

THE DEVELOPMENT OF OPTICAL SENSOR FOR INORGANIC SALTS DETECTION IN WATER

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Abstract

The main goal of this work is to create a highly sensitive optical sensor based on the principle of plasmon surface resonance (SPR) for inorganic salts. The experimental concept includes the creation of optical fiber probe with anion capturing agent (ACA) through the diazonium chemistry for selective-entrapping of targeted compounds and their trace amounts detection. The characterization of the obtained structures and their properties were performed using the SERS, AFM and UV-Vis methods. The created hybrid sensor structures were used to measure the presence and concentration of inorganic salts, which often occur in polluted wastewater. The proposed approach has a number of advantages, such as the possibility of real-time detection, high selectivity and sensitivity, and the possibility of miniaturization of the analytical device(s).

Keywords: Fiber optic, sensor, detection, anions, pollution, capturing agents

1. INTRODUCTION

Today, industrial production and agriculture development led to increasing release of inorganic anions in our environment. Released anions formed from toxic organic and inorganic waste products represents a serious ecological risk. [1,2]. These compounds show potential toxic effects even at relatively low concentrations [3,4]. E.g. nitrate anion (NO_3^-) or phosphate compounds (eg H_2PO_4^-) from agricultural wastewater can lead to eutrophication of watercourses [5-7]. Nitrate and nitrite anions (NO_2^-) can cause methemoglobinemia in animals or humans organisms [8,9]. Sulphate (SO_4^{2-}) and bisulphate (HSO_4^-) anions are commonly present in radioactive waste and induce a number of problems during water storage and recycling [10,11]. Therefore, it is necessary to control and regulate the concentration of anions in various areas, such as public water mains, river water, various types of drinking water and industrial wastewater.

Effective on-site monitoring of anions requires methods that allow the determination of their low concentrations in the aqueous environment. However, anionic analysis equipment (such as ion chromatography) is very expensive, requires the transport of samples to the laboratory, and the analysis itself takes a lot of time. Recently, fluorescent anionic chemosensors have been developed for this task [12,13]. Other methods of optical detection are also being studied, including the use of chromogenic sensors [14]. However, these methods also have several disadvantages: they require preliminary sample preparation, the production of such sensors is laborious and relatively expensive. The solution to these problems is to become fiber-optic sensors with ligand groups on the surface, selective to anions. Today, fiber optic sensors are an efficient, accurate and cheap tool for the determination of various analytes [15-17].

In this work, we propose an optical approach to the detection of anions. The proposed approach have a number of advantages, such as the possibility of real-time detection, high selectivity and sensitivity, and the possibility of miniaturization of the device. In other words, the main goal of this work is to create a highly sensitive optical

sensor based on the principle of plasmon surface resonance (SPR), including a anion-selective layer based on ACA modification for the detection of trace amounts of anions in water in real time. Particular attention will be paid to anions, which often occur in polluted wastewater: NO_3^- , H_2PO_4^- , NO_2^- , SO_4^{2-} .

2. EXPERIMENTAL

2.1. Materials

Gold targets for metal deposition (purity of metals, 4 N) were purchased from Safina. Multimode plastic-clad silica optical (PCS) fiber was purchased from CeramOptec (Germany) with core and buffer/cladding diameters of 200 and 230/500 μm , respectively. Deionized water, methanol (reagent grade, $\geq 99.8\%$), acetone (97%), zinc nitrate hexahydrate ($\geq 99.0\%$), sodium dihydrogen phosphate ($\geq 99.0\%$), sodium nitrite ($\geq 97.0\%$), sodium sulfate ($\geq 99.0\%$), were purchased from Sigma-Aldrich and used without further purification.

2.2. Sample preparation.

Preparation of fiber-optical sensor.

The 2 cm of PCS fiber shell was thermally removed, and naked PCS core was purified using washing with deionized water, acetone and methanol. A thin film of Au was deposited on the PCS fiber core by vacuum sputtering (thickness approx. 40 nm). The deposition of Au was accomplished from Au target (DC Ar plasma, gas purity - 99.995 %, pressure 4 Pa, discharge power 7.5 W, sputtering time 400 sec). The fibers were fixed with the replaceable SMA connectors.

Sensor modification.

The obtained optical fibers with gold were electrochemistry modified (4 mM freshly prepared water solutions, -3.0 V applied potential) for 2 min. After modification, fibers were rinsed with water, methanol, and acetone for 20 min, and dried at ambient conditions.

2.3. Measurement Techniques

Raman spectra were measured using ProRaman-L spectrometer (Laser power 40 mW) with 785 nm excitation wavelengths. Spectra were measured 30 times, each of them with 3 s accumulation time.

UV-Vis absorbance spectra of the samples were measured using a HR2000 (Ocean Optics) spectrometer in 400-800 nm wavelengths range using the AvaLight-DHS light source (Avantes). ACA-coated Au fibers were immersed in water solutions of NaNO_2 , Na_2SO_4 , NaH_2PO_4 and $\text{Zn}(\text{NO}_3)_2$ in different concentrations 10^{-6} , 10^{-4} , 10^{-2} and 1M.

3. RESULTS AND DISCUSSION

The experimental concept is presented in **Figure 1**. An optical fiber covered with an thin layer of Au film was modified with ACA. (Step A) In the next step, the optical fiber was coupled to a light source and with spectrometer. When the sensor is immersed in water, the surface plasmon resonance effect appears on the surface, and an absorption peak as well visible. The position of absorption peak depends on the refractive index of surrounding medium (Step B). Immersion of a modified sensor in an analyte solution leads to pronounced shift of SPR wavelength position, indicating the capture of anions on surface of the sensor. (Step C) The following salts: NaNO_2 , Na_2SO_4 , NaH_2PO_4 and $\text{Zn}(\text{NO}_3)_2$ were used as analyte solutions.

The modification of the sensor surface was confirmed by Raman spectroscopy (**Figure 2**). The results of Raman spectroscopy show the appearance of characteristic vibration bands of aromatics and $-\text{CH}_3$ after modification.

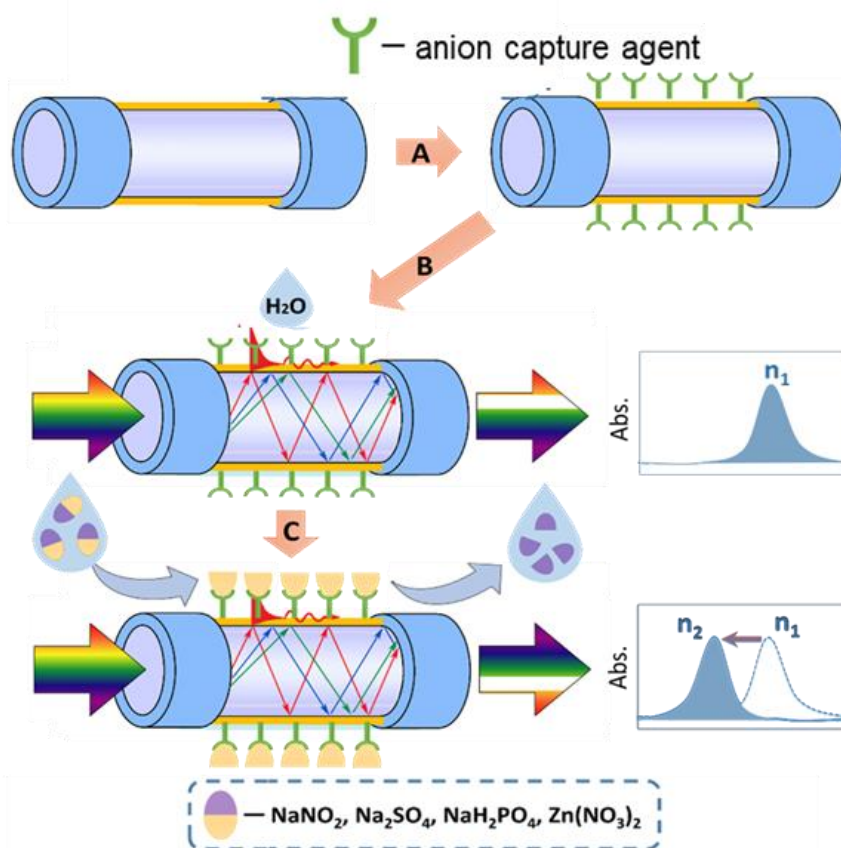


Figure 1 Scheme of preparation and use of an optical sensor. A - pre-modification of the sensor in a freshly prepared aqueous solution of the ACA, B - immersion of the sensor in the aquatic environment and the occurrence of a plasmon absorption band, C - capture of anions and subsequent shift of the absorption band.

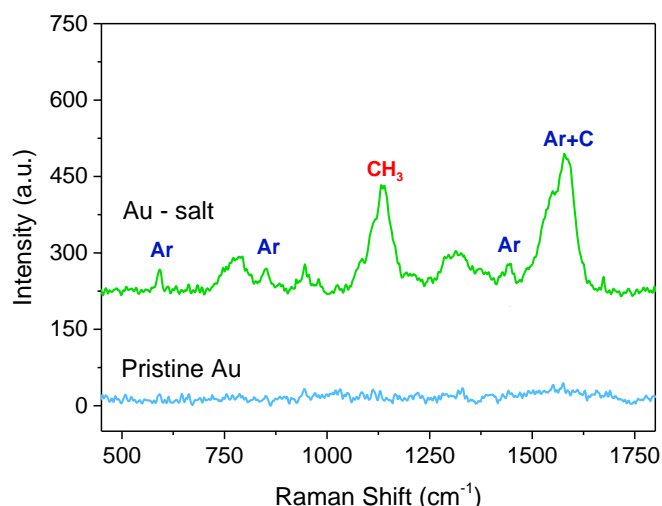


Figure 2 Raman spectra on the surface of: (i) pristine Au, (ii) Au with ACA

During the experiment, the prepared sensors were immersed in solutions of four different anions with different concentrations, which led to a change in the refractive index of the medium surrounding the plasmon-active part of the sensors. The complete sets of absorption spectra are shown in **Figure 3**. As can be seen, entrapping of anions effectively affects the position of the absorption maximum of plasmons.

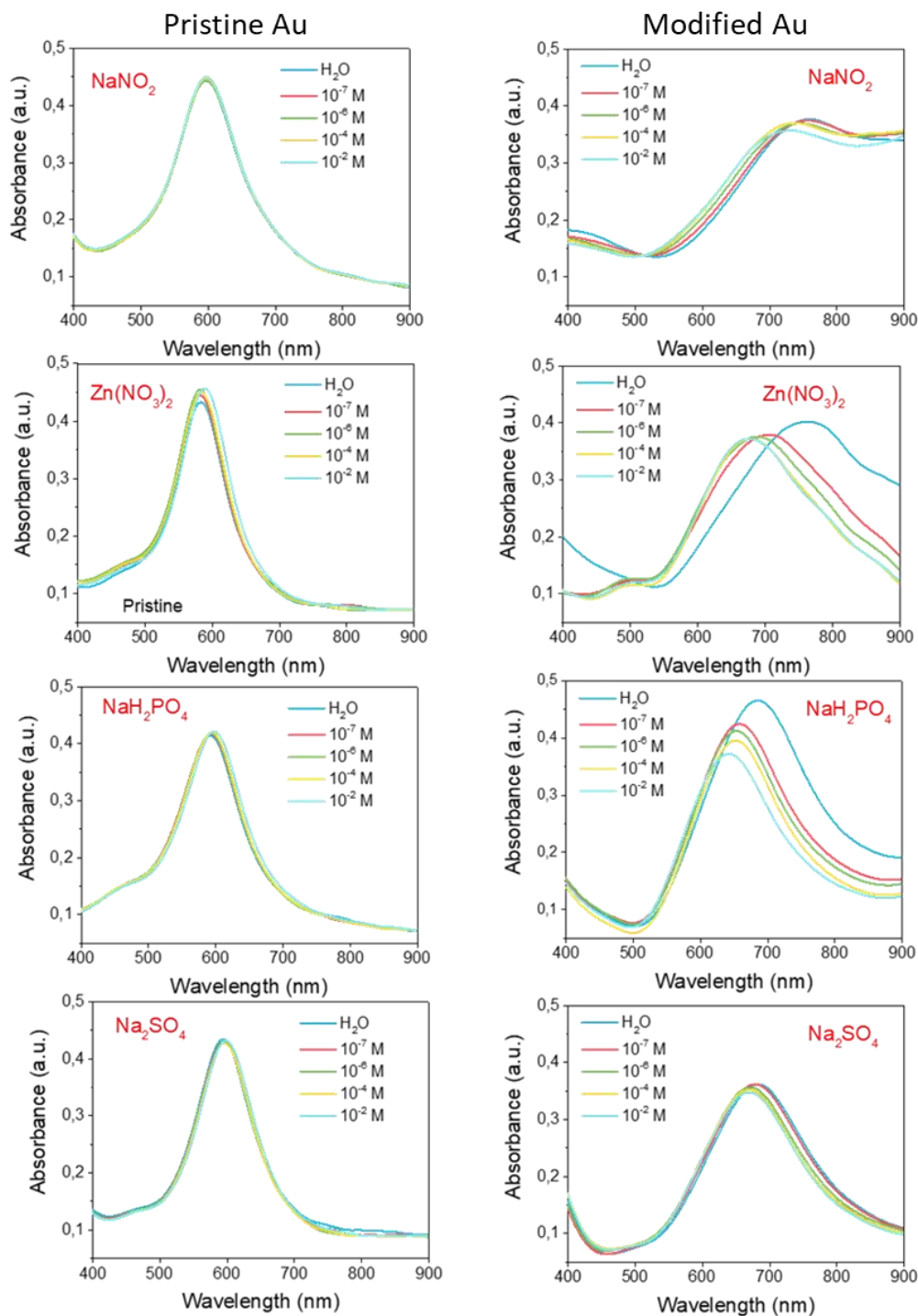


Figure 3 Results of the interaction of pristine and modified sensor with analyte solutions

4. CONCLUSION

In this work, fiber-optic sensors were developed for monitoring of anions and determining their concentrations. Our basic concept uses the functionalization of a plasmon-supported fiber surface modified with an ACA. The salt's layer ensures the extraction of anions from model solutions, which causes a shift in the position of the absorption band. The created system demonstrates high sensitivity to nitrite (NO_2^-), nitrate (NO_3^-), dihydrogen phosphate (eg H_2PO_4^-) and sulphate (SO_4^{2-}) anions. It was found that the lower detectable concentration is

only 10^{-7} M, which makes the proposed sensors comparable to the conventional analytical approach to the determination of water pollution.

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