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Supplementary Information

Ultrasensitive and selective fluorescent recognition of selenite by o-phenylenediamine functionalized carbon quantum dots

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1. Instrumentation and characterization methods

Transmission electron microscopy (TEM) was performed by a copper grid coated with thin films of carbon on a Tecnai G2 F20 microscope (FEI Co. U.S.A) at an accelerating voltage of 200 kV. Fourier-transform infrared spectra (FT-IR) were obtained for KBr pellets on Frontier-PerkinElmer FT-IR spectrometer from 4000 to 400 cm^{-1} of wavenumber. UV−vis absorption spectra were obtained on a UV-3600 UV-VIS-NIR spectrophotometer (Shimadzu, Japan) by a quartz cuvette with 1 cm path length.

Fluorescence excitation and emission spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer with a scan rate of 240 $nm \cdot min^{-1}$, which utilized a Xenon lamp of 1/5 nm slit width and equipped by a quartz cuvette with an optical path length of 1 mm, the excitation (Ex) /emission wavelengths (Em) were 400 nm and 461 nm, respectively. Fluorescence imaging experiments were performed on an FV 1000-IX81confocal laser scanning microscope (Olympus, Japan) with FV5-LAMAR for excitation at 400 nm and a variable bandpass emission filter set to 500-550 nm through a 100 × 1.4 NA objective. Fluorescent photographs were taken by a SONY DSC-W800 with ZF-20D hand-held UV lamp (Shanghai, China) under excitation at 400 nm.

X-ray photoelectron spectroscopy (XPS) survey data were obtained by a Thermo Scientific ESCALAB 250Xi equipped with an Al Kα X-ray

source (1487.2 eV), the analysis chamber was 8×10^{-8} mbar and the X-ray spot was 650 μm. Zeta potential of the OPD-CQDs aqueous solution was measured by a Zetasizer Nano ZS series (Malvern Instruments, UK) with a laser wavelength of 633 nm and a detection angle of 173° at 25 °C.

2. Experimental methods

2.1 Quantum yield calculations of the OPD-CQDs

The quantum yield (QY) of the OPD-CQDs was calculated by a reported formula utilized quinine sulfate in 0.1 mol/L H_2SO_4 as the reference sample.[1] The QY of quinine sulfate was 54% at 365 nm excitation,[2] while the QY of OPD-CQDs was calculated according to the following equation:

$$\phi_2 = \phi_1 \times \frac{F_2}{F_1} \times \frac{A_1}{A_2} \times \frac{n_2^{\,2}}{n_1^{\,2}}$$

where ϕ represents the QY of testing sample, F represents the fluorescence intensity of testing sample, A stands for the absorbance, n stands for the refractive index. The subscript “1” and “2” refer to the OPD-CQDs and quinine sulfate, respectively. In an identical solvent, $n_2/n_1 = 1$.

2.2 Stability of the OPD-CQDs

The photostability and chemical stability of OPD-CQDs were

mainly investigated under different conditions, exemplified by photobleaching experiment, inorganic salt ions and different acid-base environments. Firstly, the photostability was investigated by continuously stimulating OPD-CQDs aqueous solution (3 μg/mL) under a 150 W xenon lamp for 60 min, and the fluorescence spectra (Ex = 400 nm, Em = 461 nm) were continuously measured and recorded during this periods. Meanwhile, the resisted inorganic salt ions ability and pH stability were evaluated by the fluorescence changes of OPD-CQDs (3 μg/mL) incubated with a series concentration of NaCl solution (10^{-6}, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} and 1.0 mol/L) or a series buffer solutions with pH 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0.

2.3 The selectivity of OPD-CQDs to SeO_3^{2-}

The selectivity and anti-interference ability were investigated by the fluorescence fluctuation of OPD-CQDs (3 μg/mL) incubated with different metal ions (200 μmol/L K^+, Mn^{2+}, Na^+, Zn^{2+}, Sn^{2+}, Ba^{2+}, Fe^{2+}, Ca^{2+}, Ni^{2+}, Mg^{2+}) and anion (200 μmol/L NO_2^-, $H_2PO_4^-$, $S_2O_3^{2-}$, Cl^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, HCO_3^-, F^-, CH_3COO^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, AlO_2^-, AsO_3^{3-}, SeO_4^{2-}).

2.4 Detection of SeO_3^{2-} in actual samples

In order to further investigate the anti-interference ability and

application of OPD-CQDs in actual sample detection, real complex biological samples (such as tap water and human serum samples) were utilized to evaluate the feasibility and applicability of OPD-CQDs. Four standard concentrations SeO_3^{2-} solutions were prepared and added to tap water and human serum samples, the measured concentration and recovery rate of each sample can be calculated according to the linear fitting equation of SeO_3^{2-}. Each experiment was repeated three times.

2.5 MTT assays

The cytotoxicity of OPD-CQDs to Hela cells was examined by MTT assay. Firstly, Hela cells were seeded in culture flasks and grown in DMEM with 10% fetal bovine serum (FBS, Hyclone) and 1% penicillin/streptomycin at 37 ◦C in 5% CO_2 atmosphere for 24 h. Secondly, it was seeded in a 96-well plate (1×10^4 cells per well) and cultured for 24 h in 1000 μL complete medium, which was treated with different concentrations of OPD-CQDs (0 μg/mL, 0.1 μg/mL, 1.0 μg/mL, 5.0 μg/mL, 10.0 μg/mL, 50.0 μg/mL and 100.0 μg/mL) for 24 h. In addition, 100 μL new medium with MTT (10 μL, 5 mg/mL) was added and incubated for 4 h to form formazan dye. The absorbance at 490 nm was measured on enzyme-linked immune absorbent detector after 100 μL DMSO was added to dissolve formazan dye. The cytotoxicity of OPD-CQDs was calculated by the statistical analysis of absorbance

values.

3. Figure

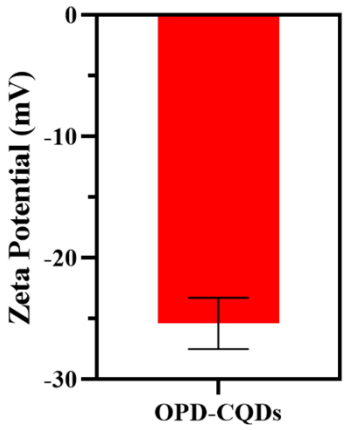

Fig. S1 Zeta potential data of OPD-CQDs.

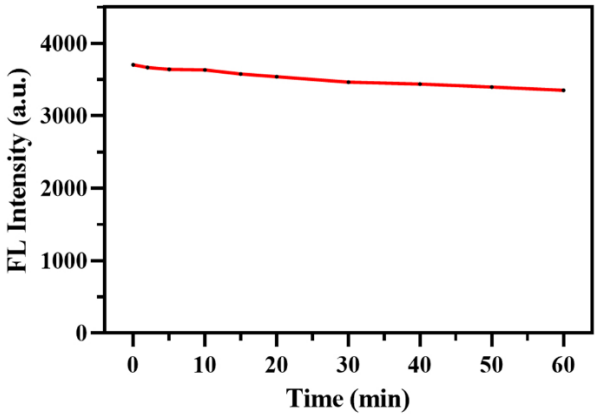

Fig. S2 The fluorescence intensity variation of the OPD-CQDs under continuous irradiation with xenon lamp for 60 min.

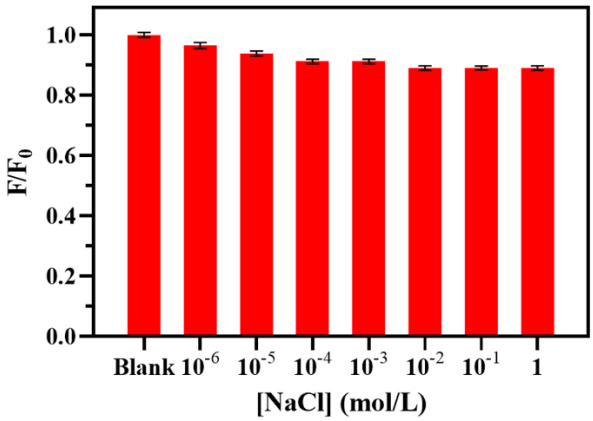

Fig. S3 The fluorescence intensity variation of OPD-CQDs under different concentrations of NaCl.

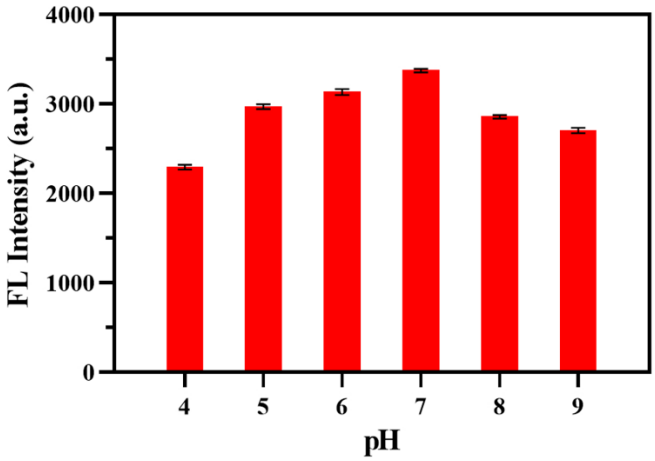

Fig. S4 The fluorescence intensity variation of OPD-CQDs under different pH.

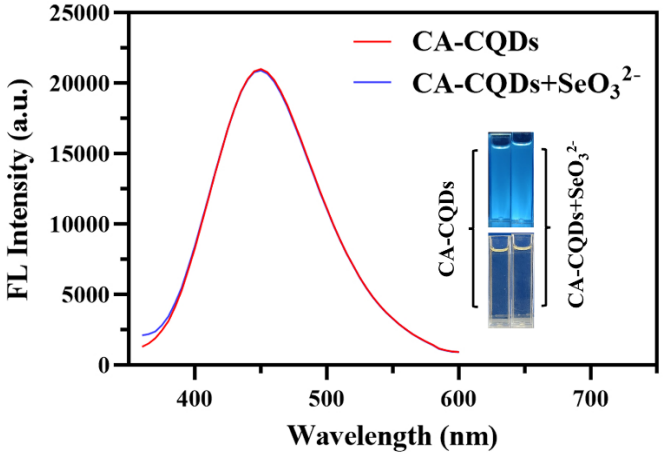

Fig. S5 The Fluorescence changes of CA-CQDs before and after adding SeO_3^{2-}.

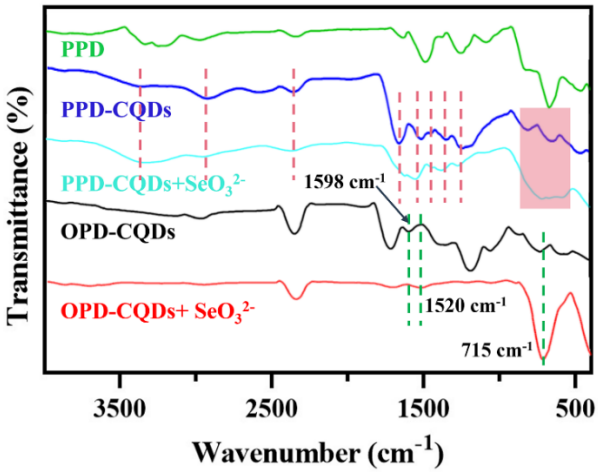

Fig. S6 The mechanism research of specific recognition between OPD-CQDs and SeO_3^{2-}. The infrared spectra of p-phenylenediamine (PPD), carbon quantum dots prepared by p-phenylenediamine (PPD-CQDs), PPD-CQDs +SeO_3^{2-} (PPD-CQDs cultured with SeO_3^{2-}), OPD-CQDs and OPD-CQDs +SeO_3^{2-} (OPD-CQDs cultured with SeO_3^{2-}).

References:

1 K. Jiang, S. Sun, L. Zhang, Y. Lu, A. Wu, C. Cai and H. Lin, *Angew. Chem. Int. Ed.*, 2015, **54**, 5360-5363.

2 Y. Wu, L. Cao, M. Zan, Z. Hou, M. Ge, W. F. Dong and L. Li, *Analyst*, 2021, **146**, 4954-4963.