

DEVELOPMENT OF NANO-POROUS SILICON PHOTONIC SENSORS FOR PESTICIDE MONITORING

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We present the results of research and development of photonic sensors based on nano-porous silicon (pSi), which are used for determination of low concentration of atrazine and alpha (α); beta (β) isomer endosulfan concentration in aquatic environment. The limit of detection (LOD) of sensors is of 1.4 pg.mL^{-1} , $0.32 \text{ }\mu\text{g.mL}^{-1}$ and $0.21 \text{ }\mu\text{g.mL}^{-1}$ for atrazine and α - and β -endosulfan, respectively. Experiment shows that atrazine's half-life in the aqueous phase ranges from 60 to 150 days in the humic acid and/or water, respectively. These pSi-sensors can contribute to the detection of persistent pesticides in the aqueous medium with short measuring time and high sensitivity for improving agricultural and food productions with sustainable environmental protection.

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1. Introduction

The wide-spread use of organic solvents, fertilizers and pesticides in industry and agriculture globally over the last sixty years has strongly polluted groundwater and soil, resulting in diseases and hardship in humans and animals [1]. The first step in the removal of harmful contaminant from soil, groundwater and food is the effective detection of these damaging elements. Photonic technology offers a lot of promise in the area of pollution sensing and prevention by exploiting novel properties of photonic materials and their structures. Photonic sensors are capable of detecting bio- and/ or chemical pollutants at very short time (at second or minute levels), high sensitivity, and high specificity. Among the photonic sensors for aqueous environment control and protection, the sensors based on porous silicon (pSi) structures have many advantages such as low-cost, small size, high sensitivity, label-free and reversible [2-4].

Porous silicon microcavity structures (PSMCs) allow realizing convenient and low-cost optical devices for the detection of organic solvents and pesticide content with very low concentration in aquatic environment, so that PSMC devices show promise for a simple and portable instruments for liquid-phase environment pollutant monitoring. Owing to high specific surface area [5], pSi is an ideal transducer material for sensors of liquids [6-8] and vapors [9,10]. The principle of pSi-sensors is a determination of the optical spectral shift caused by refractive index change of the pSi-layers in the device due to the interaction with liquid and/or gas. It is based on the principle that the response of the sensor is only dependent on refractive index and therefore lacks specificity for the studied substances. It is possible to use a physical or chemical method to overcome this drawback. A commonly used chemical and/or electrochemical method is the functionalization of the surface of silicon nanocrystals in the porous layers [11,12]. The

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functionalized pSi-sensors by chemical and/or biological materials have a problem for reversible use that increased their cost for applications. In other hand, the sensitivity and selectivity of optical sensors can be enhanced by designing suitable structural parameters such as thickness, porosity, number of pSi-layers in the device [13], by creating a stress on the sensor surface [14], and by combining chemico-physical method [15-17].

The attractive features of pSi-structures are not only the high surface area but also a controllable fabrication of porous layers via electrochemical anodization, allowing for a diversity of pores of different morphology and size from few nanometers to microns, which gives a good chance to preparing complex multilayer structures through variation of the current density, electrolyte formation, temperature, etching time and Si-substrate resistivity. These properties of pSi-structures cannot principally be achieved in other porous materials (e.g., aluminum oxides, zeolites), making pSi an ideal material for sensing applications [8]. A simple, cheap optical sensor for detecting and quantifying the presence of pesticides in water and in humic acid was reported by De Stefano et al. [18]. They used pSi and allowed permeation of liquid into its pores. pSi-structures are highly sensitive to the refractive index of a liquid within pores, which affects its optical properties. Anderson et al. [19] reported that pSi is capable of detecting the refractive index change to as low as 7×10^{-5} . The pSi optical chemical sensing in an aqueous environment has attracted great attention in the last decade due to its applications in agriculture, food quality, and drinking water control. Unfortunately, the reversibility of pSi-sensors for aqueous environment detection is not stable from their skeletal structures, which may be changed in cleaning process. The durability and stability of reversible sensors depends on their preparation process.

In this paper, we present the results of research and development in the field of photonic sensors based on nano-porous silicon (nano-pSi), which is used for detection of pesticides such as endosulfan and atrazine with low concentrations in aqueous medium. The pSi-microcavity photonic sensor was able to detect ultra-low concentration of atrazine, and alpha (α); beta (β) isomer endosulfan concentration in water using the liquid-drop method. These pSi-photonic sensors can contribute to the detection of pollutants such as persistent pesticides in solution for improving agricultural and food productions with sustainable environmental protection.

2. Materials and Methods

2.1. Preparation of pSi-microcavity sensors

pSi-microcavities were fabricated by an electrochemical method in a process that was presented in detail in our work [20,21]. For converting the surface of the silicon nano-crystals from hydrophobic to hydrophilic, we oxidized the as-prepared sample in an ozone atmosphere for 45 min. by using the ozone generator (H01 BK Ozone with a capacity of 500 mg/hour). In addition, the controlled process of pSi-oxidation improved the durability of skeletal structure and for long life time of aging pSi. Cross-sectional and top view images of the pSi-microcavity were obtained using a high resolution field-emission scanning electron microscope (FE-SEM) S-4800.

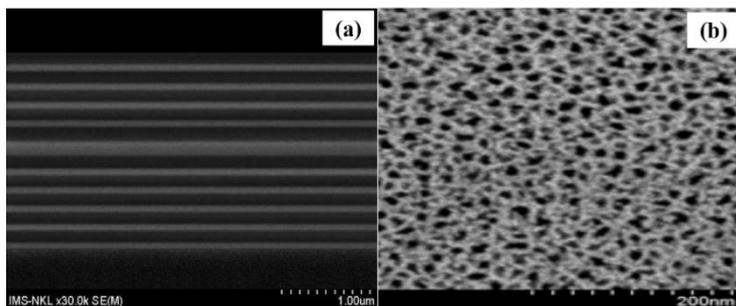


Fig. 1. (a) Cross-section and (b) SEM plan-view images of a porous silicon microcavity design in the $(HL)^{4.5} LL (HL)^3$ structure

Fig. 1 shows cross-section and plan-view images of the microcavity based on $(HL)^{4.5}LL(HL)^{5.0}$ pSi-multilayer structure, where H and L labels correspond to high and low refractive index layers, respectively, 4.5 and 5.0 mean four and half and five pairs of HL in the structure. We choose structure with few pairs (from 3/3.5 to 5/5.5 pairs) of HL, because this gives a good reflectivity spectrum, possibly controlling the porosity of layers, and easily repeatable electrochemical etching process. The thicknesses of high and low refractive layers were 70-73 nm and 90-95 nm with accuracy of ± 2 nm, respectively. This structure was obtained from anodization current density of 15-17 mA/cm² and 50-55 mA/cm² and with etching time of 5.5 sec. and 3 sec. in a 16% hydrofluoric acid (HF) solution for high and low refractive index layers, respectively. The porosity of layers can be controlled by HF concentration and current density, which influenced on the effective refractive index of pSi-layers [4]. In our experiments, we choose the porosity contrast of pSi-layers of 30-40 for liquid-drop measurement method. For measurement of reflective spectra of the samples, we used an ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer (Varian Cary 5000) with a corrected resolution of 0.05 nm and a portative spectrometer (USB-4000, Ocean Optics) with resolution of 0.2 nm, respectively. The light source was a Tungsten Halogen light Source (HL-2000 Family, Ocean Optics). From experimental results we calculated refractive indices of about 2.1 and 1.75 for high and low refractive index layers, respectively. Figure 2 demonstrates the reflection spectra of pSi-microcavity sensor in the air and in pure water. The wavelength shift measured by spectrometer USB-4000 is of 39.8 nm in water and this value is kept for referent data of used sensor for liquid-drop measurement method.

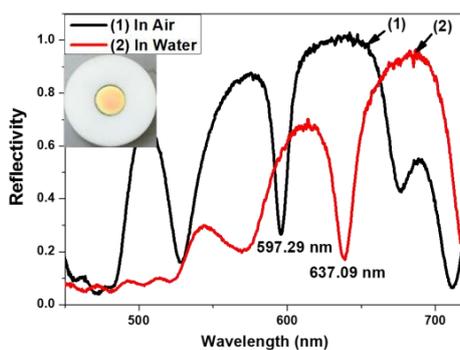


Fig. 2. The reflection spectra of pSi-microcavity sensor in air (curve 1) and in pure water (curve 2). Inset: Image of pSi-sensor with surface area of about 0.8 cm².

2.2. Experimental setup

For the liquid-drop method, the measured solutions have directly permeated through the pSi-sensors by the immersion of sensor into solution and/or drop of small solution on the sensor surface. The scheme of experimental setup is shown in Fig.3, in which would be controlled the temperature of sensor chamber for stability and repeatable of measurement. The sensor response is given by the shift of the resonant wavelength of the microcavity when sensors are immersed in the liquid. We investigate the dependence of the wavelength shift on solvent concentration at constant temperature of sensor chamber. In our experiment, we use an optical fiber splitter R200-7-VIS-NIR for light irradiation to sensor and for collecting the light reflected from this one. We have also used a LM35D integrated circuit for measuring the temperature in the sensor chamber. For an experimental data run, it takes 5 min. to 7 min. A standard deviation of the wavelength shift is obtained from the average value of 5 experimental data runs.

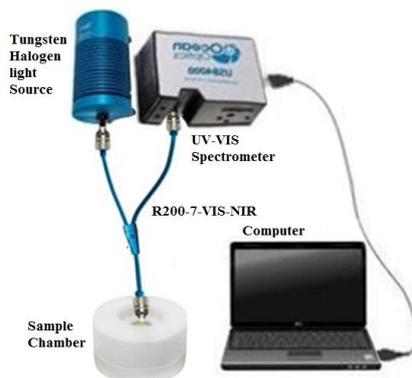


Fig.3. Schematic of the pesticide concentration measurement by liquid-drop method using the porous silicon microcavity sensor

3. Results and discussion

The basic characteristics of the PSMC and the resonant wavelength shift ($\Delta\lambda$) caused by the ambient refractive index (n) were determined experimentally by using a series of liquids with known refractive indices. The effective refractive index of the nano-pSi layer immersed into organic solvent would increase due to the substitution of air with liquid in the pores and consequently the optical thickness of layer increased. In the result, the resonant wavelength shift would be depended upon the refractive index value of the organic solvent [4], and calculated sensor sensitivity ($\Delta\lambda/\Delta n$) of about 120 nm/RIU for the porosity contrast of pSi-layers of 38. The Spectrophotometer Varian Cary 5000 is able to detect a wavelength shift of 0.05 nm, and then the minimum detectable refractive index change in the pSi-layer is of 2.5×10^{-4} .

Experiment shows that after complete evaporation of organic solvent, the reflectance spectra of the sensors return to their original waveform positions (as in the air). In our case the evaporation of organic solvents in open air at room temperature was completed for 50 minutes, but this process can occur for some tens of seconds when the samples were in the vacuum chamber with 10^{-1} torr. That means, the change of sensor reflectance spectra are temporary and it is useful for reversible optical sensing. For prevention of temperature dependence of effective refractive index of pSi-sensor, we have to keep the sensor temperature in the constant value from 14°C to 28°C .

3.1. pSi-sensor for detection of endosulfan concentration in water

Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine-3-oxide) is an organochlorine insecticide and acaricide. Endosulfan is a popular chlorinated insecticide used in many countries because of its favorable toxicological action and low persistence in comparison with other organochlorinated pesticides. Endosulfan can enter the human body by ingestion; inhalation and gives to an estrogenic effect in humans [22] and it became a highly controversial agricultural chemical due to its acute toxicity, potential for bioaccumulation, and role as an endocrine disruptor. Accidental and suicidal poisoning with endosulfan is widely reported in literatures [23,24].

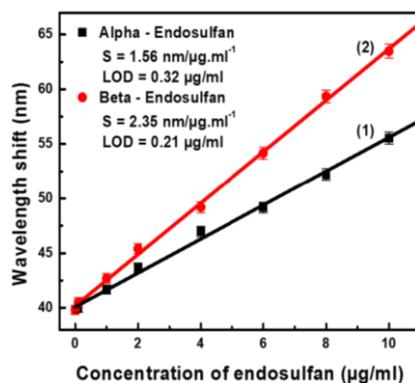


Fig. 4. Wavelength shift of pSi-sensors as a function of α - and β -endosulfan concentrations in water

Endosulfan has alpha (α) and beta (β) isomers, which are toxically different and it is non-volatile compound. We have used the liquid-drop technique for detection of endosulfan in water. In our study, the low concentrations of α - and β -endosulfan solutions were obtained by dilution from mixture in water. Concentration of α ; β -endosulfan in water is in the range between $0.1 \mu\text{g.mL}^{-1}$ and $10 \mu\text{g.mL}^{-1}$ in our experiment. Fig. 4 presents the results of detection of α - and β -endosulfan concentration in water. The endosulfan of α - and β - isomers can be specified by the different slope of the dependence between wavelength shift and endosulfan concentrations. The LOD of pSi-sensor is obtained of $0.32 \mu\text{g.mL}^{-1}$ and of $0.21 \mu\text{g.mL}^{-1}$ for α - and β -endosulfan, respectively. This LOD is still low level of detection in comparison with gas chromatography method [25] (about $0.12 - 0.15 \text{ ng.mL}^{-1}$), but the pSi-sensor method has advantage in the low cost, simple sample preparation process and that is suitable for detection of endosulfan in the out-door field work.

3.2. pSi-sensor for detection of atrazine concentration in water

Atrazine (ATZ, 1-chloro-3-ethynamino-5-isopropylamino-2, 4, 6-triazine) is a triazine herbicide commonly used to control weeds in the agricultural crops. Atrazine appears as a white solid, colourless, non-volatile, poorly soluble in water. It was reported that the indiscriminate use of atrazine may have harmful effect on the aquatic organism, the environment and human health, especially the desethylated atrazine (DEA), desisopropyl atrazine (DIA) and diaminochlorotriazine (DACT) are very toxic [26]. For the detection of atrazine in water, we should use liquid-drop method, because this herbicide is non-volatile compound. In the previous work [19], we had shown the method for preparation of atrazine solution stock in the range between 2.15 and $2.15 \times 10^6 \text{ pg.mL}^{-1}$ (10^{-11} - 10^{-4} M of atrazine in water) for experiments. We have measured wavelength shift of the pSi-sensor with conditions: (i) atrazine in pure water and (ii) atrazine in an aqueous solution of a humic acid (HA, 0.2 mg.mL^{-1}) extracted and purified from soil. Humic acid solutions were chosen to represent systems similar to natural conditions where water-containing pesticides also dissolve organic matter as component [17]. When the pSi-sensor was exposed to water (with refractive index of 1.3326) and to humic acid (with refractive index of 1.3541), the reflectance spectra promptly shifted toward longer wavelengths by about 39.8 nm and 46.5 nm, respectively, in comparison with air. After analyzing the resonant wavelength shift in the reflectance spectra of pSi-sensor in water and humic acid conditions, we performed the wavelength shift measurements for the detection of atrazine pesticide in mixtures of water and humic acid during their exposure to different concentrations (2.15 - $2.15 \times 10^6 \text{ pg.mL}^{-1}$). It is remarkable that the repeatability and reproducibility of sensor response mainly depends on the capability of filling the pSi-pores. The concentration of atrazine in the solution is determined by the wavelength peak shift of the pSi-sensor, and the capability of filling the pores is tested by the repeatability of measured values. As shown by result of our previous work [9], the resonant peak shift of pSi-sensor for atrazine concentrations in water from 2.15 to $2.15 \times 10^6 \text{ pg.mL}^{-1}$ is of 21.1 nm, but the sensor response was non-linear in this large range of atrazine concentration. The

wavelength shift of pSi-sensor is linearly increased in the very low concentration of atrazine (2.15-21.5 pg.mL^{-1}) in our measurement with total wavelength shift of 6.4 nm. Many investigations reported that atrazine in the aqueous phase had been degraded by time [27,28] and atrazine's half-life in the aqueous phase and ground-water resources ranges from tens to some hundred days (for example, the atrazine's half-life is from 41 to 237 days in the literature [27]). We measured atrazine concentration from the same mixture samples after keeping it for six months for obtaining atrazine's half-life in the aqueous environment. The atrazine solution was kept in the close box under natural condition of temperature and lighting. The wavelength shift of sensor for both atrazine/water and atrazine/humic acid had been decreased by degradation of atrazine in the mixture samples by time.

Table 1. Resonant cavity peak shift measured from different concentrations of atrazine in water at different times

Atrazine concentration (pg.mL^{-1})	Wavelength shift (nm)	
	Before	After 6 months
0 (pure water)	39.8	39.8
2.15	40.5	40.3
4.3	41.6	40.6
8.6	43.4	41.5
12.9	44.7	42.1
17.2	46.3	42.9
21.5	47.2	43.9

Table 1 presents the measurement results of resonant wavelength shift of sensor wetted by atrazine solutions with low pesticide concentrations at different time of measurement. The sensor reproducibility had been verified by the same value of wavelength shift of the same sensor in the pure water at different times.

Fig. 5 presents a linear relation between the different concentrations of atrazine in the very low concentration range from 2.15 to 21.5 pg.ml^{-1} and the resonant peak wavelength shift for sample kept for six months. In the Fig.5, each experimental point was the average value of five independent measurements, with the accuracy representing the standard deviation. We could calculate the sensitivity of the sensor as the slope of the linear curve interpolating the experimental points. Thus, we obtained the sensor sensitivity value of 0.36-0.19 nm/pg.ml^{-1} for atrazine in water, and 0.67-0.3 nm/pg.ml^{-1} for atrazine in humic acid solution, respectively. From these measurement results, we also estimated the limit of detection (LOD), as the ratio between the instrument resolution and sensitivity. LOD numerical value is 1.39-2.63 pg.mL^{-1} and 0.75-1.67 pg.mL^{-1} for atrazine in water and in humic acid solution, respectively. The atrazine's half-life in the aqueous phase can be obtained from experiments. At the first measurement, the resonant wavelength of sensor shifted on 6.4 nm and 14 nm in water and in humic acid, respectively, when the concentration of atrazine changed from 2.15 to 21.5 pg.mL^{-1} , but after six months the wavelength shift is of 4.2 nm and 6.7 nm for the same samples (similar to atrazine concentration decreased from 21.5 pg.mL^{-1} to 8.6 and 6.8 pg.mL^{-1} in water and in humic acid, respectively). The atrazine's half-life is estimated from 60 to 150 days in the humic acid and water, when the keeping condition of atrazine solution is similarly to natural condition.

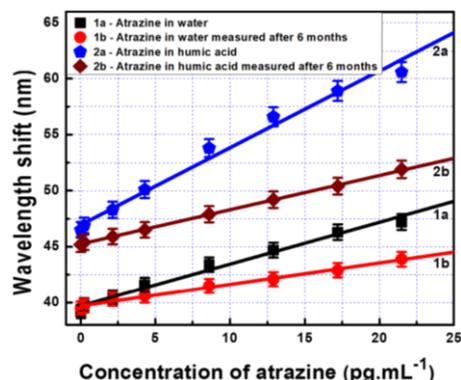


Fig.5. Wavelength shift of pSi-sensor as a function of atrazine concentration in water and humic acid solutions at different times

Table 2 presents the results of atrazine detection using different methods such as electrochemical method with different electrodes and photonic method with pSi-multilayers. LOD of electrochemical immunoassay sensor is of 0.2 pg.mL^{-1} , which is lowest in comparison of atrazine concentration founded in real underground water samples (20 ng.mL^{-1}). But the electrochemical immunoassay sensor has the disadvantage in reversible use. The photonic sensor has the LOD higher, but it has advantage in the reversible use.

Table2. Comparison of atrazine detection limits using different methods

Measurement method	Sample configuration	Limit of Detection (pg.mL^{-1})	Reference
Square wave voltammetry	Au/PJUG-HATZ/ α -ATZ	0.2	Piro et al. [29]
Impedance spectroscopy	Au/DSP/ α -ATZ-npAlm	16	Liu et al. [30]
Chronoamperometric	PhA/EI	10	Deep et al. [31]
Square wave voltammetry	Pt/PANI/Gr/ α -ATZ	43	Nguyen et al. [32]
Spectral peak shift	pSi microcavity	170	Rotiroti et al. [33]
Spectral peak shift	pSi microcavity	1.4	this work

It is remarkable that our pSi-sensor has significant improvement of magnitude of optical method for the detection of pesticide present in water in comparison with previous works (for examples with work [33]). It may be caused by different current densities and etching times for preparation of microcavity samples (i.e. difference in the porosity ratio of low- and high-refractive index layers and layer thickness) and by difference of cavity resonant wavelengths (visible versus infrared). In our case, the experiment had been done for several measurements and the results have good repetition. In addition, it was observed that, after removing the atrazine and/or endosulfan solution on the sensor surface and washing it with distilled water, the cavity-resonant wavelength in the reflectance spectra promptly returns to its original position. This is a very good quality of pSi-cavity structures, as it is helpful in the development of low-cost and reversible optical sensing devices.

4. Conclusions

In conclusion, with a rapid increase in global use of chemical fertilizers, pesticides, and organic solvents in agriculture and industry, the living environment becomes contaminated, especially in the underground water and foods. A major hurdle in the removal of harmful agents in the liquid environment is their detection in the outdoor field, which is difficult with conventional laboratory methods. Nano-photonics sensors based on photonic structures such as pSi-multilayer are capable of detecting pesticides in the aquatic environment with low concentration at very short time and high sensitivity, which adapted to the standard of safe limit of living-used water, and beverage products.

Nevertheless, challenges of pSi-sensors still remain associated with high accurate quantification and specification of various mixture liquid analyses and their reliability in the real environment. We believe that photonic sensor technique, in particular the pSi-sensor based on microcavity structures, will take advantage of the powerful tools for environment protection and pollution, which is addressed with urgency for living conditions.

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