

Ultraselective Detection of Nitrogen Oxides over a Nanoporous Membrane

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A nitrogen oxide (NO_x ; $x = 1, 2$) optical sensor with an extremely low detection limit in the range of fractions of ppbV (0.3 ppbV for 20 s sample injection) is presented. Phenylenediamine derivatives are utilized as molecular probes in the solid state on a nanoporous membrane to produce a miniaturized and low cost sensing platform for use as a wearable personal monitor.

In spite of significant advances in sensor development, a portable device that can reliably detect personal exposure of chemicals in a real environment still faces many challenges.¹ These challenges include extremely low yet potentially toxic levels of chemicals in many practical scenarios, variable environmental conditions, and the need of low-cost and highly portable detection methods. To address these challenges, we present here a nitrogen oxide (NO_x ; ($x = 1, 2$)) sensor based on new solid-state molecular probes, alumina nanoparticles, and a low-cost and high performance webcam-sensing platform. NO_x are studied here because they are among the most toxic pollutants from traffic and industrial processes, which affect a large population.^{1,2} Detection of NO_x has been a leading priority for environmental monitoring agencies, industrial hygienists, and epidemiologists.^{3–6} This is also important for pulmonologists because NO in exhaled breath has been identified as an asthma biomarker.

The molecular probes are phenylenediamine derivatives, *o*-phenylenediamine and diethyl-*p*-phenylenediamine, immobilized on 50 nm alumina nanoparticles (Figure 1A) supported on a microporous cellulose membrane. The nanocomposite sensing

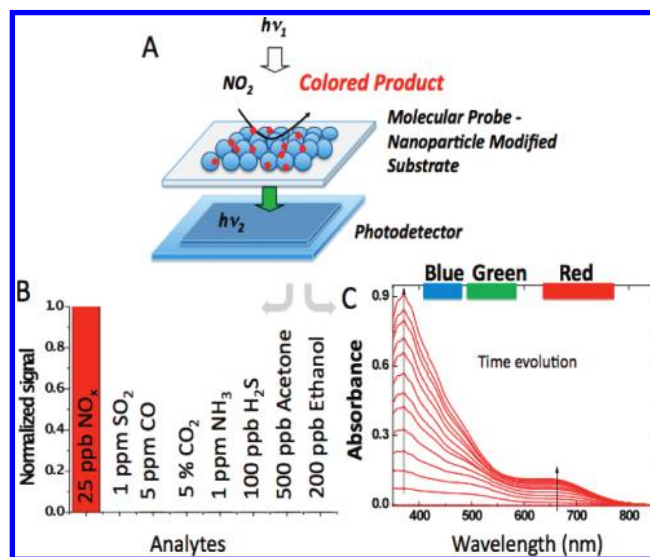


Figure 1. (A) Schematic representation of the sensing platform. (B) Normalized response of *o*-phenylenediamine upon exposure to NO_2 and various environmental gases. A similar response pattern is found for diethyl-*p*-phenylenediamine. (C) UV–visible spectrum of *o*-phenylenediamine upon reaction with NO_2 (part-per-million (ppm) level) taken at increasing reaction times.

material provides a large effective surface area, which is one of the key factors for the high sensitivity. Exposure of the phenylenediamine derivative-modified nanoparticles to NO_2 produces distinctive color changes and allows for unambiguous detection of the analyte. The sensing mechanism is immune to most common compounds present in polluted ambient air, except ozone, which can also trigger a reaction but can be scrubbed with a simple ozone filter. Figure 1B shows the response of one of the molecular probes, *o*-phenylenediamine, to 25 ppb NO_2 compared to the response of interfering agents at concentrations typically found in polluted environments. In addition, selectivity coefficients of both molecular probes (obtained at much larger concentrations of interfering agents and calculated as the NO_2 sensitivity/interfering agent sensitivity) are higher than 10^4 (Supporting Information, Section 1, Selectivity of the Molecular Probes). Figure 1C shows visible spectrophotometric changes of the molecular probe, *o*-phenylenediamine, upon reaction with NO_2 . Increases of absorbance in the range of 350–550 nm are clearly observed, which forms the basis of the sensing

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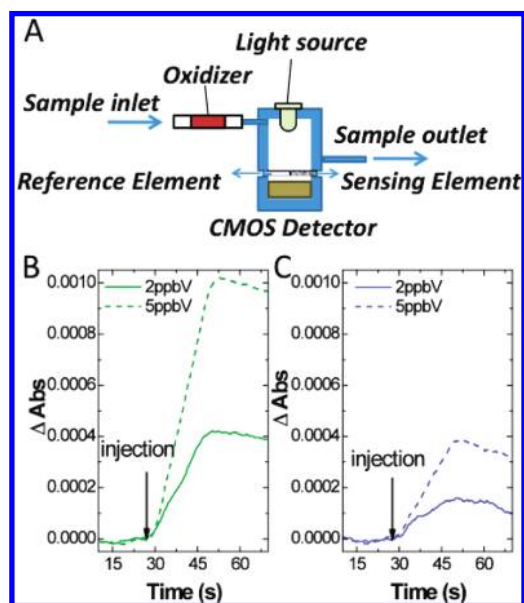


Figure 2. (A) Configuration of the sensing platform. (B) Green- and (C) Blue-component signal corresponding to the injections of 2 and 5 ppbV of NO_2 . The sensor probe is diethyl-*p*-phenylenediamine, and the signal is the $-\log(\text{sensing area light intensity}/\text{reference area light intensity})$. Flow rate = $\sim 450 \text{ mL/min}$.

mechanism⁷ (see below). Similar features of increasing absorbance upon exposure for NO_2 are found for diethyl-*p*-phenylenediamine. The reaction of the highly selective probes is fast, and the response of the sensor is mass transport controlled even at high flow rates of $500 \text{ mL} \cdot \text{min}^{-1}$ (Supporting Information, Section 2, Mass Transport Study). This renders a NO_2 capture efficiency of $\sim 90\%$ and an apparent reaction efficiency of $\sim 95\%$ (Supporting Information, Section 9, Apparent Reaction Efficiency).

Unlike existing detection methods for NO_2 , which involve the catalytic conversion of NO_2 into NO followed by chemiluminescence detection,⁸ the new sensing platform directly detects NO_2 without the need of additional supplies of reagents, low pressure sensing environments, and expensive photodetectors. Furthermore, with the addition of a small oxidizing tubing (based on NaMnO_4), NO can be converted into NO_2 , enabling detection of NO and total NO_x ($\text{NO}_2 + \text{NO}$) (see Supporting Information, Section 3. Oxidizing Tubing for Conversion of NO into NO_2).

Another key enabling feature of the present sensing platform is the sensor configuration, including the detector and signal processing (Figure 2A). A basic version of the sensor consists of two elements, one for sensing and one for reference correction. The optical signal is taken with an optical imaging device based on a complementary semiconductor metal oxide (CMOS) imager. The image is acquired and controlled with a program developed in our lab. The program has the capability of extracting red, green, and blue intensity values ($R(t)$, $G(t)$, and $B(t)$, respectively) from the image with a reasonably fast acquisition rate ($\sim 5 \text{ Hz}$). The logarithmic ratio between the sensing and the reference elements for each color component is evaluated as an output signal. The

overall approach affords not only increased sensitivity but also selectivity. (1) An extremely low detection limit in the range of fractions of ppbV ($\sim 0.3 \text{ ppbV}$, see Figure 2B) is achieved due to the low noise level of the system ($\sim 2 \times 10^{-5}$ absorbance units for a 20 s period (sample injection period); Supporting Information, Section 10, NO_x Field Testing); (2) Excellent selectivity against common interfering agents, such as carbon dioxide, is obtained because the molecular probes are insensitive to pH changes and have high oxidation potential, and the capability of reading individually RGB components provides a distinct color pattern for the analyte. In addition, the sensing platform is also provided with a nafion tubing, which makes the sensor immune to humidity changes (Supporting Information, Section 5, Humidity Effect Conditioning).

The new solid-state molecular probes provide the needed sensitivity, selectivity, and response time for many real-world applications. The device hardware is rather simple and compact, adding the benefit of low cost and high portability. One of the key elements of the sensing platform is the use of the new molecular probes without the need of additional binders or coreagents. The molecular probes are casted on alumina nanoparticles immobilized on a semitransparent support (Supporting Information, Section 4, Preparation of the Sensing Element). The support provides (1) an excellent host to high surface concentration of the molecular probes, enabling a high dynamic detection range and lifetime (Supporting Information, Section 7, Sensor Stability (under NO_2 Sensing)), (2) a good medium for quick diffusion and transport of NO_2 , (3) a medium that promotes the formation of colored products, and (4) a highly stable support to store the sensor for several months (4 months tested so far; Supporting Information, Section 6, Sensor Stability (under Storage)).

We have applied this new sensing platform to detect NO_2 and NO . Figure 3A shows as an example a calibration plot obtained for detection of NO_2 from a few ppbV to 200 ppbV using a diethyl-*p*-phenylenediamine molecular probe. Since the absorption wavelengths of the reaction products of both molecular probes mostly range from 350 to 550 nm (e.g., Figure 1C), we found the blue and the green components of the sensor output signal to be the most sensitive color components. This observation is consistent with the corresponding optical absorption spectra of the probes. In addition, the response curves are linear over a wide dynamic range, which enable the use of the sensor for quantitative detection and analysis of NO_2 and NO for environmental monitoring applications.

We have characterized the reaction products. In the case of *o*-phenylenediamine, the extinction coefficient of the NO_2 reaction product has been estimated to be $\sim 2000 \text{ M}^{-1} \text{cm}^{-1}$ in solid phase. The product is believed to be a phenazine derivative according to the study using liquid chromatography/mass spectrometry (LC/MS) and Fourier transform spectroscopy (FT-IR; see Supporting Information, Section 8, Reaction Product Characterization) and previously published studies.^{9–11} We note that even though the extinction coefficient of the the *o*-phenylenediamine product is

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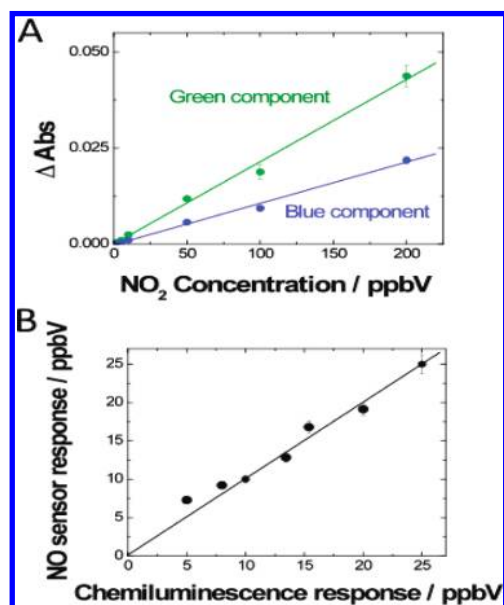


Figure 3. Analytical performance of the sensing platform. (A) Calibration plots for NO_2 using green and blue absorbance changes vs concentration of NO_2 . Signal changes were recorded upon 20 s injections of NO_2 , using diethyl-*p*-phenylenediamine as molecular probe. (B) Evaluation of the sensor accuracy for real sample analysis. The sensing platform includes an oxidizing filter made of NaMnO_4 to convert NO into NO_2 , and thus, the sensor detects NO. The molecular probe is *o*-phenylenediamine. Comparison of NO concentration determined by the present sensor vs NO concentration determined by the gold standard method (chemiluminescence). (A and B) Flow rate = ~ 450 mL/min.

modest, a high sensitivity and low detection limit are achieved because of good reference correction, efficient sample delivery and conditioning, and low noise optical detection.¹²

We have calibrated and compared our sensor with a standard reference chemiluminescence method using both artificial and real

breath and environmental samples. Levels of NO determined with the present sensing platform and the reference method are in excellent agreement as shown in Figure 3B. We have also carried out preliminary field test and demonstrated that the sensor is capable of monitoring levels of NO_x in high and low traffic areas (see Supporting Information, Section 10, NO_x Field Testing).

In summary, a highly selective, sensitive, and low-cost sensing platform is developed on the basis of new molecular probe-functionalized nanoparticles coated on a membrane and a high-performance CMOS imaging-sensing platform. High selectivity is achieved due to intrinsic chemical properties of the probes with NO_2 and distinct RGB color patterns of the reaction products. High sensitivity is possible because of the large surface concentration given by alumina nanoparticles and the fast reaction kinetics. Using an inexpensive webcam, we have achieved a detection limit of fractions of ppbV and demonstrated selective detection of NO_2 . Furthermore, the combination of the sensing platform with an appropriate oxidant preconditioning tubing has also allowed accurate detection of NO, enabling the detection of total NO_x levels.

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SUPPORTING INFORMATION AVAILABLE

Selectivity factors, sensor preparation, mass transport study, sensor stability, reaction product characterization, apparent reaction efficiency, and NO_x field testing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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