

A highly sensitive SERS method for determination of nitrogen oxide in air based on the signal amplification effect of nitrite catalyzing bromate oxidization of rhodamine 6G probe

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Experimental

Preparation of AuNPs: In a 250mL round-bottom flask containing 50 mL water and put on magnetic heat stirrer (2 mot/min), 3.5mL of 1% trisodium citrate was added after the solution boiling. Then, a 500 μ L of 1% HAuCl₄ was added quickly and maintained the solution boiling. The color turned red within 5min and the final color change to brilliant red. Boiling continued for 10 min, the flask was removed from the heating source, and the colloid was not stirred until cold ^[1]. Last the solution of 57.3 μ g/mL Au was transferred to a 50 mL volumetric flask and diluted to 50 mL with water, and stored at 4°C. There is an absorption peak of 512 nm with an average size of 10 nm.

Preparation of AgNPs: A 5.0 g PEG10000 was added to an Erlenmeyer flask containing 70 mL water to make it dissolving. Then, a 7.0 mL 10 g/L trisodium citrate and 770 μ L 2.4 \times 10⁻² mol/L AgNO₃ were added respectively. After that, 16.0 mL 0.25 mg/mL NaBH₄ was added slowly into the mixture under the vigorous stirring, during the time its color changed from pale yellow to deep yellow, which indicated that the nanosilver particles were formed ^[2]. 15 min later the mixture solution was diluted to 100 mL with water and stored in the refrigerator at 4°C, the concentration of silver particles was 19.9 mg/L with an average size of 10 nm and an absorption peak of 408 nm.

Preparation of the oxidized Rh6G (ORh6G)

Into a 100mL round-bottom flask equipped with 2.5mL H₂O, 25mL 0.01mol/L Rh6G solution, 10mL 0.5mol/L KBrO₃ solution, 10mL 1mol/L H₃PO₄ solution, 2.5mL 1.45mmol/L NO₂⁻ solution

and mixed well. The mixture heated at 65°C for 4h, after cooling in the tap water, the flask was removed to stand for 15min at room temperature. Taken the mixture solution into a 10.0mL centrifuge tube and centrifuged 30min ($150\times 100\text{r/min}$), discarded the supernatant and taken the bottom sediment drying to obtain ORh6G power.

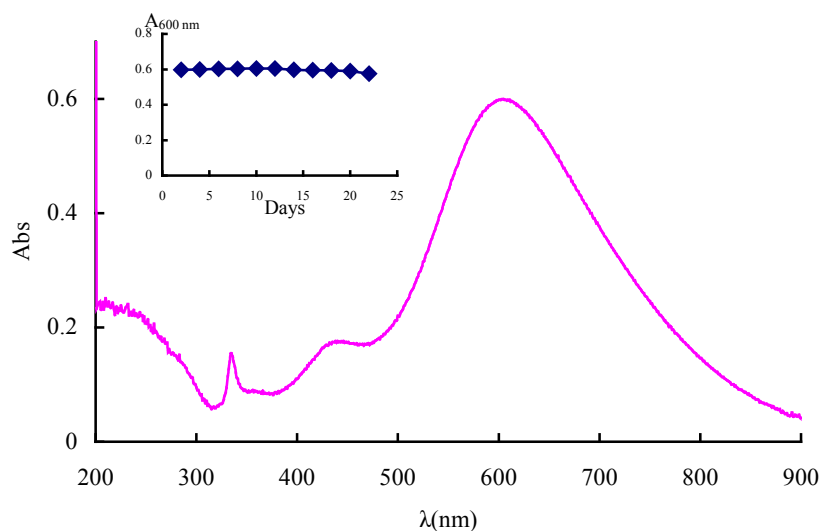


Fig.1S UV-Vis spectrum of the TA AgNP sol containing 0.050 mmol/L Ag

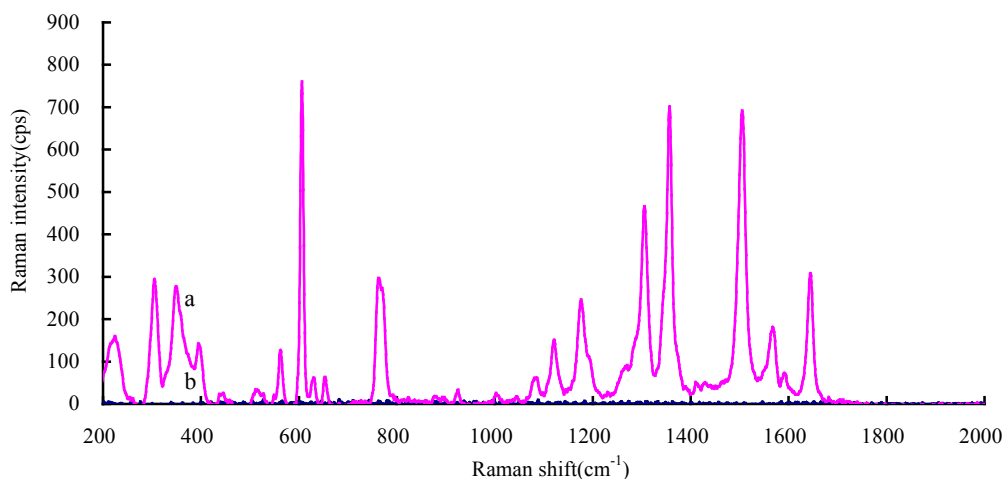


Fig.2S The normal Raman and SERS spectra of Rh6G.

a: 50mmol/L HCl + 1.0mmol/L Rh6G +15min + 60mmol/L NaCl; **b:** 50mmol/L HCl + 0.5 $\mu\text{mol/L}$ Rh6G +15min + 60mmol/L NaCl+2.97 $\mu\text{g/mL}$ TA AgNPs.

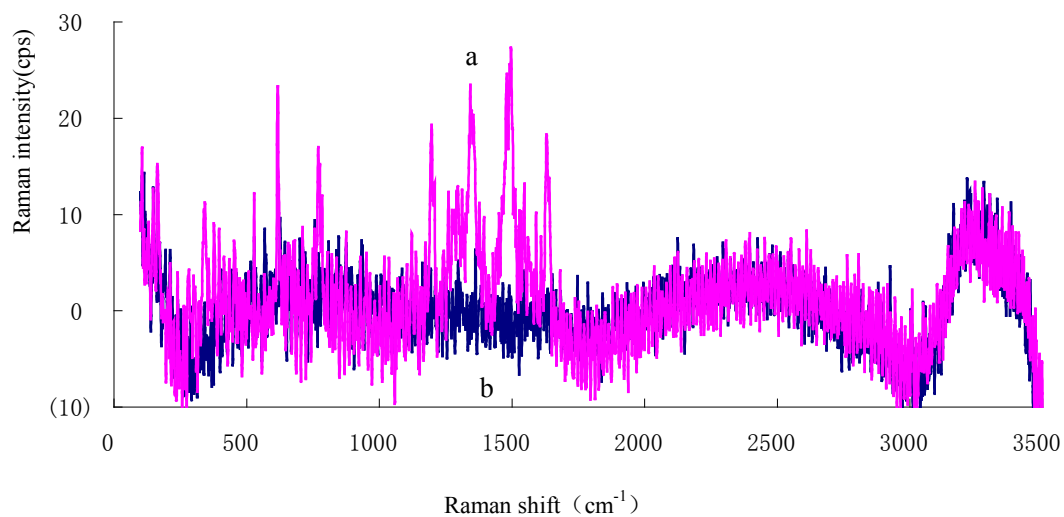


Fig. 3S The normal Raman spectra and the SERS spectra of the oxidized Rh6G

a: 50mmol/L H_3PO_4 + 0.2g/L ORh6G+ 60mmol/L NaCl; **b:** 50mmol/L H_3PO_4 + 2mg/LORh6G+ 60mmol/L NaCl+2.97 $\mu\text{g}/\text{mL}$ TAgNPs.

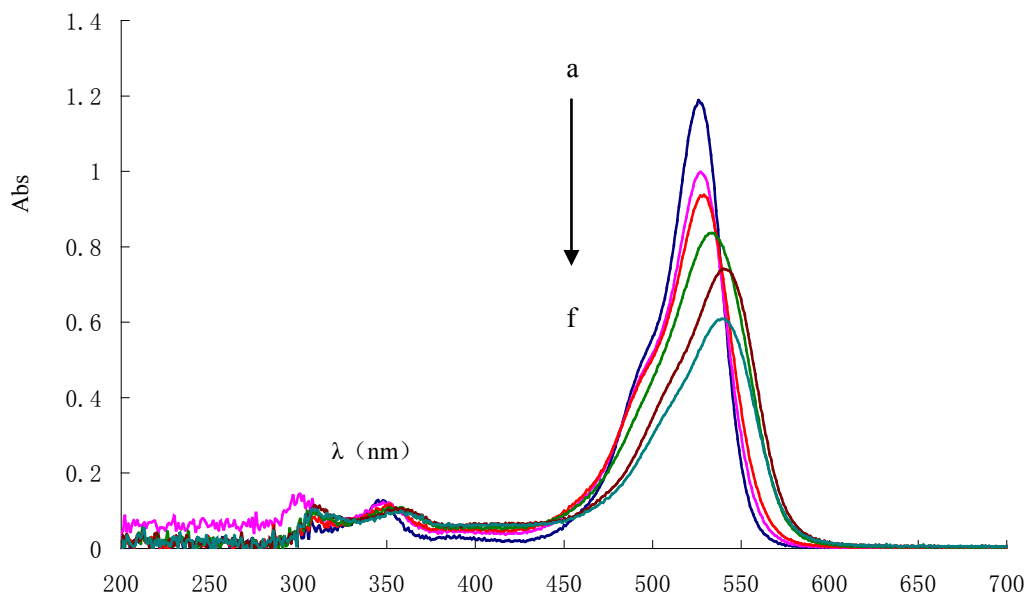


Fig.4S Absorption spectra of the NO_2^- -Rh6G- KBrO_3 system

a: 1.0 $\mu\text{mol/L}$ Rh6G+2.0mmol/L KBrO_3 +50mmol/L H_3PO_4 ; **b:** **a**+7.2 $\mu\text{mol/L}$ NO_2^- ; **c:** **a**+14.4 $\mu\text{mol/L}$ NO_2^- ; **d:** **a**+36 $\mu\text{mol/L}$ NO_2^- ; **e:** **a**+72 $\mu\text{mol/L}$ NO_2^- ; **f:** **a**+86.4 $\mu\text{mol/L}$ NO_2^-

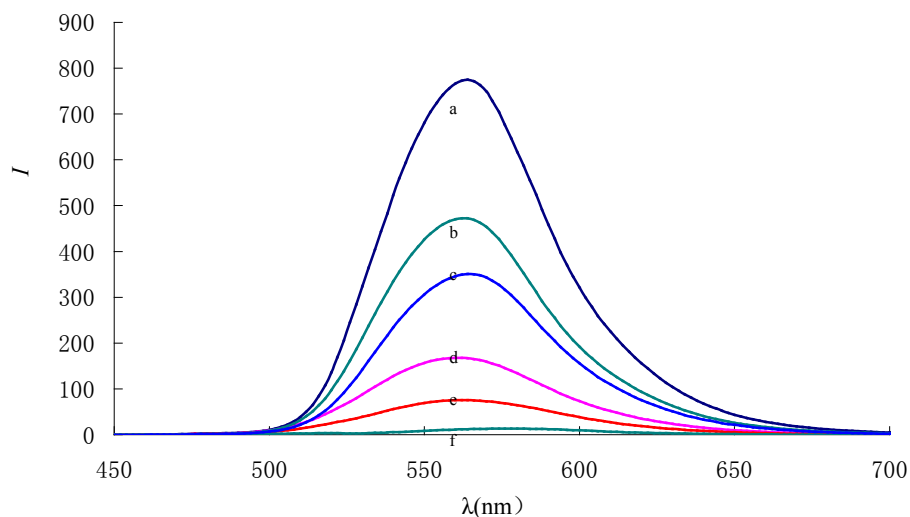
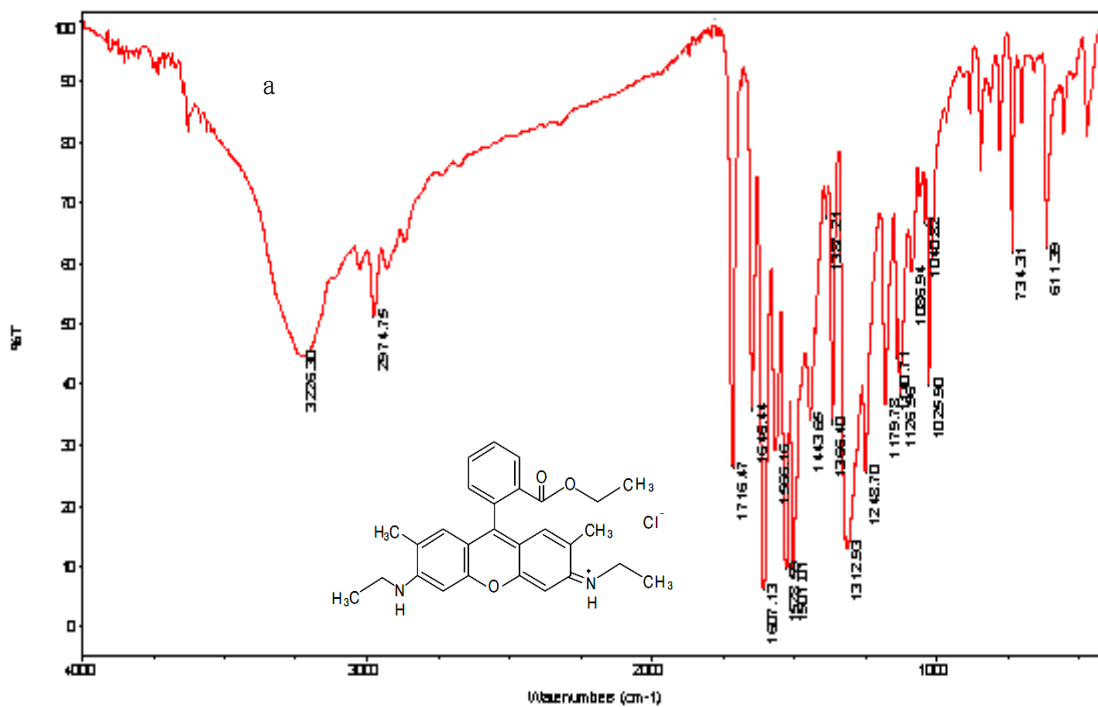


Fig.5S Fluorescence spectra of the Rh6G- KBrO_3 - NO_2^- system

a: 1.0 $\mu\text{mol/L}$ Rh6G+2.0mmol/L KBrO_3 +50mmol/L H_3PO_4 ; **b:** **a**+3.6 $\mu\text{mol/L}$ NO_2^- ; **c:** **a**+7.2 $\mu\text{mol/L}$ NO_2^- ; **d:** **a**+14.4 $\mu\text{mol/L}$ NO_2^- ; **e:** **a**+36 $\mu\text{mol/L}$ NO_2^- ; **f:** **a**+57.6 $\mu\text{mol/L}$ NO_2^-



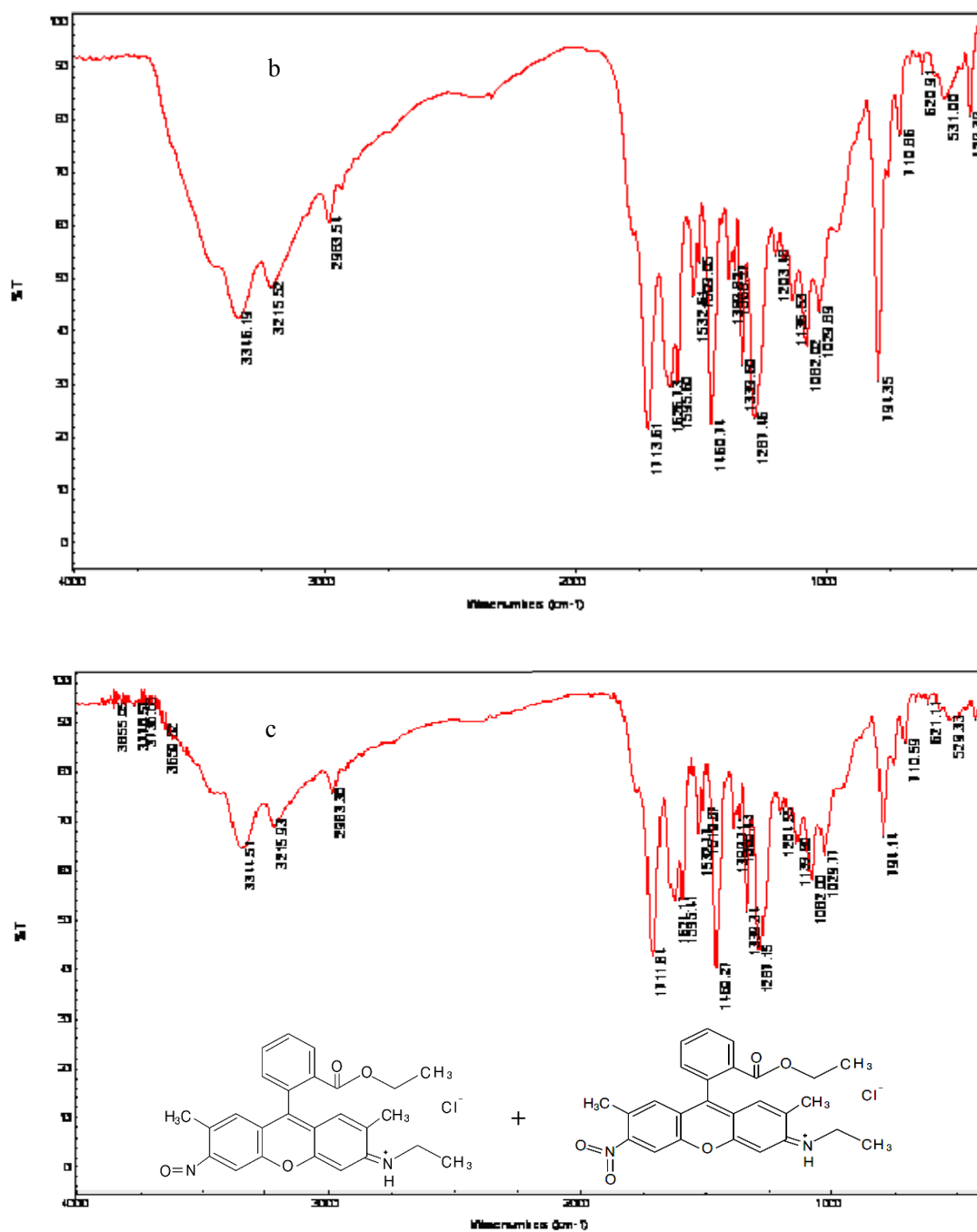


Fig.6S FTIR spectra of Rh6G and ORh6G

(a) Rh6G; b) ORh6G of the KBrO₃-Rh6G system; c) ORh6G of the KBrO₃-Rh6G-NO₂⁻ system.

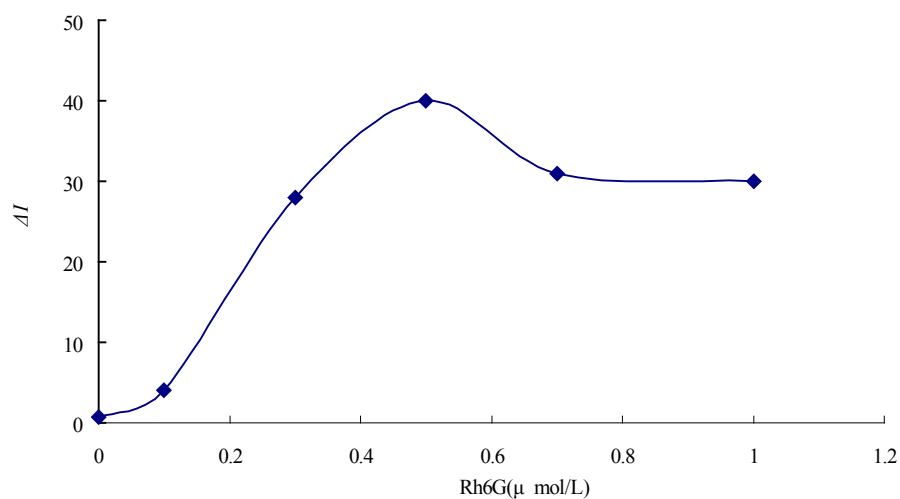


Fig.7S Effect of Rh6G concentration

1mmol/L KBrO_3 + 50mmol/L H_3PO_4 + 60mmol/L NaCl + 2.97 $\mu\text{g}/\text{mL}$ TAgNPs.

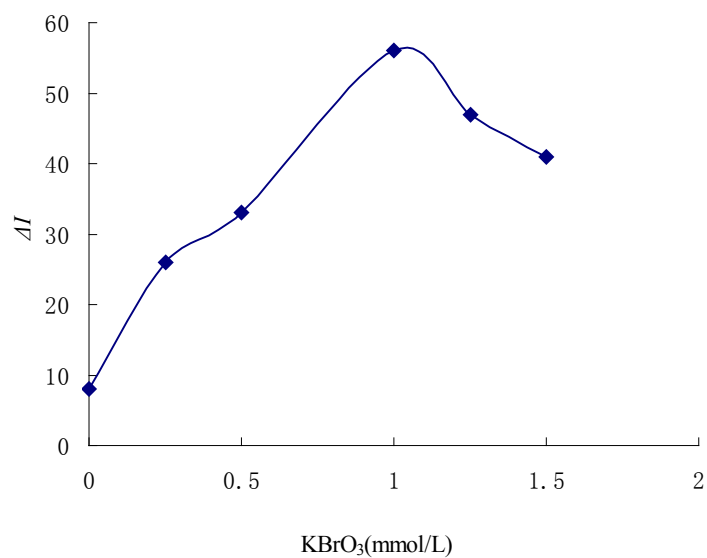


Fig.8S Effect of KBrO_3 concentration

0.5 $\mu\text{mol/L}$ Rh6G + 50mmol/L H_3PO_4 + 60mmol/L NaCl + 2.97 $\mu\text{g}/\text{mL}$ TAgNPs

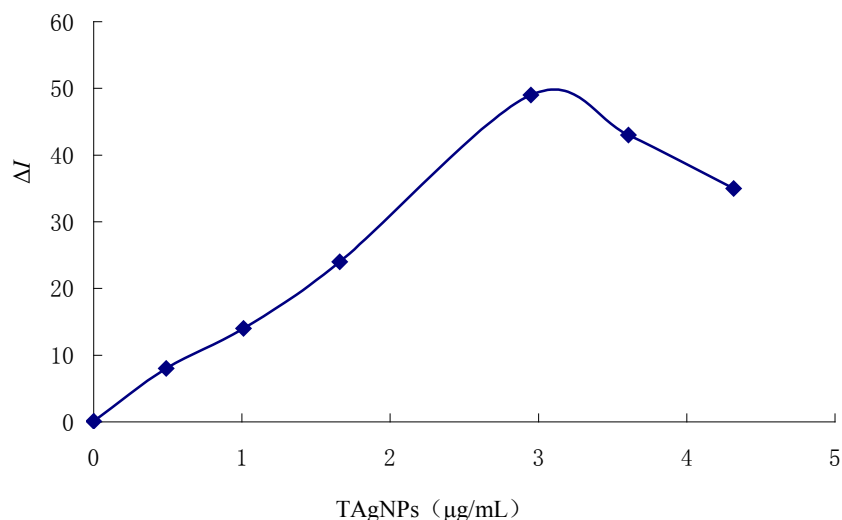


Fig.9S Effect of TAgNPs concentration

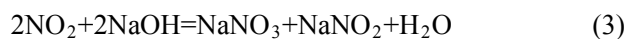
0.5μmol/L Rh6G+1mmol/L KBrO₃ +50mmol/L H₃PO₄+ 60mmol/L NaCl.

Air sample preparation

Fig.10S was the sketch of air sampling device, collect time was 2.0 h and flow speed was 0.6L/min. The mainly components of nitrogen oxide (NO_x) in the nature air were NO and NO₂, after oxidized by 10mL 0.16mol/L KMnO₄ solution, the NO_x almost complete to form NO₂, and the NO₂ can be absorbed by 25mL 0.02mol/L NaOH solution to form NO₃⁻ and NO₂⁻ (Equation 2) ^[3]. After finish the air sample collection, neutralize the remained NaOH in the absorption solution until its pH in the range of 7.0-7.5 using 0.1mol/L HCl solution, and diluted to 50 mL and mixed well. Taken 200μL the sample solution to detect and added a known amount of NO₂⁻ solution into the water sample to obtain the recovery.

$$C_{\text{NO}_x} = C_{\text{NO}} + C_{\text{NO}_2} \quad (1)$$





$$C_{\text{NO}_x} = n(\text{NO}_2) \times M(\text{NO}_2) / 2.0\text{h} \times 0.6\text{L} \cdot \text{min}^{-1} \quad (4)$$

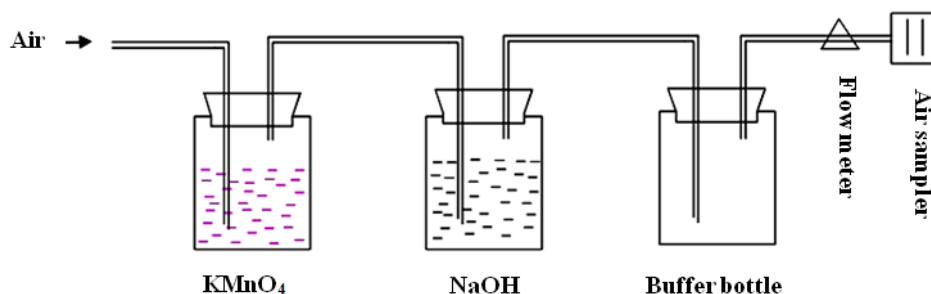


Fig.10S The sketch of air sampling device

Table 1S Analytical results of NO_x in air (n=5)

Sample	Average (nmol/L)	RSD (%)	Added NO_2^- (nmol/L)	Found NO_2^- (nmol/L)	Recovery (%)	NO_x content ($\mu\text{g}/\text{m}^3$)	Ref. results ³ ($\mu\text{g}/\text{m}^3$)	Standard method* ($\mu\text{g}/\text{m}^3$)
Sample 1	21.1	8.4	14.4	34.7	97.7	26.9	26.2	25.3
			50.4	72.3	101.1			
Sample 2	22.8	6.7	7.2	31.4	101.9	29.0	29.4	30.7
			36	58.9	98.8			
Sample 3	20.2	5.8	14.4	35.5	102.6	25.8	24.9	26.7
			57.6	77.6	99.7			
Sample 4	20.7	6.5	21.6	43.9	103.8	26.3	27.4	26.6
			57.6	75.4	96.3			
Sample 5	21.9	5.5	14.4	36.1	99.2	27.8	26.9	27.4
			57.6	77.1	97.0			

* N-(1-naphthyl)ethylene diamine dihydrochloride spectrophotometric method.

References

- [1] G. Q. Wen, C. Y. Lin, M. L. Tang, G. S. Liu, A. H. Liang, Z. L. Jiang. RSC Advan., 2013, 3, 1941-1946
- [2] Z. L. Jiang, L. P. Zhou, A. H. Liang. Chem. Comm., 2011, 47, 3162-3164.
- [3] Lu C L, Song H Y, Cai Z H, Qiu H O, Tang Z Y. Metallurgical Analysis, 2009, 29(7):49-52