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# 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<sup>2</sup> [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<sup>14</sup>), 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"><li>• The possibility of controlling the metal nanoparticles’ size and shape as well as the interparticle distance with great accuracy</li><li>• Good reproducibility at a molecular resolution range</li></ul> | <ul style="list-style-type: none"><li>• Expensive equipment</li><li>• Many steps are required to prepared one substrate</li><li>• Quite long processes, so long manufacturing time for higher areas than nm<sup>2</sup></li><li>• High cost for areas larger than few μm<sup>2</sup></li><li>• Mass production is doubtedly</li></ul> |

**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"><li>• High repeatability of microstructures</li><li>• SERS enhancement was not high</li></ul>   | 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"><li>• Durable substrates</li><li>• Restrictions on use in the excitation wavelength and laser power range</li><li>• Single-use medium</li><li>• Gain up to 10<sup>6</sup> depending on the analyte</li><li>• Temperature and humidity sensitivity</li></ul> | 175\$/ 25pieces (0.25 inch)                                     |
| Ocean Optics Inc., USA                             | Colloidal Ag nanoparticles deposited on cellulose fibers—printing   | <ul style="list-style-type: none"><li>• Single-use</li><li>• Durability 1–1.5 months</li><li>• Temperature and humidity sensitive</li><li>• Restrictions in the excitation wavelength and laser power range</li></ul>   | 64\$/piece (cellulose/Au)<br>62\$/piece (cellulose/Ag) (5.5 mm) |
| Ocean Optics Inc., USA                             | Metallic Au or Ag nanosponges   | <ul style="list-style-type: none"><li>• Reusable</li><li>• Durability up to 6 months</li><li>• Restrictions in the excitation wavelength and laser power range</li></ul>  | 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"><li>• Laser power restrictions</li><li>• Relatively high cost of substrate production</li></ul>   | 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"><li>• Measurement recommendation on a spherical area 4 mm in diameter at the center of the substrate</li></ul>  | 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"><li>• Very low durability, up to 70 hours after opening the container</li><li>• 10<sup>5</sup>–10<sup>7</sup> enhancement, depending on the analyte type</li></ul>            | 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"><li>• Only a laser with a wavelength of 785 nm</li><li>• Long shelf life</li><li>• The surface is not homogeneous, which results in lower repeatability of analyses</li></ul> | 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  $8.00 \times 10^6$  to  $1.79 \times 10^7$  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-O<sub>2</sub> 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<sup>-1</sup> was calculated at  $1.21 \times 10^7$ , 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<sup>-12</sup> M. The enhancement factor was calculated at  $1.30 \times 10^8$ . 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<sup>-12</sup> M and the enhancement factor was calculated at  $8.20 \times 10^7$ . 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 AgNO<sub>3</sub> 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  $\text{TiO}_2$  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.,  $\text{ZnO/Ag}$  [90] and  $\text{TiO}_2/\text{Ag}$  [91–94] or protected by the patent of Polish inventors  $\text{GaN/Ag}$  [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  $1.00 \times 10^{-11}$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $0.06 \text{ mg Ag/cm}^2$ , 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/ $\text{TiO}_2$ -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/ $\text{TiO}_2$ -nanotube/Ti composite.

Huang et al. [101] prepared SERS substrate consisting of Ag nanoparticles (NPs) deposited on patterned  $\text{TiO}_2$  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/ $\text{TiO}_2$ -n/Ti and Ag/ $\text{Al}_2\text{O}_3$ -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 ( $0.02 \text{ mg/cm}^2$ ), 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/ $\text{Al}_2\text{O}_3$  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  $\text{TiO}_2$ . 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  $\text{TiO}_2$  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 ( $10^{-14} \text{ M}$ ) and methyl parathion (MP) (up to  $10^{-6} \text{ M}$ ) 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  $1 \text{ mm}^2$ . 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.

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## Author details

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

\*Address all correspondence to: [marta.michalska@wat.edu.pl](mailto:marta.michalska@wat.edu.pl)

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