Supplementary Material

Facile synthesis of long-wavelength emission nitrogen-doped carbon dots for intracellular pH variation and hypochlorite sensing

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Experimental

Apparatus

The transmission electron microscopic (TEM) images were acquired on a JEOL JEM-2100 transmission electron microscope (Tokyo, Japan) with an accelerating voltage of 300 kV. The Fourier transform infrared (FTIR) spectra were conducted on a Bruker Tensor II FTIR spectrometer (Bremen,Germany) in the form of KBr pellets from 4000 to 400 cm^{-1}. The X-ray photoelectron spectra (XPS) were acquired on an AXIS ULTRA DLD X-ray photoelectron spectrometer (Kratos, Tokyo, Japan) with AlKa radiation operating at 1486.6 eV. Spectra were processed by Case XPS v.2.3.12 software using a peak-fitting routine with symmetrical Gaussian–Lorentzian functions. The atomic force microscopy (AFM) images were acquired on a Veeco Nanoscope Quadrex AFM (Bruker AFM Probes,Camarillo, CA, U.S.A.).The UV-Vis absorption spectra were performed on a PerkinElmer Lambda 365 UV-Vis spectrophotometer (PE America) at 200–700 nm. The PL spectra were recorded on Edinburgh FLS 920 spectro-fluorometer (Livingston, UK) and Varian Cary Eclipse spectrofluorometer (Palo Alto, CA, USA).

Quantum yield (QY) measurements

The relative quantum yield of N-CDs was measured with the reference to rhodamine B (QY=9.8 % at 513 nm excitation). The formula used for QY measurement is as follows:

$$QY = QY_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

QY_R represents the quantum yield of rhodamine B. Rhodamine B was dissolved in ethanol (η= 1.36) and the N-CDs was dissolved in ultrapure water (η= 1.33), A represents the absorption at the excitation wavelength of 474 nm. To avoid the self-absorption effect, absorbance must keep under 0.1.

Calculation of pKa values

pKa values of N-CDs was calculated by the following formula:

$$\log(I_{max} - I / I - I_{min}) = pH \pm pKa$$

I_{min} is minimum fluorescence intensity limiting values in base, I_{max} is maximum fluorescence intensity limiting values in acid.

MTT assays

For the cytotoxicity assay, rat adrenal medulla pheochromocytoma differentiated cells PC-12 cells were first plated on Costar @ 96-well cell culture clusters and incubated at 37°C. in 5.0% CO_2 air for 3 h to allow the cells to adhere to the surface. Wells without cells and treated with N-CDs were used as sets. The medium was then replaced with 100 μL of fresh DMEM supplemented with 10% PBS containing N-CDs and the cells were allowed to grow for a further 48 hours. Each group will have at least five parallel samples. Cells not treated with N-CDs served as controls. After adding 20 μL of 5.0 $mg \cdot mL^{-1}$ MTT reagent to each well, the cells were incubated for another 4 h. The medium containing MTT was removed and 150 μL of DMSO was added. The resulting mixture was shaken at room temperature for about 10 minutes. The optical density (OD) of the mixture was measured at 490 nm using a SunRise microplate reader (Tecan Austria GmbH, Grödig, Austria). Cell viability is estimated as:

$$\text{Cell viability (\%)} = (OD_{treatment} / OD_{control}) \times 100\%$$

The OD control and OD treatment were obtained in the absence and presence of N-CDs, respectively.

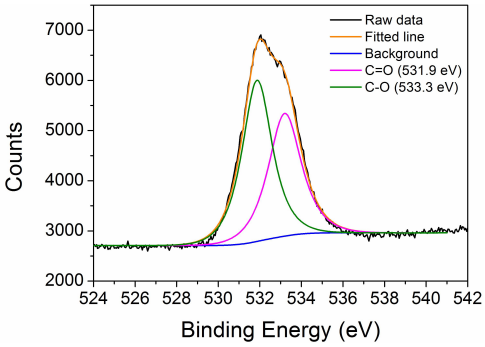


Fig.S1 O1s XPS of the N-CDs.

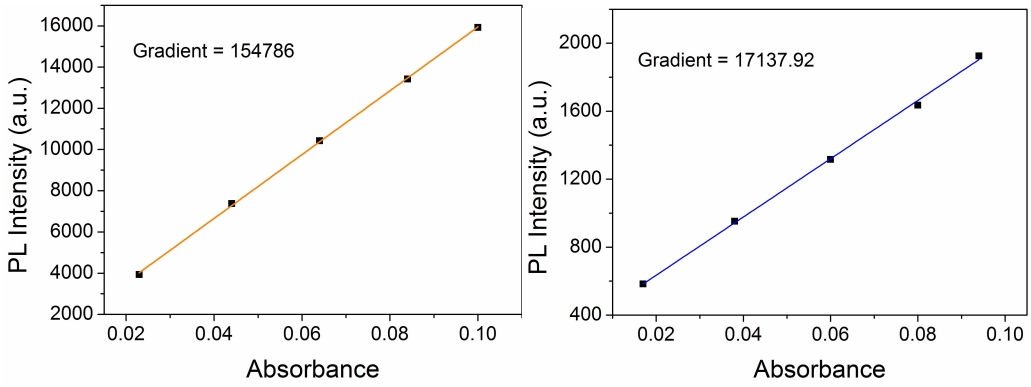


Fig.S2 Plots of integrated PL intensity against the absorbance of (A) rhodamine B and (B) N-CDs at excitation and emission wavelengths of 513 nm.

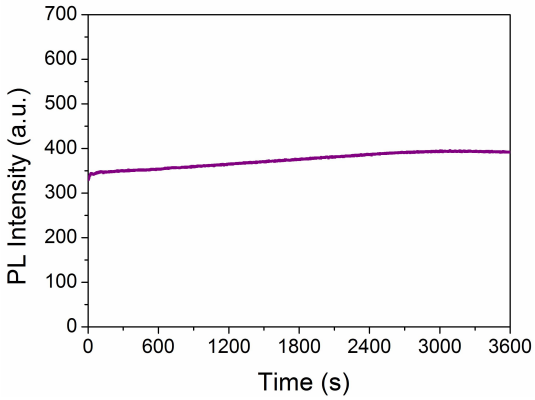


Fig.S3 Effect of Xe lamp irradiation time in room temperature on the fluorescence intensity of N-CDs aqueous.

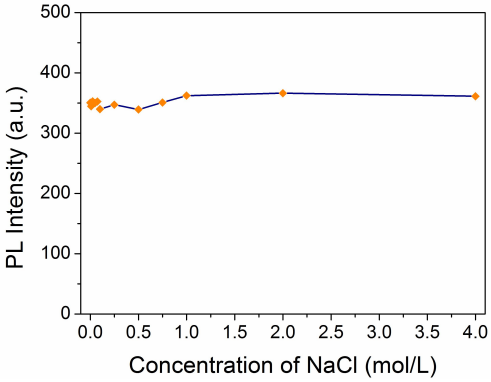


Fig.S4 Effect of ionic strength in room temperature on the fluorescence intensity of N-CDs aqueous.

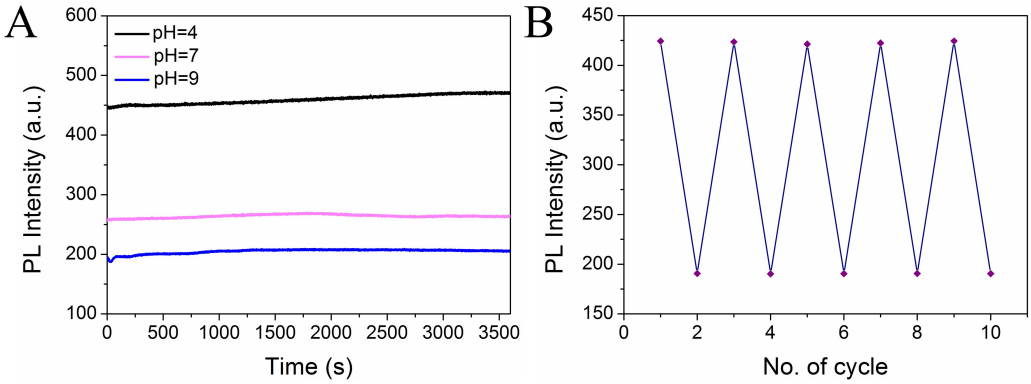
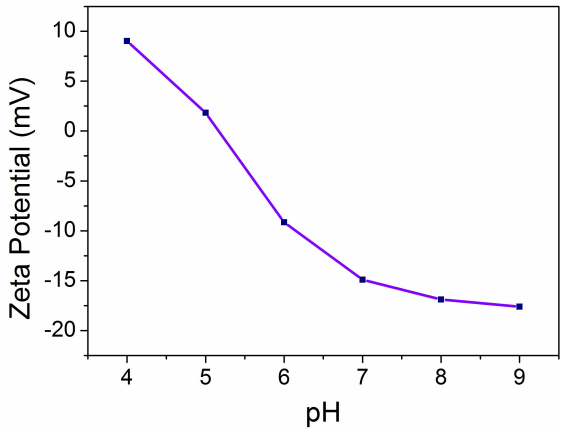
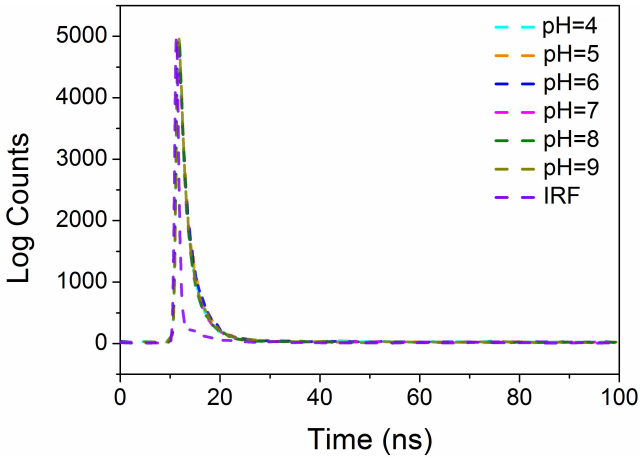


Fig.S5(A) dependence of FL intensity of N-CDs with time under Xe lamp irradiation at pH 4.0, 7.0 and 9.0, respectively; (B) fluorescence intensity upon the cyclic switching of N-CDs under alternating conditions of pH = 4.0 and pH = 9.0.



pH	4	5	6	7	8	9
Zeta potential (mV)	9.02	1.84	-9.15	-14.9	-16.9	-17.6

Fig.S6 The zeta potential of N-CDs at different pH.



pH	4	5	6	7	8	9
Time (ns)	5.30	4.35	4.00	3.72	3.61	3.54

Fig.S7 The fluorescence lifetime of N-CDs at different pH.

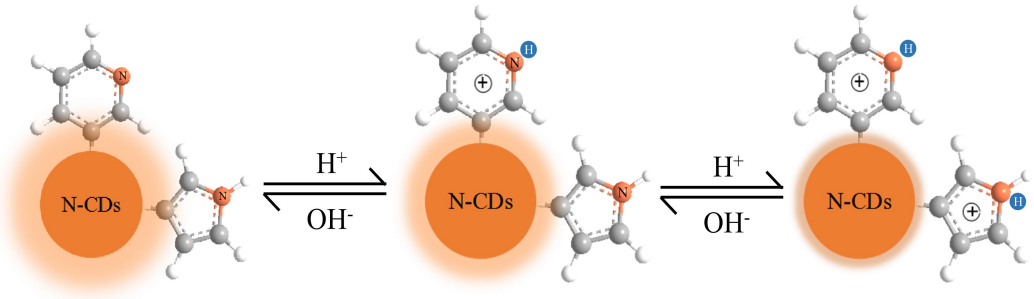


Fig.S8 The pH-response possible mechanism of as-proposed N-CDs.

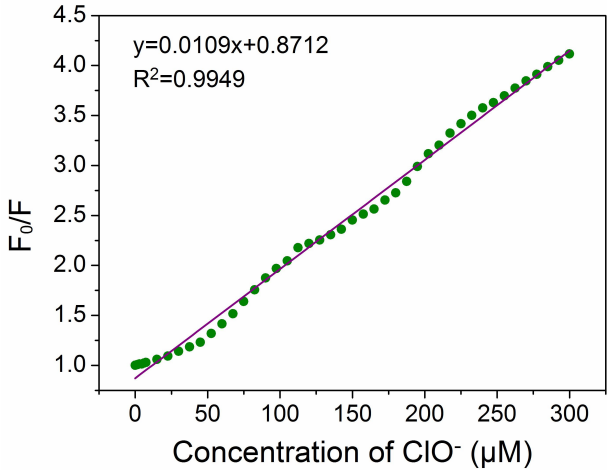


Fig.S9 The SV plot of N-CDs at different contents of ClO^-.

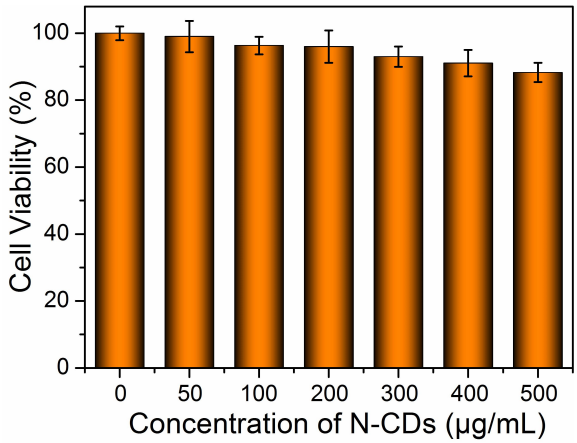


Fig.S10 Cytotoxicity test of N-CDs on PC-12 cells viability. The values represent percentage cell viability (mean% ± SD, n=6).