Electronic Supporting Information

Chitosan-stabilized gold nanoparticles decorated with thiodiacetic acid nanoprobe for selective detection of arsenic(III) in rice and water samples

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The calculation of LOD of CS/AuNPs@TDA probe

The LOD of the CS/AuNPs@TDA probe was calculated by using the following equation:

$LOD = 3.3\sigma/S$

where σ is the standard deviation of the blank sample (n = 15) and S is the slope of the linear calibration curve.[1]

Preparation of blank solution

The blank solution was prepared in 15 replicates. Each blank solution was performed by adding 250 µL of DI water to 675 µL of freshly diluted CS/AuNPs@TDA and 75 µL of 5 mM Britton-Robinson buffer at pH 4.0 in a 1.5-mL Eppendorf tube. Then, the solution was heated in a heating block at 90 °C for 90 min and after being cooled to room temperature, the UV–vis spectrum of the blank solution was recorded from 400 to 800 nm.

Preparation of the probe for the standard calibration curve

The probe was prepared by spiking the standard solution of As^{3+} in the range of 0.01 to 5.00 mg L^{-1} to 675 µL of freshly diluted CS/AuNPs@TDA and 75 µL of 5 mM Britton-Robinson buffer at pH 4.0 in a 1.5-mL Eppendorf tube. Each probe reacted at 90 °C for 90 min and after being cooled to room temperature, the UV–vis spectrum of the probe was recorded from 400 to 800 nm.

The calculation of the LOD

The absorbance value at 525 and 645 nm of each blank solution was demonstrated in Table S1. The calibration curve was linear in the range of 0.01 to 1.00 mg L^{-1}, with a linear regression equation of y (A_{645}/A_{525}) = (0.7603 ± 0.0436) x (mg L^{-1}) + (0.2361 ± 0.0264) and an R^2 of 0.9902.

Table S1 The absorbance values at 525 and 645 nm of each blank solution

Number of blank solutions	Absorbance at 525 nm (A_{525})	Absorbance at 645 nm (A_{645})	A_{645}/A_{525}
1	0.3641	0.0823	0.2260
2	0.3613	0.0810	0.2242
3	0.3610	0.0807	0.2235
4	0.3595	0.0817	0.2273
5	0.3625	0.0822	0.2268
6	0.3636	0.0810	0.2228
7	0.3630	0.0814	0.2242
8	0.3606	0.0805	0.2232
9	0.3626	0.0816	0.2250
10	0.3618	0.0815	0.2253
11	0.3619	0.0815	0.2252
12	0.3624	0.0806	0.2224
13	0.3677	0.0829	0.2255
14	0.3662	0.0825	0.2253
15	0.3649	0.0818	0.2242
		mean	**0.2247**
		σ	**0.0014**

A standard deviation of the blank solution (σ) was 0.0014 and a slope of the linear calibration curve (S) was 0.7603.

$$LOD = \frac{3.3\sigma}{S}$$

$$LOD = \frac{3.3 \times 0.0014}{0.7603}$$

$$LOD = 0.0061\ mg\ L^{-1}$$

Reference

1. ICH, Q2B Validation of Analytical Procedures: Methodology, ICH-Q2B, 1996, 1–10, https://www.fda.gov/media/71725/download, accessed June 2024

Job's plot

To determine the stoichiometry of the complex formation of CS/AuNPs@TDA with As^{3+}, the Job's plot for the absorbance after reaction was measured by keeping the sum of initial concentrations of As^{3+} and CS/AuNPs@TDA constant with a total volume of 1 mL in a 1.5-mL Eppendorf tube (125, 250, 375, 500, 625, 750, and 875 µL of 4 mg L^{-1} of As^{3+} and 875, 750, 625, 500, 375, 250, and 125 µL of CS/AuNPs@TDA (pH 4.0)). The molar ratio of As^{3+} ($X_M = \frac{[As^{3+}]}{[As^{3+}] + [CS/AuNPs@TDA]}$) is changed from 0 to 1, where X_M is a mole fraction of As^{3+}. Each solution was heated at 90 °C for 90 min and after that, it was cooled to room temperature. The spectrum was recorded by UV–vis spectrophotometer. Three repetitions of all measurements were carried out.

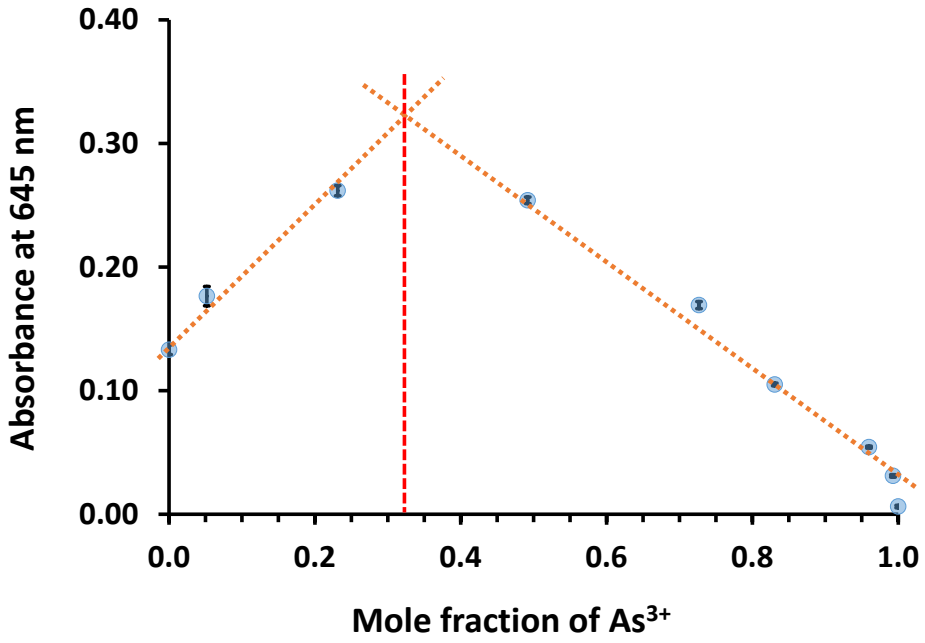

Fig. S1 Job's plot for the determination of the binding stoichiometry of As^{3+} and CS/AuNPs@TDA which absorbance is measured at 645 nm (aggregation state).

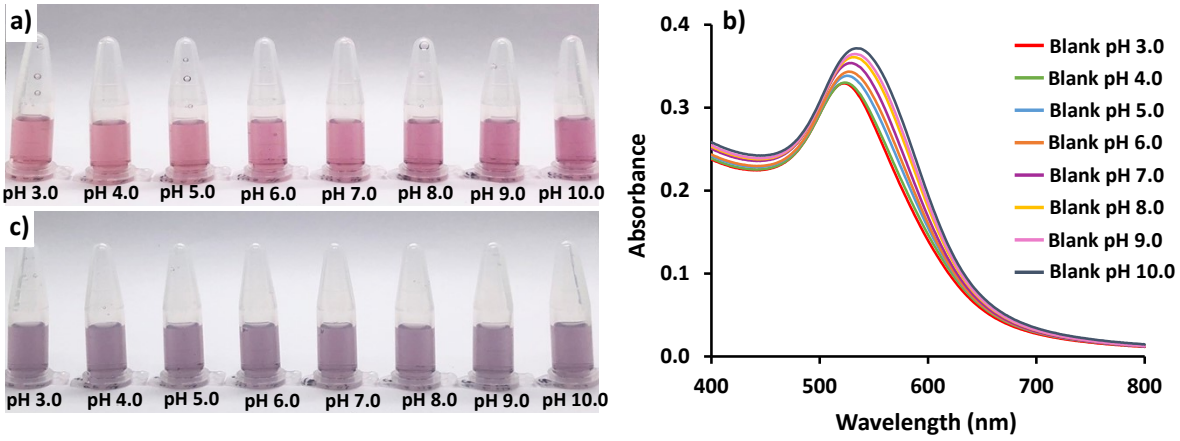

Fig. S2 Effect of pH (3.0 – 10.0) of 5 mM Britton-Robinson buffer. (a) Photographs and (b) UV–vis spectra of CS/AuNPs@TDA in the absence of As^{3+} (blank solution) at various pHs. (c) Photographs of the aggregated CS/AuNPs@TDA in the presence of 1.0 mg L^{-1} As^{3+} at various pHs.

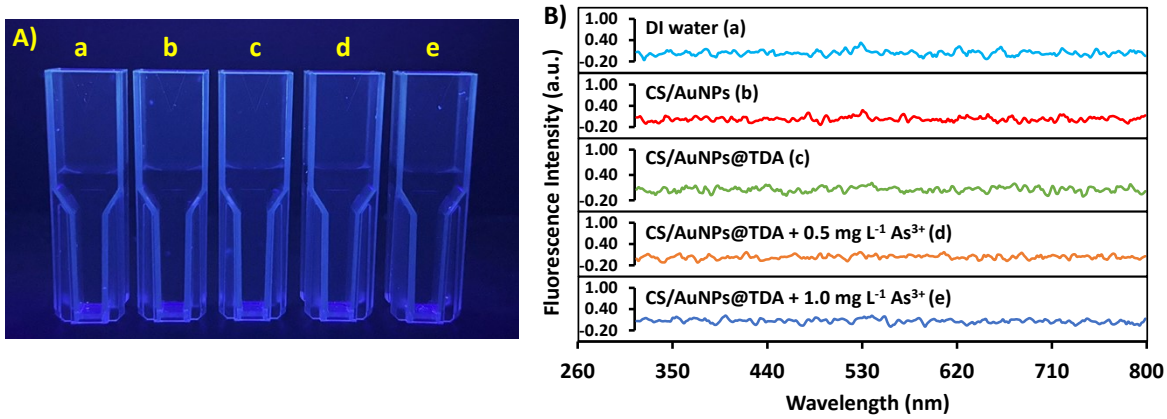

Fig. S3 (A) Fluorescence photographs and (B) fluorescence spectra of (a) DI water, (b) CS/AuNPs, (c) CS/AuNPs@TDA, (d) CS/AuNPs@TDA with 0.5 mg L^{-1} As^{3+} and (e) CS/AuNPs@TDA with 1.0 mg L^{-1} As^{3+}.

Table S2 Recoveries of As^{3+} in rice and drinking water based on the developed CS/AuNPs@TDA and ICP–OES

Sample	Spiked (mg L^{-1})	CS/AuNPs@TDA (n = 3)			ICP–OES detection[c] (n = 3)		
		Found[a,b] (mg L^{-1})	Recovery (%)	RSD (%)	Found[a] (mg L^{-1})	Recovery (%)	RSD (%)
Rice sample 1	0.00	Not detected	–	–	Not detected	–	–
	0.05	0.043±0.008	101.15	1.86	0.054±0.004	102.30	0.14
	0.20	0.203±0.007	102.98	2.89	0.206±0.001	103.60	1.62
	0.50	0.511±0.018	102.69	2.94	0.483±0.054	103.25	0.48
Rice sample 2	0.00	Not detected	–	–	0.007±0.002	–	–
	0.05	0.039±0.004	91.27	0.72	0.057±0.004	91.54	1.45
	0.20	0.195±0.009	102.64	1.45	0.207±0.014	103.42	1.68
	0.50	0.494±0.041	104.24	1.82	0.533±0.032	101.60	0.42
Drinking water 1	0.00	Not detected	–	–	Not detected	–	–
	0.05	0.045±0.008	99.18	2.91	0.048±0.004	101.50	2.09
	0.20	0.188±0.006	93.93	2.17	0.188±0.004	94.08	1.73
	0.50	0.468±0.002	93.54	0.34	0.470±0.001	93.93	0.22
Drinking water 2	0.00	Not detected	–	–	Not detected	–	–
	0.05	0.045±0.007	96.40	1.20	0.049±0.001	95.70	0.63
	0.20	0.191±0.006	95.12	1.30	0.186±0.008	94.92	2.87
	0.50	0.471±0.002	94.06	0.52	0.473±0.004	94.66	0.38

[a]Found ± standard deviation; [b]LOQ of the developed method was 0.018 mg L^{-1}; [c]LOQ of the ICP–OES method was 15.76 ng L^{-1}.

Table S3 Recoveries of As^{3+} in environmental water samples based on the developed CS/AuNPs@TDA and ICP–OES

Sample	Spiked	CS/AuNPs@TDA (n = 3)			ICP–OES detection[c] (n = 3)		
	(mg L^{-1})	Found [a,b] (mg L^{-1})	Recovery (%)	RSD (%)	Found[a] (mg L^{-1})	Recovery (%)	RSD (%)
W1	0.00	Not detected	–	–	0.063±0.001	–	–
	0.05	0.048±0.002	101.92	0.78	0.113±0.001	102.74	0.78
	0.20	0.189±0.009	93.36	0.52	0.251±0.001	94.10	0.97
	0.50	0.461±0.016	92.62	2.89	0.534±0.002	94.31	0.52
W2	0.00	Not detected	–	–	0.006±0.001	–	–
	0.05	0.044±0.005	102.98	2.99	0.058±0.001	104.00	1.92
	0.20	0.198±0.009	105.74	2.10	0.215±0.004	104.33	1.63
	0.50	0.457±0.016	93.02	2.92	0.467±0.003	92.17	0.74
W3	0.00	<LOQ[b] (0.007±0.002)	–	–	0.008±0.004	–	–
	0.05	0.052±0.001	88.22	1.95	0.052±0.003	87.33	2.32
	0.20	0.197±0.011	97.64	0.25	0.201±0.004	98.88	0.89
	0.50	0.467±0.008	92.00	1.26	0.459±0.002	90.17	1.31

W1: Water from abandoned public shallow well; W2: Water from Huai Nong Ped creek; W3: Water from an abandoned tin mine; [a]Found ± standard deviation; [b]LOQ of the developed method was 0.018 mg L^{-1}; [c]LOQ of the ICP–OES method was 15.76 ng L^{-1}.