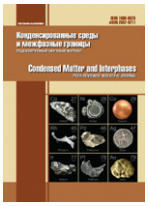

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Silicon nanowires modified with Au/Ag nanoparticles for the label-free detection of prostate-specific antigen using surface-enhanced Raman spectroscopy

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Abstract

Objective: Prostate-specific antigen (PSA) is an important biomarker widely used for the early diagnosis of prostate cancer. In this work, substrates based on silicon nanowires coated with bimetallic gold and silver nanoparticles (AuAg@SiNWs) are presented for the highly sensitive detection of PSA using surface-enhanced Raman spectroscopy (SERS).

Experimental: The fabrication of AuAg@SiNWs was based on simple and readily accessible chemical etching and metal deposition techniques, making the approach suitable for scaling and potential biomedical applications. The thickness of the silicon nanowire array was approximately 800 nm, while the bimetallic nanoparticle layer was formed predominantly in the upper region of the nanostructures and exhibited a thickness of 100–200 nm. To ensure the biospecificity of the sensor, the surfaces of the AuAg@SiNW substrates were functionalized with antibodies.

Analysis of the SERS spectra revealed a clear dependence of the intensity of characteristic amide bands (in particular, at 1294 and 1030 cm^{-1}) on the PSA concentration, starting from 1 ng/mL. The calculated calibration curve in the concentration range of 0.001–1 μg/mL demonstrated a high degree of linearity (R^2 = 0.96), while the stable presence of characteristic spectral features at a concentration of 1 ng/mL indicates the high functional sensitivity of the proposed platform.

Conclusions: The results obtained demonstrate that AuAg@SiNW-based substrates possess significant potential for label-free and highly sensitive detection of protein cancer biomarkers, including PSA, and can be used as a platform for the development of compact biosensors for laboratory diagnostics and point-of-care applications.

Keywords: Silicon nanowires, Prostate-specific antigen (PSA), Surface-enhanced Raman spectroscopy

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1. Introduction

Cancer remains one of the major threats to human survival due to its significant impact on global health. Prostate cancer is the most common malignancy among men over the age of 50. Early diagnosis of prostate cancer is closely associated with prostate-specific antigen (PSA), which is regarded as the gold-standard biomarker. PSA is a 34 kDa single-chain glycoprotein secreted by the prostate gland [1]. It is well known that an increase in serum PSA concentration in prostate cancer is caused by tumor cell proliferation, disruption of the affected organ, and subsequent leakage of the antigen into the systemic circulation. PSA concentrations exceeding 4 ng/mL are detected in approximately 80–90 % of patients with prostate cancer and in 10–20 % of patients with benign prostatic hyperplasia.

At present, several methods are used for the determination of PSA levels, including enzyme-linked immunosorbent assay (ELISA) [2], immunochromatographic analysis [3], chemiluminescent immunoassay [4], silicon nanowire-based field-effect transistor sensors [5], and Raman scattering techniques [6]. One of the increasingly popular approaches for PSA detection is surface-enhanced Raman spectroscopy (SERS) [7–9]. SERS is a modification of conventional Raman scattering in which a strong enhancement of the signal from molecules adsorbed on nanostructured noble metal surfaces, most commonly gold or silver, is observed. The efficiency of SERS is largely determined by the morphology of the nanostructure, the type of metal used, and the distance between the analyte molecules and the metal surface.

Nanostructured silicon substrates have been actively investigated in recent years as a basis for the development of SERS-active sensing chips. Their key advantage lies in a high degree of structural tunability, which enables targeted modification of the silicon morphology at the synthesis stage. Among such substrates are silicon nanowires (SiNWs) fabricated by metal-assisted chemical etching (MACE) [10, 11]. By varying the MACE parameters, it is possible to control key structural characteristics, including pore size, nanowire height and diameter, nanostructure density and orientation, as well as the degree of their mutual aggregation. To impart SERS activity, SiNWs are additionally decorated with silver and/or gold nanoparticles [12, 13]. These structures have already demonstrated their effectiveness in the detection of bacteria [12], as well as in studies of bacterial sensitivity to antibiotics [13].

In [14], the feasibility of PSA detection by SERS using aptamer-functionalized SiNWs was demonstrated. However, that study employed exclusively silver nanoparticles, which, despite their high signal enhancement efficiency, are susceptible to oxidation and structural degradation during storage. This significantly reduces the reproducibility and long-term stability of the SERS response, particularly when operating in biological fluids. Such substrates are therefore less reliable than bimetallic Au/Ag systems, which provide more stable plasmonic behavior and improved chemical stability of the surface.

The aim of the present study is to develop and evaluate the performance of SERS-active substrates based on silicon nanowires modified with gold and silver nanoparticles for highly sensitive PSA detection using immobilized antibodies as the bioselective recognition element.

2. Experimental

SiNWs modified with gold and silver nanoparticles (AuAg@SiNWs) were fabricated by metal-assisted chemical etching (MACE) of a p-type crystalline silicon (c-Si) wafer with (100) crystallographic orientation and a resistivity of 0.8–1.2 Ω·cm. Prior to etching, the c-Si wafer was sequentially cleaned in acetone and isopropanol using an ultrasonic bath, followed by immersion in 5 M HF to remove the native oxide layer from the surface.

During the first stage, gold nanoparticles were deposited onto the c-Si surface by immersing the wafer into a solution of 0.01 M $AuCl_3$ and 5 M HF mixed in a volume ratio of 1:1 for 15 s. During

the second stage of the MACE process, the gold nanoparticle-coated c-Si wafer was placed into a solution of 30 % H_2O_2 and 5 M HF with a volume ratio of 1:10 for 2 min. During this step, localized etching occurred beneath the gold nanoparticles, enabling their penetration into the c-Si substrate and resulting in the formation of SiNWs.

Afterwards, the obtained SiNW arrays were sequentially immersed in a solution of 0.02 M $AgNO_3$ and 5 M HF mixed in a volume ratio of 1:1, followed by immersion in a solution of 0.01 M $AuCl_3$ and 5 M HF with the same volume ratio, for 30 s in each solution. As a result, SiNWs modified with silver and gold nanoparticles (AuAg@SiNWs) were obtained.

The morphology of the fabricated AuAg@SiNWs was examined using a scanning electron microscope (SEM, Carl Zeiss SUPRA 40).

The feasibility of PSA signal registration by SERS under conditions of nonspecific interaction with different types of substrates was initially evaluated. It was established that, in the absence of antibodies providing specific antigen binding, PSA detection using these nanostructured substrates was not possible. Therefore, to ensure the specific interaction of PSA with the AuAg@SiNW surface, preliminary functionalization of the substrates with antibodies capable of covalent attachment to gold nanoparticles via thiol groups was required.

The reduction of disulfide bonds in antibody molecules to generate free thiol groups was performed according to the procedure described in [15]. Briefly, 12 mg of 2-mercaptoethanolamine was added to 1 mg of monoclonal antibodies (mAbs) specific to PSA (clone 5A6, HyTest) dissolved in 10 mM phosphate-buffered saline (PBS, pH 7.3) containing 5 mM EDTA, followed by incubation for 1.5 h at 37 °C. Low-molecular-weight reaction components were removed using a PD-10 desalting gel-filtration column based on Sephadex G-25 (GE Healthcare).

For long-term storage, the resulting solution of reduced antibodies was stored at –20 °C in 50 % glycerol. AuAg@SiNW substrates were incubated in a solution of reduced antibodies (10 μg/mL in physiological saline) for 1 h at room temperature under gentle agitation, followed by three washing steps (1 min each) with physiological saline containing 0.1 % Tween 20. Subsequently, the AuAg@SiNW substrates with immobilized reduced antibodies were incubated in PSA solutions prepared in physiological saline over a concentration range of 0-1000 ng/mL for 1 h at room temperature under gentle agitation, followed by three washing steps (1 min each) with physiological saline containing 0.1 % Tween 20.

SERS spectra were recorded using a confocal microscope Confotec™ MR350 with laser excitation at a wavelength of 633 nm and a laser power of 1 mW.

3. Results and discussion

An SEM micrograph of the fabricated AuAg@SiNW substrates is shown in Fig. 1. The SiNW layer has a thickness of approximately 800 nm, whereas the bimetallic nanoparticle layer formed in the upper region of the nanowires ranges from 100 to 200 nm in thickness. Such a layer thickness suggests sufficiently dense nanoparticle coverage to achieve efficient plasmonic enhancement. Larger particles observed on the surface of the SiNWs correspond to silver nanoparticles, while the bright spots on their surface are attributed to gold nanoparticles. The bright features located at the SiNW/c-Si substrate interface correspond to gold nanoparticles that penetrated into the silicon during the formation of the nanowires.

Fig. 2 presents a SERS spectrum recorded from antibody-functionalized AuAg@SiNW substrates after incubation with a PSA solution at a concentration of 1 μg/mL. The peak at 520 cm^{-1} corresponds to the optical phonon mode of c-Si, which forms the basis of the nanowire structure.

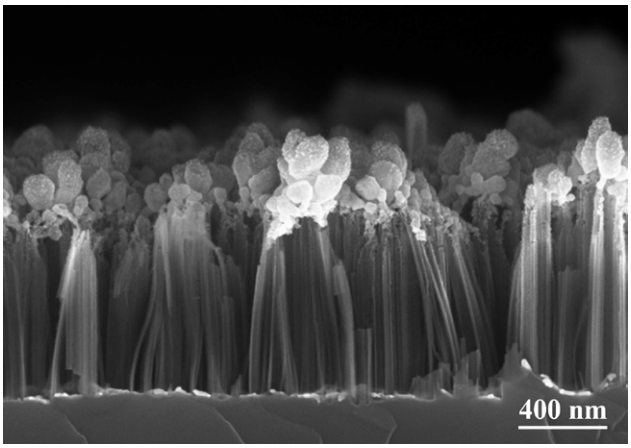

Fig. 1. SEM micrograph of a sample AuAg@SiNWs

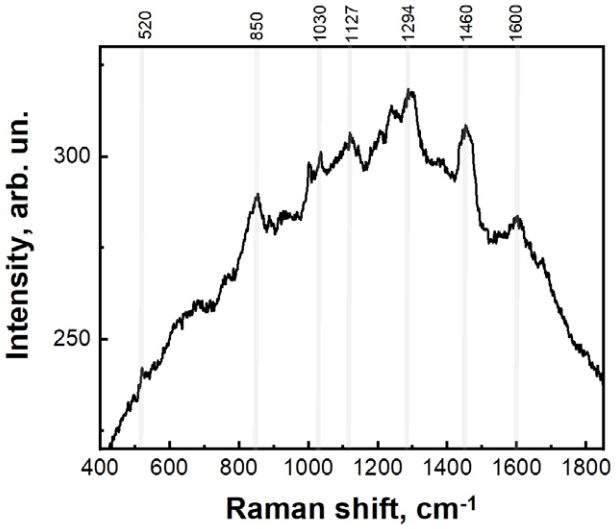

Fig. 2. SERS spectrum of PSA adsorbed on an AuAg@SiNW substrate at a concentration of 1 μg/mL

The increased background signal is attributed to photoluminescence originating from the SiNWs.

The remaining peaks in the spectrum can be attributed to vibrational modes of protein biomolecules. The band at 1000 cm^{-1} corresponds to the symmetric ring breathing mode of the phenyl group, which is characteristic of the aromatic α-amino acid phenylalanine, a constituent of most proteins. Bands in the range of 1110–1260 cm^{-1} are assigned to amide III vibrations, while the band at 1294 cm^{-1} is associated with C–N and N–H stretching modes within the amide III region. The peak at 1460 cm^{-1} is related to deformation vibrations of the C–NH bond in amide II, whereas the signal at 1600 cm^{-1} corresponds to C=O stretching vibrations of the peptide bond in the amide I region [14, 16]. These observations confirm the feasibility of efficient and reliable PSA protein detection using the developed AuAg@SiNW composite substrates via surface-enhanced Raman spectroscopy.

Fig. 3 shows SERS spectra recorded from AuAg@SiNW substrates after incubation with PSA solutions at different concentrations, ranging from 1 μg/mL to 1 ng/mL. The spectrum corresponding to the highest PSA concentration is shown at the top (black), while the spectrum of the control substrate functionalized with antibodies but without PSA is shown at the bottom (violet). The spectra are presented after subtraction of the photoluminescence background and are vertically offset for clarity.

It should be noted that the spectra of PSA and antibodies exhibit similar spectral features, which is attributable to their common protein nature. However, in the PSA spectra, pronounced bands at 1294 cm^{-1} and 1030 cm^{-1} are clearly observed, with intensities significantly exceeding those of the corresponding signals in the antibody spectra. This indicates a contribution of PSA molecules to the enhanced SERS response and confirms the possibility of their selective detection against a protein background.

Fig. 4 presents the calibration curve of the SERS signal intensity at 1294 cm^{-1} as a function of PSA concentration in the range from 1 ng/mL to 1 μg/mL. Linear fitting of the experimental data is described by the equation $y = 1969.1 + 411.4x$, with a coefficient of determination of $R^2 = 0.96$, indicating a strong correlation between antigen concentration and spectral response intensity. The observed linear relationship confirms the feasibility of quantitative PSA analysis based on the intensity of the amide band in the SERS spectrum. In the low-concentration region, starting from 1 ng/mL, a distinct specific signal

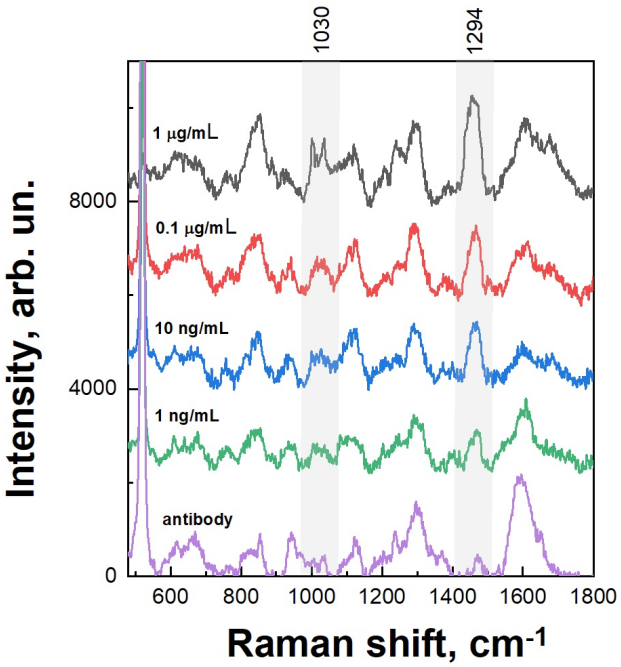

Fig. 3. SERS spectra recorded from AuAg@SiNW substrates after incubation with PSA solutions at different concentrations, ranging from 1 μg/mL to 1 ng/mL

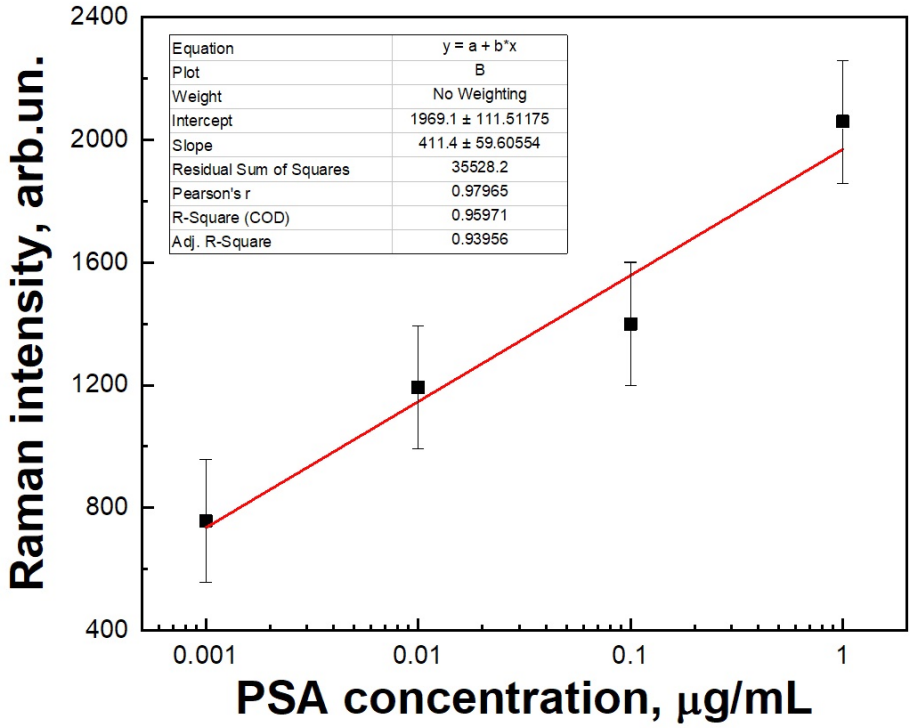

Fig. 4. Calibration curve of the SERS signal intensity at 1294 cm^{-1} as a function of PSA concentration in the range from 1 μg/mL to 1 ng/mL

is clearly detected, demonstrating the high sensitivity of the developed sensing platform.

4. Conclusions

This work presents the development and experimental evaluation of reproducible and sensitive SERS substrates based on arrays of silicon nanowires modified with bimetallic gold and silver nanoparticles (AuAg@SiNWs). The chemical etching and metal deposition methods employed are technologically simple, scalable, and compatible with silicon microelectronics, making the proposed approach promising for practical implementation.

The thickness of the SiNW arrays was approximately 800 nm, while the bimetallic nanoparticle layer was predominantly formed in the upper region of the nanostructures with a thickness of 100–200 nm. Such an architecture ensures dense and localized placement of metal nanoparticles, facilitating the formation of plasmonic hot spots and efficient signal enhancement.

To ensure biospecificity, the surface of the AuAg@SiNW substrates was functionalized with antibodies specific to prostate-specific antigen. Analysis of the SERS spectra revealed a clear dependence of the intensity of characteristic amide bands (in particular, at 1294 and 1030 cm^{-1}) on PSA concentration, starting from 1 ng/mL. The calculated calibration curve in the concentration range of 0.001–1 μg/mL exhibited a high degree of linearity (R^2 = 0.96). The stable presence of characteristic spectral features at a PSA concentration of 1 ng/mL indicates the high functional sensitivity of the developed platform.

The obtained results confirm that AuAg@SiNW-based substrates have high potential for highly sensitive detection of protein cancer biomarkers such as PSA and may serve as a basis for the development of compact biosensors for laboratory diagnostics and point-of-care applications.

Author contributions

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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