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Monomolecular-layer assembly of oligothiophene on glass wafer surface and its fluorescence sensitization by formaldehyde vapor

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ABSTRACT

A novel oligothiophene, specifically 2,2′:5′,2″-terthiophene (3T), functionalized film was fabricated by monomolecular layer assembly of 3T onto an amine-terminated glass wafer surface. Contact angle, XPS and steady-state fluorescence measurements demonstrated that the fluorophore was successfully immobilized on the substrate surface. The fluorescence emission of the film, however, is not stable in air, and it decreased along with increasing scanning number. Continuous irradiation of the film with UV light (365 nm) decreased, but stabilized the fluorescence emission of the film. Exposure of the specially treated film into formaldehyde (HCHO) vapor generated a new fluorescence emission, which appeared in a shorter wavelength in comparison with that of the original one. The intensity of the emission increased along with increasing the exposure time. Furthermore, interference experiments revealed that the sensitization is selective, and solvents including common acids, base and alcohols have little effect upon the process. More interestingly, the process is reversible. Accordingly, it is believed that the 3T functionalized film should be a strong candidate for developing a novel and sensitive HCHO fluorescent film sensor.

1. Introduction

Unlike the fluorescent films created by spin-coating, Langmuir–Blodgett film deposition, sol–gel growth, and layer-by-layer electrolyte assembly, the films fabricated by self-assembled monolayer (SAM) deposition possess a number of advantages, e.g. great stability, adjustable distance between the functional molecules and the substrate surface, and variable density of the molecules [1–3]. In fact, monomolecular layer assembly of polycyclic aromatic hydrocarbons (PAHs) and other photo- or electro-active molecules onto solid surfaces has proven to be remarkably useful for creating chemical and/or biochemical sensors, optical display materials, and nano-electronic devices [4,5], and also proven to be of value for sensitive probing interface organization and polarity [6–8]. However, most of the studies are focused on PAHs due to their characteristically high fluorescence quantum yield, their sensitivity to the properties of their local environment, and their ability to access a wide range of photophysical and electrochemical properties, depending on the PAH used. Our group is one of the groups paying interest to the creation of novel films based upon monomolecular layer chemistry, and exploration of their sensing applications. Unquestionable, utilization of novel optoelectronic active molecules as sensing elements is an important way to create novel films, and find new applications.

As other conjugated polymers, polythiophenes and its oligomers, oligothiophenes possess sophisticated electronic and optical properties, and are frequently employed for creating various optoelectronic active molecular devices, e.g. organic light-emitting diodes (OLEDs), transistor circuits, optical memories, optical modulators, and chemical and biochemical sensors, etc. [9–11]. Considering their wide applications, particularly in sensing, and reactivity of them, it was decided to employ them as sensing elements instead of PAHs for the fabrication of fluorescent films. It is out of our expectation that the fluorescence emission of the present film decreases along with increasing the scanning time. Furthermore, the emission could be totally bleached by radiating the film with an UV light. However, a new emission can be re-generated with exposing the film in formaldehyde (HCHO) vapor. Importantly, the emission increases along with increasing the exposure time. It is based upon this observation that a novel HCHO sensing film was developed.

Formaldehyde (HCHO) is widely used in industry for the preparation of paints, foams and natural and synthetic polymeric products due to its high reactivity and low cost. It is also present in the cigarette smoke, and is a by-product of combustion process [12–16]. However, very low concentrations of HCHO (∼1 ppm) in environment can irritate the eyes, nose, and respiratory organs, resulting in allergies and headaches, a condition known as sick house syndrome [13]. The World Health Organization (WHO) has

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set a standard for safe exposure of 0.08 ppm averaged over 30 min [12,14]. Therefore, sensitive and fast detection of HCHO in vapor phase has become a hot spot of research in the fields of environmental science and life science.

The traditional techniques for the detection of HCHO are based on gas chromatograph, mass spectroscopy, FTIR analysis, etc. [16–20]. Most of them, however, require bulky and expensive instruments. Obviously, to satisfy fast, in-expensive and sensitive determination of HCHO in environmental samples, developing novel approaches is of great importance. Compared with others, analytical methods based on fluorescence measurements are characterized by a number of advantages, e.g. greater sensitivity, low-cost in instrumentation, and non-contamination to the analytical systems provided films fabricated in SAM's way are used as sensors.

2. Experimental details

2.1. Materials

2,2′:5′,2″-terthiophene (3T, Puyang Huicheng Chemical Co., Ltd., 96%) and the silane coupling agent (3-aminopropyl) trimethoxysilane (APTMS, Alfa Aesar, 97%) were used directly without further purification. Toluene was purified by washing with concentrated sulfuric acid and then distilled over sodium under a nitrogen atmosphere before use. All other reagents were analytically pure. Water used throughout was de-ionized and then double distilled. Glass wafers used in the experiment were microscope slides with sizes of ~0.9 cm × 2.5 cm.

2.2. Fluorescence measurements and characterization methods

Fluorescence measurements were performed at room temperature on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS 920) with a front face method. The sensing performance of the film to HCHO vapor was examined in the following way [2]: (1) the fabricated film was inserted into a quartz cell with its surface facing the excitation light source, and PL emission of the film was recorded as usual; (2) then, two particles of a molecular sieve were added to the corner of the cell, which is far from the film, and 50 μL of HCHO solution (37–40%) was carefully added onto the molecular sieves, and the cell was sealed immediately; (3) the PL emission of the film was recorded at different evaporation times, such as 1, 3, 5, 10, 15, 20, 25, 30 min. FTIR spectra were measured with a Bruker Equinox 55 FTIR spectrometer. The ^{1}H NMR spectra of the samples were obtained on a Bruker AV 300 NMR spectrometer. Analysis of C, H and N was conducted on a PerkinElmer 2400 CHN elemental analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCA PHI 5400 (PerkinElmer) photoelectron spectrometer. The contact angles of the film surfaces were measured on video-based contact angle measuring device SCA20.

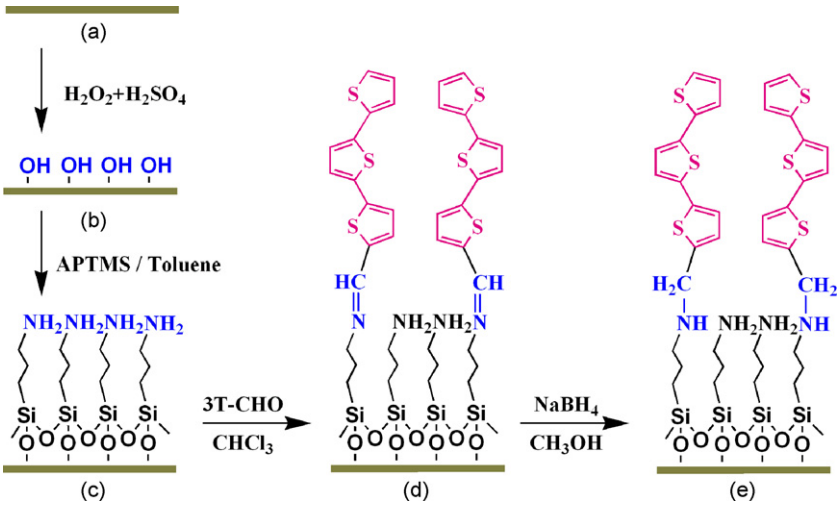
2.3. Preparation of 5-formaldehyde-2,2′:5′,2″-terthiophene

A literature method [11,21] was slightly modified and employed for the synthesis of 5-formaldehyde-2,2′:5′,2″-terthiophene (3T-CHO). To 50 mL of *N*,*N*-dimethylformamide (DMF) thermo-stated at 0 °C, 1.4 mL of $POCl_3$ (15 mmol) was added slowly. The solution was stirred for 30 min under N_2 atmosphere. Then, 50 mL of DMF solution of 2,2′:5′,2″-terthiophene (3T, 2.4 g, 10 mmol) was added dropwise. After the addition, the yellow solution was stirred for another 15 min at room temperature, and then stirred and reacted at 70 °C for 1 h. The color of the system changed into a dark red solution at the end of the reaction. Finally, 100 mL of a cold saturated aqueous solution of sodium acetate was added, and the solution was cooled. A yellow precipitate was produced, filtered, and washed repeatedly with water. The crud product was purified by chromatography on silica gel with dichloromethane as eluent. The purified 3T-CHO was collected as a yellow solid with a yield of 75% (~2.0 g); m.p. 141–142 °C; FTIR (KBr): 3085, 2792, 1645, 1448, 1218, 1044, 834, 791, 707, 662, 455 cm^{-1}; ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$): 9.86 (s, 1H, aldehyde group); 7.67, 7.66 (d, 1H, at position 4); 7.26–7.03 (m, 6H); Anal. Calcd. for $C_{13}H_8OS_3$: C, 56.49; H, 2.92; Found: C, 56.51; H, 2.73.

2.4. Fabrication of 3T-functionalized film

2.4.1. Activation and silanization of the glass wafer surface

A clean glass wafer was treated in a boiling "piranha solution" (30% H_2O_2/98% H_2SO_4: 3/7, v/v) at 98 °C for 1 h (*Caution*: piranha solution is a very strong oxidant and reacts violently with many organic materials, it must be handled with extreme care). Then, the wafer was rinsed thoroughly with plenty of water and dried. After the treatment, the wafer was immersed in a warm (50 °C) toluene solution of APTMS (0.67%, v/v) containing a trace amount of water



Scheme 1. Schematic representation of the fabrication of the 3T functionalized fluorescent film.

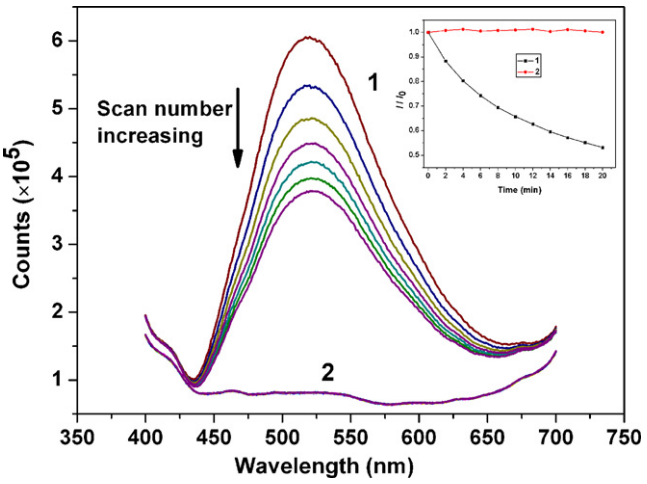


Fig. 1. Fluorescence emission spectra of the 3T-functionlized film recorded in air and at different scan numbers (1), and the one recorded after long time UV irradiation (2). The inset is the plots of the ratios of I/I_0, where I and I_0 represent the fluorescence intensities of the films at the beginning of the scans and that at a given scan time, against scan time for films 1 and 2 (λ_{ex} = 360 nm; λ_{em} = 525 nm).

for 4 h. The APTMS-modified wafer was washed successively with toluene and CH_2Cl_2 for several times to ensure that it is free of unbound APTMS [22–24].

2.4.2. Chemical coupling of 3T on the glass wafer surface

The APTMS-modified wafer was further macerated into a solution of 0.1 g 3T-CHO in 30 mL $CHCl_3$ under reflux for 6 h to generate corresponding Schiff's base. Then the glass wafer was washed by $CHCl_3$ and directly reduced with $NaBH_4$ in anhydrous methanol under reflux for 1 h. To remove un-reacted 3T-CHO, the wafer was extracted with CH_2Cl_2 in a Soxhlet extractor for 3 h. After the extraction, the wafer was further rinsed with plenty of CH_2Cl_2, acetone and water, respectively. The fabrication process was schematically shown in Scheme 1.

2.4.3. Photochemical stabilization of the fluorescent films

It was found that the fluorescence emission of the film as prepared in air decreases along with increasing the scanning numbers. This decrease has been attributed to the reaction of the sensing element 3T with oxygen. In order to improve the photochemical stability of the film, it was irradiated in air under an ultraviolet lamp (Power: 16 W; Wavelength: 365 nm; The distance between the lamp and the film is about 6 cm.) for 1 h before use. It was found that the photochemical stability of the film was significantly improved after the treatment. Fig. 1 shows the degradation of 3T-functionlized film in the presence of oxygen and the example plots of the ratio of I/I_0 of the film against scanning time before and after irradiation.

3. Results and discussion

3.1. Characterization of the 3T functionalized film

In the early 1980s, Sagiv successfully assembled a monomolecular layer film on a glass wafer surface by employing a long-chain alkyl trichlorosilane [25]. Since then, various organic silicon derivatives have been developed and widely used to build monomolecular layer films on glass wafer surface in order to alter the surface properties and introduce some reactive groups for further modification. Accordingly, APTMS was employed to react with the substrate, a glass wafer, in order to get surfaces with amino group. It is believed that these surfaces should react with 3T-CHO and form corresponding Schiff's base, and further reduction with $NaBH_4$ must enhance the chemical stability of the film because the unstable Schiff's base will be reduced into a saturated structure.

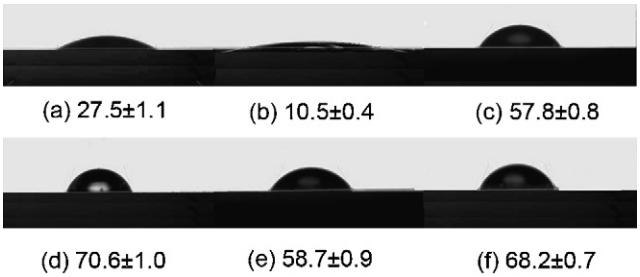


Fig. 2. Static contact angles (θ) (H_2O) for (a) the clean glass wafer; (b) the activated surface; (c) the APTMS-modified surface; (d) the Schiff's base surface; (e) the 3T functionalized film; (f) UV light-treated film.

The leaking of fluorophore moieties from the film into solution was investigated by monitoring the fluorescence emission of the remained solvent after immersion of the film in $CHCl_3$ for 18 h. No typical 3T or 3T-CHO emission was found, suggesting that leaking problem was trivial, and the sensing element had been chemically immobilized on the substrate surface.

Contact angle measurement is a simple but efficient characterization method for surface properties, which examines the wettability of surfaces and provides some useful information about the structure and composition of surface. The static contact angles with water for the surfaces at different coupling stages are shown in Fig. 2. It can be seen that activation made the contact angle decrease from 27.5° to 10.5°, indicating that more hydroxyl groups were formed after the activation, which should be favorable for

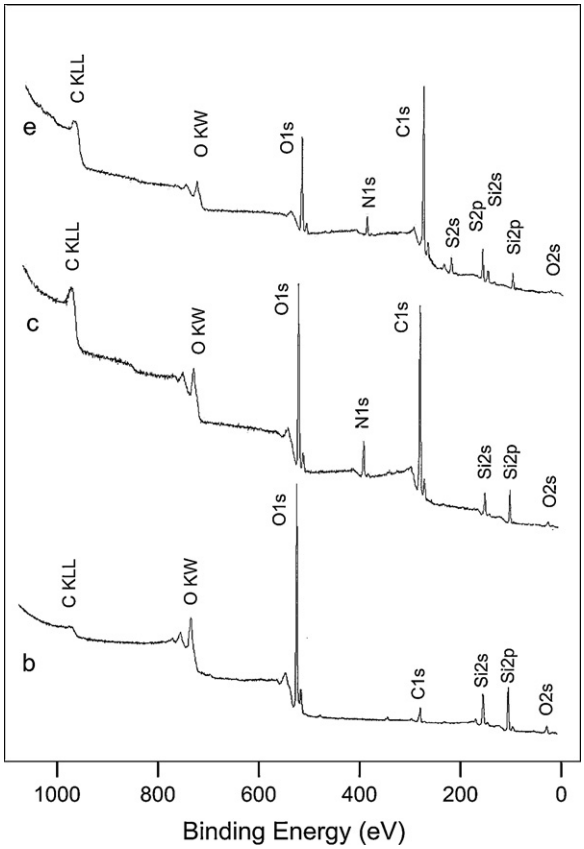


Fig. 3. The XPS traces of the films, where the meanings of b, c, and e are the same with those explained in Fig. 2.

the silanization of the surface. Further treatment of the surface with APTMS resulted in a sharp increase in the data from 10.5° to 57.8°, in support of successful introduction of the hydrophobic aminopropyl-chains onto the substrate surfaces. Reaction of 3T-CHO with the amino-groups of the modified substrate increased the contact angle to 70.6°. Reduction of the formed Schiff's base with $NaBH_4$ decreased the angle to 58.7°. These results were consistent with the expectation from the chemical compositions of the glass wafer surfaces as shown in Scheme 1. Light irradiation increased the contact angle to 68.2°, indicating that the surface is still hydrophobic. A detailed discussion will be given in a later section.

Chemical coupling of 3T on the glass wafer surface was further studied by XPS measurements. Fig. 3 depicts the XPS spectra of the glass wafer with different surface compositions and structures. Compared with the activated glass wafer, the XPS spectrum of the APTMS-modified glass wafer surface is characterized by two N1s signals, appearing at 399.6 and 401.3 eV, respectively, indicating presence of nitrogen-containing molecules on the substrate surface in accordance with the chemical modification. It can be also seen that the signal of C1s (284.6 eV) became much stronger on the amine-terminated surface, a direct evidence for the successful coupling of the organic silane agent [26]. As expected, immobilization of 3T-CHO made the signal of C1s become even stronger, and meanwhile the specific signal of S2p (170.1 eV) appeared, which is, of course, originated from the 3T moiety. Therefore, it was believed that the fluorescent 3T was successfully immobilized on the glass wafer surface.

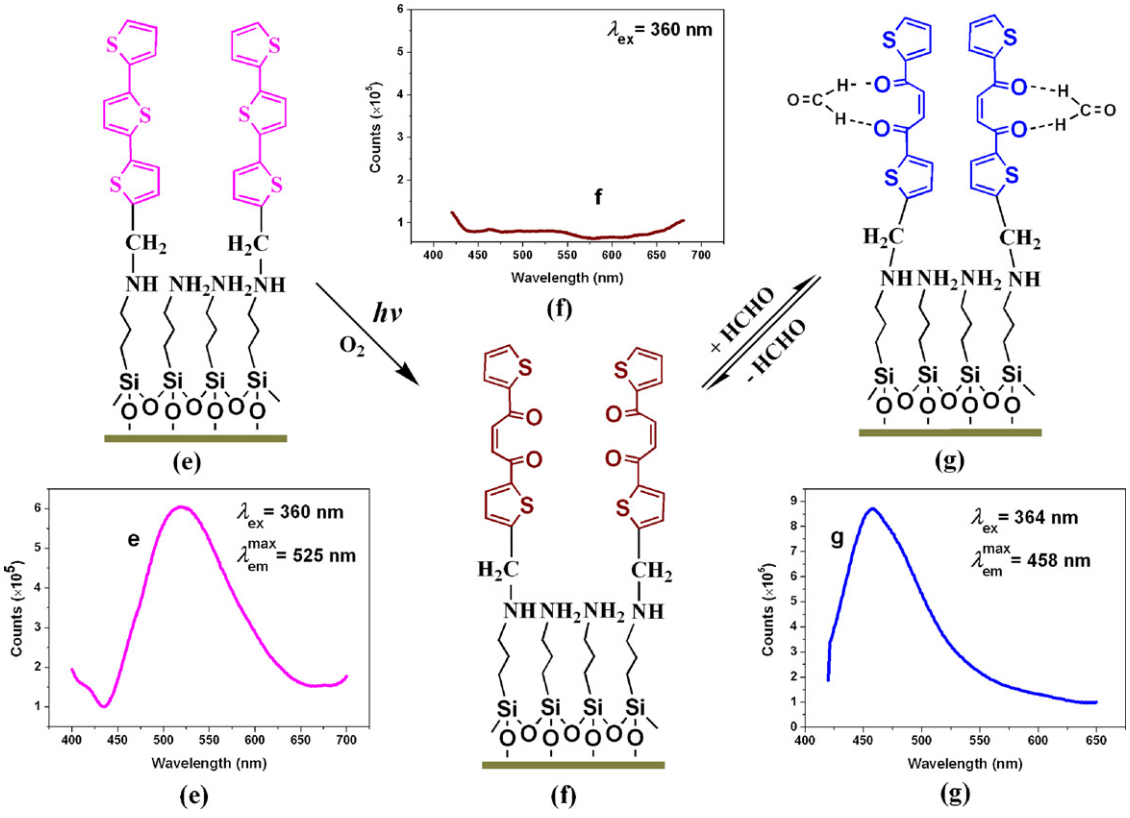
Further analysis of the XPS results could reveal the loading density of 3T on the substrate surface. It is no doubt that the relative intensity of the signal of C to that of S is determined by the loading density of the fluorophore on the substrate surface. Suppose that the graft density of 3T is x, and then the density of the un-reacted amino group should be $1-x$. With reference to the structure of the film as shown in Scheme 1, it can be seen that the formula of the two grafts are $C_{16}H_{16}S_3N$ and C_3H_8N, respectively. Then, the atomic number of carbon on the substrate surface should be $[16x+3(1-x)]\times S$, where S is the surface area of the substrate, and that of sulfur should be $(3x)\times S$. Thus, the atomic ratio of the two elements is $[16x+3(1-x)]/3x$. With reference to Fig. 3 and *via* simple calculation, it is revealed that the loading density of 3T on the substrate surface is about 0.14, a density which is suitable for sensing because higher densities would result in self-quenching and a lower density must accompany a weak fluorescence, which is also unfavorable for sensing.

It was noticed with surprising that the intensity of the fluorescence emission decreases along with increasing the scanning time (*cf.* Fig. 1). This decrease was tentatively attributed to the photodegradation of the immobilized 3T because one possible reason that is leaking of the fluorophore molecules into solution has been eliminated, and in addition a similar phenomenon was observed for oligothiophenes in solution by other groups [27–31]. The instability in fluorescence emission will undoubtedly limit the applications of the film, and thereby this problem must be resolved before it can be considered for sensing.

3.2. Stability enhancement of the 3T functionalized fluorescence film

It is well known that oxygen is a commonly found, highly efficient fluorescence quencher. During a quenching process, it can act as an electron acceptor, giving rise to radical anions, as that described in Eq. (1) with 3T as an example fluorophore [27,30–32]. It can also react with 3T and forms an oxidative product of 3T, as that shown in Scheme 2.

$$3T \xrightarrow{h\nu} {}^3 3T \xrightarrow{O_2} 3T^{\bullet+} O_2^{\bullet-} \quad (1)$$



Scheme 2. Schematic representation of the photo-chemical oxidation of the 3T functionalized film and its sensing to HCHO vapor.

Considering the photochemical nature of the reactions represented in Eq. (1) and Scheme 2, and the good stability of the two oxidative products, the 3T functionalized film was irradiated under a UV light for a sufficient long time in order to get a film with stable fluorescence emission [30–32]. As demonstrated by the inset of Fig. 1, this is an effective way to improve the fluorescence stability of the film. It is to be noted, however, that with the proceeding of the reaction, the characteristic fluorescence emission of 3T is getting weaker and weaker, which is in accordance with the decrease of the density of the fluorophore on the film surface. Participation of oxygen in the photochemical reaction was further confirmed by a reference reaction. During the reaction, the fluorescence emission of the original 3T-functionalized film was continuously monitored under an inert atmosphere (N_2), and no significant decrease in the intensity of the emission was found.

The different electrostatic property of $3T^{\bullet+}O_2^{\bullet-}$ and that of the oxidative product of 3T (*cf.* Scheme 2) must correspond to different wettability to water. In fact, light irradiation increased the contact angle of the film surface, rather than decreased it (*cf.* Fig. 2), indicating that the product of the photochemical reaction might be the one denoted in Scheme 2, as revealed by Holdcroft [33] and Holdcroft and Abdou [34].

Considering the fact that the fluorescence emission of both 3T and 3T-CHO can be sensitized by HCHO in aqueous phase (unpublished results), it was expected that the fluorescence emission of the film might be responsible to the presence of HCHO, and thereby the effect of HCHO to the fluorescence emission of the film was studied.

3.3. Fluorescence sensitization of the film by HCHO vapor

Fig. 4 shows the fluorescence emission spectra of the film recorded at different exposure times in HCHO vapor. Reference to the figure, it can be seen that a special emission around 458 nm appeared that was not found before and after the UV light irradiation, suggesting that it was neither coming from 3T nor coming from the photochemical product as shown in Scheme 2. It should originate from a new component, and the component must be well related with HCHO. On the basis of this consideration and the possible surface structure of the film shown in Scheme 2, the fluorescent active component should be a physical complex of HCHO and the photo-oxidative product of 3T (*cf.* Scheme 2).

To further confirm the tentative conclusion that it is the photo-oxidative product of 3T that is responsible for the detection of HCHO vapor, a number of reference experiments were conducted, and the corresponding results are shown in Fig. 5. With reference to

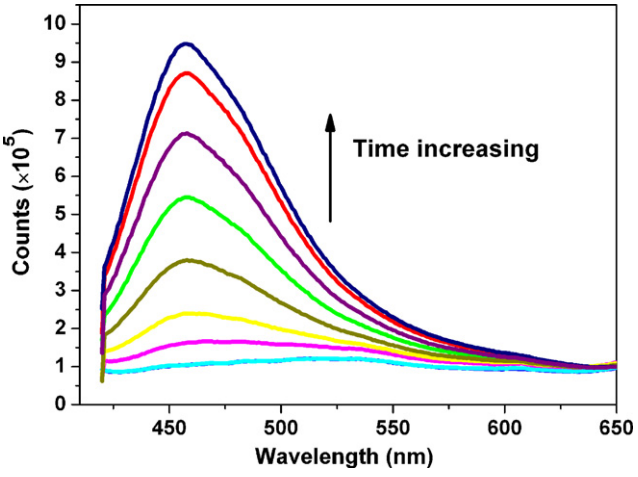


Fig. 4. The fluorescence emission spectra of the light-treated 3T functionalized film recorded at different exposure times in HCHO vapor (λ_{ex} = 364 nm).

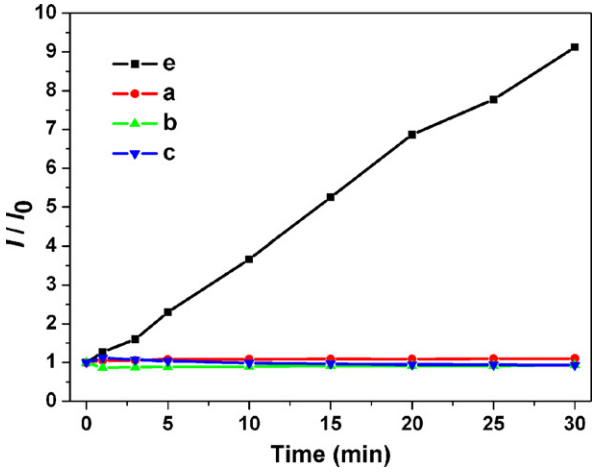


Fig. 5. Plots of I/I_0 against the exposure time of the films in HCHO vapor, where a, b, c, and e stand for the films of different surface compositions (*cf.* Fig. 2) (λ_{ex} = 364 nm; λ_{em} = 458 nm).

the figure, it is seen that presence of HCHO had not shown any significant effect upon the emission, if applicable, of the reference films, including the bare glass, the activated glass, and the amine-terminated film, indicating that 3T plays crucial rule for the performance of the film.

Further interrogation of Fig. 4, it can be also found that the intensity of the emission increases along with increasing the exposure time, and the final emission intensity after 30 min exposure in HCHO vapor is at least nine times stronger than that at the beginning (I/I_0), where I and I_0 stand for the fluorescence intensity in the presence and absence of HCHO vapor.

Considering the toxicity of HCHO vapor to the environment and the fact that it is not easy to be determined directly, it is worthwhile to study the selectivity and reversibility of the fluorescence sensitization process, which are important for real sensing applications.

3.4. Interference of other common solvents

To test the selectivity of the response of the film to HCHO vapor, the effects of common solvents, including methanol, ethanol, formic acid, acetic acid, ammonia, hydrogen chloride, benzene, toluene, dichloromethane, chloroform, acetaldehyde, benzaldehyde, ethyl acetate, etc. to the fluorescence emission of the film were examined in a similar condition as that used for the examination of the sensing performance of the film to HCHO vapor. It was found that in comparison with HCHO, the vapors of all solvents tested have much weaker effect upon the fluorescence emission of the film as shown in Fig. 6. The most pronounce influence is coming from ammonia, acetic acid, formic acid or methanol, but the maximum response of the film to these chemicals is less than 20% of that to HCHO vapor. Furthermore, the responses of the film to these interference solvents are fast, and the emission is getting stable within a few minutes, a sharp difference to that of the film to HCHO. No doubt, this difference is favorable for the selective detection of HCHO.

3.5. Reversibility of the sensitization process

The reversibility of the fluorescence sensitization process was examined in a route way as described before [2,12]. The film was first exposed to HCHO vapor at room temperature for 30 min and then its emission spectrum was recorded. After the measurements, the film was recovered by blowing in air at room temperature

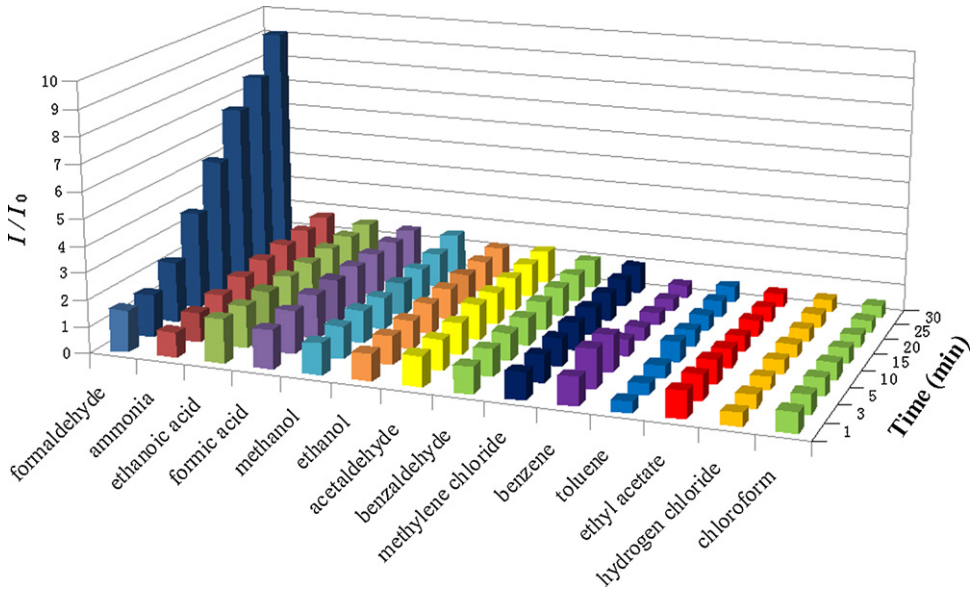


Fig. 6. The sensing performances of the UV light treated 3T functionalized film to different chemical vapors at different exposure times (λ_{ex} = 364 nm; λ_{em} = 458 nm).

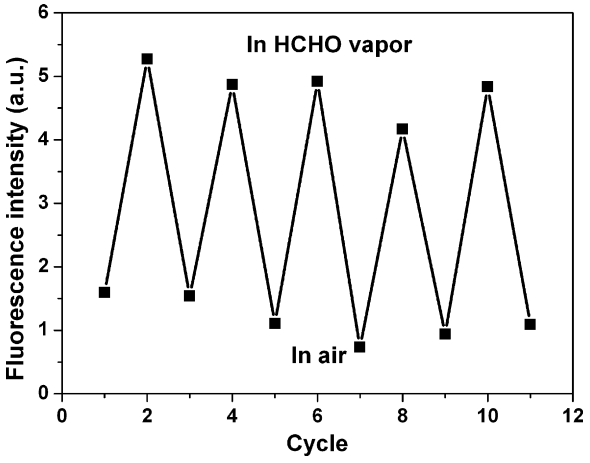


Fig. 7. The reversibility of the sensing performance of the UV light treated 3T functionalized film to HCHO vapor (λ_{ex} = 364 nm; λ_{em} = 458 nm).

(~10 min) or by washing with ethanol for several times. The emission spectrum of the film at dry state was recorded again. The whole process was repeated for five times and the results are shown in Fig. 7. It can be seen that the fluorescence sensitization process is reversible.

4. Conclusions

In the present work, a novel fluorescent sensing film with 2,2′:5′,2″-terthiophene as sensing element was fabricated in a monomolecular layer manner. It was revealed that UV light irradiation stabilizes the fluorescence emission of the film, and a new emission is generated upon exposure of the light treated film to HCHO vapor. Further examination demonstrated that the intensity of the emission is highly dependent upon the concentration of the HCHO vapor. Furthermore, the sensitization is selective and reversible. These properties guarantee that 3T functionalized film can be a strong candidate for developing HCHO specific fluorescence film sensor.

Acknowledgements

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