

A novel PH sensitive N-doped carbon dots with both long fluorescence lifetime and high quantum yield

Experimental Section:

The CDs were obtained by a simple microwave-assisted hydrothermal method by employing a microwave digestion container (XH-800C, Xianghu, China). In a typical procedure, 0.3355 g citric acid (CA) and 0.0645 g tris were dissolved in 20 ml water and transformed the solution in a microwave digestion vessel. Then they were placed in the microwave digestion container and heated at 160°C for 10 min at 900 W power. After the reaction was completed, the microwave digestion vessel was cooled down naturally. Next, the aqueous solution was dialysed through a dialysis membrane (1000 MWCO) to remove the residual precursors. Then the obtained CDs solution stored at room temperature for use.

Characterizations:

High-resolution transmission electron microscopy (HRTEM) observations were performed on a JEOL-2010 electron microscope operating at 200 kV. Atomic force microscopy (AFM) image was obtained with a Micronano New Spm atomic force microscope (Zhuolun, China). The element analysis was performed by vario EL III (Elementar, Germany). The Fourier transform infrared spectroscopy (FTIR) spectra were measured by an NICOLET iS10 (Thermo) spectrometer with the KBr pellet technique ranging from 500 to 4000 cm⁻¹. UV2450 spectrophotometer (Hitachi, Japan) was used to determine the absorbance of the CDs. The fluorescence spectra of the

CDs were measured with a F900 fluorescence spectrometer (Edinburgh, UK), with a slit width of 1 nm and 1 nm for excitation and emission, respectively. The fluorescence lifetimes were measured by F900 fluorescence spectrometer (Edinburgh, UK) with using a time-correlated single photon counting (TCSPC) technique and a nanoflash lamp. The sample was excited at a wavelength of 330nm and the fluorescence emission intensity at a fixed emission wavelength was collected in a period of time to obtain the fluorescence intensity decay profile.

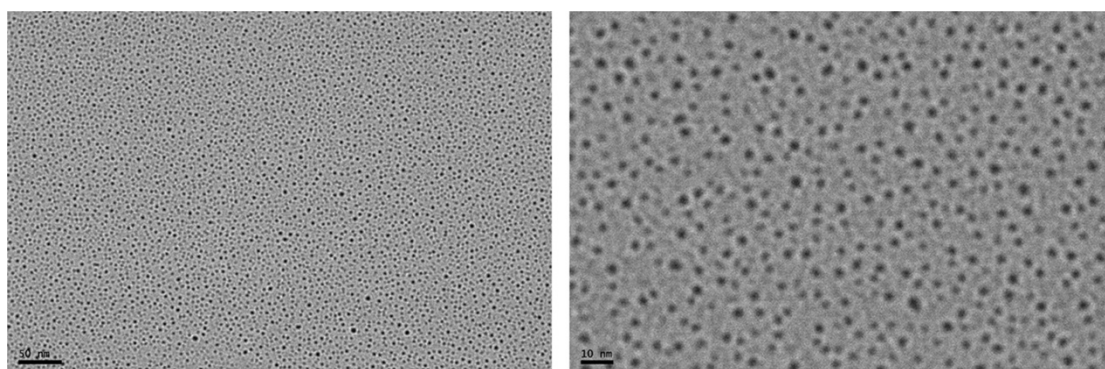


Figure. S1 TEM images of CDs

Quantum yield measurement

Fluorescence quantum yield (QY) of CDs was measured by comparing the integrated photoluminescence intensities (excited at 330 nm) and the absorbance value (at 330nm) using quinine sulfate in 0.1 M H_2SO_4 ($\Phi_F=0.54$) as standard. Different concentrations of the CDs and standards were prepared, all of which had absorbance less than 0.1 at their excitation wavelengths. The fluorescence spectra for the calculation of quantum yield should be corrected for nonlinear instrument response before the integration of their total intensities.

The detailed experimental procedure:

1. Record the UV-vis absorbance spectrum of the chosen sample. Note down the

absorbance at the excitation wavelength to be used.

2. Record the fluorescence spectrum of same solution and note down the integrated photoluminescence intensities.
3. Repeats steps 1 and 2 for five solutions with different concentrations of the chosen sample, making the absorbance at the excitataion wavelength less than 0.1 so that fluorecence measurements with minmal errors due to the “inner-filter effect” were obtained.
4. Plot a graph of intergated fluorescence intensity vs absorbance. The slops of standard and the sample were obtained to the calulitation of the fluorescence quantum yield.

QY was calculated using the following equation:

$$\Phi_x = \Phi_{ST} \left(\frac{Grad_x}{Grad_{ST}} \right) \left(\frac{\eta_x^2}{\eta_{ST}^2} \right)$$

Where the subscripts ST and X denote standard and test respectively, Φ is the fluorescence quantum yield, *Grad* the gradient from the plot of integrated fluorescence intensity vs absorbance, and η the refractive index of the solvent.

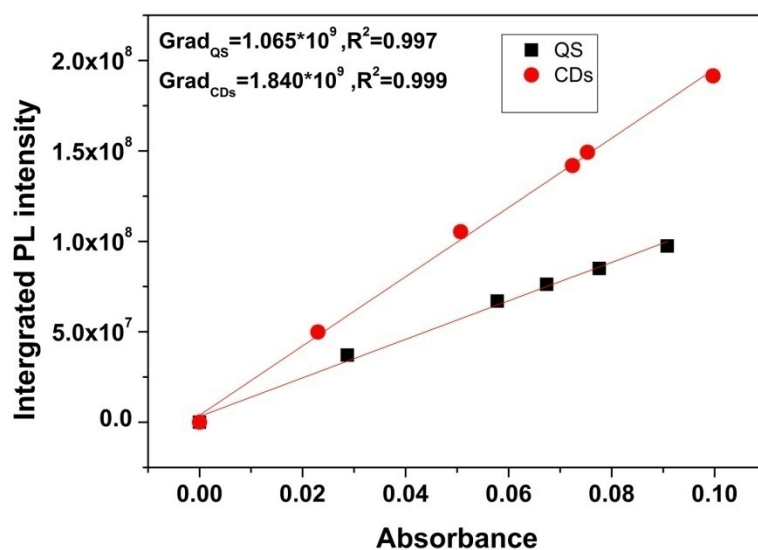


Figure. S2. Fluorescence and Absorbance of the CDs and Quinine Sulfate (QS).

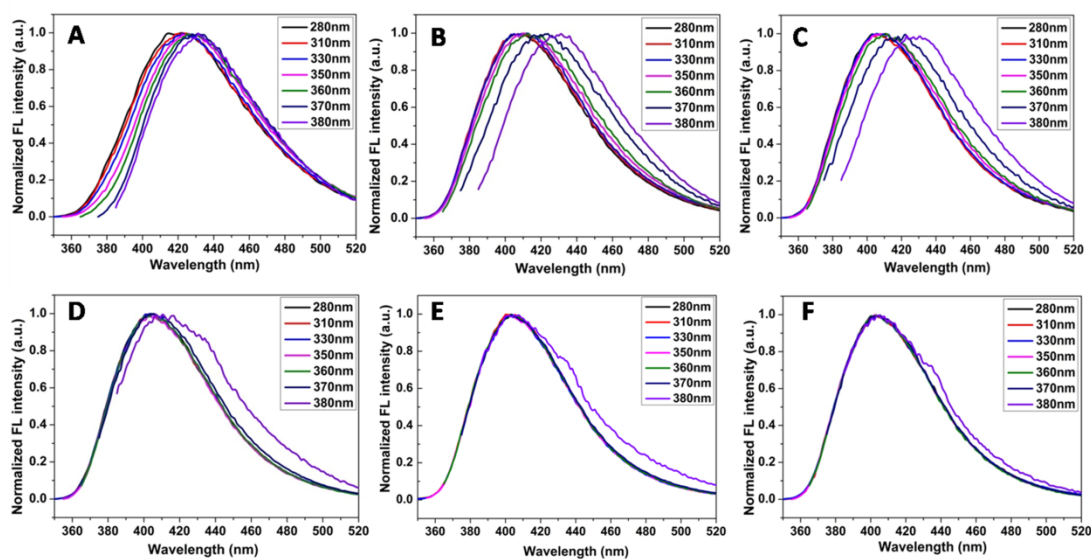


Figure. S3 Normalized fluorescence spectra of CDs-H at (A) pH=3.0, (B) pH=3.8, (C) pH=4.0, (D) pH=5.0 and CDs-OH at (E) pH=7.0, (F) pH=9.0.

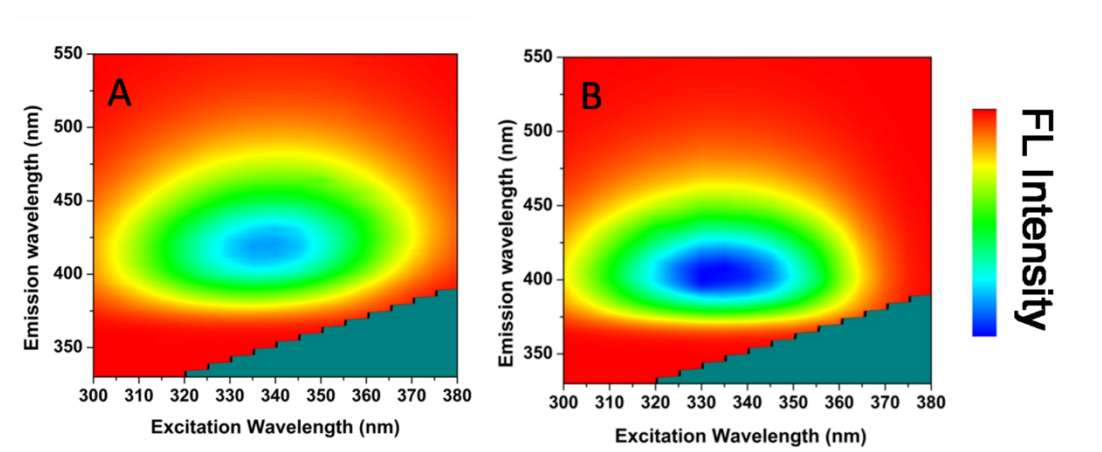


Fig. S4 Emission maps of CDs-H at pH of 3.4 and CDs-OH at pH of 7.0.

Fluorescence lifetime

The decays in the fluorescence lifetime of the CDs with different emission wathlength could be fitted using a monoexponential equation. The decay parameters, as obtained from fitting the raw decay date are given in table. S1.

Table. S1 Fitted decay lifetimes at different emission wavelengths and different pH, excitation is 330nm. The χ^2 values dictate the goodness of the exponential fits to the raw date.

pH	Lifetime (ns) (χ^2)						
	380 nm	400 nm	420 nm	440 nm	460 nm	480 nm	500 nm
3.4	11.08 (1.08)	12.79 (1.16)	15.11 (1.02)	16.96 (0.94)	18.34 (1.04)	18.70 (1.10)	19.50 (1.04)
4.0	12.08 (1.24)	12.90 (0.98)	14.00 (1.03)	15.11 (1.25)	16.36 (1.05)	17.17 (1.09)	17.77 (0.99)
5.0	13.37 (1.10)	13.34 (1.14)	13.77 (1.18)	13.94 (0.87)	14.30 (0.98)	14.53 (1.07)	14.75 (1.07)
7.0	13.67 (1.16)	13.75 (1.06)	13.68 (1.07)	13.65 (1.02)	13.66 (0.97)	13.81 (1.08)	13.75 (1.02)
11.0	13.03 (1.13)	13.02 (1.10)	13.04 (1.07)	13.05 (1.12)	13.15 (1.02)	13.16 (1.14)	13.17 (0.96)