Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information (ESI)

for

Synthesis of nitrogen-doping carbon dots with different photoluminescent properties by controlling the surface states †

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1. Quantum Yield Calculations

The materials were synthesized by tuning the molar ratios of citric acid and guanidine hydrochloride. 0.42 g (2 mmol) of citric acid was separately reacted with guanidine hydrochloride of 0.064 g and 0.191 g, making the molar ratio of citric acid to guanidine hydrochloride is 3:1 and 1:1, named the materials as CDs-1, CDs-2. Then, 0.48 g (5 mmol) guanidine hydrochloride was separately reacted with citric acid of 0.35 g, 0.175 g, 0.116 g and 0.0875 g, making the molar ratio of citric acid to guanidine hydrochloride vary from 1:3 to 1:6, 1:9, and 1:12, named the materials as CDs-3, CDs-4, CDs-5 and CDs-6.

The quantum yield (Φ) of CDs was calculated using quinine sulfate as reference. Quinine (literature Φ = 0.54) was dissolved in 0.1 M H_2SO_4 (refractive index (η) of 1.33) while the CDs was dissolved in ultra-pure water (η = 1.33). Then the quantum yield of CDs was calculated by comparing the integrated photoluminescence intensities and the absorbance values of CDs with the references Fluorescein sodium. The data was plotted and the slopes of the sample and the standards were determined. The quantum yield (QY) was calculated using the below equation:

$\Phi x = \Phi ST\ (mx\ /\ mST)\ (\eta x2\ /\eta ST2\ )$ Where Φ is the quantum yield, m is slope, η is the refractive index of the solvent, ST is the standard and X is the sample. The quantum yield for CDs-1, CDs-2, CDs-3, CDs-4, CDs-5 and CDs-6 were 3.4%, 6.3%, 11.7%, 13.6%, 53.7% and 60.5%, respectively.

2. Characterizations of CDs

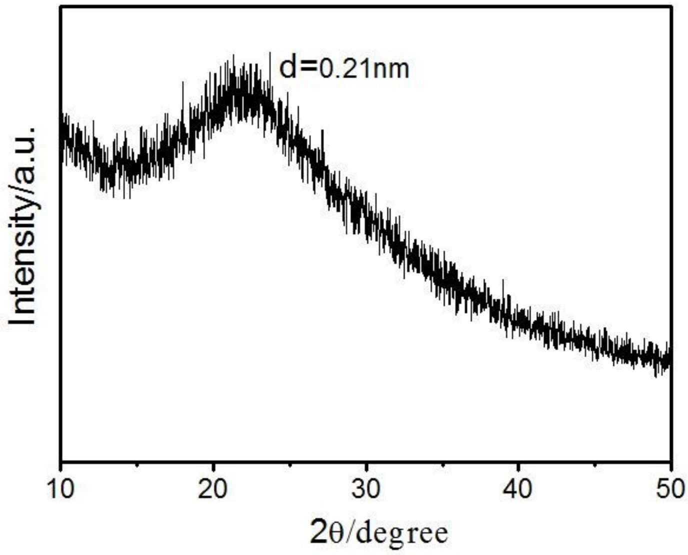

Fig.S1 XRD spectrum of the CDs. XRD pattern of CDs displaying a broad peak centered at around 21°, similar to the graphite lattice spacing, which is a typical band corresponding to highly disordered amorphous carbon

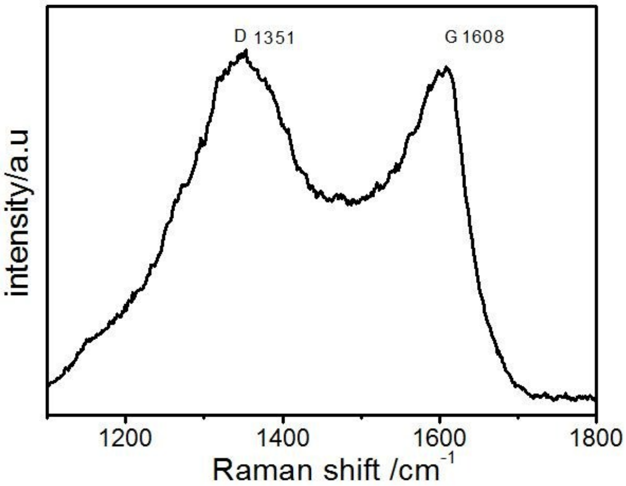

Fig.S2 Raman spectrum of the CDs. The spectrum of the CDs shows contribution from both the G band at 1608 cm^{-1}, related to in-plane vibration of sp^2 carbon, and the D band at 1351 cm^{-1}, related to the presence of sp^3 defects. The relative intensity (I_D/I_G) ratio of ~1.05, which is larger than graphene oxide and chemically, reduced graphene, suggesting the existence of defects in the CDs.

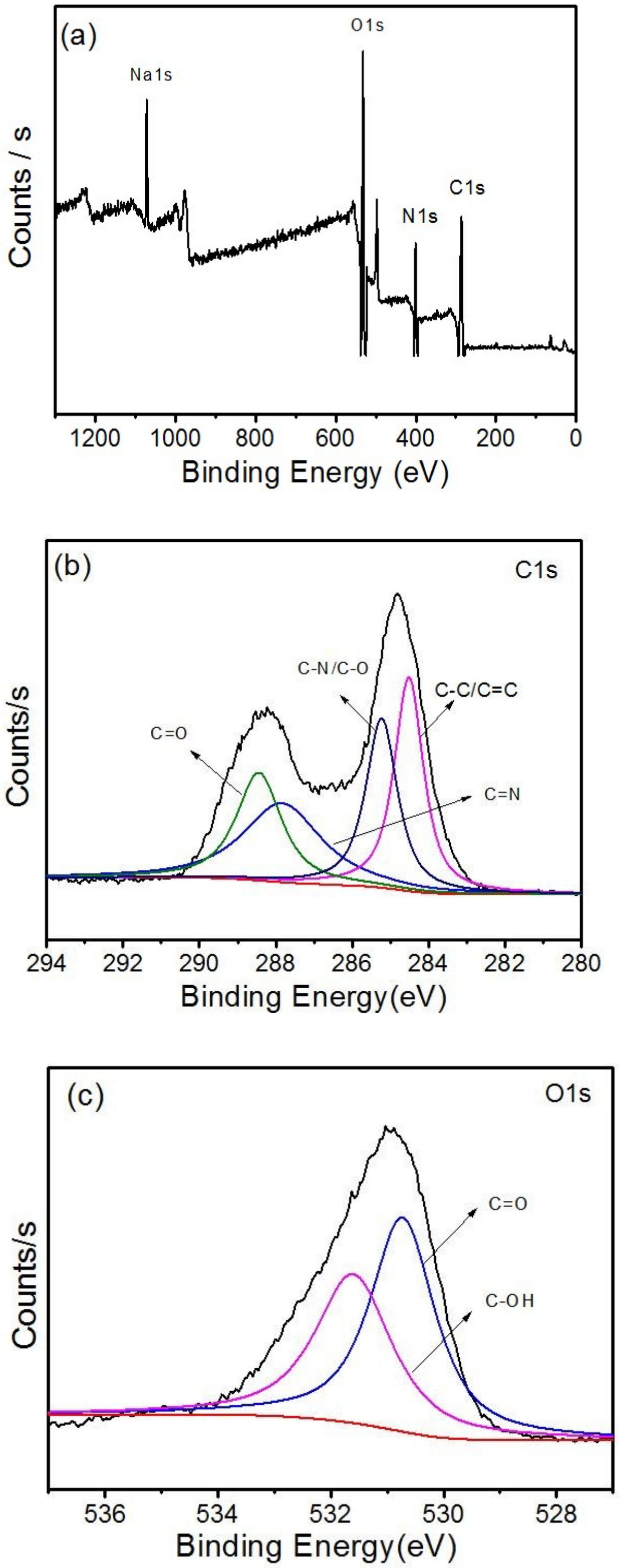

Fig.S3 The XPS of (a) full spectrum, (b) C1s and (c) O1s in the product. The O 1s spectrum exhibits two peaks at 530.7 and 531.6 eV, which can be assigned to C=O and C–OH/C–O–C groups, respectively. The C 1s XPS spectrum reveals different types of carbon atoms are contained in the as-prepared CDs, corresponding to sp^2 C in the form of C–C or C=C in graphene at 284.5 eV, sp^3 C in the form of C–N and C–O at 285.2 eV, C=N at 287.8eV, and C=O at 288.4eV.

3. Optical properties of CDs

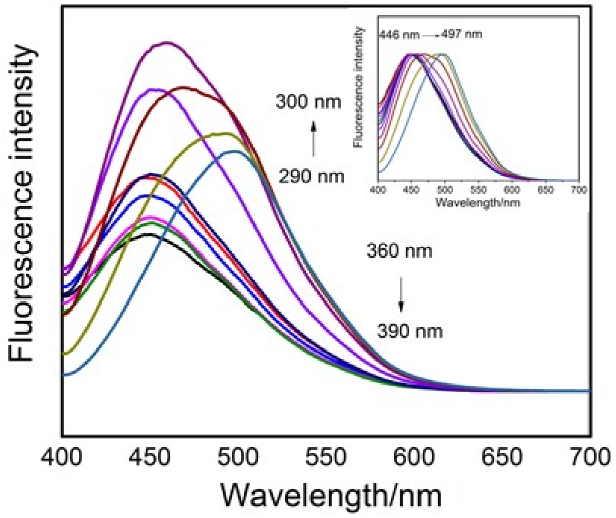

Fig.S4 Emission spectra of CDs-2 obtained at different excitation wavelengths. Inset: the normalized PL emission spectra.

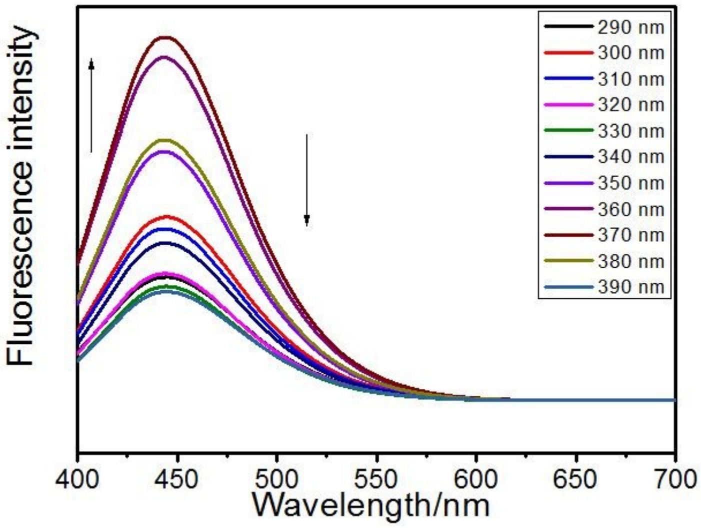

Fig.S5 Emission spectra of CDs-4 obtained at different excitation wavelengths.

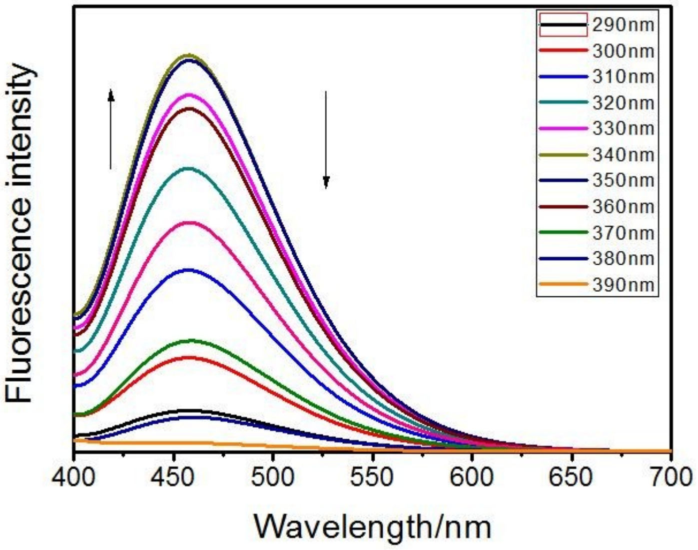

Fig.S6 Emission spectra of CDs-5 obtained at different excitation wavelengths.

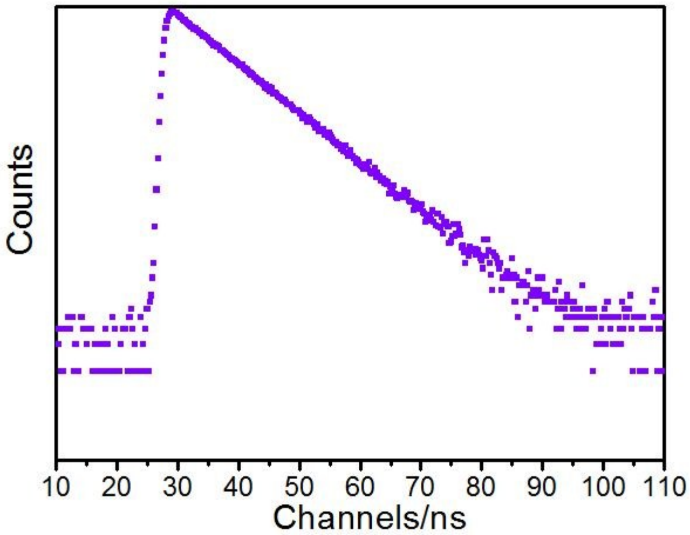

Fig.S7 Decay curve of the as-prepared CDs.

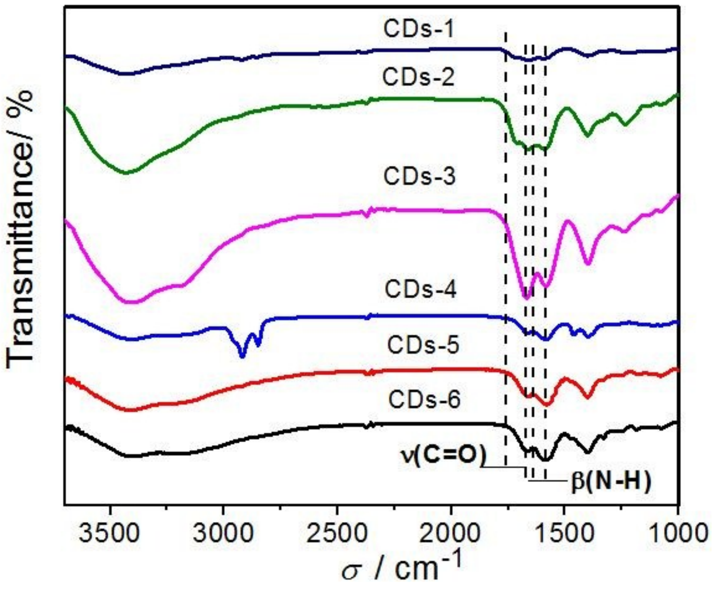

Fig.S8 FTIR spectrum of the as-prepared different C-Dots-based materials.

4. Stability of the CDs

The PL emissions of the CDs remains stable under continuous exposure of UV light for two hours (Fig. S9, ESI†), implying that the CDs cannot be photobleached under the excitation light and can be used as fluorescence probes for long-terms monitoring. Furthermore, scare changes in PL emission were found even if in salt solution of 2M (Fig. S10, ESI†), indicating that the CDs are very stable and thus can be practically applied in biomedium wherein high concentrations have to be involved. Interestingly, the N-doped CDs had strong PL in the range of pH 6 to 12 (Fig. S11, ESI†), which could be understood in terms of the change in surface charge owing to protonation-deprotonation, and thus can be used for monitoring molecular interaction events occurred in a medium of wide range of pH. The above results verify the excellent stability of the CDs, indicating that the CDs have the potential for practical applications either in biosensing, biolabelling or bioimaging fields.

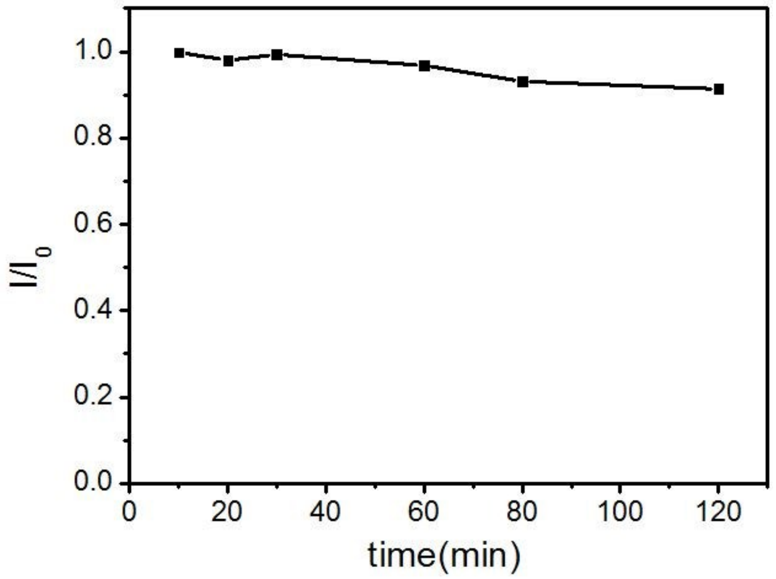

Fig.S9 The effect of UV light irradiation on CDs fluorescence (I_0 and I correspond to the fluorescence intensity of CDs at 458 nm in the absence and presence of irradiation, respectively).

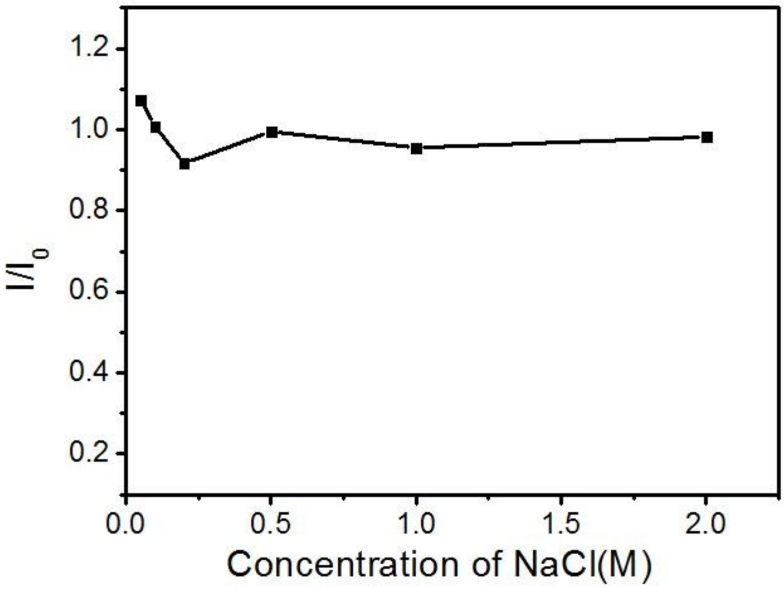

Fig.S10 The effect of the NaCl concentration (0, 0.5，0.1，0.2，0.5，1，2 M) on CDs fluorescence.

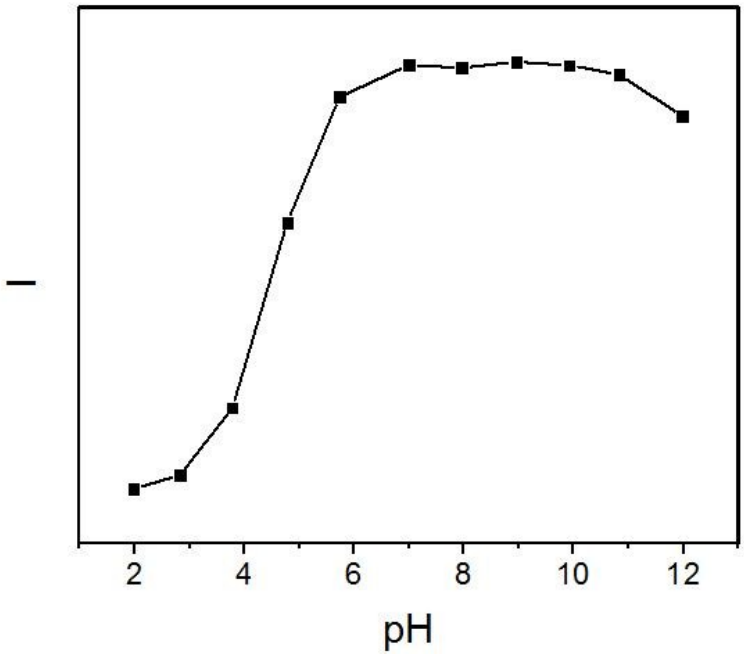

Fig.S11 The effect of the different pHs on CDs.

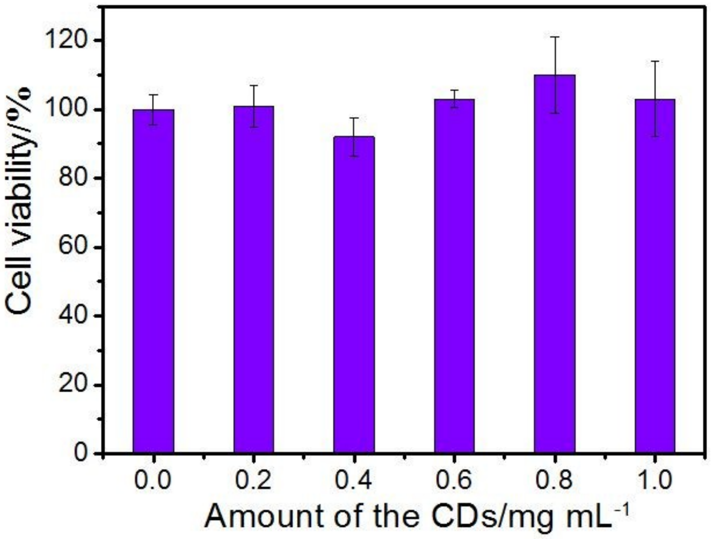

Fig.S12 Cell viability assays of the cells treated with different concentrations of the CDs. Cell Counting Kit-8 (CCK-8) assay showed that the CDs scarcely impose toxicity to the Human epidermoid cancer cells and own excellent biocompatibility even if the cells were treated by high dose of CDs of 1 mg / mL for 24 h (Fig. S12, ESI†). Hence, the N-doped CDs with small size, high selectivity, good stability, and especial biocompatibility substantially make them superior in potential bioimaging applications. In such case, Hep-2 cells were employed for semiquantitative monitoring of the intracellular Hg^{2+} level.

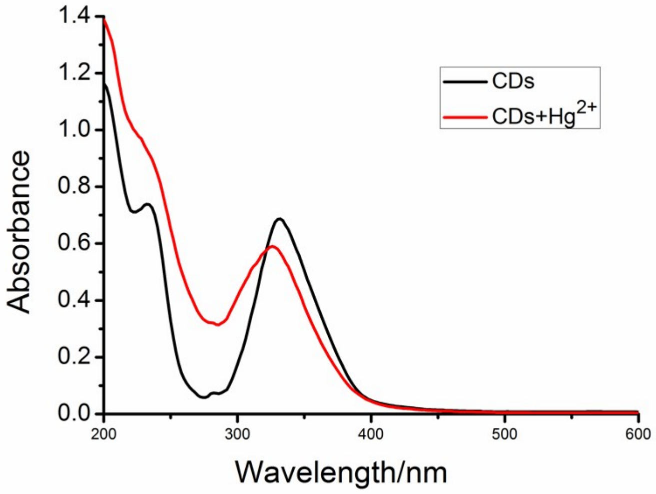

Fig.S13 The UV-vis absorption of the CDs and the CDs-Hg^{2+}.

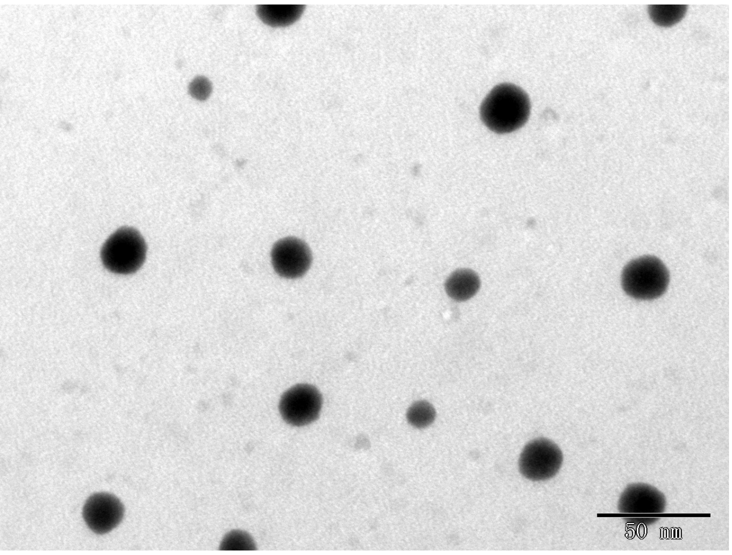

Fig.S14 The TEM image of the as-prepared CDs with Hg^{2+} ions. TEM images of the as-prepared CDs show that average size of the CDs get enlarged from 4.61 nm to 16.2 nm after interacting with Hg^{2+}, indicating that some degree of aggregations has occurred (Fig.1a and Fig. S14, ESI†).

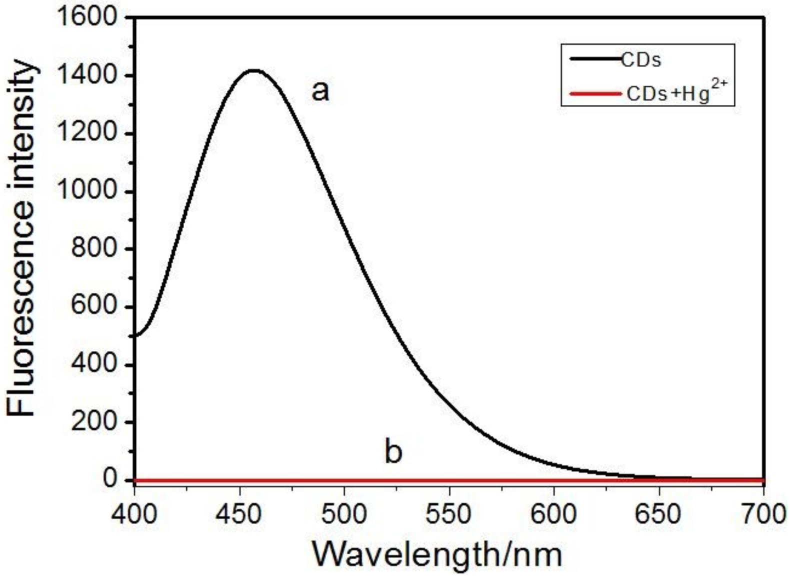

Fig.S15 FL spectra of solutions of CDs (curve a) and CDs- Hg^{2+} mixture (curve b). It could be seen that CDs solution in the absence of Hg^{2+} exhibits a strong PL peak at 458 nm (Fig. S15, curve a). In contrast, the presence of Hg^{2+} leads to a substantial decrease of fluorescence in intensity (Fig. S15, curve b), implies that the fluorescence of CDs could be quenched by the Hg^{2+} effectively. On the basis of this obvious phenomenon, CDs can be utilized as highly efficient probes for Hg^{2+} detection in the following experiments. The phenomenon "Hg^{2+} concentration-dependent quenching CDs fluorescence" was evaluated for quantitative detection of Hg^{2+}.

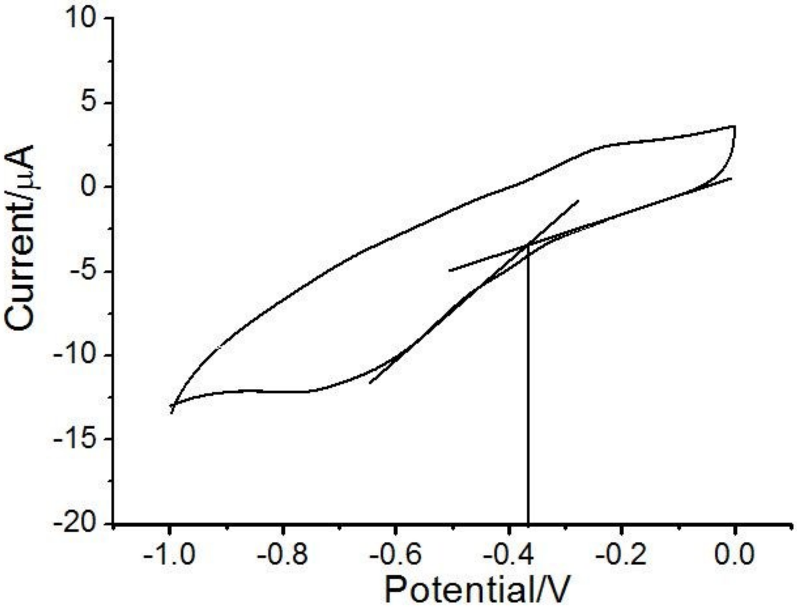

Fig.S16 Cyclic voltammograms of the N-doped C-Dots in the solution state.

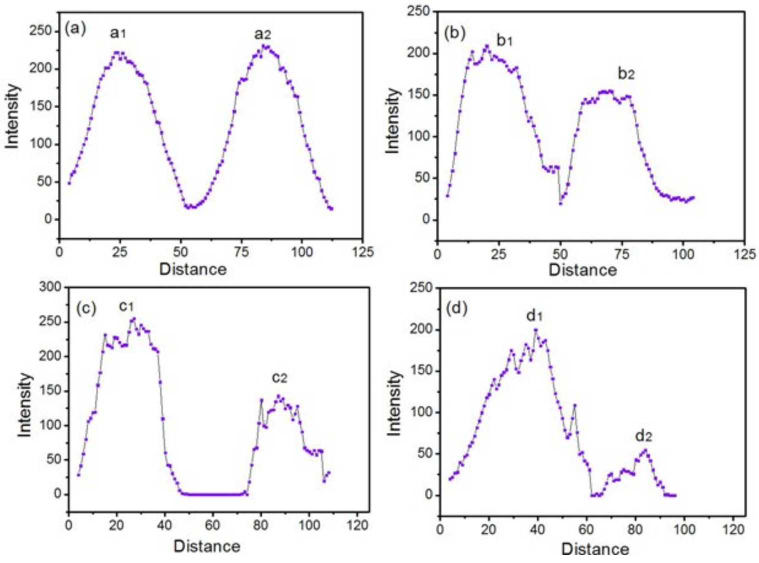

Fig.S17 Quantitative analyzed of fluorescence intensity in each group of cell with result of the bioimaging.