An Ultrasensitive SERS Method for Quantitative Analysis of Ozone Using Nanogold Sol as Substrate and Rhodamine S as Probe

Xinghui Zhang, Chenyin Li, Qingye Liu*, and Aihui Liang *

Key Laboratory of Ecology of Rare and Endangered Species and Environmental Protection,

Ministry of Education, Guangxi Normal University, Guilin 541004, P. R.China

EXPERIMENTAL SECTION

Instruments and reagents. A model of DXR smart laser Raman spectrometer (Thermo Co., USA) with a laser of 633nm, collect time of 5s and a power of 3.5 mW, a model of FEI Quanta 200 FEG scanning electron microscope (FEI Co., Holand), a model of SW-002-2g/h portable ozone generator (West Electronic Purification Equipment Limited, Qingdao, China), a model of nanometer particle size and zeta potential analyzer (Malvern, UK), and a model of TQC-1500-z atmospheric sampler (Tianrui Apparatus Limited, Yancheng, China) were used to take measurements.

AuNP was prepared by trisodium citrate producer[1]. The nanogold concentration is 47.3mg/L Au and the average size is 10 nm. The reagents are analytically pure, and the water is doubly distilled.

H_3BO_3-KI (BKI) absorbent solution: A 1.55 g H_3BO_3 and 2.5 g KI were dissolved by water and diluted to 250 mL, and stored in a brown bottle to make sure that the background absorbent absorption value drifting below the 0.010. The absorbent concentration, calculated as KI, is 0.06 mol/L. A 0.2% starch indicator: 0.2 g starch was added into 5 mL water and mixed into a paste. Then, 80 mL boiling water was added while stirring and kept boiling for 2 min before being cooled to room temperature and diluted to 100 mL. A 0.1 mol/L $Na_2S_2O_3$ solution: 6.5 g $Na_2S_2O_3$and 0.05 g Na_2CO_3 were dissolved with 20 mL water and the solution was boiled for 10 min before cooling and dilution to 250 mL. The solution was stored in a brown bottle and placed in the dark for several days and filtered before use. The calibration of $Na_2S_2O_3$ solution was done by the $K_2Cr_2O_7$ titrate procedure. O_3 standard solution: A 300 mL BKI absorbent was added into a jar and O_3 was introduced for 10min through O_3 generator. Then the solution was transferred into a brown bottle and stored in 4℃ refrigerator. And the concentration was calibrated by the $Na_2S_2O_3$ standard solution. All reagents were of analytical grade and the water was doubly distilled.

Procedure. a 100μL 5.0×10^{-4} mol/ L ozone standard solution, 40μL 1.0×10^{-5}mol/ L RhS were added into a 5mL calibrated tube, diluted to about 0.5 mL with water and mixed well. Then, a 900μL 47.3 mg/L AuNP, and 180 μL 2.0 mol/L HCl solutions were added, and diluted to 2 mL with water. The mixture was then diluted to 2.0 mL and mixed well. The solution was transferred

into a quartz cell. Under the selected conditions, the SERS intensity at 1503 cm^{-1} (I) was recorded. A blank (I_0) without O_3 was recorded and the value of $\Delta I = I_0 - I$ was calculated.

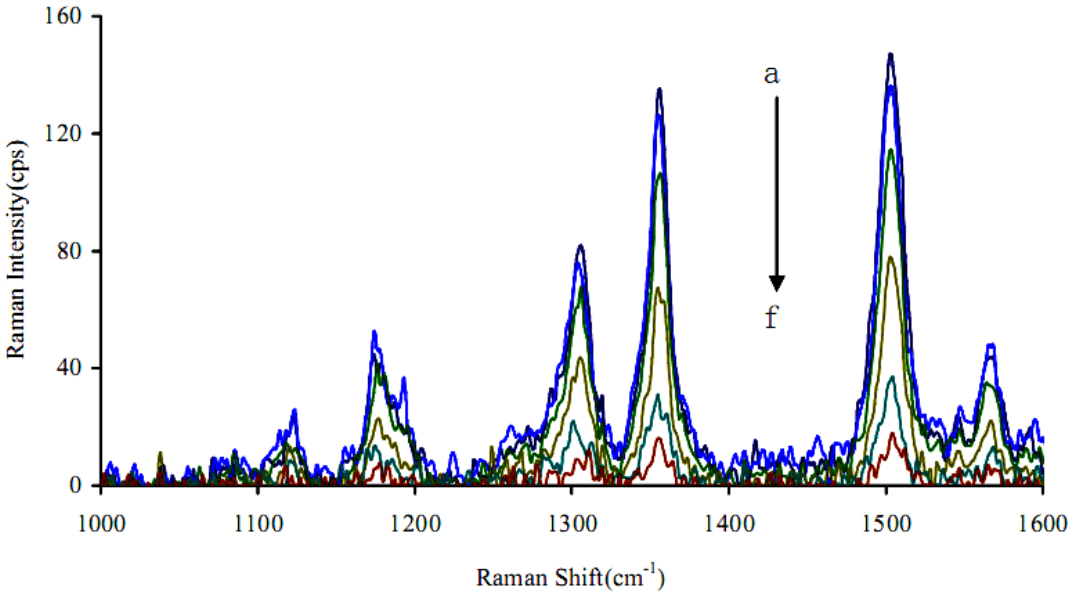


Fig. 1S SERS spectra for the Rh6G system containing different concentration of O_3
(a) 2.0×10^{-7} mol/L Rh6G-21.52 mg/L AuNPs -0.18 mol/L HCl; (b) 6.25 nmol/L O_3; (c) 25.0 nmol/L O_3; (d) 75.0 nmol/L O_3; (e) 137.5 nmol/L O_3; (f) 212.5 nmol/L O_3

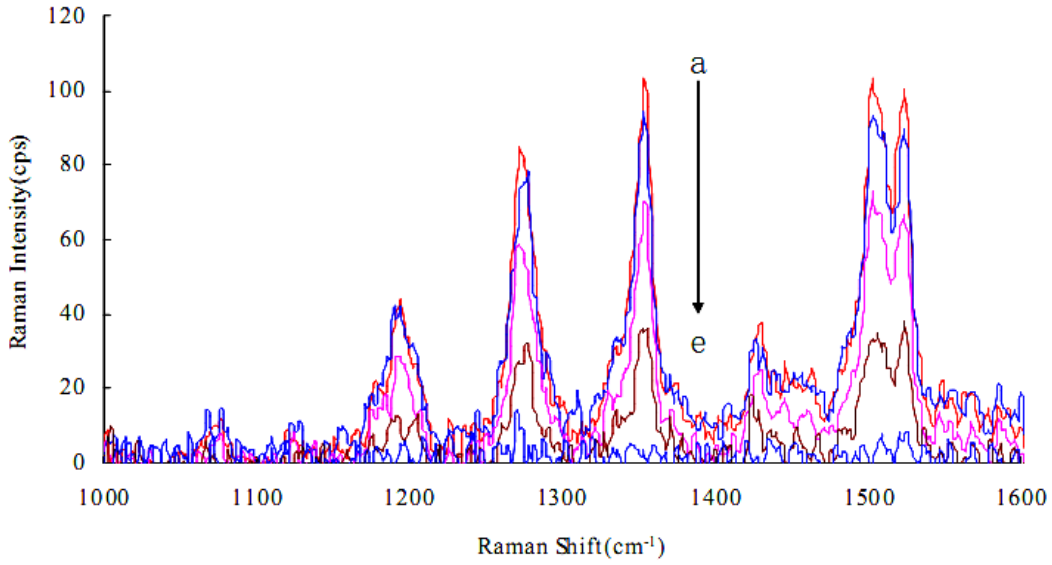


Fig. 2S SERS spectra for the RhB system containing different concentration of O_3
(a) 2.0×10^{-7} mol/L RhB-21.52 mg/L AuNPs -0.18 mol/L HCl; (b) 6.25 nmol/L O_3; (c) 25.0 nmol/L O_3; (d) 50.0 nmol/L O_3; (e) 75.0 nmol/L O_3

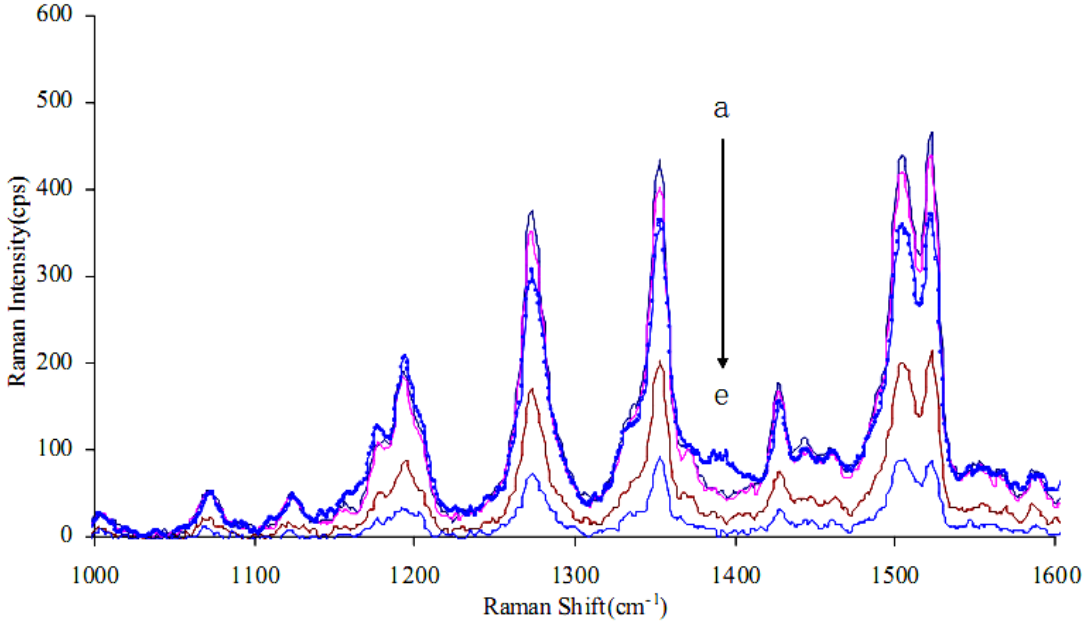


Fig. 3S SERS spectra for the b-RhB system containing different concentration of O_3
(a) 2.0×10^{-7} mol/L b-RhB-21.52 mg/L AuNPs -0.18 mol/L HCl; (b) 6.25 nmol/L O_3; (c) 25.0 nmol/L O_3; (d) 75.0 nmol/L O_3; (e) 125.0 nmol/L O_3

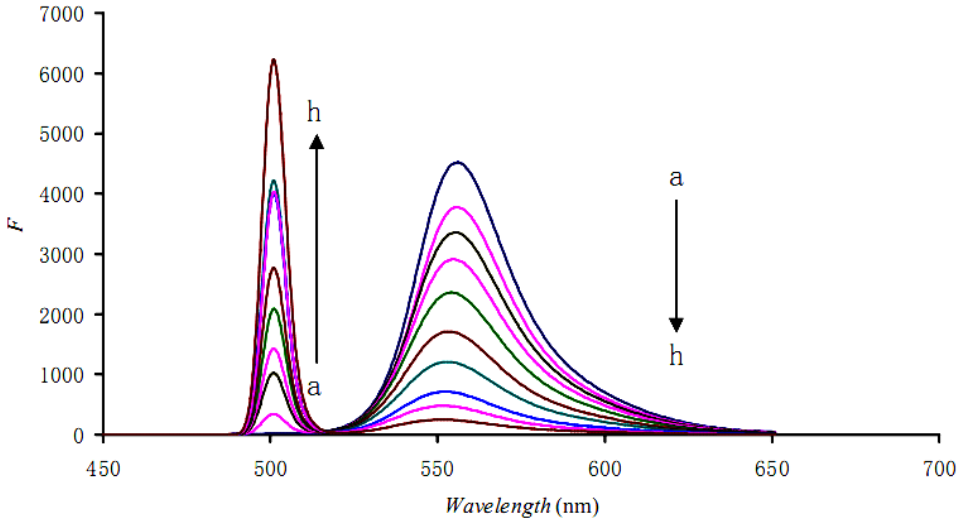


Fig. 4S Fluorescence spectra of the Rh6G associating particle system
(a) 0.18 mol/L HCl-1.33×10^{-5} mol/L Rh6G; (b) a-1.93 μmol/L O_3; (c) a-5.79 μmol/L O_3; (d) a-7.72 μmol/L O_3; (e) a-9.65 μmol/L O_3; (f) a-11.6 μmol/L O_3; (g) a-13.5 μmol/L O_3; (h) a-19.3 μmol/L O_3;

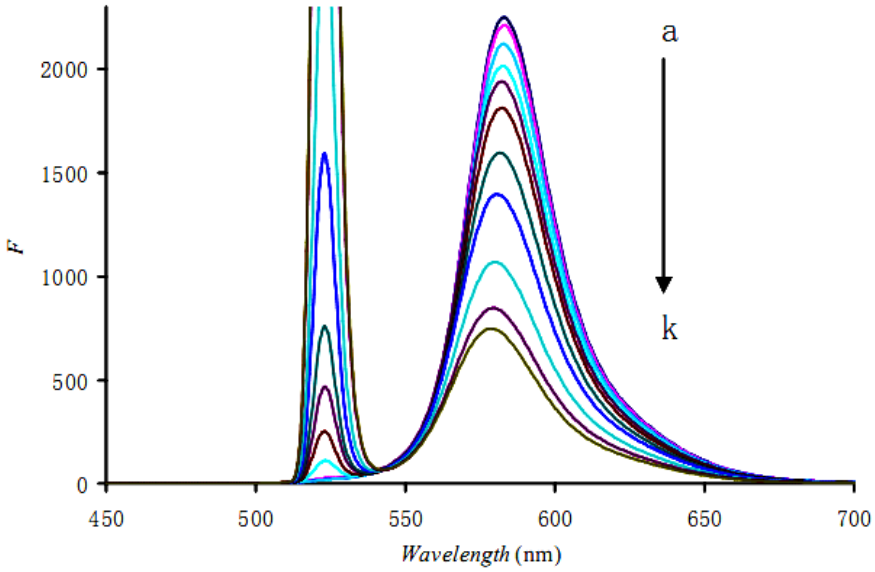


Fig.5S Fluorescence spectra of the RhB associating particle system
(a) 0.18 mol/L HCl-1.33×10^{-5} mol/L RhB; (b) a-0.83 μmol/L O_3; (c) a-6.67 μmol/L O_3; (d) a-10.0 μmol/L O_3; (e) a-13.3 μmol/L O_3; (f) a-20.0 μmol/L O_3; (g) a-26.7 μmol/L O_3; (h) a-33.3 μmol/L O_3; (i) a-40.0 μmol/L O_3; (j) a-46.7 μmol/L O_3; (k) a-53.3 μmol/L O_3

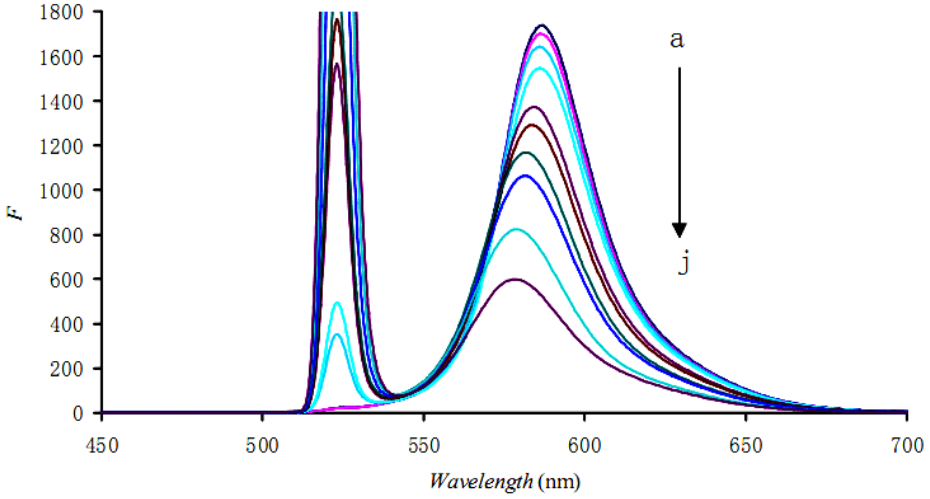
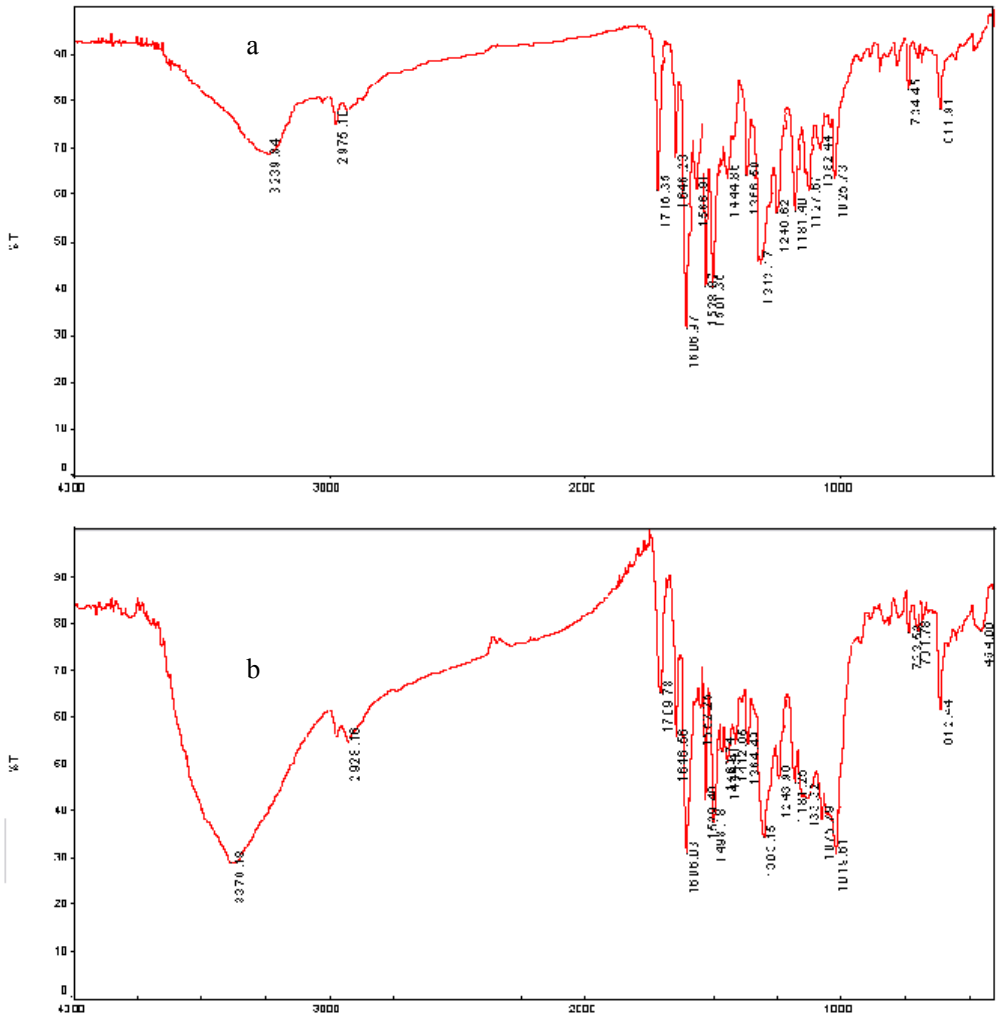


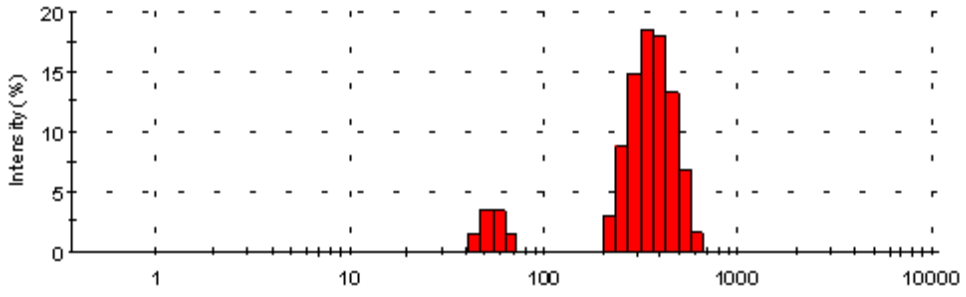
Fig. 6S Fluorescence spectra of the b-RhB associating particle system
(a) 0.18 mol/L HCl-1.33×10^{-5} mol/L b-RhB; (b) a-0.83 μmol/L O_3; (c) a-1.67 μmol/L O_3; (d) a-3.33 μmol/L O_3; (e) a-6.67 μmol/L O_3; (f) a-8.33 μmol/L O_3; (g) a-10.0 μmol/L O_3; (h) a-13.3 μmol/L O_3; (i) a-18.3 μmol/L O_3; (j) a-23.3 μmol/L O_3



Wavenumber (cm^{-1})

Fig. 7S IR spectra of the RhS and its associated particle

(a) RhS; (b) RhS-I_3.



Size/nm

Fig. 8S Laser scattering of the RhS associated particles

0.18 mol/L H Cl-1.5×10^{-7} mol/L RhS-50 nmol/L O_3

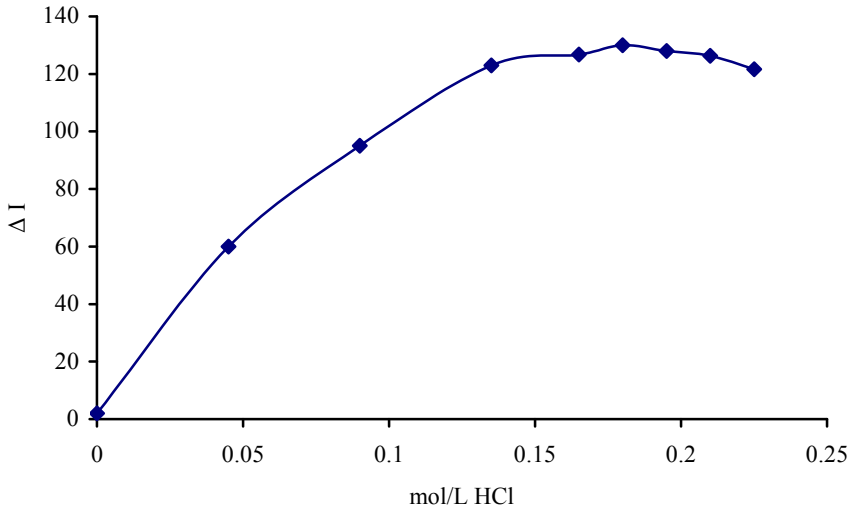


Fig. 9S Effect of HCl concentration

21.52 mg/L AuNPs -1.5×10^{-7} mol/L RhS-50 nmol/L O_3

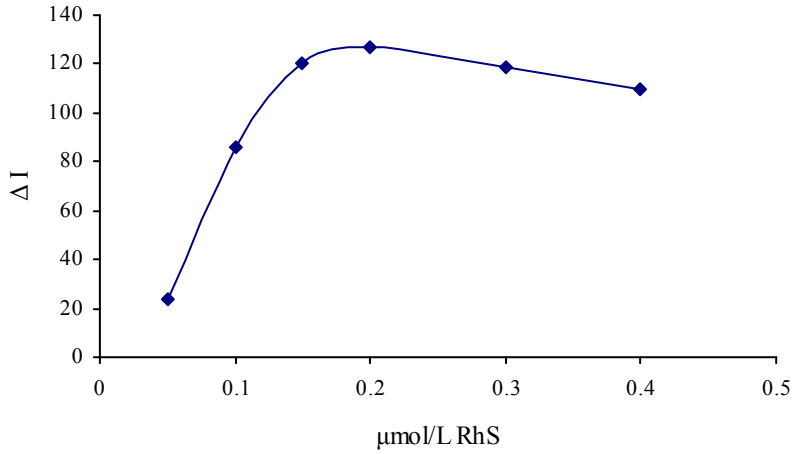


Figure 10S Effect of RhS concentration

21.52 mg/L AuNPs -0.18 mol/L HCl-50 nmol/L O_3

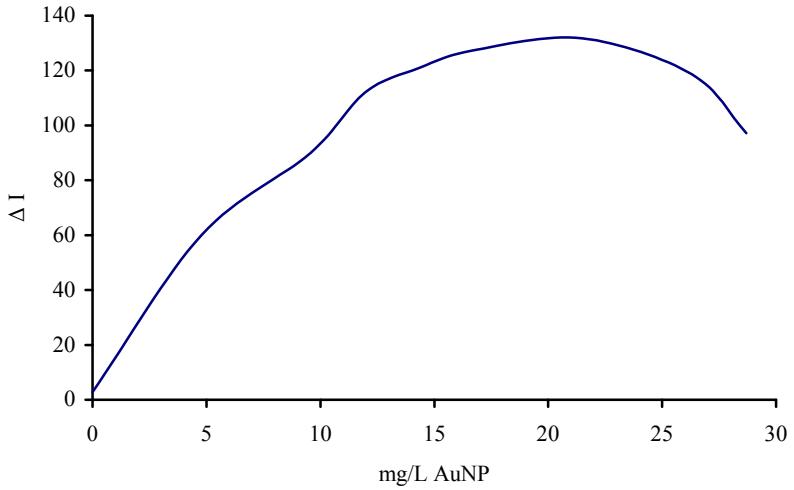


Fig. 11S Effect of AuNPs concentration

1.5×10^{-7} mol/L RhS-0.18 mol/L HCl-50 nmol/L O_3

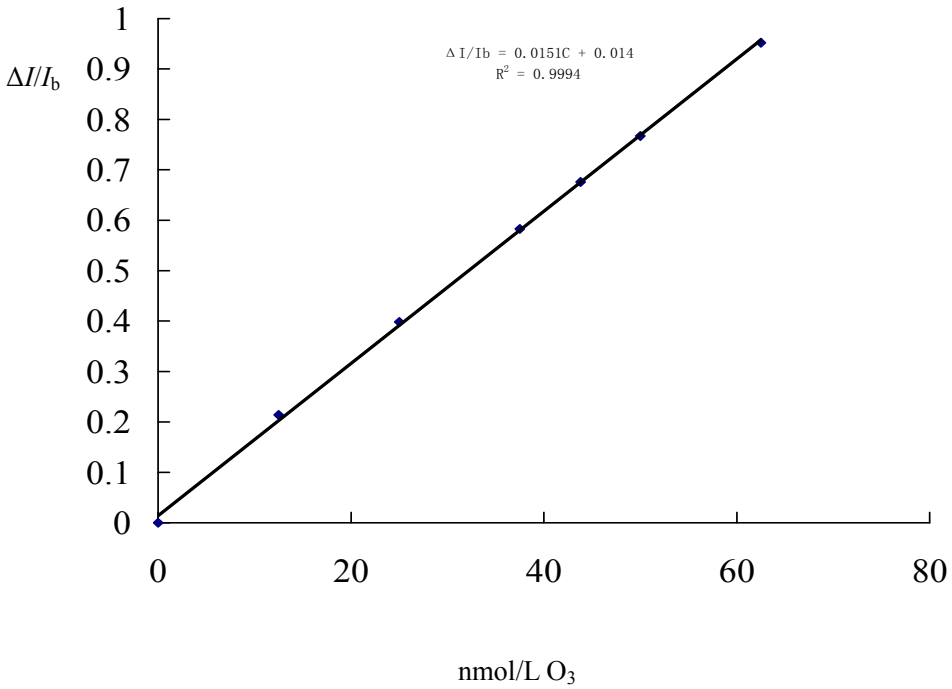


Fig. 12S Working curve of the $\Delta I/I_b$ *vs.* concentration.

Table 1S Effect of coexistence substances

Coexistent substance	Tolerance (Times)	Relative error (%)	Coexistent substance	Tolerance (Times)	Relative error (%)
Zn^{2+}	300	-3	Cu^{2+}	200	5
Ca^{2+}	300	4	Mg^{2+}	300	-5
Ag^{+}	200	3	Hg^{2+}	200	4.5
Fe^{3+}	100	-5	$Cr_2O_7^{2-}$	100	5
Cr^{3+}	200	4	Co^{2+}	200	4.8
H_2O_2	100	4	NO_2^{-}	100	5

Table 2S Analytical features of the rhodamine dye SERS and fluorescence systems

Dye	λ_{Raman} (cm^{-1})	λ_{em} (nm)	Regression equation	LR (nmol/L)	Coefficient	DL (nmol/L)
RhS	1503	-	ΔI = 2.654C+5.4	1.56~62.5	0.9974	0.9
Rh6G	1503	-	ΔI = 0.621C+2.0	6.25~212.5	0.9979	4.0
RhB	1503	-	ΔI = 1.427C-1.2	6.25~75.0	0.9935	1.7
b-RhB	1522	-	ΔI = 3.475C+7.7	6.25~350.0	0.9921	1.3
RhS	-	554	ΔF = 0.272C+0.020	30~28300	0.9992	10
Rh6G	-	585	ΔF = 0.0520C+0.05	330~23300	0.9948	90
RhB	-	583	ΔF = 0.030C-0.055	830~53.300	0.9874	490
b-RhB	-	556	ΔF = 0.275C+0.05	970~15400	0.9918	670

Sample analysis. A 6.0 mL BKI absorbing solution was added in the bottle of TQC-1500-z atmospheric sampler that collect air sample 1h with sampling flow rate of 1.0 L/min. Then, the absorbing solution was diluted to 6.0 mL with water to obtain the sample solution. A 0.20 mL of the sample solution was used to determine ozone content according to the procedure. This method results are listed in Table 3 that were agreement with that of the indigo carmine spectrophotometer [2]. The RSD is in the range of 2.0-3.7 %. The sample of 1A-3A was collected at the gate of the School of Guangxi Normal University, at a.m. 9:00~10:00, sunny, and temperature of 30 ℃. The sample of 1B-3B was collected at the gate of the School of Guangxi Normal University, at p.m. 10:10~11:10, sunny and cloudy, and temperature of 30 ℃. From the results (See ESI, Table 3S), we can see that the content of B sample is higher than the A sample, it is owing to the ozone

generated from the traffic and population flux.

Table 3S Analytical results

Samples	Found (μg/m^3 O_3)	Mean (μg/m^3 O_3)	RSD(%)	Ref. results(μg/m^3 O_3)[a]
A1	43.2, 40.0, 42.6	41.9	3.4	41.2
A2	40.5, 40.9, 38.0	39.8	3.9	39.8
A3	42.5, 43.2, 41.0	42.2	2.7	42.0
B1	47.0, 48.5, 49.0	48.2	2.2	48.4
B2	48.2, 49.8, 50.5	49.5	2.4	48.9
B3	49.6, 50.0, 52.4	50.7	3.0	50.2

[a] Indigo carmine spectrophotometry.

References

1. Z. L. Jiang, Y. Y. Fan, M. L. Chen, A. H. Liang, X. J. Liao, G. Q. Wen, X. C. Shen, X. C. He, H. C. Pan, H. S. Jiang, *Anal. Chem.,* 2009, **81**, 5439.
2. HJ 504-2009. Determination of O_3 in air-indigo carmine spectrophotometry. Beijing: Chinese Environmental Scientific Press, 2009.