Analytical Methods

Supporting Information

Ultra-sensitive fluorescent detection of strychnine based on carbon dots self-assembled gold nanocage sensing probe

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Part 1. Experimental

1.1. Reagents and materials

Tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES), o-Phenylenediamine (oPD), acetonitrile, acetic acid, absolute ethanol, chloroauric acid ($HAuCl_4$), sodium hydrosulfide (NaSH), ethylene glycol (EG), polyvinylpyrrolidone (PVP), silver trifluoroacetate (CF_3COOAg), histidine, glucose, urea, ammonium hydroxide ($NH_3 \cdot H_2O$), NaCl and KCl were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Strychnine, brucine, aconitine and cantharidin were purchased from Pufei De biotech Co., Ltd. (Chengdu, China). All commercially available chemicals are analytically grade. All aqueous solutions were prepared with ultrapure water (18.2 MΩ·cm, Millipore).

1.2. Instrumentation

Fluorescence spectra were recorded by F-4500 fluorescence spectrophotometer (Hitachi, Japan). Fourier transform infrared spectra (FT-IR) were performed on 850 spectrophotometers (Tianjin Gangdong SCI.&TECH. CO, LTD). The UV-Vis spectra were measured using the Agilent Cary 60 UV-Vis spectrophotometer. Transmission electron microscopy (TEM) images were performed with HT7800 Hitachi TEM system at 300 kV. In addition, a FLS-1000 fluorescence spectrophotometer (Edinburgh Instruments, EI) provided the fluorescence lifetime of MIPs-CDs@AuNCs.

1.3. Synthesis of silane-functionalized CDs

In brief, 0.25 mmol of oPD and 0.725 mmol of HNO_3 were dissolved in 5 mL of water, then the solution was stirred and ultrasonic shaken for 5 min. Next, the solution was put into a 25 mL Teflon-lined autoclave and heated at 200 ℃ for 10 h. Then the solution was cooled down to room temperature and through 0.22 μm polyether sulfone membrane to remove large particles, and the blue liquid was obtained. After

that, the blue liquid was dialyzed in a 500 Da dialysis bag against water for 48 h. The resulting liquid was freeze-dried, and the yellowish-brown powder was produced, which was stored at -20 °C for next use. To prepare silane-functionalized CDs, 100 mg of CDs was dissolved in 10 mL of ethanol and 350 μL of APTES was added, then the mixture was vibrated for 48 hours.
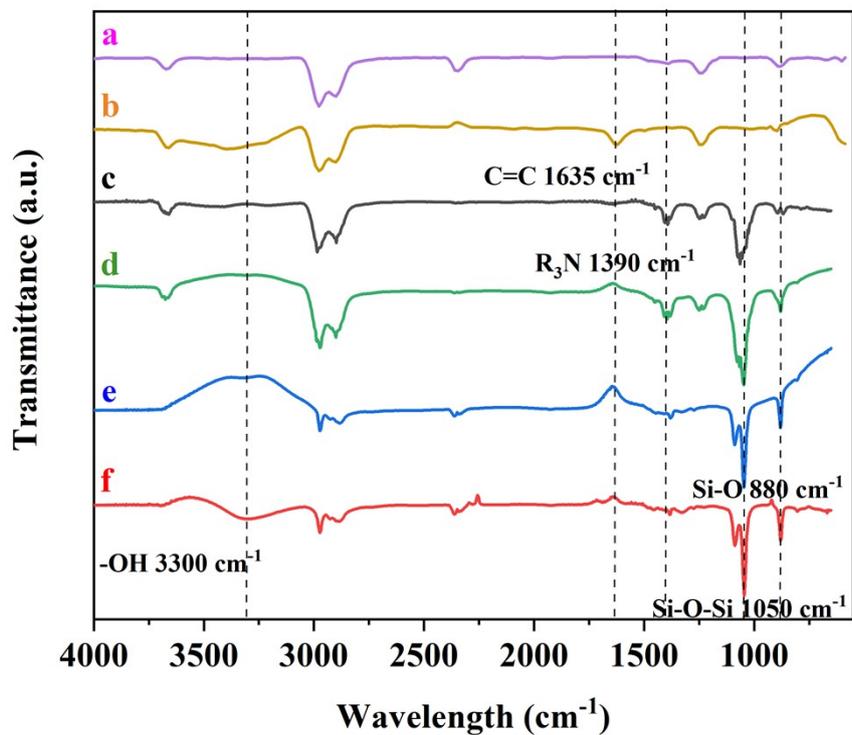
Part 2. Figures and tables

Fig. S1. Fourier-transform infrared spectra of AuNCs (a), CDs@AuNCs (b), strychnine (c), MIP-CDs@AuNCs before elution (d), MIP-CDs@AuNCs after elution (e) and NIP-CDs@AuNCs (f).
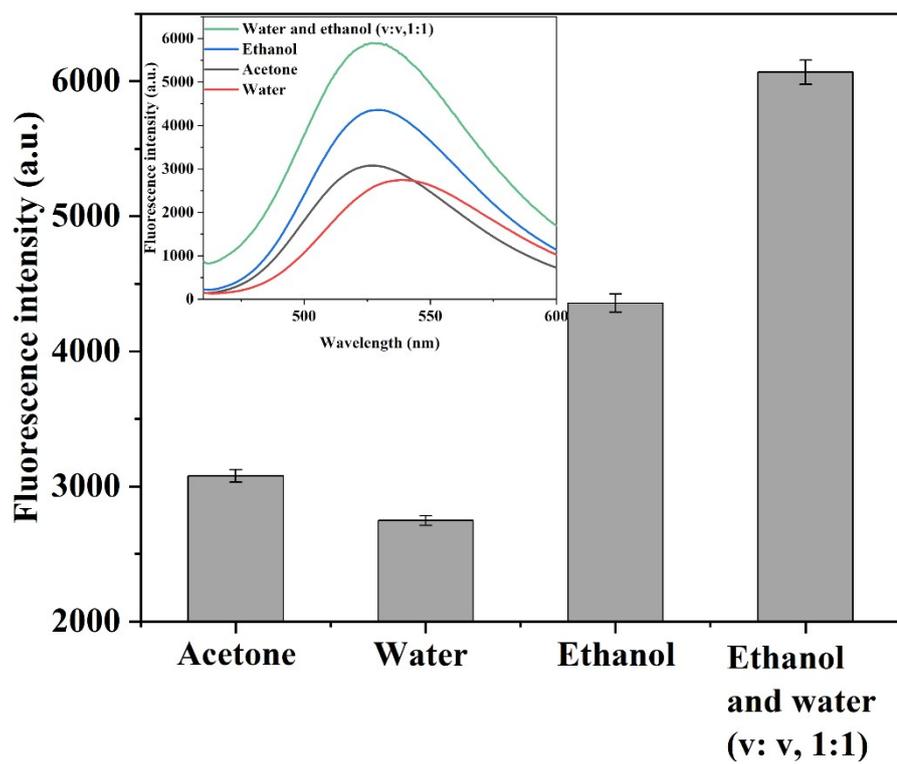
Fig. S2. The fluorescence intensities of MIPs-CDs@AuNCs under different solvents including mixture of water and ethanol (v: v, 1:1), ethanol, acetone, and water.
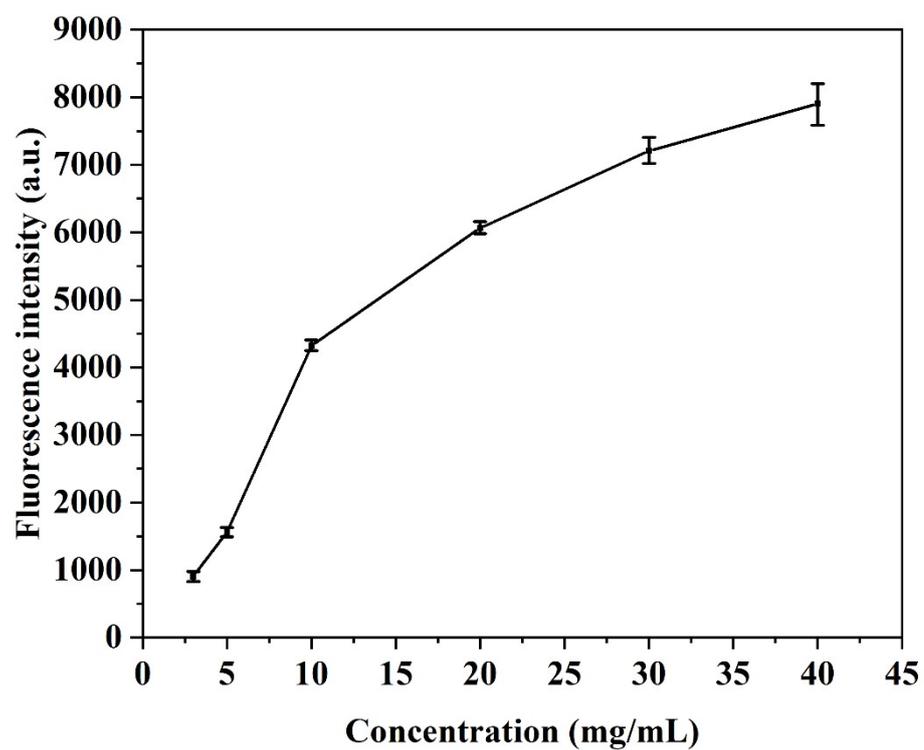
Fig. S3. The fluorescence intensities of MIPs-CDs@AuNCs with different concentrations including 3, 5, 10, 20, 30, 40 mg/mL.
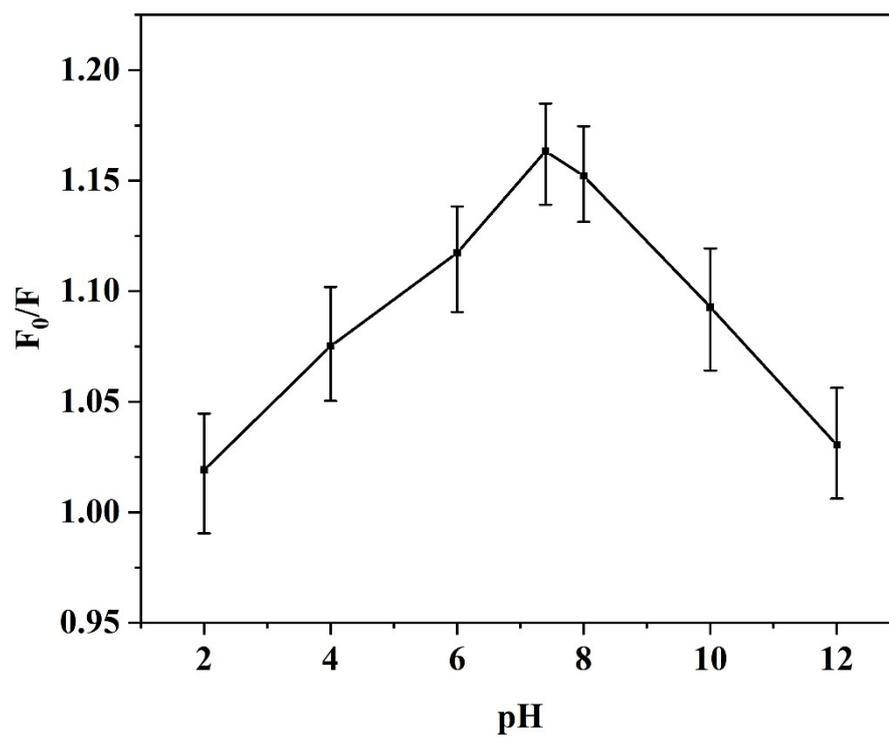
Fig. S4. The proportion of fluorescence intensities before and after the addition of strychnine (20 ng/mL) in different pH.
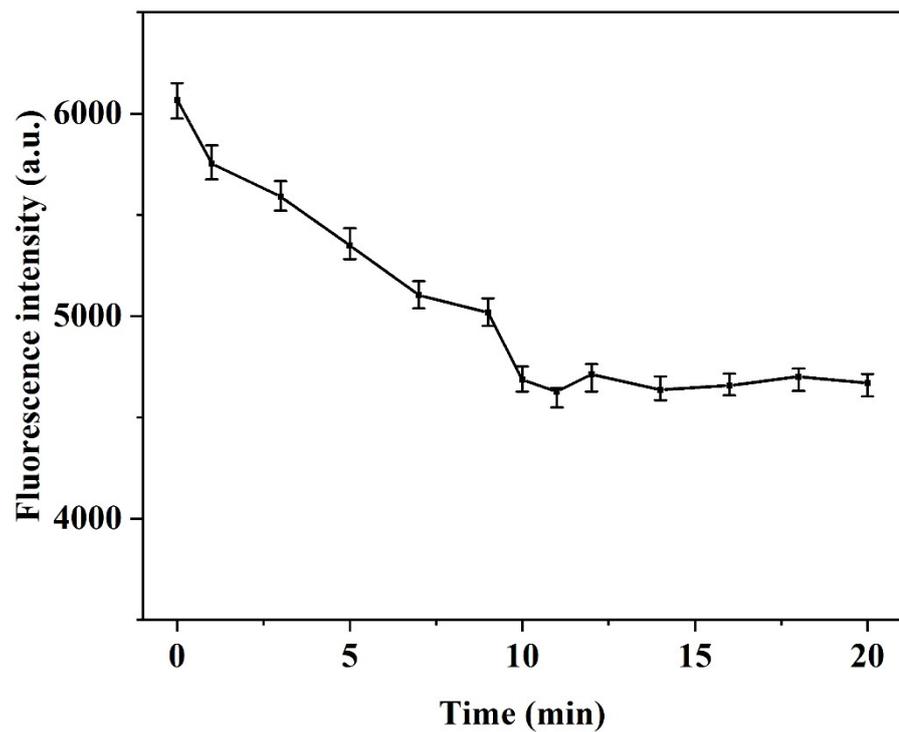
Fig. S5. The fluorescence intensities of MIPs-CDs@AuNCs with the addition of strychnine (20 ng/mL) in 0-20 min.

Table S1. Validation of strychnine detection with the MIPs-CDs@AuNCs probe in

spiked samples.

Samples	Strychnine added (ng/mL)	Strychnine found* (ng/mL)	Recovery (%)	Precision RSD (%, n = 3)	
				Intra-day	Inter-day
1	10	10.23	102.30	2.24	4.61
2	20	18.62	93.21	1.52	3.59
3	150	147.43	98.29	2.08	4.67

*Mean of three determinations.

Table S2. Comparison of the performance of MIPs-CDs@AuNCs probe and LC-MS/MS in real blood samples.

blood samples	MIPs-CDs@AuNCs		LC-MS/MS	
	Found* (ng/mL)	RSD (%, n = 3)	Found* (ng/mL)	RSD (%, n = 3)
1	40.89	1.77	42.17	1.37
2	78.42	1.91	77.26	1.42
3	61.03	2.04	61.82	1.22

*Mean of three determinations