A simple label-free rhodamine 6G SERS probe for quantitative analysis of trace As(III) in the aptamer-nanosol

Lingling Ye[§], Guiqing Wen[§], Jichao Dong, Yanghe Luo, Qingye Liu, Aihui Liang [*], Zhiliang Jiang [*]

Key Laboratory of Ecology of Rare and Endangered Species and Environmental Conservation of Education Ministry, Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology, Guangxi Normal University, Guilin 541004, China.

Preparation of gold nanoparticles

Nanogold was synthesized through reduction of $HAuCl_4$ by trisodium citrate. Into a 50 mL boiling water with stirring, a 0.5 mL 1% $HAuCl_4$ and 3.5mL 1% trisodium citrate were added rapidly successively. After boiling for 10 min, the color became from colorless to wine red. The mixture was continued stirring to room temperature, and then diluted to 50 mL to obtain a concentration of 58.0 μg/mL Au nanogold in size of about 10 nm [25].

Preparation of silver nanoparticles

Silver nanoparticle was synthesized through $NaBH_4$ reduction process [37]. A 40 mL water was added into a flask, a 3.5mL10g/L trisodium citrate and 385 μL 2.4×10^{-2} mol/L $AgNO_3$ were added into successively. Then, 4.0mL 0.5mg/mL $NaBH_4$ was dripped slowly. After 20 min, it was diluted to 50 mL to obtain a 19.9μg/mL Ag nanosilver sol that stored at 4 ℃.

Preparation of NGssDNA probe

Piped 10 mL 58.0 μg/mL NGs into a conical flask, added 2.0 mL 2.0mL 0.5μmol/L ssDNA solution under the stirring slowly, continued to stir 15 min, and stored at 4 ℃. In terms of ssDNA, the NGssDNA concentration is 83.3 nmol/L.

Preparation of NSssDNA probe

A 3.0mL 19.9μg/mL NSs was moved into a conical flask, and a 1.0mL 0.5 μmol/L ssDNA solution was added slowly to obtain the probe. In terms of ssDNA, this NSssDNA concentration is 125 nmol/L.

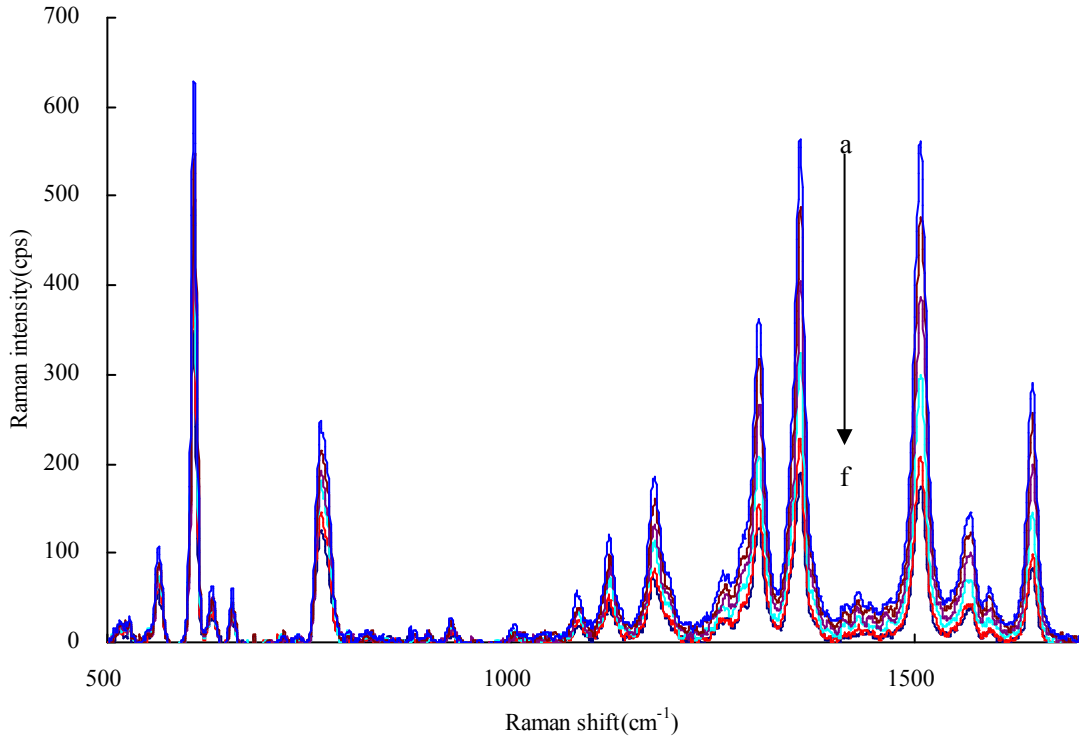

Fig. 1S SERS spectrum of AgssDNA-As^{3+}-Rh6G system

a: 25nmol/L NSssDNA+pH 8.0 HEPES+50mmol/L NaCl+5.23×10^{-6}mol/L Rh6G; b: a+0.144 ng/mL As^{3+}; c: a+5.76ng/mL As^{3+}; d: a+8.64ng/mL As^{3+}; e: a+11.52ng/mL As^{3+}; f: a+17.28ng/mL As^{3+}.

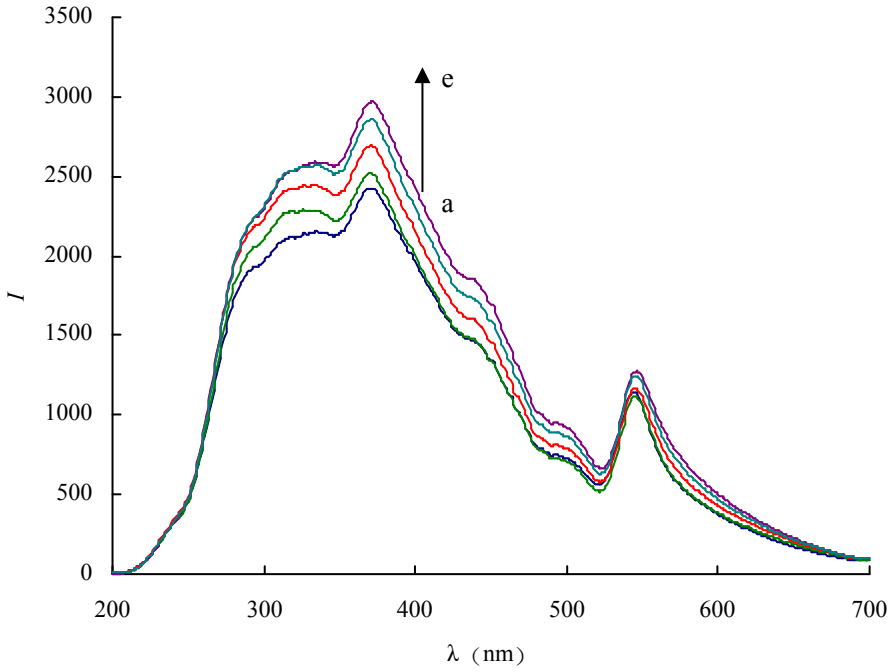

Fig. 2S RRS spectra of the NGssDNA- As^{3+}-Rh6G system

a: 25nmol/L NGssDNA +pH 8.0 HEPES+50mmol/L NaCl+5.23×10^{-6}mol/L Rh6G; b: a+2.88ng/mL As^{3+}; c: a+5.76ng/mL As^{3+}; d: a+11.52ng/mLAs^{3+}; e: a+17.28ng/mL As^{3+}.

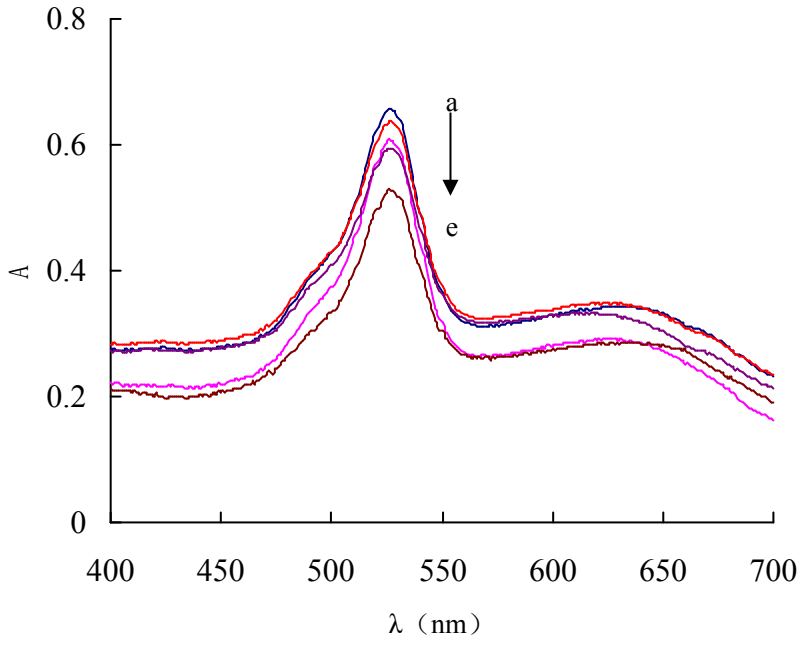

Fig. 3S UV spectrum of NGssDNA-As^{3+}-Rh6G system

a：25nmol/L NGssDNA +15min+ pH 8.0 0.75mmol/L HEPES+50mmol/L NaCl+5.23×10^{-6}mol/L Rh6G; b: a+2.88ng/mL As^{3+}; c: a+5.76ng/mL As^{3+}; d: a+11.52ng/mL As^{3+}; e: a+17.28ng/mL As^{3+}

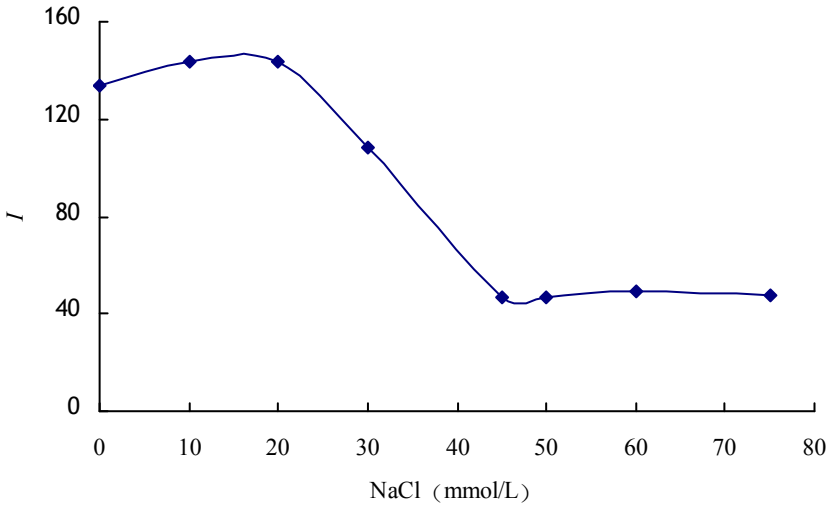

Fig. 4S Effect of NaCl

14.3μg/mL NGs+pH 8.0 HEPES + 5.23×10^{-6}mol/L Rh6G

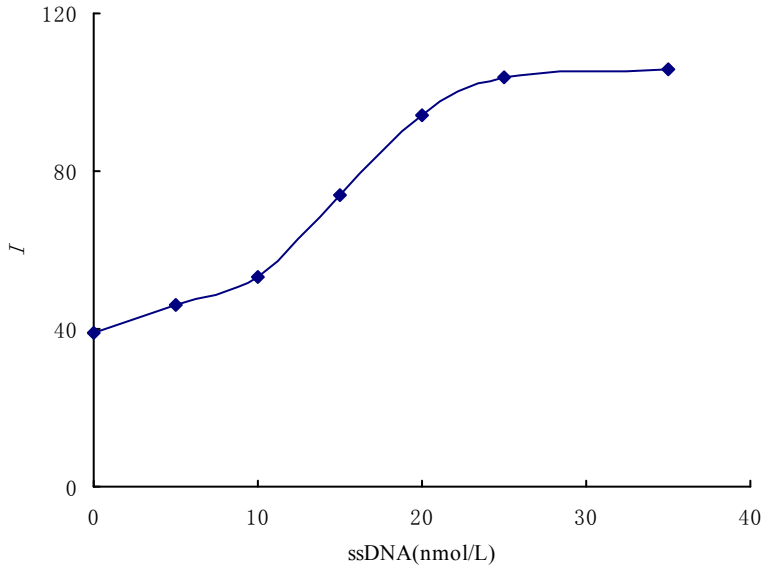

Fig. 5S Effect of ssDNA concentration

14.3μg/mL NGs+50mmol/L NaCl+pH 8.0 HEPES +5.23×10^{-6}mol/L Rh6G

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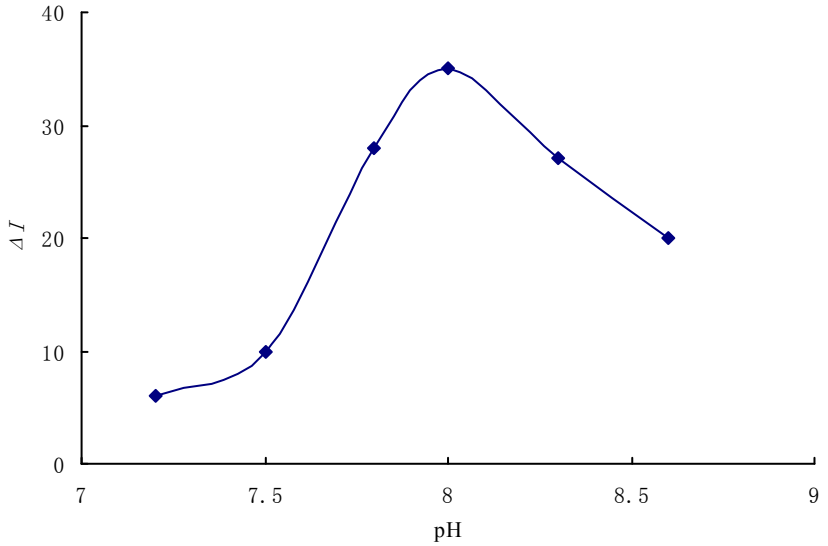

Fig. 6S Effect of pH

25nmol/L NGssDNA+50mmol/L NaCl+ 0.75mmol/L HEPES +10 ng/mL As^{3+}+5.23×10^{-6}mol/L Rh6G

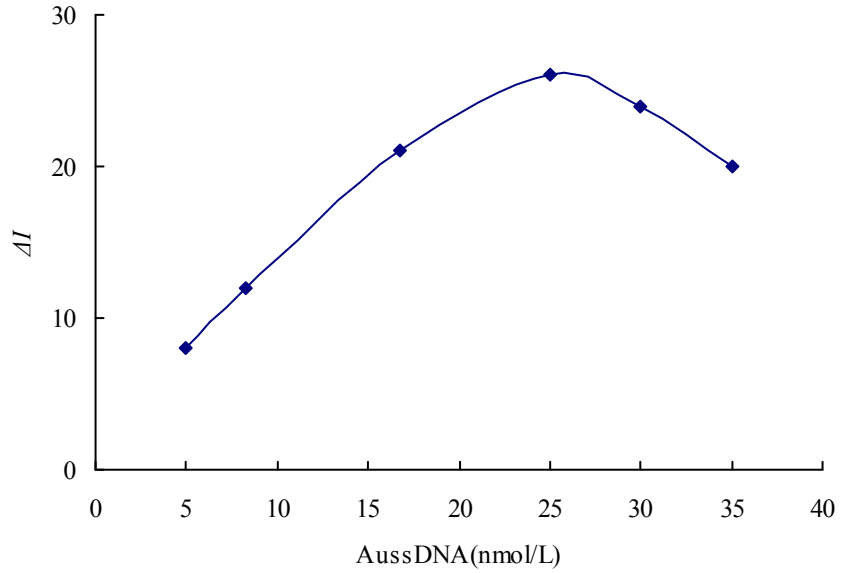

Fig. 7S Effect of NGssDNA concentration

50mmol/L NaCl+pH 8.0 HEPES+10 ng/mL As^{3+} +5.23×10^{-6}mol/L Rh6G

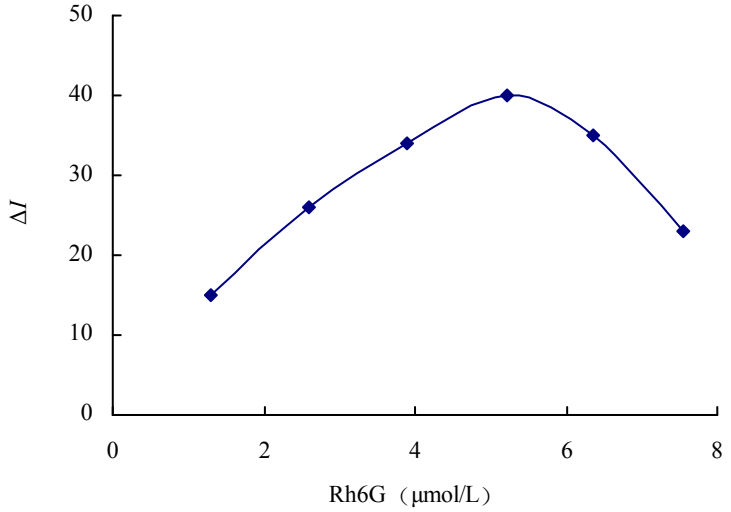

Fig. 8S Effect of Rh6G concentration

pH 8.0 HEPES +50mmol/L NaCl+25nmol/L NGssDNA+10 ng/mL As^{3+}.

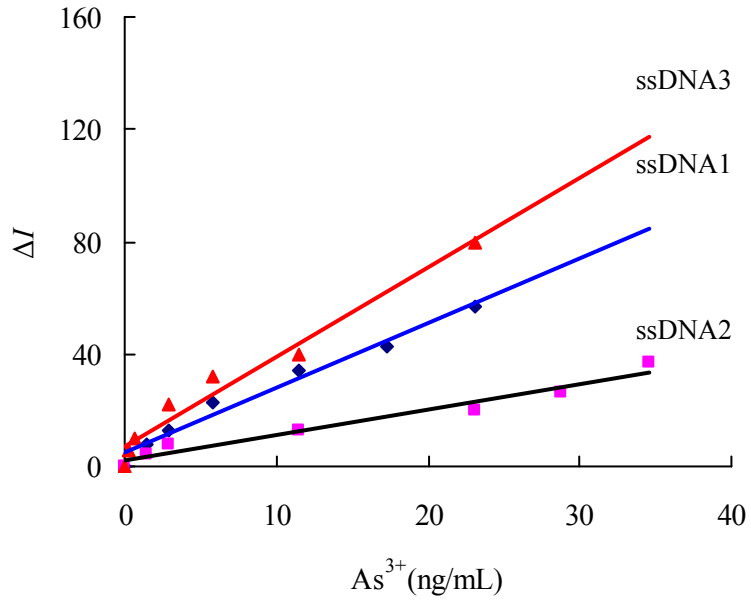

Fig. 9S Working curve of different ssDNA system

25nmol/l NGssDNA +50mmol/L NaCl+pH 8.0 HEPES +5.23μmol/L Rh6G

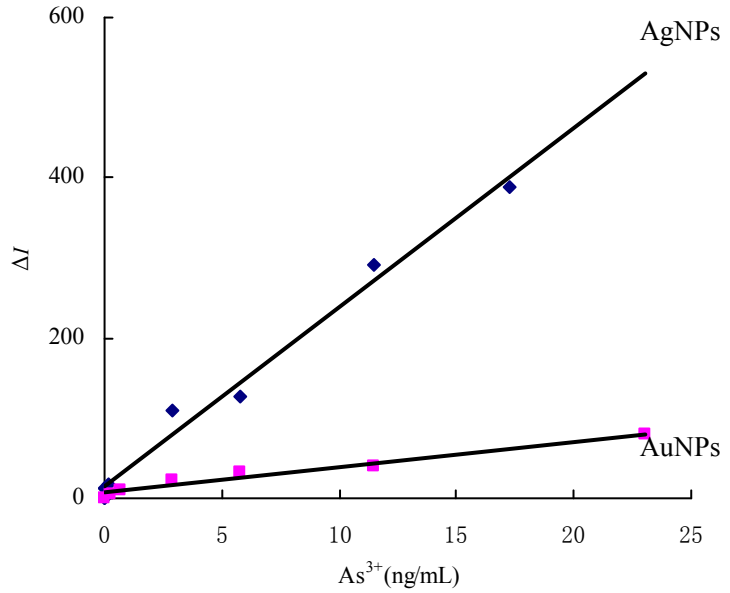

Fig. 10S Working curve of different SERS substrate system

25nmol/L Au/AgssDNA +50mmol/L NaCl+pH 8.0 HEPES +5.23μmol/L Rh6G.

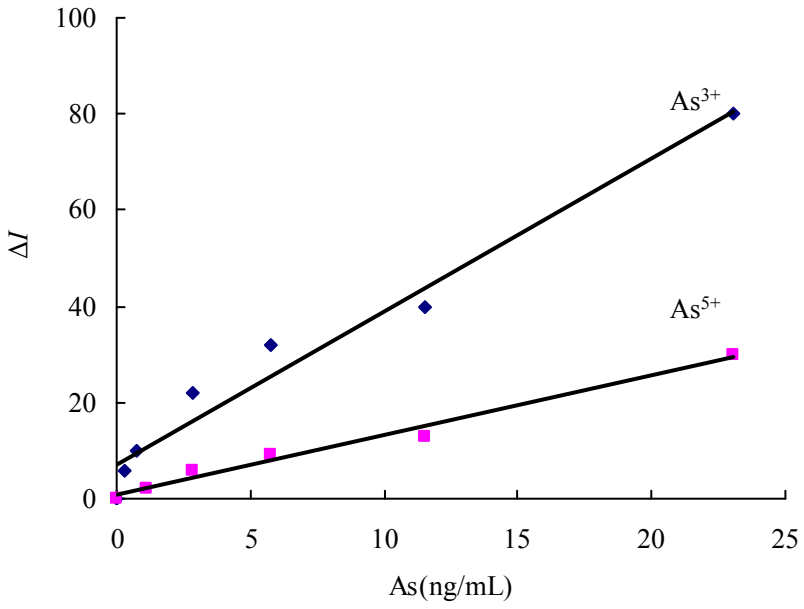

Fig. 11S Working curve of different valence state arsenic system

25nmol/l NGssDNA +50mmol/LNaCl+pH 8.0 HEPES +5.23μmol/L Rh6G.

Table 1S Effect of foreign substances

Coexistent substance	Tolerance Concentration	Relative error (%)	Coexistent substance	Tolerance Concentration	Relative error (%)
L-valine	2.5μg/mL	-5.7	Zn^{2+}	100μmol/L	3.6
L-aspartate	2.5μg/mL	3.7	K^{+}	50μmol/L	3.7
L-lysine	2.5μg/mL	1.9	Co^{2+}	10μmol/L	-8.5
glucose	15μmol/L	3.6	Hg^{2+}	10μmol/L	-1.6
BSA	120ng/mL	-4.1	Cu^{2+}	75μmol/L	-5.6
HSA	150ng/mL	1.8	Al^{3+}	7.5μmol/L	1.8
Ca^{2+}	150μmol/L	-3.5	Ba^{2+}	100μmol/L	4.2
Mg^{2+}	150μmol/L	3.6	Fe^{3+}	2.5μmol/L	-1.9

Table 2S Different ssDNA system analysis feature

System	Regression equation	Linear range (ng/mL)	Correlation coefficient	Detection limit (ng/mL)
ssDNA1	$\Delta I = 2.3C + 5.1$	1.44-23.04	0.9760	0.03
ssDNA2	$\Delta I = 0.9C + 2.2$	1.44-34.56	0.9589	0.07
ssDNA3	$\Delta I = 3.2C + 7.0$	0.288-23.04	0.9676	0.1

Table 3S Sample analysis results

Sample	Spiked As (ng/mL or ng/g)	Average (ng/mL or ng/g, n=5)	RSD (%)	Recovery (%)	HG-AAS (ng/mL or ng/g)
Li river	-	No detected	-	-	-
	12.5	11.9±0.64	5.4	95.2	
	16.7	16.1±0.68	4.2	96.3	
Rong lake	-	No detected	-	-	-
	2.50	2.40±0.16	6.8	96.2	
	5.00	4.89±0.29	5.9	97.9	
Waste water 1	-	7.90±0.51	6.4	-	7.42
Waste water 2	-	11.5±0.59	5.1	-	10.9
Milk 1	-	31.2±1.7	5.4	-	29.8
Milk 2	-	28.0±1.2	4.3	-	27.6