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Photochromic Spiropyran-Embedded PDMS for Highly Sensitive and Tunable Optochemical Gas Sensing

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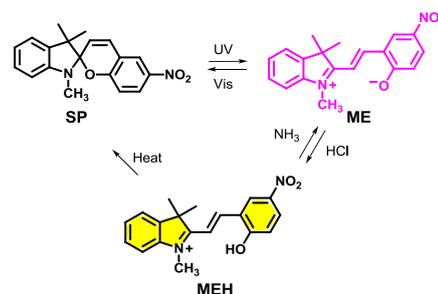
A highly sensitive, tunable, flexible and microfluidic compatible gas sensor was developed based on a photochromic spiropyran-embedded PDMS composite.

Photochromic materials undergo a reversible structural change that interconverts two distinct isomeric forms upon irradiation at specific wavelengths.¹ Owing to the light-driven molecular switching properties, photochromic compounds have been incorporated into many intriguing systems, including molecular actuators,² optical memory devices,³ holographic gratings,⁴ and drug delivery vesicles.⁵ Azobenzene, spiropyran, phenoxquinone and bisthiénylene derivatives are representative of the most common types of photochromic compounds explored to date. These molecules undergo various types of isomerization reactions, such as cis-trans isomerization (azobenzene), ring opening (spiropyran), phenyl group migration (phenoxquinone), or ring closure (bisthiénylene), upon UV irradiation. Recently, applications of photochromic materials in the chemosensor area have received much attention⁶ because molecular sensing properties can be triggered by light and, consequently, “On-Off” switching of sensory function can be readily manipulated by UV or visible light irradiation.

Among many photochromic compounds, spiropyran derivatives have garnered great attention as a result of a number of interesting features that include facile synthesis, distinct chromic transition, and fluorogenic nature of one isomeric form (usually the ring opened form) in certain environments.⁷ In the case of **SP** in Scheme 1, the spiropyran can exist in two isomeric states, including a ring-closed, less-polar spiro form (**SP**) and a ring-opened, more polar merocyanine form (**ME**) (Scheme 1). Under acidic conditions, protonation of the **ME** form occurs to give a **MEH** state which can be transformed to the **ME** form by treatment with ammonia or to the regenerated **SP** form by heat treatment.

Polydimethylsiloxane (PDMS), a low cost flexible and optically transparent polymer that is inert to many organic and inorganic compounds, has been extensively used as a template/mold for nano/microscale patterning⁸ and as a substrate for microfluidic channel formation.⁹ During a recent investigation aimed at the development of

spiropyran-based smart materials,^{6b,10} we formulated the hypothesis that embedment of photochromic spiropyran molecules in PDMS would enable fabrication of a unique, transparent, flexible, microfluidic compatible and reversible sensor system. It should be noted that photoswitching behavior of spiropyran-embedded PDMS has been reported.¹¹



Scheme 1 Three distinct states (**SP**, **ME** and **MEH**) of a spiropyran derivative.

In an effort designed to investigate the feasibility of this type of spiropyran-PDMS based sensor system, a PDMS film containing the photochromic substance was fabricated by employing a simple mixing and drying method (see ESI†). Specifically, a methylene chloride solution containing 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran (**SP**) was injected into a mixture of the PDMS elastomer base and a curing agent (10:1 wt ratio). The resulting mixture was poured into a Petri dish and the dish was placed in a vacuum oven at 70 °C for 2 h. This process generated a flexible and transparent film. In Figure 1 are shown images of the spiropyran-embedded PDMS film before (Fig. 1A, middle) and after (Fig. 1A, left) 365 nm UV irradiation (1 mW/cm²) for 3 min. The appearance of purple color upon UV irradiation of this material is indicative of the generation of the **ME** form of the spiropyran present in the film. The reverse process (decolorization) takes places upon exposure of the film to visible light. Interestingly, UV irradiation of the spiropyran-embedded film through a photomask results in the generation of patterned images (Fig. 1A, right). Analysis

of the optical microscopic image of the material shows that micron-sized patterned images are present, indicating that selective transformation of the SP form of the photochromic molecule to the ME form takes place in the exposed areas (Fig. 1B, middle). The patterned purple colored film emits red fluorescence when viewed under a fluorescence microscope (Fig. 1B, right). This observation is in accord with the one made earlier observation showing that the ME form of spiropyran is fluorescent.¹⁰ The flexible nature of the film is demonstrated by the images shown in Figure 1B (left).

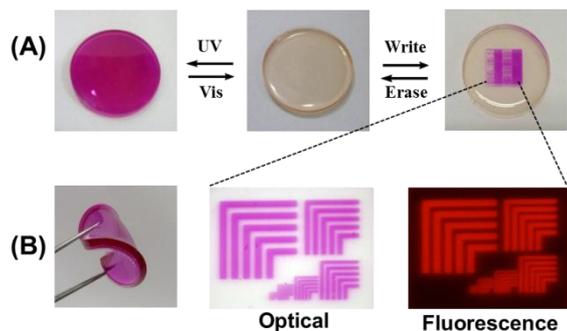


Fig. 1 (A) A spiropyran-PDMS composite film as prepared (middle), after 365 nm UV irradiation for 3 min (left), and patterned images generated by a photomasked UV irradiation (right). (B) Photograph of a UV-irradiated flexible film (left), optical (middle) and fluorescence (right) microscopic images of the patterned film.

An interesting phenomenon occurs when the purple colored UV-irradiated spiropyran-embedded PDMS film is exposed to HCl gas. As the images displayed in Figure 2A show, the area of the PDMS film that is placed on top of a vial containing concentrated HCl solution becomes yellow immediately. Visible light irradiation of the HCl vapor exposed film leads to generation of the ring-closed SP form of spiropyran in the area that is not exposed to HCl vapor. The HCl vapor treated area remains yellow, indicating that the MEH form of spiropyran does not undergo the ring forming reaction upon visible light irradiation. Heat treatment (100 °C for 10 s) of the film, however, induces decolorization and results in the generation of SP form from the MEH state of the spiropyran.

In order to gain more information about the nature of the spiropyran-embedded PDMS film, UV-visible absorption spectra were recorded (Fig. 2B). Formation of the spiropyran ME form by 365 nm UV light irradiation is evidenced by observing a new absorption peak at 550 nm. Interestingly, the complete disappearance of the absorption band at 550 nm with simultaneous appearance of a new peak at 430 nm takes place when the UV-irradiated PDMS film is exposed to HCl vapor. These results indicate that protonation of the phenolate ion in the ME form of the spiropyran by HCl occurs to yield the MEH state of the molecule. Protonation of the phenolate ion results in significant decrease in the efficiency of fluorescence emission so that the PDMS film is virtually nonfluorescent under UV light (Fig. S1, ESI†). It should be noted that the purple-to-yellow color change of the spiropyran-embedded PDMS film promoted by exposure to an aqueous HCl solution takes place very slowly. This observation indicates that the photochromic PDMS film is more sensitive to HCl in the gas phase.

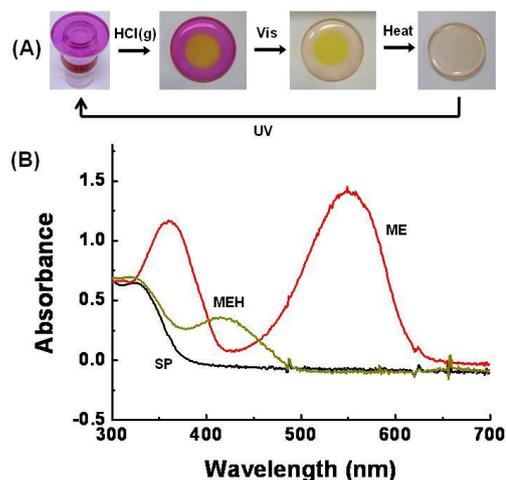


Fig. 2 (A) Chromatic changes of a UV-irradiated spiropyran containing PDMS film. (B) UV-visible spectra of a spiropyran-PDMS film before (black line), after (red line) 365 nm UV irradiation for 3 min, and after (green line) exposure of the UV irradiated film to HCl(g) for 10 min.

To address the sensitivity of the spiropyran-embedded PDMS film to HCl gas, a UV-irradiated purple-colored film was placed in a 50 mL ampule containing MgSO_4 powder and the ampule was sealed with a sure-seal cap. An aqueous HCl solution of designated concentration was injected into the ampule and placed in an oven at 30 °C for 5 h. The intensity of the yellow color developed was analyzed by utilizing a Photoshop program. The detection limit was calculated to be 18 ppb from the plots displayed in Figure S2 (ESI†).

In addition to the sensitivity a good selectivity for a specific analyte is also an important factor for a sensor system. The purple-to-yellow color change of the spiropyran-PDMS composite film in response to various acidic gases was monitored. The intensity of magenta color of the acid treated sensor film was plotted using the Photoshop program. As displayed in Figure 3, formic acid, acetic acid and trifluoroacetic acid are not capable of promoting the color change and the intensity of magenta color remains unchanged. Nitric acid is found to induce the colorimetric transition. However, the degree of the color change is much smaller than that of HCl. Thus, the quenching of the magenta color promoted by the HCl gas is superior to the nitric acid.

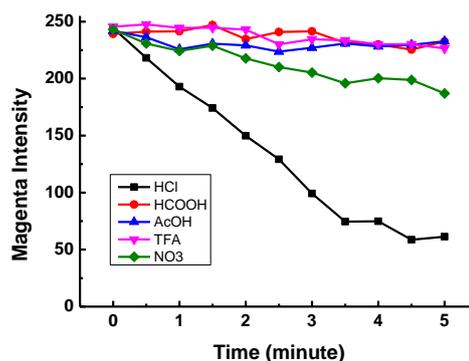


Fig. 3 Plots of magenta intensity as a function of time.

In the course of the investigation of the HCl vapor-induced chromic transition of spiropyran-embedded PDMS film, we found that HCl vapor is capable of penetrating the PDMS film. Thus, prolonged exposure of the PDMS film containing the ME form of the spiropyran to HCl vapor leads to a purple-to-yellow color transformation even on the backside of the film, which does not directly contact with the gas. This finding indicates that HCl gas diffuses into the PDMS film where it converts the ME to the MEH form of the spiropyran in the film. The facile diffusion of HCl gas through the PDMS membrane and the chromic transition induced by the gas are both unexpected and interesting since most earlier permeation studies with PDMS membranes have been focused on hydrophobic gases such as ethylene, propylene and butylene or on the non-condensable permanent gases such as nitrogen and hydrogen.¹²

Based on the facile HCl gas-induced chromic transition of the spiropyran-embedded PDMS film, we have designed and fabricated a simple microfluidic chip containing a straight microchannel comprised of spiropyran-embedded PDMS (Fig. S3, ESI†). It should be noted that metal ion binding and release properties of spiropyran modified microfluidic chips has been previously described.¹³ The microchannel dimensions are 100 μm in width and 50 μm in depth. UV irradiation (365 nm, 1 mW/cm², 3 min) of the microfluidic chip was observed to result in the formation of purple color, indicating that photoisomerization of spiropyran molecules from SP to ME form in the PDMS composite takes place (Fig. 4A, left). HCl gas was introduced to the microchannel using a specially designed gas-testing chamber with mass flow controllers that deliver dry HCl gas (2.3 ppm) at room temperature. Several parameters were measured using the gas testing chamber during repetitive cycles of exposure and recovery in order to evaluate the behavior of the HCl sensor while the gas flow rate was precisely adjusted in a range of 1- 5 mL/h using a programmable syringe pump. Introduction of the gas into the microchannel was found to result in colorimetric change of the sensor chip from purple to yellow (Fig. 4A, right). Since the conversion of the ME form of spiropyran to the MEH form promoted by HCl results in the fluorescence quenching, fluorescence microscope monitoring was carried out in the middle of the microfluidic chip, utilizing an excitation wavelength of ca. 550 nm at which the ME form of spiropyran absorbs.

An inverted fluorescence microscope was ideal for exploring the conversion (Fig. S4, ESI†) since it allows UV irradiation from the top of the microscope, as displayed in Figure S3. Since conversion of the ring-opened ME form of the spiropyran to the ring-closed state occurs during the fluorescence monitoring process, continuous 365 nm UV irradiation from the top of the fluorescence microscope was found to prevent this process. Inspection of the fluorescence images displayed in Figure 4B shows that the area and color of fluorescence quenching become wider and darker, respectively, as the HCl gas flow rate increases. This indicates that the amount of the MEH form generated by reaction of HCl with the ME form in the PDMS substrate increases with increasing HCl gas flow rate. The plot in Figure 4C summarizes the time dependent fluorescence quenching profiles measured along a line perpendicular to the flow direction at the middle of the channel at a fixed flow rate of 3 mL/h. It is clear from inspection of this figure that the distance of fluorescence quenching induced by HCl gas becomes longer as the exposure time increases. Figure 4D contains plots of diffusion length and fluorescence intensity variation measured at 4 min

as a function of flow rate. As expected, the plots show that gas permeates farther into the PDMS substrate and promotes the ME-to-MEH transformation more efficiently with increasing the flow rate.

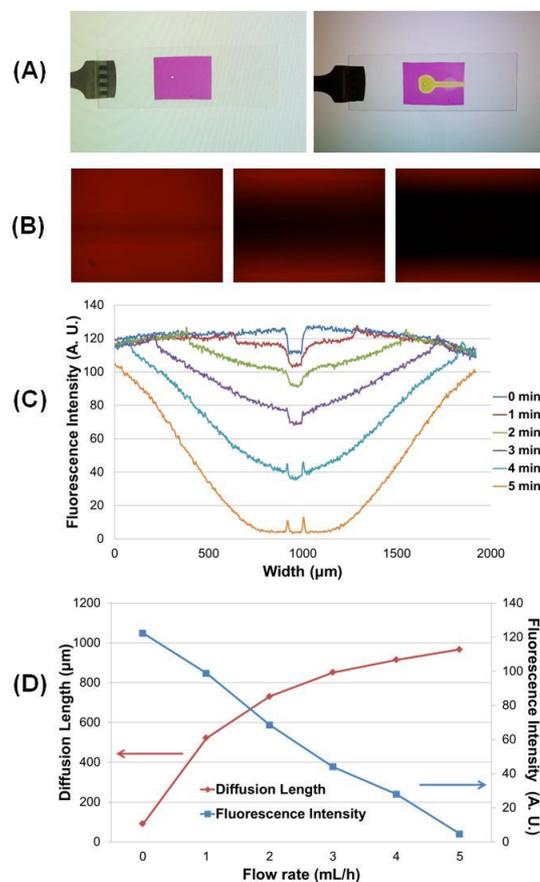


Fig. 4 (A) Photographs of a spiropyran-embedded microfluidic sensor chip before (left) and after (right) exposure to HCl gas. (B) Fluorescence images recorded 4 min after introduction of HCl gas at flow rates of 1 (left), 3 (middle) and 5 (right) mL/h. (C) Fluorescence intensity profiles measured at the middle of the channel (flow rate: 3 mL/h). (D) Plots of diffusion length and fluorescence intensity measured at 4 min as a function of flow rate.

Estimating gas diffusivity in a porous media is important especially when the media is utilized for a diffusion-based sensor system. The plot in Figure 4D shows that the diffusion length increases logarithmically with the time. This is a consequence of the fact that diffusion of HCl gas is augmented by a finite channel pressure. According to Klinkenberg analysis for diffusion augmented by pressure in porous media, an effective gas diffusivity is a linear function of pressure as demonstrated by the relationship given in Eq. 1,¹⁴

$$\alpha = \frac{k_g p}{\phi \mu} \quad (1)$$

where α , k_g , p , ϕ and μ , are effective gas diffusivity, effective gas permeability, pressure, porosity, and viscosity, respectively. Also, pressure is a linear function of flow rate for a pressure-driven laminar flow (see ESI†), and diffusion length scales with square root of diffusivity (Eq. 2).

$$L = \sqrt{4\alpha t} \quad (2)$$

Consequently, the diffusion length increases logarithmically with increasing flow rate. In order to estimate effective HCl diffusivities in spiropyran-embedded PDMS, we calculated channel pressures at the measurement point for six flow rates (See ESI†). The relationship obtained is given in Figure S5 (ESI†). The effective diffusivity was calculated using Eq. 2 and the diffusion length using the data in Figure 4D. The relationship between these parameters was found to be fairly linear in agreement with the Klinkenberg analysis (Eq. 1), indicating that estimation of the effective diffusivity is quite reliable. To our knowledge, this is the first experimental result demonstrating the effective HCl gas diffusivity in spiropyran-embedded PDMS.

Although we used a continuous irradiation method to prevent conversion of the ring-opened MC form of the spiropyran to the ring-closed state, the ME form of the spiropyran was found to be stable for a 10 min period which is enough for the sensor test (Fig. S6, ESI†). In addition, the HCl promoted MEH form was found to be more stable, and the initial yellow color remained for 40 min (Fig. S6, ESI†). These results indicate that the colorimetric sensing of the acid gas also can be carried out without continuous irradiation although it is more desirable if detection of the gas require a prolonged (> 10 min) time period after initial UV irradiation.

In conclusion, in this investigation we have developed a straightforward method for the preparation of photochromic compound-embedded PDMS membranes. The flexible and transparent spiropyran-PDMS composite film was observed to display a reversible colorimetric transition upon photoirradiation. More interestingly, the photochemically generated ring-opened ME form of the spiropyran is rapidly protonated by HCl gas to form the nonfluorescent MEH form in the PDMS membrane. It is both unexpected and interesting that HCl gas penetrates the spiropyran-embedded PDMS substrate and effectively converts the fluorescent ME form of the photochromic compound to the protonated nonfluorescent MEH form. Moreover, the spiropyran-embedded PDMS membrane was found to be recyclable. Thus, the HCl treated yellow-colored PDMS membrane becomes colorless upon heat treatment and the purple colored PDMS film is regenerated upon 365 nm UV light irradiation. In addition, the spiropyran-PDMS sensor system has excellent sensitivity (18 ppb) to the HCl gas.

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† Electronic Supplementary Information (ESI) available: Experimental details. See DOI: 10.1039/c000000x/

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