SUMMARY

Electrochemical sensors are a class of sensors in which a chemical signal is converted into electrical whose value depends on the concentration of the analyte. Electrochemical sensors are most often used in the manufacturing, chemical, marine, and automotive sectors to monitor production processes, machines, gases, and fuel efficiency, as well as inbiomedical applications including medical diagnostics, in the frame of which research on new diagnostics and therapies monitoring methods, devices and systems, such as point of care systems (POCs) is undertaken.Currently, the development of electrochemical sensors focuses on the search for new materials and the use of innovative material combinations - the production of composite and hybrid materials to improve specific properties of analytical instruments, i.e., sensitivity, selectivity, limit of detection, repeatability, and stability. Therefore, there is an unwavering interest in nanostructures and nanomaterials, which important feature is a high surface-to-volume ratio ensuring the development of the active surface area. An interesting material used in electrochemical sensor systems is titanium dioxide (TNT) nanotubes, characterized by chemical and thermal stability and resistance, biocompatibility, good electrical conductivity, and the possibility of low costs productionand the possibility of and the possibility of choosing the conditions of the manufacturing process depending on the application.

Although the literature contains a number of studies on the use of TiO_2 nanotubes as substrates for various types of sensors, only a few reports concern their use in this area in combination with silver nanoparticles (AgNPs). The developed composite electrochemical sensors based on AgNPs/TNT enabled the detection of hydrogen peroxide and glucose. Importantly, this platform has not been used in systems where analyte detection is based on antibody-antigen interaction. Therefore, studies were carried out to confirm the possibility of using this AgNPs/TNT nanocomposite in such systems. Based on literature studies, it was also found that there are no methods of producing spherical, well-dispersed, non-agglomerated silver nanoparticles of high purity on TNT substrates using fast one-step processes. Instead, the procedures proposed in the literature resulted in obtaining nanosilver on TiO_2 nanotubes in the form of nanowires, nanodendrites, or fractal nanostructures with various levels of complexity (agglomerates) and often with very heterogeneous, uneven, and chaotic dispersion. Moreover, these methods often required reducing, stabilizing, and other agents, the addition of which contaminated the nanoparticles. Suppose composite is used as the sensor substrate. In that case, the formation of agglomerates should be avoided as their presence may block the channels of the nanotubes, resulting in a reduction of the specific

surface area. On the other hand, the presence of impurities (compounds remaining after the AgNPs production process) often adversely affects the properties of nanomaterials.

Therefore, the aim of the doctoral dissertation was to produce a composite electrochemical sensor substrate based on titanium dioxide nanotubes and spherical silver nanoparticles (AgNPs) using a fast, one-step, direct synthesis without the need to use auxiliary substances in addition to the silver nanoparticle precursor.

The following research theses were presented:

- **it is possible to produce spherical silver nanoparticles on titanium dioxide nanotubes in a one-step synthesis process without the need to use other factors apart from the AgNPs precursor,**
- **it is possible to improve titanium dioxide nanotubes' electrical conductivity and adsorption properties by modifying them with silver nanoparticles,**
- **produced AgNPs/TNT composites can be used as platforms for electrochemical sensors.**

The following studies were carried out to develop methods of:

- manufacturing of the sensor platform, i.e., TiO_2 nanotubes on a titanium foil,
- thermal modification of TNT - to determine the influence of the annealing temperature on the material and electrochemical properties of TNT,
- modification of TNT with silver nanoparticles - to study the influence of AgNPs production process parameters on the material and electrochemical properties of TNT.

The final stage of the research was to confirm the possibility of the practical application of the developed AgNPs/TNT composite as a platform of an electrochemical sensor, based on the example of impedance detection of heat shock protein 70 (HSP70) - a marker of neoplastic diseases.

TNTs were produced by anodizing, which enables the growth of nanotubes on a titanium foil substrate, ensuring their self-assembly. In this way, the proper electrical connection of the nanotubes with the substrate is achieved, and further processing is facilitated. Based on the literature, the range of diameters of the tested TiO_2 nanotubes from 25 to 75 nm was selected due to the good adsorption properties for proteins and cells. To increase the specific surface area of the nanotubes as much as possible, the conditions for their production were selected that made it possible to obtain the longest TNT possible while avoiding the formation on their surface of a disorderly layer of thin needle-like structures called "nanograss", which arise as a result of the chemical dissolution of the tops of TiO_2 nanotubes and the collapse of their thin walls. Since the literature does not present any studies on the influence of the nanotube diameter (while maintaining the same height of the TNT layer) on their material and electrochemical properties, their height was assumed to be constant, which was 1000 nm.

The next stage was related to research on improving the conductive properties of TNT through thermal treatment of amorphous TiO_2 formed in the anodizing process, resulting in its transformation into a crystal structure. TiO_2 occurs in three polymorphs: anatase, rutile, and brookite. An argon atmosphere and annealing temperature range from 450°C to 550°C were selected for the thermal modification of TiO_2 nanotubes. As shown in the literature, these conditions do not change the morphology of nanotubes and lead to a structure composed predominantly of anatase, which offers the highest electron mobility and has better adsorption properties than rutile. As a result of the research, it was found that TNT with a diameter of 50 nm and a height of 1000 nm, annealed at 450°C, has an electrical conductivity increased by about 50% in relation to the amorphous forms. Moreover, the thermal treatment increased the reproducibility and repeatability of the produced electrodes.

The last stage of the research was to develop a methodology for the production of spherical, non-agglomerated silver nanoparticles on TNT using vacuum sputtering and photo- and electro-reduction without the need to use other substances apart from the AgNPs precursor. The factor determining the coverage with silver nanoparticles is the nucleation centers formed on the surface of titanium dioxide nanotubes, which usually occur at the edges of the nanotubes. Based on XPS results (X-ray photoelectron spectrometry), it has been proposed that as a result of the reduction of silver ions near the TiO_2 surface, silver nanoparticles are deposited on TNT through the formation of a Ti – Ag and Ti – O – Ag bond.

By modifying the parameters of the AgNPs production process, AgNPs/TNT nanocomposites were obtained with electrical conductivity greater by about 50% than annealed TNT without silver nanoparticles. In addition, based on the research it has been shown improved adsorption properties of composites. AgNPs/TNT enabled impedimetric detection of the HSP70 protein showing a linear response in the concentration range from 0.48 to 100 ng/ml. The detection limit of the developed sensor was 1.61 ng/ml, while the sensitivity was 18.16 Ω/(ng/ml).

Keywords: electrochemical sensors, electrochemical impedance spectroscopy, nanocomposites, silver nanoparticles, titanium dioxide nanotubes