

ENHANCED SENSOR TECHNOLOGIES UTILIZING POROUS SILICON FOR PRECISE DETECTION OF PERFLUOROCTANOIC ACID AND BEYOND

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Abstract

Single-crystalline silicon with a porous structure at the micrometer to nanometer level is currently used as a sensor for electrochemical or optical-based detection because of its exceptional optical, surface, and electronic properties. However, further research into this structured nanomaterial is ongoing and points to its potential use in other detection and sensor fields. This work focuses on the preparation and application of porous silicon sensor substrates for the dual-mode detection of perfluorooctanoic acid (PFOA). PFOA is captivating because it is a known contaminant and a substance that the human body cannot naturally excrete, which over time leads to the accumulation of this compound in the blood and organs and can cause health complications. In the first step of the realization of this work, a number of samples with different morphologies and sizes of the porous structure were prepared and the best ones were subsequently used. Then, the porous Si (pSi) surface was coated with a thin layer of gold by a vacuum sputtering method to increase the surface conductivity and introduce plasmon-active properties. The sample surface was modified with amino-containing organic moieties to ensure high surface affinity towards PFOA molecules (and their selective capture). The successful modification of the surface morphology, chemistry, and properties was verified by scanning electron microscopy (SEM) and UV-Vis. PFOA detection was subsequently performed in two modes, using electrochemical impedance spectroscopy (EIS) and surface-enhanced Raman spectroscopy (SERS) approaches. The EIS and SERS experiments showed that the sensor is reliable for determination of the PFOA in water at a significant concentration. In conclusion, the successful experiments in the detection of PFOA give us hope that the developed sensor could be used for the detection of other hazardous substances with similar size, structure, and functional groups.

Keywords: Porous silicon, nanomaterial, sensor technologies, PFOA, EIS, SERS, environmental detection, health implications

1. INTRODUCTION

In this work, a porous silicon substrate was used to detect an important industrial contaminant: perfluorooctanoic acid. As a representative of the larger group of perfluoroalkyl compounds, this substance is not only harmful to the environment, but also has major impacts on human health [1]. It often appears in wastewater from factories engaged in, for example, the production of waterproof clothing, food packaging or fire-fighting foams [2-3]. Nowadays, the use of substances and materials which form PFOA during the production process or subsequent utilization are often prohibited. PFOA as a biopersistent compound once it gets to human body, accumulates in important organs and stays there for several years, since the body is not able to sufficiently excrete it in any normal way [4-5]. These are strong enough reasons to find a reliable sensor that would be able to successfully detect and quantify the given substance even in very small amounts. PFOA is attributed, among others, to immunotoxicity, neurotoxicity, developmental toxicity and hepatotoxicity, while the basic mechanisms of their action are extensively studied [1]. Its presence in the human body is then

specifically associated with some other health problems such as increased cholesterol, thyroid diseases or cancer of kidneys and testicles [6-7]. The half-life of PFOA in the human body was calculated as 2.4 years and it is estimated to be at least 10-15 years in the environment [2]. In the European Union, a limit of 0.5 $\mu\text{g/l}$ was set for all perfluorinated substances in drinking water, valid according to the directive of January 12, 2021 [8]. Based on these numbers the emerging need for detection of PFOA has raised but the current analytical methods are challenged to detect such PFOA concentration without utilization of sophisticated analytical techniques and equipment.

Commonly, analytical laboratories use chromatographic methods together with mass spectrometry for the detection of PFOA [9]. These methods are capable of sensitive measurement even of relatively low detection limits. On the other hand, they are methods that can only be performed in laboratory conditions, using expensive and non-portable equipment. Therefore, there is a current need for easier on-site and real-time detection options, cheaper, with acceptable reproducibility and an acceptable detection limit.

The aim of this work was to use a porous silicon substrate as a dual PFOA sensor for surface-enhanced Raman spectroscopy [10,11] and electrochemical impedance spectroscopy. SERS was primarily intended to confirm the presence of PFOA in the sample using the large surface area of pSi and sputtered gold on the surface to achieve intensive SERS signal. The SERS method has considerable potential even for the detection of trace amounts of the analyte as it is very sensitive [12]. EIS was used to quickly and easily determine the amount of the desired compound. EIS can be used to analyze the complex resistance of the system and to determine the parameters of the electrochemical processes that take place on the surface of the electrode i.e. the PFOA concentration that was captured by the sensor [13]. Both, EIS and SERS methods are favoured by their sensitivity, simplicity, and variability.

2. EXPERIMENTAL

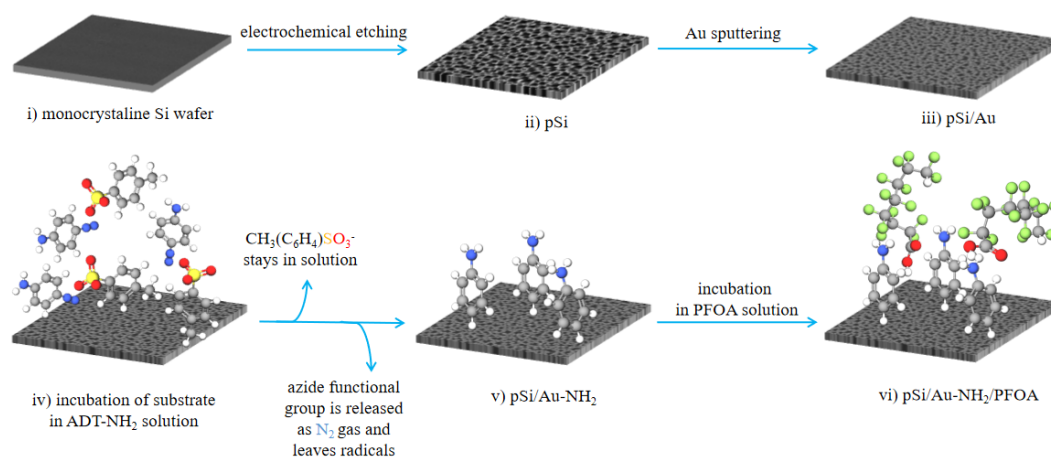


Figure 1 Schematic representation of the process of substrate production and surface modification.

First step of substrate preparation is represented by **Figure 1**. In particular i) - iii) steps include the electrochemical etching of a p-type monocrystalline silicon wafer using a solution of hydrofluoric acid under application of external bias. The Si wafers were inserted into the etching cell and connected as the anode, the platinum electrode was used as the cathode, and the 48% HF solution in DMF was used as the electrolyte. Based on literature, there were different etching conditions used during pSi preparation which shaped the morphology and porous size of the sample [14]. The appearance of porous silicon structure was monitored using SEM. The iii) step composed of sputtering of thin Au layer on porous surface to ensure surface plasmon resonance and surface electrical conductivity. During this step the pSi samples were placed in the sputtering chamber and the parameters were entered: current 40 mA, dispersion factor 1.3, and sputtering time 600 s.

For better capture of the analyte on the sensor, its surface was grafted with 4-aminobenzenediazonium tosylate (ADT-NH₂) [15]. The task was to create a bond between the substrate and analyte and ensure selective capture of PFOA. In particular, the amino group attached to pSi/Au surface through benzene ring has the ability to interact with anionic group of PFOA. For sensing, the modified substrate pSi/Au-NH₂ was placed in PFOA solution for 30 min, gently washed with distilled water, dried and subjected to SERS or EIS measurements. These steps are shown in **Figure 1 iv) - vi)**.

UV-Vis absorption spectra of the samples were obtained using an HR2000 spectrometer (Ocean Optics). Measurements were performed in the wavelength range 300–800 nm using an AvaLight-DHS light source (Avantes) in reflection mode.

The SERS spectra were collected using a ProRaman-L spectrometer (Enwave optronics) with an excitation wavelength of 785 nm and the laser power of 60 mW. A PalmSens 4 device (PalmSens BV) and PStTrace software were used to measure EIS. Electrochemical measurements were performed in three-electrode set-up, where the sample was used as the working electrode, platinum wire was used as the counter electrode, and standard Ag-electrode was chosen as the reference electrode. As an electrolyte the 0.5 mol/l H₂SO₄ and the frequency range was set as 1 MHz – 0.001 Hz.

3. RESULTS AND DISCUSSION

3.1 Characterization of Prepared Substrates

The optimization process showed the sample of etching conditions set as 2 mA for 15 minutes as the one most suitable for SERS and was used in the subsequent steps. By using these conditions, a pSi of squared porous morphology was created and can be seen in **Figure 2 (left)**.

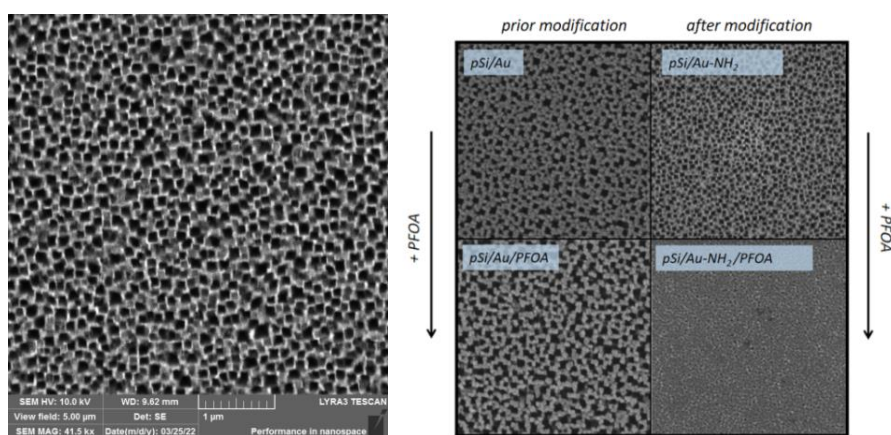


Figure 2 SEM picture of the pSi morphology used for sensing (left) and a comparison of substrate surface morphology of unmodified and modified samples before and after PFOA incubation (right).

The pore size of prepared samples of pSi was in range 30–50 nm and the structure showed homogeneous size and distribution of pores. The surface morphology was also verified using SEM for samples prior and after modification with ADT-NH₂ and before and after incubation in PFOA water solution. The two samples, unmodified and modified, in **Figure 2 (right)** interacted with PFOA and showed changes of the surface morphology, especially apparent in the case of sample grafted with ADT-NH₂. Thus it can be concluded that ADT-NH₂ grafting really introduce the ability to capture PFOA.

The positions of the SPP absorption band was detected using UV-Vis spectroscopy and the spectra are shown in **Figure 3**. The wide absorption band, located between 500 and 600 nm is well evident on UV-Vis spectra of pSi/Au. Grafting of samples surface with -C₆H₄-NH₂ does not have a significant effect on the position of the

plasmon absorption maximum, as this salt can be spontaneously grafted only in a form of monolayer. However, it can be seen that the entrapment of PFOA onto the surface results in significant red shift of plasmon absorption band position and in band widening, which can be related to capture of “larger” PFOA molecules.

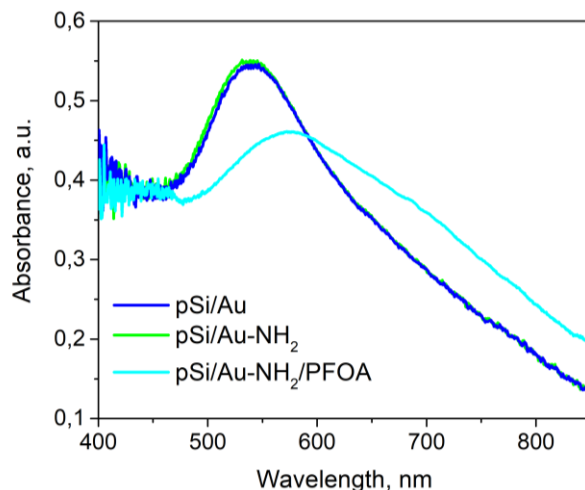


Figure 3 Measurement of UV-Vis absorption spectra of pristine pSi/Au and grafted pSi/Au-NH₂ samples before and after PFOA entrapment

3.2 FUNCTIONALITY AND SENSING

3.2.1. EIS

The EIS spectra were measured before and after PFOA entrapment. Measured spectra can be approximated using an equivalent circuit and the information relevant to the individual elements can be assigned their physical equivalent to the ongoing electrochemical events. Hence the presence of PFOA in solution and its capture on the substrate influenced the EIS spectra curves as can be seen in **Figure 4**. EIS showed that the impedance of the pSi/Au-NH₂ electrode in electrochemical cell increases after incubation in PFOA solution. Observed changes can be attributed to the increase of charge transfer resistance (between analyte solution and electrode surface) due to electrode blocking by entrapped PFOA molecules. Increasing the charge transfer resistance is a desirable effect for the possible determination of the analyte presence and, potentially, the concentration.

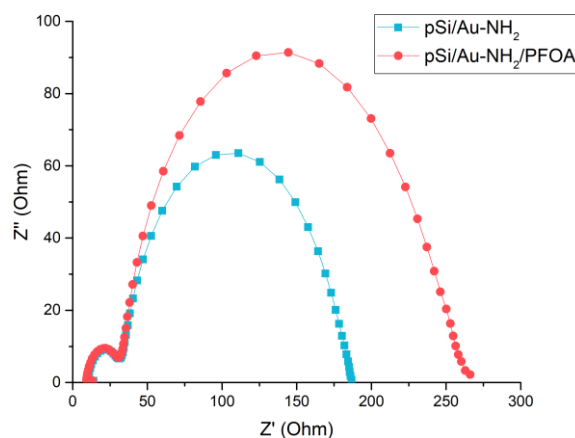


Figure 4 EIS curves measured on pSi/Au-NH₂ and pSi/Au-NH₂/PFOA samples, incubated in solution of CPFOA=10⁻⁸ mol/l

3.2.2. SERS

The aim of the SERS measurement was to find significant vibrational bands in the spectra to confirm the surface modification and PFOA entrapment on samples surface. Measured spectra are presented in **Figure 5**, while vibration bands affiliation is summarized in **Table 1**.

Table 1 SERS peaks affiliation for PFOA

Assignment	Band position [cm ⁻¹]
CF ₃ band	360
	735
	1343

In particular, from **Figure 5** the characteristic fingerprints of C–F bonds are well evident (these bonds are abundantly present in the structure of PFOA). So, SERS approach is also suitable for confirming the presence of PFOA.

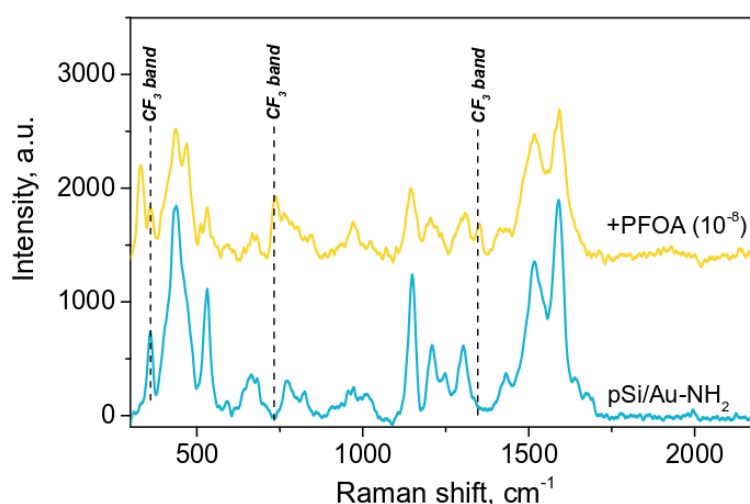


Figure 5 SERS spectra of pSi/Au-NH₂ and pSi/Au-NH₂/PFOA ($C_{\text{PFOA}}=10^{-8}$ mol/l) samples.

4. CONCLUSION

In this work, a porous silicon substrate was prepared and proved to be a suitable tool for the detection of PFOA in water. Detection was performed using dual-mode approach with implementation of SERS and EIS analytical techniques. The surface squared morphology of porous Si (pore size distribution: 30-50 nm) was created by electrochemical etching of p-type silicon. Samples proved reproducibility and homogeneity of the structure. The mesoporous structure with a sputtered layer of Au produces a strong plasmon effect due to the structured surface. After sample interaction with PFOA, subsequently measured SERS spectra show significant peaks assigned to C–F bond and proves the bonding of PFOA to the substrate. In the EIS measurement, the selected sample also showed the ability to quantify the PFOA presence in solution. Successful experiments in the detection of PFOA give us hope that the created sensor could also be used to detect other dangerous substances with similar size, structure and functional groups. It is planned to perform experiments similar to those in this work with another environmentally significant analyte.

ACKNOWLEDGEMENTS

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