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A portable fluorescence detector for fast ultra trace detection of explosive vapors

Yunhong Xin, Gang He, Qi Wang, and Yu Fang

1 School of Physics and Information Technology, Shaanxi Normal University, Xi’an 710062, People’s Republic of China
2 Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Materials Science, Shaanxi Normal University, Xi’an 710062, People’s Republic of China

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This paper developed a portable detector based on a specific material-based fluorescent sensing film for an ultra trace detection of explosives, such as 2,4,6-trinitrotoluene (TNT) or its derivate 2,4-dinitrotoluene (DNT), in ambient air or on objects tainted by explosives. The fluorescent sensing films are based on single-layer chemistry and the signal amplification effect of conjugated polymers, which exhibited higher sensitivity and shorter response time to TNT or DNT at their vapor pressures. Due to application of the light emitting diode and the solid state photomultiplier and the cross-correlation-based circuit design technology, the device has the advantages of low-power, low-cost, small size, and an improved signal to noise ratio. The results of the experiments showed that the detector can real-time detect and identify of explosive vapors at extremely low levels; it is suitable for the identification of suspect luggage, forensic analyses, or battlefields clearing. © 2011 American Institute of Physics. [doi:10.1063/1.3642661]

I. INTRODUCTION

During the past 10 years, violence of terrorist bombings, with the most alarming increase in number, has made the task of standoff detection of improvised explosive devices extremely urgent. Yet, because of the variety of explosive materials available, cleverness of packaging, variability of venue, and the (mostly) low vapor pressures of explosives, the task of detection is extremely difficult. There already exist various valid technologies for the analysis of explosives: high-performance liquid chromatography, electrochemical detection, gas chromatography/mass spectroscopy (GC/MS), IR, x-ray imaging, NMR, and ion mobility spectrometry. However, because of the cost, the portability, and the complexity, these methods are unfit for on-site monitoring devices.

As a result, much interest has been focused on the development of portable, low-cost, and more reliable detection devices. First of all, the sensor is the critical component for developing the detectors. Up to now, a wide variety of chemical sensors have been developed based on various transductions. Although mass sensors have suitable detection properties, in most cases they fail to detect explosives with very low vapor pressures. Optical devices based on immune sensors exhibit high selectivity, thanks to the specific reaction of antibodies with explosive molecules. The enzyme-linked immunosorbent assays (ELISAs) device exhibits a detection sensitivity of 1–15 ng/ml of TNT, in 5 h. This technique is dedicated to the detection of explosives in a liquid matrix. Despite these advances, there is currently a strong demand for explosives vapor sensors that are more suitable for the inspection of landmine detection, forensic analysis, and suspicious luggage.

Recently, the fluorescent sensing films for detection of TNT have received a great deal of attention. Caron et al. developed a system for the detection of nitroaromatic explosives consisting of a portable detector based on a specific fluorescent material. The system was able to perform an ultra trace detection of explosives, such as TNT or its derivate DNT, in ambient air or on objects tainted by explosives. However, its response speed is very slow and it will take many minutes for an efficient test. Swager and co-workers have continued to advance the ability of semiconductive organic polymers to detect explosives vapors at extremely low levels. Selectivity between explosives and interferents is being improved in the devices via a fundamental understanding of the energy transport mechanism along the poly(arylene ethynylene) backbone and its response to polymer structure, assembly architecture, and receptor characteristics. Fisher et al., at Nomadics, have continued to provide novel packaging and testing of the Fido sensor based on Swager’s fluorescent polymers. They have recently reported successful detection of simulated vehicle-borne ion energy distribution (IED) targets using both vapor and swipe sampling. Cross-reactive chemical sensors using fluorescent polymers with both narrow and broad specificity are being utilized in an artificial olfactory system for landmine detection. These devices rely on the transport of trace vapor, but active air movement can produce detection within a few seconds.

Compared with the other sensors, the special process and structure guarantee the advantages of the single-layer chemistry and conjugated polymer-based fluorescent sensing films: (1) fast response based on the design strategy of directly exposing fluorophores to the testing solution, (2) high stability coming from the chemical bond among the components, (3) so-called “molecule wire effect,” which result in “super quenching effect,” and (4) multiple measurable photo physical parameters.
In this paper, based on our specific material-based fluorescent sensing film,\textsuperscript{16} we develop a low-cost, low-power, high sensitivity, and small size device for the detection of nitroaromatic explosives and give an elaboration on the design process and relative technology. The results of the experiments showed that the developed detector was able to perform an ultra trace detection of explosives, such as 2,4,6-trinitrotoluene (TNT) or its derivate 2,4-dinitrotoluene (DNT).

II. FLUORESCENT FILM SENSOR

A. Synthesis of fluorescent film sensor

The fluorescent film was prepared in the same way as reported in Ref.\textsuperscript{16}. Poly (diphenylsilane) (0.04 g) was dispersed in tetrahydrofuran (THF) (20 ml), and then stirred for 20 min. To the suspensions, a few drops of \textit{n}-butyl-lithium were added under stirring. The scission reaction was completed within a few minutes, and the solution was then poured onto the substrates with reactive anchors, and reacted for another 15 min. After coupling, the substrates were collected and rinsed repeatedly with THF and toluene. Further cleanout was conducted by immersing the substrates in toluene overnight, and then separated and refluxed in THF for 5 h to make sure that all physically adsorbed oligomer and other impurities are removed from the plate surface. The synthesis of poly(diphenylsilane) and its coupling onto a glass plate surface is schematically shown in Fig. 1.

B. Steady-state excitation and emission spectra of the film

The excitation and emission spectra of the oligomer-functionalized film in dry state are shown in Fig. 2. The maximum excitation and emission of the film appeared at 370 nm and 410 nm, respectively. Lots of experiments revealed that the fluorescent films have a fast, sensitive, and selective response to nitroaromatic compounds (NACs) in vapor phase; it is suited to sense DNT and TNT vapors. The film characterization and fluorescence quenching process is described in detail in Ref.\textsuperscript{16}.

III. SYSTEM DESIGN PRINCIPLES

This measurement system is in nature a kind of weak optical signals detecting device; it involves fluorescent materials, optics, computer, signal processing, and many other technologies. Its work principle is as follows: the light emitting diode (LED) emits an optical signal with specific wavelength, by which the fluorescent sensing film is excited to emit a certain intensity of fluorescent signal. If the sample air contains explosive material, such as the TNT vapors, the fluorescent materials would interact with explosive vapors, which would...
result in the fluorescence intensity decreased, so by measuring the fluorescence intensity, the sample material which contains explosive can be detected.

A. System frame

The frame of the measurement system is schematically shown in Fig. 3. It is shown in Fig. 3 that the system is composed of a sample unit, an optical sensor unit, an excitation module, a solid state photomultipliers (SSPMs) readout unit, a signal conditioning circuit, a microcontroller unit (MCU), a communications unit, and some other units or components.

B. Sample unit

The sample unit is consisted of a pump and its driven circuit, an airtight quartz cuvette, and the air input and output channels. The pump used is an ordinary miniature air pump (GminiP-3*, Beijing Jinshou Mini Pump Center, China), and its flow pressure can be adjusted within 30–50 kPa range. The size of the pump is 24 mm × 16 mm × 41 mm. To prevent dust and other solid polluter, an air filter with a meshy structure has been introduced into the air input pipe.

C. The excitation module

The circuit of the excitation module is shown as Fig. 4. It is composed of a signal shaping circuit and a LED constant current control circuit. A low-cost LED (YCL-UV360–370, Shenzhen YuanChuang Electronic Co. Ltd., China (Ref. 17)) delivering an optical power of 3 mW at a wavelength of 365 nm. Compared with the iodine tungsten lamp, the LED is superior in many respects. We set the LED intensity with a style of pulse-width modulation, which allows the apparent intensity of a LED to be controlled by driving LED with a high frequency square wave with a varying duty cycle. This technique can avoid changes of the emission spectra, which occur when intensity is controlled by current.

1. Signal shaping circuit

Signal shaping circuit uses an Op Amp (U10A, AD8032, Texas Instruments) as a comparator to shaping the signal from the control processor; the AD8032 is a rail to rail Op Amp of which the output signal amplitude can approximately equal to the voltage source.

2. Constant current control circuit

Constant current control circuit is composed of three Op Amps (U11A, U10B, U11B). This circuit is used to control the current flowing the LED1 to a constant value, which made LED emit a constant light. The current value is determined by the resistor $R_{m3}$ and input voltage, the LED current and $R_{m3}$ are related by the simple equation

$$I_{LED} = -\frac{V_{in}}{R_{m3}},$$

where $V_{in}$ is the output signal of Op Amp U10A.

D. Optical sensor unit

The diagram of optical sensor unit is shown as Fig. 5. Light is focused on the fluorescent sensing film through a convex lens (uncoated, 20 mm diameter) with a spot diameter
of 9 mm, a single bandpass filter (370/10/OD4, Mega-9, China\textsuperscript{18}) is incorporated to reject wavelengths below 360 nm and above 380 nm. Fluorescence is collected by a convex lens (uncoated, 20 mm diameter) and focused at the end-face by a solid state photomultiplier (SSPM, SSPM\_0611B4MM, Photonique SA\textsuperscript{19}) with a spot diameter of 6 mm. To suppress the remaining excitation radiation, the detector had been interfaced with a bandpass filter (410/20/OD4, Mega-9).

**E. SSPM readout circuit**

SSPM is a new type of photon counting device made up of multiple avalanche photodiode pixels operated in Geiger mode. It is essentially an opto-semiconductor device with excellent photon counting capability and great advantages such as low voltage operation and insensitivity to magnetic fields. 0611B4MM is a blue and UV light sensitive SSPM specifically designed for positron emission tomography and optical emission spectroscopy applications. Incorporating 1700 microcells, it offers sufficient dynamic range to handle the actual application.

Figure 6 shows the SSPM readout circuit for 0611B4MM. The circuit will provide negative signal polarity at the input to the amplifier. Depending on the expected brightness of the events to be observed, $R_{48}$ can be adjusted according to the actual application: For high photon rates, which give rise to higher currents drawn by the SSPM, $R_{48}$ should be chosen smaller in order to assure good signal gain stability. Yet, $R_{48}$ should not be selected smaller than 5 k\textOmega\textsuperscript{1} in order to protect the SSPM during bias ramp-up. The couple capacitor C57 isolates the dark current or the background light current of the SSPMs, and the optional shaping capacitor C56 serves to differentiate away signal tails, which for certain types of SSPMs, can be quite long (100 ns to 1 \mu s).

**F. Signal conditioning circuit**

Compared with the photomultiplier tube, a significant disadvantage of the SSPMs is its high noise. To overcome this shortcoming, a cross-correlation-based signal conditioning circuit is used to suppress the noise. It is consisted of an analog multiplexers and an integrator. The principal diagram of signal conditioning circuit is shown as Fig. 7.

In the diagram, $x(t)$ and $c(t)$ are the input signal and control signal, respectively, $c(t)$ is the channel select signal of the analog multiplexer, $x(t)$ is the combination of the actual signal $s(t)$ and the system random noise $n(t)$, as derived below

$$x(t) = s(t) + n(t),$$ (2)
FIG. 8. (Color online) The schematic diagram of cross-correlation-based circuit.

where

$$s(t) = \begin{cases} A, & 0 \leq t < \tau_1 \\ 0, & \tau_1 \leq t < T_1 \end{cases}, \quad (3a)$$

$$s(t) = s(t + nT_1), \quad n = -\infty, \ldots, -1, 0, 1, \ldots, +\infty. \quad (3b)$$

The control signal \(c(t)\) is set as

$$c(t) = s(t)v(t), \quad (4)$$

where

$$v(t) = \begin{cases} C, & 0 \leq t < \tau_2 \\ 0, & \tau_2 \leq t < T_2 \end{cases}, \quad (5a)$$

$$v(t) = v(t + nT_2), \quad n = -\infty, \ldots, -1, 0, 1, \ldots, +\infty. \quad (5b)$$

In Eqs. (3a) and (5a), the parameter \(T_1, T_2\) are the period of the signal \(s(t)\) and \(v(t)\), respectively, where \(T_1 \ll T_2\). When \(0 \leq t < \tau_2\), the integrator output \(y(t)\) will be

$$y(t) = -\int x(t)dt = -\int [s(t) + n(t)]dt. \quad (6)$$

The negative symbol in Eq. (6) is because of the integrator being an anti-phase one. If \(n(t)\) is a zero mean random signal and the integral time constant is much larger than the period \(T_2\), \(y(t)\) can be found as follows:

$$y(t) = -\int [s(t) + n(t)]dt = -\int s(t)dt = -A \frac{\tau_1 T_2}{T_1} + C_0, \quad (7)$$

where \(C_0\) is the initial value of integrator and it is approximate to the value of the voltage source \((V_{cc})\) in actual.

When \(\tau_2 \leq t < T_2\), \(y(t)\) will be

$$y(t) = -\int (-V_{cc})dt = \int V_{cc} dt. \quad (8)$$

Due to the saturation of electronic devices, \(y(t)\) will at final reach and stabilize at the voltage source value \(V_{cc}\).

Figure 8 shows the actual circuit, where \(V_1\) is the output signal of the SSPMs readout circuit, CD4051 is a single 8-Channel CMOS analog multiplexer having three binary control inputs: A, B, and C. Here, only 0–2 Channels were used: CHAL0 and CHAL1 are the channel selected logical control signal coming from the MCU. USA, C12, and R15 construct an integrator which is a key component of the circuit, the peak value of the output of the integrator V3 stands for the fluorescence intensity, the smaller the peak value, the higher the density of explosives vapors. The signal sequence diagrams were shown as Fig. 9.

G. The control module

The system is controlled by a fully integrated mixed-signal system-on-a-chip MCU (C8051F350 Silicon Laboratories Inc., USA (Ref. 20)). It is a high-speed pipelined 8051-compatible microcontroller core (up to 50 MIPS) and has a 24-bit single-ended or differential analog-to-digital converter with analog multiplexer and two 8-bit current output DACs. And the system had been programmed using C51 language. The MCUs is interfaced with a personal computer (PC) using a Zigbee wireless sensor network, and the developed

FIG. 9. (Color online) The signal sequence diagram.
IV. EXPERIMENTS AND RESULTS

A. The bias voltage setup

The SSPM multiplication ratio (gain) depends on the electric field applied across the avalanche layer. Normally, the higher the reverse voltage, the higher the gain will be. However, if the reverse voltage is increased further, a voltage drop occurs due to the current flowing through the device series resistance and load resistance, causing the voltage applied to the avalanche layer to decrease. On the other hand, the higher gain will lead to a higher noise level. So, we use 27.5 V bias voltage in practice.

B. LED intensity control

We set the apparent intensity of the LED by driving it using a high frequency square wave with a varying duty cycle, i.e., $\tau_1$ and $T_1$ in Eq. (3a), by which the excited fluorescent intensity can be controlled. We can also set the tested signal strength by setting a varying integral time constant and period, i.e., $\tau_2$ and $T_2$ in Eq. (5a). Experiments were conducted using a varying duty cycle (1:1, 1:4,) square wave with a varying frequency (10 kHz, 20 kHz) to drive the LED. Figure 10 shows the photograph of the signal sample system and the measured signal waves is shown as Fig. 11.

In practice, we can set the parameters $\tau_1$, $T_1$, $\tau_2$, and $T_2$ by the keyboard of the device or by the interface of the PC to match the actual test conditions.

C. Explosives vapor detection

The photograph of the developed device is shown in Fig. 12. To verify its performance, we have experimented many times, the experimental results which showed that the detector has a very high sensitivity and a short response time. The following is an example of the experimental process: the lid of a vial containing 1 g TNT was used as detection samples, and in order to demonstrate the sensitivity of the device, the lid was washed several times before test; three continuous tests were made, and the result was shown as Fig. 13. In the curve in Fig. 13, there are three peaks, which stand for the different sample time of the lid: the first one is sampled about 2 s, the second is about 3 s, and the third is about 5 s. From the experiment and real-life test, it is seen that the detector...
possesses extremely high sensitivity and rapid response to the vapor of the explosives. Its estimated detection limit (threshold concentration) to TNT is less than $10^{-15}$ g/ml.\textsuperscript{21}

Additionally, from the point of real-life applications, detection of NACs-contained explosives is almost unaffected by the presence of common organic solvents, daily chemicals, and fruit juice, such as benzene, toluene, methanol, ethanol, perfume, and apple juice. This is because the response of the film to these compounds is much weaker than that to the explosives and thereby their interference can be easily screened by the set up of a suitable threshold. False alarm can be only found when the system is not properly used, for example, contamination of the sampling unit or un-suitable set up of a threshold.

V. CONCLUSION AND DISCUSSION

In this paper, we dealt with the development of a portable, low-power, and low-cost vapor phase explosive detector based on a specific materials-based fluorescent sensing film. The instrument has been designed by using a LED as the light source and a SSPM as the photosensitive device. As the components chosen in the design are not as good as those used in the commercially available instruments, such as Edinburgh Instrument FLS920, some special circuits with superior performances and advanced signal processing techniques, e.g., low noise preamplifier, code pulse-width modulation technique, and cross-correlation-based signal conditioning circuit, have been employed to suppress the system’s noise and guarantee the performances of the system. With all these efforts, even though the system is much smaller and cheaper, it shows comparable sensing performances to the machine, which is commercially available but of much larger size and cost more than 10 times.

Caron \textit{et al.}\textsuperscript{5} have done the efficient work in the ultra trace detection of explosives. Comparison to the work conducted by Caron \textit{et al.}, the design adopted and the components used in the construction of our instrument are very different from those employed by them, and furthermore, the sensing component is also different. Among others, the most important fact is that our system is superior because of its much faster response to the presence of NACs, specifically a few seconds to a few minutes.

As the device is developed for the ultra trace detection of explosive vapors, it is very difficult to quantify the concentration of an explosive in vapor phase. The actual readout of the detector is not the real density value and it is only a reference value, which is relative to the initial parameter we set. The future work is to find an appropriate way to calibrate the test data and make it be consistent with the real value.

Another problem is that the effect of temperature and humidity on the performance of the device is not fully investigated, and this effect will be studied later on.

As a continuation of our efforts in the past, we have been trying to develop even more and powerful fluorescent sensing films for the detection of variety of poisonous, harmful, incendive, and explosive compounds, and combine them into sensor arrays, which should possess multiple sensing abilities. Based on these sensing platforms, we will develop the new system that can detect many kinds of compounds and have a better performance. This is our main objective in the future.

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19See http://www.photonique.ch/Prod_0611B4MM.html for basic performance parameters and performance graphs of the chip SSPM_0611B4MM.