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Determination of trace glyphosate in water with a prism coupling optical waveguide configuration

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ABSTRACT

We herein discuss a prism coupling hollow-core metal-cladded waveguide (HCMW) sensor that uses ultrahigh-order modes (UHM) for sensitive absorption detection of glyphosate. In our method, modified chromogenic glyphosate in the hollow-core serves as guiding medium for high-power wave propagation. Prism coupling is employed to generate attenuated total reflection (ATR) dips of the UHM. The depths of the dips are closely related to the extinction coefficient of chromogenic glyphosate. A glyphosate detection limit below1.4 nm/l is experimentally demonstrated with low consumption and solution-free operation. The calibration curve has been found linear in the concentration range of 0.0–5.0 nm/l.

To improve outputs of agricultural crops, organophosphorus pesticides have been extensively researched [1–3]. Most are harmful to human health because they interfere with the synthesis of neuraminidase and its function [4]. Glyphosate (N-(phosphonomethyl)glycine) is an organophosphorus pesticide developed in 1971 by Monsanto. It has since become one of the most widely used herbicides in the world because of its excellent performance in weed control [5], its relatively low toxicity to mammals [6], and the introduction of transgenic plants with an anti-glyphosate capability [7], such as soya, corn, canola, wheat, sugar beets, and cotton [8,9]. However, glyphosate is a toxic endocrine disruptor, and its accumulation will impact the environment [10] and pose a threat to human health [11]. Specifically, the connection is broken between the enzymatic hydrolysis of n-acetyl neuraminic acid residues and α2–3, α2–6 or α2–8 key from glycoproteins and oligosaccharides [12]. Therefore, monitoring small concentrations of glyphosate in food and drinking water has gained increasing importance.

Analytical methods for the quantitative determination of low glyphosate concentrations in water and other environmental matrices include electrothermal atomization atomic absorption spectrometry [13,14], flame atomic absorption spectrometry [15,16], fluorimetry [17,18], and fade spectrophotometric methods [19]. These spectroscopic techniques are sensitive and accurate, but suffer from system complexity, long testing times, and the need for laboratory environments. Other widely used methods are molecularly interactive, such as enzyme-linked immunosorbent assays [20–23], capillary electro-phoresis [24,25], and surface plasmon resonance (SPR) [26,27]. Cartigny et al. [28] used ^{31}P and ^{1}H nuclear magnetic resonance (NMR) to detect the presence of glyphosate in biological fluids to within 0.005 ~ 1 μg/L. Recently, Xiaokang Ding et al. [18] employed oligopeptide functionalized SPR to detect glyphosate at a limit of 0.58 μM. Although SPR is much more sensitive than NMR, the immobilization of binding partners creates several issues. In particular, the molecular binding site may be near the surface [29] and induce steric hindrances that could affect binding energetics and/or kinetics, and the surface layers often exhibit decreased activity over time.

Here, we discuss a prism coupling hollow-core metal-cladded waveguide (HCMW) sensor for glyphosate detect. In this design, double metal claddings are used that exhibit a negative dielectric constant. This implies that the effective refractive index of guided modes can be $0 < N < 1$, which is usually prohibited for conventional guided and SPR modes [30]. Chromogenic glyphosate in the hollow core serves as guiding medium for high-power wave propagation,

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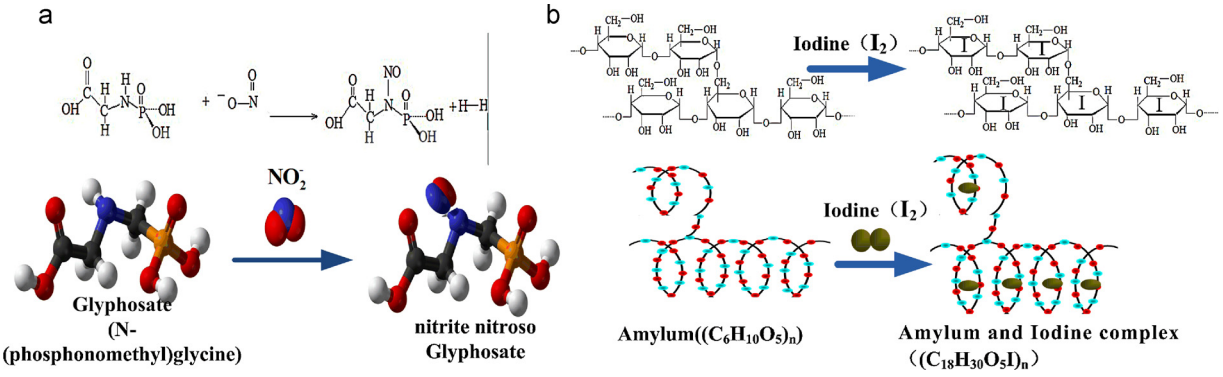

Fig. 1. Schematic illustration of proposed reaction mechanism: (a) reaction between glyphosate and nitrite nitroso ion; (b) reaction between amylum and iodine.

making it possible to excite highly sensitive ultrahigh-order modes [31] *via* small incident angle coupling. It is shown that glyphosate concentrations as low as 1.4 nm/l (1.4 nm) are unambiguously identified within several minutes. In addition to the relatively high detection efficiency, the platform has a small analyte volume, it is label-free and performed in real-time, and it is environmentally friendly, compact, and inexpensive.

1. Experimental

1.1. Chemicals

Glyphosate (N-(phosphonomethyl)glycine), sulfuric acid (H_2SO_4), sodium nitrite ($NaNO_2$), potassium iodide (KI), and amylum were analytical reagent grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Reactions are depicted in Fig. 1.

1.2. Preparation and measurement

Sulfuric acid (3 mol/l) was prepared by diluting 40 ml of acid in 140 ml of water, and a sodium nitrite solution was prepared by dissolving 1.2 g in 1 l of water. Samples are stored in a cold refrigerator. Chromogenic reagents were potassium iodide and amylum, which were prepared by dissolving 1.0 g of potassium iodide in 1 ml water and 4 mg of amylum in 1 ml water. A 1.42 μmol/l glyphosate stock solution was prepared by dissolving 0.2513 ± 0.0001 g of glyphosate in 250 ml water. A 1.42 nmol/l glyphosate standard solution was prepared by diluting 1 ml of glyphosate stock solution in 100 ml water. The glyphosate standard solutions were prepared by appropriate dilution by water. All the water was de-ionized in an ultra-pure water system (Milli-Q Direct-Q8, EMD Millipore Corporation, Billerica, MA, USA).

The glyphosate reaction process flow chart is show in Fig. 2(a). The reaction occurs at pH 4.0 ± 0.3, and forms a complex having an absorption spectrum as shown in Fig. 2(b), which was obtained with a UV-vis spectrophotometer (TU-1901, Purkinje General, Beijing, China). The absorption peak is at 532 nm, thus a laser emitting at this wavelength was used for sensing.

1.3. HCMW sensor chip

As shown in Fig. 3(a), the HCMW is composed of three parts: (i) an optical prism with the vertex angle of 150°, (ii) an 40 nm silver film deposited on the bottom side of the prism to act as a coupling layer and the cladding of the hollow-core guide, (iii) a ring-like glass gasket with the thickness of 1 mm sandwiched between

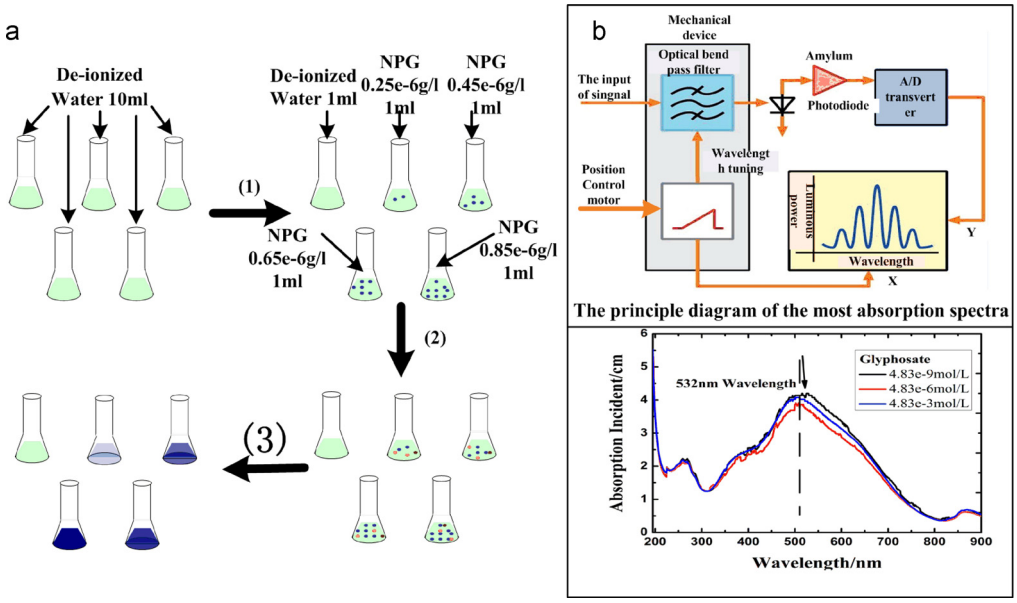

Fig. 2. (a) Schematic illustration of procedure. (1) In each bottle, the same amount of glyphosate solution with different concentrations was injected, followed by (2) 0.5 ml of a 1.2 g/L $NaNO_2$ solution and 6 ml of a 3.0 mol/L sulfuric acid solution. After 20 min to ensure full reaction between sodium nitrite and glyphosate, (3) 2.0 ml of potassium iodide solution and 2.0 ml of amylum solution were added, respectively, and shaken immediately. (b) Absorption spectrum of chromogenic glyphosate.

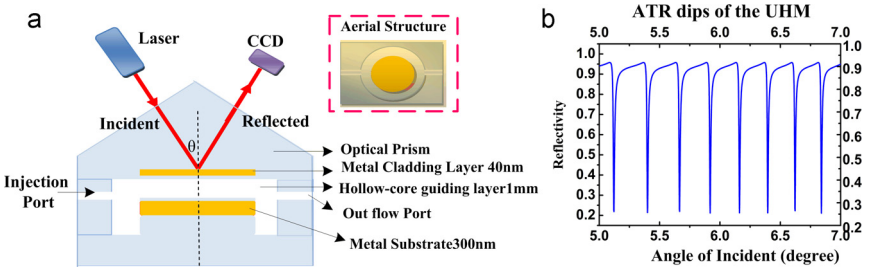

Fig. 3. (a) Schematic diagram of the HCMW sensor, where the analyte serves as the guiding layer and is sandwiched between two silver films (cladding layers). (b) Calculated reflectivity of the UHM with respect to the incident angle (effective RI N); the simulation parameters are given in the text.

the prism and the glass substrates with a rounded glass island of 980 μm thick to form a sample cell, and (iiii) a >300 nm silver film deposited on the top side of the glass island to act another cladding of the guide. The silver cladding films are sputter-deposited in vacuum (SPF-210B, Anelva Corporation, Tokyo, Japan). Analyte to be detected in the sample cell with 20 μm thick acts as the guiding layer of the HCMW. All the glass slides in the HCMW sensor (BK7, $n = 1.516$, Shanghai Optics Engine Inc. Shanghai, China) are optically contacted together to meet the conditions of parallelism.

1.4. Experiment configuration

A schematic of the experimental arrangement is shown in Fig. 4. To excite the UHM of HCMW, a transverse-excitation-polarized laser beam from a 30-mW, 532-nm solid-state laser (MW-SL-532/30 mW, Shanghai Optics Engine Inc. Shanghai, China), with a 0.4 mrad divergence (a 1-mm aperture further reduces the divergence) impinges on the prism bottom. The sample solution is pumped through the cell by an injector with a pipe having a 0.5 mm inner radius. A computer-controlled $\theta/2\theta$ goniometer performs angular scans while the intensity of the reflected beam is detected by a photodiode. The attenuated total reflection (ATR) dip is recorded for a specific UHM.

1.5. HCMW action principle

According to electromagnetic field boundary conditions, the reflectivity [32] can be expressed as:

$$R_{\min} \propto \left\{ 1 - \frac{4Im(\beta^0)Im(\Delta\beta^L)}{[Im(\beta^0) + Im(\Delta\beta^L)]^2} \right\} \quad (1)$$

where $Im(\beta^0)$ and $Im(\beta^L)$ are intrinsic and radiative damping, respectively [33]. $\beta^0 = k_0 N = k_0 n_0 \sin\theta$ is the propagation constant for an effective index N of the guided modes, $k_0 = 2\pi/\lambda$ is the wavenumber of light with wavelength λ in free space, and θ is incident angle. The intrinsic damping is the transmission loss of the guided wave, which is closely related to the extinction coefficient of the guiding layer [34]. Radiative damping is the leakage loss of the guided wave back into free space, which is strongly dependent on the thickness of the top silver film. When

$$Im(\beta^0) = Im(\Delta\beta^L) \quad (2)$$

the minimum reflectivity of the system $R_{\min}$ becomes zero. Eq. (2) also represents the matching condition for the excitation of the guided modes [35]. There are two methods to determine the analyte concentration with optically resonant mode-based sensors. One is to determine the real part of the complex refractive index of the analyte and the other is to determine the extinction coefficient of the analyte (imaginary part of the complex refractive index). In the first case, an increase in analyte concentration increases the refractive index of the solution, which increases the resonance angle and shifts the ATR dips to the right. In the second case, the depth of the dip will rise or fall with an increased extinction coefficient of the analyte. Whether the depth rises or falls is dependent on the difference between the intrinsic and radiative damping. Two different situations are shown in Fig. 5, where the parameters of the waveguide are fixed except for the thickness of the top silver film.

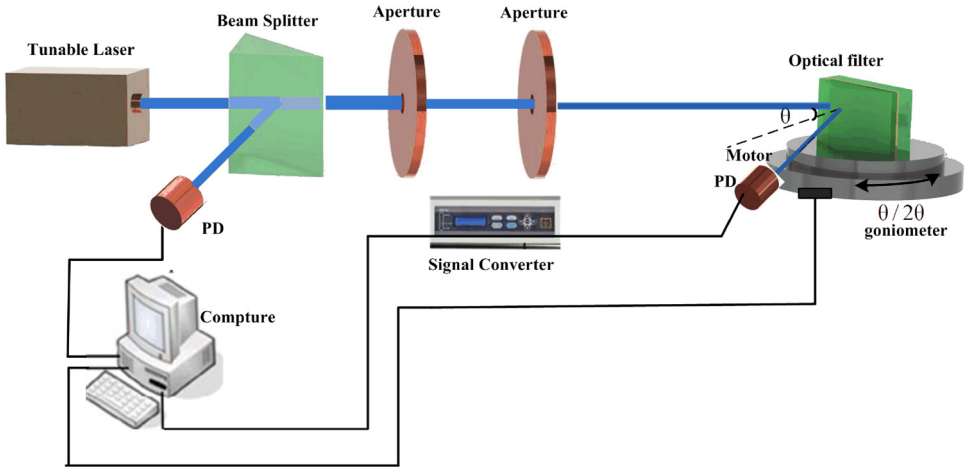

Fig. 4. Experimental configuration for glyphosate detection.

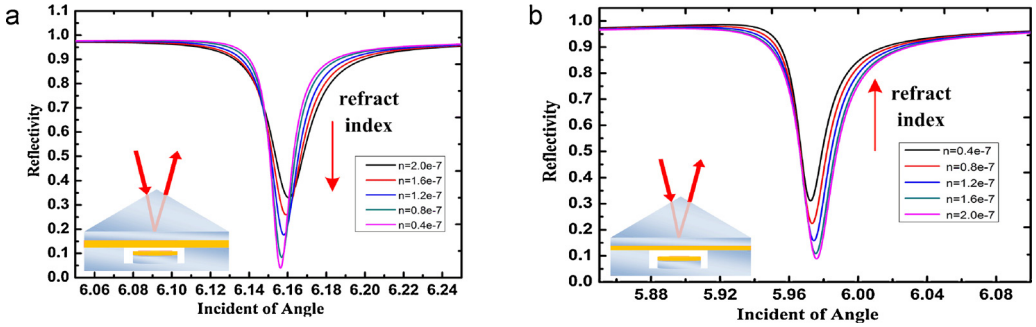

Fig. 5. R_{min} dependence on the sample concentrations with two different thicknesses of the top silver film ($\lambda = 760$ nm) (a) thickness $d = 40$ nm, $\varepsilon = -17.8 + 0.78i$, R_{min} increases with increasing extinction coefficient. (b) thickness $d = 18$ nm, $\varepsilon = -17.8 + 0.78i$, R_{min} decreases with increasing extinction coefficient.

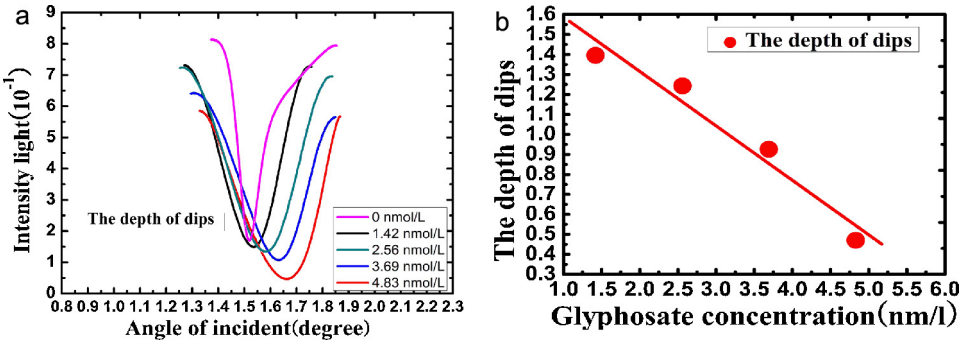

Fig. 6. (a) ATR spectra for different glyphosate concentrations; (b) depths of the ATR dips at coupled angles for different glyphosate concentrations. The concentration response curve is the line fit.

2. Results and discussion

2.1. Detection of glyphosate

Fig. 6(a) shows the ATR spectra for the glyphosate analyte. As the concentration increases from 0.00 to 4.38 nm/l, the depth of the dip at the coupled angle decreases from 0.169 to 0.046. Fig. 6(b) shows the linear relationship between the minimum reflectivity and the concentration of glyphosate from 1.42 to 4.38 nm/l, where $R_{min} = (1.81 \pm 0.014) - (0.23 \pm 0.046) * C_{(NPG)}(\text{nm/l})$. The limit of detection is 1.42 nM $C_{(NGP)} = (m_{(NGP)}/M_{(NGP)}V) = (2.0 \times 10^{-4}\,\text{g}/156\,\text{g/mol} \times 1\,\text{l}) = 1.42\,\text{nm/l} = 1.42\,\text{nM}$. The sample size is the small volume of the sensor cell.

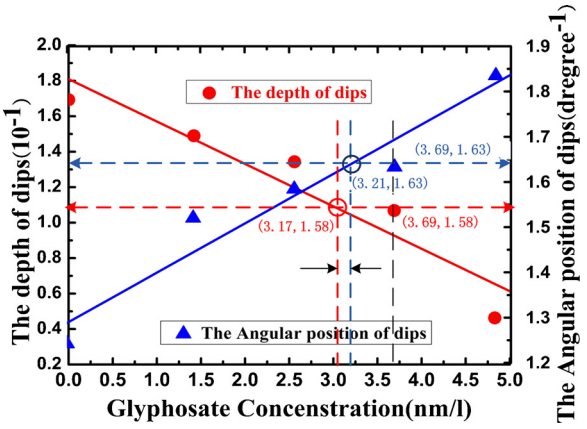

Fig. 7. Numerical simulations of the linear responses, along with experiment results.

2.2. Dip position and dip depth

As shown in Fig. 7, the dip position increases and the dip depth decreases with increasing glyphosate concentration. Two linear responses for glyphosate concentrations over 0.0–5.0 nm/l result, where:

$\theta = (1.29 \pm 0.051) + (0.21 \pm 0.017) * C_{(NPG)}(\text{nm/l})$ and $R_{min} = (1.81 \pm 0.014) - (0.23 \pm 0.046) * C_{(NPG)}(\text{nm/l})$. From these dependences the results of numerical simulations are depicted in Fig. 7.

The red and blue lines represent the linear responses of the dip depths and dip positions, respectively, and the red circles and blue triangles are the respective experimental results. The detection schemes for glyphosate concentrations are in good agreement.

This work describes a simple, convenient and sensitive method to detect glyphosate. HCMW is used as a sensor to improve the detection sensitivity of the change in extinction coefficient associated with chromogenic glyphosate. The detection limit was accurately determined to be 1.42 nm/l (1.42 nM). In general, this system is potentially able to detect other materials, and requires very small sample sizes.

Acknowledgments

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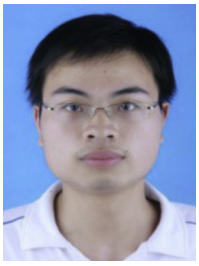
Biographies



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