Detection of Nitrobenzene, DNT, and TNT Vapors by Quenching of Porous Silicon Photoluminescence

Stéphane Content, William C. Trogler,* and Michael J. Sailor*[a]

Abstract: The detection of nitroaromatic molecules in air by the quenching of the photoluminescence of porous silicon (porous Si) films has been explored. Detection is achieved by monitoring the photoluminescence (PL) of a nanocrystalline porous Si film on exposure to the analyte of interest in a flowing air stream. The photoluminescence is quenched on exposure to the nitroaromatic, presumably by an electron-transfer mechanism. Detection limits of 500 parts-per-billion (ppb), 2 ppb, and 1 ppb were observed for nitrobenzene, 2,4-dinitrotoluene (DNT), and 2,4,6-trinitrotoluene (TNT), respectively (exposure times of 5 min for each, in air). Specificity for detection is achieved by catalytic oxidation of the nitroaromatic compound. A platinum oxide (PtO_2) or palladium oxide (PdO) catalyst at 250 °C, placed in the carrier gas line upstream of the porous Si detector, causes oxidation of all the nitroaromatic compounds studied. The catalyst does not oxidize benzene vapor, and control experiments show no difference in the extent of PL quenching by benzene with or without an upstream catalyst. The PL quenching by NO_2, released in the catalytic oxidation of nitroaromatic compounds, is less efficient than the quenching of the intact nitroaromatic compound. This provides a means to discriminate nitro-containing molecules from other organic species.

Keywords: IR spectroscopy · nitroaromatic compounds · photoluminescence quenching · sensors · silicon

Introduction

A device capable of rapidly detecting volatile chemical emissions from explosives is highly desirable since there are about 120 million unexploded land mines worldwide.[1] Metal detectors are becoming increasingly unreliable because the amount of metal used in modern land mines is becoming very small and the amount of spurious metal debris in suspect areas can be quite large. Detection of vapor signatures of the explosive, such as 2,4,6-trinitrotoluene (TNT) or its degradation product dinitrotoluene (DNT), is an attractive alternative. Dogs can be trained to detect these vapor signatures; however, dogs are expensive to train and are easily tired.[2] Approaches involving the detection of the specific explosive or its signature vapors include gas chromatography coupled to a mass spectrometer, neutron activation analysis, and electron capture detection.[1] These techniques are highly selective, but they are cumbersome and not easily fielded in a small, low-power package. The detection of nitroaromatic compounds based on adsorption into chemoselective polymers has also been reported. For example, a chemically selective silicone polymer layer on a SAW (surface acoustic wave) device has been shown to provide a detection limit of 235 ppt for DNT.[3] Quenching of the fluorescence in a chemoselective polymer has been used to detect DNT and TNT under static (no flow) conditions with a detection limit in the parts-per-billion (ppb) range for exposure times of less than ten seconds.[4] Finally, cyclic voltammetry that uses a gold microelectrode covered with a small volume of a nonvolatile electrolyte, has been used to detect TNT-saturated air (7 ppb).[5] Such simple techniques are promising because they can be incorporated into inexpensive and portable microelectronic devices. The work described herein represents an attempt to develop an inexpensive solid-state sensor that can provide a sensitive and selective response to nitroaromatic compounds. The sensor is based on photoluminescence quenching of nanocrystalline porous silicon (porous Si).

Porous silicon is a high surface area network of Si nanocrystallites which is produced by an electrochemical etch of single-crystal Si wafers.[6] The nanocrystallites in porous Si exhibit quantum confinement effects, and emit visible photoluminescence (PL) with an external quantum efficiency of up to 5 %.[7] Previous work has shown that the intensity of PL depends on the presence of surface adsorbates.[8–11] For example, molecules capable of acting as energy or charge acceptors can quench the PL of porous Si at diffusion-controlled rates.[8, 12] In addition, corrosive molecules, such as NO_2, can quench luminescence by introducing nonradiative

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defects on the surface of the silicon nanocrystallites.[13, 14] Introduction of a very small number of defects can have a dramatic effect on luminescence; in the case of NO_2, detectable changes are observed with exposures as low as 70 ppb.[13]

Nitroaromatic molecules have two features that are relevant to the detection methods outlined above. First, they are good electron acceptors and the quenching of PL from porous Si by an electron transfer process has been demonstrated for a variety of nitro-substituted molecules, in particular dinitrobenzene.[12] This can be considered to be a "direct detection" method. The second feature of interest is that nitro compounds can be catalytically oxidized to CO_2, H_2O, and NO_2 at temperatures lower than those needed to oxidize most other potential organic interferents. This second feature allows the discrimination of nitro- and non-nitro-containing organic compounds. It is shown in this work that NO_2 does not quench PL from porous Si as efficiently as DNT or TNT. By incorporating a catalyst (PtO_2 or PdO at 250 °C) upstream of the detector, discrimination of the nitroaromatic molecules from benzene is achieved. A detection scheme is demonstrated that couples selective catalytic oxidation to a sensitive porous Si detector to achieve both sensitivity and selectivity.

Experimental Section

Sample preparation: Luminescent porous Si samples were prepared by an electrochemical etch of *n*-type Si (phosphorous-doped, ⟨100⟩ orientation, International Wafer Service) of resistivity between 0.75 and 0.95 Ω cm. The etching solution was prepared by the addition of an equal volume of pure ethanol (Quantum Chemicals) to an aqueous solution of HF (48% by weight; Fisher Scientific). The etching cell was constructed of Teflon and was open to air. Silicon wafers were cut into squares with a diamond scribe and mounted in the bottom of the Teflon cell with a Viton O-ring seal, exposing 0.2 cm^2 of the Si surface. Electrical contact was made to the backside of the Si wafer with a strip of heavy Al foil. A loop of Pt wire was used as a counter electrode. The exposed Si was illuminated with $\approx 120\ mW\,cm^{-2}$ of white light from a 300 W tungsten lamp for the duration of the etch. Etching was carried out as a two-electrode galvanostatic procedure at an anodic current density of $50\ mA\,cm^{-2}$ for 5 min. After etching, the samples were rinsed in ethanol and dried under a stream of N_2. The porous Si chip was then placed in a chamber where it was exposed to a flow of the carrier gas under consideration.

Photoluminescence measurements: Steady-state photoluminescence spectra were obtained with an Ocean Optics S2000 spectrometer fitted with a fiber optic probe. The excitation source was a blue LED ($\lambda_{max} = 480$ nm) focused on the sample (at a 45° angle to the normal of the surface) by means of a separate fiber optic and lens assembly. Light was collected along the axis normal to the front surface of the porous Si sample with a microscope objective lens and focused onto a fiber optic. A 520 nm cut-off filter placed in front of the detection fiber optic prevented the excitation light from entering the emission detection optics. Spectra were recorded with a CCD-detector in the wavelength range of 400 to 900 nm. Throughout this paper, values of percent quenching are reported as $(I_0 - I)/I_0$, where I_0 is the intensity of the luminescence of porous Si, integrated between 400 and 900 nm, in the absence of quencher and I is the integrated intensity of luminescence of porous Si in the presence of a quencher at a given concentration. Values reported as the ratio I/I_0 use the same definition of I and I_0 given above. Five experiments were performed for each analyte studied. The error (95% confidence level) in all percent quenching and I/I_0 values reported in this paper are less than 6% of the values quoted.

Infrared spectroscopic measurements: Fourier-transform infrared spectra (FTIR) were collected with a Nicolet Magna 550 infrared spectrometer operating in the transmission mode. Spectral resolution was $4\ cm^{-1}$, and typically 32 interferograms per spectrum were acquired. The sample chamber was purged with nitrogen during spectral acquisition. Gas-phase reactants and products were analyzed with a Nicolet 510 FTIR spectrometer fitted with a liquid-nitrogen-cooled MCT (mercury cadmium telluride) detector optimized for the 800–4000 cm^{-1} region.

Preparation of gas samples: For the nitrobenzene and benzene exposure studies, air that was saturated with nitrobenzene (99%, Aldrich) or benzene (99.9%, Aldrich) by means of a fritted glass gas bubbler, was diluted with dry synthetic air (80% N_2, 20% O_2) in a specially designed flowmeter/mixer. The flow rates were adjusted independently to obtain the different concentrations used in the study. For the 2,4-dinitrotoluene (DNT) (97%, Aldrich) and 2,4,6-trinitrotoluene (TNT) studies, the solid dispersed on glass beads was introduced into a glass tube and placed in one arm of the flowmeter/mixer apparatus. This was then exposed to a flow of dry synthetic air (80% N_2, 20% O_2, $100\ mL\,min^{-1}$). All the experiments were performed at atmospheric pressure, under a controlled flow of the appropriately dosed air. In order to determine the limits of detection for DNT and TNT, the saturated vapor of each substance in an electropolished stainless steel bottle was diluted by the addition of high-pressure dry air. Further expansion–repressurization cycles were performed to obtain the desired dilution. NO_2 (99.5%, Aldrich) was used as received and diluted by means of the above procedures. 2,4,6-TNT was synthesized as described elsewhere[15] and purified by recrystallization twice from methanol and dried overnight in a vacuum. Purity was confirmed by NMR spectroscopy.

Preparation and treatment of the catalyst: Platinum(IV) oxide and palladium(II) oxide (Aldrich, 99.9%) were dispersed on glass beads (2 mm diameter) and placed in a glass tube in the flow stream of the desired gas, upstream of the porous Si detector. The tube containing the catalyst was wrapped with heating tape and the temperature was monitored with a thermocouple which was in direct contact with the outside surface of the tube. The gas was passed through a 30 cm loop of glass tubing in a room-temperature water bath in order to cool it before it reached the sample chamber which contained the porous Si.

Results and Discussion

Direct detection of nitroaromatic compounds by photoluminescence quenching

Photoluminescence quenching by benzene and nitrobenzene: The intensity of the photoluminescence from freshly etched porous Si is reduced upon exposure to benzene[11] or nitrobenzene in air, and reaches steady-state values within a few minutes. The percentage of PL intensity lost after 5 min of exposure to 420 ppm of analyte is 55% for nitrobenzene and 8% for the same concentration of benzene. Quenching of PL is totally reversible with benzene, but only partially reversible with nitrobenzene. Thus only 45% of the initial PL intensity was recovered after 30 min in a stream of pure air when the sample had been exposed to 420 ppm of nitrobenzene in air for 5 min. FTIR spectra taken of the porous Si samples before and after exposure to either benzene or nitrobenzene showed no change in the Si–O, Si–H, and C–H stretching regions. This indicated that there was no appreciable irreversible adsorption or oxidation of the sample. However, when a porous Si sample was exposed to 420 ppm of nitrobenzene in air for an extended period of time (1 h), the FTIR spectrum showed that the porous Si sample was slightly oxidized (Figure 1). In addition to the $\nu_{(Si-H)}$, $\nu_{(Si-H2)}$, and $\nu_{(Si-H3)}$ absorptions at 2091, 2116, and 2141 cm^{-1}, respectively (observed on the freshly etched porous Si surface), the sample exposed to nitrobenzene displayed a new feature assigned to $\nu_{(Si-O)}$ centered at 1061 cm^{-1}, which is characteristic of surface oxide and suboxide species. Moreover, the two strongest IR

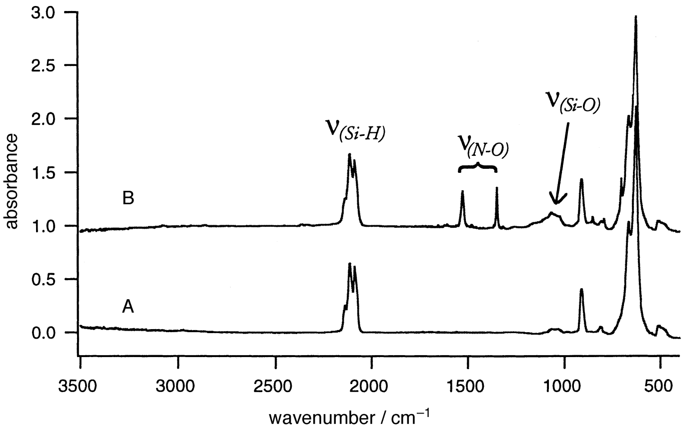


Figure 1. FTIR spectra of a freshly etched porous Si chip (A) and after a 1 h exposure to nitrobenzene in air followed by a 30 min flush in pure air (B).

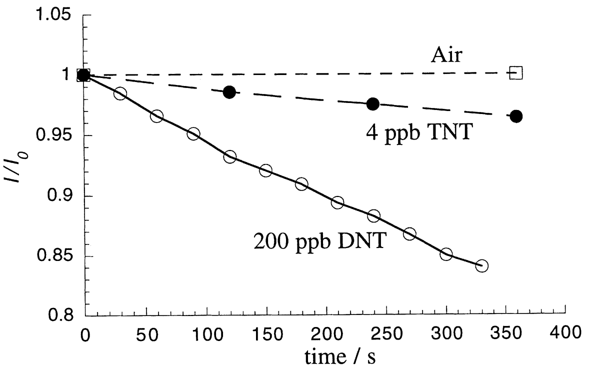


Figure 3. Variation of I/I_0 for *n*-type porous Si as a function of the time of exposure to different gas mixtures. I_0 is defined as the integrated intensity of porous Si photoluminescence in air before exposure ($t = 0$), and I is defined as the integrated intensity of photoluminescence in the analyte stream after a given exposure time.

absorptions of nitrobenzene were detectable (at 1550 and 1360 cm^{-1}) on the surface of the porous Si sample. These bands that are associated with nitrobenzene do not disappear after exposure to flowing air for 30 min; however, they do disappear if the sample is rinsed with ethanol. Up to 85 % of the initial PL intensity is irreversibly quenched and a 20 nm red shift in λ_{max} of PL occurs under the above conditions.

The same nitrobenzene exposure experiment was carried out in nitrogen instead of air as the carrier gas. Traces of oxide on the surface of the porous Si chip were observed in the FTIR spectrum after 4 h of exposure. This data indicates that nitrobenzene is able to oxidize porous Si in the absence of oxygen, although to a lesser extent. The percent PL quenching is slightly less (80 %) under anaerobic conditions.

Photoluminescence quenching by DNT and TNT: The intensity of PL of freshly etched porous Si is reduced upon exposure to DNT or TNT. Figure 2 shows the PL spectra of a sample exposed to 4 ppb of TNT in an air stream. The decrease in PL intensity with increasing time of exposure to TNT, DNT, and pure air is given in Figure 3. After 5 min, the percentage of quenching for DNT-saturated air (vapor pressure = 200 ppb at 25 °C[16]) was 12 %, and 4 % in the case of TNT-saturated air (vapor pressure = 4 ppb at 25 °C [16]). As a control experiment, the intensity of photoluminescence of a porous Si sample was found to be completely stable for one hour under a flow of pure air. The value of the slope of the curve of I/I_0 as a function of time for DNT is 3.5 times greater than for TNT. The slope of the curve for TNT is thus significantly larger than that expected from the relative vapor pressures of these two gases (which differ by a factor of 50). This enhanced sensitivity towards TNT is ascribed to a larger electron transfer quenching rate and a larger adsorbate binding constant for TNT, as discussed below.

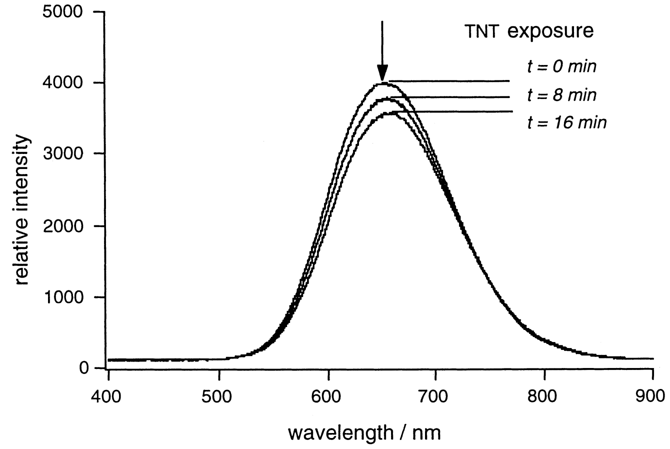


Figure 2. Steady-state photoluminescence spectra of *n*-type porous Si showing the quenching of photoluminescence that occurs on exposure to TNT (≈4 ppb in air) for the indicated times. The photoluminescence was stable in pure air for 1 h.

As was observed for nitrobenzene above, PL quenching by the nitroaromatic compounds TNT and DNT was found to be only partially reversible. After exposure to the relevant analyte, exposure to a flow of pure air for 30 min resulted in the recovery of only 60 % of the original PL intensity for DNT and only 35 % for samples exposed to TNT. If either of the samples were rinsed with ethanol at this point, then 85 % of the original PL intensity was recovered.

Long-term exposure of porous Si to DNT or TNT in air resulted in irreversible oxidation of the sample. The FTIR spectrum of porous Si exposed to 200 ppb of DNT for 16 h displayed bands characteristic of surface oxidation (Figure 4). In addition to the $\nu_{(Si\text{–}H)}$, $\nu_{(Si\text{–}H2)}$, and $\nu_{(Si\text{–}H3)}$ bands at 2091, 2116, and 2141 cm^{-1}, respectively, present on the freshly etched porous Si surface, the sample exposed to DNT displayed a large new (Si–O) band centered at 1061 cm^{-1}, assigned to surface oxide and suboxide species. Features assigned to $\nu_{(OSi\text{–}Hx)}$ are observed at 2255 and 2195 cm^{-1}. These higher energy Si–H$_x$ vibrations are characteristic of Si–H species that have oxygen atoms bound to the Si atom.[17] Figure 4 also shows that the loss in intensity of the $\nu_{(Si\text{–}Hx)}$ band is offset by increased intensity in the $\nu_{(OSi\text{–}Hx)}$ band. Traces of surface-adsorbed DNT are also detected in the FTIR spectrum as absorptions at 1550 and 1340 cm^{-1}, which resemble those in the FTIR spectrum in a KBr pellet sample of DNT. The adsorbed DNT observed by FTIR spectroscopy can also be removed with an ethanol rinse. After the 16 h DNT exposure, 95 % of the PL intensity was quenched. The

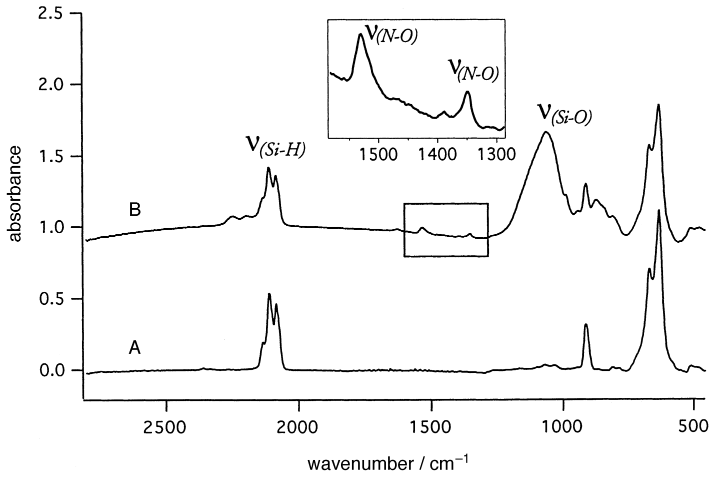


Figure 4. FTIR spectra of a freshly etched porous Si chip (A) and after exposure to a flow of DNT overnight showing the formation of Si–O bonds and the ν_{NO} of adsorbed DNT (B).

PL intensity recovered to 75 % of the original value after the ethanol rinse.

The behavior of TNT was qualitatively similar to that of DNT. Exposure of a porous Si sample to a flowing stream of 4 ppb of TNT in air for 16 h resulted in a luminescence quenching of 65 %, which is somewhat less than the percentage observed in the experiment with a higher concentration of DNT for the same time period. No trace of adsorbed TNT was observed on the surface of the sample by FTIR analysis, although a significant absorption of silicon oxide was observed.

The purity of the TNT sample was found to be important in order to obtain reproducible results. The results presented above were obtained after two successive recrystallizations of the TNT from methanol. A third recrystallization produced the same result as with the twice-recrystallized material. When the quenching experiment was undertaken without recrystallization of TNT (synthesized by nitration of dinitrotoluene)[15] higher (ca. 10 ×) quenching percentages were observed. Presumably, impurities with higher vapor pressures or higher quenching efficiencies are present in the as-synthesized TNT. Alternatively, the vapor pressure of the TNT crystals may be increased by the presence of impurities, leading to a lower quenching efficiency with the pure material.

Quenching response to multiple analyte exposure cycles: The intensity of PL from porous Si samples was also recorded in a flow stream in which the gas composition was alternated between pure air and a nitroaromatic vapor in air (Figure 5). In each experiment, the sample chip was exposed to a flow of one of the nitroaromatic compounds (nitrobenzene, DNT, or TNT) in air for a fixed amount of time and then the flow stream was switched to pure air for the same amount of time. The experiment was performed for six analyte/air cycles over a total time period of 6 h. Each experiment was conducted with a saturated concentration of the analyte in air (nitrobenzene, DNT, and TNT concentrations of 420 ppm, 200 ppb, and 4 ppb, respectively).

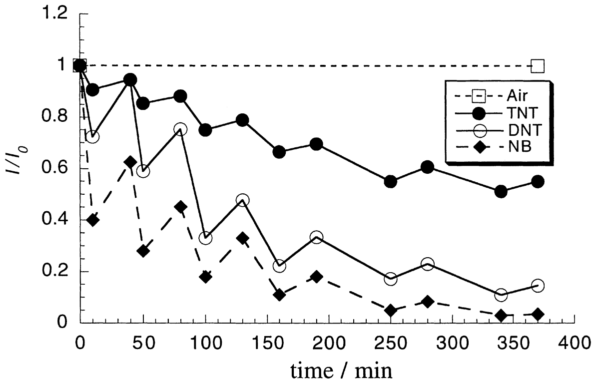


Figure 5. Variation of I/I_0 for n-type porous Si samples as a function of time, alternating between exposures to nitrobenzene, DNT, TNT, and pure air mixtures. Oxidation of the sample leads to incomplete recovery of photoluminescence after each successive exposure to the nitroaromatic. The control experiment for air exposure is also shown. I_0 is defined as the integrated intensity of porous Si photoluminescence in air before exposure ($t = 0$), and I is defined as the integrated intensity of photoluminescence in the analyte stream after a given exposure time.

A control experiment performed with pure air shows no significant change in PL intensity over 6 h. As has been described above, exposure to a nitroaromatic vapor resulted in significant quenching of PL which was not completely recovered during the air-flushing cycle. With each subsequent exposure to the analyte, the intensity of PL decreased further. The most efficient quenching was observed with nitrobenzene, for which the vapor pressure was the highest; DNT is less efficient, and TNT, with the lowest vapor pressure, is the least efficient.

Limits of detection: The detection limits for DNT and TNT were determined for a 5 min exposure of the relevant gas in a flowing air stream. The quenching of photoluminescence from porous Si as a function of analyte concentration is presented in Figure 6. A detection criterion of 2 % quenching, corresponding to five times the noise level of the spectrometer system (spectral integration time of 800 ms), was applied. Under these conditions, the detection limit was 2 ppb for DNT and 1 ppb for TNT. Photoluminescence quenching was always greater for TNT than for DNT at equivalent concentrations.

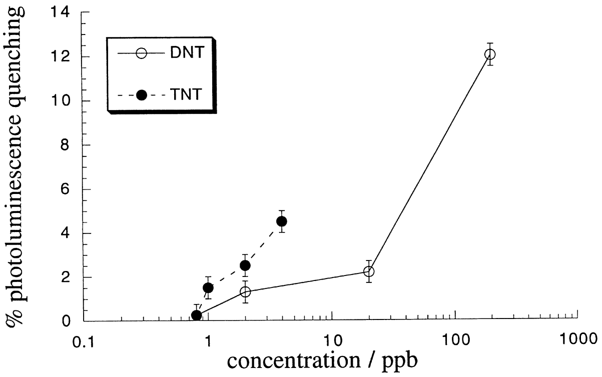
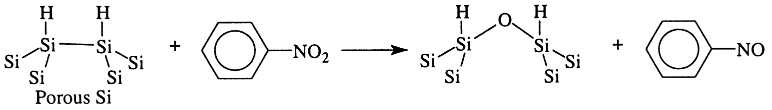


Figure 6. Variation of the percentage of quenching for n-type porous Si samples as a function of the logarithm of the concentration of the gas.

Effect of illumination on irreversible quenching: In order to test whether the irreversible quenching process originates from a photochemical reaction, quenching runs were run in the dark and under continuous irradiation with the 480 nm LED excitation source. For the dark runs, the sample was only illuminated during spectral acquisition, typically 5 s. The decay of photoluminescence was monitored over a period of 20 min for samples exposed to 200 ppb of DNT in a flowing air stream. Quenching of 40% was observed for both the irradiated sample and the one held in the dark. This indicated that the quenching mechanism is not highly photosensitive. As a control, the PL of porous Si in a flowing air stream was monitored with continuous 480 nm irradiation. No significant change in PL intensity was observed over the same 20 min time period.

Mechanism of irreversible quenching of photoluminescence: For all the nitroaromatic molecules studied, PL quenching is only partially reversible. The data provide a clear indication that the porous Si surface is oxidized upon exposure to the nitroaromatic compounds, either in the presence or absence of O_2. Prolonged exposure to either nitrobenzene, DNT or TNT was found to result in the appearance of oxide-related absorptions in the infrared spectra of the porous Si samples (Figure 1 and Figure 4). The irreversibility of PL quenching is attributed to this oxidation reaction. Nitrobenzene, DNT, or TNT, are proposed to react with porous Si according to Equation (1).



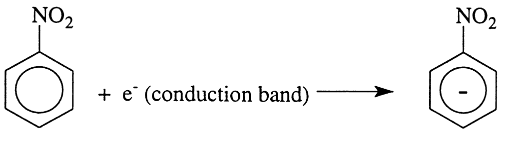
(1)

The integrated area of the bands associated with Si–H stretching modes in the FTIR spectrum did not change appreciably upon oxidation by the nitroaromatic (Figure 1 and Figure 4). This is consistent with the proposed oxidation mechanism, in which oxygen is inserted into a Si–Si surface bond. A similar reaction mechanism has been proposed for the oxidation of porous Si by dimethyl sulfoxide, which results in oxidized porous Si and dimethyl sulfide.[18] In the present case, the initial organic product is proposed to be a nitroso aromatic. Nitroaromatics have been shown to act as oxygen atom donors in some solid-state reactions. For example, nitrobenzene reacts with cobalt aluminum oxides to insert an oxygen atom into the lattice. That reaction results in a mixture of organic products, although the principle product is nitrosobenzene.[19]

Several experiments designed to identify the organic products of the silicon oxidation reaction were performed. A freshly etched porous Si chip was exposed to a solution of nitrobenzene for several days and the sample and solution were analyzed. The FTIR spectrum of the chip showed the appearance of a new peak attributed to Si–O bonds; however, no change was detected in the nitrobenzene solution either by UV/Vis spectroscopy or gas chromatographic–mass spectrometric analysis. Another freshly etched porous Si chip was exposed to a solution of [D_5]nitrobenzene for the same amount of time. The NMR spectrum was identical to that of a solution which was not in contact with any porous Si. No organic by-products of the surface modification process were detected in any of the experiments.

The irreversible quenching of photoluminescence is proposed to arise from a combination of the surface oxidation reaction and strongly physisorbed organic molecules that are not removed under a flow of air. Although silicon oxide generally acts as a passivating layer on silicon in MOSFET circuitry, there are many examples of defective oxides or suboxides that serve to decrease the overall quantum efficiency of emission from Si nanoparticles. The slow growth of the oxide layer is thought to be responsible for the net decrease in photoluminescence intensity observed with each additional exposure cycle (Figure 5). The fact that some of the photoluminescence intensity can be recovered at the end of the experiment by rinsing the sample with ethanol supports the hypothesis that an additional contributor to the observed irreversible quenching comes from strongly physisorbed molecules. It is the less strongly physisorbed molecules that are thought to be responsible for the reversible quenching of photoluminescence, which is discussed in more detail below.

Mechanism of reversible quenching of photoluminescence: A variety of photoluminescence quenching mechanisms have been shown to be accessible to porous Si. The mechanisms can be separated into four basic categories: interfacial charge transfer, interfacial energy transfer, introduction of nonradiative surface traps, and dielectric medium effects. Interfacial charge transfer can occur when a molecular electron donor or acceptor of the appropriate energy comes in contact with an excited silicon nanocrystallite in the porous Si matrix.[12, 20] Likewise, interfacial energy transfer can occur if the molecular quencher has accessible singlet or triplet energy levels.[8, 21–23] Nonradiative surface traps can be introduced by a chemical reaction at the porous Si surface that generates mid-gap defects.[10, 14, 18, 24] Finally, it has been shown that the dielectric constant of the medium surrounding the nanocrystallites in porous Si modifies the efficiency of geminate recombination,[25] which results in a loss of photoluminescence upon immersion of porous Si into any liquid dielectric medium.[10, 11, 25, 26] The first three modes of quenching can occur with very low concentrations of quencher (typically ppm or lower), while the dielectric effect occurs at relatively high surface coverages, corresponding to large concentrations of quencher (parts per thousand or greater). Fauchet and McLendon have previously studied the quenching of luminescence of porous Si by nitroaromatic compounds, and the mechanism of quenching was attributed to an electron transfer pathway based on the observed correlation with reduction potentials. Data in this work support the interpretation given in Equation (2).



(2)

Fauchet and McLendon have shown that the conduction band of porous Si is negative with respect to the reduction potential of 1,4-dinitrobenzene (−0.8 V vs. NHE).[12] Therefore, electron transfer is expected to be exergonic (negative free energy) for the nitroaromatic molecules DNT and TNT, based on their similar reduction potentials (−0.9 and −0.7 vs NHE, respectively).[4] We have also observed that nitrobenzene is an effective quenching agent. The quenching efficiency is expected to arise from a combination of three factors: the partial pressure of the nitroaromatic vapor, the free energy (ΔG^0) of the electron transfer, and the binding constant between the gas and porous Si. Assuming Arrhenius-type behavior, the relationship between the quenching constant (K_q), the vapor pressure (v_p), the free energy (ΔG^0) and the binding constant (K_b) can be approximated by Equation (3), where A is a constant. This relationship has also been used in the interpretation of oxidative quenching of PL from conjugated polymers by nitroaromatic compounds[4].

$$K_q \propto v_p(A \exp - \Delta G^0)K_b \tag{3}$$

The quenching of porous Si photoluminescence is more efficient with TNT than with DNT at comparable pressures of analyte. The reduction potential of TNT is less negative than that of DNT, so TNT has a larger driving force for electron transfer than DNT. Nitrobenzene, which has the most negative reduction potential (−1.15 V vs NHE) of the three nitro-containing analytes studied, exhibits the lowest quenching at a similar partial pressure. Thus the simple Arrhenius relationship of Equation (3) qualitatively predicts the relative efficiencies of quenching that were experimentally observed for TNT, DNT, and nitrobenzene.

Infrared measurements indicate that nitrobenzene (Figure 1) and DNT (Figure 4) persist on the porous Si surface even after extensive flushing of the sample chamber with pure air. Thus the analytes strongly adsorb to the surface of porous Si. Adsorption will also influence the efficiency of electron transfer quenching because it determines the surface concentration of the quencher, as indicated in Equation (3). The relative binding affinities of nitrobenzene, DNT, and TNT have not been determined, so a more quantitative analysis of quenching rates is precluded at this point.

Indirect detection of nitroaromatic compounds by catalytic decomposition

The large number of quenching pathways accessible to porous Si makes the development of chemically specific sensors a challenge. Quenching by the dielectric medium mechanism can occur with any adsorbate,[25] although the greater efficiency of quenching seen for energy transfer and charge transfer quenching suggests that molecules without the appropriate redox or electronic states only become interferents at high concentrations. This is borne out by the benzene results in the present work; detectable PL quenching only occurred at benzene concentrations above 400 ppm, while DNT and TNT were detectable at ppb levels. In an attempt to improve the chemical specificity for nitro-containing compounds, a method which uses selective catalytic oxidation upstream of the porous Si detector was attempted. We anticipated that each nitro group would be released as NO_2 during catalytic oxidation over catalysts, such as palladium and platinum oxides, that are commonly used to oxidize organic substances.[27–29] Although PL from porous Si was quenched by $NO_{2(g)}$,[13] the process was less efficient than quenching by DNT or TNT. Thus, catalytic combustion can be used to determine the presence of nitroaromatic compounds in the analyte stream. By the use of two porous Si detectors, one with catalyst and one without, a differential signal specific to each NO_2-containing species can presumably be achieved.

Catalytic oxidation of nitrobenzene to NO_2: Initial studies focused on the development of the catalytic reaction with nitrobenzene. A dry air stream that contained 420 ppm of nitrobenzene vapor (a simple model for TNT, DNT and other nitroaromatic explosives) was passed through a glass tube that contained glass beads coated with a platinum oxide or palladium oxide catalyst. The outflow from the catalyst was passed into an IR cell (pathlength 10 cm) and the spectral signatures of CO_2, H_2O and NO_2 were observed. A decrease in nitrobenzene concentration was evident in the difference-FTIR spectrum (Figure 7, symmetric and asymmetric stretches of the nitro group at 1551 and 1357 cm^{-1}, respectively), while a concomitant increase in the FTIR signature of free NO_2 was observed (Figure 7, double peak from rotational fine structure centered at 1620 cm^{-1}). Lower oxides of nitrogen (NO and N_2O) were not observed. The efficiency of decomposition of nitrobenzene was similar with either the platinum or the palladium catalyst. About 90 % of the nitrobenzene was oxidized at a catalyst temperature of 200 °C while 100 % was oxidized at 250 °C. This indicates the stoichiometry of the combustion reaction as given in Equation (4).

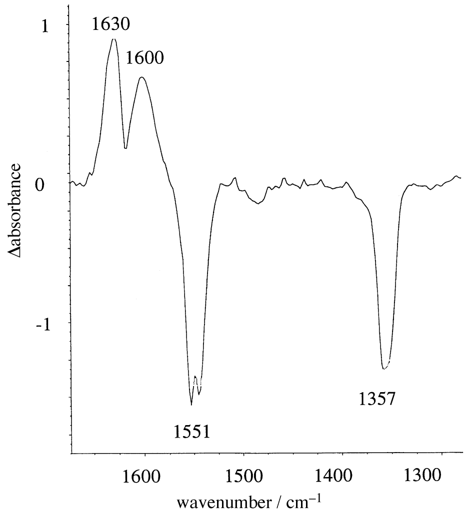


Figure 7. Difference FTIR spectrum of the products formed and reactants consumed when air saturated with nitrobenzene vapor is passed over PtO_2-coated glass beads at 250 °C. Rotational lines from overlapping water vapor (also a product) were removed by subtraction to show only the behavior of the nitrobenzene reactants (negative peaks) and nitrogen dioxide products (positive peaks).

$$2\,C_6H_5NO_2 + 14.5\,O_2 \longrightarrow 12\,CO_2 + 5\,H_2O + 2\,NO_2 \tag{4}$$

When a flowing stream of nitrobenzene (420 ppm) in air was passed through the apparatus in the absence of catalyst, the efficiency of the decomposition of nitrobenzene was much weaker. As a control experiment, nitrogen was used as a carrier gas instead of air. In this case, there was no detectable decomposition of the nitrobenzene below 400 °C.

As a comparison, the same experiments were performed with benzene. In the presence of either catalyst heated to 250 °C, traces of CO_2 and H_2O were detected; however, the FTIR signal from benzene did not diminish noticeably. At catalyst temperatures of 400 °C, approximately 5 % of the benzene in the air stream was observed to disappear. The ability to selectively catalyze the low-temperature combustion of nitrobenzene is unexpected. Electron-withdrawing substituents generally deactivate an organic compound towards oxidation, and nitrobenzene is even less reactive than chlorobenzene in catalytic solution oxidation processes.[30] The unexpectedly efficient heterogeneous catalytic oxidation of nitroaromatic compounds is useful, because many potential organic interferents will not be oxidized at low catalyst temperatures. Furthermore, the reaction products (CO_2 and H_2O) from the oxidation of simple organics, exhibit weak quenching of PL on porous Si, and therefore offer little interference. One possible reason for the high reactivity of nitrobenzene and other nitroaromatic compounds under conditions of heterogeneous catalytic oxidation, is the inherent high reactivity observed between nitroaromatic compounds and metal oxide surfaces.[19, 31] This has been most often observed in the context of the reduction of nitroaromatic compounds; however, the surface binding/activation processes apparently also facilitate oxidation when dioxygen is present in excess. The efficient heterogeneous catalytic oxidation observed here for NB, DNT, and TNT is noteworthy given the interest in remediation of these compounds, when they are found as environmental pollutants.[32–38]

Detection of nitrobenzene using an upstream catalyst: The rate of quenching of the luminescence of porous Si by nitrobenzene was slower when a catalyst was inserted upstream. After 5 min in the flowing nitrobenzene/air stream, the quenching efficiency was about 40 % with a catalyst, and 55 % without a catalyst. In either case, quenching was predominantly irreversible since only 70 % of the initial PL intensity was recovered after a 30 min air purge. There is no detectable change in the FTIR spectrum of the chips compared to freshly etched porous Si. As a control experiment, the quenching of PL was recorded in nitrogen instead of air with a catalyst (held at 250 °C) and without a catalyst upstream of the porous Si detector. Under these conditions, there is no change in the efficiency of quenching. The behavior was the same with the catalyst held at 400 °C. There was also no change in the PL intensity when wet air was used with a catalyst held at 250 °C.

Although the oxide was not detectable after short (5 min) exposures, evidence for oxidation was apparent on porous Si chips exposed to nitrobenzene/air mixtures for longer time periods. The FTIR spectrum obtained after a 1 h exposure of a chip to a nitrobenzene/air mixture in the presence of an upstream catalyst, followed by a 30 min air flush, displayed a new (Si – O) band centered at 1061 cm^{-1}, that is characteristic of surface oxide and suboxide species. The extent of oxidation (as determined by the area of the $\nu_{(Si-O)}$ vibrational band) is not as great when the same experiment is performed in the absence of catalyst. The samples that have been exposed to nitrobenzene/air for longer times also displayed a greater loss in PL intensity. After 1 h in the flowing nitrobenzene/air stream, the quenching efficiency was close to 100 % both with or without a catalyst (no detectable PL spectrum was observed above the baseline under the conditions used for acquisition).

The irreversibility of PL quenching for the experiments with an upstream catalyst was attributed to the generation of a small number of surface oxide defects upon reaction with the NO_2 produced according to Equation (3), as has been previously postulated.[13] Surface defects can act as highly efficient nonradiative electron-hole recombination centers. At short exposure times, the oxide defects are at a concentration too low to be detectable by FTIR, although they are detected at longer exposure times.

The efficiency of quenching of PL by nitrobenzene in the absence of a catalyst (without catalytic oxidation to NO_2) is unexpected. The measured detection limit for nitrobenzene in air without a catalyst is 500 ppb. A comparison was made of the quenching of porous Si obtained after 10 min of exposure to nitrobenzene/air without an upstream catalyst, 10 min of exposure to nitrobenzene/air with an upstream catalyst (at 250 °C), and 10 min of exposure to NO_2/air. At comparable analyte concentrations, the efficiency of quenching was within the error limits for all three. In all three cases the efficient irreversible quenching could be attributed to the oxidation of the porous Si surface. Thus, for the purpose of detecting nitrobenzene, there is no advantage in the use of an upstream catalyst. In contrast, the use of a catalyst is worthwhile in the detection of TNT and DNT because it provides specificity, as discussed below.

Detection of DNT and TNT with an upstream catalyst: Quenching of PL from porous Si by a flow of DNT/air or TNT/air passed through a catalyst at 250 °C was monitored by the use of the same experimental protocol as that used for the nitrobenzene/air experiments discussed above. The efficiency of PL quenching by DNT and TNT was significantly higher than for their catalytic combustion products NO_2, CO_2, and H_2O. The percent quenching of 200 ppb of DNT in the absence of the catalyst was 12 %. In the presence of the catalyst, the percent quenching by the DNT/air mixture was only 2 %. Complete combustion of the DNT would produce a concentration of 400 ppb of NO_2. Separate experiments with 500 ppb of NO_2 in air showed the percent quenching of NO_2 to be 5 %, consistent with the results of catalytic combustion.

For 4 ppb of TNT in air, no detectable quenching (< 1 %) was observed with the upstream catalyst at 250 °C, while 4 % PL quenching was observed either with no catalyst or with the upstream catalyst held at room temperature (no catalytic reaction). The concentration of NO_2 expected to be produced by the active catalyst (12 ppb) was well below the detection limit for NO_2.[13] Similar responses were observed with the upstream catalyst (either PtO_2 or PdO) held at either 250 °C or 400 °C, which indicated that combustion was complete at catalyst temperatures as low as 250 °C. The vapor pressures of DNT and TNT were so low that the NO_2, CO_2, and H_2O combustion products were not detectable by FTIR as they were in the nitrobenzene experiments.

Mechanism for selective detection of DNT and TNT with an upstream catalyst: Figure 8 summarizes the results obtained with and without a catalyst at 250 °C. The quenching of PL was clearly more efficient in the absence of the catalytic reaction. This demonstrates the high sensitivity of porous Si to electron transfer quenching by nitroaromatic compounds. The data also show that selective detection of TNT and DNT can be achieved by comparison of the catalytic and noncatalytic responses from the porous Si detector. When a catalyst is used, the nitroaromatic compound is decomposed to NO_2, H_2O and CO_2 as shown in Equation (4) for nitrobenzene. It has been shown that CO_2 and H_2O have no significant influence on the quenching efficiency of porous Si, so the observed quenching resulted only from the NO_2 produced.[13] Nitrobenzene quenched the PL with roughly the same efficiency as NO_2; thus no discrimination could be obtained by the use of a catalyst with this analyte. Because PL quenching by DNT and TNT was so much more efficient than by NO_2, the catalytic reaction allows discrimination of these analytes. It has also been demonstrated that oxygen is needed for the catalyst to work, since no reaction was observed by FTIR when nitrobenzene in nitrogen was used as the carrier gas.

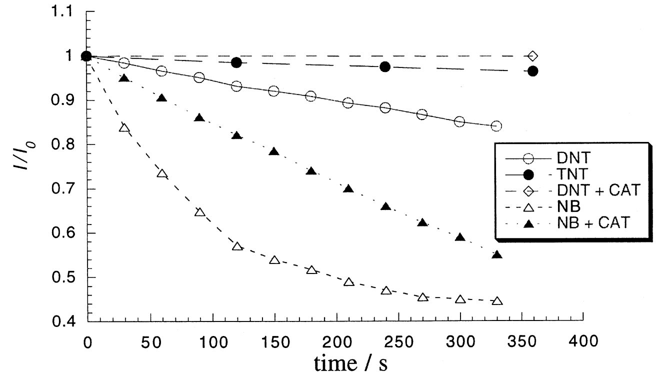


Figure 8. Variation of I/I_0 for *n*-type porous Si samples as a function of time after exposure to nitrobenzene (NB), DNT and TNT gas mixtures, to illustrate the sensitivity differences between direct and indirect detection. In a control experiment, the air flow for the duration of the experiment, gave a stable signal. I_0 is defined as the integrated intensity of porous Si photoluminescence in air before exposure ($t = 0$), and I is defined as the integrated intensity of photoluminescence in the analyte stream after a given exposure time.

In order to explore the specificity of the catalyst for the oxidation of nitroaromatic compounds, potential interferent gases were tested. A flow of benzene (80 Torr), hexane (110 Torr), toluene (28 Torr), isooctane (48 Torr), and isoprene (400 Torr) vapor/air mixtures were independently passed through a catalyst held at 250 °C. These gases were chosen because they are typical organics found in the atmosphere, since they are present in automotive fuels. Isoprene is a natural hydrocarbon emitted by plants that has significant atmospheric concentrations.[39]

The reactivity of the different gases was recorded in the absence and presence of the catalyst held at 250 °C. No new signals were detected in the FTIR spectrum of the gas stream when a catalyst was employed, although the absorption assigned to CO_2 increased slightly. A slight increase in the background CO_2 was also observed in the carrier stream without added organics; this was attributed to outgassing from the heated apparatus. The intensity of PL from a downstream sample of porous Si was also monitored. The percentage of quenching was the same in the absence or presence of a catalyst when benzene, hexane, toluene, isooctane, and isoprene were present in the carrier gas.

The reactivity of nonaromatic nitro compounds nitromethane (36 Torr) and nitropropane (7.5 Torr) in the carrier gas were also investigated. FTIR measurements indicated that the catalyst at 250 °C completely decomposed these compounds into NO_2, CO_2 and H_2O. The quenching of PL from porous Si was also monitored in the absence and presence of the catalyst. In the absence of a catalyst the extent of PL quenching reached 80 % after 25 s for these gases, whereas in the presence of a catalyst, it took only 5 s to reach a steady state in which 80 % of the PL was quenched. This behavior indicates that nitromethane and nitropropane are not detected with as high a sensitivity as TNT or DNT, presumably because they quench the luminescence of porous silicon by adsorption rather than by electron transfer quenching.[25, 26, 40] Catalytic oxidation produces NO_2, however, which can be detected with greater sensitivity. A similar increase in quenching efficiency after oxidation was observed for simple amines, such as aniline. FTIR studies showed that catalytic oxidation also yielded NO_2 for these nonaromatic nitro compounds. Among the likely interferents examined, DNT and TNT are unique because their catalytic oxidation results in a strong decrease in the efficiency of the luminescence quenching of porous silicon and they can be detected at very low concentrations.

Conclusions

Sensitive direct detection of DNT, TNT, and nitrobenzene in a flowing air stream has been achieved by means of photoluminescence quenching of porous Si. The mechanism of quenching is attributed to reversible electron transfer quenching of quantum-sized nanocrystallites in the porous Si matrix, although there is also a contribution from chemical oxidation of porous Si by the nitroaromatic compounds that leads to an irreversible response at long exposure times (>5 min). The use of an oxidation catalyst specific for nitroaromatic compounds allows the selective decomposition into NO_2, CO_2 and H_2O at low temperatures. Since the PL of porous Si is less sensitive to these combustion products than to DNT or TNT, selectivity for these analytes can be achieved by comparison of the relative response between two porous Si chips, one with and one without an upstream catalyst. The catalyst provides discrimination between the nitroaromatic compounds and several common atmospheric interferents: benzene, hexane, toluene, isooctane and isoprene. The limits of detection for DNT and TNT are 2 ppb and 1 ppb, respectively.

Acknowledgements

We thank Dr.Honglae Sohn for the synthesis of TNT, Dr. Sonia Létant for helpful discussions, as well as the Belgian and American Exchange Foundation and The Rotary Foundation for a post doctoral fellowship. This research was supported through DARPA's tactical sensors program through a Space and Naval Warfare Systems Center Contract (No. N66001-98-C-8514). The technical point of contact for this DARPA program is Dr. Edward Carapezza.

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Received: November 2, 1999 [F2114]