

## Supplementary Information

### Nitrogen-doped Carbon Dots as fluorescent probe for Detection of Curcumin Based on the Inner Filter Effect

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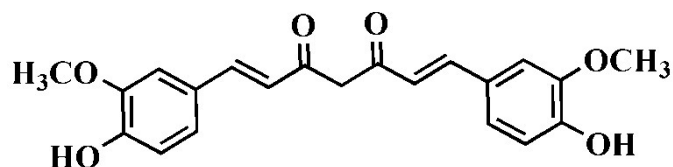


Fig. S1 Chemical structures of curcumin

The fluorescent property and the quantum yield of the N-doped CDs

prepared from citric acid and urea with a molar ratio of 6:1, 3:2, 1:1, 2:3 and 1:6 was investigated. As shown in Fig.S2, with the decrease of the molar ratio from 6:1 to 1:6, the PL intensity of the as-prepared CDs gradually increased under the same excitation wavelength. The corresponding PL spectra from different molar ratios of citric acid to urea was also shown in Fig.S3 and Fig.2A. It was observed that the molar ratios of citric acid to urea has little effect on the maximum excitation and emission wavelengths of CDs. And all of the N-doped CDs obtained from different molar ratios exhibited strong similar blue fluorescence under 365nm UV light. In our preliminary experiments, the molar ratios of citric acid to urea was found crucial for the fluorescence quantum yield (QY) of N-doped CDs. With the decrease of molar ratio (from 6:1 to 1:6), the QY of N-doped CDs increased and then remained basically unchanged. First, if the precursor contained less NH<sub>2</sub> groups (from urea), the QY of the as-prepared N-doped CDs was only 8.9% (6:1) or 9.6% (3:2). However, if NH<sub>2</sub> groups continued to increase, the QY of the N-CDs were above 20.00%. These results revealed that doping more N atoms into CDs can greatly increase the QY of CDs.[S1]

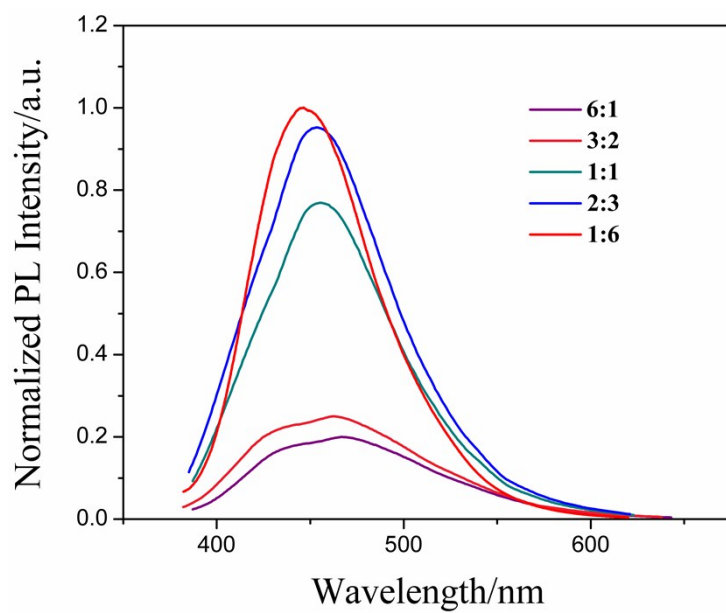
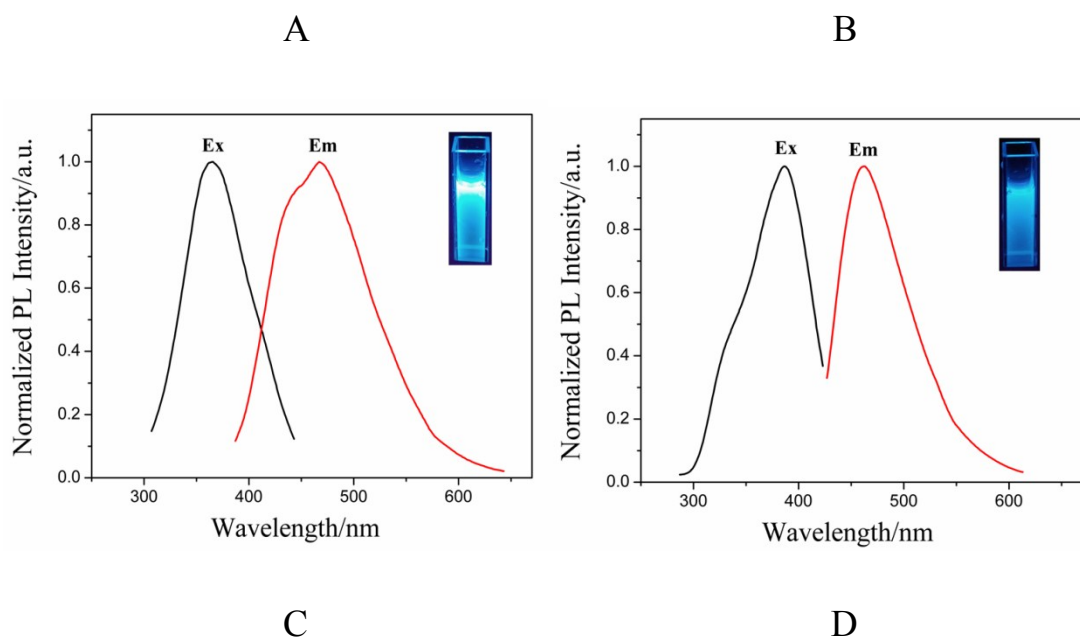


Fig.S2 The UV-vis spectra of the obtained N-doped CDs from different molar ratios of citric acid to urea.



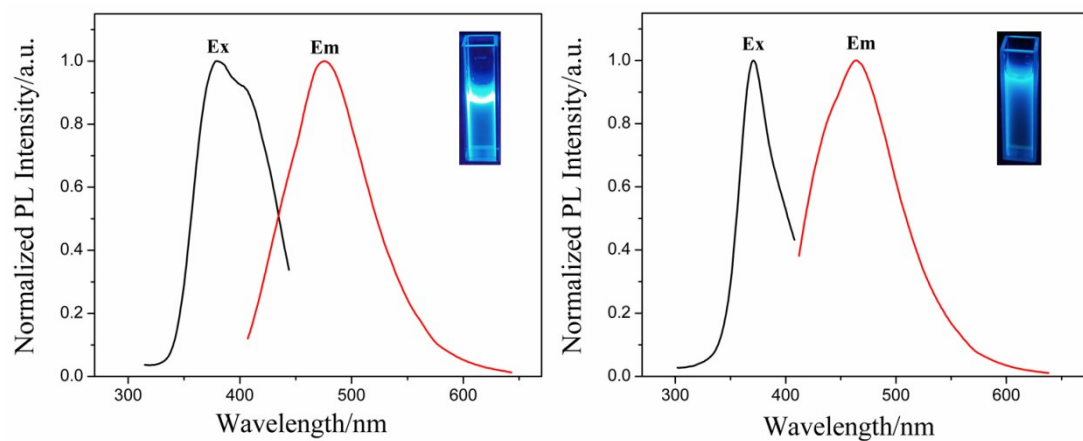


Fig.S3 PL spectra of the N-doped CDs obtained from different molar ratios of citric acid to urea: 1:6 (A), 2:3 (B), 1:1 (C), 3:2 (D). Inset:photographs taken under 365 nm UV light.

Table S1 Physicochemical parameters of the N-doped CDs.

Molar ratios of citric acid to urea	Ex (nm)	Em (nm)	QY(%)	Color under UV light

6:1	365	467	8.9	blue
3:2	385	461	9.6	blue
1:1	380	475	20.6	blue
2:3	370	465	24.8	blue
1:6	360	445	25.4	blue

As shown on the DLS measurement (Fig.S4), the average hydrodynamic size of N-doped CDs was 10.93nm. The hydrodynamic diameter of nanoparticle obtained by DLS was larger than those by TEM due to presence of solvation layer around the N-doped CDs in aqueous solution.

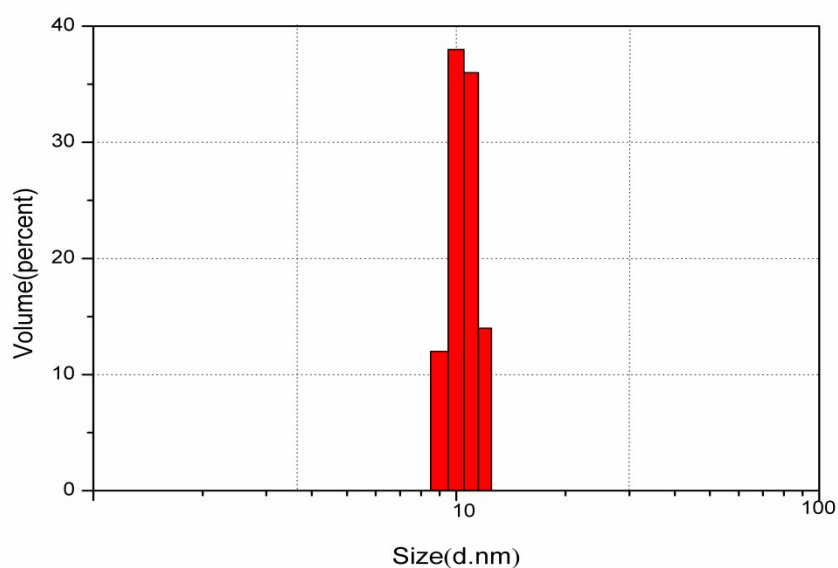


Fig.S4 Hydrodynamic diameter distribution of N-doped CDs.

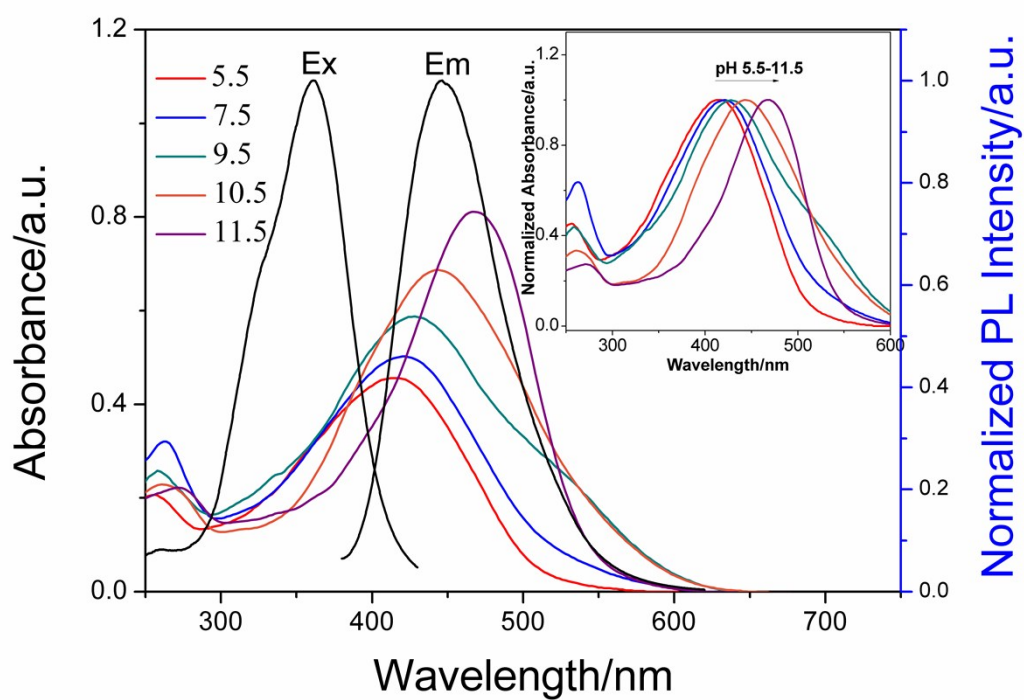


Fig.S5 The spectral overlap between the absorption band of the curcumin and the excitation and emission band of the N-doped CDs at different pH values. Inset : Normalized UV-Vis spectra of curcumin at different pH. The value of pH was 5.5, 7.5, 9.5, 10.5 and 11.5 from left to right.

Table S2. Comparison of different methods for curcumin detection.

<b>Methods</b>	<b>Linear range (<math>\mu\text{M}</math>)</b>	<b>Detect limit (<math>\mu\text{M}</math>)</b>	<b>reference</b>
HPLC	0.6 - 271	0.18	S2
MALDI-TOF-MS	2.7 - 270	0.27	S3
Voltammetry	9.9 - 107	4.1	S4
RP-HPLC	0.27 - 27	0.027	S5
UV	0 - 40.7	0.2	S6
LC-MS	0.014 - 2.7	0.014	S7
RLS	1.08 - 162.9	0.19	S8
Capillary Electrophoresis(CE)	1080 - 4340	27	S9
QDs-based ratiometric fluorescence probe	0.16 - 16.9	0.037	S10
this method	0.2 - 10	0.084	this work



A HPLC method for determination of curcumin in human urine samples was performed to compare with our proposed method. As shown in Fig.S6, the blank and control samples were injected, the result indicated that blank urine showed no significant interfering to detection of curcumin in human urine samples.

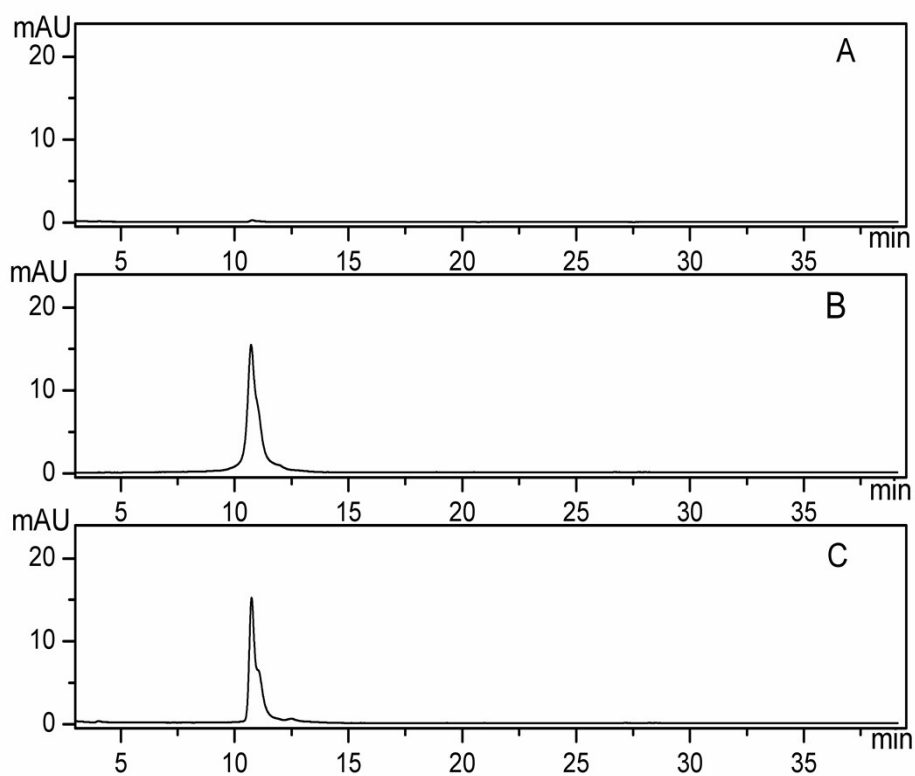


Figure S6 HPLC chromatograms : (A) blank urine, (B) curcumin standard substance, (C) urine sample

### Supporting References

- [S1] X.Y. Zhai, P. Zhang, C.J. Liu, T. Bai, W.C. Li, L.M. Dai, W.G. Liu, *Chem. Commun.*, 2012, **48**, 7955-7957.
- [S2] M. Rahimi, P. Hashemi, F. Nazari, *Anal.Chim.Acta*, 2014, **826**, 35- 42.
- [S3] Y.S. Huang, T.J. Hsieh, C.Y. Lu, *Food Chem.*, 2015, **174**, 571-576.
- [S4] G. K. Ziyatdinova, A. M. Nizamova, H. C. Budnikov, *J. Anal. Chem.*, 2012, **67**, 591-594.
- [S5] A. Mishra, G. Dewangan, W. R. Singh, S. Hazra, T. K. Mandal, *J. Adv. Pharm. Technol. Res.*, 2014, **5**, 147-149.
- [S6] B. Tang, L. Ma, H.Y. Wang, G.Y. Zhang, *J. Agric. Food Chem.*, 2002, **50**, 1355-1361.
- [S7] K.Y. Yang, L.C. Lin, T.Y. Tseng, S.C. Wang, T.H. Tsai, *J. Chromatogr. B*, 2007, **853**, 183-189.
- [S8] Z.G. Chen, L. Zhu, T.H. Song, J.H. Chen, Z.M. Guo. *Spectrochim. Acta, Part A.*, 2009, **72**, 518-522.
- [S9] M. Lechtenberg, B. Quandt, A. Nahrstedt, *Phytochem. Anal.*, 2004, **15**, 152-158.
- [S10] X.J. Zhao, F.X. Lia, Q.Y. Zhang, Z.B. Li, Y.H. Zhou, J. Yang, C. Dong, J.P. Wang, S.M. Shuang, *RSC Adv.*, 2015, **5**, 21504-21510.