

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

5,900

Open access books available

145,000

International authors and editors

180M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



An Overview of Anodic Oxides Derived Advanced Nanocomposites Substrate for Surface Enhance Raman Spectroscopy

Marta Michalska-Domańska

Abstract

Surface-enhanced Raman spectroscopy (SERS) is an analytical technique, which allows to identify traces of chemical or biological substances in many field, like pharmaceutical and food industries, homeland security, nanosensors, or environmental protection. The analytes are identified based on their vibrational spectra, unique for a given compound. The advantage of SERS is effective qualitative analysis of trace amounts of analyte, but the disadvantages are stability of substrate and repeatability of measurements. The challenge is to improve SERS substrates to minimize these drawbacks. Nowadays high-precision electron beam lithography or focused ion beam is used in SERS substrate fabrication, which is impractical for large-scale production. In recent years, researchers' attention has focused on porous anodic oxides, with inexpensive and scalable production method, as potential materials for SERS substrates. This chapter will discuss the progress of anodic oxides used as a SERS substrate, and the brief description of conventional SERS substrate fabrication methods will be presented.

Keywords: nanocomposites, anodization, anodic oxide, titanium anodic oxide, aluminum anodic oxide, porous, plasmon, hot spots, surface-enhanced Raman spectroscopy, SERS substrate

1. Introduction

Raman spectroscopy is a technique based on measuring Raman scattering, i.e., inelastically scattered photons. It belongs to the techniques of testing the oscillatory spectra of materials. Thanks to its application, it is possible to obtain information about the type and structure of various chemical and biological compounds, including explosives, drugs, molecules of poisonous compounds, as well as bacteria, viruses, and even cancer cells. This technique has a lot of advantages, but the biggest disadvantage is the low sensitivity of the method, which can be solved by the use of surface-enhanced Raman spectroscopy (SERS). It increases the intensity of the Raman signal up to 10^{14} times compared to the signal received in a classic Raman experiment [1]. The first observations of the surface-amplified Raman signal for

pyridine were made on the rough silver surface as early as 1974 [2]; however, the authors did not recognize the observed phenomenon as an extraordinary amplification or phenomenon. Since the discovery of SERS in 1977 [3], interest in this research technique has grown exponentially.

SERS is a well-known technique for detecting trace amounts (or even individual molecules) of chemical and organic substances in real time, using a specific structural and vibration “fingerprint” of the analyte being tested. By using this technique, it is possible not only to efficiently qualitatively analyze the particles adsorbed on the surface of the substrate but also to obtain valuable information on the structure of the detected compounds. SERS can be used, among others, in medicine, pharmaceutical and food industry, internal security, the detection of terrorist threats, nanosensors, or environmental protection [1, 4].

SERS is a noninvasive technique; it can be used for solid, liquid, and gas samples and does not require sample preparation before measurement; and it does not require vacuum. In biological analysis, it is possible to work in vitro and in situ. Analyses can be carried out in a wide range of measurement conditions (temperature, pressure) and are short-lived (lasts for seconds); a small amount of the analyzed substance (up to one molecule) is sufficient. It is possible to detect many components of a sample at the same time because the spectra obtained are characterized by high resolution.

A few years ago, SERS measuring equipment (based on confocal microscope, monochromator, and detector—cooled silicon matrix) was expensive and has significant dimensions. Nowadays, there are more and more inexpensive, portable technical solutions with increasingly better parameters (although their spectral resolution is still relatively low). Despite the advantages, one should take into account the limitations of this research methodology: problems with quantitative analysis, problems with the determination of fluorescent materials, and the inability to determine metals and alloys, as well as the stability and repeatability of measurements. The latter one problem can be solved by improving the SERS substrates used.

SERS substrate can be classified by structure of substrate surface, fabrication method, or application. According to the used structure, the SERS substrates can be divided based on:

- a. Metal nanoparticles (e.g., colloids)
- b. Metal thin films
- c. Nanowires
- d. Composites

Generally, all fabrication methods of the SERS substrate production can be divided into four main categories [5]:

- a. Chemical synthesis (like synthesis of colloids by microwave heating method) (1)
- b. Deterministic patterning (including all lithographic techniques, like electron beam lithography and focused ion beam fabrication) (2)
- c. Template-assisted methods (3)
- d. Other methods not mentioned above, which can be classified as nonconventional (4)

The two first categories (1, 2) can be classified as a “bottom-up” approach, while the third (3) is typical “top-down” approach [5]. The fourth category (4) collects all new technologies, which present new proposal and are based on new ideas, not used traditionally. For example, when anodic aluminum oxide (AAO) is used as a template for nanofabrication of metallic nanostructures, one can classify that method to the third category (3), while AAO decorated by metallic nanoparticles and used as an active SERS substrate will be included in nonconventional method (4). In summary, the classification of the fourth category depends on what experimental actions are included there, so the decision whether it is “bottom-up” or “top-down” approach should be taken after the analysis of the method.

SERS substrate can be divided according to application:

- a. Military utilization and internal security, e.g., detection and identification of illicit or dangerous materials such as explosives
- b. Quality control in the food and pharmaceutical industry
- c. Medicine, e.g., detection of cancer cells or defects in DNA
- d. Biology
- e. Environmental science
- f. Single molecule detection

To describe SERS substrate, the following parameters have to be taken under consideration: enhancement factor of signal for a given analyte, repeatability of measurements, shelf life/durability, required excitation wavelength and laser power range, temperature, and humidity sensitivity. To define SERS substrate efficiencies, the specific application, where the substrate is planned to be used, should be included. For example, when we plan to use SERS in blue or green-orange region (cover visible and NIR light), we can take an Au or Ag nanocolloids, but for UV region we need to use Al nanoparticles [6]. Generally, for detection of microorganisms and living cells, the colloidal nanoparticles are typically preferred as SERS substrates. Also, for detection of specific sequence of DNA or RNA and Ag or Au nanoparticles, Raman-active dyes can be applied, while in detecting pancreatic cancer biomarkers, the SERS in body fluids is required [7, 8]. Detection of bacteria *E. coli* can be made on SERS substrate with gold nanoparticles [9]. For detection of explosive materials, traditionally silver- or gold-based nanostructure is typically used [10–12], but Cu-based nanoobjects fabricated by laser ablation were also tested [13]. Another important factor that influenced the Raman enhancement is the environment, in which the detected molecules are embedded, such as body fluid, ethanol water, or other solvent.

Enhancing Raman scattering over ordinary ones, spectrum registration conditions are on the order of 10^6 or greater. It is assumed that the observed signal enhancement is the resultant of two mechanisms: chemical strengthening and electromagnetic field amplification.

Generally, the Raman enhancement depends on electromagnetic and chemical amplification in the presence of metallic nanostructure (Ag, Au, Cu, Al, etc.). Chemical strengthening arises as a result of the overlapping of valence orbitals of the adsorbed molecule and the metal conductivity bands. Then a charge transfer from the adsorbate analyze to the metal (or vice versa) becomes possible. The strength of the SERS enhancement is strongly dependent on the shape and size as well as

dielectric constant of the metal (plasmonic) nanoparticles on SERS substrate [14, 15], because this affected the ratio of absorption and scattering events. When the particles are too large, the excitation of nonradiative multipoles can appear, and a decrease in the overall efficiency of the enhancement may occur. On the other hand, too small particles lose their electrical conductance and did not enhance the field. When the particle size move toward few atoms, we do not have plasmon anymore at the surface, because we do not have large collection of electrons oscillated together. Each experiment has an ideal particle size and ideal surface thickness to achieve best performance [16]. The strength of chemical enhancement is much lower than electromagnetic ones, but it is very important in determination of spectral pattern of SERS spectra, i.e., Raman shift or intensity ratio [17]. When the interaction between molecule and the metal produces a metal-molecule charge transfer (CT) state and the Raman scattering is excited with a laser source in resonance with that state, some Raman modes can be strongly enhanced. In summary, the critical issue for the improvement of SERS sensitivity and reproducibility is the rational design of a stable and uniform SERS-active substrate, because the Raman enhancement is susceptible to the composition, size, and morphology of the substrate [18–20]. Higher SERS substrate surface area favors obtaining enhanced higher signal, and for this reason the work is underway on obtaining SERS substrates constructed of nanostructures coated with metallic plasmonic nanoobjects.

The high local electromagnetic field near plasmonic nanostructures, when the tested molecules are in their immediate vicinity, provides enhanced high Raman signal. The degree of electric field enhancement depends on the composition, morphology, and geometric parameters of surface nanostructures, as well as the amount of the so-called hot spots (regions of intense local field enhancement believed to be caused by local surface plasmon resonances (LSPR) [21]), and decreases sharply as the distance between the ground and the analyte under test increases above a dozen nm. There are a lot of publications described in detail in the LSPR phenomenon [22–28], which justified not taking up this issue in this chapter.

Plasmon hot spots spread over the entire surface of the SERS substrate to ensure high sensitivity and repeatability of spectroscopic measurements; however, several conditions must be filled: (1) homogeneous distribution of plasmon nanostructures on a large surface with a strictly controlled distance, which effectively produces hotspot points; (2) it is necessary to efficiently and homogeneously deposit the studied molecules on the entire SERS substrate [29].

The main features of both the abovementioned mechanisms of SERS enhancement are different and will be given below. Chemical reinforcement can be characterized as follow:

- The enhancement of Raman scattered light intensity in relation to the usual Raman spectrum registration conditions is of the order of 10^2 .
- Enhancement occurs only for particles that interact directly with the metal—as a consequence the range is limited to the monolayer adsorbate (high surface specificity).
- Chemical enhancing does not depend on the optical properties of the metal but on the nature of the metal-adsorbate interactions; for that reason they are also observed for other metals than traditionally used in SERS, like Ag, Au, or Cu.
- The amount of chemical enhancing depends on the location of the Fermi level of the metal and changes depending on the applied electrode potential.

Electromagnetic field enhancement can be characterized as follow:

- The field enhancement effect depends mainly on the optical properties of metal and is the strongest for Ag, Au, and Cu
- Field amplification increases the scattering intensity of Raman order of 10^4 in relation to normal condition registration of Raman spectrum.
- This enhancement is felt up to several dozen nm from the surface of metal (range covers several atomic layers).
- The effect strongly depends on the size, shape, and roughness, the surface morphology of the metal, or the size of the aggregates of metal atoms.

To be able to take full advantage of the possibilities of the SERS technique, and even expand its application, it is necessary to develop effective SERS substrates that will provide Raman dissipation signal enhanced up to 10^6 and larger. These SERS substrates have to be time stable and mechanically durable and ensure repeatable analysis results. To realize this aim, the SERS substrates based on nanostructures, including metallic nanostructures, have to be developed. The main trends in the matter of searching suitable nanostructures are as follow:

- Colloids
- Layers of metals
- Layers covered by nanoobjects
- Nanostructures covered by metallic nanoobjects/plasmonic nanoparticles
- Mix of form mentioned above

Brief descriptions of conventional fabrication methods and new directions to production of nanostructures for application in SERS are presented as follows:

In recent years ideas and attempts of using the anodic aluminum oxide and anodic titanium oxide as SERS substrate were made. The ideas can be divided into the following groups:

1. Using AAO as a matrix for the nanofabrication of nanostructures (like nanodots or nanowires) which can act as SERS substrates
2. AAO coated by metals (mainly by silver, AAO/Ag) in many forms directly used as the composite SERS substrate
3. ATO coated by metals (Ag or Au) which can act as recyclable SERS-active substrate

More detailed information about research of anodic oxides using as SERS substrate will be given in Part 4 of this chapter.

In this chapter, the main emphasis will be on a new type of SERS substrates based on anodic metal oxides, which is the perspective and future direction of SERS substrates. Generally, AAO and ATO consist of arrays of regularly arranged nano-tubes/nanopores, which can be filled or covered by other materials. Moreover, ATO

after annealing can act as a semiconductor and be used, for example, as a photocatalyst for removal of residual particles left on the substrate after SERS measurements. Due to the listed above advantages, the anodic oxides in SERS applications become more and more popular but up to now only in the research area. It is worth to notice that aluminum and/or titanium anodic oxides as a SERS substrate are not commercially produced now, so as a consequence its fabrication methods can be classified as unconventional fabrication SERS substrate method. The possibilities of application of anodic aluminum oxide and anodic titanium oxide as SERS substrates will be described and discussed in details below.

2. Conventional SERS substrate fabrication methods

Conventional SERS substrate types are nanostructures covered by metallic nanoobjects (NS/PLA), including nanoparticles or colloids. The fabrication methods of that substrate are briefly summarized below.

The SERS substrates in a type of nanostructures covered by metallic nanoobjects (NS/PLA) are produced by the application of the physical vapor deposition (PVD) technique of thin discontinuous metallic layers on nanostructures [30], using lithographic techniques (photolithography, electron or ion beam lithography) [31], nanoprinting or lithography supported by a template (matrices of porous polymers or shadow lithography—nanosphere lithography (NSL)) [31]. However, the methods listed above are relatively expensive and time-consuming for areas larger than the range of mm^2 [32]. The limitation of using lithography method in SERS substrate production is connected with fabrication cost of nanostructures on large area [33] and resolution [34] of this technique. Below, in **Table 1**, the main disadvantages of that approach are presented.

The use of Au, Ag, or Cu metal colloids, with a diameter in the range of 10–80 nm, which are produced by chemical reduction, requiring the use of expensive chemical reagents, but the largest enhanced SERS (up to 10^{14}), is shown for highly aggregated colloids [31]. The biggest disadvantages of using colloids are storage (usually they should be used immediately after preparation), difficulties in use in portable spectrometers, high cost, problems with repeatability, and the limited range of materials that can be determined due to colloids' dimensions. The use of colloidal metallic particles or nanowires on a glass substrate ensures a relatively homogeneous size of nanoobjects; however, their placement on the substrate is random and unique.

Since few years, the interest on new kind of flexible SERS substrates grows linearly. The new interesting group of SERS substrates constitutes flexible and highly sensitive multiparticle complexes. They are mainly based on metal nanoparticles

Advantages	Disadvantages
<ul style="list-style-type: none"> • The possibility of controlling the metal nanoparticles' size and shape as well as the interparticle distance with great accuracy • Good reproducibility at a molecular resolution range 	<ul style="list-style-type: none"> • Expensive equipment • Many steps are required to prepared one substrate • Quite long processes, so long manufacturing time for higher areas than nm^2 • High cost for areas larger than few μm^2 • Mass production is doubtedly

Table 1.

Main positive and negative features of using lithography methods in SERS substrate production.

combined with different kinds of fibers, thanks to which they possess new properties. To prepare that kind of SERS substrate, many approaches are taken under consideration, including the use of polymer nanofabric [35, 36], cellulose [37, 38], or flexible piezoelectric-modulated layer [39] decorated by silver or gold nanoparticles or nanowires. Few of these substrates can find its application in food industry, especially for pesticide detection [37, 38, 40], and others in explosive materials detection [41]. Despite many unquestionable advantages, such as high sensitivity, that kind of substrates can be temperature and humidity sensitive as well as still has short lifetime. In this chapter other issues related to this type of SERS substrate will not be addressed.

3. Commercially available SERS substrate

There are several commercially available SERS substrates. They are manufactured based on silicon etching and metal deposition techniques (Klarite substrates (discontinued), Renishaw), colloid distribution on cellulose fiber substrate (Ocean Optics substrate), or ion etching (Silmeco substrates). For more information on these solutions, see **Table 2**. All data were taken from the companies' websites.

Company name/SERS substrate name	Fabrication technology	Features	Price/active area
Renishaw-Klarite substrate (production terminated)	Silicon etching and coating of 300–500 nm Au	<ul style="list-style-type: none"> • High repeatability of microstructures • SERS enhancement was not high 	Around 75 EUR/ piece (4 × 4 mm)
Diagnostic anSERS Inc., USA	Colloidal Ag nanoparticles deposited on cellulose fibers, printed	<ul style="list-style-type: none"> • Durable substrates • Restrictions on use in the excitation wavelength and laser power range • Single-use medium • Gain up to 10⁶ depending on the analyte • Temperature and humidity sensitivity 	175\$/ 25pieces (0.25 inch)
Ocean Optics Inc., USA	Colloidal Ag nanoparticles deposited on cellulose fibers—printing	<ul style="list-style-type: none"> • Single-use • Durability 1–1.5 months • Temperature and humidity sensitive • Restrictions in the excitation wavelength and laser power range 	64\$/piece (cellulose/Au) 62\$/piece (cellulose/Ag) (5.5 mm)
Ocean Optics Inc., USA	Metallic Au or Ag nanosponges	<ul style="list-style-type: none"> • Reusable • Durability up to 6 months • Restrictions in the excitation wavelength and laser power range 	80\$/piece, Au or Ag nanosponge (4 × 4 mm)
Silmeco ApS, Denmark	Si nanostructures coated by Ag or Au, ion digestion and vapor deposition, solution deposition or incubation	<ul style="list-style-type: none"> • Laser power restrictions • Relatively high cost of substrate production 	350\$/5pieces (4 × 4 mm)

Company name/SERS substrate name	Fabrication technology	Features	Price/active area
Horiba Ltd., Japan	Nanobludgeons, vapor deposition, dynamic evaporation at an angle	<ul style="list-style-type: none"> • Measurement recommendation on a spherical area 4 mm in diameter at the center of the substrate 	No information about the price (4 × 3 mm or 5 × 7 mm)
Enhanced Spectroscopy, Inc., USA	Ag layers, physical vapor deposition	<ul style="list-style-type: none"> • Very low durability, up to 70 hours after opening the container • 10⁵–10⁷ enhancement, depending on the analyte type 	No information about the price
Nanova Inc., USA	Au nanoparticles with bimodal diameter distribution (60 nm and 15 nm)—larger particles are probably colloids and smaller ones are probably vapor deposited	<ul style="list-style-type: none"> • Only a laser with a wavelength of 785 nm • Long shelf life • The surface is not homogeneous, which results in lower repeatability of analyses 	25\$/piece

Table 2.

Commercially available SERS substrates with company name, main features, and oriented price.

4. Anodic oxides used as a SERS substrate

Anodic oxides are the group of materials which can be described as layered material made on the top of valve metal (like Al, Ti, Zn, Sn, W, etc. [42–47]) or its alloy (like Ti6Al7Nb, FeAl, etc. [48–51]) by electrooxidation, called anodization. Nowadays it was discovered that it is also possible to anodize copper foil which leads to production of anodic oxide layer which consists of nanobundle or nanorods [52–54]. Anodization is the only method for anodic oxide production. The main morphologies possible to obtain by anodization are:

- Nanopores
- Nanotubes
- Nanowires/nanofibers

The most popular anodic oxides are aluminum anodic oxide (AAO) and titanium anodic oxide (ATO).

AAO is a layer of nanocapillaries, perpendicular to the Al substrate, with a diameter in the range of nanometer scale (nanoporous morphology).

Two main applications of AAO are:

1. Used as a template for nanofabrication of AAO made in two-step anodization process, when the nanocapillaries are hexagonally arranged [55–57]
2. Used as a protective, anticorrosion layer on the top of aluminum alloys [58, 59]

ATO can be made by anodization in two morphologies: nanoporous (similar to AAO, but in worse nanopore arrangement) or nanotubular [60–62].

The morphological features of ATO can be relatively easily controlled by parameters of titanium anodization process. ATO is mainly used as a photocatalyst (after annealing) [63], but new applications of that material are still developed. Below, the way of using AAO and ATO as a SERS substrate will be discussed.

The nanofabrication of nanostructures using the anodic aluminum oxide (AAO) template is one of the methods leading to the production of uniformly distributed nanoobjects on the substrate. The AAO is system of hexagonally ordered nanocapillaries, which are vertically oriented to the substrate surface. AAO matrix is produced during an electrochemical oxidation of aluminum foil. It is possible to control geometric parameters of AAO (such as pore diameter, distance between them, matrix thickness, degree of nanopore ordering, etc.), implemented by appropriate selection of matrix production process parameters (e.g., type, concentration and temperature of electrolyte, applied voltage, anodization time) [64–71]. It provides wide possibilities of controlling the morphology and distribution of metallic nanostructures fabricated by AAO template-assisted method, which provoked the multiple use of the AAO matrix in research aimed at making SERS substrates. Below one can find examples of using AAO in preparation of SERS substrate.

Because of the advantages of using AAO in nanostructure fabrication (like low cost, facile, and recurrent), a lot of research groups study the possibility of utilizing these materials in SERS substrate production. An ultrathin AAO membrane (up to 100 nm thick) was used to produce nanodots, nanowires, or metallic nanowires with plasmonic properties, and samples prepared in this way were used as SERS substrates [72–79]. Successful attempts were also made to produce SERS flexible substrates using AAO matrices [20, 80, 81]. AAO was also used as a matrix for the production of composite SERS substrates [82, 83] or after coating with silver (AAO/Ag) directly as the SERS substrate [84–86].

Nguyen et al. [73] built SERS substrate based on hexagonally ordered Au nanodisks, which was deposited on quartz by ultrathin AAO used as a shadow mask. The tested molecule was methamidophos (MAP) at various concentrations ranging from 1 ppb to 10^3 ppm. It was found that SERS signal depends on the morphological features of nanodisks: diameter and distance between nanostructures. The authors observed clearly the tendency of shifting the plasmon resonance to the longer wavelength with increasing the size of Au nanodisks and with decreasing the distance between them.

Liu et al. also reported correlation between the size of Au nanocones and its SERS properties in rhodamine 6G (R6G) detection [74]. They prepared highly ordered Au nanocone arrays with a diameter in the range of 36–77 nm and the distance between the centers of nanocones about 100 nm. To prepare this substrate, the AAO mask was used and Au was evaporated on glass. It was experimentally proven that the spectral position of plasmon resonances was seen to slightly blue-shift with increasing the nanocone size, which coincided well with the result of finite-difference time-domain (FDTD) simulation. Moreover, compared with the bulk sample, the estimated SERS enhancement factor in R6G detection was boosted from 8.00×10^6 to 1.79×10^7 as the diameter of Au nanocones increased from 36 to 77 nm [74].

Kim et al. [76] fabricated a highly ordered array of Au nanorod arrays consisted of agglomerated nanoparticles by porous anodic aluminum oxide (AAO) template-assisted electrochemical deposition. That prepared SERS substrate was tested for 1 mM 4-methylbenzenethiol (4-MBT) detection in three systems: Au nanorod arrays with agglomerated structures after removing AAO template, smooth structures after removing AAO template, and agglomerated structures before removing AAO template. It was shown that the Au nanorod arrays with agglomerated

structures demonstrated a higher activity in SERS effect as abundant nanogaps are created uniformly by combination of hot spots caused by both agglomerated porous structures on each nanorod and inter-rod gaps. Interestingly, that SERS substrate tested before removing AAO template exhibits the lowest signal intensity.

Liu et al. described a universal method to fabricate large-area regularly ordered gold nanodots using an AAO mask [79]. The Au nanodots were patterned on different substrates such as silicon wafer, gold, and graphene substrates, and then the films were used as SERS-active cathodes in Li-O₂ batteries. The discharge products on the different electrodes (graphene and gold) were analyzed, and the results indicated that the cathode reactions on these two electrodes are distinct from each other. The SERS electrodes are so sensitive that even a small amount of product formed on the nonporous, planar electrode can be detected clearly. The authors ensured that SERS-active electrode provided a uniform enhancement of the Raman spectra over the entire substrate, which is more suitable for detecting the intermediates and by-products formed on the electrode.

Several research groups work on developing flexible SERS substrates based on polymer and metallic layers, which are fabricated with the use of AAO membranes as a template for giving the shape to polymer. Zhang et al. [20] tested flexible SERS substrate made by Au sputtering on the surface of the polymer nanostructure arrays, which was made by R2R imprinting UV-NIL process where AAO was used as the mold. The thickness of sputtering Au layer was optimized, and finally the substrate with a 30-nm Au coating was chosen as it showed the highest SERS enhancement for R6G detection. The largest enhancement factor for R6G at 1366 cm⁻¹ was calculated at 1.21×10^7 , and the SERS performance showed no obvious differences under different bending angles and different bending cycles. The tested substrate demonstrated excellent SERS performance and flexibility.

Zhao et al. [80] have transferred three-dimensional nanoparticle array to polymer film with the use of AAO mask. As a result, polymer-nanocone-based 3D Au nanoparticle array SERS substrate was obtained. The new class of SERS substrate presented displays a high SERS sensitivity to R6G in a concentration up to 10⁻¹² M. The enhancement factor was calculated at 1.30×10^8 . In the other paper, Zhao et al. have reported fabrication of polymer nanopillar array with Au nanoparticle inlays used as a flexible and efficient SERS substrate [81]. The substrate was prepared by nanoimprint lithography (NIL) method using an anodic aluminum oxide (AAO) template. It was found that substrate shows high SERS sensitivity to R6G identification with concentration up to 10⁻¹² M and the enhancement factor was calculated at 8.20×10^7 . Moreover, both tested SERS substrates [80, 81] exhibit remarkable reproducibility, excellent flexibility (the SERS intensity acquired from the substrate almost remains constant after 200 bending times), and transparency in visual and infrared range, are lightweight and can be easily handled.

Chen et al. have used AAO with silver nanoparticles entrapped in the nanopores as a SERS substrate [86]. The Ag nanoparticles were seeded growth from aqueous AgNO₃ solution inside the AAO pore channels and treated at elevated temperature. It was shown that Ag nanoparticles entrapped in the pore channels exhibit significant structural stability and are less susceptible to oxidation than Ag NPs on the surface of a planar substrate at high temperatures. It was revealed that Ag NPs in AAO retain substantial SERS activity after heat treatment at 500°C for 5 days and even 600°C for 3 hours. The authors claim that geometric confinement of Ag NPs in the pore channel structure of AAO has clearly played a significant role in endowing them with the enhanced stability. It seems to be likely that the stability region may well be expanded to higher temperature and longer durations with reduced dimensions of the pore channels and decreased porosity

of AAO. The SERS activity of tested samples with 10^{-6} M R6G was studied. It was shown that SERS spectra made on as-prepared and annealed samples are basically the same, which suggests that the coalescence of adjacent Ag NPs occurring at this stage has insignificant impact on the overall hot spots available for SERS enhancement.

Lim and Ng [87] compared the SERS enhancement level for 2-naphthalenethiol obtained on AAO nanofibers coated with a thin Ag layer and on a metallic thin Ag layer deposited on nanoparticles and showed that the SERS signal enhancement on a properly selected length of AAO nanofibers is almost three times higher than on a thin Ag layer.

Dan et al. used AAO as a template for Ag nanorod array fabrication and then removed the oxide and decorated nanorods by Au nanoparticles [88]. As-prepared substrate was used as a SERS substrate for R6G. The detection limit is as low as 10^{-16} M with excellent recyclability. According to the authors, the Raman enhancement occurs in the gap between the nanorods and the top of the nanorod bundle. The authors believe that this synthesis method can be used to prepare other metallic materials with outstanding structure, which can be used in many fields.

Zhong et al. [89] reported fabrication of Fe nanorod arrays by AAO template-assisted method and covered them by Au nanoparticles by sputtering approach to produced large-area urchin-like Au nanospheres for testing as SERS substrate for rhodamine 6G detection. The lower concentration of detected R6G with the use of as-prepared SERS substrate was 10^{-12} M. Moreover, this substrate exhibits excellent reusability after being cleaned. Based on the analysis of three-dimensional finite-difference time-domain (FDTD) simulations, the strong SERS activity is mainly due to the high density of hot spots induced by the gaps between the neighboring Au-NSs. According to the authors, the urchin-like arrays exhibit promising potential as new platforms to realize novel optoelectronic devices and have a great potential for more application in other fields.

Despite the AAO popularity, scientists also found interest within the ATO matrix as a production part of composite SERS substrate. Arrangement of ATO nanopores or nanotubes is not so regular like in AAO, but crystal form of TiO_2 shows photocatalytic properties, which can be of advantage in construction of reusable SERS substrates. Recently, there have been reports of nanocomposites composed of semiconductor and noble metal, e.g., ZnO/Ag [90] and TiO_2/Ag [91–94] or protected by the patent of Polish inventors GaN/Ag [95, 96], used as SERS substrate. Below possibility of composite SERS substrate build of anodic titanium oxide and metallic nanoparticles will be discussed.

Jakubowicz et al. [93] prepared ATO membranes with Ag nano-trees embedded in the pores. They found that the Ag nano-trees have a uniform branched symmetry independent of the applied substrate. In the cited paper, the SERS activity has not been studied; however other groups reported production of similar Ag nano-trees in AAO membrane and used this as a SERS substrate for R6G identification [84]. The SERS detection limit for R6G was estimated to 1.00×10^{-11} M. Moreover, unlike the case of conventional modification of hydrophobic functional groups, the Ag dendrite-integrated AAO membrane substrates have potentials in simple, rapid, direct, and sensitive detection of pollutants with low affinity for noble metal surface, such as fluoranthene. The authors ensure that Ag-dendrites/AAO membrane exhibited excellent SERS performance with high sensitivity, good reproducibility, and tenability [84].

Sun et al. [97] recognized Ag-coated ATO as a low-cost, uniform, and recyclable SERS-active substrate for 2-mercaptobenzoxazole (MBO) detection. The tested composite consisted of ATO made by two-step anodization of Ti foil with deposited Ag nanoparticles on the top of ATO by e-beam evaporation. The clear SERS signal

was observed for very low concentration of MBO like 10^{-8} M. Utilizing photocatalytic properties of titanium dioxide, the SERS substrate after using was illuminated by UV light by 20 minutes and rinsed in distilled water to remove residual ions and molecules and dried at room temperature. SERS substrate cleaned in that way was reused for MBO detection with success.

Wen et al. described ATO coupling with Au nanostructures as a reliable SERS substrate with application in medicine, for chronic myeloid leukemia drug evaluation [98]. A critical biomarker of apoptosis, caspase-3, was detected by SERS analysis in real samples with reasonable recoveries. The authors assumed that SERS substrate developed by them has a lot of advantages (like cost-effectiveness, excellent reproducibility, and high sensitivity), which endows it with promising potential in apoptosis monitoring and anticancer drug development.

Ling et al. reported the use of Ag embedded in TiO_2 nanotube array as a recyclable SERS substrate for R6G molecule detection [99]. Concentration of R6G in SERS measurements was 10^{-6} M. It was found that the morphology of deposited Ag is strongly affected by the diameters of ATO nanotubes and the UV irradiation induced Ag aging process, especially the self-migration of silver along the tubular wall. The SERS activity is not proportional to the ATO diameters, and the enhancement factors on various roughened metallic surfaces strongly depend on the size, shape, distribution, and interaction of Ag nanoparticles with ATO.

In the other research, Roguska et al. [100] investigated Ag, Au, and Cu nano-clusters deposited on TiO_2 nanotubes/Ti as SERS substrate for pyridine detection. The influence of ATO nanotube diameters as well as the amount of deposited metal on SERS performance was studied. It was found that SERS activity of composite substrate was strongly dependent on the amount of deposited metal on ATO; for example, above 0.06 mg Ag/cm^2 , the SERS intensity signal was higher than for referential substrate consisting of bulk activated Ag. Moreover, this high SERS activity of tested substrate, according to the authors, is mainly the merit of their specific morphology. The SERS activity depends also on the type of metal used and the increase in the following order $\text{Cu} < \text{Au} < \text{Ag}$, wherein composite made of Cu/TiO_2 -nanotube/Ti was less active than referential samples made from activated Cu bulk substrate. This observation could be attributed to an instantaneous oxidation of Cu clusters and particles on ATO surface, which result in quenching of SERS signals from the adsorbed molecules. Additionally, the highest substrate stability was observed for Au/TiO_2 -nanotube/Ti composite.

Huang et al. [101] prepared SERS substrate consisting of Ag nanoparticles (NPs) deposited on patterned TiO_2 nanotube films through pulse-current (PC) electrodeposition. The resultant substrate exhibited particle-size-dependent as well as density-correlated UV-vis absorbance and SERS enhancement effect. It was shown that SERS signal of R6G molecules obtained on the tested sample was highly enhanced.

Differences in ATO and AAO matrices are not only in their morphology. Kudelski et al. compared SERS substrate behavior consisting of Ag nanoparticles deposited on AAO and ATO nanotubes [102] for pyridine and two various selected dyes. The recorded average SERS enhancement factors on Ag/TiO_2 -n/Ti and $\text{Ag/Al}_2\text{O}_3$ -n/Al composites was at least equal to the SERS enhancement factor on standard electrochemically roughened Ag substrates (i.e., about 10^6 – 10^7) or higher by a factor of 2. The authors proven that SERS spectra for examined molecules are distinctly different for those two composite substrates. They proposed that observed differences may be caused by specific interaction between the Ag nanoparticles and the oxides, especially different location of Fermi level in the Ag nanoparticles deposited on two tested nanostructured oxides, AAO and ATO. Moreover, the authors suggested that the critical influence on the shape of the spectrum (the

position of individual SERS signals) and most probably on the “chemical” part of SERS enhancement is the electronic properties of the composites, not the specific surface area of substrate.

In other paper from the same group, Pisarek et al. reported [85] the influence of the size of the nanotubes/nanopores of AAO and ATO decorated by Ag nanoparticle as well as the structure of the porous oxide layers on the SERS enhancement factor (EF) for pyridine and mercaptobenzoic acid detection. It was shown that for the same amount of deposited Ag (0.02 mg/cm^2), the size of the nanopores significantly affects the EF, which reaches distinctly higher values at an optimal nanopore size (wherein the higher the EF, the smallest the nanotube diameter) than on a standard silver surface roughened by electrochemical cycling, i.e., $\text{EF} > 10^6$. Moreover it was shown that for Ag/Al₂O₃ NT/Al material the EF is significantly higher than that for Ti-based composite and an order of magnitude higher than that for commonly used in SERS measurements roughened silver. It was proven that porous alumina interact with Ag nano-deposits, hence affecting the electronic structure of the Ag-nanoparticles, which may be most useful in detecting small amounts of certain organic compounds.

Other researchers, Bao et al. [82] and Zhou et al. [83], combined advantages of using AAO matrix to fabricate ordered nanostructures with catalytic activity of TiO₂. Based on the photocatalytic properties of titanium dioxide, the authors have obtained promising self-cleaning effect of adsorbed molecules from composite SERS substrates made of Ag nanowires (made by AAO template-assisted fabrication method) coated with a TiO₂ layer. That composite was used as a SERS substrate as prepared as well as after cleaning realized by UV light irradiation. SERS effect was tested successfully for R6G (10^{-14} M) and methyl parathion (MP) (up to 10^{-6} M) on both, fresh and recycled samples [83]. The authors gave reasons why tested composite showed high SERS enhancement [83]:

1. Ag provided much higher SERS enhancement than Au and other metals.
2. Between collapsing nanowire tips, the gaps are created and they act as many “hot spots,” where analyte molecules are positioned.
3. High aspect ratio (length/width) of Ag nanowires is a major factor to achieving high SERS enhancement.

5. Future of SERS substrate

The challenge that needs to be solved in order to use the SERS spectroscopy method on a wider scale than now is to develop a cheaper and repeatable method for the synthesis of uniformly distributed homogeneous nanostructures enabling the production of SERS substrates significantly enhancing the signal ($>10^6$) in a repeatable manner.

The ideal SERS substrate should be characterized by enhanced high electromagnetic field, not have a fluorescent background, and operate in a wide wavelength range and with unlimited laser power. In addition, it should have a long shelf life, be repeatable and uniform throughout its entire surface, be able to operate in different environments, and be available in different sizes. The future SERS substrates will be a commercially produced, cheap, and repeatable substrate, using new plasmonic materials (e.g., semiconductors, graphene), possible to use in portable Raman spectrometers. It is very likely that databases for the interpretation of standardized SERS spectra will be created in the future.

Taking into account all the requirements for an ideal SERS substrate, which are mentioned above, the anodic oxide-based nanocomposites as SERS substrate can become an efficient and popular product. Nowadays, the possibility of applying this material as a highly active SERS substrate is in the research phase, and the results are very promising. The prospective role of advanced anodic oxide based nanocomposites as SERS substrate can be attributed to the following features:

- No fluorescence and very low background, similar to the values recorded for quartz and silicon.
- The production of anodic oxides is relatively easy and fast process, so the cost of such production would be significantly lower than the cost of now commercially available SERS substrates.
- The structures obtained by anodization are characterized by a large specific surface area, repeatability, and the ability to control geometric parameters by means of manufacturing process parameters (e.g., anodization potential or process temperature), which ensure the repeatability of SERS analyses.
- It is possible to increase the production scale of anodic oxide-based SERS substrates relatively quickly and easily.

6. Conclusion

Despite the undoubted advantages and potentially large possibilities of the widespread use of SERS spectroscopy in many field, its progress has been hampered by the inability of scientists and industry to produce SERS substrates with high sensitivity, stability, and repeatability. Currently commercially available SERS substrates are characterized by obtaining enhancement of 10^5 – 10^7 and durability between several days and 6 months. The above limitations appear due to the relatively small control over the morphology of substrate structures at the nanoscale, which are responsible for the observed enhancement of SERS [103].

It is important to have the reproducible and homogeneous distribution of nanostructures over the entire surface of the SERS substrate, while obtaining large areas that meet these conditions. The next step is to find technology to transfer these results from the laboratory to the industrial scale providing some technological problems. The use of conventional nanostructures in fabrication methods becomes less attractive because they are relatively expensive, time-consuming, difficult, and not effective for areas larger than 1 mm^2 . The use of anodic aluminum oxide template for the production of nanostructures, despite promising results at the nanoscale, is fraught with many problems arising when attempting to increase the scale of production, including a complicated, multi-stage, and difficult process for producing ultrathin membranes; ordering structures only in the domain area; and difficulties in obtaining repetitive systems of nanostructure. On the other hand, the outstanding array structure made by AAO template-assisted method has a promising practical application in SERS field, so this direction will be probably developed in the future. Also using the ATO for SERS substrate production seems to be a promising solution: the possibility of combining relatively ordered nanopores/nanotubes with its photocatalytic properties to utilize SERS substrates self-cleaning effect gives a big perspective of application on that material. In the future probably the composite SERS substrates based on AAO/ATO and Ag or Au will be commercially available.

Acknowledgements

This work was financed by the National Centre for Research and Development (Poland) under program LIDER IX (Nr LIDER/50/0199/L-9/17/NCBR/2018). M. Michalska-Domańska cordially acknowledges financial support from the Polish Ministry of Science and Higher Education (Scholarship for Young, Outstanding Researchers 2016–2019, agreement no. 1013/E-410/STYP/11/2016). The author thanks Dr. P. Nyga for the help in finding information about commercially available SERS substrates.

IntechOpen


IntechOpen

Author details

Marta Michalska-Domańska
Institute of Optoelectronics, Military University of Technology, Warsaw, Poland

*Address all correspondence to: marta.michalska@wat.edu.pl

IntechOpen

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Douketis C, Haslett TL, Wang Z, Moskovits M, Iannotta S. Self-affine silver films and surface-enhanced Raman scattering: Linking spectroscopy to morphology. *The Journal of Chemical Physics*. 2000;**113**:11315-11323
- [2] Fleischmann M, Hendra PJ, McQuillan AJ. Raman spectra of pyridine adsorbed at a silver electrode. *Chemical Physics Letters*. 1974;**26**(2):163-166
- [3] Jeanmaire DL, Van Duyne RP. Surface Raman spectroelectrochemistry: Part I. heterocyclic, aromatic, and aliphatic amines adsorbed on the anodized silver electrode. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*. 1977;**84**(1):1-20
- [4] Tu Q, Chang C. Diagnostic applications of Raman spectroscopy. *Nanomedicine: Nanotechnology, Biology, and Medicine*. 2012;**8**:545-558
- [5] Culha M, Cullum B, Lavrik N, Klutse CK. Surface-enhanced Raman scattering as an emerging characterization and detection technique, Hindawi Publishing Corporation. *Journal of Nanotechnology*. 2012;**2012**:971380. DOI: 10.1155/2012/971380
- [6] Jha SK, Ekinici Y, Agio M, Loffler JF. Towards deep-UV surface-enhanced resonance Raman spectroscopy of explosives: Ultrasensitive, real-time and reproducible detection of TNT. *Analyst*. 2015;**140**:5671-5677. DOI: 10.1039/C4AN01719F
- [7] Cao YWC, Jin R, Mirkin CA. Nanoparticles with Raman spectroscopic fingerprints for DNA and RNA detection. *Science*. 2002;**297**(5586):1536-1540. DOI: 10.1126/science.297.5586.1536
- [8] Nariman B, Foley A, Houghton JM, Sun Y, Kim B. Multiplex detection of pancreatic cancer biomarkers using a SERS-based immunoassay. *Nanotechnology*. 2017;**28**(45):455101. DOI: 10.1088/1361-6528/aa8e8c
- [9] Satpathy G, Chandra GK, Manikandan E, Roy Mahapatra D, Umamathy S. Pathogenic *Escherichia coli* (*E. coli*) detection through tuned nanoparticles enhancement study. *Biotechnology Letters*. 2020;**42**:853-863. DOI: 10.1007/s10529-020-02835-y
- [10] Ben Jaber SS, Peveler WJ, Quesada Cabrera R, Sol CWO, Papakonstantinou I, Parkin IP. Sensitive and specific detection of explosives in solution and vapour by surface-enhanced Raman spectroscopy on silver nanocubes. *Nanoscale*. 2017;**9**:16459-16466. DOI: 10.1039/C7NR05057G
- [11] Shanthil M, Fathima H, Thomas KG. Cost-effective plasmonic platforms: Glass capillaries decorated with Ag@SiO₂ nanoparticles on inner walls as SERS substrates. *ACS Applied Materials & Interfaces*. 2017;**9**:19470-19477. DOI: 10.1021/acsami.6b12478
- [12] Zhang C, Wang K, Han D, Pang Q. Surface enhanced Raman scattering (SERS) spectra of trinitrotoluene in silver colloids prepared by microwave heating method. *Spectrochimica Acta Part A*. 2014;**122**:387-391. DOI: 10.1016/j.saa.2013.11.066
- [13] Hamad S, Podagatlapalli GK, Mohiddon MA, Soma VR. Cost effective nanostructured copper substrates prepared with ultrafast laser pulses for explosives detection using surface enhanced Raman scattering. *Applied Physics Letters*. 2014;**104**:263104. DOI: 10.1063/1.4885763

- [14] Lu H, Zhang H, Yu X, Zeng S, Yong K-T, Ho H-P. Seed-mediated plasmon-driven regrowth of silver nanodecahedrons (NDs). *Plasmonics*. 2011;**7**(1):167-173
- [15] Coluccio ML, Das G, Mearini F, Gentile F, Pujia A, Bava L, et al. Silver-based surface enhanced Raman scattering (SERS) substrate fabrication using nanolithography and site selective electroless deposition. *Microelectronic Engineering*. 2009;**86**:1085-1088
- [16] Bao L-L, Mahurin SM, Liang C-D, Dai S. Study of silver films over silica beads as a surface-enhanced Raman scattering (SERS) substrate for detection of benzoic acid. *Journal of Raman Spectroscopy*. 2003;**34**(5):394-398
- [17] Pilot R, Signorini R, Durante C, Orian L, Bhamidipati M, Fabris L. A review on surface-enhanced Raman scattering. *Biosensors*. 2019;**9**:57. DOI: 10.3390/bios9020057
- [18] Wang Z, Zong S, Wu L, Zhu D, Cui Y. SERS-activated platforms for immunoassay: Probes, encoding methods, and applications. *Chemical Reviews*. 2017;**117**(12):7910-7963
- [19] Hasna K, Antony A, Puigdollers J, Kumar KR, Jayaraj MK. Fabrication of cost-effective, highly reproducible large area arrays of nanotriangular pillars for surface enhanced Raman scattering substrates. *Nano Research*. 2016;**9**(10):3075-3083
- [20] Zhang CP, Yi PY, Peng LF, Lai XM, Chen J, Huang MZ, et al. Continuous fabrication of nanostructure arrays for flexible surface enhanced Raman scattering substrate. *Scientific Reports*. 2017;**7**:39814-39822
- [21] Maher RC. SERS Hot Spots. In: Kumar CSSR, editor. *Raman Spectroscopy for Nanomaterials* Characterization. Berlin, Heidelberg: Springer; 2012
- [22] Pacaud M, Hervé-Aubert K, Soucé M, Makki A, Bonnier F, Fahmi A, et al. One-step synthesis of gold nanoflowers of tunable size and absorption wavelength in the red & deep red range for SERS spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2020;**225**:117502. DOI: 10.1016/j.saa.2019.117502
- [23] Wan Y. Modulation of localized surface plasmon resonance of the titanium nitride nanoparticle array based on graphene. *Optik*. 2020;**200**:163420. DOI: 10.1016/j.ijleo.2019.163420
- [24] Araujo TP, Quiroz J, Barbosa ECM, Camargo PHC. Understanding plasmonic catalysis with controlled nanomaterials based on catalytic and plasmonic metals. *Current Opinion in Colloid & Interface Science*. 2019;**39**:110-122. DOI: 10.1016/j.cocis.2019.01.014
- [25] Mejía-Salazar JR, Oliveira ON Jr. Plasmonic biosensing. *Chemical Reviews*. 2018;**118**:10617-10625. DOI: 10.1021/acs.chemrev.8b00359
- [26] Zhu C, Xu Q. Amorphous materials for enhanced localized surface plasmon resonances. *Chemistry, an Asian Journal*. 2018;**13**(7):730-739. DOI: 10.1002/asia.201701722
- [27] Agrawal A, Cho SH, Zandi O, Ghosh S, Johns RW, Milliron DJ. Localized surface plasmon resonance in semiconductor nanocrystals. *Chemical Reviews*. 2018;**118**(6):3121-3207. DOI: 10.1021/acs.chemrev.7b00613
- [28] Csáki A, Stranik O, Fritzsche W. Localized surface plasmon resonance based biosensing. *Expert Review of Molecular Diagnostics*.

2018;**18**(3):279-296. DOI:
10.1080/14737159.2018.1440208

[29] Huang Z, Meng G, Huang Q, Chen B, Zhu C, Zhang Z. Large-area Ag nanorod array substrates for SERS: AAO template-assisted fabrication, functionalization, and application in detection PCBs. *Journal of Raman Spectroscopy*. 2013;**44**:240-246

[30] Chettiar UK, Nyga P, Thoreson MD, Kildishev AV, Drachev VP, Shalaev VM. FDTD modeling of realistic semicontinuous metal films. *Applied Physics B: Lasers and Optics*. 2010;**100**(1):159-168. DOI: 10.1007/s00340-010-3985-y

[31] Wang AX, Kong X. Review of recent progress of plasmonic materials and nano-structures for surface-enhanced Raman scattering. *Materials*. 2015;**8**:3024-3052

[32] Bang D, Chang YW, Park J, Lee T, Park J, Yeo J-S, et al. One-step electrochemical fabrication of vertically self-organized silver nanograss. *Journal of Materials Chemistry A*. 2013;**1**:4851-4857

[33] Lan H, Ding Y. Nanoimprint lithography. In: Wang M, editor. *Lithography*. IntechOpen; 2010. DOI: 10.5772/8189. Available from: <https://www.intechopen.com/books/lithography/nanoimprint-lithography>

[34] Vieu C, Carcenac F, Pépin A, Chen Y, Mejias M, Lebib A, et al. Electron beam lithography: Resolution limits and applications. *Applied Surface Science*. 2000;**164**(1-4):111-117

[35] Lushi K, Nanxi D, Guofeng T, Shengli Q, Dezhen W. Highly enhanced Raman scattering with good reproducibility observed on a flexible PI nanofabric substrate decorated by silver nanoparticles with controlled size. *Applied Surface Science*. 2020;**511**:145443

[36] Shi J, You T, Gao Y, Liang X, Li C, Yin P. Large-scale preparation of flexible and reusable surface-enhanced Raman scattering platform based on electrospinning AgNPs/PCL nanofiber membrane. *RSC Advances*. 2017;**7**(75):47373-47379

[37] Chen X, Lin H, Xu T, Lai K, Han X, Lin M. Cellulose nanofibers coated with silver nanoparticles as a flexible nanocomposite for measurement of flusilazole residues in oolong tea by surface-enhanced Raman spectroscopy. *Food Chemistry*. 2020;**315**:126276

[38] Parnsubsakul A, Ngoensawat U, Wutikhun T, Sukmanee T, Sapcharoenkun C, Pienpinijtham P, et al. Silver nanoparticle/bacterial nanocellulose paper composites for paste-and-read SERS detection of pesticides on fruit surfaces. *Carbohydrate Polymers*. 2020;**235**:115956

[39] Lu J, Song Y, Lei F, Du X, Huo Y, Xu S, et al. Electric field-modulated surface enhanced Raman spectroscopy by PVDF/Ag hybrid. *Scientific Reports*. 2020;**10**:5269

[40] Liou P, Nayigizik FX, Kong F, Mustapha A, Lin M. Cellulose nanofibers coated with silver nanoparticles as a SERS platform for detection of pesticides in apples. *Carbohydrate Polymers*. 2017;**157**:643-650

[41] Gao R, Song X, Zhan C, Weng C, Cheng S, Guo K, et al. Light trapping induced flexible wrinkled nanocone SERS substrate for highly sensitive explosive detection. *Sensors and Actuators B: Chemical*. 2020;**314**:128081

[42] Stepniowski WJ, Norek M, Michalska-Domańska M, Bombalska A, Nowak-Stepniowska A, Kwaśny M, et al. Fabrication of anodic aluminum oxide with incorporated chromate

ions. Applied Surface Science. 2012;**259**:324-330

[43] Macak JM, Tsuchiya H, Schmuki P. High-aspect-ratio TiO₂ nanotubes by anodization of titanium. *Angewandte Chemie, International Edition*. 2005;**44**(14):2100-2102

[44] Macak JM, Tsuchiya H, Taveira L, Aldabergerova S, Schmuki P. Smooth anodic TiO₂ nanotubes. *Angewandte Chemie, International Edition*. 2005;**44**(45):7463-7465

[45] Mika K, Socha RP, Nyga P, Wiercigroch E, Małek K, Jarosz M, et al. Electrochemical synthesis and characterization of dark nanoporous zinc oxide films. *Electrochimica Acta*. 2019;**305**:349-359

[46] Zaraska L, Gawlak K, Wiercigroch E, Malek K, Koziel M, Andrzejczuk M, et al. The effect of anodizing potential and annealing conditions on the morphology, composition and photoelectrochemical activity of porous anodic tin oxide films. *Electrochimica Acta*. 2019;**319**:18-30

[47] Syrek K, Zaraska L, Zych M, Sulka GD. The effect of anodization conditions on the morphology of porous tungsten oxide layers formed in aqueous solution. *Journal of Electroanalytical Chemistry*. 2018;**829**:106-115

[48] Chilimoniuk P, Michalska-Domańska M, Czujko T. Formation of nanoporous mixed aluminum-iron oxides by self-organized anodizing of FeAl₃ intermetallic alloy. *Materials*. 2019;**12**(14):2299

[49] Łazińska M, Durejko T, Michalska-Domańska M, Bojar Z. Characterization of titanium oxide formed on biomedical Ti₆Al₇Nb alloy fabricated by laser engineered net shaping (LENS). In: *Proceedings Euro PM2017: International Power Metallurgy Congress and Exhibition 2017*. Milan, Italy: Additive Manufacturing; 2017. p. 140833

[50] Stępniewski WJ, Choi J, Yoo H, Oh K, Michalska-Domańska M, Chilimoniuk P, et al. Anodization of FeAl intermetallic alloy for nanoporous mixed aluminum-iron oxide. *Journal of Electroanalytical Chemistry*. 2016;**771**:37-44

[51] Stępniewski WJ, Choi J, Yoo H, Michalska-Domańska M, Chilimoniuk P, Czujko T. Quantitative fast Fourier transform based arrangement analysis of nanoporous anodic oxide formed by self-organized anodization of FeAl intermetallic alloy. *Materials Letters*. 2016;**164**:176-179

[52] Stępniewski WJ, Paliwoda D, Chen Z, Landskron K, Misiołek WZ. Hard anodization of copper in potassium carbonate aqueous solution. *Materials Letters*. 2019;**252**:182-185

[53] Stępniewski WJ, Yoo H, Choi J, Chilimoniuk P, Karczewski K, Czujko T. Investigation of oxide nanowires growth on copper via passivation in NaOH aqueous solution. *Surface and Interface Analysis*. 2019;**14**:15-18

[54] Stępniewski WJ, Yoo H, Choi J, Norek M, Jozwik P, Misiołek WZ. Fabrication and characterization of oxide nano-needles formed by copper passivation in sodium hydroxide solution. *Thin Solid Films*. 2019;**671**:111-119

[55] Stępniewski WJ, Moneta M, Karczewski K, Michalska-Domańska M, Czujko T, Mol JMC, et al. Fabrication of copper nanowires via electrodeposition in anodic aluminum oxide templates formed by combined hard anodizing and electrochemical barrier layer thinning. *Journal of Electroanalytical Chemistry*. 2018;**15**:59-66

[56] Stępniewski WJ, Salerno M. Fabrication of nanowires and nanotubes by anodic alumina template-assisted electrodeposition. In: *Manufacturing*

Nanostructures. UK: One Central Press; 2014

[57] Stępniewski WJ, Bojar Z. Nanoporous anodic aluminum oxide: Fabrication, characterization, and applications. In: Handbook of Nanoelectrochemistry: Electrochemical Synthesis Methods, Properties, and Characterization Techniques. Switzerland: Springer; 2016. pp. 593-646

[58] Abrahami ST, de Kok JMM, Terryn H, Mol JMC. Towards Cr(VI)-free anodization of aluminum alloys for aerospace adhesive bonding applications: A review. *Frontiers of Chemical Science and Engineering*. 2017;**11**(3):465-482

[59] Abrahami ST, Hauffman T, de Kok JMM, Mol JMC, Terryn H. XPS analysis of the surface chemistry and interfacial bonding of barrier-type Cr(VI)-free anodic oxides. *Journal of Physical Chemistry C*. 2015;**119**(34):19967-19975

[60] Kulkarni M, Mazare A, Schmuki P, Iglic A. Influence of anodization parameters on morphology of TiO₂ nanostructured surfaces. *Advanced Materials Letters*. 2016;**7**(1):23-28

[61] Naghizadeh M, Abdizadeh H, Golobostanfard MR. Effect of fluoride concentration and water content on morphology of titania nanotubes in ethylene glycol solution. *Advanced Materials Research*. 2013;**829**:907-911

[62] Michalska-Domańska M, Nyga P, Czerwiński M. Ethanol-based electrolyte for nanotubular anodic TiO₂ formation. *Corrosion Science*. 2018;**134**:99-102

[63] Zhang S, Li Y, Xu P, Liang K. Effect of anodization parameters on the surface morphology and photoelectrochemical properties

of TiO₂ nanotubes. *International Journal of Electrochemical Science*. 2017;**12**(11):10714-10725

[64] Michalska-Domańska M, Stępniewski W, Salerno M. Effect of inter-electrode separation in the fabrication of nanoporous alumina by anodization. *Journal of Electroanalytical Chemistry*. 2018;**823**:47-53

[65] Michalska-Domanska M, Stępniewski WJ, Jaroszewicz LR. Characterization of nanopores arrangement of anodic alumina layers synthesized on low-(AA1050) and high-purity aluminum by two-step anodizing in sulfuric acid with addition of ethylene glycol at low temperature. *Journal of Porous Materials*. 2017;**24**(3):779-786

[66] Stępniewski WJ, Moneta M, Norek M, Michalska-Domańska M, Scarpellini A, Salerno M. The influence of electrolyte composition on the growth of nanoporous anodic alumina. *Electrochimica Acta*. 2016;**211**:453-460

[67] Stępniewski W, Norek M, Budner B, Michalska-Domańska M, Nowak-Stępniewska A, Mostek A, et al. In-situ electrochemical doping of nanoporous anodic aluminum oxide with indigo carmine organic dye. *Thin Solid Films*. 2016;**598**:60-64

[68] Stępniewski WJ, Florkiewicz W, Michalska-Domańska M, Norek M, Czujko T. A comparative study of electrochemical barrier layer thinning for anodic aluminum oxide grown on technical purity aluminum. *Journal of Electroanalytical Chemistry*. 2015;**741**:80-86

[69] Stępniewski WJ, Forbot D, Norek M, Michalska-Domańska M, Król A. The impact of electrolyte's viscosity on the formation of nanoporous anodic aluminum oxide. *Electrochimica Acta*. 2014;**133**:57-64

- [70] Stępniewski WJ, Norek M, Michalska-Domańska M, Forbot D, Król A. Study on the correlation between criterion number derived from Rayleigh-Bénard convective cells and arrangement of nanoporous anodic aluminum oxide. *Materials Letters*. 2014;**125**:124-127
- [71] Michalska-Domańska M, Norek M, Stępniewski WJ, Budner B. Fabrication of high quality anodic aluminum oxide (AAO) on low purity aluminum – A comparative study with the AAO produced on high purity aluminum. *Electrochimica Acta*. 2013;**105**:424-432
- [72] Wang Y, Wang Y, Wang H, Wang X, Cong M, Xu W, et al. Hierarchical ultrathin alumina membrane for the fabrication of unique nanodot arrays. *Nanotechnology*. 2016;**27**:025302. DOI: 10.1088/0957-4484/27/2/025302
- [73] Nguyen TT, Ung TDT, Nguyen QL. Square-inch 2D-arrays of Au nanodisks fabricated by sputtering Au onto anodic aluminum oxide templates for SERS applications. *Advances in Natural Sciences: Nanoscience and Nanotechnology*. 2016;**7**:045017
- [74] Liu D, Wang Q, Hu J, Chen L. Size correlation of optical and SERS properties for highly ordered Au nanocone arrays with sub-100 nm feature size. *Journal of Optics*. 2016;**18**:085006
- [75] Li ZP, Xu ZM, Qu XP, Wang SB, Peng J, Mei LH. Fabrication of nanopore and nanoparticle arrays with high aspect ratio AAO masks. *Nanotechnology*. 2017;**28**:095301
- [76] Kim Y-T, Schilling J, Schweizer SL, Wehrspohn RB. Morphology dependence on surface-enhanced Raman scattering using gold nanorod arrays consisting of agglomerated nanoparticles. *Plasmonics*. 2017;**12**:203-208. DOI: 10.1007/s11468-016-0250-1
- [77] Feng Y, Kim K-D, Nemitz CA, Kim P, Pfadler T, Gerigk M, et al. Uniform large-area free-standing silver nanowire arrays on transparent conducting substrates. *Journal of the Electrochemical Society*. 2016;**163**(8):D447-D452
- [78] Hao Q, Huang H, Fan X, Hou X, Yin Y, Li W, et al. Facile design of ultra-thin anodic aluminum oxide membranes for the fabrication of plasmonic nanoarrays. *Nanotechnology*. 2017;**28**:105301
- [79] Liu K, Yu Z, Zhu X, Zhang S, Zou F, Zhu Y. A universal surface enhanced Raman spectroscopy (SERS)-active graphene cathode for lithium-air batteries. *RSC Advances*. 2016;**6**:102272. DOI: 10.1039/c6ra23331g
- [80] Zhao W, Wu Y, Liu X, Xu Y, Wang S, Xu Z. The fabrication of polymer-nanocone-based 3D Au nanoparticle array and its SERS performance. *Applied Physics A: Materials Science & Processing*. 2017;**123**:45. DOI: 10.1007/s00339-016-0665-8
- [81] Zhao WN, Liu XG, Xu YB, Wang SB, Sun TY, Liu SS, et al. Polymer nanopillar array with Au nanoparticle inlays as a flexible and transparent SERS substrate. *RSC Advances*. 2016;**6**:35527-35531
- [82] Bao Z, Wu Y. TiO₂ thin layer coated Ag nanoarrays complex for surface-enhanced Raman scattering substrate. *Key Engineering Materials*. 2013;**562-565**:1037-1042. DOI: 10.4028/www.scientific.net/kem.562-565.37
- [83] Zhou Y, Chen J, Zhang L, Yang L. Multifunctional TiO₂-coated Ag nanowire arrays as recyclable SERS substrates for the detection of organic pollutants. *European Journal of Inorganic Chemistry*. 2012;**2012**:3176-3182
- [84] Zhang C-y, Lu Y, Zhao B, Hao Y-w, Liu Y-q. Facile fabrication of Ag

- dendrite-integrated anodic aluminum oxide membrane as effective three-dimensional SERS substrate. *Applied Surface Science*. 2016;**377**:167-173
- [85] Pisarek M, Holdynski M, Roguska A, Kudelski A, Janik-Czachor M. TiO₂ and Al₂O₃ nanoporous oxide layers decorated with silver nanoparticles—Active substrates for SERS measurements. *Journal of Solid State Electrochemistry*. 2014;**18**:3099-3109
- [86] Chen H, Ohodnicki P, Baltrus JP, Holcomb G, Tylczak J, Henry D. High-temperature stability of silver nanoparticles geometrically confined in the nanoscale pore channels of anodized aluminum oxide for SERS in harsh environments. *RSC Advances*. 2016;**6**:86930
- [87] Lim L-K, Ng B-K. Large scale AAO nano-fiber substrate for SERS application. In: *Photonics North (PN)*. Quebec City, QC; 2016. pp.1-2. DOI: 10.1109/PN.2016.7537899
- [88] Dan Y, Zhong C, Zhu H, Wang J. Highly ordered Au-decorated Ag nanorod arrays as an ultrasensitive and reusable substrate for surface enhanced Raman scattering. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*. 2019;**560**:360-365
- [89] Zhong C, Dan Y, Zhang P, Wang J. Self-assembly urchin-like Au-NSs arrays and application as surface-enhanced Raman scattering substrates. *Materials Letters*. 2019;**234**:125-128
- [90] Yang L, Ruan W, Jiang X, Zhao B, Xu W, Lombardi JR. Contribution of ZnO to charge-transfer induced surface-enhanced Raman scattering in Au/ZnO/PATP assembly. *Journal of Physical Chemistry C*. 2009;**113**:117-120
- [91] Yang L, Jiang X, Ruan W, Yang J, Zhao B, Xu W, et al. Charge-transfer-induced surface-enhanced Raman scattering on Ag-TiO₂ nanocomposites. *Journal of Physical Chemistry C*. 2009;**113**:16226-16231. DOI: 10.1021/jp903600r
- [92] Yang L, Jiang X, Ruan W, Zhao B, Xu W, Lombardi JR. Observation of enhanced Raman scattering for molecules adsorbed on TiO₂ nanoparticles: Charge-transfer contribution. *Journal of Physical Chemistry C*. 2008;**112**:20095-20098
- [93] Jakubowicz J, Koper JK, Adamek G, Połomska M, Wolak J. Silver Nano-trees deposited in the pores of anodically oxidized titanium and Ti scaffold. *International Journal of Electrochemical Science*. 2015;**10**:4165-4172
- [94] Belich NA, Grigor'eva AV, Petukhov DI, Sidorov AV, Gołdt AE, Gudilin EA. Immobilization of nanostructured metal silver at the surface of anodic titanium dioxide for the creation of composites with the surface plasmon resonance. *Nanotechnologies in Russia*. 2015;**10**(5-6):345-352
- [95] Witkowska E, Szymborski T, Waluk J, Michota-Kamińska A. The platform for testing of chemicals and microorganisms via surface enhanced Raman spectroscopy and method of its preparation; 2014. p. 409210
- [96] Kamińska A, Sivanesan A, Witkowska E, Gołąb J, Winiarska M, Nowis D, et al. Detection of DNA mutations using novel surface-enhanced Raman spectroscopy (SERS) diagnostic platform. *Journal of Chemistry and Chemical Engineering*. 2013;**7**:199-208
- [97] Sun Y, Yang L, Liao F, Dang Q, Shao M. Parameter optimization for Ag-coated TiO₂ nanotube arrays as recyclable SERS substrates. *Applied Surface Science*. 2018;**443**:613-618
- [98] Wen S, Su Y, Wu R, Zhou S, Min Q, Fan G-C, et al. Plasmonic Au nanostar

Raman probes coupling with highly ordered TiO₂/Au nanotube arrays as the reliable SERS sensing platform for chronic myeloid leukemia drug evaluation. *Biosensors and Bioelectronics*. 2018;**117**:260-266

[99] Ling Y, Zhuo Y, Huang L, Mao D. Using Ag-embedded TiO₂ nanotubes array as recyclable SERS substrate. *Applied Surface Science*. 2016;**388**:169-173

[100] Roguska A, Kudelski A, Pisarek M, Opara M, Janik-Czachor M. Surface-enhanced Raman scattering (SERS) activity of Ag, Au and Cu nanoclusters on TiO₂-nanotubes/Ti substrate. *Applied Surface Science*. 2011;**257**:8182-8189

[101] Huang Y, Sun L, Xie K, Lai Y, Liu B, Ren B, et al. SERS study of Ag nanoparticles electrodeposited on patterned TiO₂ nanotube films. *Journal of Raman Spectroscopy*. 2011;**42**:986-991. DOI: 10.1002/jrs.2830

[102] Kudelski A, Pisarek M, Roguska A, Hołdyński M, Janik-Czachor M. Surface-enhanced Raman scattering investigations on silver nanoparticles deposited on alumina and titania nanotubes: Influence of the substrate material on surface-enhanced Raman scattering activity of Ag nanoparticles. *Journal of Raman Spectroscopy*. 2012;**43**:1360-1366

[103] Banholzer MJ, Millstone JE, Qin L, Mirkin CA. Rationally designed nanostructures for surface-enhanced Raman spectroscopy. *Chemical Society Reviews*. 2008;**37**:885-897