Supplementary Information

Nitrogen-doped Carbon dots for the Sensitive Detection of Ferric Ions and Monohydrogen Phosphate by Naked Eye and Imaging in Living Cells

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1. Determination of fluorescence quantum yield

Fluorescence quantum yield was measured by a standard method in air-equilibrated sample at room temperature. The fluorescence quantum yield was determined by using Rhodamine B (Φ=0.31 in water) as reference. [1, 2]

$$\Phi_{sam} = \Phi_{ref} \frac{I_{sam}}{I_{ref}} \cdot \frac{A_{ref}}{A_{sam}} \cdot (\frac{n_{sam}}{n_{ref}})^2 \qquad (1)$$

Where Φ is the fluorescence quantum yield, I is the integrated emission intensity, A is the absorbance, and n is the refractive index. The subscripts $_{sam}$ and $_{ref}$ stand for sample and reference, respectively. Herein, the N-CDs and Rhodamine B were dissolved in ultrapure water (n =1.33) and excited under 420 nm and kept the absorbance below 0.05.

2. Supplementary figures

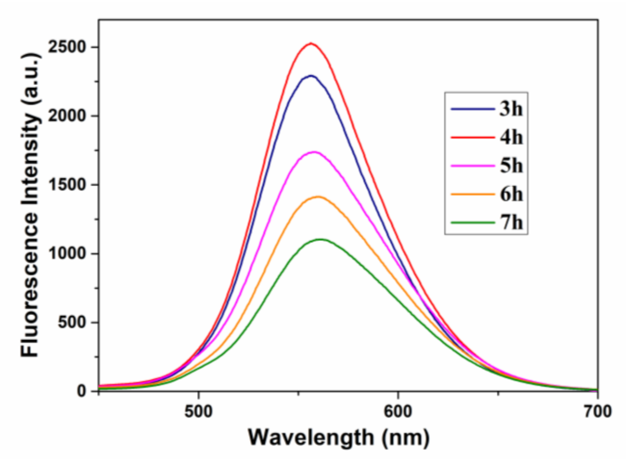

Fig.S1 Fluorescence emission spectra of the N-CDs based on o-phenylenediamine and formamide as the precursors with the mole ratio1:1.5 at 150 ℃ for the different reaction times.

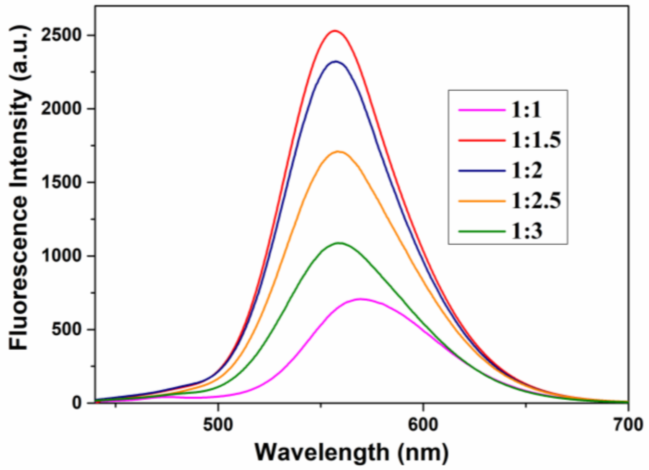

Fig.S2 Fluorescence emission spectra of the N-CDs based on o-phenylenediamine and formamide as the precursors at 150 ℃ for 4h with the different mole ratios between o-phenylenediamine and formamide.

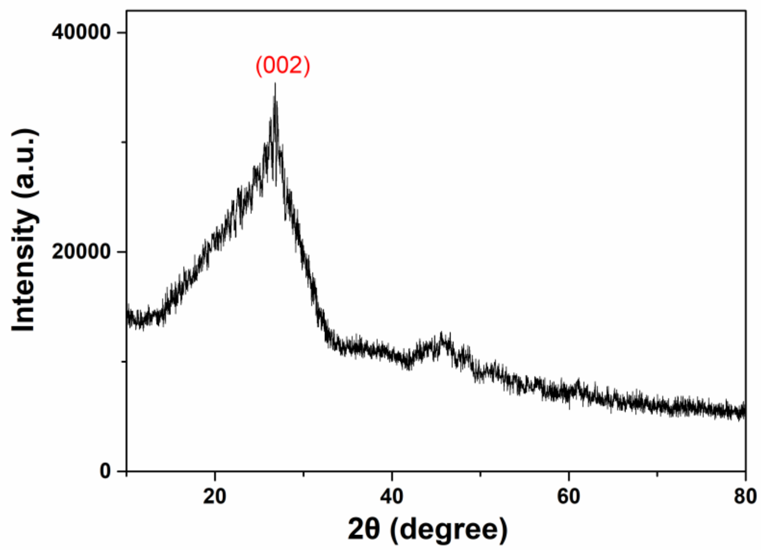

Fig.S3 XRD diffraction pattern of the N-CDs.

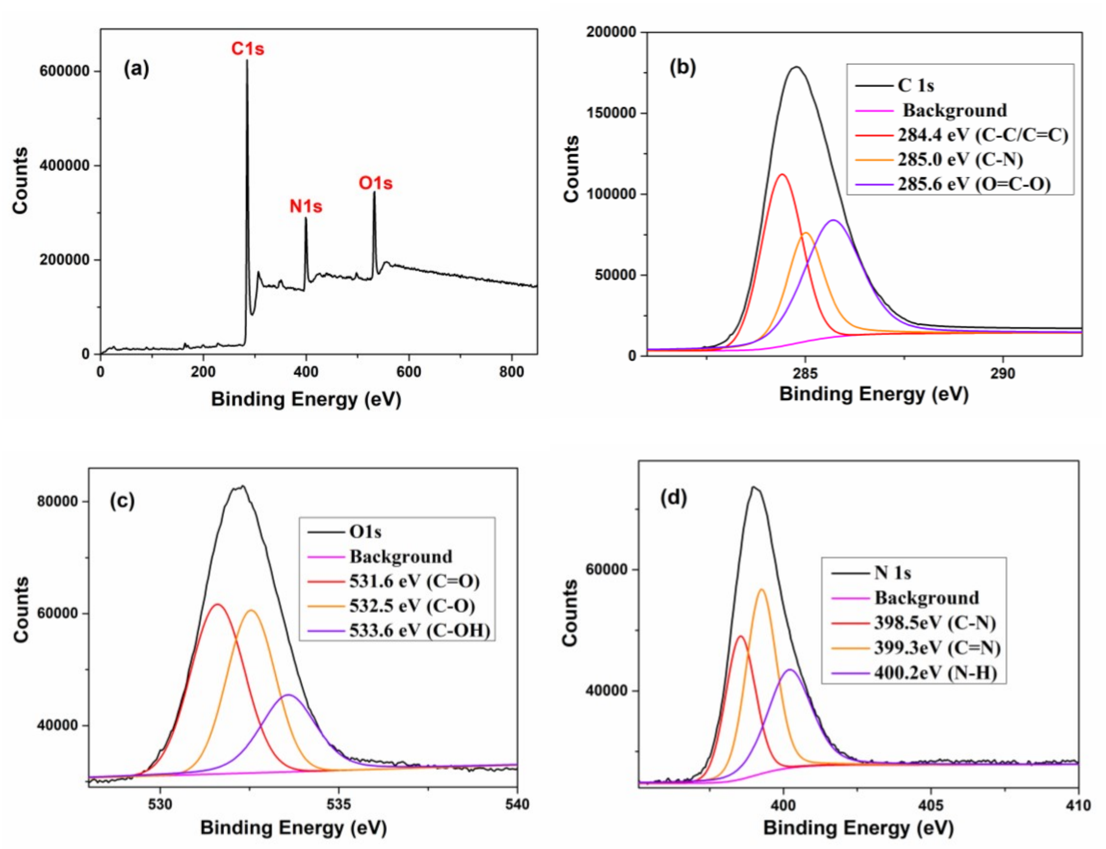

Fig.S4 (a) The full scan XPS of the N-CDs. High resolution XPS of C 1s (b), O 1s (c) and N 1s (d).

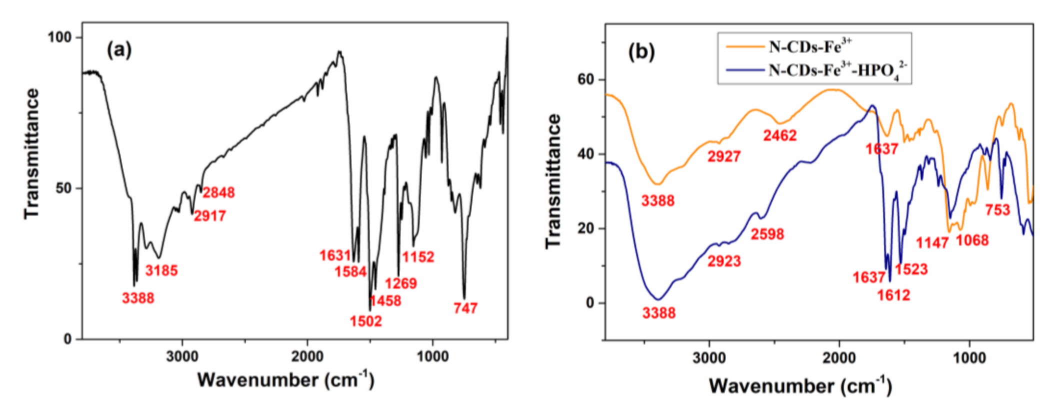

Fig.S5 Fourier transformed infrared spectra of the N–CDs (a) and the complexes of the N-CD-Fe^{3+} and the [N-CD-Fe^{3+}-HPO_4^{2-}] (b).

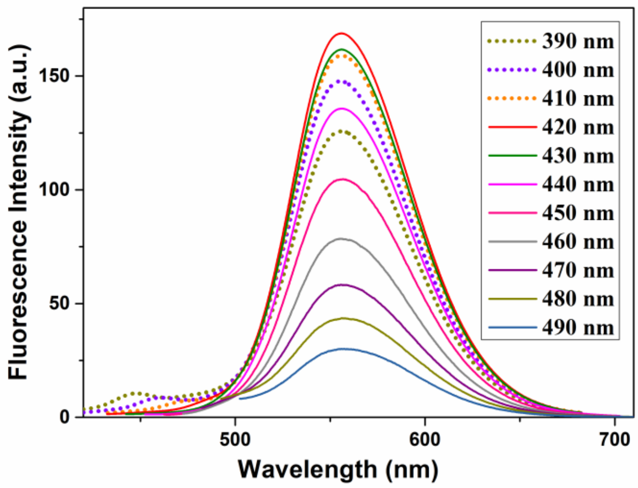

Fig.S6 The fluorescence emission spectra of the N-CDs at different excitation wavelengths.

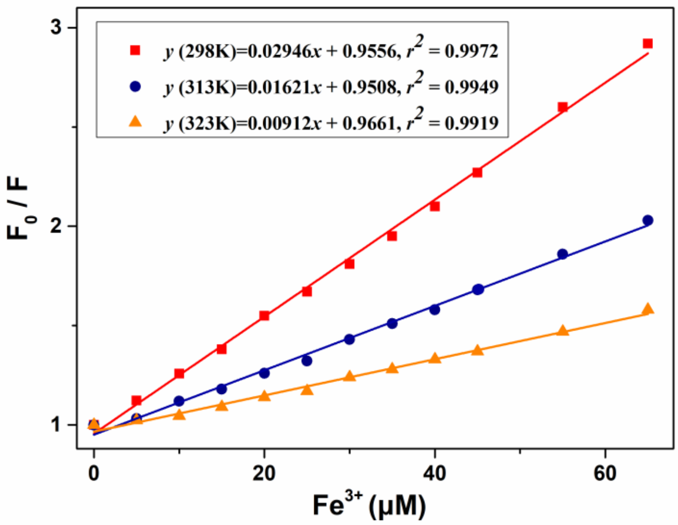

Fig.S7 Stern-Volmer plot at different temperatures (298 K, 318 K and 323K) and different concentrations of Fe^{3+} (0.3–65.0 μM).

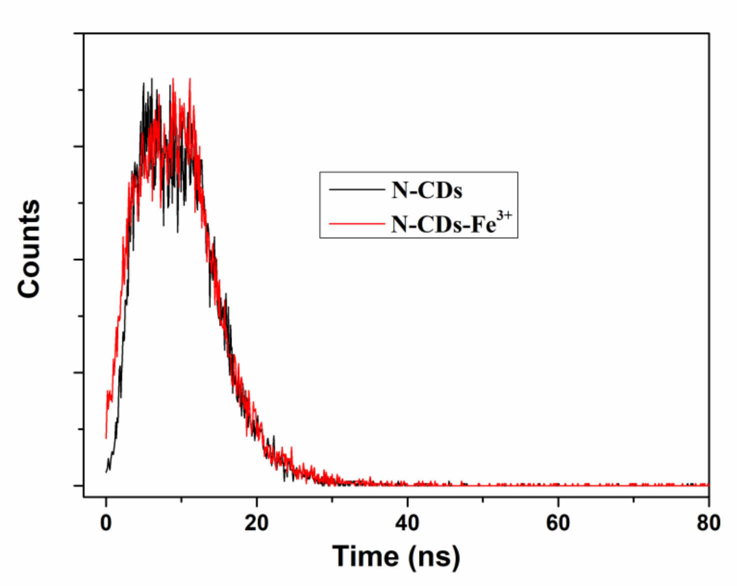

Fig.S8 Fluorescence lifetime decays of the N-CDs in the absence (black line) and presence (red line) of Fe^{3+} under excitation of 450 nm.

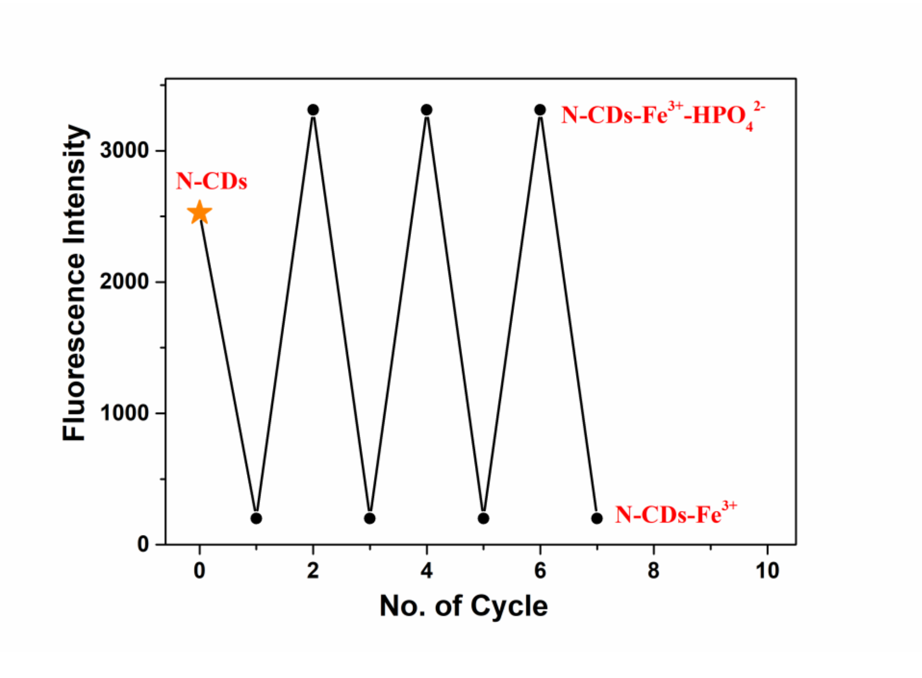

Fig.S9 Reversible fluorescence responses between N-CDs-Fe^{3+} and HPO_4^{2-} at 556 nm.

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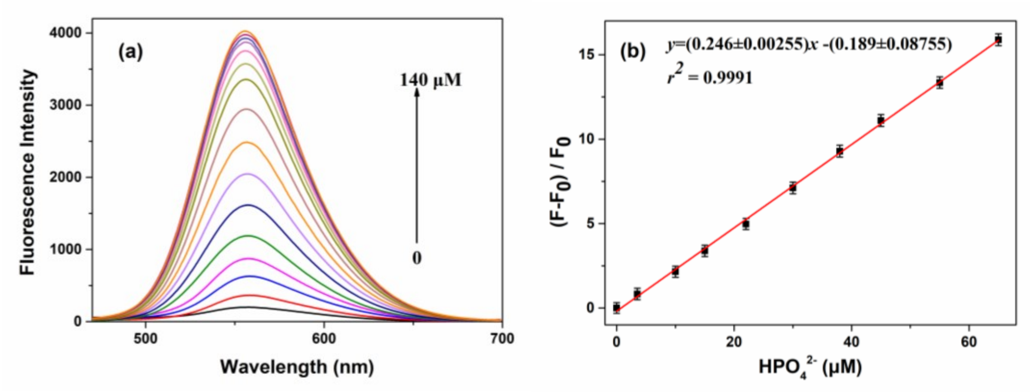

Fig.S10 (a) Fluorescence emission spectra of the N-CDs-Fe^{3+} complex in the presence of different concentrations of HPO_4^{2-} (0-140 μM). (b) Linear relationship between $[(F-F_0)/F_0]$ and the concentration of HPO_4^{2-}, where F_0 and F are the fluorescence intensities of the N-CDs-Fe^{3+} complex at 556 nm in the absence and presence of HPO_4^{2-}, respectively. The excitation wavelength is 415 nm.

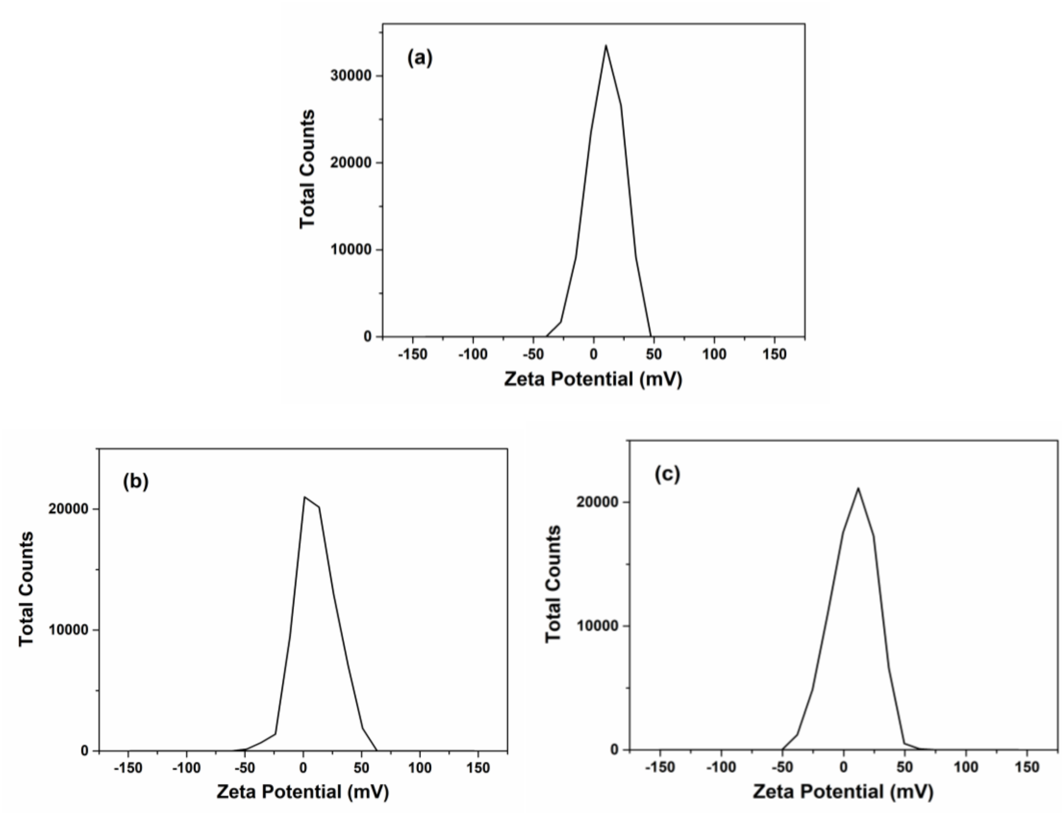

Fig.S11 Zeta potential plots of the N-CDs (a), the complexes of the N-CDs-Fe^{3+} (b) and the [N-CDs-Fe^{3+}-HPO_4^{2-}] (c).

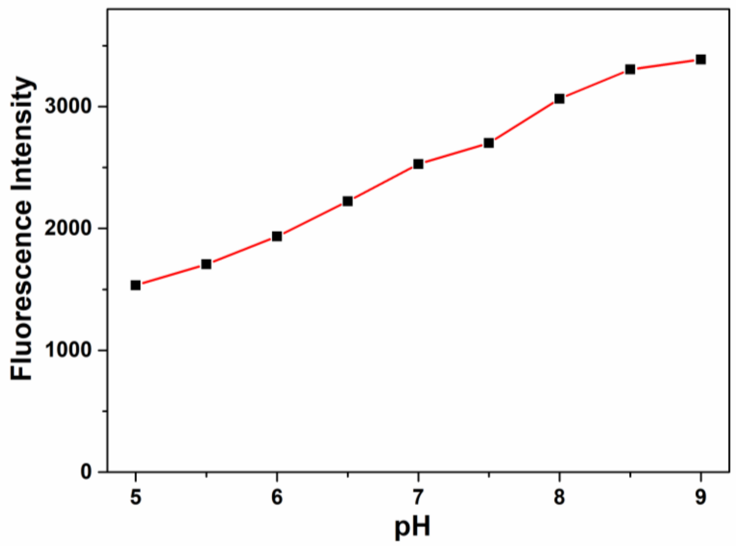

Fig.S12 Effect studies of pH on the fluorescence intensities of the N-CDs (0.04 mg/ mL) at 556 nm.

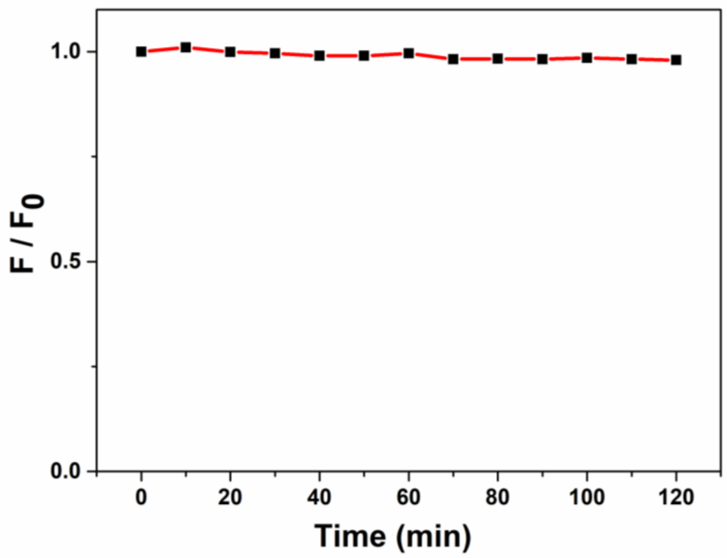

Fig.S13 Photostability studies of the N-CDs as a function of the continuous ultraviolet light at 365 nm for 120 min at 420 nm excitation wavelength.

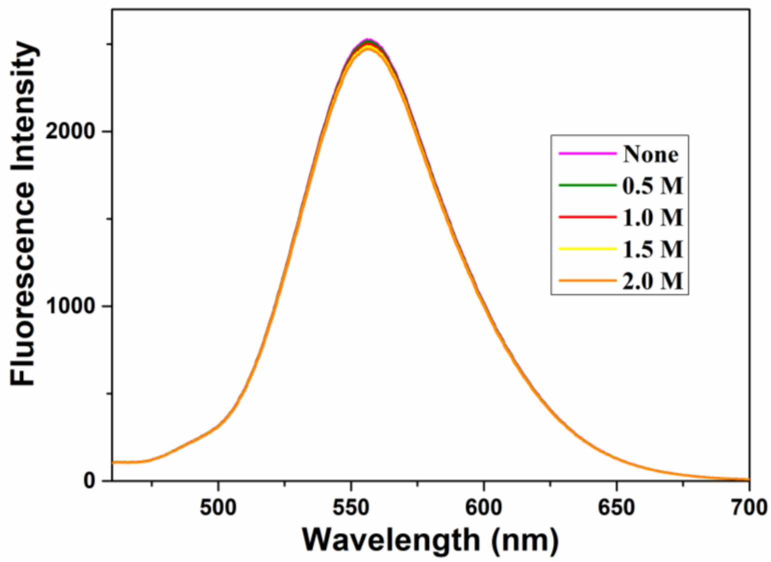

Fig.S14 The effect studies of the different ionic strengths (0.0-2.0 M KCl) on the fluorescence emission spectra of the N-CDs (0.04 mg/mL) at 420 nm excitation wavelength.

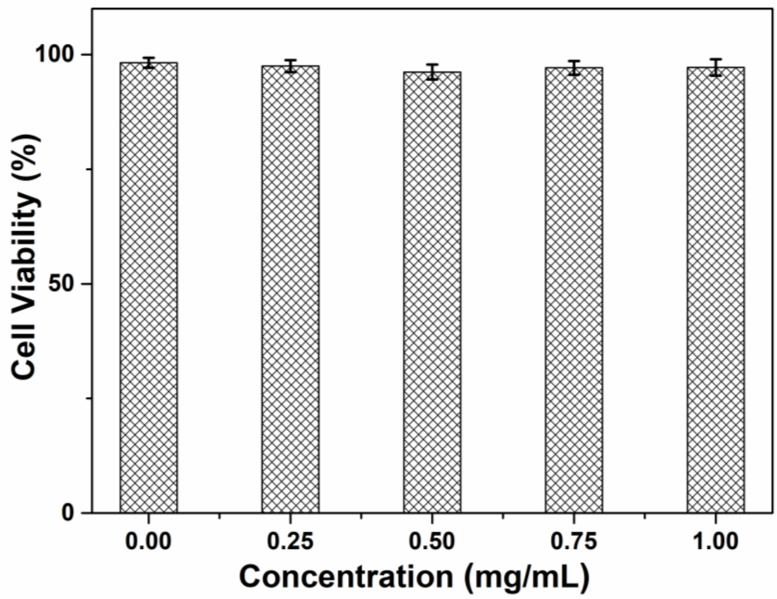

Fig.S15 Cytotoxic assays of the different concentrations of the N-CDs on HEp-2 Cells.

Table S1 Comparison between the reported carbon dots for Fe^{3+} sensing and the N-CDs

Kinds of carbon dots	Ex/Em (nm)	Stokes shift	QYs	Detection limit (μM)	ref
N/P-CDs	320/408	88	43.2 %	0.33 μM	3
CDs	360/442	82	8.64 %	0.32 μM	4
N-CDs	350/420	70	14 %	0.9 μM	5
Si-CDs	390/520	130	27.2 %	13.7 nM	6
CDs	340/426	86	10.5 %	0.2 μM	7
N-CQDs	360/440	80	23.48 %	0.7462 μM	8
CDs	360/436	76	6.2 %	128 nM	9
CDs	380/450	70	10.85 %	9.55 μM	10
N-GQDs	332/440	108	23.3 %	90 nM	11
N-CDs	330/420	90	13.6 %	0.13 μM	12
N-CDs	340/450	110	70 %	107 nM	13
CDs	360/450	90	9.8 %	0.0154 μM	14
N-CDs	355/442	87	27 %	0.01 μM	15
N,Zn-CDs	350/450	100	63.28 %	0.027 μM	16
N,S-CDs	360/443	83	28.9 %	0.16 μM	17
F-CDs	320/447	127	35.2 %	10 nM	18
N-CDs	360/438	78	54 %	42nM	19
CQDs	400/510	110	15 %	50 nM	20
BNS-CDs	500/600	100	5.44 %	90 nM	21
N-CDs	420/510	90	21.5 %	0.18 μM	22
N-CDs	450/556	106	20 %	0.85 μM.	This work

Table S2. Comparison between the organic dyes and the N-CDs

Anion	E_x / E_m (nm)	Stokes shift	Detection limit (μM)	Ref.
$[H_2PO_4]^-$	365/495	131	0.176	23
$[H_2PO_4]^-$	365/401	36	0.046	24
$[H_2PO_4]^-$	330/535	205	0.0165	25
$[H_2PO_4]^-$	365/450	85	0.12	26
$[H_2PO_4]^-$.	480/550	70	3.5	27
$[H_2PO_4]^-$	534/560	26	0.015	28
$[H_2PO_4]^-$	554/612	58	0.0169	29
$[HPO_4]^{2-}$	256/368	112	0.071	30
$[HPO_4]^{2-}$	460/496	36	0.025	31
$[HPO_4]^{2-}$	494/ 526	32	0.0621	32
$[HPO_4]^{2-}$	440/595	155	0.312	33
$[HPO_4]^{2-}$	450/556	106	0.80	This work

3. References

1. M. Zhang, Y. Gao, M. Li, M. Yu, F. Li, L. Li, M. Zhu, J. Zhang, T. Yi, C. Huang, *Tetrahedron Lett.* **2007**, *48*, 3709-3712.

2. Z. Qu, X. Zhou, L. Gu, R. Lan, D. Sun, D. Yu, G. Shi, *Chem. Commun.*, **2013,** *49*, 9830-9832.

3. J. Shangguan, J. Huang, D. He, X. He, K. Wang, R. Ye, X. Yang, T. Qing, J. Tang, *Anal. Chem.*, 2017, 89, 7477–7484.

4. J. Shen, S. Shang, X. Chen, D. Wang, Y. Cai, *Mater. Sci. Eng. C*, 2017, 76, 856-864.

5. R. Atchudana, T. N. J. I. Edison, K. R. Aseer, S. Perumalc, N. Karthika, Y. R. Lee, *Biosens. Bioelectron.,* 2018, 99, 303-311.

6. M. Shamsipur, K. Molaei, F. Molaabasi, M. Alipour, N. Alizadeh, S. Hosseinkhani, M. Hosseini, *Talanta,* 2018, 183, 122-130.

7. C. Sun, Y. Zhang, P. Wang, Y. Yang, Y. Wang, J. Xu, Y. Wang, W. W. Yu, *Nanoscale Res. Lett.*, 2016, 11, 110.

8. H. Qi, M. Teng, M. Liu, S. Liu, J. Li, H. Yu, C. Teng, Z. Huang, H. Liu, Q. Shao, A. Umar, T. Ding, Q. Gao, Z. Guo, *J. Colloid Interf. Sci.,* 2019, 539, 332-341.

9. S. Jayaweera, Y. Ke, X. Hu, W. J. Ng, *J. Photoch. Photobio. A*, 2019, 370, 156-163.

10. M. Zulfajri, G. Gedda, C. J. Chang, Y. P. Chang, G. G. Huang, *ACS Omega*, 2019, 4, 15382-15392.

11. J. Ju, W. Chen, *Biosens. Bioelectron.,* 2014, 58, 219-225.

12. W. Liu, H. Diao, H. Chang, H. Wang, T. Li, W. Wei, *Sensor. Actuat. B,* 2017, 241, 190-198.

13. L.J. Mohammed, K.M. Omer, *Sci. Rep.,* 2020, 10, 3028.

14. W. Zhang, L. Jia, X. Guo, R.Yang, Y. Zhang and Z. Zhao, *Analyst,* 2019, 144, 7421-7431.

15. Q. Huang, Q. Li, Y. Chen, L. Tong, X. Lin, J. Zhu, Q. Tong, *Sensor. Actuat. B*, 2018, 276, 82-88.

16. S. K. Tammina, D. Yang, X. Li, S. Koppala, Y. Yang, *Spectrochim. Acta A*, 2019, 222, 117141.

17, K. K. Chan, C. Yang, Y. H. Chien, N. Panwara and K. T. Yong, *New J. Chem.,* 2019, 43, 4734-4744.

18. D. Hong, X. Deng, J. Liang, J. Li, Y. Tao, K. Tan, *Microchem. J,*. 2019, 151,104217.

19. L. Li, L. Shi, J. Jia, D. Chang, C. Dong, S. Shuang, *Analyst,* 2020, 145, 5450-5457.

20. K. M. Omer, D. I. Tofiq, A. Q. Hassan, *Mikrochim Acta.* 2018, 185, 466.

21. Y. Liu, W. Duan, W. Song, J. Liu, C. Ren, J. Wu, D. Liu, H. Chen, *ACS Appl. Mater. Interfaces,* 2017, 9, 12663-12672.

22. H. Deng, C. Tian, Z. Gao, S. W. Chen, Y. Li, Q. Zhang, R. Yu, and J. Wang, *Analyst,* 2020,145, 4931-4936.

23. B. Turfan, E. U. *Org. Lett.,* 2002, 4, 2857-2859.

24. T. Mineno, T. Ueno, Y. Urano, H. Kojima, T. Nagano, *Org. Lett.,* 2006, 8, 5963-5966.

25. K. Du, J. Liu, R. Shen, P. Zhang, *Luminescence,* 2019, 34, 407-414.

26.C. Guo, S. Sun, Q. He, V. M. Lynch, J. L. Sessler, *Org. Lett.,* 2018, 20, 5414-5417.

27. L. He, R. P. Zuo, B. Wei, H. Tao, Q. Y. Cao, *Dyes. Pigments,* 2019, 168, 205-211.

28. J. Wu, X. Zhao, Y. Gao, J. Hu, Y. Ju, *Sensor. Actuat. B,* 2015, 221, 334-340.

29. S. Sen, M. Mukherjee, K. Chakrabarty, I. Hauli, S. K. Mukhopadhyay, P. Chattopadhyay, *Org. Biomol. Chem.,* 2013, 11, 1537-1544.

30. K. P.Wang, S. J. Zhang, C. D. Lv, H. S. Shang, Z. H. Jin, S. Chen, Q. Zhang, Y. B. Zhang, Z. Q. Hu, *Sensor. Actuat. B,* 2017, 27, 791-796.

31. T. Wei, G. Wu, B. Shi, Q. Lin, H. Yao, Y. Zhang, *Chin. J. Chem.,* 2014, 32, 1238-1244.

32. H. Tavallali, G. Deilamy-Rad, A. Moaddeli, K. Asghari, *Spectrochim. Acta A,* 2017, 183, 319-331.

33. M. R. Ganjalia, M. Hosseini, Z. Memari, F. Faridbod, P. Norouzi, H. Goldooz, A. Badiei, *Anal. Chim. Acta*, 2011, 708, 107-110.