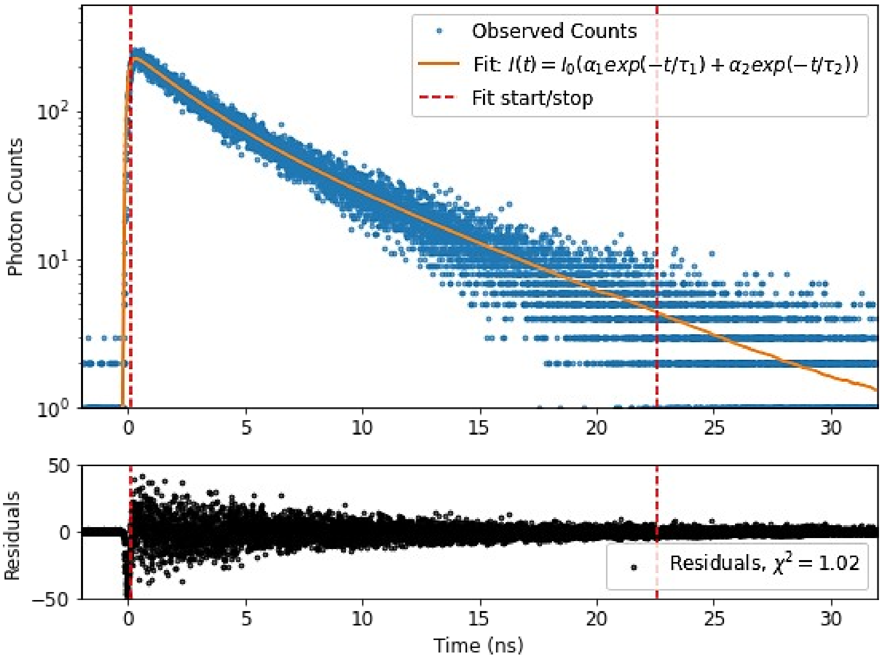
Measurement	α_1	τ_1	α_2	τ_2	τ_{avg}
1	0.62	2.61	0.38	7.06	4.32
2	0.58	2.43	0.42	6.80	4.29
3	0.66	2.81	0.34	7.46	4.38
Mean	0.62	2.62	0.38	7.11	4.33
Std. Dev.	0.04	0.16	0.04	0.27	0.04

Measurement 1:



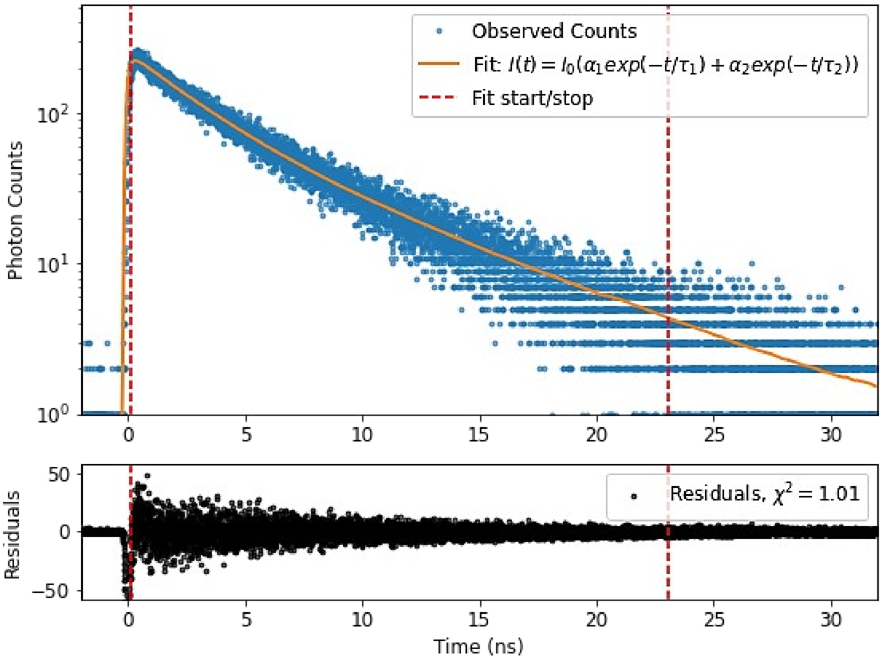
Parameter	Value
α_1	0.62
τ_1	2.61
α_2	0.38
τ_2	7.06
$\langle\tau\rangle_a$	4.32

Measurement 2:



Parameter	Value
α_1	0.58
τ_1	2.43
α_2	0.42
τ_2	6.80
$\langle\tau\rangle_a$	4.29

Measurement 3:



Parameter	Value
α_1	0.66
τ_1	2.81
α_2	0.34
τ_2	7.46
$\langle\tau\rangle_a$	4.38

pH-sensitive fluorescence of N-CDs

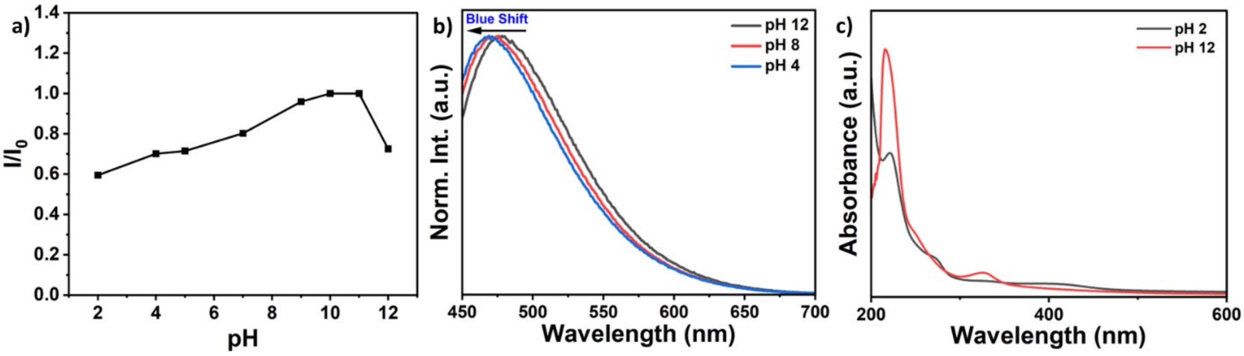


Figure S3. (a) The fluorescence intensity of N-CDs at different pH considering the emission wavelength corresponding to the maximum fluorescence (520 nm) at the excitation wavelength of 410 nm. The red square shows the range in which the N-CDs fluorescence remain

The PL emission color change was studied to be irreversible. The alkaline N-CDs solution was acidified using HCl 1.2 M, passing from pH 12 to pH 4, and a further blue shift instead of a red shift is observed, as shown in Figure S3.b.

UV-vis absorption spectra of the 1 mg/ml N-CDs solutions were recorded at pH 2 and at pH 12, as shown in Figure S3.c. The observed modifications in the UV-vis spectrum above 300 nm with increasing pH suggest that pH variations may influence the surface states of the N-CDs and, therefore, the changes in the fluorescence emission spectra. The sensitivity of fluorescence to pH and solvents is often attributed to nitrogen- and oxygen-containing functional groups on the surface of CDs (1).

In particular, the protonation and deprotonation of the surface functional groups, such as carboxylic and amine groups, is what may trigger the response to different pH values (2).

NaCl Stability

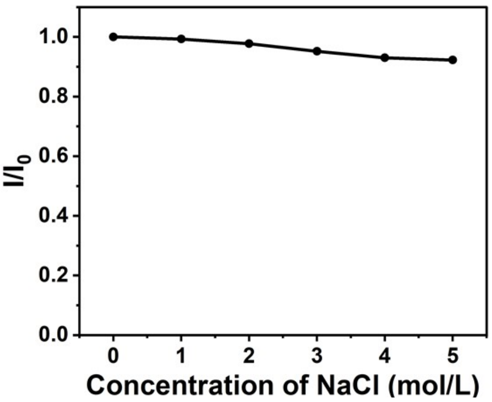


Figure S4. Fluorescence intensity of N-CDs under different ionic strengths of NaCl aqueous solutions.

Figure S4 shows that the N-CDs demonstrate a good stability from 0 to 5 mol/L NaCl as they keep 92% of the initial fluorescence intensity.

Solvent Stability

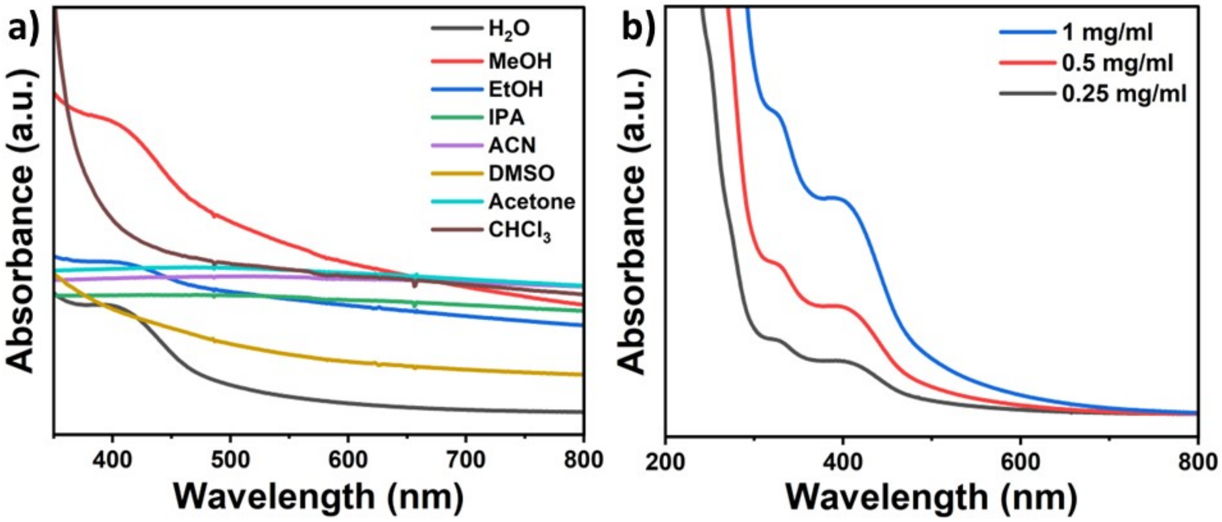


Figure S5. (a) UV-vis absorption of N-CDs in different solvents at a concentration of 1 mg/ml. (b) UV-vis absorption of aqueous solutions at different concentrations of N-CDs powder.

Considering the UV-vis spectra of the N-CDs in the different solvents (Figure S5), it is observed that the absorbance at 410 nm changes as the polarity of the solvent increases. This indicates that the N-doped Carbon Dots have different surface states in different solvents.

Fluorescence stability of N-CDs in various solvents

Table S4. Fluorescence stability of N-CDs in various solvents.

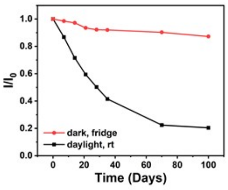
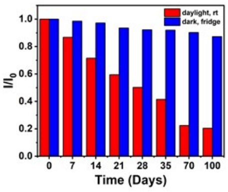
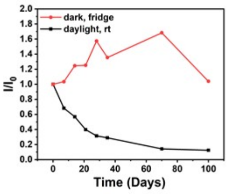
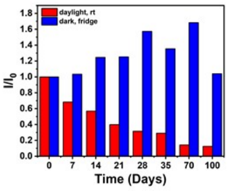
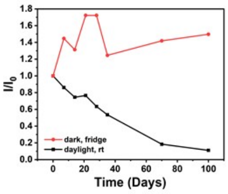
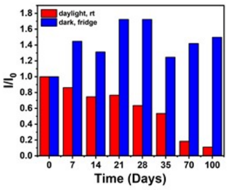
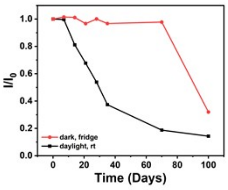
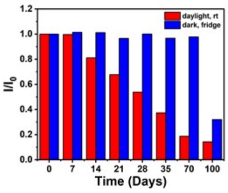
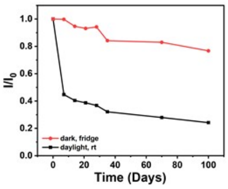
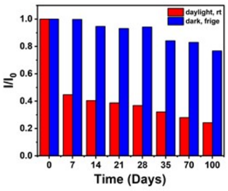
	Wavelength maximum emission (λ_{ex} = 410 nm)		
Water	520 nm		
Methanol	516 nm		
Ethanol	512 nm		
Isopropanol (IPA)	515 nm		
Dimethyl sulfoxide (DMSO)	498 nm		

Table S4 shows the stability of the N-CDs fluorescence in diverse solvents. Generally, the fluorescence intensity was better preserved in time by storing the solutions in the dark at low temperatures.

The fluorescence of the solutions of N-CDs in acetonitrile, acetone, and chloroform was not detectable after 28 days, 35 days, and 21 days, respectively. This demonstrates the instability of the N-CDs in non-polar solvents.

Concentration-dependent emission of N-CDs

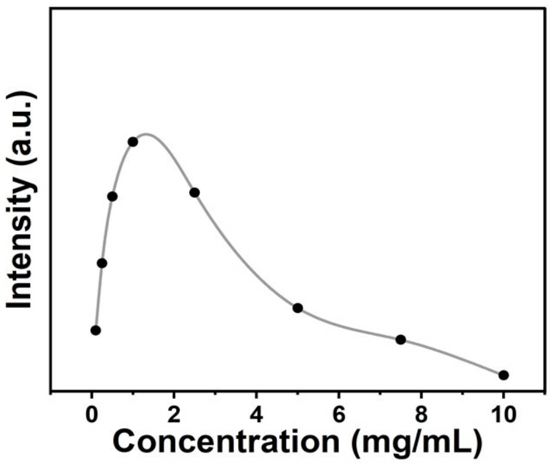


Figure S6. Trend of the fluorescence intensity of the N-CDs at different concentrations.

Figure S6 shows the fluorescence intensity increasing up to N-CDs concentrations of 1 mg/ml and then started to decrease progressively, likely due to an Inner Filter Effect (IFE) (3).

Invisible fluorescent N-CDs ink

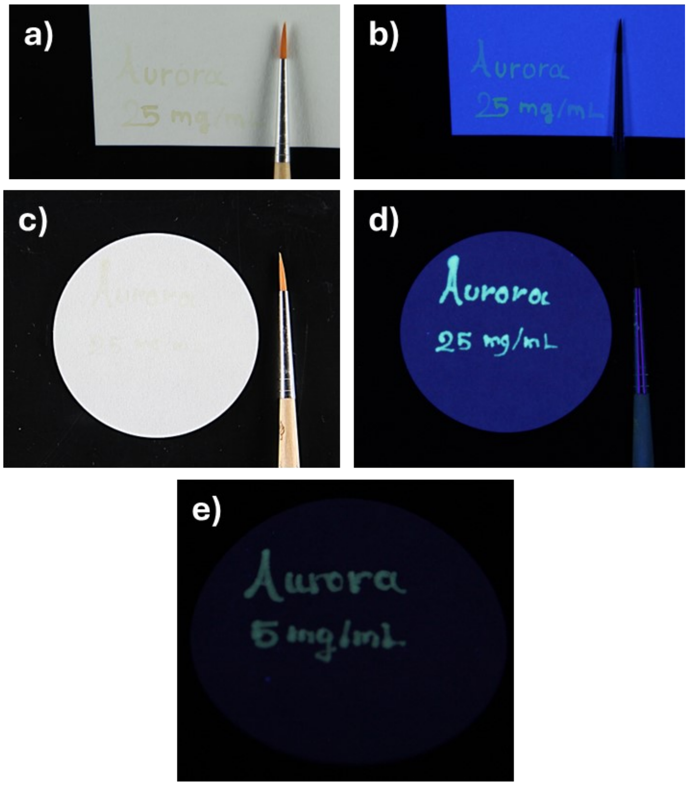


Figure S7. Aqueous solution 25 mg/ml of N-CDs brushed on Whatman® filter paper, shown (a) under daylight and (b) under 365 nm UV light. Aqueous solution 25 mg/ml of N-CDs brushed on Whatman® filter paper, shown (c) under daylight and (d) under 365 nm UV light. Aqueous solution 5 mg/ml of N-CDs brushed on Whatman® filter paper, shown (e) under 255 nm UV light.

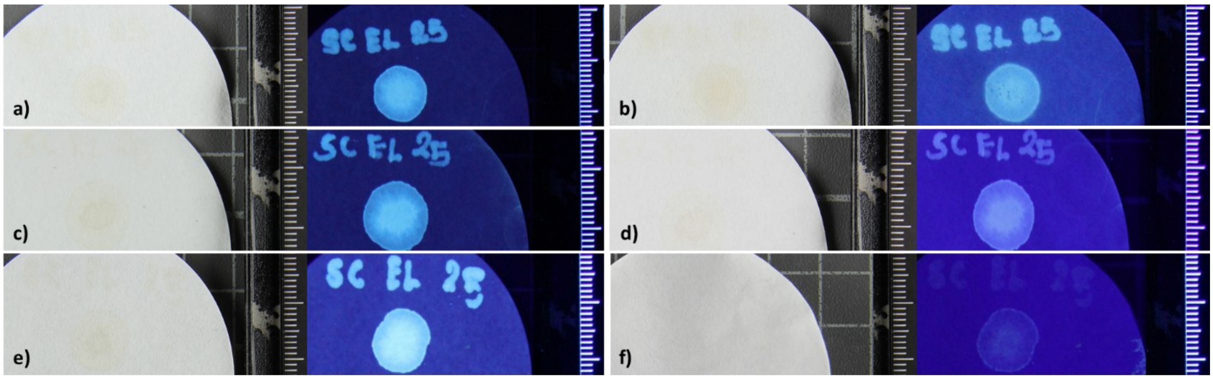


Figure S8. Aqueous solution of N-CDs (25 mg/mL) handwritten and drop cast on filter paper: (a) before hydrothermal aging under daylight (left) and UV light (right); (b) after hydrothermal aging under daylight (left) and UV light (right); (c) before indoor photoaging under daylight (left) and UV light (right); (e) before sunlight-accelerated aging under daylight (left) and UV light (right); (f) after sunlight-accelerated aging under daylight (left) and UV light (right).

PVA-N-CDs and PVP-N-CDs inks UV-vis and PL characterization

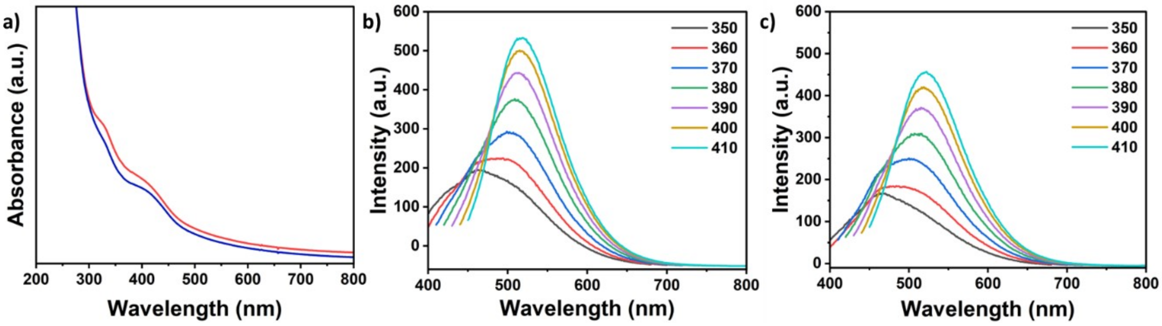


Figure S9. (a) UV-vis absorption of the N-CDs and 4% w/v PVA in water (red line) and of the N-CDs 3% w/v PVP, prepared using a mixture of water and ethanol in equal proportions (blue line). Fluorescence spectra at different excitation wavelengths for (b) N-CDs and 3% w/v PVP in water and ethanol and (c) N-CDs and 4% w/v PVA in water.

References

1. Moniruzzaman M, Kim J. N-doped carbon dots with tunable emission for multifaceted application: solvatochromism, moisture sensing, pH sensing, and solid state multicolor lighting. Sensors and Actuators B: Chemical. 2019 Sep;295:12–21.

2. Bai J, Ma Y, Yuan G, Chen X, Mei J, Zhang L, et al. Solvent-controlled and solvent-dependent strategies for the synthesis of multicolor carbon dots for pH sensing and cell imaging. J Mater Chem C. 2019;7(31):9709–18.

3. Lai S, Jin Y, Shi L, Zhou R, Zhou Y, An D. Mechanisms behind excitation- and concentration-dependent multicolor photoluminescence in graphene quantum dots. Nanoscale. 2020;12(2):591–601.