Chloroform-sensing properties of plasmonic nanostructures using poly(methyl methacrylate) transduction layer

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The design and development of a sensitive, fast and selective chloroform vapour sensor based on a poly(methyl methacrylate) (PMMA) transduction layer and a plasmonic nanostructures transducer is presented. The PMMA layer swelled when it was in exposure to the vapours, which would in turn bring in an extinction efficiency change in the localised surface plasmon resonance (LSPR) spectrum for triangular silver nanoprisms. The LSPR spectral response to chloroform and other vapours was measured by a UV–vis spectrometer in real time. Experiment results showed that the PMMA–LSPR sensor indicated a sensitivity of 4.76×10^{-5} ppm^{-1} and a detection limit of 21 ppm. A fast, stable and reversible response was observed during positive and negative test cycles upon variations of the environment in the gas cell between clean air and saturated chloroform contained air. The PMMA–LSPR sensor also showed good selectivity of chloroform when it was exposed to vapours with different functional groups. It has been demonstrated that plasmonic nanostructures coated with PMMA transduction films can be applied to chloroform sensing and vapour classifying applications.

1. Introduction: In recent years, volatile organic compounds (VOCs) have been commonly involved in environment detection as a result of their extensive use in industrial and commercial applications. Owing to their toxic characteristics, the potential risk of accidental leakage is very dangerous for human health and the environment. Development of rapid, sensitive and well selective VOC sensors becomes an important issue and attracts growing interest among researchers [1, 2]. VOC sensors are schematically composed of two parts, namely a transduction layer and a transducer device [3]. The transduction layer is a sensitive element, which interacts with the surrounding environment, collects and concentrates vapour molecules, with its surface undergoing some physical changes. The transducer device detects these changes and converts them into an interpretable signal. In this sense, a fast, sensitive and reliable transducer is the heart of a successful sensor design.

Transducers of VOC sensors generally operate under different principles, and various techniques have been developed in the past year. Widely used are electrical techniques like those usually referred to as semiconductor transducers (e.g. ZnO, SnO_2) [4] and piezoelectric transducers [5]. However, they have high power consumption [6] or are easily influenced by the exterior environment [7]. Transducers of optical technique such as surface plasmon resonance (SPR) [8] are good alternatives because of their improved durability and stability. However, because of the complexity of the instrumentation, SPR sensors are cumbersome to implement in large arrays and it is hard to meet the highly miniaturised and high-throughput screening applications [9]. The SPR phenomenon is also found in noble metal nanoparticles (MNPs), namely the localised SPR (LSPR). The LSPR spectrum can be readily measured by a UV–vis spectrometer and does not require a delicate optical coupler [10]. Much cheaper and more easily integrated in large arrays, this sensing method becomes a potential candidate for providing improvements over the current SPR sensing technique [9].

In the past few years, a significant amount of research has been published on LSPR techniques for the detection of biomolecules [11, 12] and chemicals [13, 14]. Also, several papers have been published in gas-phase molecule detection. Chen and Lu [15] proposed MNPs as transducers for VOC sensing applications because of their unique LSPR properties. In 2010, Van Duyne and co-workers [16] reported the first inert gas sensing studies based on LSPR spectroscopy. Moreover, our previous study demonstrated good adsorption of alcohol vapours and the LSPR responses to ethanol, acetone, benzene, hexane and propanol for triangular nanoprisms [17]. In each of these LSPR sensors, MNPs are acting as both the transduction element that absorbs the VOCs molecules and the transducer that converts vapour quantities to refractive index changes. Although the large surface area of MNPs effectively facilitated quantitative adsorption, there is no specific selectivity towards VOCs inherently.

In this Letter, a sensitive and selective VOCs sensor, namely a PMMA–LSPR sensor, is developed by integrating a poly(methyl methacrylate) (PMMA) transduction layer with a silver triangular nanoprisms transducer. Chloroform was chosen to be the analyte because of its toxic characteristic for human living and its selective adsorption on PMMA films. Silver triangular nanoprisms were fabricated by the nanosphere lithography (NSL) technique, and the PMMA transduction layer was prepared using the spin-coating method. The optical response to chloroform vapour was measured by a UV–vis spectrometer in real time, and the sensitivity and repeatability were further analysed. The selectivity of the PMMA–LSPR sensor was also investigated by observing the maximum spectral response to the presence of six vapours with various functional groups, and effects that influence the selectivity were also discussed.

2. Experiment setup and method: K9 glass substrates ($20 \times 10 \times 1.5$ mm) were used to provide good light transmissivity and a physical support for the triangular nanoprisms. The NSL nanofabrication technique is employed here to create the regular ordered silver triangular nanoprisms array. The substrates were prepared and the nanostructures were fabricated following the process in our previous publication [17].

A layer of PMMA thin film over triangular nanoprisms was prepared by the spin-coating method. PMMA is an excellent transduction material for optical sensors because of its characteristics such as long-term stability, low optical loss and no particular light absorption in the visible spectrum. By using a microsyringe, a small

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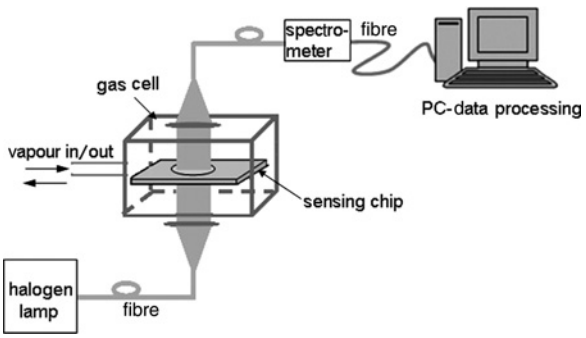


Figure 1 *Schematic presentation of detection system*

amount (~50 µl) of PMMA solution (AR-P639.04, ALLRESISIT Inc., Germany) molecules (molecular weight is 50 kg/mol, refractive index is 1.49) in ethyl lactate was dispensed onto the fabricated transducer from a distance of 5 mm above the chip surface. A sample of PMMA film was prepared with a spin speed of 6000 rpm for 30 s. The thickness was measured to be 42 nm by a profiler (NewView 7300, Zygo Inc., USA).

A detection system was constructed to test the optical response of the LSPR sensor upon being exposed to the vapour samples of different concentrations. The prepared sensing chip was fixed in the small airproof gas cell, which was especially designed and fabricated with a specific kind of polymer to enhance light transmission. In addition to vapour flowing, the gas cell also provided a platform where the PMMA transduction layer collects and concentrates the test vapour molecules. As shown in Fig. 1, optical responses were studied by transmitting the light source (HL2000 halogen lamp, Dong Yang Fan Co. Ltd, Korea) into one fibre system, reaching the gas cell to illuminate the sensing chip. The transmitted light was then collected by another optical fibre system and was measured and recorded using the spectrometer (QE65000, Ocean Optics Inc., USA) with associated data processing software (SpectraSuite, Ocean Optics Inc., USA).

3. Results and discussion: Triangular silver nanoprisms have been directly grown on the glass substrate surface using the presented approach, as shown in the scanning electron microscopy image in Fig. 2*a*. Triangular nanoprisms were arranged regularly in a hexagonal form, indicating a uniform size and shape. According to the surface profile measurement, the array period was 430 nm and the average side length of the triangle is ~115 nm. This regular pattern will give an excellent LSPR spectrum with a considerable resonance peak that is sensitive to small changes of refractive index nearby. According to the spectrometer test results shown in Fig. 2*b*, the peak of the LSPR spectrum of the bare transducer locates at 626 nm, with a maximum extinction efficiency of 0.28.

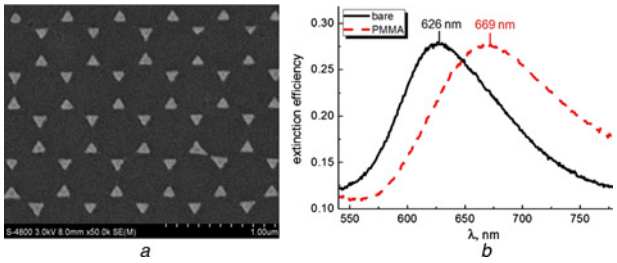


Figure 2 *Scanning electron microscopy image of fabricated transducer (Fig. 2a); LSPR spectra test for bare transducer and 42 nm PMMA functionalised transducer in clean air (Fig. 2b)*

In the case of the transducer functionalised with PMMA film, the LSPR spectrum presents a resonance peak at 669 nm, differing by 43 nm from that for bare nanoprisms. This great red-shift was induced by the large refractive index of the PMMA layer covered on the surface of triangular nanoprisms. It should also be noted that because of the slight optical absorption of PMMA film, the maximum extinction efficiency is 0.275, a little lower than that for bare nanoprisms.

3.1. LSPR spectrum response to chloroform vapour concentrations: The optical response of the prepared sensor to various chloroform concentrations was tested. Fig. 3 gives examples of the spectral responses of the PMMA–LSPR sensor in five different concentrations of chloroform vapour. The extinction efficiency in the spectra is found to be more sensitive compared with the peak wavelength to vapour concentrations. This can be explained in terms of both changes in the refractive index of the PMMA layer because of chloroform adsorption and increases in film thickness because of film swelling [18]. The refractive index of chloroform is 1.45, slightly smaller than that of PMMA film and the effect of chloroform adsorption on the refractive index is not expected to be significant. Thus, shifts in peak wavelength can be hardly observed. It is therefore believed that the changes in extinction efficiency are primarily caused by increases in PMMA film thickness because of swelling.

As indicated in Fig. 3*b*, the extinction efficiency of the LSPR spectrum decreases from 0.275 to 0.242 gradually when the concentration varies from 0 to 680 ppm, suggesting a linear relationship. Hence, we define a sensitivity m to directly evaluate the sensing performance of PMMA–LSPR sensors

$$m = \Delta E^*/\Delta C \tag{1}$$

where ΔE^* denotes the maximum extinction efficiency changes in the LSPR spectrum with ΔC being the corresponding concentration variations. According to the best-fit straight line in Fig. 3*b*, the chloroform sensing sensitivity is $\sim 4.76 \times 10^{-5}$ ppm^{-1}. The detection limit, determined by LSPR sensor sensitivity m as well as the operational resolution ($\sim 10^{-3}$) of the applied spectrometer, is ~21 ppm for the chloroform test in our experiment based on the results in Fig. 3. It will be improved if a spectrometer with greater test resolution is used.

3.2. Response time and repeatability: The dynamic LSPR spectral response to chloroform vapour was examined in both positive and negative response. Saturated chloroform vapour flow was switched on for 30 s for the positive response and switched off for 330 s for the negative response by closing or opening the riser of the gas cell. A fast and reversible response of LSPR spectra was observed upon variation of the environment in the gas cell between saturated chloroform vapour-containing air and clean air, as shown in Fig. 4.

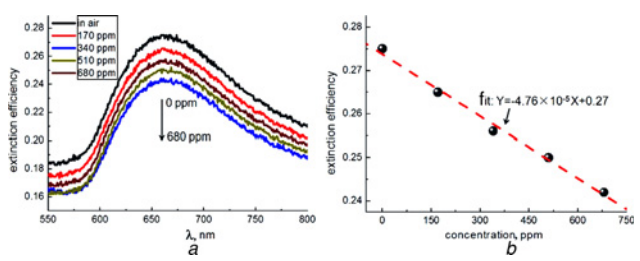


Figure 3 *LSPR spectral response to chloroform of different concentrations (Fig. 3a); sensitivity calibrated with five different chloroform concentrations (Fig. 3b)*

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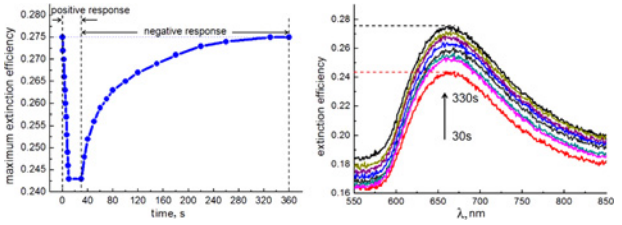


Figure 4 *Time response to saturated chloroform vapour of PMMA–LSPR sensor (Fig. 4a); LSPR spectra during negative test cycle (Fig. 4b)*

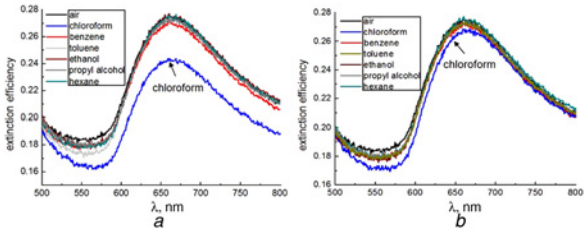


Figure 5 *Spectral responses of PMMA–LSPR sensor to six saturated VOCs (Fig. 5a) and six VOCs of 100 ppm in concentration (Fig. 5b)*

According to Fig. 4*a* which plotts maximum extinction efficiency against time, during the positive response test cycle, the maximum time required for reaching the saturated value on maximum extinction efficiency change (response time) was considered to be very fast, namely 10 s. After that, the maximum extinction efficiency will stay unchanged at 0.245 before a negative response test cycle begins, indicating a stable optical response of the LSPR sensor. During the negative response test cycle, which begins at 30 s, spectrum recovery is observed, as indicated in LSPR spectrum movements in Fig. 4*b*. The time of reaching the initial condition (recovery time) was tested to be 300 s, which is much longer than the response time.

The large difference between response time and recovery time can be explained in two aspects. Firstly, the mixing time (diffusion rate) of chloroform and air are different for the two reverse responses. When switched on, the concentration of chloroform in the tiny closed gas cell grows from 0 ppm to saturate in a short time; when switched off, saturated chloroform vapour diffused into the exterior environment with a concentration in the gas cell grows from saturated to ~0 ppm in a much longer time. Secondly, the interaction of chloroform and PMMA can be described as: $A + X \underset{K2}{\overset{K1}{\rightleftharpoons}} AX$ [19], where A denotes chloroform and X is PMMA. $K1$ and $K2$ are reaction rate constants for the absorption and desorption process, and they obviously differ greatly in values. Moreover, the thinner the PMMA transduction layer, the bigger the values. Therefore the response time and recovery time will be improved when a much thinner PMMA transduction layer is used for the LSRP–PMMA sensor.

3.3. Selectivity: Six VOCs with various functional groups were chosen to test the selectivity of the LSPR sensor. Besides the chloroform vapour, we also included two compounds with the phenyl group (i.e. benzene and toluene), two alcohols namely ethanol and propyl alcohol and one hydrocarbon compound, hexane. These VOCs are often mixed with chloroform in the environment. Fig. 5*a* shows the maximum spectral response to the presence of six saturated vapours. It was found that the LSPR sensor was much more sensitive to chloroform vapour than to the five other analyte vapours, indicating good selectivity of the sensor.

The selectivity in more cases was evaluated by the spectral response to vapours of the same concentration. The test results of the spectrum responses to six analyte vapours of 100 ppm are shown in Fig. 5*b*. Although the distinction of spectral response between chloroform and other VOCs is not as obvious as that shown in Fig. 5*a*, relative good chloroform selectivity can be also observed.

To resolve the selective characteristics of the sensor in a better manner, we further summarised the magnitude of extinction efficiency response to the concentration of the six test vapours, as shown in Table 1. According to the calculated sensitivity, it is easily found that chloroform vapour is much more sensitive than the five other vapours. Besides, it can also be observed that the response of compounds with the phenyl group is greater than that with the alcohol and hydrocarbon group. This selectivity can be attributed to the specific affinities between the functional groups of VOCs and the transduction layer of the sensor [20]. Moreover, as mentioned in previous publications, a higher refractive index of VOCs also contributes to the selectivity of the PMMA–LSPR sensor [21]. Although the test results in this experiment are only preliminary, the response analysis showed that the PMMA–LSPR sensor could provide initial vapour classifications.

4. Conclusions: A sensitive, rapid and well selective chloroform vapour sensor based on triangular silver nanoprisms and PMMA transduction films has been developed and the experimental results are evaluated. The sensor works based on PMMA layer swelling and LSPR spectrum responses because of exposure of the vapours. The optical response of the PMMA–LSPR sensor to vapours like chloroform, benzene and ethanol of various concentrations was measured by a UV–vis spectrometer. A maximum extinction efficiency change in spectrum can be observed as the concentration of the test vapours varies. The sensitivity, defined as the slope of the best fitting line for maximum extinction efficiency change against vapour concentration function, is $\sim 4.76 \times 10^{-5}$ ppm^{-1} for chloroform. The detection limit, determined by the sensitivity of the sensor and the extinction efficiency resolution of the applied spectrometer, is ~21 ppm in our experiment. A fast (10 s for response time), stable and reversible optical response was observed during the positive and negative test cycle for chloroform sensing. The PMMA–LSPR sensor also shows good selectivity to chloroform vapour in the presence of six vapours with different functional groups, and this selective property is explained based on different chemical affinities between the test vapours and PMMA films as well as refractive index contributions. This study indicates that the PMMA–LSPR sensors have great potential for practical applications in indoor monitoring and outdoor detection.

Table 1 Comparison of optical response of six test vapours

VOCs	**Chloroform**	Benzene	Toluene	Propyl alcohol	Ethanol	Hexane
refractive index	**1.446**	1.501	1.497	1.385	1.362	1.375
saturated response, %	**3**	0.5	0.2	0	0	0
100 ppm response, %	**0.5**	0.2	0.1	0	0	0
sensitivity, 10^{-5}/ppm	**4.76**	1.36	1.28	0	0	0

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