Highly sensitive carbon dots fluorescent probe with ratiometric emission for the determination of ClO^-

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Preparation method of CDs

3 g citric acid were dissolved in 30 mL doubly deionized water and the solution was added into a 50 mL Teflon autoclave matched with stainless steel and reacted at 180 ℃ for 12 h. When the temperature drops to room temperature, the suspensions were centrifuged for 15 min at 8000 rpm for separation and dialyzed against doubly deionized water for 24 h with dialysis membrane (MWCO=500-000). Finally, the treated pure aqueous solution was vacuum freeze-dried to collect dried CDs.

Quantum yield (QY) measurement

QY of the CDs was determined by a widely accepted relative method. Specially, rhodamine 6G (QY =95% in ethanol) was selected as the reference. The QY of a sample was calculated according to the following equation:

$$\varphi=\varphi'\times\frac{A'}{I'}\times\frac{I}{A}\times\frac{\eta^2}{\eta'^2}$$

Where φ is the QY of the testing sample, I is the testing sample's integrated emission intensity, n is the refractive index (1.33 for water and 1.36 for ethanol), and A is the optical density. The prime symbol (′) refers to the referenced dye of known QY. To minimize reabsorption effects, absorption was always kept below 0.1 at the excitation wavelength.

Cytotoxicity Assay

Human hepatic carcinoma SMMC7721 cells were cultured in DMEM medium containing 10% fetal calf serum, 100 U•mL^{-1} penicillin, 100 μg•mL^{-1} streptomycin, and cultured in an incubator at 37 °C, 5% CO_2. The cells in the logarithmic growth phase were seeded in a 96-well culture plate (100 μL well) at a cell number of 8×10^4•mL^{-1}. After 24 hours of routine culture, the cells were divided into a blank control group and a drug-administered group with 6

$$\text{Cell viability}(\%)=\frac{OD_{test\ group}-OD_{blank\ control\ group}}{AOD_{Normal\ control\ group-OD_{blank\ control\ group}}}\times100\%$$

sets of duplicate holes in each group. After 24 h, the liquid in the well was aspirated, and 100 μL of DMEM medium containing 0.5 mg•mL^{-1} MTT was added to each well. After further incubation for 4 h, the supernatant was aspirated, and 100 μL of DMSO was added to each well to dissolve the precipitate. The microplate shaker was mixed for 10 min, and the absorbance (OD) value was measured at 570 nm. The survival rate of the cells was measured by the MTT method, and was calculated by the following formula:

The experiment was repeated three times. SMMC7721 cells were obtained from Chinese Academy of Sciences Shanghai Cell Bank.

Preparation of N, S-CDs-dyed paper strips and ions sensing test

Cellulose-based filter paper was wetted in N, S-CDs solution and dyed yellow under UV lamp with excitation at 365 nm. After 1 min, the filter paper was extracted from the solution and naturally dried in the air. Then, NaClO aqueous solution was dyed on the strip containing N, S -CDs in the same way. The change of the fluorescence on the strips was observed under a UV lamp with 365 nm excitation.

Table S1. Lifetime calculations from the time-resolved decay profiles of N, S-CDs and N, S-CDs-ClO^-.

Sample	τ_1（ns）	Percent (%)	τ_2（ns）	Percent (%)	Ave. T(ns)
N, S-CDs	3.1347	81.62	15.1230	18.38	5.34
N, S-CDs-ClO^-	2.4005	60.82	9.2313	39.18	5.07

Table S2 Comparison of N, S-CDs with other CDs probe for ClO- detection.

Probe	Linear range (μM)	LOD (μM)	Ref.
Biomass CDs	0.1-10 and 10-300	0.05 and 0.06	25
Fluorescent SNCDs	0.18-4.22	0.021	26
BN-CDs	0.1-1000	0.045	27
Ruthenium complex-modified CDs	0.05-7	0.012	36
fluorescein labelled-CDs	0-70	0.093	32
N, S-CDs	0.067-60	0.0091	This work

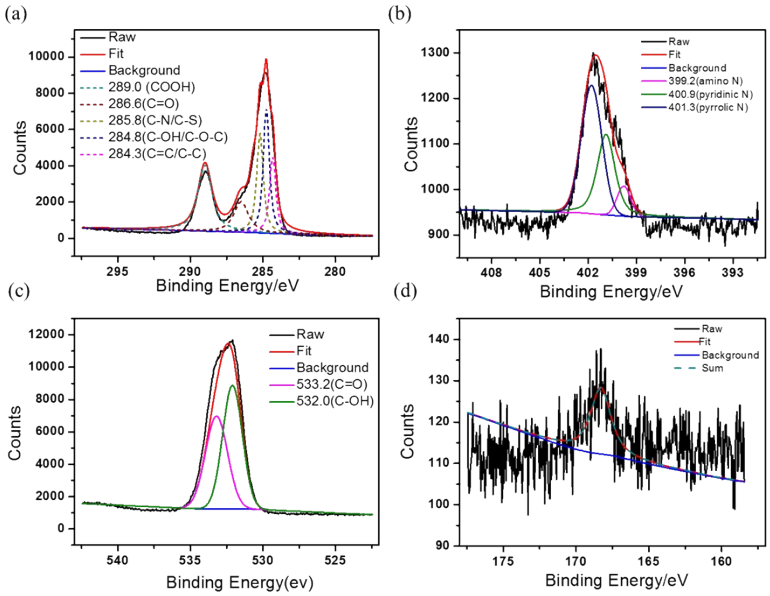

Fig. S1 (a) High-resolution XPS data of C 1s; (b) N 1s (c) O 1s and S 2p of N, S-CDs.

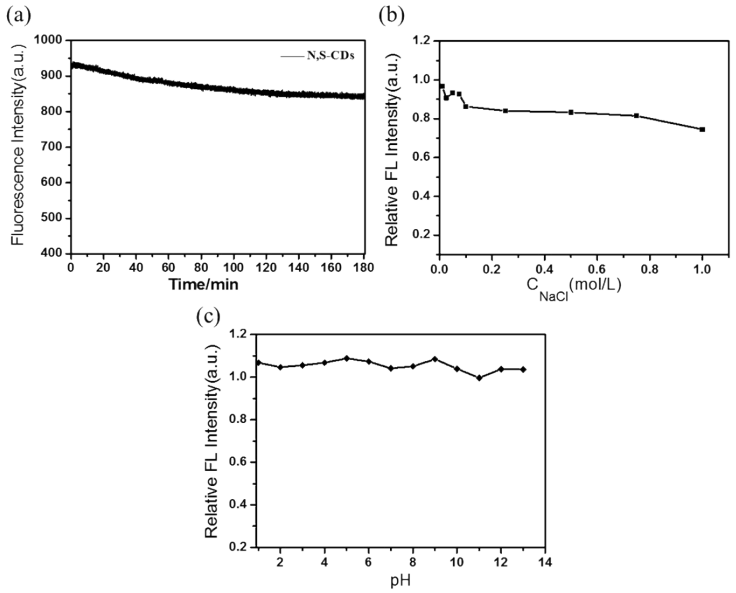

Fig. S2 (a) Effect of time intervals of irradiation with xenon arc light on fluorescence intensity of N, S-CDs; (b) Effect of ionic strength on fluorescence intensity of N, S-CDs. The ionic strengths are controlled by various concentrations of NaCl. (c) Effect of pH on FL intensity of N, S-CDs. The pH is adjusted by the PBS buffers.

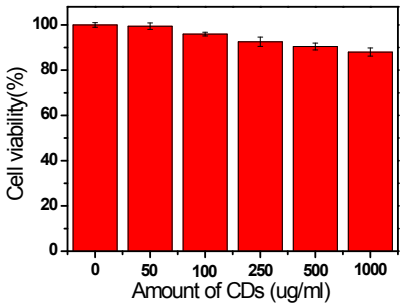

Fig. S3 Cytotoxicity testing results of N, S-CDs on SMCC 7721 cells viability. The values represent percentage cell viability (mean% ± SD, n=6).

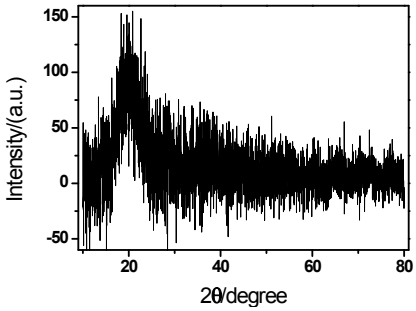

Fig. S4 X-ray diffraction (XRD) pattern of the N, S-CDs.

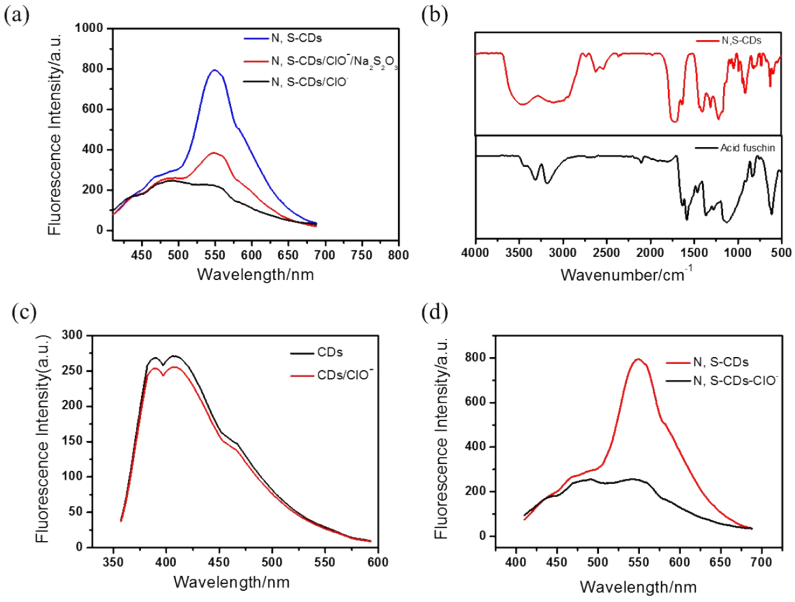

Fig. S5 (a))Fluorescence spectra of N, S-CDs, N, S-CDs-ClO^- and N, S-CDs-ClO^--$Na_2S_2O_3$; (b) FT-IR spectra of N, S-CDs and acid fuchsin; (c) Fluorescence spectra of CDs and CDs-ClO^-; (d) Fluorescence spectra of N, S-CDs and N, S-CDs-ClO^-.

Scheme S1. Working Mechanism of N, S-CDs for ClO^- sensing.