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Fluorescent polymer-porous silicon microcavity devices for explosive detection

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Conjugated polymers entrapped in porous silicon microcavity have been studied as optical sensors for low volatility explosives such as trinitrotoluene. The fluorescence spectra of entrapped polymers were modulated by the microcavity via a spectral “hole” that matches the resonance peak of the microcavity reflectance. Exposure of the porous silicon microcavity containing entrapped polymer to explosives vapor results in a red shift of the resonance peak and the spectral hole, accompanied by the quenching of the fluorescence. This multiplexed response provides multiple monitoring parameters, enabling the development of an optical sensor array for the detection of target explosive vapor. © 2007 American Institute of Physics. [DOI: 10.1063/1.2432247]

Porous silicon (PSi) chemical and biological optical sensors have been intensively studied for the past decade^{1–10} because of the high surface area of PSi and the variety of optical transduction mechanisms upon exposure to different analytes. The sorption of the target molecules and biopolymers into the silicon pores modifies the refractive index and consequently optical properties of PSi. Optical sensors based on PSi thin layer,⁴ waveguides,¹⁰ Bragg mirrors,¹ luminescent,^{3,5} and reflective^{2,6,8,9} microcavities (MCs) have been reported in literature. However, most of these sensors demonstrate no specificity for target molecules. Furthermore, most of the tested organic gaseous analytes (alcohols, saturated hydrocarbons, and chloromethanes) must display high vapor pressures [$\sim(1-100) \times 10^{-5}$ mm Hg] in order for the change in the reflectance or luminescence of PSi structures to be detected. The detection of analytes with low vapor pressure ($\sim 10^{-5}$ mm Hg and lower) such as some nitroexplosives [e.g., trinitrotoluene (TNT) and cyclonite] is a challenge by these methods since nonspecific sorption coupled with low analyte concentration in the pores is not sufficient to uniquely alter PSi optical properties.

It is known that some conjugated polymers exhibit a high sensitivity to nitroaromatic explosives resulting in strong quenching of their emission.^{11–14} Thus, it is expected that entrapping these polymers inside the PSi microcavity should significantly improve sensor efficiency due to specific binding of TNT to the sensory polymers, high quantum fluorescence yield of the polymers (higher than PSi self-luminescence), amplification mechanism as a result of the energy migration,¹⁵ and the fine spectral patterning of the broad fluorescence band induced by the MC structure. Moreover, the MC reflectivity can also be sufficiently sensitive to detect explosive vapors if a sensory polymer is entrapped inside the pores.

As we report in this letter, a chemosensitive polymer entrapped in PSi MC allows detection of vapors of explosive nitroaromatics via a modulation in both fluorescence and reflectance signals. The MC resonant peak in the reflectance spectra is shifted upon vapor exposure. The broad polymer fluorescence shows patterning by the narrow MC peak, which is also sensitive to the vapor exposure. Such spectral patterning provides an additional parameter for recognition, namely, the dependence of fluorescence quenching on the detection wavelength. Conventional fluorescence-based chemosensors to detect explosives^{11–14} employ flat substrates and hence do not display these spectral features. As a result, their fluorescence quenching exhibits no wavelength dependence.

The PSi MCs were prepared by anodic etching of *p*-type (100)-oriented Si wafers (resistivity of $\sim 0.01 \Omega \text{ cm}$) in 15% solution of HF with ethanol. The microcavity structure consists of a Fabry-Pérot resonator between two distributed Bragg reflectors (DBRs) which are fabricated from alternating layers of high and low porosities. By choosing appropriate layer thicknesses, the MC resonance peak in the reflectance spectrum [Fig. 1(a)] can be tuned to the desired wavelength. In fabricated samples, the first DBR consists of 5 periods while the second has 20 periods; each period contains two layers, high and low porosities. For most samples, the low and high porosity layers were fabricated at a current density of 6 and 50 mA/cm². Poly(2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV) was purchased from ADS, Inc. (molecular weight=139 000) and used as received. The polyiptycene containing polymer was synthesized according to Ref. 11. Devices were prepared by spin casting onto or vacuum filling into the substrate (flat Si or PSi MC) from chloroform solution. Vacuum filling was achieved by dropping MEH-PPV in CHCl₃ solution onto a PSi MC that has been under active vacuum in a flask followed by pressurizing the flask with nitrogen. The fluores-

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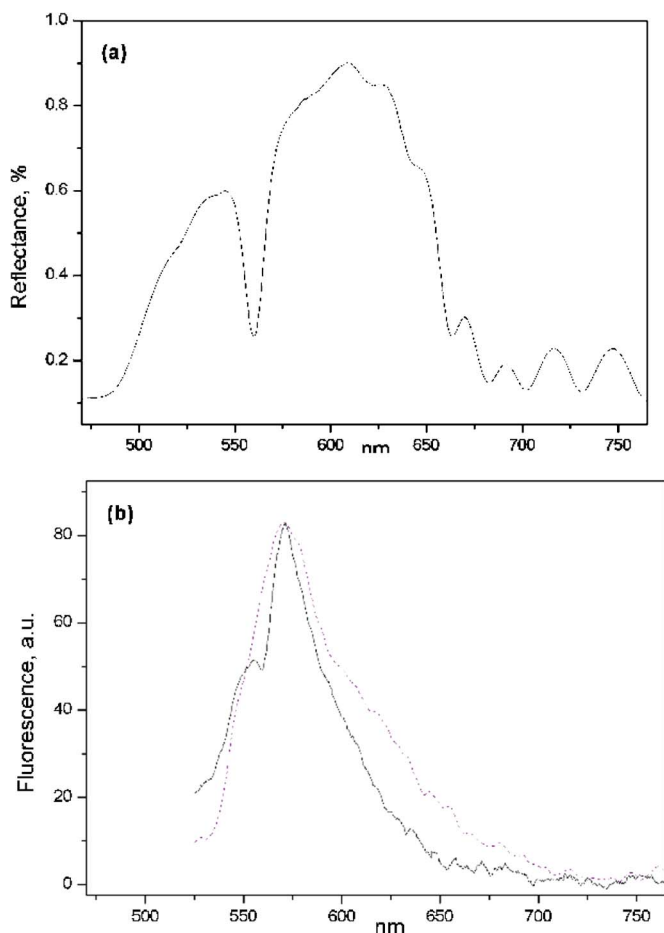


FIG. 1. (Color online) (a) Reflectivity spectra of PSi MC after filling with MEH-PPV by vacuum trapping. (b) Fluorescence spectra of the same sample (solid curve) and MEH-PPV spun cast onto flat Si (dash curve). Excitation wavelength is 490 nm.

cence and reflectance were measured with an Ocean Optics spectrometer coupled with an optical fiber positioned normal to the sample surface. The filled microcavities were placed into a sealed cuvette containing saturated vapor of TNT. Fluorescence (reflectance) spectra and time traces (at specific wavelengths) were recorded immediately after sealing.

Figure 1(a) shows the reflectivity of MC (resonance peak at 560 nm) filled with MEH-PPV via vacuum trapping. The fluorescence spectrum of the sample [Fig. 1(b)] demonstrates a broad band, typical for a MEH-PPV film, patterned with a narrow spectral “hole” matching with the resonance peak in the reflectivity. By comparison, the fluorescence of MEH-PPV spun cast on the flat Si [Fig. 1(b)] exhibits no resonant effects at 560 nm. The appearance of the spectral hole in the MC device indicates that the polymer is entrapped near the surface of the first DBR. In the case of near-surface trapping the polymer emission at the resonance wavelength has a minor reflection for fluorescence that is directed toward the MC depth [as distinct from other wavelengths inside the stop band, Fig. 1(a)] resulting in a reduction of fluorescence intensity at 560 nm. In the case of deep entrapping (throughout the entire MC depth) a narrow fluorescence peak should be observed, similar to that reported for MCs filled with dye,¹⁶ with Er ion,¹⁴ and from self-PSi luminescence.³ The schematic in Fig. 2 illustrates the reflectance and fluorescence features for a polymer entrapped near the first DBR surface (top two layers of gray color).

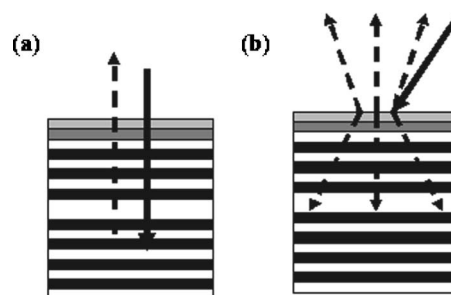


FIG. 2. Schematics show (a) reflectance and (b) fluorescence of DBR/MC/DBR structure filled with polymer. Black and white strips correspond to PSi layers with low and high porosities. Gray color (first two layers) shows the area filled with polymer. Solid arrow is an incident light and dash arrows are reflected (a) and fluorescent light (b).

Figure 3 demonstrates the redshift of MC resonance peak in the reflectance spectra upon exposure TNT saturated vapors. In contrast, without MEH-PPV MC peak does not exhibit spectral shift. Thus, the entrapping of the sensory polymer inside MC allows the detection of analytes with low pressure of saturated vapors while the “empty” MC does not exhibit any response to the vapor exposure.

The exposure of MC filled with MEH-PPV to TNT also affects the fluorescence of the sample, resulting in redshift of the spectral hole. This shift is concomitant with fluorescence quenching [Fig. 4(a)] leading to different time traces for different detection wavelengths. The largest attenuation occurs at 562 nm [Fig. 4(b)], a combination of diminished fluorescence and a spectral shift of the hole (~ 1 nm) toward the longer wavelengths. The gradual shift of the hole in the fluorescence and reflectance occurs due to a change in refractive index as TNT molecules bind to the MEH-PPV inside the MC. In contrast, Fig. 4(c) shows the fluorescence quenching of MEH-PPV spin cast onto flat Si detected at three wavelengths. The time traces of the quenching are the same for all wavelengths, indicating the uniform decrease of the fluorescence signals. However, the PSi device still demonstrates lower quenching [$\sim 45\%$ for 300 s, 562 nm, Fig. 4(b)] than flat Si device [$\sim 75\%$ for 300 s, Fig. 4(c)]. The reason for that can be related to PSi pore clogging by polymer, which prevents the access of TNT molecules to remote polymer layers inside MC.

The observed redshift in reflectivity is larger (~ 2 – 3 nm) than the redshift in fluorescence (~ 1 nm), and

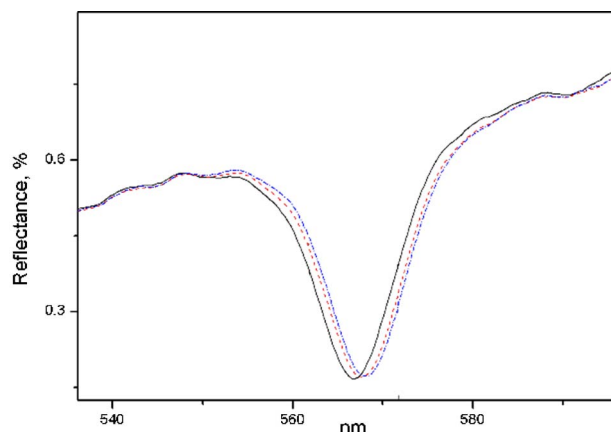


FIG. 3. (Color online) Evolution of reflectance of PSi MC filled with MEH-PPV under TNT vapors: (a) solid—initial, dash—after 50 s and dash dot—after 250 s.

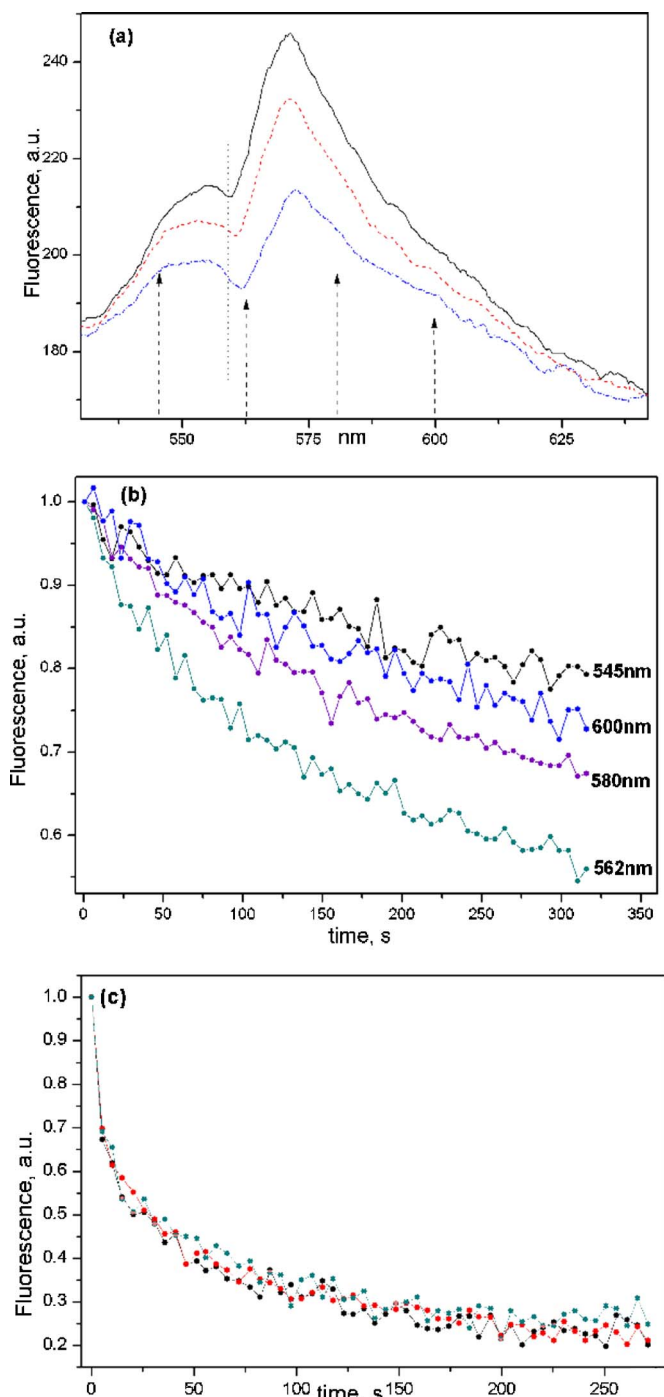


FIG. 4. (Color online) Evolution of fluorescence upon exposure to TNT vapors for MEH-PPV. (a) entrapped into PSi MC: solid—initial, dash—after 50 s, dash dot—after 250 s. Dotted straight line corresponds to an initial spectral position of the MC “hole;” (b) time traces of the fluorescence for four wavelengths [shown by arrows in Fig. 3(a)] and (c) time traces of the fluorescence for MEH-PPV spun cast onto flat Si for 550, 570, and 600 nm [spectrum is shown in Fig. 1(b)].

MC reflectance resonance peak is narrow and more pronounced than the spectral hole in the corresponding fluorescence spectrum. A possible explanation is related to the inhomogeneous broadening inherent in the polymer fluorescence. If the profile of the reflectance resonance peak is described as $F(\lambda)$, then the corresponding profile of the spectral hole can be presented as $S(\lambda) = \int g(t)F(t-\lambda)dt$, where $g(t)$ is the function of inhomogeneous broadening. Such a convolution should lead to broadening of the fluorescence profile $S(\lambda)$ and a reduction in the redshift.

We observed similar trends in reflectivity, fluorescence spectra, and time traces of polyipticene containing polymer exposed to TNT vapor. In this case, the polymer was spun cast onto surface of PSi MC and demonstrated similar photophysical modulations as observed in vacuum filled MEH-PPV samples (i.e., spectral hole and emission redshift upon TNT exposure). However, when MEH-PPV is spin cast, the resulting devices do not demonstrate a sizable redshift as compared with vacuum entrapping method. We suggest that because of the porous structure of polyipticene polymer film,¹¹ TNT molecule were able to diffuse inside the MC and change the refractive index, resulting in observed spectral responses whereas MEH-PPV does not permit this diffusion. More detailed investigations are currently underway.

In conclusion, we have demonstrated that PSi microcavities filled with conjugated emissive polymers can be used as chemical sensors to detect nitroaromatic explosives with low vapor pressures. These sensors can work simultaneously in reflective and in fluorescence regimes. Upon exposure to TNT vapor, fluorescence is attenuated differently at different wavelengths, as compared to the uniform quenching of polymers deposited on a flat substrate in a typical emissive chemosensor.^{11,12,14} Our scheme allows the introduction of an additional set of parameters (detection wavelengths) to uniquely characterize specific explosive vapors and their interferants that could be beneficial in the design of next generation sensor arrays for explosive detection. The sensor array can be designed as a set of different sensory polymers entrapped in microcavity or one polymer entrapped into spatially distributed microcavity.¹⁷

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