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Electronic Supplementary information

Preparation and utilization of carbon dots as nanoprobe for sensitive tartrazine and palladium(II) determination

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Table of Contents

Experimental

Reagents and chemicals

Instruments

Synthesis of Cdots

Quantum yield measurement of the Cdots

Optimizing the experimental conditions

Fluorescence detection procedure for Trz and Pd(II)

Real sample analysis

Fig. S1 The high-resolution TEM of Cdots.

Fig. S2 FL emission spectra of Cdots in water (red dot-line, λex = 325 nm) and quinine sulfate (black line, λex = 360 nm) in 0.1 M H_2SO_4 solution as the standard.

Fig. S3 (A) FL intensities at 325 nm of the Cdots at various pH values and (B) FL intensities of the Cdots in the presence of different concentrations of NaCl.

Fig. S4 The UV-vis spectra of Cdots, Trz and Cdots/Trz mixed solution.

Fig. S5 pH-dependent FL signals of Cdots at various pH values (PBS buffer, 50 mM) containing 50 μM Trz (A) or 50 μM Pd(II) (C). The relative FL intensity of Cdots at 325 nm wavelength in the presence of 50 μM Trz (B) or 50 μM Pd(II) (D) at various pH values.

Table S1. Comparison of analyte, technology, materials, linear range and detect limit for Trz analysis using different detection methods.

Table S2. Comparison of analyte, technology, materials, linear range and detect limit for Pd(II) analysis using different detection methods.

Experimental

Reagents and chemicals

Furadantin (FDT) was obtained from the Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Palladium chloride ($PdCl_2$), tartrazine (Trz), D-fructose (Fru), dextran (Dex), nicotinic acid (NA), ascorbic acid (AA), glutathione (GSH), citric acid (CA), glucose (Glu), L-sucrose (Suc), sodium citrate (SC), phenylalanine (L-Phe), L-alanine (L-Ala), histidine (His) and lysine (Lys) were purchased from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other solvents and chemicals are of analytical grade using without further purification. Ultrapure water was used throughout the experiment.

Instruments

The ultraviolet-visible (UV-vis) and fluorescence (FL) spectra were measured on a Shimadzu UV-2550 spectrophotometer (Tokyo, Japan) and a Jasco FP-6500 spectrofluorometer (Japan), respectively. Transmission electron microscopy (TEM) and high-resolution TEM images were obtained on a Jeol JEM-2100. Fourier transform infrared (FT-IR) spectrum was obtained using a Nicolet 5700 IR spectrophotometer (USA). X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo ESCALAB 250 X-ray photoelectron spectrometer (USA). The fluorescent lifetimes were obtained using an Edinburgh Instruments FLS980 spectrophotometer with excitation at 300 nm.

Synthesis of Cdots

Firstly, 0.05 g of FDT was dispersed in 8.0 mL of CH_3OH. Subsequently, the dispersed precursor was transferred into a 25 mL Teflon reactor and kept at 180 °C for 20 h, followed by cooling to room temperature. After centrifugation at 12000 rpm for 20 min, the supernatant was collected, that is Cdots.

Quantum yield measurement of the Cdots

Reference on quantum yield measurements: Lakowicz, J. R. *Rinciples of Fluorescence Spectroscopy*, 2nd Ed., **1999**, Kluwer Academic/Plenum Publishers, New York. The optical densities were measured on a Shimadzu UV-2550 spectrophotometer (Tokyo, Japan) in the range of 200-700 nm. Quinine sulfate in 0.1

M H_2SO_4 (literature quantum yield 0.54 at 360 nm) was chosen as a standard. Absolute values are calculated using the standard reference sample that has a fixed and known fluorescent quantum yield value, according to the following equation:

$$\Phi_x = \Phi_s \left[\frac{Fu}{Au}\right] \left[\frac{As}{Fs}\right] \left[\frac{\eta u}{\eta s}\right]^2$$

where Φ is the quantum yield, *Fu* and *Fs* are the measured integrated emission intensity of Cdots and quinine sulfate, respectively. *Au* and *As* are the optical density of Cdots and quinine sulfate, respectively. And *ηu* and *ηs* are the refractive index of Cdots and quinine sulfate, respectively. In order to minimize re-absorption effects, absorbencies in the 10 mm fluorescent cuvette were kept under 0.05 at the excitation wavelength (360 nm).

Optimizing the experimental conditions

In order to achieve highly sensitive detection of Trz and Pd(II), we optimized the pH value of the detection system. Firstly, 5 µL Cdots solution (5.0 mg mL^{-1}) and 25 µL Trz or Pd(II) solution (1mM) were incubated within 50 µL PBS buffer (50 mM) at different pH values for 10 min. Then the final volume of the mixture was adjusted to 500 µL with ultrapure water. Finally, the FL spectra of these mixtures were measured after standing for 10 min. Test conditions: λex= 325 nm, excitation and emission slit widths are 5 and 3 nm, respectively.

Fluorescence detection procedure for Trz and Pd(II)

For the determination of Trz and Pd(II), 5 µL Cdots stock solution (5.0 mg mL^{-1}) and 50 µL PBS buffer (pH 7.0, 50 mM) were successively added in a centrifuge tube (2 mL). Next, different concentrations of Trz and Pd(II) solutions (0 - 300 µM) were separately added to the above solution. Then, the final volume was determined with ultrapure water to 500 µL. After 10 min of standing reaction, the FL spectra were measured using the above conditions. For the selectivity of the Cdots-based constructed Trz and Pd(II) sensor, Trz and Pd(II) was replaced by other possible competitive interfering substances. The analysis conditions are shown above.

Real sample analysis

Orange juice was purchased at a local supermarket. Before opening, beverages were

shaken to ensure their uniformity and then diluted with water to produce 10-fold dilution. The dilution was sonicated for 10 min followed by filtrating through a 0.22 μM filter membrane and collecting the filtrate. The filtrate was stored at 4 °C. The tap-water samples from our school were first centrifuged at 11 000 rpm for 30 min and then filtered three times through a 0.22 μM filter membrane for subsequent analysis. The standard addition method was used to determine the concentration of Trz or Pd(II) in the actual samples. That is, 5 μL of Cdots (5.0 mg mL^{-1}), 50 μL of PBS buffer (pH = 7.0), 200 μL of diluted real samples and different amounts of Trz and Pd(II) solution were in turn added to a centrifuge tube. The volume of the above mixture was set with ultrapure water to 500 μL. After being mixed with a vortex mixer, the mixture was balanced for 10 min before FL spectrum measurements were performed.

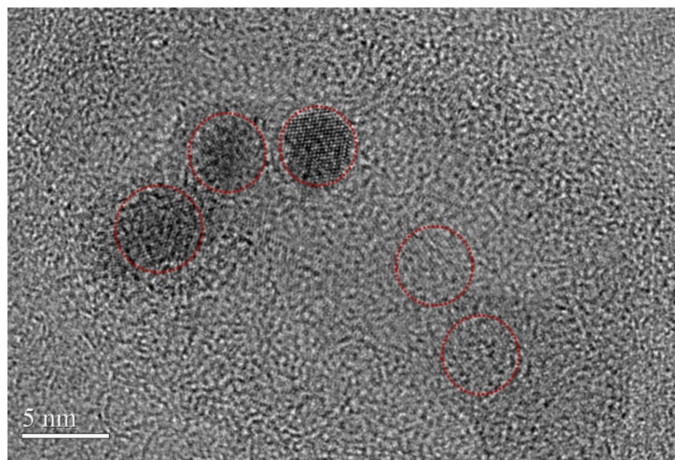


Fig. S1 The high-resolution TEM of Cdots.

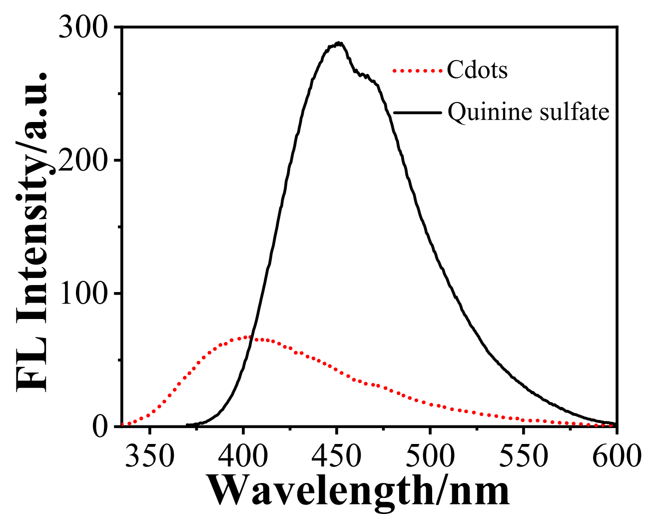
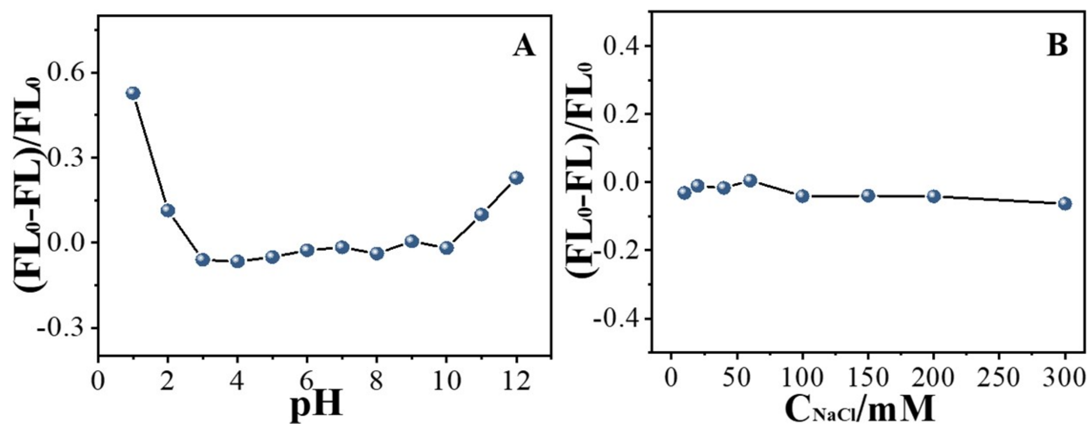


Fig. S2 FL emission spectra of Cdots in water (red dot-line, λex = 325 nm) and quinine sulfate (black line, λex = 360 nm) in 0.1 M H_2SO_4 solution as the standard.



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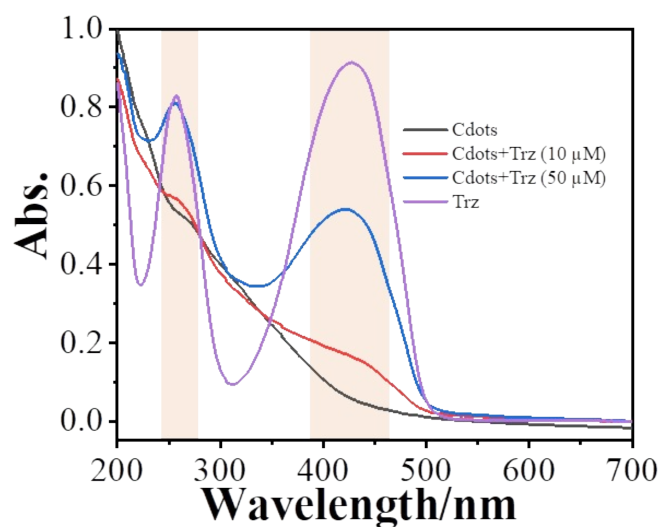

Fig. S4 The UV-vis absorption spectra of Cdots, Trz and Cdots/Trz mixed solution.

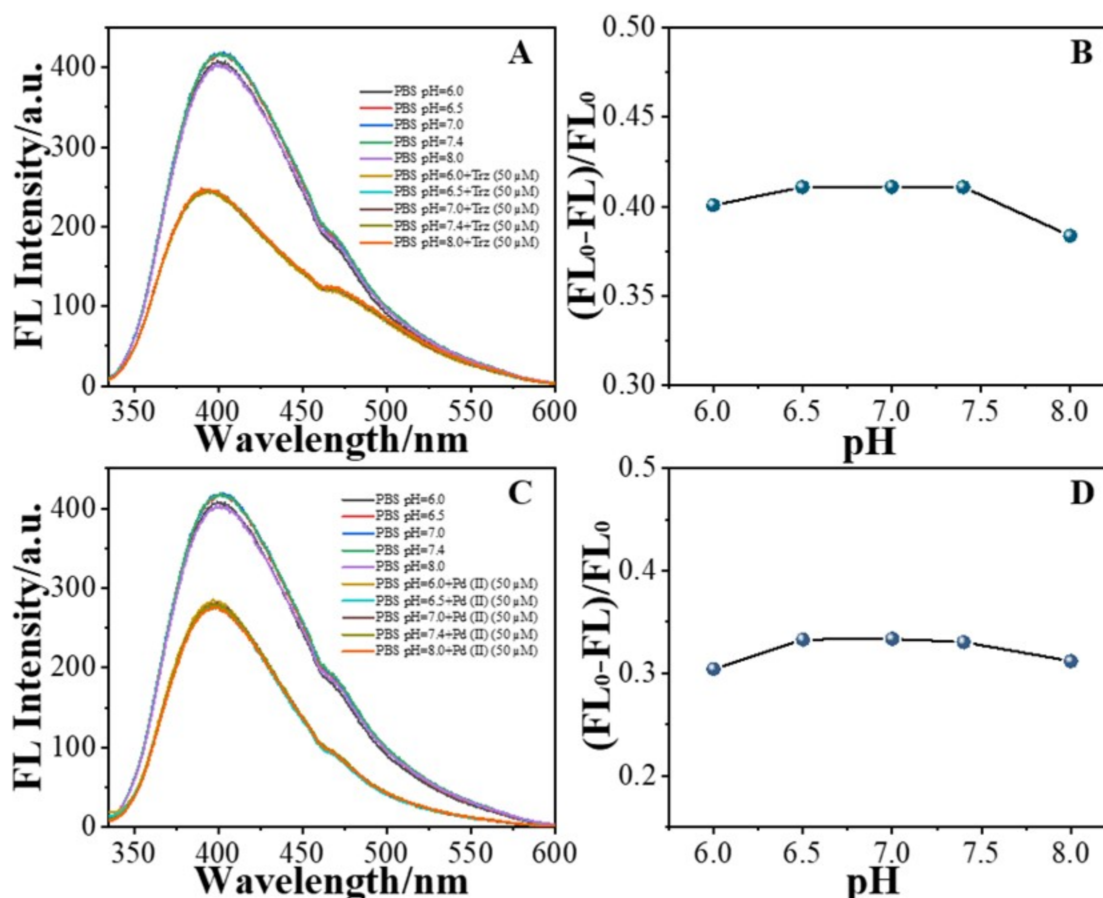

Fig. S5 pH-dependent FL signals of Cdots at various pH values (PBS buffer, 50 mM) containing 50 μM Trz (A) or 50 μM Pd(II) (C). The relative FL intensity of Cdots at 325 nm wavelength in the presence of 50 μM Trz (B) or 50 μM Pd(II) (D) at various pH values.

To achieve the optimum detection sensitivity, we investigate the impact of pH on the determination of Trz and Pd(II). Form the Fig. S5, only a minor change in the FL intensity was observed under weakly acid-base environments. The reason might be that the detection between the probe and the analytes is through energy or electron transfer, and does not involve the process of chemical reaction between the probe and analytes. The change in the optical properties of the probe is also mitigated by the functional groups on its surface through protonation or deprotonation. Considering the complexity of the analysis systems, the pH 7.0 PBS buffer was selected as the par excellence analysis condition.

Table S1 Comparison of analyte, technology, materials, linear range and detect limit for Trz analysis using different detection methods.

Analyte	Technology	Materials	Linear range	Detect limit	Ref
Trz	Fluorescent	Citrus limon CQDs	0.6-23.5 μM	200 nM	[1]
Trz	Fluorescent	Crayfish shell carbon quantum dots	0-70.0 μM	0.48 M	[2]
Trz	Electrochemical	Electrochemical paperbased analytical device	4.0-60.0 μM	2.09 μM	[3]
Trz	Fluorescent	Fe_3O_4@SiO_2@QDs@ms-MIPs	0.05-80 μM	23.7 nM	[4]
Trz	Electrochemical	Samarium niobate Anchored carbon nanofibers	0.0012-163.3 μM	1.2 nM	[5]
Trz	Fluorescent	Cdots	0.05-300 μM	33.48 nM	Our method

Table S2 Comparison of analyte, technology, materials, linear range and detect limit for Pd(II) analysis using different detection methods.

Analyte	Technology	Materials	Linear range	Detect limit	Ref
Pd(II)	Fluorescent	CDs-Pc probe	2.7-90.4 μM	0.19 μM	[6]
Pd(II)	Fluorescent	Biomass ionic liquid smart materials fluorescent probe	0-20.0 μM	0.23 μM	[7]
Pd(II)	Fluorescent	Nitrogen-doped carbon dots	0-33.0 μM	60 nM	[8]
Pd(II)	Fluorescent	Near-infrared carbon dots	0-200.0 μM	85.3 nM	[9]
Pd(II)	Fluorescent	Sulfur-chlorine-doped Carbon quantum dots	5-40 μM	0.1 μM	[10]
Pd(II)	Fluorescent	Cdots	0.01-300 μM	9.21 nM	Our method

References

[1] T. Chatzimitakos, A. Kasouni, L. Sygellou, A. Avgeropoulos, A. Troganis, C. Stalikas, *Talanta*, 2017, **175**, 305-312.

[2] L. He, H. Du, *J. Food Compos. Anal.*, 2023, 118, 105200.

[3] A. G. Figueira, D. F. L. Vinícius, L. T. Pedrosa, D. S. C. Cunha, M. F. B. Luiz, C. M. M. Auxiliadora, M. R. Camargo, *Microchem. J.*, 2022, **181**, 107799.

[4] S. Luo, X. Sun, L. Zhang, Y. Miao, G. Yan, *Food Chem.*, 2024, **430**, 137096.

[5] D. P. I. Jenisha, S. F. Wang, *Food Chem.*, 2023, **422**, 136230.

[6] T. Arslan, S. Güney, O. Güney, *Sens. Actuators B Chem.*, 2023, **377**, 133079.

[7] K. Kang, B. Liu, G. Yue, H. Ren, K. Zheng, L. Wang, Z. Wang, *Ecotox. Environ. Safe.*, 2023, **255**, 114795.

[8] S. Pawar, S. Kaja, A. Nag, *ACS Omega*, 2020, **5**, 8362-8372.
[9] Y. Qu, D. Li, J. Liu, F. Du, X. Tan, Y. Zhou, S. Liu, W. Xu, *Microchem. J.*, 2022, **178**, 107375.
[10] S. Gao, H. Zhang, H. Li, Y. Pei, *Opt. Mater.,* 2023,**139**, 113746.