

Ultrasensitive detection of nitrogen oxides over a nanoporous membrane

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Supporting information

1. Selectivity of the molecular probes: the selectivity of the sensor was directly evaluated by measuring the response towards several compounds commonly found in environmental samples. Given the low responses of the molecular probes to the interferents, these tests were carried out in the presence of interferents with concentrations from tens to hundreds ppm, which are much higher than those regularly found in air. The selectivity coefficient is defined as the ratio between the sensor responses to nitrogen dioxide and to a given interferent at the same concentration. For *o*-phenylenediamine and diethyl-*p*-phenylenediamine molecules, the selectivity coefficients are greater than 1.3×10^4 for all tested interferents, except for ozone, which is also a strong oxidant. However, we were able to remove ozone using a simple filter based on molybdenum oxide derivative (2B Technologies, Boulder, Co.) (Table S1).

Table S1. Interferent Test for *o*-phenylenediamine

Compound	Selectivity coefficients
SO ₂	6.1×10^4
CO	3.1×10^5
CO ₂	1.5×10^7
NH ₃	1.3×10^4
H ₂ S	1.7×10^4
Acetone	4.5×10^4
Ethanol	5.6×10^4
Ozone	0.9

2. Mass transport study: The responses of the sensor for o-phenylenediamine and diethyl-*p*-phenylenediamine were characterized as a function of the sample flow rate. A linear dependence was found, indicating mass transport control of the sensor response (see Fig. S1 as example for o-phenylenediamine). A flow rate of 450 mL min⁻¹ was used in this work.

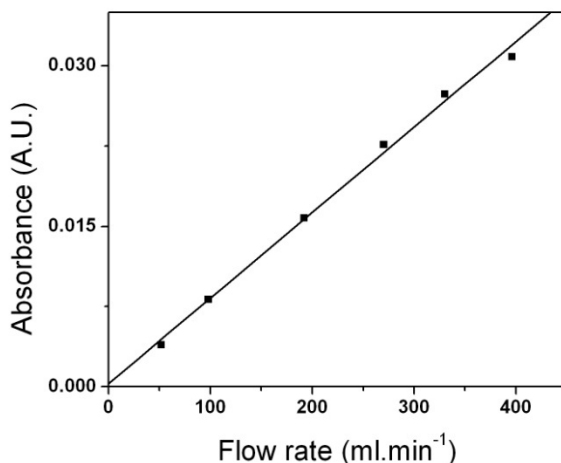


Figure S1. Response of a sensor towards 200ppbV NO₂ at different sample flow rates. Injection time = 20 seconds. Molecular probe: o-phenylenediamine.

3. Oxidizing tubing for conversion of NO into NO₂: Samples containing nitric oxide (NO) were oxidized by a tubing containing a solid porous substrate (alumina) impregnated with sodium permanganate to provide optimum gas adsorption, absorption and oxidation. The media works under a wide range of humidity levels (10 to 95% RH), which makes it suitable for environmental purposes. Since the converter could also absorb nitrogen oxides, the amount, particle size and packing of sodium permanganate were optimized to have the least NO_x absorption and maximum NO oxidation efficiency. The oxidizing filter is designed with 3 mg of oxidizing material packed inside 3-mm length polytetrafluoroethylene tubing with a 2-mm inner

diameter. The full oxidation efficiency of this oxidizing tubing is 90% and has been tested to have a capacity of 25 ppmV·day NO.

4. Preparation of the sensing elements: Cellulose microporous membrane was dipped in 2.5 mg ml⁻¹ aqueous alumina suspension with particle diameter of 0.05 μm. The alumina coated membrane was later dipped into a o-phenylenediamine or N,N-diethyl-p-phenylenediamine solution in acetonitrile and kept for one hour with mild shaking. After this, the sensing element was dried under vacuum and kept in a nitrogen atmosphere.

5. Humidity effect conditioning: Since absorbance signal changes were observed upon exposure of the sensor to high humidity environments (~100% relative humidity) (probably due to water condensation on the sensing platform optics), a nafion tubing (Perma Pure, LLC) was incorporated before the inlet of the sensing chamber to avoid interference of humidity. This produced a sensing platform with high immunity to humidity changes (Fig. S2).

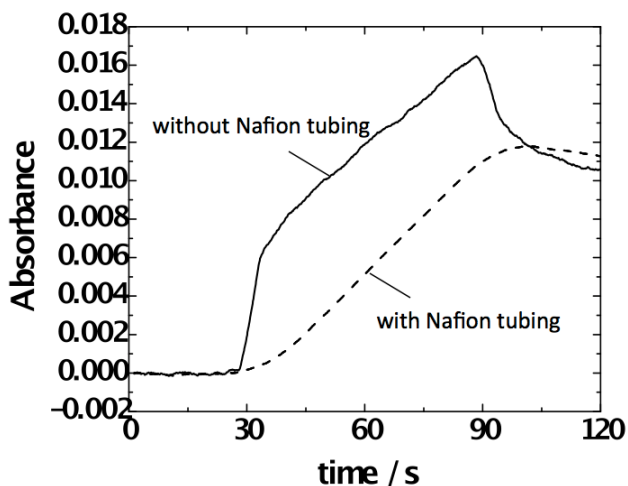


Figure S2. Sensing platform response to NO₂ at ~100 % relative humidity. Curves obtained with and without a nafion tubing located at the inlet of the sensing chamber.

6. Sensor stability (under storage): a batch of several sensing elements was prepared and stored at ambient temperature in a clean nitrogen atmosphere to test their stability. After different periods of time, the sensor was taken out from the storing chamber and used to measure the concentration of a 50 ppbV standard NO₂ sample (Fig. S3). The response of the sensors was tested for a period of 4 months and the response had 10% variation.

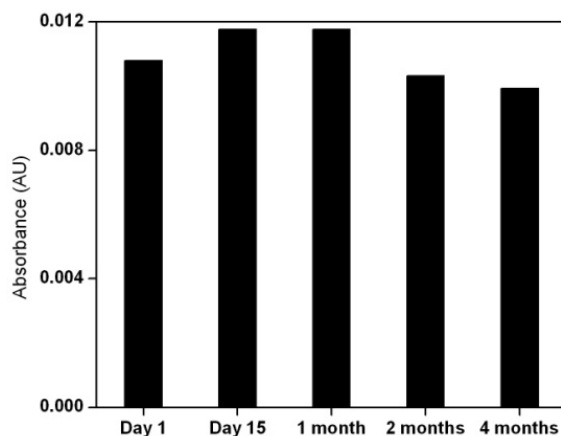


Figure S3. Response of different sensing elements prepared in one batch and kept at room temperature in a nitrogen atmosphere. Tests performed with 50ppbV standard NO₂ samples. Injection time = 20 seconds.

7. Sensor stability (under NO₂ sensing): The chemical reactions of the molecular probes are not reversible, and the sensing elements have limited availability over long time exposure to NO₂ samples. Fig. S4A-B shows the response of two different sensing elements with o-phenylenediamine under continuous and intermittent injections of 100 ppbV NO₂, respectively. From these experiments, the total capacity for detection of a sensing element was evaluated to be 80 ppbV.hour, i.e. the sensing element can be used continuously when exposed to 80 ppbV NO₂ for one hour.

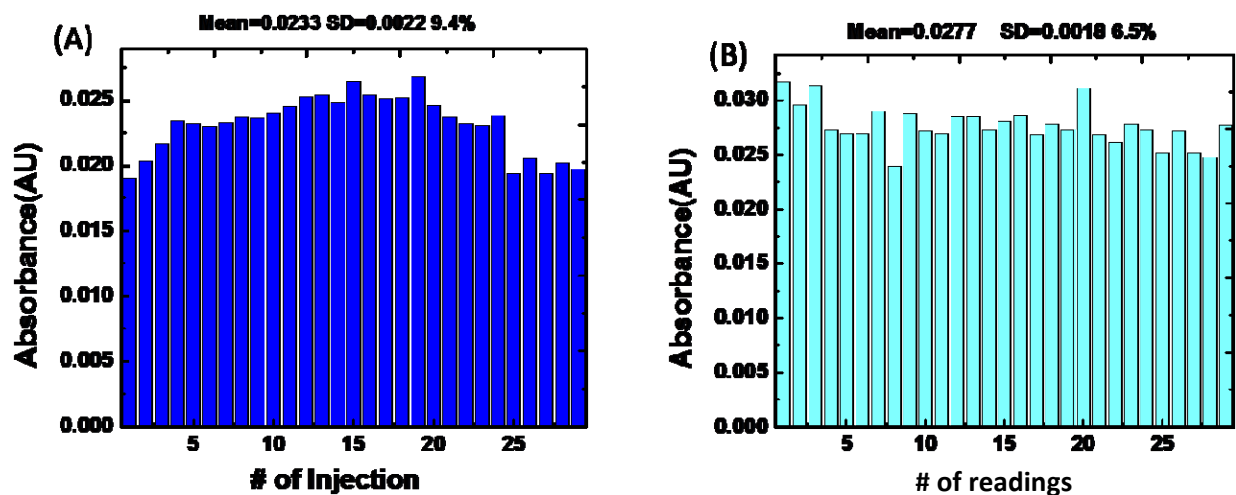


Figure S4. (A) Response of the sensor to consecutive injections of 100 ppbV NO₂ for 100 s. The system was purged with clean air for 30 s between the injections. (B) Response of the sensor when exposed continuously for 2900s to 100ppbV NO₂ without purging with air.

Considering the low detection limit achieved with a short injection time, one sensing element can be used for long periods of time for environmental samples. For instance, a concentration of 53 ppbV NO₂ (EPA regulation) could be safely monitored more than 1000 times if the injection time is only 5 seconds. In this way, several hundreds of measurements can be performed during a full day test by controlling the purging time.

8. Reaction product characterization: High Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS), and Fourier transform infrared (FTIR) spectroscopy were used to characterize the reaction products.

HPLC/MS studies: Two sensing elements (Control A and Sensing element B) were treated according to the following protocol:

Control A: A sensing membrane prepared with o-phenylenediamine was dipped in 2 mL of acetonitrile (HPLC grade) and shaken for 5 minutes. After this, the liquid extract was

centrifugated and the supernatant was injected into a HPLC for separation and collection of the separation products. The main product fraction was analyzed by MALDI-TOF spectrometry (Fig. S5, red line).

Sensing element B: A sensing membrane prepared with o-phenylenediamine was used to test a high NO₂ concentration (1ppmV) for a long period of time until a clear color development was visually observed. Then, the sensing element was dipped in 2 mL of acetonitrile (HPLC grade) and mildly shaken for 5 minutes. The liquid extract was centrifugated and the supernatant was injected into a HPLC. The separated products were collected, and the main product fraction was analyzed by MALDI-TOF spectrometry (Fig. S5, green line).

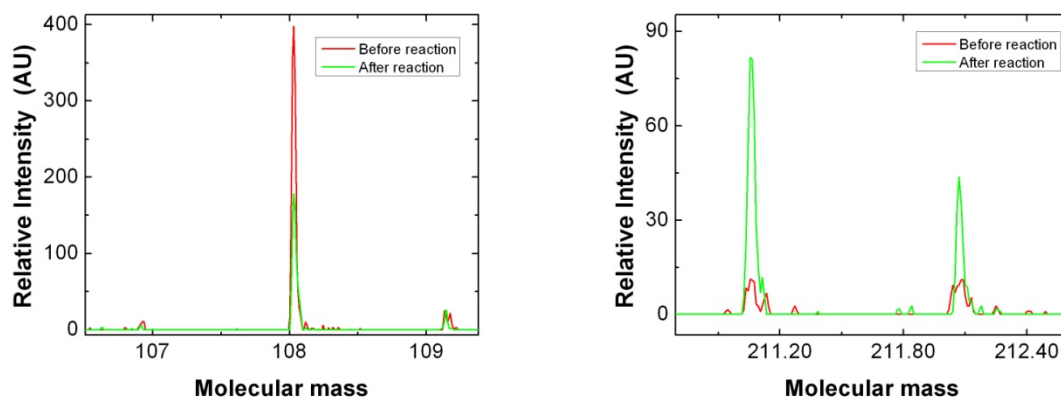


Figure S4. MALDI-TOF spectrometry of main products found on the control A (red) and sensing element B (green) before and after reaction with NO₂ at 1ppmV.

It is clear that the main compound in control A (before the reaction with NO₂) corresponds to o-phenylenediamine with a molecular weight of 108 a.m.u., and that the main product after the reaction in Sensing element B has a molecular weight of 211 a.m.u.

FTIR spectroscopy: FTIR spectra of *o*-phenylenediamine before and after the exposure to 50 ppm of NO₂ for 15 min were obtained (Fig. S5A), and the formation of a reaction product with features matching those found for phenazine¹⁻⁴ were observed: C=N at 1,633-1637 cm⁻¹,¹⁻⁴ 1,2,4,5-tetrasubstituted ring at 836-871 cm⁻¹,^{1,4} and 2,3-disubstituted benzene ring at 752-754 cm⁻¹.^{1,3} In addition, no formation of important signatures from 2,2'-diaminoazobenzene (N=N at 1408 cm⁻¹), another potential product of the reaction, could be identified.⁵ These studies together with other former studies published by others before¹⁻⁴ allow us to identify 2,3-diaminophenazine (chemical structure shown below) as NO₂ reaction product.

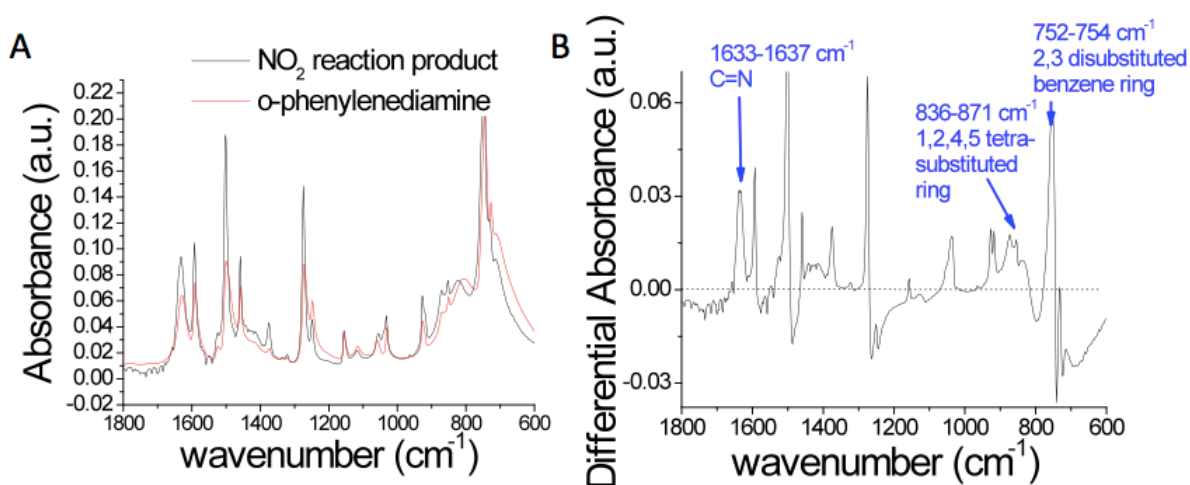
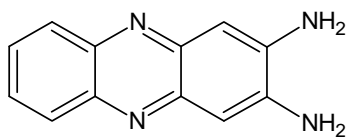


Fig S5. (A) FTIR spectrum of *o*-phenylenediamine before (red) and after (black) reaction with 50 ppm NO₂. (B) FTIR differential spectrum from spectra in (A) (after NO₂ spectrum – before NO₂ spectrum), indicating vibrational modes reported for phenazine. The range between (3600-2000) cm⁻¹ showed typical features of N-H vibrational modes (not shown).



Formula Weight = 210.2346

2,3-diaminophenazine

9. Apparent reaction efficiency: We have estimated the apparent efficiency of NO₂ to oxidize o-phenylenediamine immobilized in the nanoporous membrane to be ~ 95 %. The estimation has considered the total amount of o-phenylenediamine immobilized on the membrane (~ 50-60 uL of 100 mM o-phenylenediamine solution), and the total amount of o-phenylenediamine used in the reaction, considering sensor lifetime (80 ppb NO₂.hour as indicated above), NO₂ capture in the membrane (~ 90%), flow rate of the system (0.45 L/min), and a 1:1 reaction stoichiometry. The high efficiency clearly demonstrates benefits of the new solid-state molecular probes, and their use in the sensing platform assembled with an integrative approach.

10. NO_x field-testing:

It is important to mention that the short-time noise level is low ($\sim 2 \times 10^{-5}$ a.u.) and the long-term stability is excellent ($\sim 4 \times 10^{-4}$ a.u for a period of ~ 30 min.), which is essential for operating the sensor in field-testing. A field test was performed in Tempe, Arizona on Dec.15, 2009. The test was carried out by sampling environmental air while driving around in a Phoenix area. The driving route covered busy traffic regions (highways) where more pollutants were present and also park areas (Papago park) where the air was cleaner. Fig. S6 (A) shows the absorbance change during the test (black curve), and the derivative of the absorbance is proportional to the instantaneous concentration of NO₂ in air (red curve). Fig. S6 (B) summarizes the results with NO₂ concentrations at certain points along the field trip marked on a map. It can be seen that the NO₂ concentrations near or on the highway (~ 45 -ppbV average) are higher than those concentrations recorded in the park and at the ASU campus (~ 25 -ppbV average). The results from the field test were in agreement with the averaged concentration published by Maricopa County Mobile Monitoring System located in a nearby area on the same day. Further field-

testing has been conducted with the implementation of an internal sampling and purging mechanism to control the sensor exposure, which can extend the use of the sensor for 8-9 hours (not shown).

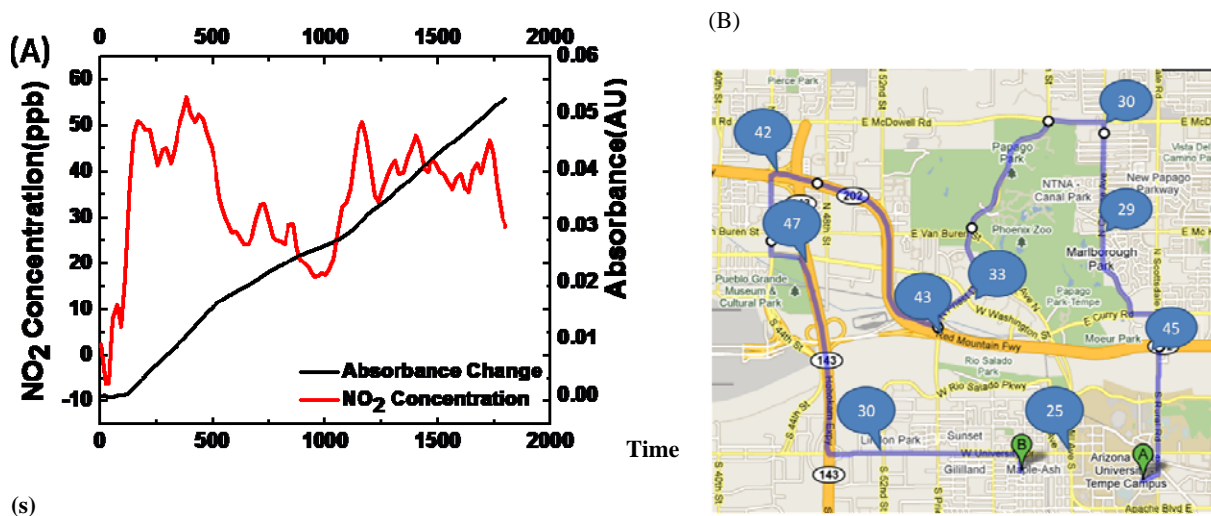


Figure S6. (A) Results obtained from an environmental test performed in the Tempe-Phoenix area. (—) absorbance change of the sensor, (—) NO₂ concentration in ppbV. (B) Map of the covered route during the field-testing. Numbers indicate the concentrations of NO₂ at selected locations expressed as ppbV.

References

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