

Plasmonic Optical Fiber-based Sensor for Monitoring Toxic Nitrophenolic Compounds

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Abstract. The detection of nitrophenolic compounds, including 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP), is essential because of their significant environmental persistence and toxic effects on living organisms. In this work, we present a sensitive and selective approach based on a polyaniline (PANI)-coated fiber optic-surface plasmon resonance (FO-SPR) sensor for real-time monitoring of these pollutants in aqueous environments. The PANI layer was fabricated directly onto the gold-coated sensing region of an unclad optical fiber via chemical oxidative polymerization, ensuring uniform coverage and strong adhesion. The PANI layer was characterized using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), which provided detailed information on its morphological features and chemical composition. Moreover, the sensor performance was evaluated by tracking the shifts in the SPR wavelength upon analyte interaction. The developed sensor exhibited a clear linear response to both target compounds, achieving detection limits of 33 nM for 4-NP and 14 nM for 2,4-DNP. Moreover, the proposed FO-SPR sensor offers key advantages, including low cost, label-free operation, and rapid response, making it highly suitable for continuous environmental monitoring. Overall, this FO-SPR sensing technology represents a promising and practical solution for detecting hazardous nitrophenolic contaminants in water systems.

Key-words: Chemical polymerization; fiber optic plasmonic sensor; nitrophenolic compounds; polyaniline.

1. Introduction

Nitrophenolic compounds represent a significant class of environmental contaminants, widely recognized for their persistence and toxicity in the ecosystems. Among them, 4-nitrophenol (4-NP) and 2,4-dinitrophenol (2,4-DNP) are of particular concern due to their widespread use in industrial processes, including the production of dyes, pharmaceuticals, pesticides, and explosives [1]. Their toxicological profile includes mutagenic behavior and the potential to disrupt endocrine functions, raising serious concerns regarding both ecological balance and human health [2]. Consequently, the monitoring of such pollutants has become a priority in environmental analysis and public safety [3].

Conventional detection methods, including high-performance liquid chromatography and mass spectrometry, are well established for the high-accuracy, high-sensitivity identification of nitrophenolic compounds [4]. However, these techniques often require sophisticated instrumentation, extensive sample preparation, and trained personnel, which limits their applicability for rapid, on-site analysis [5]. Moreover, the need for real-time monitoring under dynamic environmental conditions has driven the development of efficient, cost-effective sensing strategies.

In this context, optical sensing technologies have emerged as promising tools for environmental monitoring. Surface plasmon resonance (SPR), in particular, has attracted considerable attention for its ability to detect changes in refractive index at a metal-dielectric interface with high sensitivity [6]. When coupled with fiber-optic (FO) configurations, FO-SPR sensors offer additional advantages, including compactness, flexibility, and remote sensing capability [7]. These features make FO-SPR systems especially suitable for in-situ applications, where continuous, real-time measurements are necessary. The performance of the FO-SPR sensors can be further enhanced through surface functionalization with materials that provide selective interactions with target analytes [8]. Conductive polymers have proven to be highly effective in this context, owing to their tunable chemical properties and strong affinity for specific molecular species. Among these materials, polyaniline (PANI) stands out as a versatile and attractive candidate. It combines environmental stability with ease of synthesis and exhibits unique electronic properties that enable interactions with electron-deficient compounds, such as nitrophenols [9].

This study explores the development of a PANI-functionalized FO-SPR sensor for the detection of 4-NP and 2,4-DNP in aqueous environments. The PANI layer was fabricated directly onto the gold-coated sensing region of an unclad optical fiber via chemical oxidative polymerization, ensuring uniform coverage and strong adhesion. Additionally, the polymer film was characterized using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), which provided detailed information on its morphological features and chemical composition. Moreover, the sensor performance was evaluated by tracking the shifts in the SPR wavelength upon analyte interaction. The proposed PANI-functionalized FO-SPR sensor exhibited a clear linear response to both 4-NP and 2,4-DNP, achieving detection limits in the nanomolar range. In conclusion, the proposed FO-SPR sensing platform provides a rapid, sensitive, and practical solution for detecting hazardous nitrophenolic pollutants in environmental samples.

This manuscript differs from the previously published CAS 2025 Proceedings paper [10] through several significant improvements and additions. The Introduction and Results and Discussion sections have been substantially expanded to provide a more comprehensive context and deeper interpretation of the findings. New XPS measurements have been performed, thoroughly analyzed, and incorporated into the manuscript, adding valuable insight into the surface properties of the sensor. In addition, Fig. 3 and Fig. 4 from this paper have been revised and updated to improve clarity and better support the presented results. Finally, the reference list has been enriched with additional relevant literature, strengthening the scientific background and positioning of the

study within the field.

The structure of this paper is structured as follows. Section 2. outlines the materials used, the fabrication process of the FO-SPR sensors, the methods employed for surface characterization, and the procedures for detecting the nitrophenols compounds. Section 3. presents the main experimental results, including SEM and XPS analyses as well as the data obtained for nitrophenol detection using the prepared FO-SPR sensors. Finally, Section 4. summarizes the key findings and provides the overall conclusions of the study.

2. Materials and Methods

2.1. Reagents and materials

All the reagents, including aniline, 4-nitrophenol, 2,4-dinitrophenol, hydrochloric acid, ammonium persulfate, acetone, and toluene, were bought from Merck. The multimode optical fiber with a silica core diameter of 400 μm was supplied by Thorlabs. A magnetron sputtering device (Quorum Q150R ES) was used to coat the FO with a thin gold film.

2.2. Fabrication of the FO-SPR sensor

A 0.5 cm section of the optical fiber (FO) was stripped of its protective jacket and cladding using a mechanical stripper, then cleaned with acetone. Subsequently, a 50 nm layer of gold (Au) was deposited onto the exposed fiber surface via magnetron sputtering. Polyaniline (PANI) films were then formed on the Au-coated FO-SPR substrates through chemical oxidative polymerization. To achieve this, the Au-coated fibers were first immersed in an aqueous solution containing 1 M ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and 1 M hydrochloric acid (HCl). A 0.1 M aniline solution in toluene was then added to the mixture. The sensors were maintained in this solution for 5 minutes at 25°C. The appearance of a green film confirmed the successful deposition of PANI in its emeraldine form on the Au-coated FO. After polymerization, the sensors were rinsed and dried prior to use.

The FO-SPR portable sensing system is illustrated schematically in Fig. 1 as outlined in our prior publications [13]. In summary, the setup includes an ultraviolet-visible spectrophotometer (AvaSpec ULS2048, Avantes), a tungsten-halogen light source (AvaLight, Avantes), a bifurcated fiber-optic cable, and the interchangeable FO-SPR sensor. The spectrophotometer is connected to a laptop and is used to detect the light reflected from the FO sensing tip. Any variation at the Au surface of the sensor leads to a shift in the SPR signal. Finally, the as-prepared PANI/Au-coated FO sensors were used to detect 4-NP and 2,4-DNP at various concentrations in deionized water.

2.3. FO-SPR surface characterisation

A field-emission scanning electron microscope (FE-SEM, JEOL 7600F) and an X-ray photoelectron spectroscopy setup (XPS, Thermo Fisher Scientific ESCALAB Xi+) were used to investigate the surface morphology and chemical composition, respectively, of the PANI film deposited on the Au-coated FO-SPR sensors. The resulting XPS spectra were interpreted with reference to the NIST X-ray Photoelectron Spectroscopy Database and The Handbook of X-ray Photoelectron Spectroscopy by J. F. Moulder et al. [11].

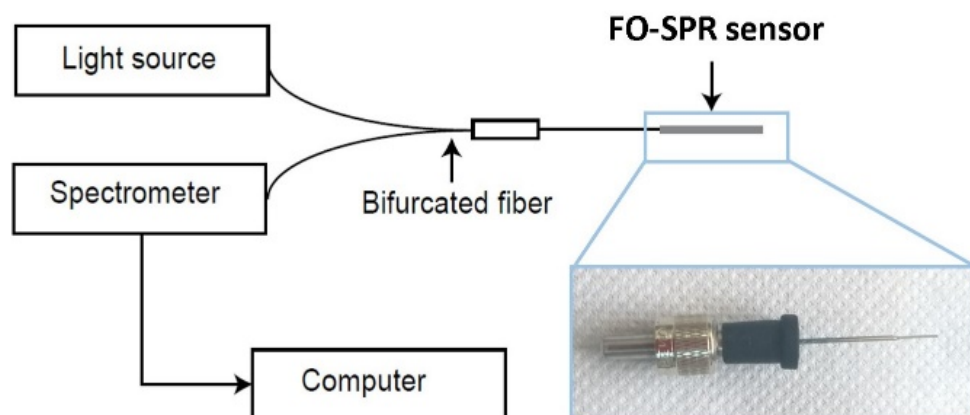


Fig. 1. Schematic of the FO-SPR experimental setup, together with an image of the fabricated Au-coated FO-SPR sensor inserted into the SMA connector.

2.4. Detection of the nitrophenolic based compounds

The PANI/Au FO-SPR sensors were utilized to detect various concentrations of 4-NP and 2,4-DNP in deionized water, ranging from 0, 0.06, 0.12, 0.25, 0.5 to 1 μM . For each concentration, the FO-SPR sensor was immersed in the solution for 1 minute. Each nitrophenol concentration was measured in duplicate to ensure reliability. The sensitivity of the PANI/Au FO-SPR sensor to 4-NP and 2,4-DNP was assessed by plotting the shift in SPR wavelength against the corresponding analyte concentration and fitting the calibration curve with a linear model. The limit of detection (LOD) was determined using the formula $3\sigma/S$, where σ is the standard deviation of the lowest measured concentration, and S is the slope of the linear regression line [12].

3. Results and Discussion

3.1. SEM and XPS measurements

Fig. 2 presents SEM micrographs of the surface of an Au-coated FO-SPR sensor following a 5-minute chemical oxidative polymerization of PANI at room temperature. The PANI film exhibits a uniformly roughened texture on the Au-coated FO-SPR sensor, as illustrated in the inset of Fig. 2.

Corresponding XPS spectra of the FO-SPR surface presented in Fig. 2 are shown in Fig. 3. The XPS survey spectrum confirms the presence of carbon (C), nitrogen (N), oxygen (O), chlorine (Cl), and gold (Au) on the sample surface (see Fig. 3A). The Au 4f and Au 3d signals originate from the gold substrate used during the measurement, while C, N, O, and Cl are associated with the polyaniline (PANI) film synthesis and the residual precursor.

High-resolution XPS spectra of the C 1s and N 1s regions were recorded to investigate the chemical environments of the elements in pristine PANI (see Figs. 3B and 3C). The C 1s spectrum (Fig. 3B) was deconvoluted into several components characteristic of the polymer backbone. The dominant peak located at ~ 285.5 eV corresponds to C–C/C=C bonds in the aromatic rings of the polyaniline chain. A second component centered at ~ 287.7 eV is attributed to C–N bonds, which are characteristic of the benzenoid and quinoid units of PANI. Additional contributions observed at ~ 286.4 eV, ~ 287.1 eV, and ~ 288.9 eV are assigned to carbon atoms bonded to heteroatoms, corresponding to C–OH/C–O/C=N, C=O, and O–C=O functional groups, respectively. The

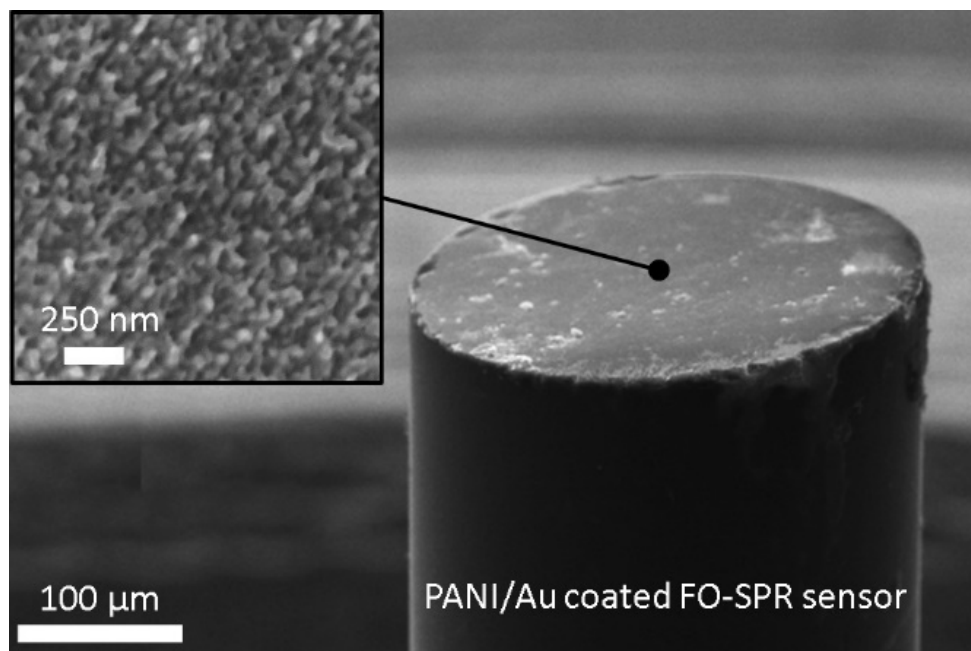


Fig. 2. SEM micrograph of the Au-coated FO-SPR sensor surface after PANI oxidative chemical synthesis for 5 minutes at room temperature. The inset is a magnified SEM image of the PANI/Au-coated FO-SPR surface.

presence of these oxygen-containing species is commonly attributed to slight surface oxidation of the polymer or to adsorption during sample preparation and exposure to air.

The N 1s spectrum (Fig. 3C) reveals multiple nitrogen chemical states characteristic of polyaniline. The component located at ~ 398.8 eV is assigned to imine nitrogen ($=N-$) associated with the quinoid segments of the polymer chain. The peak centered at ~ 399.6 eV corresponds to amine nitrogen ($-NH-$) belonging to the benzenoid units. A higher binding energy component at ~ 401.0 eV is attributed to protonated nitrogen species ($-N^+$), which indicates the presence of the doped emeraldine salt form of PANI. Finally, a weak contribution around ~ 402.0 eV can be assigned to oxidized nitrogen species, possibly originating from interactions with oxygen or slight surface oxidation.

Overall, the coexistence of imine, amine, and protonated nitrogen species confirms the typical emeraldine structure of polyaniline, where benzenoid and quinoid units coexist along the polymer backbone.

3.2. Detection of nitrophenolic-based compounds

The PANI-coated Au FO-SPR sensors were employed to detect concentrations of two nitrophenol compounds, specifically 4-NP and 2,4-DNP, dissolved in deionized water [10]. The concentrations tested were 0, 60, 120, 250, 500, and 1000 nM, allowing for the evaluation of the sensor's sensitivity and performance across a broad range of analyte levels.

The SPR spectra for varying concentrations from 0 to 1000 nM of 4-NP using a PANI/Au-coated FO sensor are plotted in Fig. 4A. Furthermore, Fig. 4B shows the linear calibration curve acquired after 1 minute of detection of each 4-NP concentration with the PANI/Au-coated

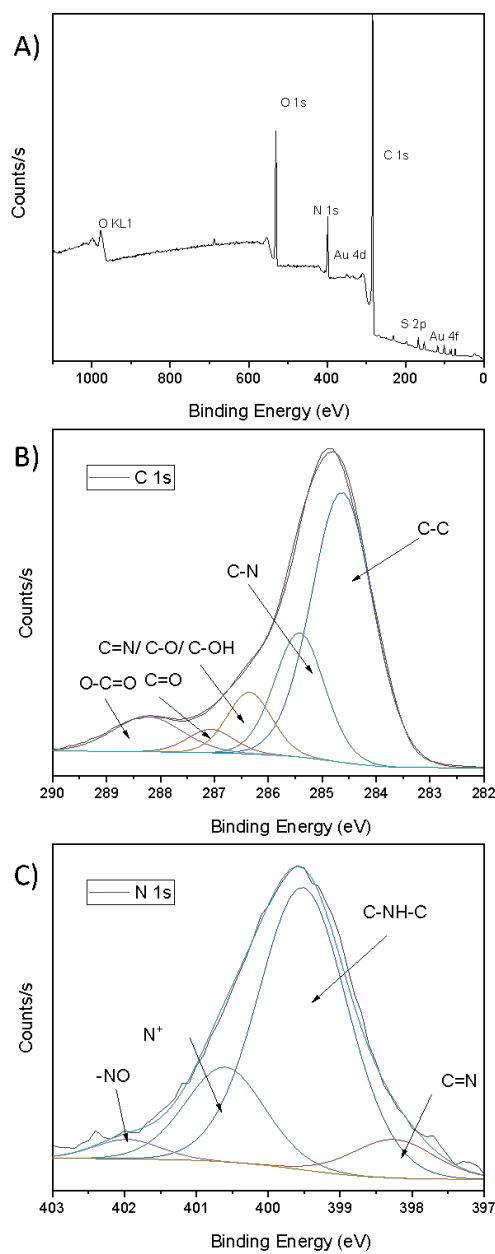


Fig. 3. XPS spectra: (A) Wide scan of the synthesized PANI film via chemical oxidative polymerization; (B) PANI C 1s and (C) PANI N 1s core-level spectra of the film obtained by chemical synthesis.

FO-SPR sensor. The linear relationship was given by a regression equation with a coefficient of determination (R^2) of 0.979 and a slope of 0.018 nm/nM. As previously noted, the slope value corresponds to the sensitivity of the sensor, which was determined to be 0.018 nm/nM. Additionally, the limit of detection (LOD) was estimated at 33 nM.

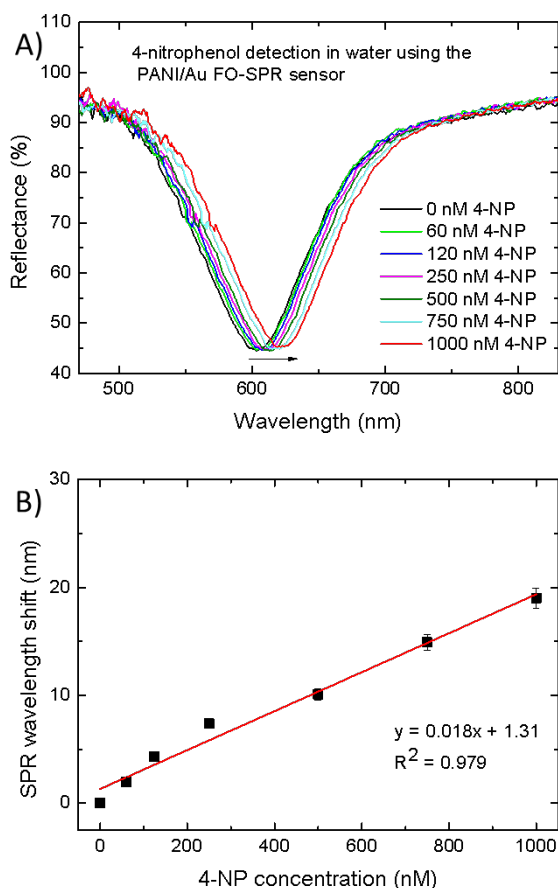


Fig. 4. Detection of 4-NP in water. A) SPR spectra for varying concentration from 0 to 1000 nM of 4-NP using a PANI/Au-coated FO sensor; B) SPR wavelength shift variation with the 4-NP concentration.

The SPR spectra for varying concentrations from 0 to 1000 nM of 2,4-DNP using a PANI/Au-coated FO sensor are plotted in Fig. 5A. Moreover, Fig. 5B shows the linear calibration curve acquired after 1 minute of detection of each 2,4-DNP concentration with the PANI/Au-coated FO-SPR sensor. The linear relationship was described by a regression equation with a coefficient of determination (R^2) of 0.978 and a slope of 0.026 nm/nM. The LOD was estimated to be 14 nM.

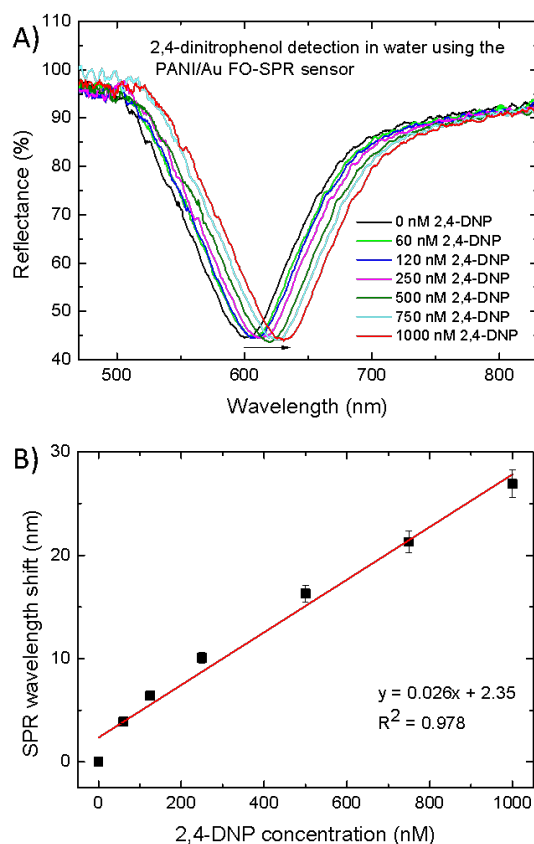


Fig. 5. Detection of 2,4-DNP in water. A) SPR spectra for varying concentration from 0 to 1000 nM of 2,4-DNP using a PANI/Au-coated FO sensor; B) SPR wavelength shift variation with the 2,4-DNP concentration.

As shown in Figs. 4B and 5B, the PANI/Au-coated FO-SPR sensor exhibits higher sensitivity to 2,4-DNP than to 4-NP. This might be attributed to the presence of two electron-withdrawing nitro groups in 2,4-DNP, which enhance π - π interactions and hydrogen bonding with the PANI backbone. The lower LOD and higher slope of the calibration curve for 2,4-DNP confirm its stronger affinity for the PANI-coated surface.

Table 1 presents a comparison between FO-SPR sensors, HPLC, and UV-Vis spectroscopy used for analytical detection of nitrophenolic compounds (i.e., 4-NP) [10, 14, 15]. The FO-SPR sensor developed herein demonstrates significantly lower limits of detection (33 nM for 4-NP and 14 nM for 2,4-DNP), outperforming both HPLC (2.5 μ M for 4-NP) and UV-Vis spectroscopy (100 nM – 1 μ M for 4-NP) [10]. In terms of analysis time, the FO-SPR sensor enables real-time monitoring within seconds to minutes, whereas HPLC requires considerably longer processing times (20-60 minutes per run), and UV-Vis analysis typically takes 10-20 minutes. Additionally, the FO-SPR system offers high portability, making it suitable for on-site applications, unlike HPLC systems, which are bulky and laboratory-bound, and unlike UV-Vis instruments, which provide only moderate portability. From a cost perspective, the FO-SPR sensor is relatively economical,

with low to moderate expenses primarily for reagents and maintenance. In contrast, HPLC incurs high operational costs due to solvent consumption and column use, while UV-Vis falls in a moderate cost range. Furthermore, the FO-SPR method requires minimal sample preparation, allowing direct analysis of aqueous samples. In contrast, HPLC requires extensive pretreatment steps, including extraction and filtration, and UV-Vis requires only moderate preparation, including pH adjustment and dilution.

Table 1. The detection of nitrophenolic compounds (i.e., 4-NP) using FO-SPR sensors, HPLC and UV-Vis spectroscopy

Parameter	FO-SPR sensor	HPLC	UV-Vis spectroscopy
Limit of detection	33 nM 4-NP; 14 nM 2,4-DNP herein	2.5 μ M 4-NP	100 nM – 1 μ M 4-NP
Analysis time	Real-time (sec. to min.)	20-60 min. per run	10-20 min. (depending on the cuvette)
Portability	High	Low	Medium
Cost per analysis	Low to moderate (reagents, maintenance)	High (solvents, columns)	Medium (standard cuvettes, light sources)
Sample preparation	Minimal (aqueous samples were directly tested)	Extensive (extraction, filtration)	Moderate (pH adjustment, dilution)

Overall, the results demonstrate that the FO-SPR sensor offers a compelling combination of high sensitivity, rapid response, portability, and reduced sample preparation, making it a highly competitive alternative to classical analytical methods for the detection of nitrophenolic compounds.

4. Conclusions

A PANi/Au bilayer FO-SPR sensor capable of detecting trace levels of both 4-NP and 2,4-DNP in aqueous solutions was developed. The method is label-free, highly sensitive and selective, and enables real-time monitoring. Future work will focus on integrating this sensor into a portable device and validating its performance in complex environmental samples.

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