Supporting information

High Time-Resolution Optical Sensor for Monitoring Atmospheric Nitrogen Dioxide

Yong Tian,[†] Xiaomin Zhang,[‡] Huiyan Shen,[‡] Aifeng Liu,[†] Zongshan Zhao,[*,†] Ming-Li Chen,[‡] and Xu-Wei Chen[*,‡]

[†] CAS Key Laboratory of Biobased Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, 266101, China

[‡] Research Center for Analytical Sciences, and Department of Chemistry, College of Sciences, Northeastern University, Shenyang, 110819, China

[*] Corresponding author:

Dr. Zongshan Zhao, Fax/Tel: +86 532-80662709, E-mail: zhaozs@qibebt.ac.cn

Prof. Xu-Wei Chen, Fax: +86 24 83676698, Tel: +86 24 83688944, E-mail: chenxuwei@mail.neu.edu.cn

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Reagents and Samples

All chemicals used were at least of analytical reagent grade. Sulfanilic acid, n-(1-naphthyl)-ethylenediamine dihydrochloride, and aceticacid were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Deionized water (DI water obtained by Milli-Q water purification system, Billerica, USA) of 18.2 MΩ cm was employed in the experiments. The stock solution of n-(1-naphthyl)-ethylenediamine dihydrochloride (1.00 g L^{-1}) was prepared in a 50 mL volumetric flask. Sulfanilic acid solution (20.0 g L^{-1}) was prepared by dissolving 0.40 g of sulfanilic acid into 20 mL of hot water (ca. 80℃) and then cooled to room-temperature for storage. The regular Griess-Saltzman (GS) reagent solution was prepared by transferring the prepared sulfanilic acid solution into a volumetric flask containing 4 mL acetic acid, 4 mL the prepared n-(1-naphthyl)-ethylenediamine dihydrochloride solution and then diluted to 100 mL. The high purity of NO_2 (50 ppmv, prepared by 99.99% of NO_2 and 99.999% of N_2, Dalian Special Gases Co., Ltd, Dalian, China, www.dl-gas.com/en/index.html) with appropriate dilution by high purity of N_2 (99.999%, Qingdao Haideweiye Technology Co., Ltd., China) was employed as the standard gas for NO_2 calibration.

FEP Teflon gas sample bags (purchased from Hao Chen Tian Cheng Environment Protection and Technology Company, Beijing, China) are employed for urban air gas collection. The air samples were collected near the Songling road in rush hours (close to QIBEBT at about 6:00 p.m.). Two sampling sites were at distances of 3 m and 50 m from the roadbed, respectively. The field analysis of urban air was carried out in the campus of QIBEBT that was about 70 m away from the roadbed.

Experimental Procedures for Standard NO$_2$ Detection

Before the NO$_2$ detection, the dark signal (U$_d$) was acquired with the LED off. Then, the PPMT was filled with the color reagent, the LED and SVs was turned on for acquisition of the initial signal before NO$_2$ standard gas injection. The signal was recorded for 20s (U$_0$ ~ U$_{20}$), and the average of the last half of the signal (U$_{10}$ ~ U$_{20}$) was record as U$_0$. Meanwhile, as showing in **Figure S1**, the standard gas of NO$_2$ was prepared and loaded into the sample loop via the sample injection system. At the data acquisition time of 20s (t = 20 s), the SVs were switched to power off for injecting the standard NO$_2$ into the detection cell. After 180 s, the system was reset for the next run.

Experimental Procedures for Urban Air Analysis

The device was adjusted as **Figure 1** when analyzing air samples. Similar to the standard NO$_2$ detection, the PPMT was filled with the fresh color reagent, and then the whole system was turned on for recording the U$_0$ for 20 s. Meanwhile, the collected urban air or the field urban air was loaded into the sample loop. After 20 s, the SVs were switched to power off channel, the air sample began to be analyzed. After 180s, the color reagent was refilled, air sample were changed and SVs were turned on for the next run. After analysis processes have been finished, the PPMT was refreshed and filled with DI water, and the detection cell was refreshed by N$_2$.

Data Analysis

As refer to the previous report[1], U_d was the average value of potentials acquired when the LED was turned off. The average value from 10 to 20 s ($U_{10} \sim U_{20}$) was used as U_0 to avoid data fluctuation when filling color reagent at the beginning of each test. The temporal absorbance A_t was calculated by using the equation of $A_t = \log((U_0 - U_d)/(U_t - U_d))$. To reduce errors that generated by single point quantitation, the slope of the signals between 100 s to 180 s ($(A_{180} - A_{100})/80)$) were used for quantitation.

Reference

(1) Tian, Y.; Dasgupta, P. K.; Mahon, S. B.; Ma, J.; Brenner, M.; Jian, H.; Boss, G. R. *Anal. Chim. Acta* **2013**, *768*, 129-135.

Figure S1. Schematic representation of the device used for standard NO_2 detection. MFC: mass flow controller; SV: solenoid valve; F: sodium hydroxide filter; SL: sample loop; OF: optical fiber; LED: light emitting diode; JT: jacket tube; PPMT: porous polypropylene membrane tube; PD: photodiode; PT: peek tube; P1 and P2: air pump; W: waste.
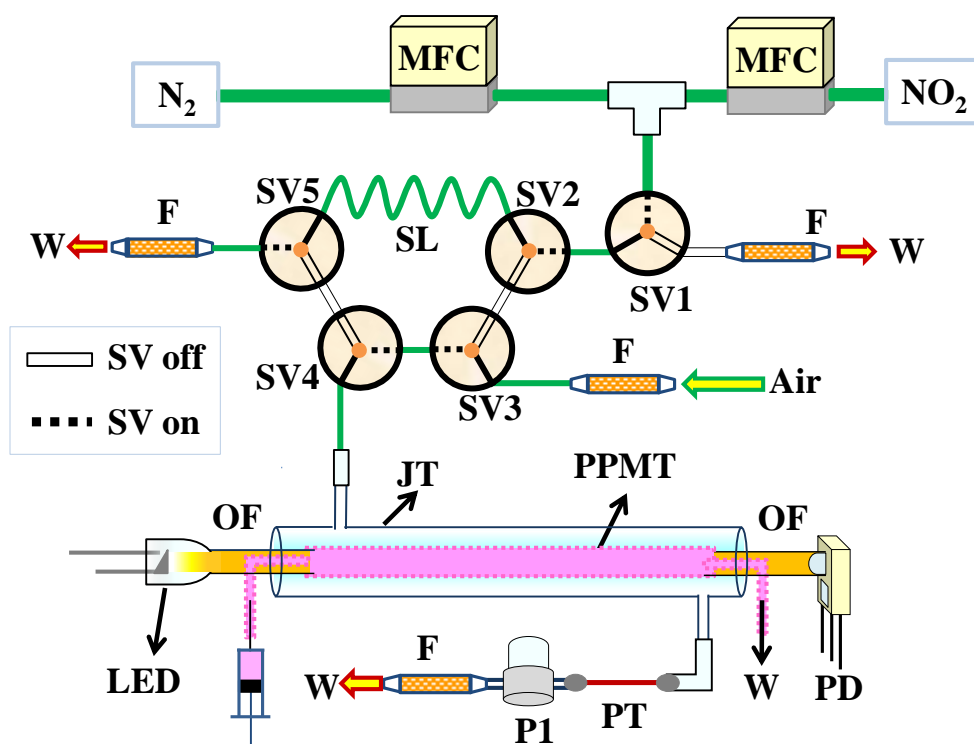
Figure S2. The circuit diagrams for LED, PD and DAQ (A), and three-way solenoid valves (B). LED: light emitting diode; PD: photodiode; DAQ: data acquisition board.
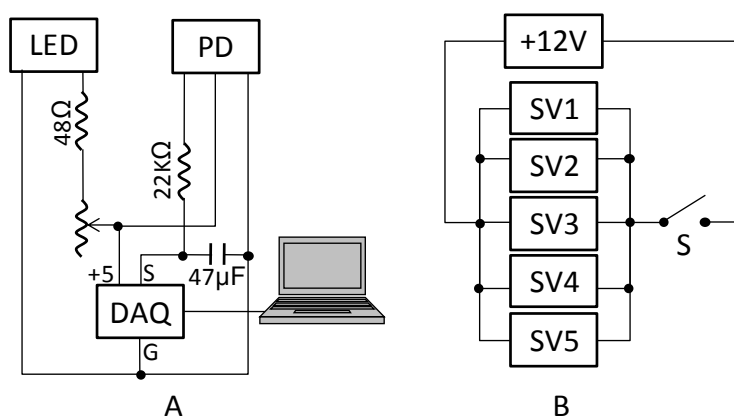
Figure S3. The schematic illustration for the chromogenic reaction of Griess-Saltzman (GS) reagent with NO_2.
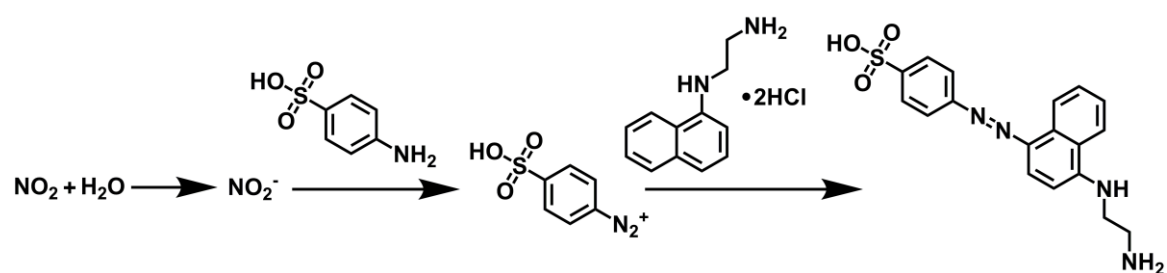
Figure S4. (a) Effect of the GS reagent solution concentration on a 100 ppbv of NO_2 detection (TRC: times of regular GS solution concentration); (b) effect of the length of peek tube used as the gas flow rate limiter on 100 ppbv of NO_2 detection.
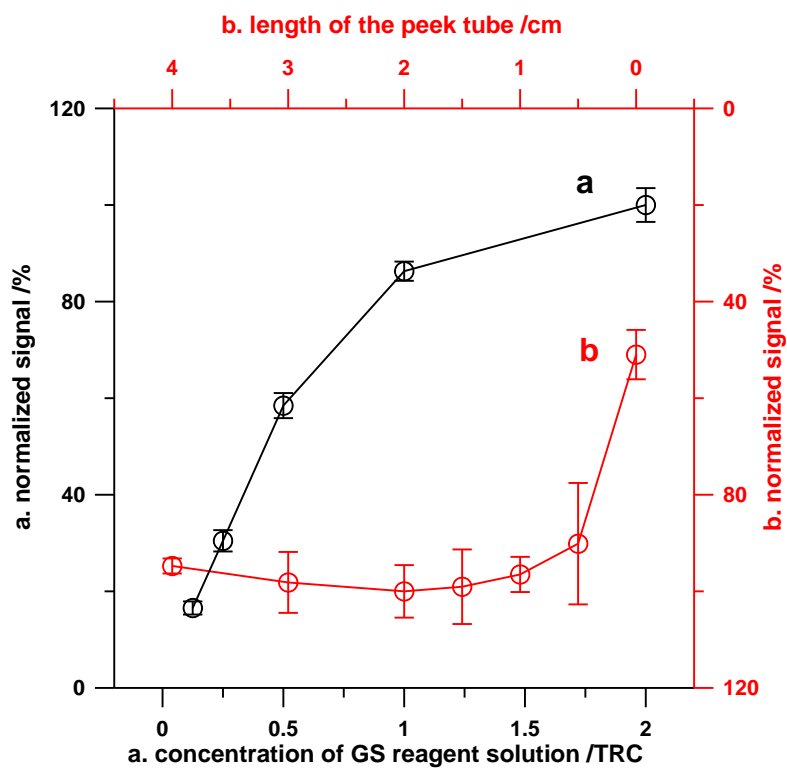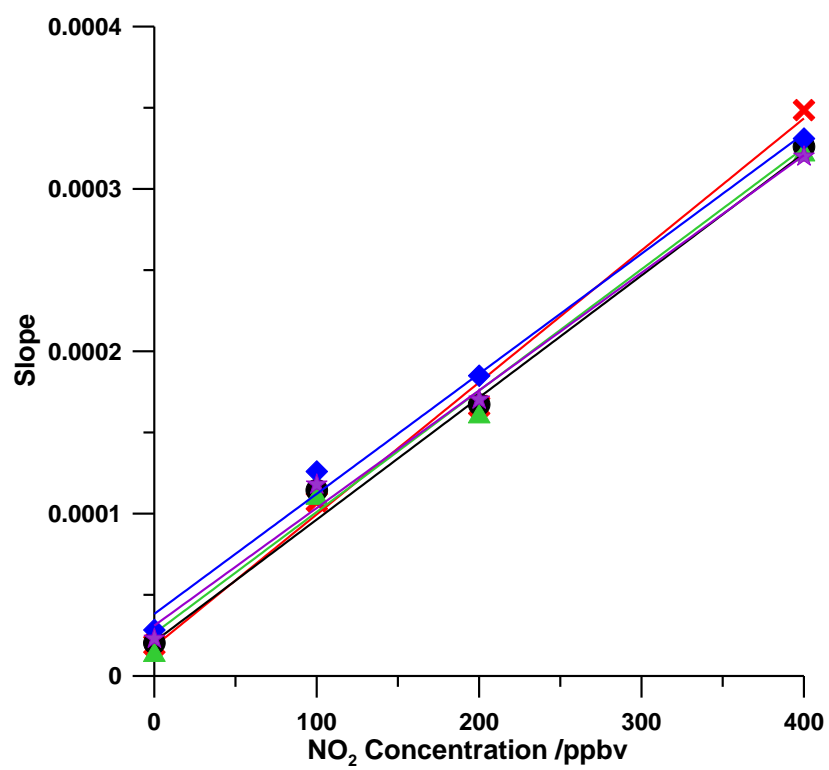
Figure S5. The analytical signals of the assembled device in detection of standard NO_2 (NO_2 concentration: 0 ~1000 ppbv).

$S = (1.356E\text{-}6 \pm 5.27E\text{-}8) * C_{NO_2} + (1.391E\text{-}4 \pm 1.67E\text{-}5)$

$R^2 = 0.9925$
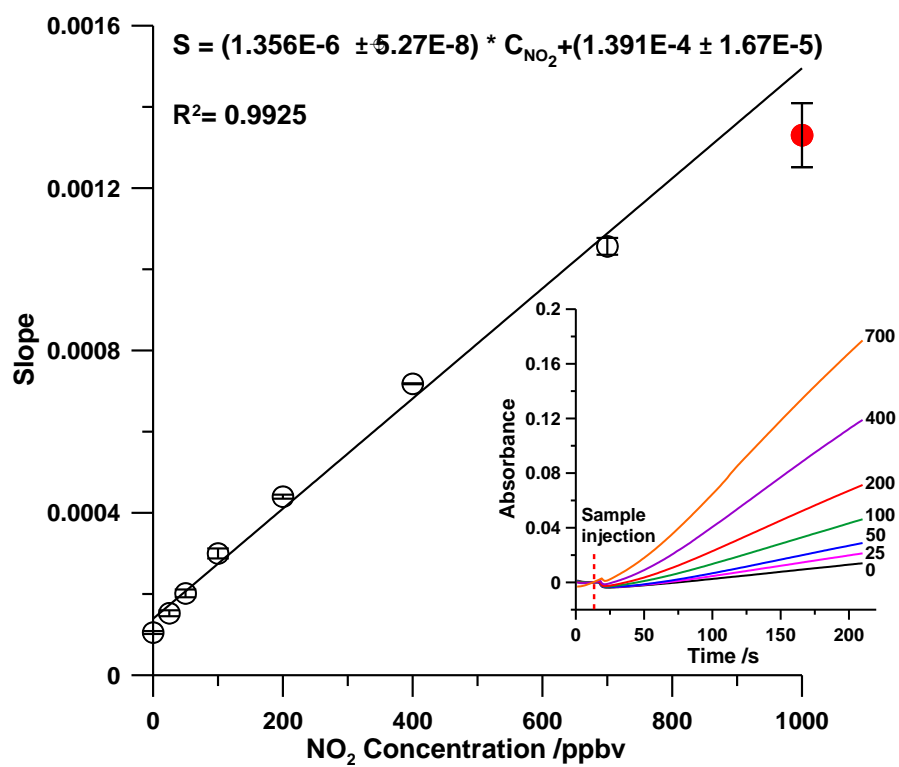
Figure S6. The inter-day calibration curves in five days.

Table S1. The equations of the inter-day calibration cures in five days.

No.	Calibration curves	R^2	RSS
1	$S=(8.13E\text{-}07\pm4.15E\text{-}08)C_{(NO2)}+(1.82E\text{-}05\pm9.52E\text{-}06)$	0.9948	3.02E-10
2	$S=(7.47E\text{-}07\pm4.07E\text{-}08)C_{(NO2)}+(2.63E\text{-}05\pm9.32E\text{-}06)$	0.9941	2.90E-10
3	$S=(7.52E\text{-}07\pm4.60E\text{-}08)C_{(NO2)}+(2.12E\text{-}05\pm1.05E\text{-}05)$	0.9925	3.70E-10
4	$S=(7.39E\text{-}07\pm4.12E\text{-}08)C_{(NO2)}+(3.82E\text{-}05\pm9.44E\text{-}06)$	0.9938	2.97E-10
5	$S=(7.24E\text{-}07\pm4.18E\text{-}08)C_{(NO2)}+(3.10E\text{-}05\pm9.59E\text{-}06)$	0.9933	3.06E-10

R^2: the coefficient of the determination, RSS: residual sum of squares