

*Research Article*

Silver-Coated Cobalt Microtubes for Surface-Enhanced Raman Sensing

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Abstract: In this study, magneto-plasmonic Co@Ag microtubes were developed as controllable substrates for surface-enhanced Raman sensing. Cobalt microtubes were synthesized by template-assisted electrochemical deposition in track-etched polyethylene terephthalate membranes with an average pore diameter of 400 ± 20 nm, followed by template removal and electroless deposition of silver on the Co surface. The silver coating was performed using a solution containing AgNO₃, potassium sodium tartrate, and pyridine, resulting in the formation of nanostructured Ag layers on the cobalt microtube framework. The obtained structures' morphology, elemental distribution, crystal structure, surface composition, and magnetic properties were investigated using scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and vibrating sample magnetometry. The results confirmed the formation of hollow Co microtubes uniformly coated with a crystalline metallic Ag layer. Magnetic measurements showed that silver deposition changed the coercivity and squareness ratio of the microtubes while preserving their magnetic responsiveness. The Co core enabled external-field-assisted alignment and local organization of the microtubes on the substrate, whereas the Ag shell provided plasmonic activity and hot-spot formation for Raman signal enhancement. Using rhodamine 6G as a model analyte, the Co@Ag microtubes demonstrated surface-enhanced Raman detection down to 10^{-9} M, with enhancement factors on the order of 10^6 . These results highlight the potential of magnetoplasmonic Co@Ag microtubes as efficient and tunable platforms for surface-enhanced Raman spectroscopy applications.

Keywords: Cobalt microtubes; Magneto-plasmonic structures; Rhodamine 6G detection; Surface-enhanced Raman scattering; Track-etched membranes

1. Introduction

Surface-enhanced Raman scattering (SERS) is a highly sensitive spectroscopic technique that enables the detection of molecules at low concentrations, often down to the single-molecule level (Bahlol et al., 2024; Blackie et al., 2009; Xu et al., 2020). SERS has found wide application in chemical sensing, biosensing, catalysis monitoring, and environmental analysis since its discovery (Chen et al., 2021; Huang et al., 2023; Sharma et al., 2012; Song et al., 2017; Yan et al., 2016). The principle of SERS relies on the enhancement of Raman scattering by localized surface plasmon resonances (LSPR), which arise when electromagnetic radiation interacts with nanostructured metallic surfaces (Sharma et al., 2012).

The intrinsically weak nature of conventional Raman scattering limits its practical application for trace analysis of low-concentration analytes. Therefore, the development of SERS-active substrates capable of generating strong and reproducible local electromagnetic fields remains a key challenge in modern Raman-based sensing.

The efficiency of SERS strongly depends on the morphology, composition, and surface

structure of plasmonic nanomaterials. Noble metals, such as silver and gold, are most frequently employed owing to their strong visible plasmonic activity and well-developed synthesis strategies (Chen et al., 2021; Kalachyova et al., 2017). Considerable efforts have been devoted to the development of reproducible SERS-active substrates by controlling the nanostructure geometry, dimensionality, and distribution of “hot spots” (Han et al., 2024; Wei et al., 2024; Zhou et al., 2025).

The introduction of magnetic functionality into plasmonic nanostructures has opened new avenues for SERS-active substrates in recent years. Magnetic-plasmonic hybrids, typically based on ferromagnetic cores (Fe, Ni, Co) decorated with plasmonic metals (Au, Ag), combine strong electromagnetic enhancement with the ability to be manipulated by external magnetic fields (Huynh et al., 2021; Serafinelli et al., 2022; Tiryaki et al., 2024; Wang et al., 2020). This dual functionality not only improves the reproducibility of SERS analysis but also enables spatial alignment, concentration, and magnetic separation of analytes. Several studies have demonstrated that gold- or silver-coated magnetic nanoparticles can serve as efficient multifunctional SERS platforms for biosensing, pollutant detection, and bioimaging (Du & Jing, 2011; Du et al., 2014; Hou et al., 2012). Thus, magnetic-plasmonic systems offer an important advantage over purely plasmonic substrates: they allow not only signal enhancement but also active control over the SERS-active material’s position, distribution, and local concentration.

Particular attention has also been paid to one-dimensional nanostructures, such as nanowires and nano- and microtubes, due to their high aspect ratios, anisotropic properties, and large active surfaces (Kozhina et al., 2021b, 2021a; Perales-Rondon et al., 2020). Another important feature of micro- and nanotubular architectures is their hollow one-dimensional geometry. Magnetic microtubes possess a higher aspect ratio, larger accessible surface area, pronounced shape anisotropy, and improved orientability in an external magnetic field than small magnetic nanoparticles. These properties make them promising not only for the detection of small model molecules but also for the future analysis of large organic molecules and biological objects, including proteins, biomacromolecules, and complex molecular assemblies, whose interaction with small nanoparticles may be spatially limited or poorly controlled. Perales-Rondon et al. (2020) synthesized silver microtubes in polycarbonate track-etched membranes and demonstrated their applicability as SERS substrates for the quantitative detection of Rhodamine 6G. In our previous studies (Korolkov et al., 2022; Shumskaya et al., 2021, 2022), we investigated the gold coating of Ni nanotubes. The resulting structures demonstrated encouraging results for their application as SERS-active substrates for the detection of dyes and nitro compounds.

Template-assisted synthesis using track-etched membranes (TeMs) is one of the most versatile and scalable approaches for the fabrication of one-dimensional nanostructures, including nanowires, nanotubes, and microtubes (Korolkov et al., 2017; Kozlovskiy et al., 2019; Kozlovskiy et al., 2017; Shakayeva et al., 2025; Yeszhanov et al., 2018). The high density and uniformity of channels in TeMs allow precise control over the deposited nano- and microstructure geometry. Electrochemical deposition through such templates enables the synthesis of cobalt microtubes with tunable wall thickness, diameter, and length. Cobalt is an attractive material because of its strong ferromagnetic properties, which ensure high coercivity and magnetic anisotropy, making it suitable for external alignment and manipulation. At the same time, plasmonic coatings from silver or gold play a key role in enhancing the sensitivity of Raman-based detection techniques, as they can generate strong localized electromagnetic fields on the nanostructure surface. Recent studies have demonstrated that Co-Ag and Ni-Ag hybrids show promising magnetoplasmonic properties and can be efficiently used in SERS (Fan et al., 2017; Lv et al., 2021; Petruš et al., 2021).

In this study, we report the fabrication of cobalt microtubes by electrochemical deposition in PET track-etched membranes, followed by electroless silver deposition to obtain magnetoplasmonic Co@Ag structures. The obtained microtubes were characterized using SEM/EDX, XRD, XPS, and VSM analyses to confirm their morphology, structure, surface composition, and magnetic properties. The Co@Ag microtubes were tested as SERS-active substrates using

rhodamine 6G as a model analyte, demonstrating detection down to 10^{-9} M. The novelty of this study lies in the fabrication of hollow Co@Ag microtubes that combine the magnetic responsiveness and structural anisotropy of cobalt with the nanostructured silver shell's plasmonic activity. To the best of our knowledge, Co@Ag hollow microtubes obtained by template-assisted synthesis have not been previously investigated as magnetically controllable SERS-active substrates. The combination of magnetic responsiveness, hollow one-dimensional geometry, and Ag-based plasmonic activity makes these microtubes promising candidates for the development of tunable and reproducible SERS platforms for chemical, environmental, and future bioanalytical applications.

2. Materials and Methods

2.1 Chemicals

Silver nitrate (AgNO_3 , $\geq 99.0\%$) and rhodamine 6G (R6G) were purchased from Sigma-Aldrich (Gillingham, Dorset, United Kingdom). Cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), boric acid (H_3BO_3), sodium hydroxide (NaOH), sodium chloride (NaCl), acetic acid (CH_3COOH), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), ethanol ($\text{C}_2\text{H}_5\text{OH}$), ammonia solution (NH_4OH), potassium sodium tartrate tetrahydrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), and pyridine ($\text{C}_5\text{H}_5\text{N}$) were purchased from OAO Reaktiv (Novosibirsk, Russia). All chemicals were of analytical grade and were used as received without additional purification. Deionized water with $18.2 \text{ M}\Omega \cdot \text{cm}$ resistivity was produced using an Aquilon-D301 water purification system (Aquilon, Podolsk, Russia).

2.2 Co microtube template synthesis

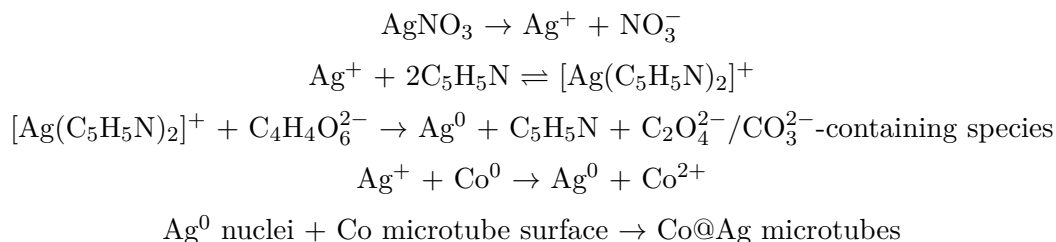
Polyethylene terephthalate (PET) track-etched membranes (TeMs) were used as templates. The membranes had a thickness of $12 \mu\text{m}$, an average pore diameter of approximately $400 \pm 20 \text{ nm}$, and a pore density of $4 \times 10^7 \text{ pores cm}^{-2}$. Cobalt microtubes were fabricated via electrochemical deposition in potentiostatic mode within a two-electrode cell at a constant potential of 1.5 V . A thin gold layer ($10\text{--}20 \text{ nm}$) sputtered onto the backside of the PET TeM served as the cathode. This coating was too thin to fully seal the pores but enabled the formation of a metallic rim around each opening, guiding the growth of hollow structures. The electrolyte used for Co microtube formation contained $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (120 g L^{-1}), H_3BO_3 (45 g L^{-1}), and $\text{C}_6\text{H}_8\text{O}_6$ (3 g L^{-1}). Deposition was performed at 25°C with the pH adjusted to 3. The process was monitored by recording the voltage-time response using a VersaSTAT3 potentiostat (AME-TEK Scientific Instruments, Oak Ridge, TN, USA). Under these conditions, the pore channels remained open during deposition, forming hollow microtubular structures.

2.3 Electroless Ag deposition on Co microtubes

Upon completion of microtube growth, the PET template was eliminated by chemical etching in 5 M NaOH for 4 hours, which ensured complete polymer matrix dissolution. Silver coating of the Co microtubes was performed using a solution containing 34 mM AgNO_3 , 120 mM potassium-sodium tartrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), and 50 mM pyridine. The deposition process was conducted in Eppendorf-type tubes under continuous mixing on a vortex agitator at room temperature for 16 hours. After the reaction, the samples were thoroughly rinsed with water and ethanol and subsequently stored in ethanol until further use.

The proposed scheme of Ag deposition on Co microtubes is shown below. At the initial stage, Ag^+ ions may be adsorbed on the Co surface. Ag^+ ions are stabilized in solution by pyridine. Potassium sodium tartrate tetrahydrate acts as a reducing agent, promoting the further reduction of Ag^+ species to Ag^0 atoms. The generated Ag^0 atoms subsequently nucleate and grow on the initially formed Ag sites, forming Ag nanoparticles and a nanostructured Ag shell on the Co microtube surface. Partial reduction of Ag^+ may also occur in solution, and free Ag particles can be formed as a by-product. Magnetic separation was applied after the deposition process to separate Ag-coated Co microtubes from non-magnetic free silver particles.

It should also be noted that the XPS analysis shows that the surface of the Co microtubes contains a CoO layer. Therefore, the direct galvanic replacement between Ag^+ and metallic Co is limited. However, a partial surface-assisted redox interaction between Ag^+ and metallic Co at defect sites or locally exposed Co areas cannot be excluded.



2.4 Characterization methods

X-ray diffraction (XRD) measurements were performed at room temperature using a Smart-Lab diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The obtained diffraction patterns were processed and interpreted using the DIFFRAC.EVA software (version 4.2.1; Bruker AXS GmbH, Karlsruhe, Germany). The average crystallite size was calculated from the broadening of the XRD reflections using the Scherrer equation (1):

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D is the average crystallite size, K is the shape factor taken, λ is the X-ray wavelength of Cu $K\alpha$ radiation ($1.5406 \text{ \AA}$), β is the full width at half maximum of the diffraction peak in radians, and θ is the Bragg diffraction angle.

Surface morphology and elemental composition were examined by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using a Hitachi TM 3030 microscope equipped with a Bruker XFlash MIN SVE microanalysis system operating at 15 kV. Magnetic properties were evaluated from magnetization hysteresis loops recorded using a vibrating sample magnetometer integrated into a liquid helium-free high-field measurement system (Cryogenic Ltd.). Measurements were performed at ambient temperature in magnetic fields up to 2 T.

2.5 The SERS assay

Surface-enhanced Raman scattering measurements were performed using Rhodamine 6G (R6G) as a model analyte. Before measurements, Co@Ag microtubes were dispersed in ethanol to obtain a suspension with a concentration of 10 mg mL^{-1} . A drop of the Co@Ag suspension was deposited onto a single-crystal silicon substrate and distributed over the surface using an external magnetic field to improve the spatial organization of the magnetic microtubes. The substrate was then dried under ambient conditions. Then, 0.1 mL of R6G aqueous solution with concentrations ranging from 10^{-3} to 10^{-9} M was applied to the prepared Co@Ag microtube substrate and dried again before analysis. The SERS spectra were recorded using a Senterra Raman microscope (Bruker) in the spectral range of $600\text{--}1800 \text{ cm}^{-1}$. A 532-nm laser with a laser power of 2 mW was used as the excitation source. The acquisition time for each spectrum was 2 s . Spectra were collected from five different positions on the substrate for each concentration, and the final intensity values were calculated as the arithmetic mean of these measurements. The silicon substrate and Co@Ag microtubes without R6G were measured as reference samples to confirm the absence of interfering Raman bands in the analytical spectral region.

3. Results and Discussion

3.1 Co microtube synthesis and electroless silver deposition

Figure 1 shows SEM images of the initial Co microtubes, showing uniform shape and smooth wall surfaces. The average length of microtubes is $10 \pm 1 \mu\text{m}$, diameter is $\sim 400 \pm 20 \text{ nm}$. The morphology and elemental composition of the Co@Ag microtubes are shown in Figure 2. The SEM image in panel (a) shows a characteristic cluster of microtubes whose surfaces are covered with nanostructured silver agglomerates. The inset presents an elemental mapping, where cobalt is marked in green and silver in red, revealing a uniform coating of the cobalt framework with silver nanoparticles. Panel (b) illustrates a single microtube; the inset shows the elemental distribution with cobalt forming the core and silver localized on its outer surface. The EDS spectrum in panel (c) confirms the presence of only cobalt and silver in the sample. According to the quantitative analysis (Table 1), the mass contents of silver and cobalt are 77.53% and 22.47%, respectively, indicating the formation of a continuous silver layer on the surface of the cobalt microtubes.

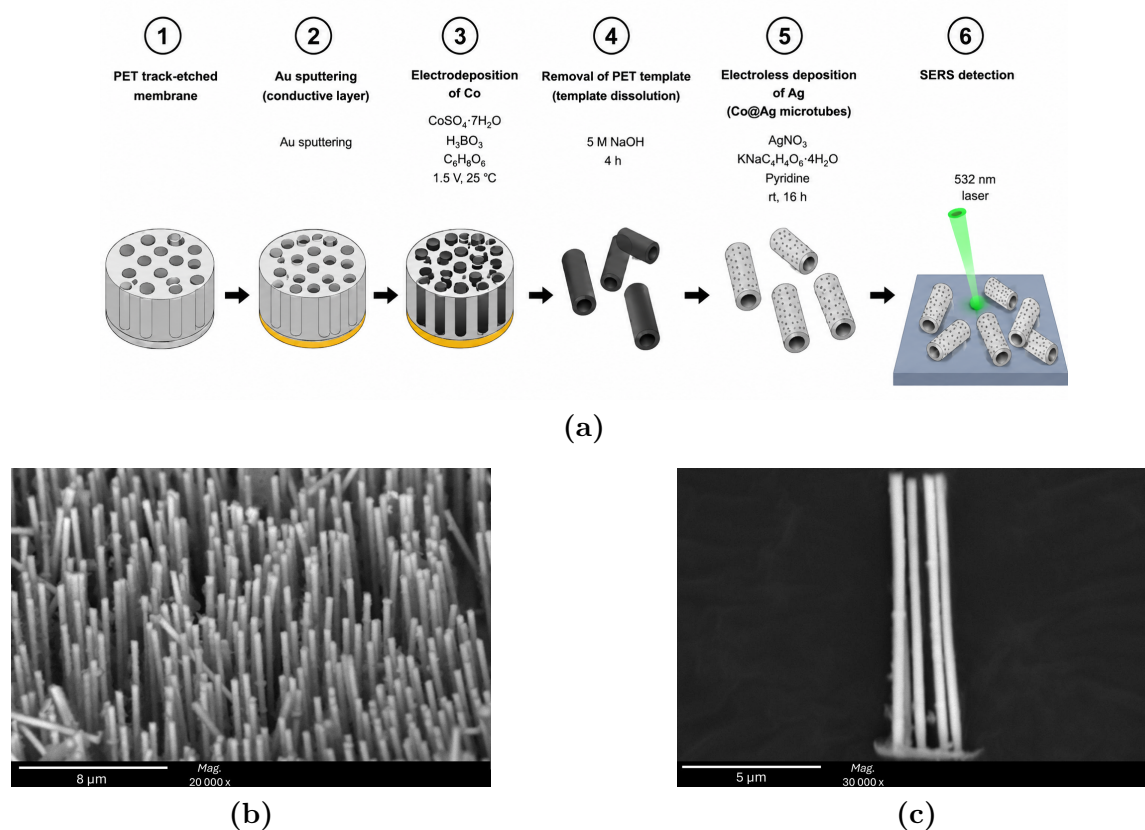


Figure 1 (a) Scheme of preparation of Co@Ag microtubes and SEM images of the Co microtubes: microtube collection area (b) and area of individual microtubes (c)

Table 1 Elemental analysis of the Co@Ag microtubes

Element	Type of the line	Weight %	Atom. %
Co	K-line	22.47	34.66
Ag	L-line	77.53	65.34

Figure 3a shows the X-ray diffraction (XRD) patterns of the obtained Co and Co@Ag microtubes. The pristine Co microtubes exhibit characteristic diffraction peaks at 2θ 44.2° , 51.5° , 75.9° , and 92.4° , which can be indexed to the (111), (200), (220), and (311) planes of face-centered cubic cobalt (Fm-3m) (PDF 01-077-7451).

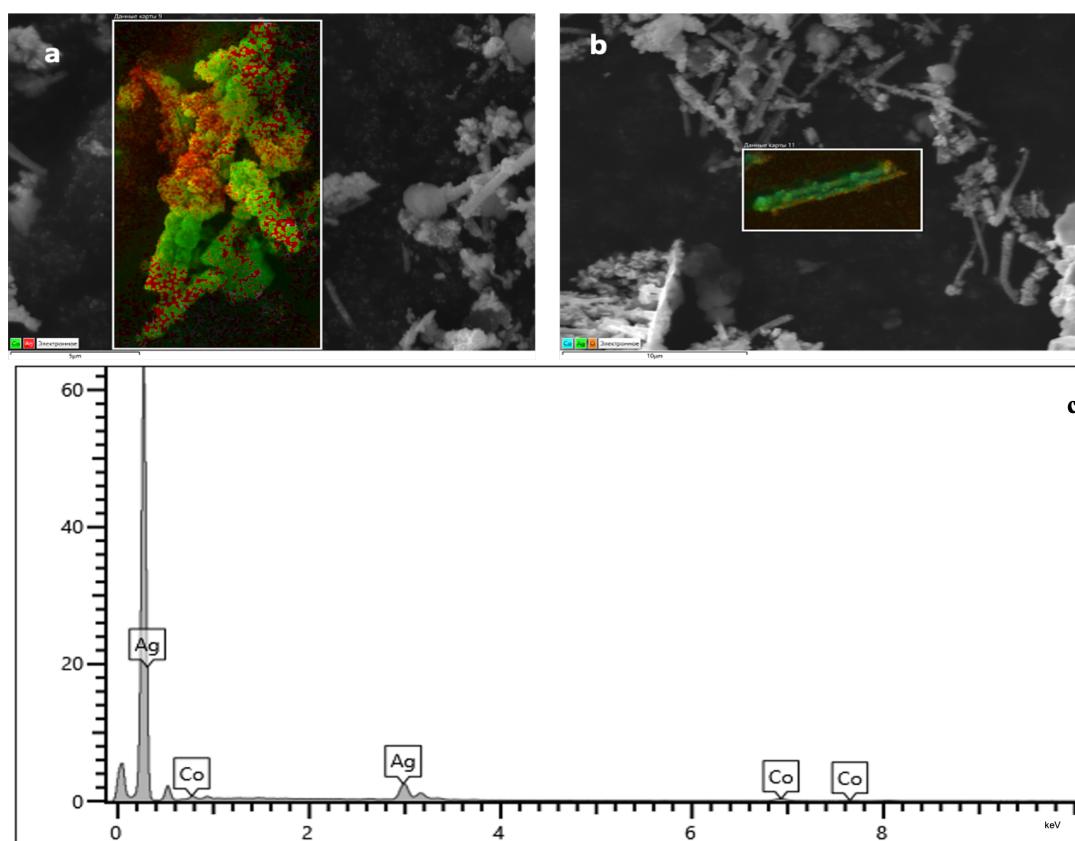


Figure 2 (a) SEM image, (b) SEM image, and (c) EDX spectrum of the Co@Ag microtubes

Although bulk cobalt is commonly associated with the hexagonal close-packed structure at room temperature, fcc Co formation can occur under nonequilibrium conditions during electrochemical deposition. In the present case, cobalt was deposited inside the confined nanochannels of PET track-etched membranes, where rapid nucleation, restricted crystal growth, small crystallite size, and internal microstrain can stabilize the metastable fcc Co phase. Whole pattern profile fitting analysis (WPPF) confirmed the presence of a single cobalt phase (100 wt%) with a refined lattice parameter of $a = 3.5490(18)$ Å and an average crystallite size of 10.6 nm, accompanied by a microstrain value of 0.5%. The relatively small crystallite size and sharp diffraction reflections indicate high crystallinity within the Co microtubular framework. After silver deposition, the diffraction pattern reveals additional strong reflections at 2θ 38.1°, 44.3°, 64.4°, 77.4°, 81.5°, 110.5°, and 114.9°, which are assigned to the (111), (200), (220), (311), (222), (331), and (420) planes of fcc Ag (PDF 04-0783). Rietveld refinement confirmed the coexistence of both phases in the composite: 83 wt% Ag and 17 wt% Co. The lattice parameters were refined as $a = 4.0860(3)$ Å for Ag and $a = 3.555(2)$ Å for Co. The average crystallite size of silver calculated by the Scherrer equation (1) was 14.6 nm, whereas the crystallite size of cobalt in the coated Co@Ag sample could not be reliably determined due to the overlap of Co diffraction reflections with the intense Ag peaks. Therefore, to avoid overinterpretation of the XRD data, the Co crystallite size in the Co@Ag sample is not reported in Table 2.

The coexistence of fcc Co and fcc Ag phases is important for understanding the functional behavior of Co@Ag microtubes. Because cobalt and silver have different lattice parameters, the formation of the hybrid structure should not be interpreted as the formation of a Co-Ag solid solution. Instead, the XRD results indicate that the crystalline cobalt microtube preserves its structural integrity and supports the growth of crystalline Ag nanostructures. The Ag coating forms a rough nanocrystalline outer shell, which is responsible for localized surface plasmon excitation under laser irradiation. The Co core provides magnetic responsiveness and allows the microtubes to be oriented, concentrated, or spatially organized by an external magnetic field.

The combination of a ferromagnetic Co scaffold and a plasmonic Ag shell is the key determining factor.

Table 2 XRD data of Co and Co@Ag microtube samples

Sample	Phase	Lattice parameter, Å	Crystallite size (nm)	Phase concentration (%)
Co microtubes	Co – Cubic, Fm-3m	$a=3.5490(18)$	10.6	100
Co@Ag microtubes	Co – Cubic, Fm-3m	$a=3.555(2)$	n.d.*	17
	Ag – Cubic, Fm-3m	$a=4.0860(3)$	14.6	83

* Note: n.d. – not reliably determined due to the overlap of Co reflections with intense Ag diffraction peaks.

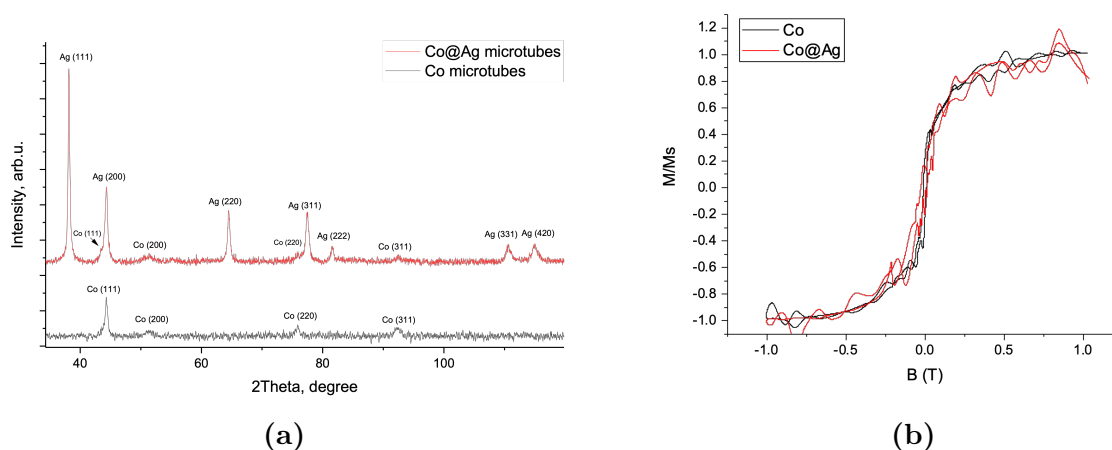


Figure 3 (a) XRD and (b) hysteresis loops for Co and Co@Ag microtubes

The emergence of well-defined Ag peaks combined with an increased crystallite size demonstrates the successful formation of a crystalline Ag shell on the Co microtube surface. Simultaneously, the persistence of Co reflections confirms that the cobalt framework remains structurally stable after coating. Overall, these findings highlight the dual-phase nature of the Ag/Co system and highlight the role of Co microtubes as a robust support for the growth of crystalline silver, which may enhance their functional properties in applications such as SERS.

Figure 3b shows the results of magnetic property measurements for Co microtubes and Co@Ag microtubes. The coercivity and squareness ratio of the hysteresis loops for Co@Ag microtube samples show noticeable variations compared with the corresponding parameters of powder Co microtubes. Such changes can be attributed to the partial disruption of the continuous magnetic structure of the ferromagnetic material, which is explained by the mutually influencing antagonism between ferromagnetic and plasmonic metals. For the pristine Co microtubes, the coercivity and squareness ratio are 96 Oe and 0.229, respectively, whereas these values are 195 Oe and 0.146 for the Co@Ag microtubes. The presence of silver on the cobalt surface and the possible chemical processes occurring during silver deposition led to a twofold increase in coercivity and a decrease in loop squareness.

The relatively high coercivity of cobalt microtubes may promote the formation of agglomerates when deposited on a substrate, which complicates their spatial orientation in a magnetic field. Simultaneously, the ferromagnetic nature of the powder samples offers opportunities for precise manipulation using an external magnetic field. On the one hand, this makes it possible

to concentrate them in a specific area of the substrate, creating local zones with an increased amount of analyte for SERS analysis. On the other hand, magnetic anisotropy ensures the ordered distribution of individual plasmon-active Co@Ag microtubes along the magnetic field lines during the fabrication or application of SERS-active substrates.

Figure 4 shows the XPS survey and high-resolution spectra revealing the elemental composition and electronic states of Co and Co@Ag microtubes. The Co 2p region in the Co microtubes (Figure 4a–d) shows two major components at 780.8 eV (Co 2p_{3/2}) and 796.9 eV (Co 2p_{1/2}), with a spin-orbit separation of 16.1 eV, consistent with Co²⁺ species. In addition, characteristic shake-up satellites were observed at 786.1 and 803.1 eV, confirming the presence of Co²⁺ in the octahedral CoO-like coordination. The absence of additional Co³⁺-related components (typically near 779.6 eV) indicates that cobalt exists mainly as Co²⁺. Considering that XRD revealed only metallic cobalt reflections, the oxidized component detected by XPS is attributed to a thin surface CoO layer formed upon air exposure. Such a layer is amorphous or thin, making it invisible in the XRD pattern but easily detected by surface-sensitive XPS.

The O 1s spectrum consists of a main peak centered at 530.8 eV, which is attributed to lattice oxygen (O²⁻) in CoO, and a weaker shoulder at 532.1 eV, which corresponds to surface hydroxyl or adsorbed oxygen species. In addition, low-intensity Ag signals are detected, originating from a thin conductive Ag layer unintentionally formed during the template-assisted synthesis. This layer was deposited to improve the conductivity of the track-etched membrane template, and after cobalt deposition and template removal, only residual Ag remained on the surface. The weak Ag 3d_{5/2}–3d_{3/2} doublet appears at 368.1 and 374.1 eV, respectively, with a spin-orbit splitting of 6.0 eV, typical for metallic Ag⁰.

In contrast, Co@Ag microtubes (e–h) exhibited a pronounced increase in the intensity of the Ag-related signal. The Ag 3d_{5/2} (368.0 eV) and Ag 3d_{3/2} (374.0 eV) peaks are sharp and symmetric, which are characteristic of metallic Ag⁰, confirming the successful deposition of a continuous silver shell on the cobalt microtubes. No shake-up satellites (typical for Ag⁺ in Ag₂O or AgO near 367.6 or 368.5 eV) were observed, further supporting the metallic state. The Co 2p spectral shape remained similar to that of the pristine Co sample, suggesting that Co²⁺ was still present in the Co²⁺ state in the near-surface region but was largely covered by the Ag overlayer, reducing its relative intensity. Overall, these XPS data confirm that the Co microtubes possess a thin surface oxide film (CoO) with traces of Ag contamination, whereas the Co@Ag microtubes are characterized by a metallic Ag coating, effectively forming a Co@Ag structure.

3.2 SERS using the Co@Ag microtubes

Surface-enhanced Raman scattering (SERS) is a highly sensitive analytical approach based on the amplification of Raman signals from molecules located near nanostructured plasmonic surfaces. In the present Co@Ag system, this enhancement is mainly provided by the Ag shell, which generates localized electromagnetic fields and plasmonic “hot spots” near nanoscale surface irregularities, interparticle gaps, and tube-tube contact regions. The Co core does not act as the main plasmonic component but provides magnetic responsiveness and enables the microtubes to be organized on the substrate via external-field-assisted organization. The Ag-induced electromagnetic enhancement and Co-assisted spatial control of the SERS-active structures jointly determined the SERS activity of the Co@Ag microtubes.

To achieve this, ethanol suspensions of Co@Ag nanotubes were deposited onto single-crystal silicon substrates. Figure 5 shows the Raman spectra of the Co@Ag samples and the silicon wafer. In the Raman spectra of the nanotubes deposited on the silicon substrate, the characteristic Raman peak of single-crystal silicon (512–517 cm⁻¹) is recorded, while the microtubes themselves are not detected, which will be considered as a baseline in further spectral analysis. Moreover, the fact that the microtubes are transparent throughout the spectral range is a favorable prerequisite for their further use as plasmon-active structures in SERS measurements because the signal from the microtubes will not interfere with SERS results.

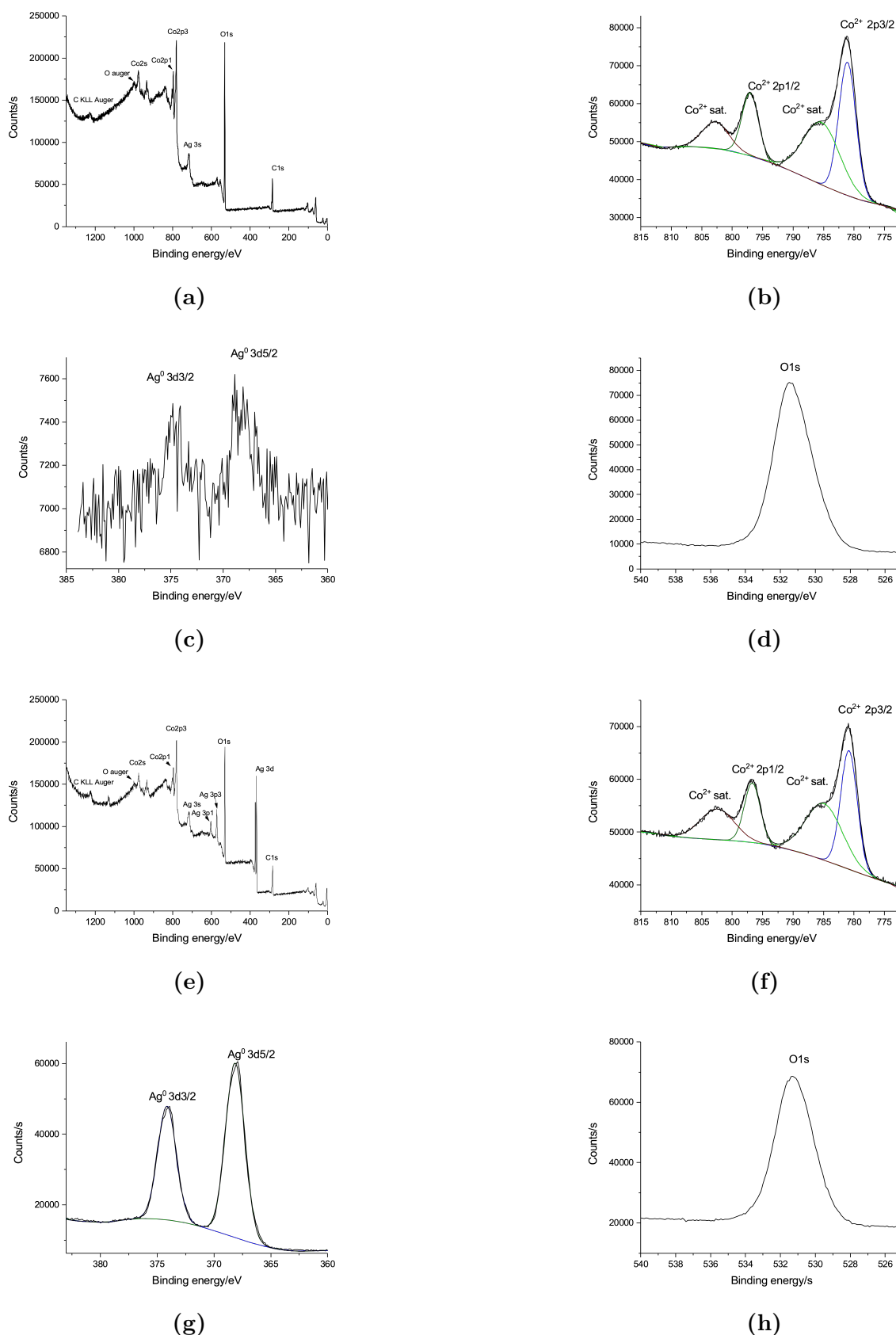


Figure 4 XPS spectra of Co microtubes (a–d) and Co@Ag microtubes (e–h)

Rhodamine 6G (R6G), a dye traditionally used for testing the sensitivity of SERS-active systems, was employed as a model analyte to evaluate the efficiency of substrates with magneto-

optical microtubes because its Raman spectrum is well characterized and highly responsive to surface enhancement effects. The tests were conducted at concentrations ranging from 10^{-3} to 10^{-9} mol/L. Suspensions of Co@Ag microtubes were suspended in ethanol at a concentration of 10 mg/mL. A drop of the microtube suspension was evenly distributed on the surface of a silicon substrate with the aid of an external magnetic field and then dried. Subsequently, 0.1 mL of the analyte solution was added to the prepared surface and dried again. Magnified images of SERS substrates with deposited dye at various concentrations were obtained. Rhodamine 6G exhibits six characteristic peaks that are clearly visible in the spectra presented in Figure 6 (Mohammadi et al., 2018). As the concentration decreases, their positions shift slightly toward lower wavenumbers.

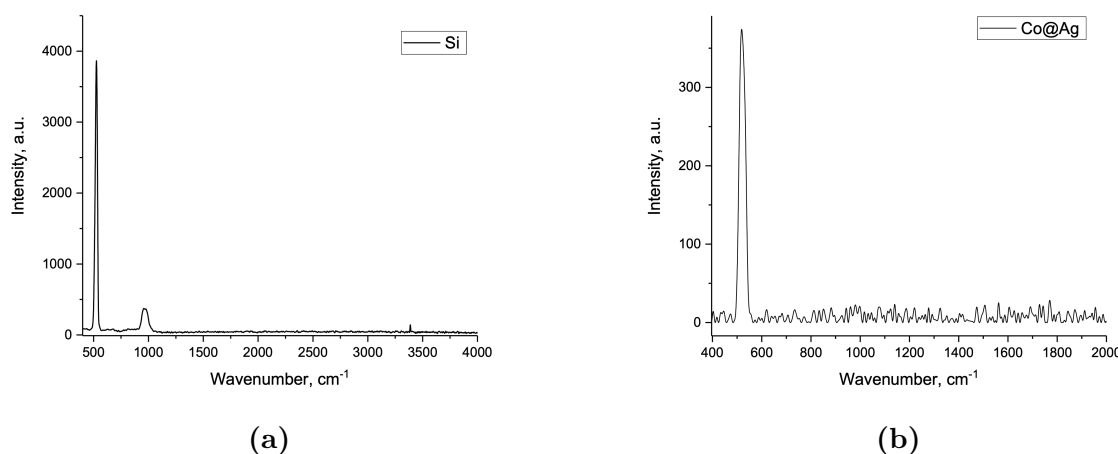


Figure 5 (a) Raman spectra of the silicon substrate and (b) Co@Ag microtubes on the silicon substrate

The conducted experiments demonstrated that the investigated microtubes can be effectively used for detecting low analyte concentrations. To determine the value of the Raman enhancement factor (EF), the following equation (Yakimchuk et al., 2019) was used:

$$EF = \frac{I_{SERS}C_R}{C_{SERS}I_R} \quad (2)$$

where I_R and I_{SERS} are the intensity of Raman scattering and SERS; C_R and C_{SERS} are the concentration of the R6G test analyte in the scattering volume for Raman measurement (10^{-2} M) and SERS measurement (10^{-9} M) (Le Ru et al., 2007). The value of EF_{1641} of the SERS signal is $\sim 4.9 \cdot 10^6$, $EF_{1511} = 4.5 \cdot 10^6$, and $EF_{1352} = 6.4 \cdot 10^6$.

The enhancement of the Raman signal in the Co@Ag microtubes can be attributed mainly to the nanostructured Ag shell's electromagnetic mechanism. Localized surface plasmon oscillations are generated on the Ag surface under 532-nm laser excitation, leading to amplification of the local electric field near nanoscale asperities, interparticle gaps, and tube-tube contact points. The magnetic Co core contributes indirectly to this enhancement by enabling magnetic-field-assisted alignment and local concentration of the Ag-coated microtubes on the substrate. Such a controlled organization can increase the probability of reproducible plasmonic hotspot formation. Therefore, the magneto-plasmonic character of the Co@Ag microtubes arises from the combination of Ag-induced local electromagnetic enhancement and Co-induced magnetic organization of the SERS-active structures.

The obtained results can be compared with previously reported pure Ag microtubes used for SERS detection of R6G (Perales-Rondon et al., 2020). Perales-Rondon et al. (2020) synthesized roughened Ag microtubes using a template-assisted electrosynthesis approach and demonstrated reproducible quantitative SERS detection of R6G in the range of 0.25–25 μ M using 633 nm excitation. Their study confirmed that Ag microtubular structures are efficient and reproducible

SERS substrates. However, SERS performance is strongly dependent not only on the plasmonic metal but also on morphology, surface roughness, tube diameter, hot-spot distribution, excitation wavelength, and substrate preparation. Therefore, a direct comparison with a separately prepared pure Ag sample would not isolate only the effect of Co. In the present Co@Ag system, the Ag shell provides plasmonic enhancement, whereas the Co core introduces magnetic responsiveness, allowing magnetic-field-assisted alignment and local concentration of the SERS-active microtubes. This additional magnetic functionality represents the main advantage of Co incorporation over pure Ag microtubes.

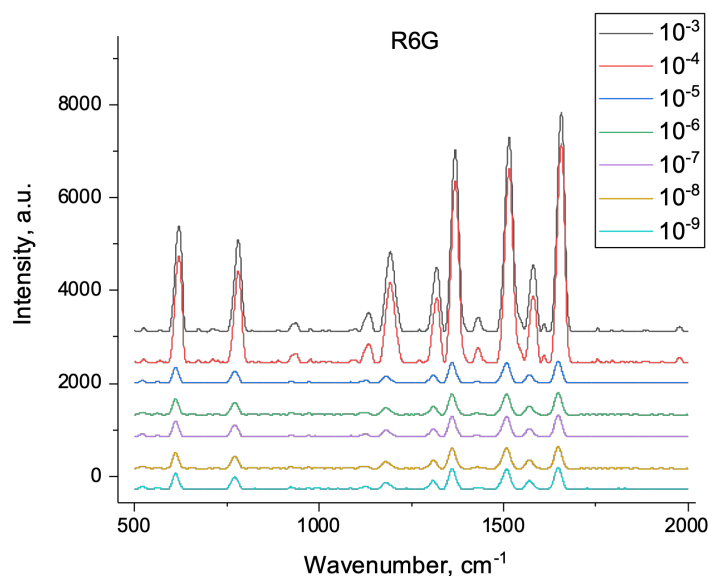


Figure 6 SERS spectra of R6G at concentrations of 10^{-3} – 10^{-9} mol/L on magneto-optical Co@Ag microtube substrates

4. Conclusions

Cobalt microtubes were successfully fabricated in PET track-etched membranes by template-assisted electrochemical deposition and subsequently coated with silver via an electroless plating method to obtain magneto-plasmonic Co@Ag hybrid structures. Morphological, structural, and surface analyses confirmed the formation of a nanostructured silver layer on the cobalt framework, while magnetic measurements revealed changes in coercivity and squareness ratio after silver deposition, indicating the interaction between ferromagnetic and plasmonic components. The Co core provides magnetic responsiveness and enables the microtubes' external-field-assisted alignment and local organization, whereas the Ag shell is responsible for plasmonic activity and the formation of SERS-active hot spots. Using rhodamine 6G as a model analyte, the developed Co@Ag microtubes demonstrated high SERS sensitivity with a detection limit down to 10^{-9} M and enhancement factors on the order of 10^6 . These results show that Co@Ag microtubes are promising tunable magneto-plasmonic platforms for SERS, combining magnetic manipulation, structural reproducibility, and high sensitivity, with potential applications in chemical sensing, biosensing, environmental monitoring, and future detection of larger organic or biological molecules.

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Author Contributions

Conceptualization, I.V.K., A.S.; methodology, I.V.K., A.S.; validation, Z.A.B., A.B.K., and A.K.S.; formal analysis, Z.A.B., N.K.Z., A.B.K.; investigation, I.V.K., A.S., Z.A.B., N.K.Z., A.B.K., and A.K.S.; writing—original draft preparation, I.V.K. and A.S.; writing—review and editing, I.V.K., A.S.; supervision, I.V.K.; project administration, I.V.K.; funding acquisition, I.V.K. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest

The authors declare no conflicts of interest.

Declaration of AI

In preparing this manuscript, the authors utilized ChatGPT-5 to enhance the English grammar and style for improved clarity and readability. The original draft and subsequent revisions were written by the authors themselves. Following the use of these tools, the authors thoroughly reviewed and edited the output and assume full responsibility for the final content of this publication.

References

- Bahlol, H. S., Li, J., Deng, J., Foda, M. F., & Han, H. (2024). Recent progress in nanomaterial-based surface-enhanced Raman spectroscopy for food safety detection. *Nanomaterials*, 14(21), Article 1750. <https://doi.org/10.3390/nano14211750>
- Blackie, E. J., Le Ru, E. C., & Etchegoin, P. G. (2009). Single-molecule surface-enhanced Raman spectroscopy of nonresonant molecules. *Journal of the American Chemical Society*, 131(40), 14466–14472. <https://doi.org/10.1021/ja905319w>
- Chen, D., Zhang, L., Ning, P., Yuan, H., Zhang, Y., Zhang, M., Fu, T., & He, X. (2021). In-situ growth of gold nanoparticles on electrospun flexible multilayered PVDF nanofibers for SERS sensing of molecules and bacteria. *Nano Research*, 14(12), 4885–4893. <https://doi.org/10.1007/s12274-021-3530-9>
- Du, J., Cui, J., & Jing, C. (2014). Rapid in situ identification of arsenic species using a portable Fe₃O₄@Ag SERS sensor. *Chemical Communications*, 50(3), 347–349. <https://doi.org/10.1039/c3cc46920d>
- Du, J., & Jing, C. (2011). Preparation of Fe₃O₄@Ag SERS substrate and its application in environmental Cr(VI) analysis. *Journal of Colloid and Interface Science*, 358(1), 54–61. <https://doi.org/10.1016/j.jcis.2011.02.044>
- Fan, C.-Z., Zhu, S.-M., & Xin, H.-Y. (2017). Controllable optical activity of non-spherical Ag and Co SERS substrate with different magnetic field. *Chinese Physics B*, 26(2), Article 023301. <https://doi.org/10.1088/1674-1056/26/2/023301>
- Han, Q., Li, Y., Chen, Y., Fan, S., Hu, Y., Yan, R., Gao, W., & Zhang, C. (2024). Fabrication of 3D popcorn-like Ag microstructures film array substrate: SERS and catalytic property. *Surfaces and Interfaces*, 44, Article 103760. <https://doi.org/10.1016/j.surfin.2023.103760>
- Hou, X., Zhang, X., Chen, S., Kang, H., & Tan, W. (2012). Facile synthesis of Ni/Au, Ni/Ag hybrid magnetic nanoparticles: New active substrates for surface enhanced Raman scattering. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 403, 148–154. <https://doi.org/10.1016/j.colsurfa.2012.04.005>
- Huang, H., Zhang, Z., & Li, G. (2023). A review of magnetic nanoparticle-based surface-enhanced Raman scattering substrates for bioanalysis: Morphology, function and detection application. *Biosensors*, 13(1), Article 30. <https://doi.org/10.3390/bios13010030>
- Huynh, K.-H., Hahm, E., Noh, M. S., Lee, J.-H., Pham, X.-H., Lee, S. H., Kim, J., & Rho, W.-Y. (2021). Recent advances in surface-enhanced Raman scattering magnetic plasmonic par-

- articles for bioapplications. *Nanomaterials*, 11(5), Article 1215. <https://doi.org/10.3390/nano11051215>
- Kalachyova, Y., Mares, D., Jerabek, V., Ulbrich, P., Lapcak, L., Svorcik, V., & Lyutakov, O. (2017). Ultrasensitive and reproducible SERS platform of coupled Ag grating with multi-branched Au nanoparticles. *Physical Chemistry Chemical Physics*, 19(22), 14761–14769. <https://doi.org/10.1039/c7cp01828b>
- Korolkov, I. V., Borgekov, D. B., Mashentseva, A. A., Güven, O., Atıcı, A. B., Kozlovskiy, A. L., & Zdorovets, M. V. (2017). The effect of oxidation pretreatment of polymer template on the formation and catalytic activity of Au/PET membrane composites. *Chemical Papers*, 71(12), 2353–2358. <https://doi.org/10.1007/s11696-017-0229-1>
- Korolkov, I. V., Shumskaya, A., Kozlovskiy, A. L., Kaliyekperov, M. E., Lissovskaya, L. I., & Zdorovets, M. V. (2022). Magnetic-plasmonic Ni nanotubes covered with gold for improvement of SERS analysis. *Journal of Alloys and Compounds*, 901, Article 163661. <https://doi.org/10.1016/j.jallcom.2022.163661>
- Kozhina, E. P., Bedin, S. A., Nechaeva, N. L., Podoyunitsyn, S. N., Tarakanov, V. P., Andreev, S. N., Grigoriev, Y. V., & Naumov, A. V. (2021a). Ag-nanowire bundles with gap hot spots synthesized in track-etched membranes as effective SERS-substrates. *Applied Sciences (Switzerland)*, 11(4), 1–13. <https://doi.org/10.3390/app11041375>
- Kozhina, E. P., Kulesh, E. A., Bedin, S. A., Doludenko, I. M., Piryazev, A. A., Korolkov, I. V., Kozlovskiy, A. L., & Zdorovets, M. V. (2021b). 1D magnetic-optical nanostructures: Template synthesis, structure and properties, application in spectroscopy based on plasmon resonance. *IEEE Magnetism Letters*, 11, 1–6.
- Kozlovskiy, A., Borgekov, D., Kenzhina, I., Zdorovets, M., Korolkov, I., Kaniukov, E., Kutuzau, M., & Shumskaya, A. (2019). PET ion-track membranes: Formation features and basic applications. In *Springer proceedings in physics* (pp. 461–479, Vol. 221). https://doi.org/10.1007/978-3-030-17759-1_31
- Kozlovskiy, A. L., Korolkov, I. V., Kalkabay, G., Ibragimova, M. A., Ibrayeva, A. D., Zdorovets, M. V., Mikulich, V. S., & Yakimchuk, D. V. (2017). Comprehensive study of Ni nanotubes for bioapplications: From synthesis to payloads attaching. *Journal of Nanomaterials*, 2017. <https://doi.org/10.1155/2017/3060972>
- Le Ru, E. C., Blackie, E., Meyer, M., & Etchegoin, P. G. (2007). Surface enhanced Raman scattering enhancement factors: A comprehensive study. *The Journal of Physical Chemistry C*, 111, 13794–13803. <https://doi.org/10.1021/jp0687908>
- Lv, Y., Sun, H., Lian, X., Shi, P., Zhang, H., & Wang, G. (2021). Influence of Co contents on the microstructure and SERS performance of self-formed Ag nanoparticles/Ag-Co alloy films on flexible substrates. *Applied Surface Science*, 563, Article 150286. <https://doi.org/10.1016/j.apsusc.2021.150286>
- Mohammadi, A., Nicholls, D. L., & Docoslis, A. (2018). Improving the surface-enhanced Raman scattering performance of silver nanodendritic substrates with sprayed-on graphene-based coatings. *Sensors*, 18(10), Article 3404. <https://doi.org/10.3390/s18103404>
- Perales-Rondon, J. V., Colina, A., González, M. C., & Escarpa, A. (2020). Roughened silver microtubes for reproducible and quantitative SERS using a template-assisted electrosynthesis approach. *Applied Materials Today*, 20, Article 100710. <https://doi.org/10.1016/j.apmt.2020.100710>
- Petruš, O., Macko, J., Oriňaková, R., Oriňak, A., Múdra, E., Kupková, M., Farka, Z., & Pastucha, M. (2021). Detection of organic dyes by surface-enhanced Raman spectroscopy using plasmonic NiAg nanocavity films. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 249, Article 119322. <https://doi.org/10.1016/j.saa.2020.119322>
- Serafinelli, C., Fantoni, A., Alegria, E. C. B. A., & Vieira, M. (2022). Plasmonic metal nanoparticles hybridized with 2D nanomaterials for SERS detection: A review. *Biosensors*, 12(4), Article 225. <https://doi.org/10.3390/bios12040225>

- Shakayeva, A. K., Omertasov, D. D., Zhatkanbayeva, Z. K., Zhumazhanova, A. T., Zdorovets, M. V., & Korolkov, I. V. (2025). Graft polymerization of allylamine for the modification of PET track-etched membrane. *Eurasian Journal of Chemistry*, 3, 85–92.
- Sharma, B., Frontiera, R. R., Henry, A. I., Ringe, E., & Van Duyne, R. P. (2012). SERS: Materials, applications, and the future. *Materials Today*, 15(1–2), 16–25. [https://doi.org/10.1016/S1369-7021\(12\)70017-2](https://doi.org/10.1016/S1369-7021(12)70017-2)
- Shumskaya, A., Korolkov, I., Rogachev, A., Ignatovich, Z., Kozlovskiy, A., Zdorovets, M., Anisovich, M., & Bashouti, M. (2021). Synthesis of Ni@Au core-shell magnetic nanotubes for bioapplication and SERS detection. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 626, Article 127077. <https://doi.org/10.1016/j.colsurfa.2021.127077>
- Shumskaya, A., Kozhina, E., Bedin, S., Andreev, S., Kulesh, E., Rogachev, A., Yarmolenko, M., & Korolkov, I. (2022). Detection of polynitro compounds at low concentrations by SERS using Ni@Au nanotubes. *Chemosensors*, 10(8). <https://doi.org/10.3390/chemosensors10080306>
- Song, W., Yang, Z., Ma, F., Chi, M., Zhao, B., & Lu, X. (2017). Electrospun magnetic CoFe₂O₄/Ag hybrid nanotubes for sensitive SERS detection and monitoring of the catalytic degradation of organic pollutants. *RSC Advances*, 7(64), 40334–40341. <https://doi.org/10.1039/c7ra07786f>
- Tiryaki, E., Zorlu, T., & Alvarez-Puebla, R. A. (2024). Magnetic-plasmonic nanocomposites as versatile substrates for surface-enhanced Raman scattering (SERS) spectroscopy. *Chemistry (Weinheim an der Bergstrasse, Germany)*, 30(24), Article e202303987. <https://doi.org/10.1002/chem.202303987>
- Wang, L., Wang, Z., Li, L., Zhang, J., Liu, J., Hu, J., Wu, X., & Weng, Z. (2020). Magnetic-plasmonic Ni@Au core-shell nanoparticle arrays and their SERS properties. *RSC Advances*, 10(5), 2661–2669. <https://doi.org/10.1039/C9RA10354F>
- Wei, Q., Pan, C., Wang, T., Pu, H., & Sun, D.-W. (2024). A three-dimensional gold nanoparticles spherical liquid array for SERS sensitive detection of pesticide residues in apple. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 304, Article 123357. <https://doi.org/10.1016/j.saa.2023.123357>
- Xu, Y., Kutsanedzie, F. Y. H., Hassan, M. M., Zhu, J., Li, H., & Chen, Q. (2020). Functionalized hollow Au@Ag nanoflower SERS matrix for pesticide sensing in food. *Sensors and Actuators B: Chemical*, 324. <https://doi.org/10.1016/j.snb.2020.128718>
- Yakimchuk, D. V., Kaniukov, E. Y., Lepeshov, S., Bundyukova, V. D., Demyanov, S. E., Arzumanyan, G. M., Doroshkevich, N. V., & Mamatkulov, K. Z. (2019). Self-organized spatially separated silver 3D dendrites as efficient plasmonic nanostructures for surface-enhanced Raman spectroscopy applications. *Journal of Applied Physics*, 126(23). <https://doi.org/10.1063/1.5129207>
- Yan, M., Shen, Y., Zhang, G., & Bi, H. (2016). Multifunctional nanotube-like Fe₃O₄/PANI/CDs/Ag hybrids: An efficient SERS substrate and nanocatalyst. *Materials Science and Engineering C*, 58, 568–575. <https://doi.org/10.1016/j.msec.2015.09.029>
- Yeszhanov, A. B., Mashentseva, A. A., Korolkov, I. V., Gorin, Y. G., Kozlovskiy, A. L., & Zdorovets, M. V. (2018). Copper nanotube composite membrane as a catalyst in Mannich reaction. *Chemical Papers*, 1–6. <https://doi.org/10.1007/s11696-018-0539-y>
- Zhou, X., Liu, S., Xiang, H., Li, X., Wang, C., Wu, Y., & Li, G. (2025). Three-dimensional SERS substrates: Architectures, hot spot engineering, and biosensing applications. *Biosensors*, 15(9), Article 555. <https://doi.org/10.3390/bios15090555>