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Track-Etched Membranes for Gold Nanowire SERS Substrates

In this study, a novel and reliable method for the production of bimetallic Ni–Au segmented nanowires by template-assisted electrochemical deposition was developed. Track-etched membranes were used as templates for the synthesis of gold nanowires with a diameter of about 100 nm by electrochemical deposition. To enhance structural stability, a modified approach was proposed, wherein gold nanowires were grown on nickel nanowire cores instead of being deposited directly onto the copper layer, as is commonly practiced. The morphology and composition of the resulting nanostructures were characterized by scanning electron microscopy (SEM) combined with energy-dispersive X-ray analysis (EDX). Elemental mapping analysis was performed to visualize the spatial distribution of constituent metals within the nanowires, revealing a well-defined segmented architecture: copper was localized at the base, nickel occupied the central region, and gold was selectively deposited on the top surface. The Surface-Enhanced Raman Scattering (SERS) activity of the substrates was evaluated using Rhodamine 6G at the concentration of 10^{-4} M, confirming their effectiveness for signal enhancement. The developed approach allows precise control of the nanostructures morphology and composition by separating the deposition stages for nickel and gold segments. By eliminating direct contact between gold and copper layers, this strategy effectively suppresses intermetallic diffusion, thereby enhancing the structural stability of the resulting bimetallic nanowires.

Keywords: track-etched membrane, template synthesis, gold nanowires, copper layer, SERS substrates, electrochemical deposition, nanostructures, signal enhancement, intermetallic diffusion

Introduction

Development of stable and reproducible SERS substrates is critical for rapid and reliable detection of organic compounds in field conditions [1]. While silver-based substrates provide higher signal enhancement due to superior plasmonic response in the visible region, gold substrates are preferred for practical applications due to their better chemical stability and biocompatibility [2]. Au inertness under ambient conditions prevents oxidation and sulfidation. That preserves its surface integrity and plasmonic properties over time, thereby ensuring consistent SERS performance and signal reproducibility.

Conventional methods of SERS substrates fabrication include chemical reduction and physical deposition techniques, which are commonly employed due to their simplicity and scalability [3]. However, these methods often lack precise control over the size, shape, and spatial distribution of gold nanostructures, leading to inhomogeneous surface morphologies and inconsistent signal enhancement across the substrate. To address these limitations and enable the development of reproducible and reliable SERS platforms, template-assisted synthesis in porous materials has emerged as a promising approach. Specifically, porous alumina oxide and track-etched membranes allow a controlled fabrication of ordered gold nanowire arrays with well-defined dimensions and improved uniformity of a SERS signal [4–6].

Due to the optical transparency of anodic aluminum oxide (AAO) in the visible spectral range it serves as a suitable template for the direct fabrication and in situ characterization of gold nanostructures. Study [4] demonstrates that variations in the size and aspect ratio of gold nanoparticles synthesized within AAO pores result in a pronounced color shift of the template, attributed to the localized surface plasmon resonance. Furthermore, research [5] reported the emergence of a magneto-optical effect in hybrid gold–nickel nanostructures, suggesting their potential for applications in optoelectronic and spintronic devices.

In comparison to AAO, polymer track-etched membranes fabricated via ion-track technology offer greater versatility and control over pore morphology. These polymer membranes allow precise tailoring of the pore geometry, including cylindrical, conical, and other predefined shapes [7, 8]. Moreover, this method enables forming a calibrated metallic nanostructure array, including multi-material and composite ones [9]. An

additional advantage is the ability to fabricate three-dimensional nanowire networks, which can be integrated as polymer-based composites [10] or employed as self-supporting porous metallic meshes [6, 11]. Such a structural flexibility makes track-etched membranes a promising platform for the development of reproducible and functionally tailored SERS substrates.

Several studies have reported the fabrication of gold nanostructures as SERS-active substrates using track-etched membranes as templates [12, 13]. However, a key limitation of such approaches lies in the usage of copper as a conductive base layer which is unsuitable for direct gold electrodeposition due to the interdiffusion between the two metals, leading to structural and chemical instability [14, 15].

A method for fabricating hollow conical gold nanostructures was demonstrated, exhibiting strong SERS performance with detection of Rhodamine 6G at concentrations as low as 10^{-8} M [16]. But, a long-term stability of the resulting substrates was compromised by the choice of copper as a base material, which facilitates interfacial diffusion and degradation over time.

To address this issue, alternative strategies have been proposed. One common solution involves a deposition of a thin metallic coating, not copper, onto the polymer template prior to the electrochemical growth. In [17], electrodeposition from sulfide-based electrolytes was shown to yield predominantly polycrystalline gold nanoparticles, whereas cyanide-based electrolytes favored the formation of (110)-textured monocrystalline structures. The process included sputtering a thin gold film onto a polycarbonate template, followed by galvanic strengthening with a copper layer. Also, gold sputtering is described in the work [18].

An alternative approach was proposed in [19], where a mercury drop was used as a liquid cathode base, eliminating the need for any intermediate metal coating. This method enables a synthesis of stable gold nanowires within polymer templates without diffusion-related degradation.

In this work, we demonstrated a structurally stable alternative through the electrochemical growth of gold onto pre-formed nickel nanowire cores, effectively preventing interfacial diffusion and phase transformation of gold. The resulting bimetallic Ni–Au segmented nanowires exhibit both chemical robustness and pronounced SERS activity, as evidenced by consistent signal enhancement of Rhodamine 6G at concentrations as low as 10^{-4} M. This approach enables the fabrication of scalable, uniform, and functionally reliable SERS substrates, suitable for high-performance sensing applications where stability, reproducibility, and environmental resistance are critical.

Experimental

Polyethylene terephthalate (PET) track-etched membranes (TMs) with a pore diameter of 100 nm were selected as a templates for the synthesis. The membranes were fabricated at the Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research (JINR, Dubna). The film thickness was 12 μm for two types of the TMs with intersecting and parallel pore systems. The surface density of the pore was $1.2 \times 10^9 \text{ cm}^{-2}$.

Nickel deposition was carried out using a Watts-type electrolyte with the following composition: $\text{NiSO}_4 \times 7 \text{ H}_2\text{O}$ — 300 g/l; $\text{NiCl}_2 \times 6 \text{ H}_2\text{O}$ — 45 g/L; H_3BO_3 boric acid — 38 g/L. The pH of the nickel electrolyte was 4. Electrodeposition was performed at an electrolyte temperature of 60 °C, using a nickel anode grade NPA1 (purity above 99 %).

Gold deposition was conducted using a commercial gold plating electrolyte. The pH of the solution was maintained at 9, and the deposition temperature was set to 70 °C. A gold wire was used as an anode.

Thermally stable electrochemical cells for deposition were fabricated from polycarbonate using 3D printing [20].

The obtained nanostructures were characterized using a JEOL JSM-6000 plus electron microscope in secondary and backscattered electron scanning modes. The accelerating voltage was 15 kV. The survey was carried out using a special holder to set the samples at different angles. Elemental analysis was performed using an attached EDX spectroscopy system.

Raman and surface-enhanced Raman scattering (SERS) spectra of Rhodamine 6G (R6G) at a concentration of 10^{-4} M were recorded on aluminum foil and SERS substrates based on Ni–Au segmented nanowires. The measurements were carried out using a Horiba LabRam Evolution confocal spectrometer equipped with a single-mode continuous-wave (CW) laser operating at 633 nm, with a maximum output power of 100 mW. A 100 \times objective lens was used to focus the laser beam, resulting in a spot size of approximately 1 μm in diameter.

For conventional Raman measurements on aluminum foil, the laser power was attenuated to 1 mW to minimize thermal effects and photodegradation of the analyte. In SERS experiments, two excitation power levels — 0.1 mW and 1 mW — were employed to assess signal dependence on laser intensity and to ensure

reliable detection under low-power conditions. Each spectrum was obtained by averaging five individual acquisitions, with an integration time of 20 seconds per scan, to enhance spectral reproducibility and signal-to-noise ratio.

Spectra were additionally recorded from rhodamine deposited on nickel nanowires at laser powers of 1 mW and 5 mW in order to demonstrate the absence of any significant signal enhancement, confirming the lack of SERS activity in nickel-based structures.

Results and Discussion

Growth and Deposition Curves

Bimetallic Ni–Au segmented nanowires were grown in several stages (Fig. 1). In the first step, a 100 nm thick copper layer was sputtered onto the surface of the track-etched membrane to provide a conductive base. Subsequently, an additional copper layer with a thickness of 3–5 μm was electrodeposited onto the initial sputtered layer (Fig. 1b). This step was carried out to mechanically improve the copper layer and ensure its structural integrity during further processing. In the second step, nickel was deposited into the pores of the track-etched membrane (Fig. 1c). The deposition was performed in a galvanostatic mode at a current density of 2 mA/cm². The deposition time was chosen such that the pores were filled approximately halfway.

The deposition rate of nickel nanoparticles is 225 nm/min.

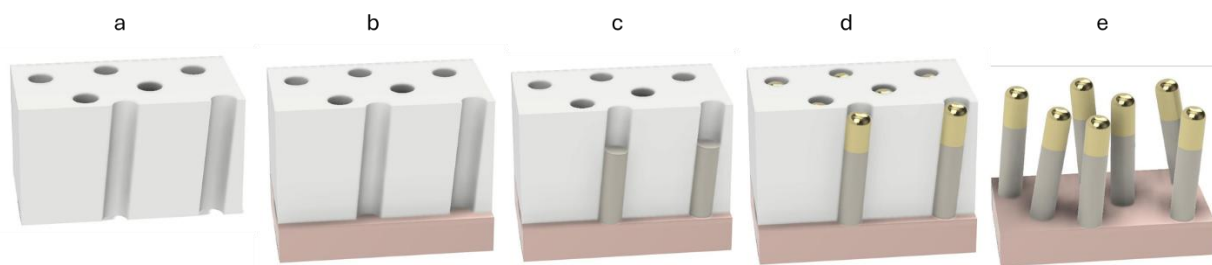


Figure 1. Stages of bimetallic Ni–Au segmented nanowire deposition

The degree of pore filling can be determined experimentally, taking into account the time required for complete pore filling, or theoretically based on the total charge passed through the electrochemical cell.

Examples of volts of time dependencies removed during nickel and gold deposition are shown in Figure 2.

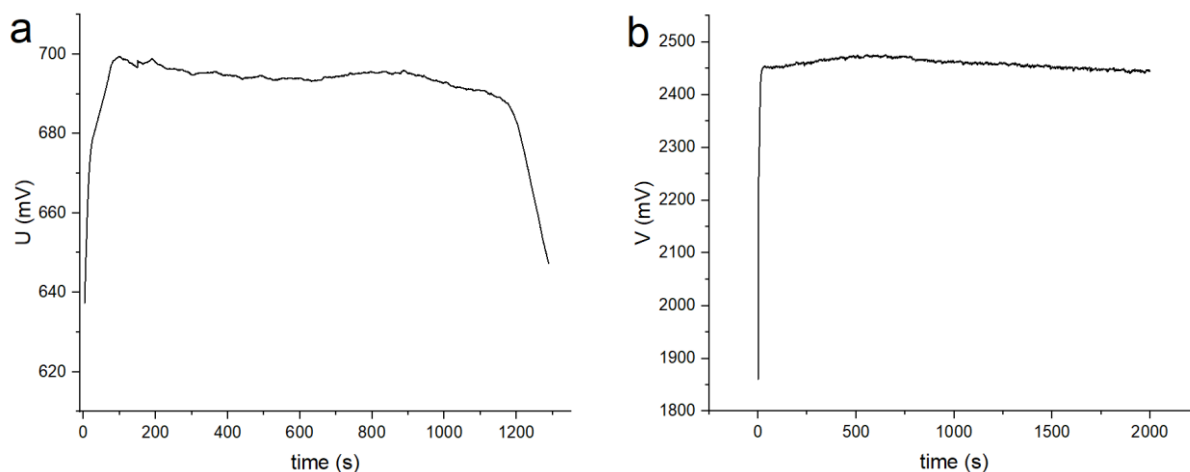


Figure 2. Changes in the electrochemical cell potential during metal deposition into 100 nm pores of track-etch membranes at a fixed current density of 2 mA/cm²: a) complete pore filling with nickel; b) partial pore filling with gold

At the third step, a gold segment was electrodeposited onto the nickel nanowires core (Fig. 1d). The deposition was carried out in a galvanostatic mode at a current density of 2 mA/cm². The deposition time varied

between 500 and 2000 seconds. Figure 2b presents the deposition curve for the gold segment. The deposition rate of gold nanoparticles is 60 nm/min.

After deposition of the gold segments, the polymer template was dissolved in a concentrated alkaline solution (6M NaOH) at 80 °C for 2 hours (Fig. 1e).

Following membrane dissolution, the resulting nanostructures were characterized using electron microscopy techniques.

Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) analysis revealed that the synthesized nanowires had an average total length of approximately 6.5 μm and a diameter of 100 nm (Fig. 4). Backscattered electron scanning clearly showed distinct contrast along the nanowire axis, indicating the presence of multiple metallic segments. The nickel segment was measured to be approximately 4.5 μm in length, while the gold segment is about 2 μm .

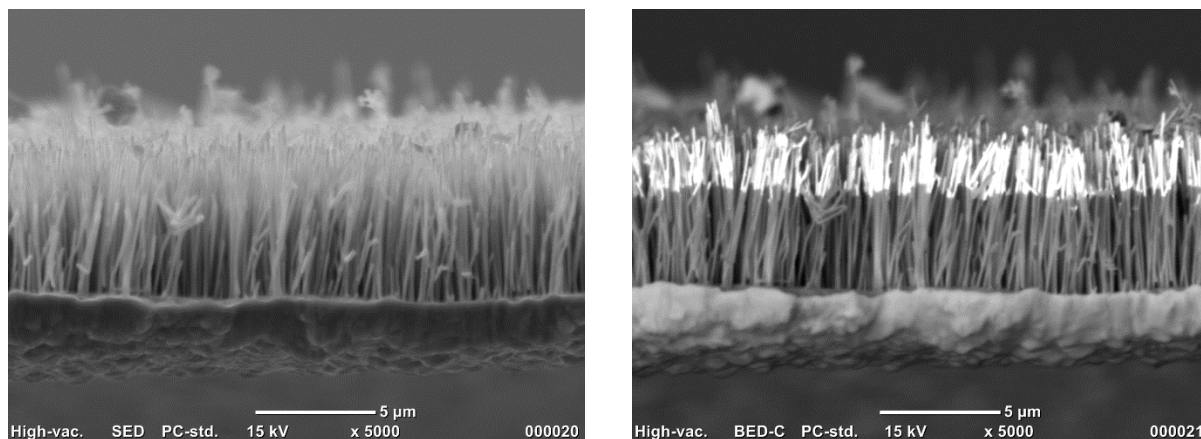


Figure 4. SEM images of the substrate with nanowires in secondary electron (SED) mode and backscattered electron (BED-C) mode

Energy-dispersive X-ray spectroscopy (EDX) analysis confirmed the presence of copper, nickel, and gold along the nanowire structure (Fig. 5). Furthermore, elemental mapping was performed to visualize the spatial distribution of constituent metals (Fig. 6). The results demonstrate a well-defined architecture, with copper localized at the base, nickel in the central segment, and gold selectively deposited at the top surface of the nanowires.

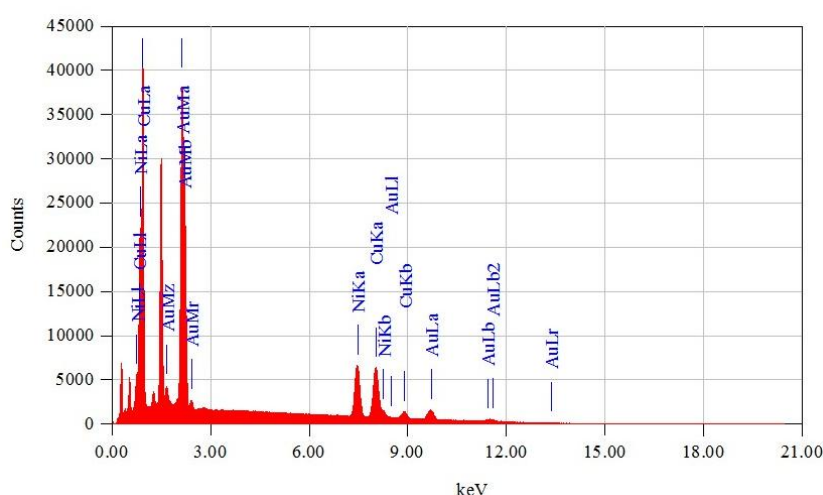


Figure 5. EDX analysis results for the bimetallic Ni–Au segmented nanowires

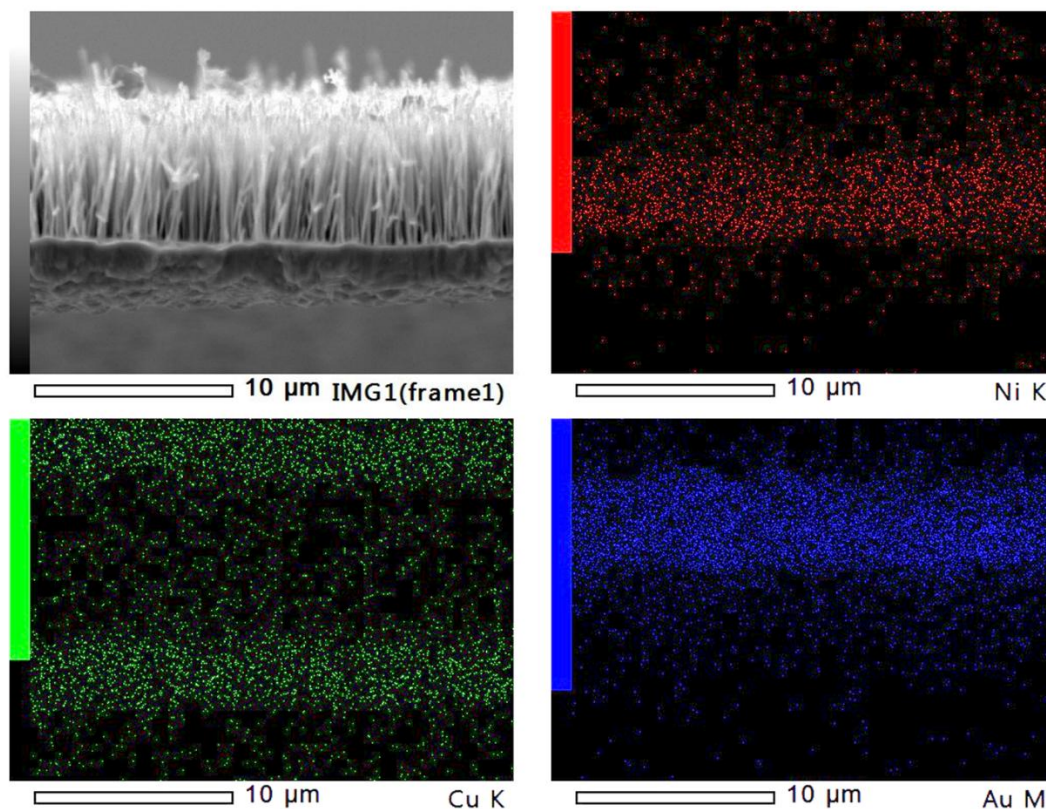


Figure 6. Elemental mapping of the nanowires showing spatial distribution of copper (green), nickel (red), and gold (blue)

Raman Scattering

Raman and SERS measurements of Rhodamine 6G (R6G) at a concentration of 10^{-4} M were performed on aluminum foil and Ni–Au segmented nanowire-based substrates. The results are summarized in Figure 7.

Figure 7a presents Raman spectra obtained from a dried droplet of R6G on aluminum foil. Clear vibrational features are observed only at the droplet edge, where the analyte is concentrated due to the coffee-ring effect, but signal still is dominated by a strong photoluminescence background. In contrast, no distinct spectral features are detected at the center of the droplet. These findings highlight the limitations of conventional Raman spectroscopy for detection that analyte concentration without plasmonic enhancement. All observed Raman bands are consistent with previously reported data for R6G known in literature.

As shown in Figure 7b, Raman spectra collected from R6G adsorbed on nickel nanowires exhibit no signal enhancement. This confirms that nickel nanostructures alone do not provide measurable SERS activity under the given experimental conditions.

In contrast, Figure 7c demonstrates a substantial improvement in spectral quality when using Ni–Au segmented nanowires as SERS-active substrates. The photoluminescence background is effectively suppressed, and the characteristic Raman peaks of R6G become clearly resolved. Spectra were acquired at two different laser powers — 0.1 mW and 1 mW — to evaluate the sensitivity and feasibility of low-power operation. Even at the reduced power level, the Raman signal remains well above the noise floor, indicating high substrate sensitivity. This feature is particularly relevant for practical sensing applications, including portable or field-deployable devices where low-power excitation is often required.

The overall performance of the Ni–Au segmented nanowire substrates suggest potential for the detection of even lower analyte concentrations and for the analysis of fluorescent compounds, which are typically challenging to detect using conventional Raman spectroscopy.

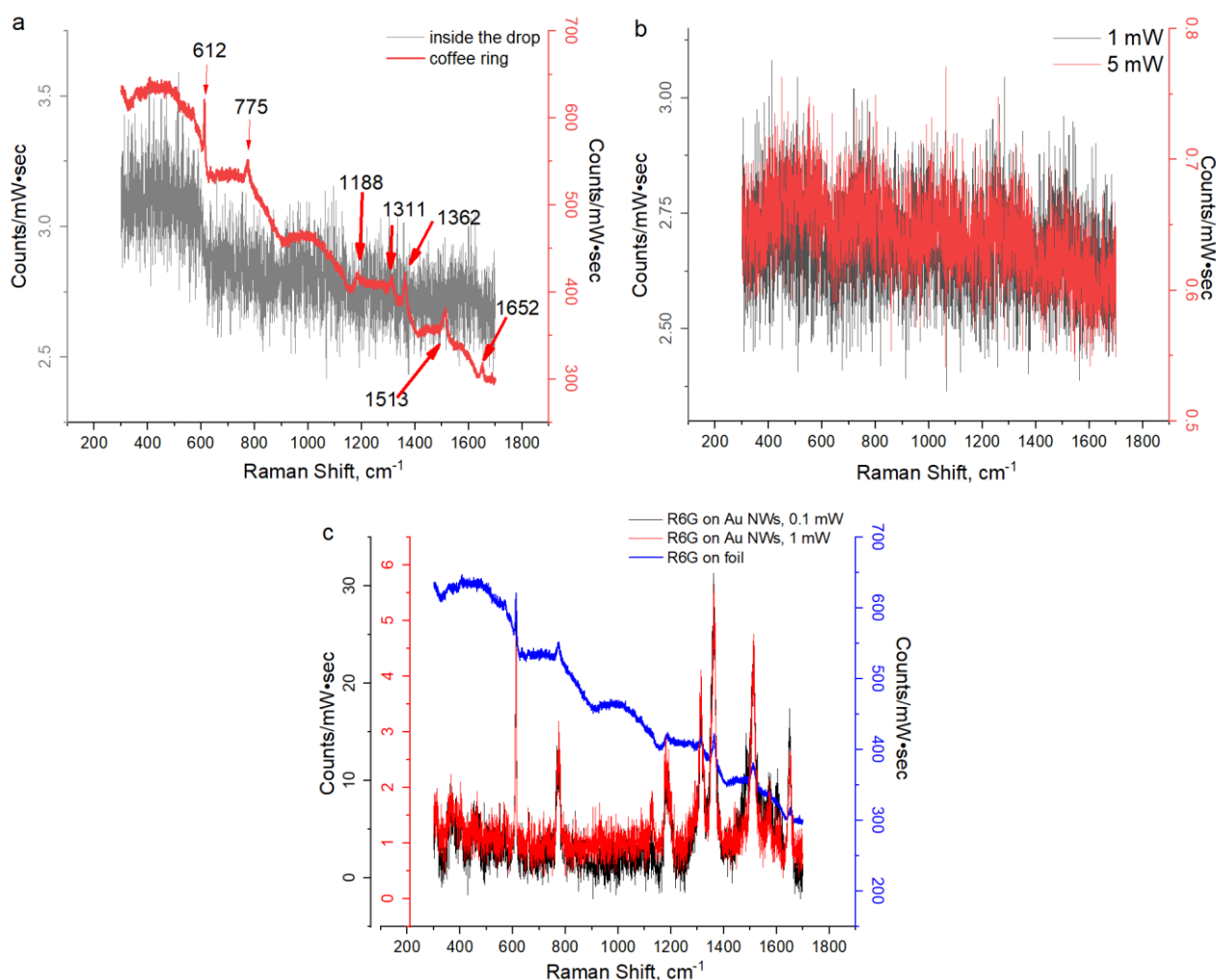


Figure 7. *a* — Raman spectra of R6G (10^{-4} M) on aluminum foil, showing signal variation at the droplet edge (coffee-ring region) and center. *b* — Raman spectrum of R6G (10^{-4} M) on Ni NWs. *c* — Comparison of R6G spectra on Al foil and Ni–Au segmented nanowires

Conclusions

In this work, a novel and reliable approach for the fabrication of bimetallic Ni–Au segmented nanowires via template-assisted electrochemical deposition was developed. The proposed method enables precise control over the morphology and composition of the nanostructures by separating the deposition stages for nickel and gold segments. This strategy effectively avoids direct contact between gold and copper layers, thereby preventing intermetallic diffusion and significantly improving structural stability.

The resulting Ni–Au segmented nanowires demonstrated strong SERS activity, allowing for the sensitive detection of 10^{-4} M Rhodamine 6G. Notably, SERS signals were obtained even at very low laser power (0.1 mW), highlighting the potential of these substrates for portable and field-deployable sensing applications. This study demonstrates that the combination of controlled template-based synthesis and bimetallic design offers a promising route toward the development of stable, reproducible, and highly sensitive SERS substrates suitable for practical analytical tasks, including trace-level detection of organic compounds with inherent fluorescence.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. **CRedit**: **Sergey Aleksandrovich Bedin** conceptualization, data curation, investigation, methodology, validation, visualization, writing-review & editing; **Elizaveta Pavlovna Kozhina** conceptualization, data curation, formal analysis, funding acquisition, resources, validation, writing-original draft, writing-review & editing.; **Ilya Mikhailovich Doludenko** investigation, methodology, validation, editing; **Vladimir Prokopevich Drachev** formal analysis, funding acquisition, resources, supervision, validation, writing-review & editing.

Conflicts of Interest

The authors declare no conflict of interest.

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