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Substantial effort has been devoted to the synthesis of molecular receptors that can function as chemosensors for nitroaromatic explosives. In spite of several advantages, these receptors suffer from low sensitivity and difficulties translating the response into the gas phase. We have combined tetrathiafulvalene-functionalized calix[4]pyrrole, a colorimetric receptor, with a polyimide microcantilever, that includes a mechanical stress sensing element. The resulting system is capable of detecting 10 ppb trinitrobenzene vapor. This represents a 30-fold improvement relative to the receptor in halogenated solvents, suggesting that this approach can provide a solution to translating the chemical response of colorimetric chemosensors into practical devices. © *2011 American Institute of Physics*. [doi:10.1063/1.3567011]

Recently, considerable effort has been devoted to the synthesis of molecular receptors that can function as so-called chemosensors for nitroaromatic explosives.[1–4] Within this context, colorimetric systems, agents that signal the presence of a nitroaromatic analyte via a color change, have a certain appeal.[2–5] Their ease of use and their ability to function in the absence of any supporting instrumentation could make them applicable in certain-situations, where a qualitative yes/no indication involving the presence or absence of a targeted explosive is required. However, in spite of their potential advantages, the colorimetric sensors for nitroaromatic explosives reported to date suffer from disadvantages. Prime among these is low sensitivity and difficulties with translating the colorimetric response seen in solution (where most function well) into the gas phase. This has made them less than ideal for stand-off detection of nitroaromatic explosive vapors. To address this deficiency, we have combined a well-studied colorimetric sensor that responds to trinitrobenzene (TNB) in organic media, namely, the thienofused, tetrathiafulvalene-functionalized calix[4]pyrrole (TTF-C4P; see scheme shown in Fig. 1), with a cantilever sensor. This receptor has previously been demonstrated to bind TNB in organic solution.[5] However, although superior to earlier TTF-functionalized calixpyrrole receptors, is capable of detecting TNB in solution with a limit of detection of approximately 0.3 ppm in halogenated solvents. We have now incorporated this receptor on a cantilever sensor in the hopes of improving the sensitivity and creating a device capable detecting TNB vapors. The resulting sensor system is capable of detecting TNB in commercially available gas mixtures containing TNB vapor at the 10 ppb level; this represents considerable operational improvement in the sensitivity compared to what is seen in bulk organic media and leads us to suggest that the present approach could provide a general solution to the long-standing problem of translating the chemical response of colorimetric chemosensors into practical devices.

Cantilever based sensors are well established in the area of trace chemical detection, including in the area of explosives detection, due in part to their high sensitivity.[6–10] We thought, therefore, that they would offer a suitable platform for creating sensing devices based on molecular receptors. Our goal was to determine whether the basic receptor-derived analyte specificity is retained while concurrently increasing the sensitivity. To achieve this objective, we developed a polymer microcantilever with an integrated deflection sensing element. We coated the cantilever with a layer of TTF-C4P, a colorimetric sensing material, which represents a generalized class of receptors[5] that is known to provide a colorimetric response to nitroaromatic explosive TNB. The device presented in this paper was found capable of detecting TNB in vapor phase via process that involves a change in the surface stress of the cantilever. The level of sensitivity is greatly enhanced compared to what was previously found with TTF-C4P.

The optical lever method[11] is commonly used to detect nanoscale bending of cantilevers in atomic force microscopy and in chemical sensing.[10] However, this method requires a bulky optical setup, which results in lack of portability and high manufacturing costs. There are also challenges associated with applying the optical lever method when the cantilever is in liquid environments or when the cantilever is too small to reflect the laser. In an effort to address these deficiencies, piezoresistive Si-based deflection elements were embedded on cantilevers to detect change in stress/strain due
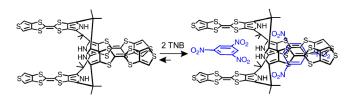

FIG. 1. (Color online) Molecular structure of thieno-TTF-calix[4]pyrrole (TTF-C4P) and its TNB binding mode observed in organic solutions.

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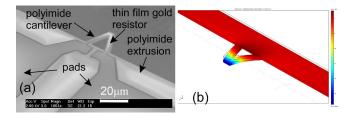
FIG. 2. (Color online) (a) Scanning electron microscopy image of the polyimide cantilever. (b) FEM simulation of the surface stress of cantilever.

to bending[12,13] eliminating the need for an optical system. Recently, polymeric cantilevers[14,15] have been developed for different applications and have displayed enhanced sensitivities, however, these systems have yet to be used for explosive detection.

For a cantilever embedded with a piezoresistor for deflection (bending) detection, the relative resistance change ($\Delta R/R$) of the piezoresistor due to surface stress is proportional to the gauge factor (the gauge factor is the ratio of relative change in electrical resistance to the mechanical strain), and inversely proportional to the Young's modulus of the cantilever material. Therefore, the sensitivity of a cantilever sensor can be increased by using a material with low Young's modulus values, such as a polymer. Such a reduction, coupled with a high gauge factor, can lead to increased sensitivity. Furthermore, at a few micron or smaller scales the signal to noise ratio (SNR) of the output signal, rather than the gauge factor, can be the dominant factor determining sensitivity.[7] Metallic thin film piezoresistors are particularly attractive because the noise and drift are much lower than what is typically seen in semiconductor piezoresistors.

The V-shape polyimide cantilever we report here has near submicron dimensions and high surface stress sensitivity. It contains an ultrathin film gold sensor integrated within the top of the cantilever. The device in question was manufactured using a simple and low-cost microfabrication process. The resulting cantilever can be used to measure very small deflections, and detect TNB gas vapor at a vapor concentration of 10 ppb when coated with a layer of TTF-C4P. This represents an improvement in the detection limit of at least 30-fold compared to the ca. 0.3 ppm level achievable when TTF-C4P is used as a bulk receptor in organic solution.

The cantilever was prepared using a three-mask process. Briefly, a 100 nm silicon dioxide layer was thermally grown on a silicon substrate. A 1.45 μm thick PI2610 polyimide (HD Microsystem™) layer was then coated on top of the oxide layer. The polyimide was patterned with reactive ion etching using oxygen to form the cantilever structure. Then, a 0.2/10 nm Cr/Au layer was evaporated on the polyimide and patterned using lift-off to form the sensing element. The silicon substrate was etched from the back side using a standard deep reactive ion etching (DRIE) process. Here, the etching ceases when the thermal oxide layer is reached. Finally, the cantilever was released by removing the thermal oxide layer using a buffered oxide etch process. The device has a length of 17.5 μm and each leg has a width of 5 μm [Fig. 2(a)]. The 0.2/10 nm Cr/Au sensing element is 2 μm wide and has a nominal resistance of 265 Ω. A 10 μm wide polyimide suspended extrusion that extends from the root of the cantilever to the chip arises from the back side DRIE. According to our finite element method (FEM) simulation, this extrusion reduces the sensitivity of the cantilever by

10%, as well as the spring constant by 60%. The spring constant was estimated to be 4.1 N/m using a Young's modulus value of 8.5 GPa for the polyimide cantilever. The actual Young's modulus of the polyimide layer depends on curing conditions.

TTF-C4P was used as a receptor for the cantilevers of this study. It has been demonstrated previously that TTF-C4P binds to nitroaromatic TNB via a combination of π-electron rich surfaces provided by the TTF subunits and hydrogen bonding interactions provided by the pyrrole NH protons.[5] This receptor also displays a high inherent specificity for flat, electron deficient species, such as TNB. In fact, little evidence of "false positives" has been seen when less highly substituted nitroaromatic compounds were used instead of TNB. Further, TNB binding is seen even in the presence of water and other polar solvents. Therefore, this particular receptor is useful in developing a working sensor device. Here, we are driven in part by the fact that while, TTF-C4P will respond to TNB in solution, the actual response is not that strong; incorporating the sensor into a device product leads to enhanced sensitivity.

To provide a basis for analyzing our systems, a simplified FEM model (modified from a model developed by Ricci *et al.*[16]) for surface stress was developed. In this model, the thin film gold layer is excluded from consideration because of its relative thinness to the polyimide cantilever structure. The change in surface strain due to the adsorption of the molecules on the cantilever is attributed to various interactions including: Lennard-Jones interactions, Coulomb repulsion between adsorbed molecules or adsorption-induced changes in the electronic charge density at the metal's surface.[17] The specific correlation between the average surface strain and the absorbed TNB vapor is unclear and requires further characterization. To simplify the model, a surface stress is applied on the top surface of the polyimide cantilever. The gold layer was excluded due to its negligible thickness. Figure 2(b) shows that the displacement of the V-shape cantilever is about 28.6 nm when 1 N/m compressive stress is applied. According to the FEM simulation, a 1 mN/m surface stress results in an average strain of about 3.6×10^{-7}.

The displacement sensitivity ($\Delta R/R$/displacement) of the cantilever was calibrated by measuring the response of the sensing element when the cantilever is deflected by a piezoelectric stage (PiezoJena, Tritor 100). A multimeter (Agilent, 34401A) was used to determine the resistance via the four point measurement method. Here, the free end of the cantilever was in contact with the piezoelectric stage. The measured displacement sensitivity proved to be 1.1 $\times 10^{-6}$/nm (0.11%/μm), while the corresponding gauge factor for the 10 nm thin film gold was found to be about 3 (Fig. 3), which is higher than the gauge factor of bulk gold.

To conduct measurements in the presence of vapor TNB two identical cantilevers are used to form a Wheatstone bridge circuit as shown in Fig. 4(a). One side of the sensing cantilever is coated with a TTF-C4P, while the reference cantilever is left uncoated. The supply voltage of the bridge circuit is set to 0.05 V to ensure low current values through the cantilever and reduce Joule heating effects. The data is recorded with a data acquisition system in real time without amplification. The noise of the readout is about 2 μV. Small temperature drifts after the Wheatstone bridge is balanced
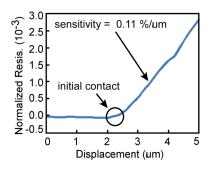
FIG. 3. (Color online) Response of the V-shape polyimide cantilever with displacement.

[Fig. 4(a)] are attributed to ambient temperature fluctuations and differences in the nominal resistance between the reference and the sensing cantilevers.

A saturated mixture of TNB vapor in 99% pure nitrogen was used to test the system. The saturated vapor employed contains TNB at 6.44×10^{-6} Torr and 25 °C. The equivalent concentration of TNB in the gas mixture is 10 ppb. Figure 4(b) shows the response of the V-shape polyimide cantilever when a 20 mL TNB gas mixture is slowly injected in the chamber, which contains the cantilever. An initial readout response occurs within 5 s following TNB injection. The differential voltage output peaks at 13 μV after several minutes. The corresponding surface stress calculated from the FEM model is approximately 1.4 N/m (tensile). The response to peak value can be further improved by reducing the dead volume. Additional experiments reveal that the cantilever does not respond to air or acetone-saturated vapors.

In conclusion, we developed a polyimide microcantilever with a thin film gold sensing element for the stress-based
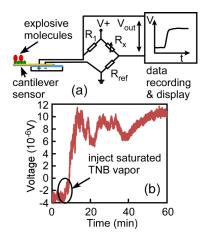

FIG. 4. (Color online) (a) Schematic diagram of the experimental setup, which includes a Wheatstone bridge circuit with a reference and a detection cantilever. (b) Graph of the response of the V-shape polyimide cantilever when exposed to TNB. The vertical axis corresponds to the normalized values of the change in resistance of the sensing element and the horizontal axis represents time in minutes.

sensing of molecular analytes. The displacement sensitivity of this device is 1.1×10^{-6}/nm. The potential utility of the device for explosive detection was explored further by coating the cantilever with TTF-C4P, a colorimetric receptor, to detect TNB vapor at 10 ppb level. It is important to note that this concentration is set by the vapor pressure of TNB, and is not the actual detection limit of our device, which is expected to be much lower. Nevertheless, even at this concentration, this new setup provides a marked improvement on the detection limit (low ppm level) seen for organic solutions containing TTF-C4P. The system can be used for the detection of other nitroaromatic explosives, including 2,4,6-trinitrotoluene, by using a modified TTF-C4P receptor with improved sensitivity. The response time and detection limits can be further improved by reducing the dead volume of the device, increasing the sensitivity of the cantilever, and improving the SNR in the readout circuit. Studies along these lines are in progress. The present results lead us to suggest that the present approach can provide a solution to the problem of translating the chemical response of colorimetric chemosensors into practical devices.

[1]M. Stepień, B. Donnio, and J. L. Sessler, Angew. Chem. **119**, 1453 (2007).
[2]Y. Jiang, H. Zaao, N. Zhu, Y. Lin, P. You, and L. Mao, Angew. Chem. **120**, 8729 (2008).
[3]E. Ercağ, A. Üezer, and R. Apak, Talanta **78**, 772 (2009).
[4]Y. H. Lee, H. Liu, J. Y. Lee, S. H. Kim, S. K. Kim, J. L. Sessler, Y. Kim, and J. S. Kim, Chem.-Eur. J. **16**, 5895 (2010).
[5]J. S. Park, F. Le Derf, V. M. Lynch, C. M. Bejger, J. L. Sessler, K. A. Nielsen, C. Johnsen, and J. O. Jeppesen, Chem.-Eur. J. **18**, 848 (2010).
[6]A. L. Pinnaduwage, H.-F. Ji, and T. Thundat, IEEE Sens. J. **5**, 774 (2005).
[7]M. Li, H. X. Tang, and M. L. Roukes, Nat. Nanotechnol. **2**, 114 (2007).
[8]R. Berger, E. Delamarche, H. P. Lang, Ch. Gerber, J. K. Gimzewski, E. Meyer, and H.-J. Güntherodt, Science **276**, 2021 (1997).
[9]J. Fritz, M. K. Baller, H. P. Lang, H. Rothuizen, P. Vettiger, E. Meyer, H.-J. Güntherodt, Ch. Gerber, and J. K. Gimzewski, Science **288**, 316 (2000).
[10]A. M. Moulin, S. J. O'Shea, and M. E. Welland, Ultramicroscopy **82**, 23 (2000).
[11]G. Meyer and N. M. Am, Appl. Phys. Lett. **53**, 1045 (1988).
[12]P. Li, X. Li, G. Zuo, J. Liu, Y. Wang, M. Liu, and D. Jin, Appl. Phys. Lett. **89**, 074104 (2006).
[13]A. Boisen, J. Thaysen, H. Jensenius, and O. Hansen, Ultramicroscopy **82**, 11 (2000).
[14]R. Katragadda, Z. Wang, W. Khalid, Y. Li, and Y. Xua, Appl. Phys. Lett. **91**, 083505 (2007).
[15]R. H. Ibbotson, R. J. Dunn, V. Djakov, P. K. Ferrigno, and S. E. Huq, Microelectron. Eng. **85**, 1314 (2008).
[16]A. Ricci, E. Giuri, and C. Ricciardi, Presentation at the COMSOL Users Conference, Milano, 2006.
[17]M. Godin, V. Tabard-Cossa, Y. Miyahara, T. Monga, P. J. Williams, L. Y. Beaulieu, R. B. Lennox, and P. Grutter, Nanotechnology **21**, 075501 (2010).