

Fabrication of ultrafine nanogroove array structures with “sharp” edges in 2D multilayer 2H-WS₂ for enhanced surface-enhanced Raman scattering

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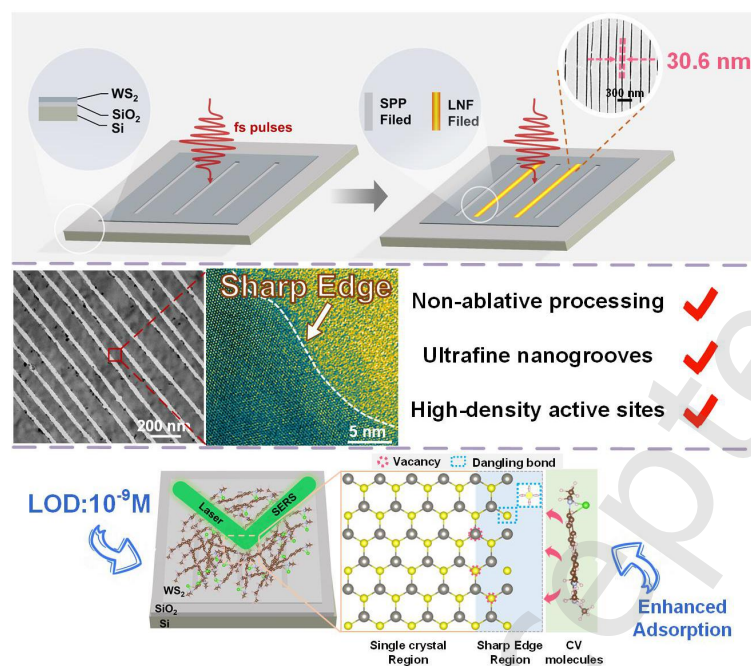
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This study utilizes a non-ablative femtosecond laser technique to fabricate ultrafine nanogroove arrays with pristine "sharp" edges on 2D multilayer 2H-WS₂. These high-density active sites significantly enhance molecular adsorption and charge transfer, achieving an ultra-sensitive SERS trace detection limit of 10⁻⁹ mol/L.

Fabrication of ultrafine nanogroove array structures with “sharp” edges in 2D multilayer 2H-WS₂ for enhanced surface-enhanced Raman scattering

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ABSTRACT: Edges of two-dimensional (2D) materials are generally more chemically reactive than their basal planes. Accordingly, engineering ultrafine edge architectures in 2D semiconductors is a compelling route to boost surface-enhanced Raman scattering (SERS). This work proposes an approach to enhance SERS sensing by fabricating ultrafine nanogroove array (NGA) structures on 2D multilayer 2H-WS₂ using femtosecond (fs) laser processing. Based on the fs laser-induced surface plasmon polariton-local near-field (SPP-LNF) effect, NGA structures with ultrafine groove widths are successfully fabricated. The processed regions remain a single-crystalline structure and exhibit “sharp” edges free of obvious amorphous or oxide layers, thereby achieving a breakthrough in non-ablation laser processing of 2D material edges. Compared with the unprocessed 2H-WS₂ regions, the NGA regions demonstrate significantly enhanced SERS sensing performance, achieving a detection limit down to 10⁻⁹ mol/L for crystal violet (CV) molecules, which is three orders of magnitude lower than that of pristine 2H-WS₂. Through combined theoretical and experimental analyses, the enhanced SERS performance of the NGA structures is attributed to the more active molecular adsorption at nanostructure edges and the intrinsic defects associated with sharp edges. This work offers a robust strategy for the controllable fabrication of edge structures and high-performance SERS sensing.

KEYWORDS: nanogroove array (NGA) structures; femtosecond laser; multilayer 2H-WS₂; sharp edge engineering; surface-enhanced Raman scattering (SERS)

1 Instruction

Surface-enhanced Raman scattering (SERS) is a highly sensitive and highly selective analytical technique that has been extensively applied in chemical analysis [1], food safety [2,3], medical diagnostics [4,5], and environmental monitoring [6]. Conventional SERS substrates are predominantly based on noble-metal nanostructures, such as gold and silver, whose enhancement mechanisms primarily rely on localized electromagnetic field amplification. However, these substrates suffer from high cost, poor uniformity, and instability, which severely restricts their practical applications. In recent years, two-dimensional (2D) transition metal dichalcogenides (TMDs) have been widely regarded as promising noble-metal-free SERS substrates owing to their atomically flat surfaces, excellent chemical stability, and tunable electronic structures [7,8]. SERS

enhancement in 2D materials is mainly governed by the chemical enhancement mechanism, originating from the charge transfer between the substrate and the adsorbed molecules [9]. Nevertheless, the absence of dangling bonds on pristine 2D material surfaces results in weak molecular adsorption and low charge-transfer efficiency, thereby hindering the realization of high-sensitivity detection.

2D TMDs generally exhibit both metallic and semiconducting phases. The metallic phases of 2D TMDs demonstrate considerable potential for SERS applications due to their large charge-transfer ability, yet their poor air stability and intrinsic thermal phase instability severely limit their widespread use [10-12]. In contrast, monolayer semiconducting TMDs, such as monolayer 2H-WS₂, exhibit relatively strong SERS performance; however, the complexity and low scalability of

monolayer fabrication hinder their practical implementation. Multilayer semiconducting TMDs are comparatively easy to fabricate and possess excellent air stability, but their SERS performance is often unsatisfactory owing to unfavorable energy-level alignment. In recent years, numerous strategies, including defect engineering [13,14] and heterostructure construction [15,16], have been reported to enhance the SERS performance of 2D semiconducting materials. Nevertheless, how to achieve a more flexible, efficient, and facile enhancement of SERS performance in multilayer semiconducting TMDs remains a significant scientific challenge. Edge engineering is widely recognized as an effective strategy for enhancing the gas-sensing performance of 2D multilayer semiconducting TMDs [17,18]. This strategy introduces abundant edge sites to replace chemically inert basal planes. These edge regions exhibit intrinsically higher chemical reactivity, which significantly enhances molecular adsorption and improves sensing sensitivity. However, the application of this strategy to SERS sensing in multilayer 2D semiconductors remains largely unexplored. Compared to traditional lithography, which inherently relies on photoresists and etchants that inevitably contaminate surface-sensitive active sites, femtosecond laser direct writing offers a maskless, dry, and strictly chemical-free alternative. This cleavage optimally preserves the intrinsic high-activity states of the exposed boundaries, enabling the creation of pristine "artificial sharp edges" without any chemical degradation to maximize SERS sensitivity. Previously, we reported a method for fabricating ultrafine nano-groove array (NGA) structures on 2D NbOI₂ by utilizing the fs laser-induced surface plasmon polariton-local near-field (SPP-LNF) effect[19]. The NGA structures exhibit ultrafine groove widths and exceptionally high structural density, with extensive exposure of edge sites that provides a robust and stable platform for molecular adsorption. It is worthwhile to explore the feasibility of using fs laser processing to fabricate ultrafine NGA structures on multilayer TMD semiconductors and to enhance SERS sensing by the abundant edge sites introduced by these structures.

This study reports a femtosecond laser-induced SPP-LNF approach for fabricating ultrafine NGA structures on 2D multilayer 2H-WS₂. The fabricated nanogrooves exhibit widths to ~30 nm, corresponding to $< \lambda/30$ of the incident laser wavelength. Structural characterizations reveal that the processed regions retain a single-crystalline structure, and the nanogrooves possess "sharp" edges free from obvious amorphous or oxide layers. The SERS performance of NGA structures was systematically investigated. The results demonstrate that the nanogroove-rich regions exhibit significantly superior SERS sensing performance for crystal violet (CV) molecules compared with the unprocessed regions. By modulating the laser fluence, NGA structures with different periodicities were fabricated, confirming that the SERS performance can be effectively tuned by the structural density. Finally, experiments and calculations verified that CV molecules adsorbed at the nanogroove edges exhibit stronger charge-transfer interactions and higher adsorption energies, which, in combination with the intrinsic defects associated with sharp edges, provides a mechanistic origin for the enhanced SERS performance.

2 Results and Discussion

Based on our previous report,[19] the mechanism of the fs-laser-induced SPP-LNF effect in 2D materials can be divided into three important stages: (1) the initiation of a periodic SPP field, (2) the activation of LNF enhancement induced by preformed nanogrooves, and (3) the establishment of a stable SPP-LNF coupling field. A typical characteristic of this process is the secondary splitting and synchronous lateral propagation of the nanogroove structures. To verify the feasibility of fabricating WS₂ nanogroove structures via the fs-laser-induced SPP-LNF effect, systematic laser-processing experiments were conducted. The processing mechanism is schematically illustrated in Figure 1a. Multilayer 2H-WS₂ nanosheets obtained by mechanical exfoliation followed by dry transfer were employed as the processing targets, with their thickness controlled within the range of 10–15 nm. A Gaussian-profile fs laser combined with a 2D high-precision translation stage was used for direct laser writing. All experiments were performed under ambient air conditions. The laser fluence was set to 22.75 mJ cm⁻², and the scanning speed was fixed at 0.1 mm s⁻¹. The resulting structures are presented in Figure 1b–c and Figure S1. Under optical microscopy, the laser-scanned regions exhibit distinct color-contrast variations, indicating clear structural differences between the irradiated and non-irradiated areas.

Subsequently, the processed samples were characterized by scanning electron microscopy (SEM) (Figure 1b–c). Upon high-magnification observation, well-defined and highly ordered NGA structures are clearly visible. By comparing the contrast between the SiO₂ substrate and the enlarged groove profiles, it can be observed that the nanogrooves fully penetrate the entire 2H-WS₂ nanosheet, confirming that complete material removal was achieved by the fs-laser irradiation. The most prominent feature of the NGA is their ultranarrow groove width. As shown in Figure 1c, the measured groove width is as low as ~30.6 nm, which is less than 1/30 of the incident laser wavelength, demonstrating that fs-laser patterning enables the successful fabrication of super-resolution NGA structures. Further statistical analyses of the groove width and period are presented in Figure 1d and Figure S2. The groove period (D) is distributed in the range of approximately 130–400 nm, while the groove width (W) falls within 23–43 nm. After Gaussian fitting, the groove widths exhibit an average value of approximately 32 ± 7.4 nm. Notably, no obvious thermal ablation or resolidification phenomena were observed during processing. Only a small amount of nanoparticle splashing was detected, indicating that the fs-laser-induced NGA structures of 2H-WS₂ exhibit excellent processing quality. In addition, the effects of laser fluence and scanning speed on the structural evolution were systematically investigated (Figure S3, S4, and S5). The results reveal that the nanostructure period gradually decreases with increasing laser fluence or decreasing scanning speed, confirming the tunability of the structural periodicity.

Finally, to further verify the SPP-LNF mechanism, quasi-in-situ structural evolution experiments were conducted. NGA with relatively small periodicity were first fabricated using a low laser fluence of 22.75 mJ cm⁻². Subsequently, a second scan was performed at the same location using a higher laser fluence of 29.25 mJ cm⁻². The corresponding results are shown in Figure S6 and Figure 1e. The results demonstrate that, while the positions of the primary NGA remain unchanged, the secondary nanogrooves predominantly emerge at the midpoints between

adjacent primary nanogrooves. Under the SPP field, nanogrooves continuously grow and laterally propagate. With increasing laser fluence, the initially formed nanogrooves induce new LNF enhancement centers, thereby triggering secondary

splitting of the nanostructures. These experimental observations provide direct evidence for the existence and validity of the SPP-LNF field mechanism.

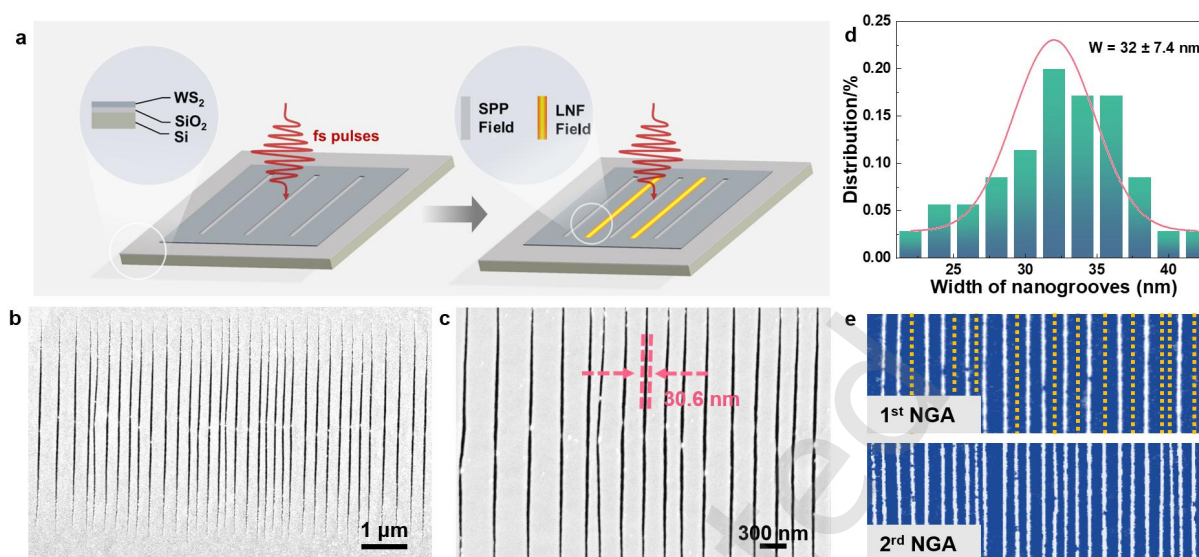


Figure 1. Fabrication of ultrafine NGA structures on 2D multilayer WS₂ via fs laser-induced SPP-LNF effect. (a) Schematic illustration of the NGA fabrication mechanism. (b–c) SEM images of the fabricated NGA structures. (d) Statistical distribution of nanogroove widths from (b) and the corresponding Gaussian fitting results. (e) Quasi-in-situ SEM observation of the secondary evolution of the NGA structures.

A comprehensive structure characterization of the NGA structures was performed. Transmission electron microscopy (TEM) was employed to evaluate the crystal structure of the NGA. Exfoliated 2H-WS₂ nanosheets were transferred onto heat-resistant silicon nitride substrate for laser processing. As shown in Figure 2a, complete material removal is achieved within the nanogroove regions, while the intergroove areas remain structurally intact without noticeable damage. Figure 2b reveals that the nanogrooves exhibit a characteristic width of ~25.1 nm. Selected-area electron diffraction (SAED) patterns collected from the processed regions (Figure 2c) confirm that the crystalline structure remains single-crystalline WS₂, with no noticeable lattice distortion or symmetry breaking induced by the laser processing. The high-resolution TEM images in Figure 2d–f further demonstrate that the WS₂ nanosheet retains a well-resolved single-crystal lattice. The measured lattice spacing is 0.271 nm, corresponding to the (010) plane of 2H-WS₂. These results indicate that the super-resolution nanogroove fabrication does not cause significant crystallographic damage, and that the nanogroove regions preserve single-crystalline characteristics, partially benefiting from the intrinsically minimal heat-affected zone of the femtosecond laser. In addition, Raman spectra (Figure S7) and X-ray photoelectron spectroscopy (XPS) analyses (Figure S8) were collected from both the processed and unprocessed regions. The comparative results demonstrate that the processed regions maintain pristine single-crystalline 2H-WS₂ characteristics, with no detectable defect formation or impurity incorporation.

The edge state of nanostructures is a critical metric for evaluating the capability of nanofabrication techniques. Edge analyses were conducted on the fabricated 2H-WS₂ NGA structures. Figure 2f presents a false-colored high-resolution TEM lattice image of the nanostructure edges, which clearly

shows that the edges exhibit no detectable amorphous layers or oxide layers. This observation highlights the presence of sharp edge states, which have not been previously reported in laser- or ion-beam-based nanofabrication of 2D materials. In our previous work on fs-laser-fabricated NbOI₂ super-resolution nanostructures, a narrow oxide layer was still observed at the edges [19]. For focus ion-beam processing, the formation of tens-of-nanometers-thick amorphous layers at the edges is unavoidable due to high-energy ion irradiation. In traditional fs-laser processing, the excitation of high-density free electrons and subsequent electron–lattice thermalization causes rapid surface heating, leading to melt zones as well as the formation of amorphous and oxide layers, which further deteriorate the surface quality. In this work, edges that are free of amorphous and oxide layers are defined as “artificial sharp edges.” Unlike the natural edges of 2H-WS₂, the formation of artificial sharp edges inevitably introduces structural defects and abundant dangling bonds. Consequently, these sharp edges inherently provide a high density of molecular adsorption sites, which have attracted increasing interest in catalysis and molecular sensing.[20] These findings lay a solid foundation for subsequent investigations of the molecular sensing properties of NGA structures.

In addition, to confirm the complete penetration of the nanogrooves, energy-dispersive X-ray spectroscopy (EDS) mapping was performed. The EDS results show that the distributions of W and S elements closely follow the nanogroove patterns, while no W or S signals are detected within the nanogroove regions. This observation confirms that the nanogrooves fully penetrate the 2D WS₂ nanosheets, demonstrating that fs-laser-induced SPP-LNF processing enables through-etching of 2H-WS₂. Crucially, due to the complete removal of material within the nanogrooves, the

formation of LIPSS does not increase the effective surface area of the WS₂ substrate.

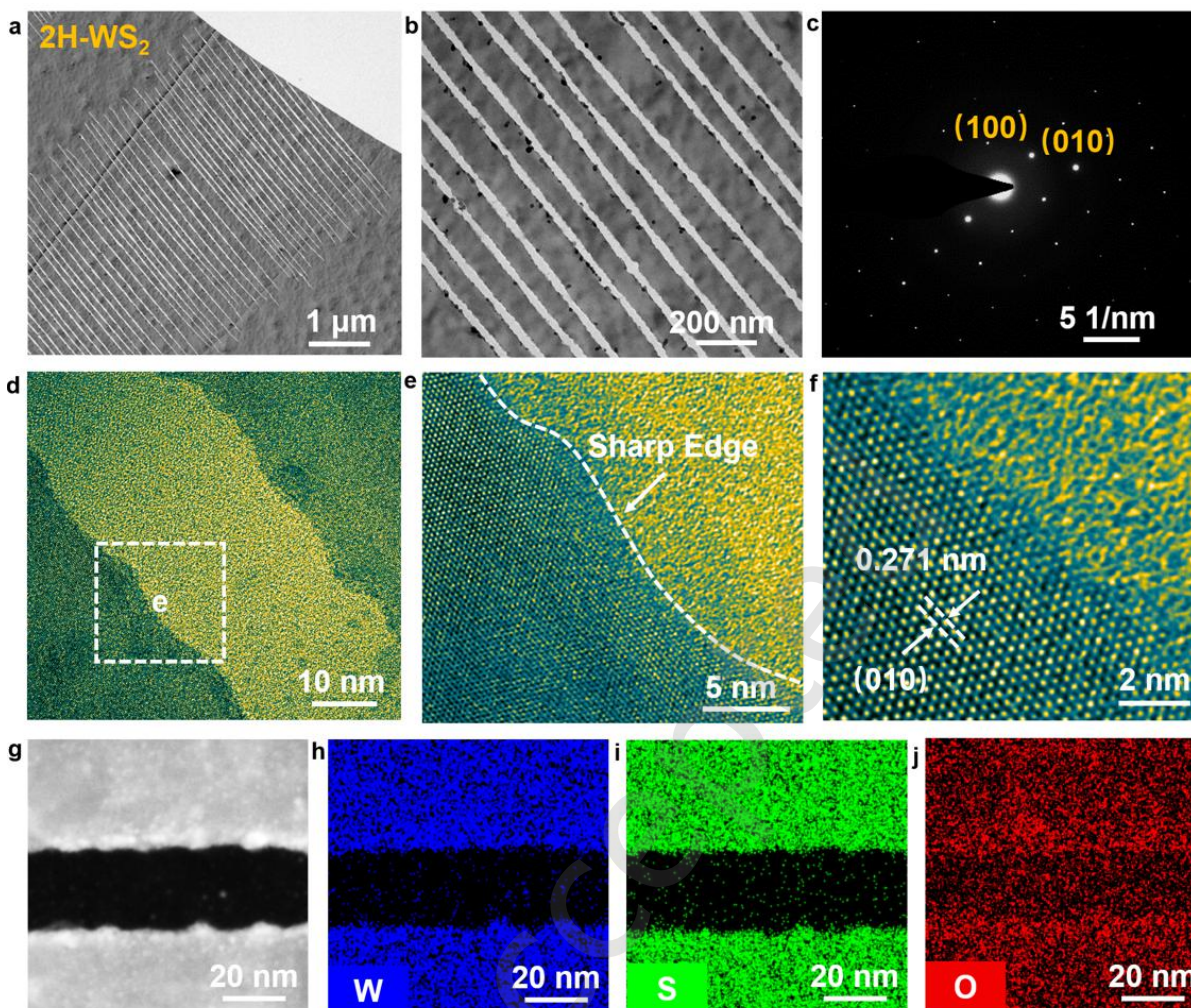


Figure 2. TEM characterization of the multilayer WS₂ NGA structures. (a–b) Low-magnification TEM images of the NGA structures. (c) SAED pattern taken from the region shown in (b). (d–f) High-resolution TEM images of the nanogroove regions and the processed edges. (g–j) EDS elemental mapping of a single nanogroove.

The high-density artificial “sharp” edges, free of amorphous and oxide layers, provide abundant molecular adsorption sites, making them a highly favorable substrate for SERS sensing. To demonstrate this, crystal violet (CV) molecules were used as a model analyte. CV is classified as a restricted food additive in both the EU and China and is considered a potential carcinogen. Large-area NGA structures were fabricated on silicon dioxide substrates. The optical image of the fabricated structures is shown in Figure 3a. The yellow dashed lines indicate the NGA regions, while the remaining areas correspond to pristine 2H-WS₂. The silicon substrates with transferred nanosheets were immersed in a 10^{−6} mol/L CV solution for two hours, followed by drying and subsequent SERS measurements. Raman spectra were collected using a 532 nm excitation laser. To clearly visualize the SERS enhancement provided by the NGA, Raman mapping of the entire nanosheet was performed, targeting the characteristic CV peaks at 1620, 1369, and 1180 cm^{−1}. The results are shown in Figure 3b–d. Notably, the signal distributions for all three peaks are consistent, with strong Raman intensity observed exclusively within the NGA regions. In contrast, the pristine 2H-WS₂ areas and the silicon substrate show no detectable SERS signal, directly confirming that the NGA enhances the Raman response of CV molecules. Next,

Raman spectra were collected from the NGA region, the unprocessed 2H-WS₂ region, and the bare silicon substrate (Figure 3e). While no CV signals were detected from the pristine or substrate regions, the NGA region exhibited clear CV Raman signatures, confirming the SERS enhancement effect induced by the nanostructures. Furthermore, the detection range of the NGA for CV molecules was evaluated by measuring SERS signals at different CV concentrations. The results (Figure 3f) demonstrate that the NGA can reliably detect CV at concentrations as low as 10^{−9} mol/L.

To evaluate the SERS enhancement of the NGA structures compared to unprocessed regions, the NGA performance was compared with that of multilayer pristine 2H-WS₂ (P-2H-WS₂). To ensure observable SERS signals from P-2H-WS₂, a 10^{−5} mol/L CV solution was used as the analyte. The SERS results from multilayer P-2H-WS₂ nanosheets are shown in Figure S9, which indicate poor detection performance, with detectable CV signals only at 10^{−5} mol/L. The Raman intensities of CV characteristic peaks from the processed NGA and unprocessed regions, along with their intensity ratios, are summarized in Figure S10 and Figure 3g. Clearly, the NGA exhibits substantially enhanced SERS performance, with CV signal intensities increased by approximately 12–53 times

compared to the pristine regions, confirming the superior SERS sensitivity of the NGA. Furthermore, repeatability tests (Figure S11) demonstrate that the NGA maintains good uniformity in SERS performance, attributed to the fs-laser fabrication process which avoids significant structural ablation or nanoparticle splashing. Stability in air, a critical metric for SERS substrates, was also evaluated (Figure S12). After one month of storage in ambient conditions, the NGA exhibits no significant degradation in performance, confirming the excellent SERS stability of 2H-WS₂ NGA. To demonstrate the versatility of the NGA for molecular detection, methylene blue (MB) brilliant cresyl blue (BCB), and Eosin molecules were further tested. MB is classified as a Group 3 carcinogen by the International Agency for Research on Cancer. The results (Figure S13) show that the

NGA region exhibits significant signal enhancement for MB molecules compared to unprocessed regions, with detectable concentrations down to 10^{-9} mol/L. Furthermore, the SERS performance was evaluated using BCB and Eosin (Figure S14). The NGA substrates achieved an impressive detection limit of 10^{-8} mol/L for both molecules. These findings confirm that the NGA can effectively detect other large organic molecules, demonstrating its broad applicability for molecular sensing. To further benchmark the sensing capability of the proposed NGA substrate, Table S1 summarizes the detection limits of different probe molecules and compares them with those of previously reported 2D-material-based SERS substrates. The results demonstrate that the 2H-WS₂ NGA exhibits competitive molecular detection performance.

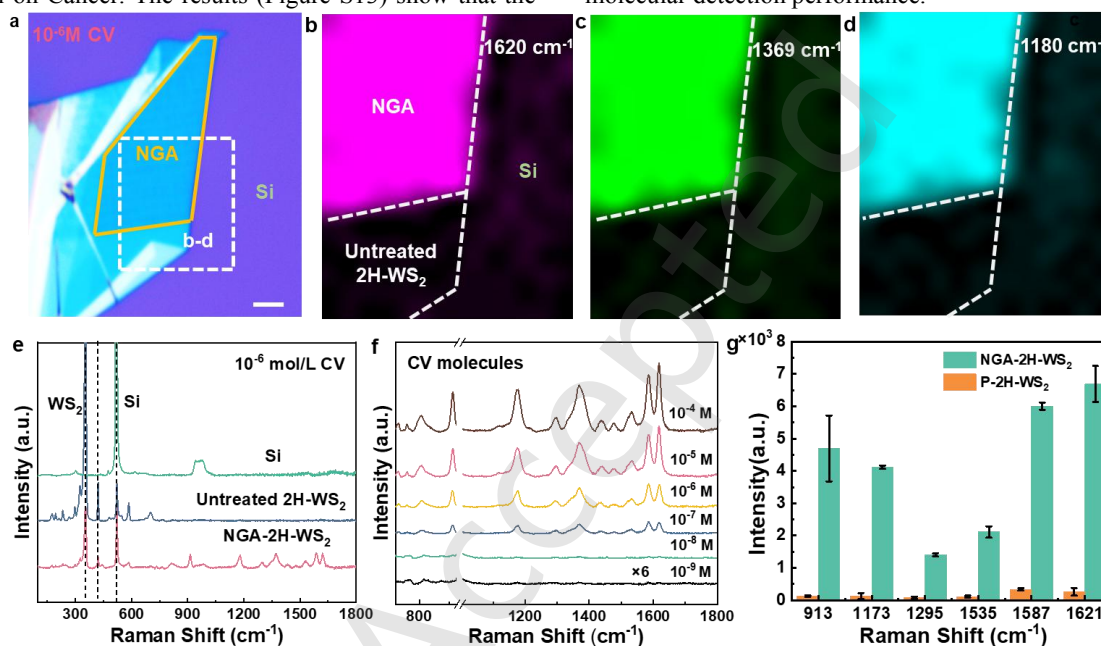


Figure 3. SERS performance characterization of the multilayer 2H-WS₂ NGA structures. (a) Distribution of the fabricated NGA regions. (b-d) SERS mapping images of CV molecules (10^{-6} mol/L) on the NGA structures, corresponding to the characteristic peaks at 1620 cm^{-1} , 1369 cm^{-1} and 1180 cm^{-1} . (e) Comparison of CV detection performance on the NGA structures, P-2H-WS₂, and bare Si substrate. (f) Detection range of CV molecules using the NGA structure. (g) SERS performance comparison between multilayer 2H-WS₂ nanostructures and P-2H-WS₂ for CV (10^{-5} mol/L).

As described above, the enhancement of SERS performance is directly related to the presence of nanogrooves. Investigating the effect of nanogroove density on SERS performance is therefore crucial for understanding the underlying enhancement mechanism. To ensure consistent detection of CV molecules, NGA with different periods were fabricated on the same 2H-WS₂ nanosheet. Six NGA structures (labeled I–VI) were prepared by varying the fs-laser fluence at 19.5, 22.75, 26.0, 29.25, 32.5, and 35.0 mJ cm⁻², respectively. After fabrication, the samples were immersed in a 10^{-6} mol/L CV solution, and their states are shown in Figure 4a–b. It can be observed that as the laser fluence increases, the average NGA period gradually decreases until saturation. Raman signals were collected from the regions indicated by red dashed boxes, targeting the CV characteristic peaks at 1620, 1369, and 1180 cm⁻¹. The results are shown in Figure 4c. All detectable CV signals originate from the NGA regions (I–VI), whereas the unprocessed areas show no detectable CV signal. The NGA I region exhibits relatively weak Raman intensity, while NGA II and III show gradually increasing CV signal intensity. NGA IV–VI display the strongest Raman signals, indicating that a smaller NGA period

favors enhanced molecular detection performance. These observations suggest that increasing the nanogroove density improves the SERS sensitivity of the structures.

The Raman mapping of CV molecules demonstrates that the period of the NGA modulates SERS performance. To more clearly compare the detection capability across different regions, Raman spectra were collected from NGA regions I–VI, as shown in Figure 4d. With progression from region I to VI, the Raman intensity initially increases significantly, reaches a saturation point, and then gradually decreases. The CV characteristic peaks at 913, 1180, 1297, 1369, 1476, 1587, and 1620 cm⁻¹ were analyzed for intensity comparison (Figure 4e). All peaks follow the same trend of initial enhancement followed by slight reduction, confirming that decreasing the NGA period (i.e., increasing nanogroove density) enhances SERS performance, but only up to a saturation point. Beyond this, excessively high nanogroove density can lead to a slight decline in SERS sensitivity. As shown in Figure 4b, when the laser fluence is sufficiently high, the NGA period becomes extremely small, reducing the effective 2H-WS₂ area. This reduction may limit the charge transfer between the substrate and analyte

molecules, which could explain the observed decrease in SERS performance at very high nanogroove densities.

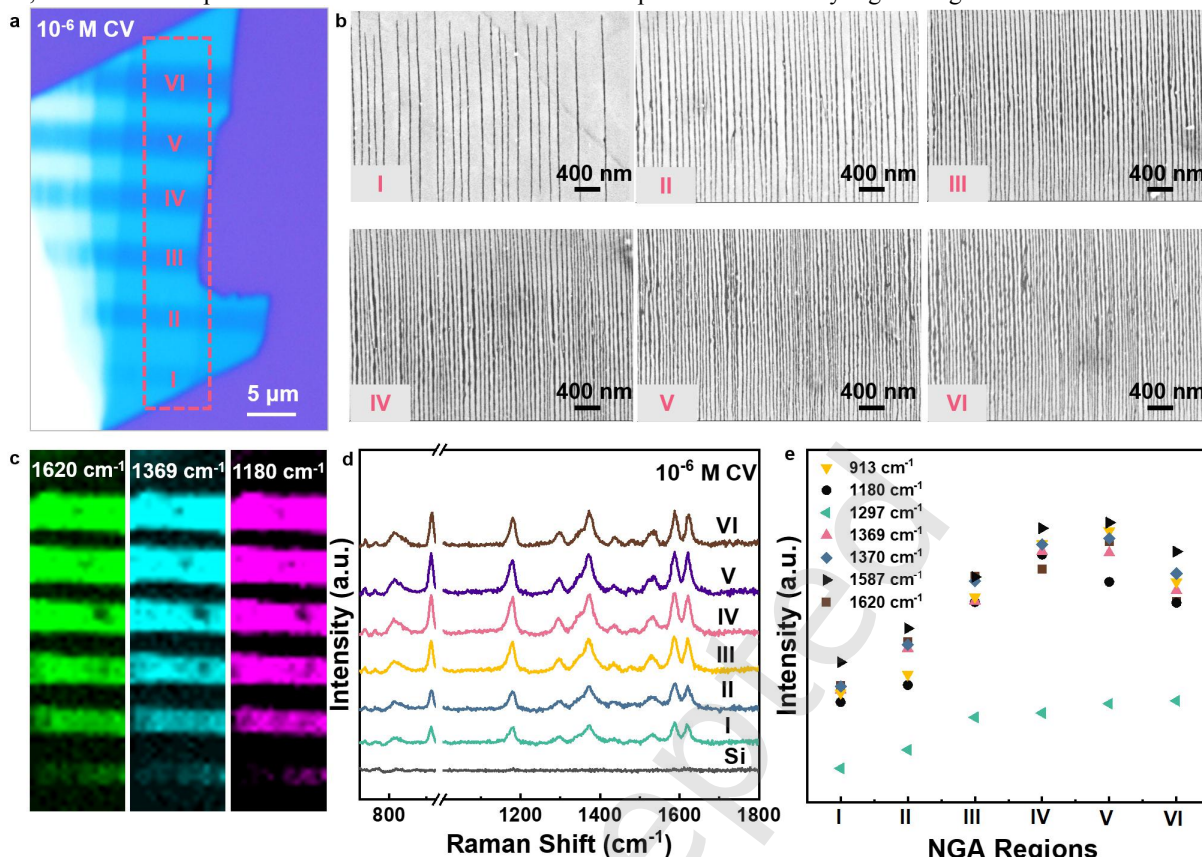


Figure 4. Characterization of SERS performance for 2H-WS₂ NGA structures with varying periods. (a) SEM images of NGA structures fabricated under laser fluences of 19.5, 22.75, 26.0, 29.25, 32.5, and 35.0 mJ cm^{-2} , respectively (after immersion in 10^{-6} mol/L CV solution). (c) SERS mapping of CV (10^{-6} mol/L) on NGA structures with different periodicities. (d) Comparison of Raman spectra corresponding to Regions I–VI. (e) Comparison of the characteristic peak intensities of CV molecules across Regions I–VI.

To elucidate the mechanism underlying the SERS enhancement of NGA, the discussion focuses on two aspects: (1) the adsorption activity of 2H-WS₂ edges relative to the basal plane, and (2) the activity of the “sharp” edges of the NGA compared to conventional natural edges. First, we consider the enhancement mechanism due to edges relative to the basal plane. Atoms at the edges of 2D materials are generally more chemically active than basal plane atoms due to several factors, including differences in the local chemical environment, charge redistribution at interfaces, and lower coordination numbers. Edge atoms often exhibit properties distinct from interior surface atoms (here, “interior” refers to surface atoms not located at edges), thereby providing abundant active sites [20–22]. Because edges possess intrinsically high surface energy, they are typically rare surface sites in layered materials. The fs-laser-fabricated 2H-WS₂ NGA contains a high density of nanogrooves per unit area, exposing a large number of edge sites. This ensures sufficient contact and adsorption between the substrate and molecules, thereby enhancing SERS performance. To validate this hypothesis, DFT calculations were performed to simulate the charge density difference of CV molecules adsorbed on the 2H-WS₂ NGA structure. As illustrated in Figure 5d, the CV molecules exhibit a strong spatial preference to adsorb within the nanogroove vicinity, with negligible adsorption occurring on the flat non-groove basal plane. Adsorption energies and charge transfer quantities were also computed. The differential charge density map is shown in

Figure S15. Significant charge transfer is observed between the CV molecule and the 2H-WS₂ edge, confirming strong interaction. The calculated adsorption energy of CV on the 2H-WS₂ edge is -0.72 eV, with a charge transfer of $0.88 e^-$. In comparison with previously reported DFT results for CV adsorption on the basal plane of 2H-WS₂ [23], both the adsorption energy and charge transfer at the edge are larger than those on the basal plane. These results demonstrate that CV adsorption is energetically more favorable at edges, providing a mechanistic explanation for the SERS enhancement observed in NGA due to the high density of exposed edge states. Furthermore, FDTD simulations demonstrate negligible electromagnetic enhancement (Figure S16).

In addition, the artificial sharp edges of the NGA differ from naturally passivated edges, as they inevitably introduce more point defects and dangling bonds, which enhance molecular adsorption. Etching processes remove atoms from the lattice, creating vacancies, broken bonds, and undercoordinated atoms at the edges [24]. These defect sites exhibit high adsorption affinity for external molecules. Furthermore, during etching, chemical bonds between atoms are disrupted, exposing reactive dangling bonds at the edge. Therefore, it is reasonable to infer that these dangling bonds readily interact with molecules, facilitating adsorption [25], as illustrated schematically in Figure 5e and Figure S14. Compared with naturally formed edges, the laser-etched NGA edges contain more defects and dangling bonds, including W and S vacancies and unpaired electrons,

which further enhance molecular adsorption at the edge.

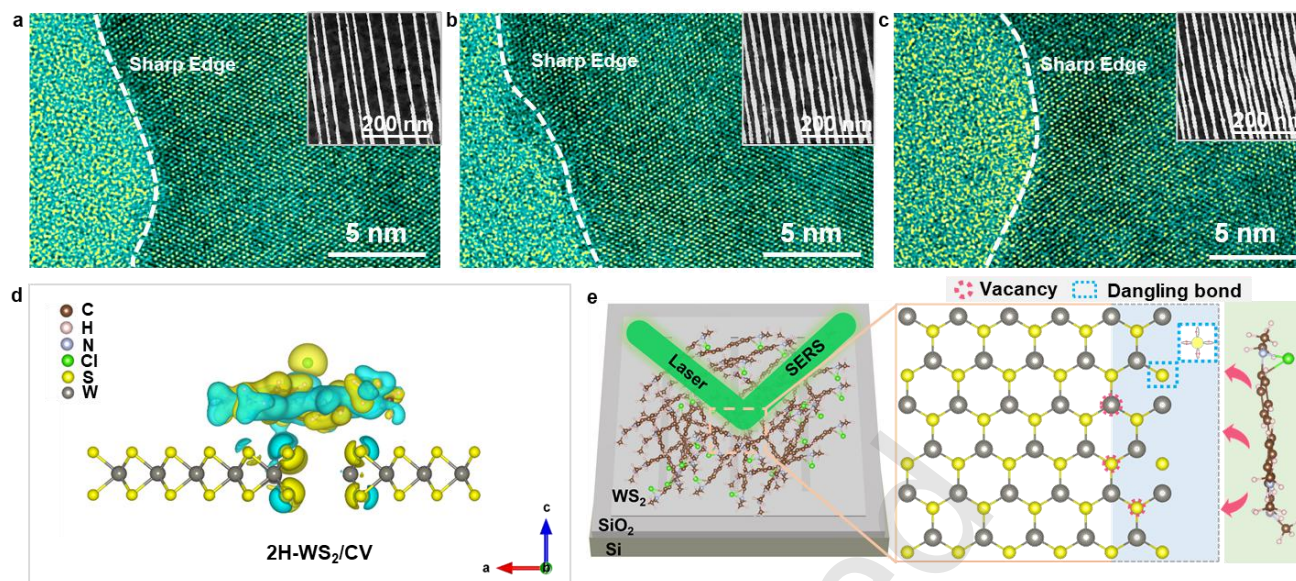


Figure 5. Investigation into the mechanism of SERS enhancement by 2D WS₂ NGA structures. (a–c) TEM characterization and SAED patterns taken from the edges of NGA structures with different periodicities. (d) Charge density difference of a CV molecule adsorbed within the 2H-WS₂ -NGA gap. (e) Schematic illustration of the enhanced adsorption mechanism of CV molecules facilitated by the "sharp" edges of 2H-WS₂.

3 Conclusion

In summary, we successfully fabricated ultrafine NGA structures on multilayer 2H-WS₂ nanosheets using fs-laser irradiation. The nanogrooves exhibit widths as small as 30.6 nm, less than 1/30 of the incident laser wavelength. Structural characterization confirms that the nanogroove regions retain the single-crystalline WS₂ lattice without noticeable defects, and the groove edges are free of obvious amorphous and oxide layers, demonstrating the successful formation of artificial "sharp" edges, which represents a significant improvement over existing laser fabrication quality. The NGA regions were further shown to possess excellent SERS performance. The detection limit for CV molecules reaches 10^{-9} mol/L, corresponding to an enhancement of three orders of magnitude compared with pristine 2H-WS₂, with Raman signal intensity increased by 12–53 times. Moreover, the tunability of the NGA period is further demonstrated to play a critical role in regulating the SERS performance and decreasing the NGA period further enhances SERS sensitivity, up to a saturation point. Finally, experimental observations and theoretical calculations demonstrate that the enhanced edge charge transfer and higher adsorption energy induced by the sharp edges, together with the intrinsic defects generated during the edge-etching process, are the key factors responsible for the observed SERS enhancement.

Data availability

Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Ye Ding: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft. He Zhou: Methodology, Investigation, Validation. Yanchao Guan: Conceptualization, Formal analysis, Writing – review & editing, Supervision. Hao Liu: Investigation, Visualization. Cheng-Yan Xu: Resources, Validation. Liang Zhen: Resources, Supervision. Yang Li: Conceptualization, Writing – review & editing, Supervision, Funding acquisition. Liangliang Xu: Methodology, Investigation. Lijun Yang: Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

References

- [1] Xu Y, Aljuhani W, Zhang Y, et al. A practical approach to quantitative analytical surface-enhanced Raman spectroscopy[J]. Chemical Society Reviews, 2025, 54(1): 62-84.
- [2] Peng W, Liu Y, Lu M, et al. Advances in surface-enhanced Raman scattering detection of foodborne pathogens: From recognition-based fingerprint to molecular diagnosis[J]. Coordination Chemistry Reviews, 2024, 518: 216083.
- [3] Lin C, Liang S, Peng Y, et al. Visualized SERS imaging of single molecule by Ag/black phosphorus nanosheets[J]. Nano-Micro Letters, 2022, 14(1): 75.

- [4] Laing S, Sloan-Dennison S, Faulds K, et al. Surface enhanced Raman scattering for biomolecular sensing in human healthcare monitoring[J]. ACS Nano, 2025, 19(9): 8381-8400.
- [5] Zhang D, Cheng Z, Song Y, et al. Rapid and sensitive acute leukemia classification and diagnosis platform using deep learning-assisted SERS detection[J]. Cell Reports Medicine, 2025, 6(9): 102320.
- [6] Srivastava S, Wang W, Zhou W, et al. Machine learning-assisted surface-enhanced Raman spectroscopy detection for environmental applications: a review[J]. Environmental Science & Technology, 2024, 58(47): 20830-20848.
- [7] Li Z, Zhai W, Yang H, et al. Phase engineering of two-dimensional transition metal dichalcogenides for surface-enhanced Raman scattering[J]. Matter, 2025, 8(9): 102210.
- [8] Tang X, Hao Q, Hou X, et al. Exploring and engineering 2D transition metal dichalcogenides toward ultimate SERS performance[J]. Advanced Materials, 2024, 36(19): 2312348.
- [9] Li W, Qian X, Li J. Phase transitions in 2D materials[J]. Nature Reviews Materials, 2021, 6(9): 829-846.
- [10] Wang L, Liu X, Luo J, et al. Self - optimization of the active site of molybdenum disulfide by an irreversible phase transition during photocatalytic hydrogen evolution[J]. Angewandte Chemie, 2017, 129(26): 7718-7722.
- [11] Ge Y, Wang F, Yang Y, et al. Atomically Thin TaSe₂ Film as a High - Performance Substrate for Surface - Enhanced Raman Scattering[J]. Small, 2022, 18(15): 2107027.
- [12] Lv Q, Wu X, Tan J, et al. Ultrasensitive molecular sensing of few-layer niobium diselenide[J]. Journal of Materials Chemistry A, 2021, 9(5): 2725-2733.
- [13] He H, Zhao M, Xu H, et al. Engineering nanopore in monolayer WS₂ for single-molecule imaging on the atomic-scale flat 2D surfaces[J]. Science Advances, 2025, 11(38): eady2148.
- [14] Song G, Gong W, Cong S, et al. Ultrathin two - dimensional nanostructures: surface defects for morphology - driven enhanced semiconductor SERS[J]. Angewandte Chemie International Edition, 2021, 60(10): 5505-5511.
- [15] Pei J, Yang F, Zhao H. Plasma-induced enhancement of light-matter interaction on graphene-MoS₂ heterostructure for sensitive SERS sensing[J]. Nano Research, 2025, 18(5): 94907376.
- [16] Lv Q, Tan J, Wang Z, et al. Ultrafast charge transfer in mixed-dimensional WO₃-x nanowire/WSe₂ heterostructures for attomolar-level molecular sensing[J]. Nature Communications, 2023, 14(1): 2717.
- [17] Yang Y, Cheng X, Wang Y, et al. Unrevealing the impact of edge states in MoS₂ thin film to NO₂ excellent selectivity[J]. Sensors and Actuators A: Physical, 2025, 383: 116233.
- [18] Zhao Q, Zhou W, Zhang M, et al. Edge - enriched Mo₂TiC₂Tx/MoS₂ heterostructure with coupling interface for selective NO₂ monitoring[J]. Advanced Functional Materials, 2022, 32(39): 2203528.
- [19] Guan Y, Ding Y, Fang Y, et al. Far-field femtosecond laser-driven $\lambda/73$ super-resolution fabrication of 2D van der Waals NbOI₂ nanostructures in ambient air[J]. Nature Communications, 2025, 16(1): 4149.
- [20] Zhou L, Li M, Wang W, et al. Edge engineering in chemically active two-dimensional materials[J]. Nano Research, 2022, 15(11): 9890-9905.
- [21] Kong D, Wang H, Cha J J, et al. Synthesis of MoS₂ and MoSe₂ films with vertically aligned layers[J]. Nano Letters, 2013, 13(3): 1341-1347.
- [22] Ni B, Wang X. Face the edges: catalytic active sites of nanomaterials[J]. Advanced Science, 2015, 2(7): 1500085.
- [23] Guan Y, Chen M, Ding Y, et al. Phase transformation on multilayer 2M-WS₂ for improved surface-enhanced Raman scattering[J]. ACS Nano, 2024, 18(26): 17339-17348.
- [24] Wang Z, Li Q, Xu H, et al. Controllable etching of MoS₂ basal planes for enhanced hydrogen evolution through the formation of active edge sites[J]. Nano Energy, 2018, 49: 634-643.
- [25] Rani R, Yoshimura A, Das S, et al. Sculpting artificial edges in monolayer MoS₂ for controlled formation of surface-enhanced Raman hotspots[J]. ACS Nano, 2020, 14(5): 6258-6268.

Electronic Supplementary Material

Fabrication of ultrafine nanogroove array structures with “sharp” edges in 2D multilayer 2H-WS₂ for enhanced surface-enhanced Raman scattering

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1. Experimental Section

Sample Preparation: 2H-WS₂ flakes were obtained from bulk single crystals via mechanical exfoliation. Subsequently, the exfoliated flakes were transferred onto a 10mm×10mm silicon substrate capped with a 300nm thick oxide layer using a dry transfer technique.

Laser Processing: The femtosecond laser used in this study has an output wavelength of 1030 nm and a pulse duration of 255 fs, producing horizontally linearly polarized light. Since the energy density required for structural modulation of the 2D materials is relatively low, an energy attenuation module, composed of a Glan prism and a half-wave plate, was added to suppress fluctuations in laser energy during processing. The output power of the attenuated laser was measured at the exit of the focusing lens using a laser power meter. After attenuation, the laser beam was expanded and collimated, achieving a beam diameter of approximately 10mm before being focused onto the sample stage via a focusing lens, resulting in a Gaussian spot with a diameter of ~10 μm. The SiO₂ substrates with 2D materials were mounted on a 3D translation stage equipped with a manual rotation platform. The 3D translation stage allows controlled movement along the X, Y, and Z axes with a positioning accuracy of 1 μm, while the manual rotation stage is used to adjust the substrate orientation.

Structural Characterization: The fabrication state of the nanogroove array (NGA) structures was initially examined using an optical metallurgical microscope, followed by scanning electron microscopy (SEM) for detailed structural imaging and dimensional measurements. Exfoliated 2H-WS₂ nanosheets were transferred onto thermally stable Si₃N₄ thin films using a dry transfer method. The Si₃N₄ films, supported on silicon substrates, were used for TEM imaging, which characterized the crystal structure distribution and electron diffraction patterns in both processed and unprocessed regions. Energy-dispersive X-ray spectroscopy (EDX) was employed to analyze the spatial distribution of W, S, and O elements. Raman spectra of both processed and unprocessed regions were collected using a Raman spectrometer, and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Al Kα radiation) was employed to characterize the valence states of the materials.

SERS Measurement: First, a 10⁻⁴ M CV solution was prepared using deionized water as the solvent. The initial CV solution was then serially diluted to obtain a range of concentrations from 10⁻⁴ M to 10⁻¹⁰ M. Subsequently, Si substrates with 2H-WS₂ nanosheets were immersed in the CV solutions of different concentrations for 2 hours, ensuring that the substrates were fully submerged in the solution. After incubation, the substrates were thoroughly rinsed with deionized water. SERS measurements were performed using a Raman spectrometer with a 532 nm excitation laser, set at 1% of the maximum laser power, and a collection time of 10 s per measurement. Each measurement point was tested three times, and the average value was taken to ensure reliability.

2. Preparation and Structural Characterization of NGA Structures

The fabrication results are shown in Supplementary Fig. 1. Under optical microscopy, the laser-scanned regions exhibit pronounced color-contrast variations, indicating distinct structural differences between the irradiated and non-irradiated areas. Subsequently, SEM characterization further confirms the formation of well-defined NGA structures, whose orientation is perpendicular to the laser polarization direction. Upon high-magnification observation, highly regular NGA are clearly resolved. Through contrast comparison with the underlying SiO_2 substrate and enlarged groove images, it can be observed that the nanogrooves penetrate through the entire 2H- WS_2 nanosheet, demonstrating that complete ablation of the nanosheet has been achieved. Furthermore, the orientation of the NGA is strictly perpendicular to the laser polarization direction.

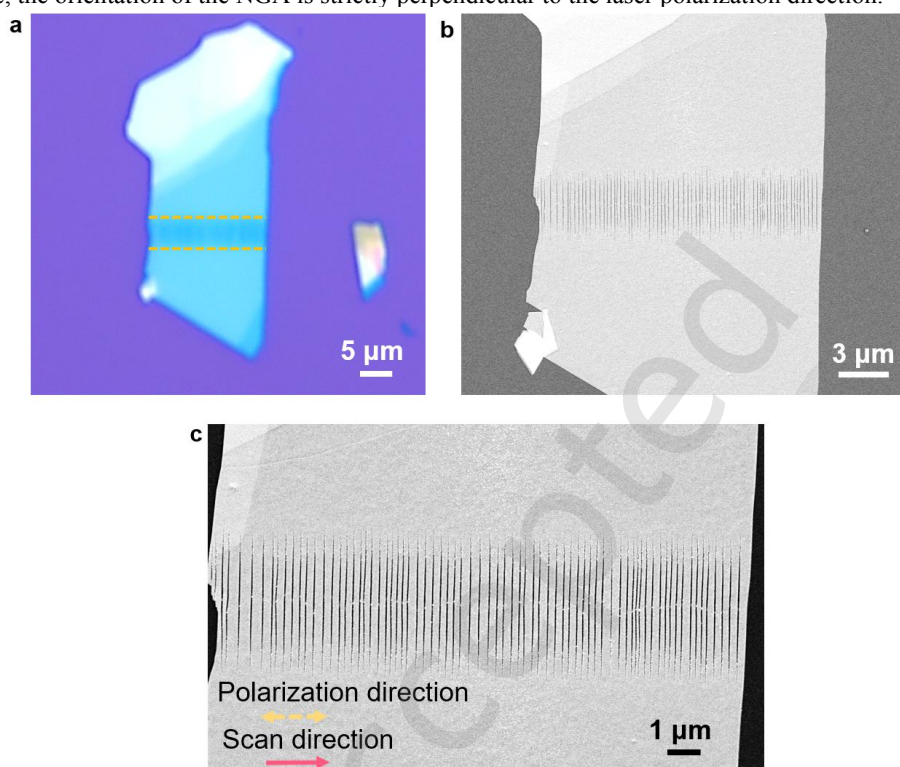


Fig. S1 Formation of super-resolution structures in 2H- WS_2 induced by fs laser. (a) Optical image. (b) SEM image. (c) High-magnification SEM image.

To achieve more accurate and quantitative characterization of the nanogroove width and average spacing, statistical image analysis was performed using the open-source image-processing software Gwyddion. First, pseudo-color processing was applied to the original SEM images to enhance image contrast. Compared with the original grayscale images, the processed images exhibit a markedly improved visual clarity (Supplementary Fig. 2), allowing a clearer visualization of the local uniformity of the nanogrooves and the resolution of the minimum achievable groove width. By statistically extracting the color-contrast information, the results show that the spacing (D) of the surface nanogrooves ranges from approximately 130 to 400 nm, while the groove widths are distributed between 23 and 43 nm.

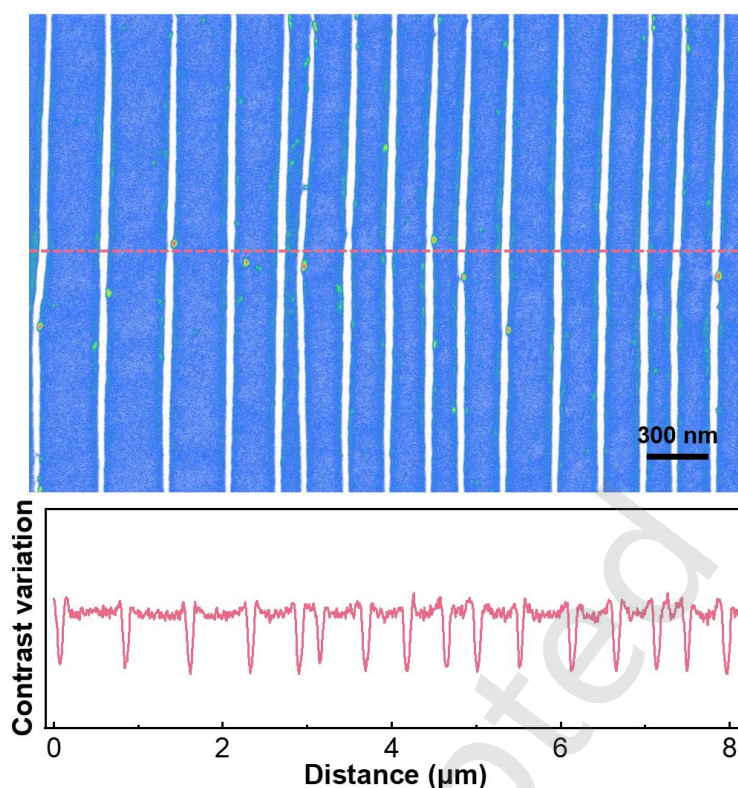


Fig S2. Structural statistics of super-resolution nanogrooves. (a) Pseudocolor SEM image. (b) Contrast distribution along the horizontal centerline of the image in (a).

In the experiments, the laser fluence was set to 19.5, 22.75, 26.0, and 29.25 $\text{mJ}\cdot\text{cm}^{-2}$, while the scanning speed was fixed at $0.01\text{ mm}\cdot\text{s}^{-1}$ and all other processing parameters were kept constant. This parameter design eliminates the influence of other variables on structural formation, ensuring that laser fluence is the sole varying factor. The fabrication results are shown in Supplementary Fig. 3, which clearly illustrate the NGA structures formed under different fluence conditions. The results demonstrate that the average spacing of the nanostructures gradually decreases with increasing laser fluence, verifying the feasibility of tuning the average periodicity of the nanostructures by adjusting the laser spot fluence.

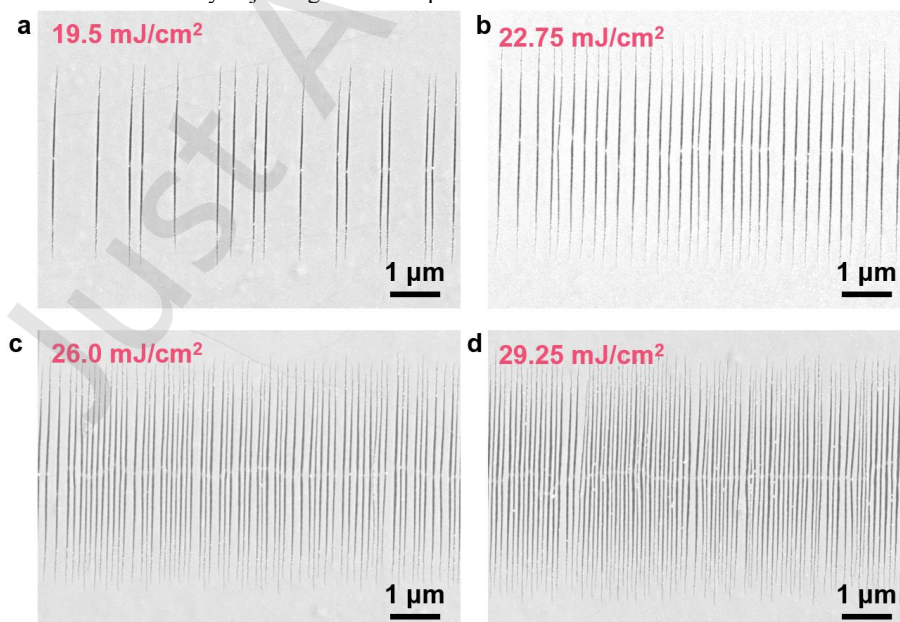


Fig S3. Nanogroove array structures at different laser fluences. (a) 19.5 mJ/cm^2 . (b) 22.75 mJ/cm^2 . (c) 26.75 mJ/cm^2 . (d) 29.25 mJ/cm^2 .

Raman spectral characterization shown in Supplementary Fig. 4 further confirms the structural integrity of the NGA nanostructures with different periodicities. As observed from the spectra, the Raman peak intensities of 2H- WS_2 gradually decrease, whereas the signals from the silicon substrate progressively increase. This trend indicates that, although the 2H- WS_2 signal is partially weakened at higher groove densities due to the enlarged ablated area, the overall crystalline structure remains well preserved, with no evident material degradation or destruction.

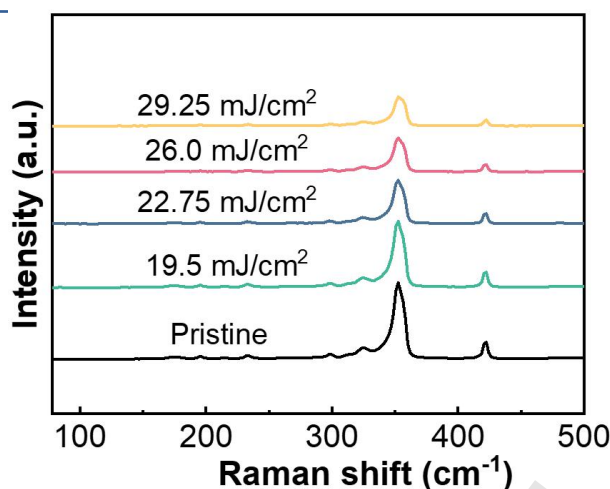


Fig. S4. Raman spectral characterization of NGA structures under different laser fluences.

Furthermore, the number of incident laser pulses was indirectly varied by adjusting the scanning speed to investigate its influence on structural formation. As shown in Supplementary Fig. 5, when the scanning speed was set to 0.001, 0.01, and 0.05 $\text{mm} \cdot \text{s}^{-1}$, the structural density was correspondingly modulated in a periodic manner. With an increasing number of pulses, the density of the nanostructures increases, resulting in a reduced structural periodicity.

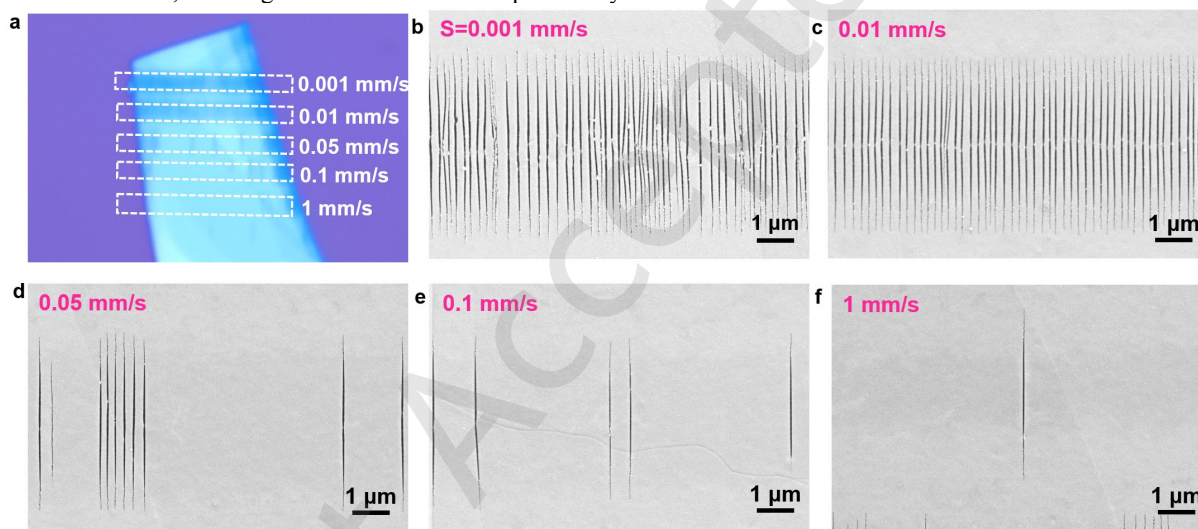


Fig S5. Structural changes at different scanning speeds. (a) Optical image. (b) Scanning speed of 0.001 mm/s. (c) Scanning speed of 0.01 mm/s. (d) Scanning speed of 0.05 mm/s.

First, NGA structures with relatively small periodicity were fabricated using a low laser fluence of $22.75 \text{ mJ} \cdot \text{cm}^{-2}$, and the structures were subjected to an initial SEM characterization to record their morphological state. Subsequently, a second laser scan was performed at the same positions using a higher fluence of $29.25 \text{ mJ} \cdot \text{cm}^{-2}$, which generated a denser NGA structure. By comparing the structures formed after the first and second scans, the formation behavior of the secondary nanostructures was investigated, as shown in Supplementary Fig. 6. The yellow dashed lines indicate the spatial differences between the primary and secondary structures. Notably, while the positions of the primary nanogrooves remain unchanged, the newly formed secondary nanogrooves predominantly emerge at the midpoints between adjacent primary grooves.

This observation demonstrates that, during structural evolution, the secondary nanogrooves originate from the localized near-field regions induced by the primary grooves, i.e., the inter-groove midpoints. This provides direct experimental evidence for nanogroove-induced localized near-field enhancement, under which nanogroove growth is initiated and progressively propagates through plasmonic field coupling. With increasing laser fluence, the initially formed nanogrooves further induce new localized near-field enhancement centers at their central regions, thereby triggering the generation of secondary nanogrooves. The concurrent action of these two field components ultimately leads to the formation of highly ordered NGA structures.

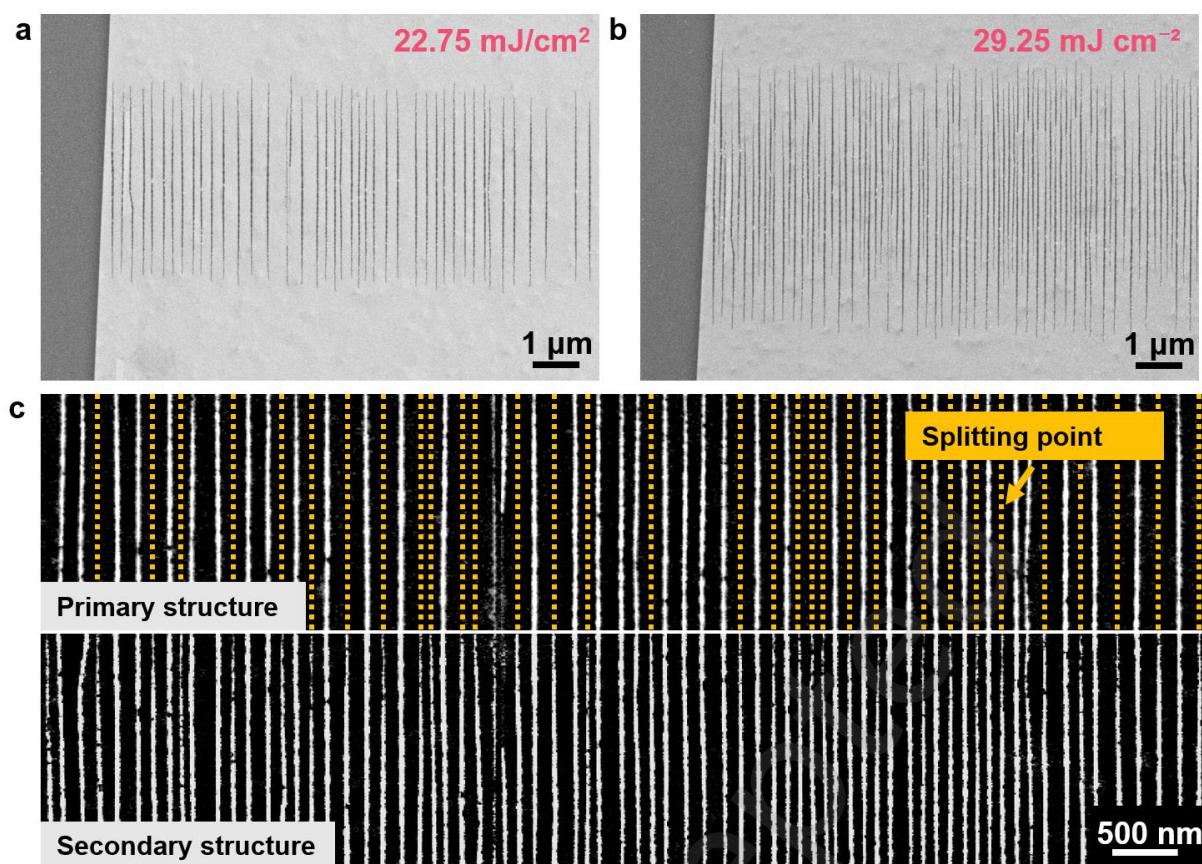


Fig S6. Observation of the secondary evolution of nano-groove array structures. (a) First scan (22.75 mJ/cm²). (b) Second scan (29.25 mJ/cm²). (c) Local black-and-white pseudocolor SEM image of (a)-(b).

Raman spectra were collected from both the processed and unprocessed regions of the 2H-WS₂ nanosheets using a Raman spectrometer. The results are shown in Supplementary Fig. 7. Both the unprocessed pristine region and the laser-processed region exhibit the characteristic A_{1g} and E_{2g} Raman modes, and neither their intensities nor peak positions show noticeable changes. Moreover, no additional oxidation-related peaks or signals from newly formed phases are observed, indicating that the super-resolution NGA region retains the intrinsic crystalline structure of 2H-WS₂. This demonstrates that the formation of nanogrooves does not cause significant damage to the crystal symmetry or structural characteristics of 2H-WS₂. In addition, no redshift or blueshift of any Raman peaks is detected, confirming that no structural strain is introduced during femtosecond laser-induced nanostructure formation.

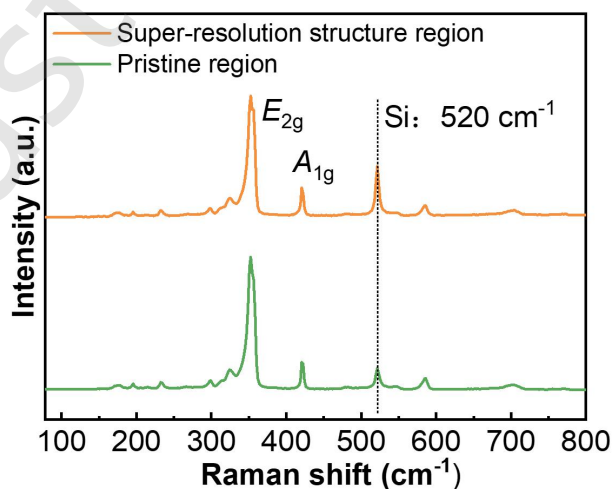


Fig S7. Raman spectra comparison of with and without nanogroove array structures.

XPS spectra were collected from both the unprocessed regions and the NGA regions, as shown in Supplementary Fig. 8. In the XPS spectra of the unprocessed region, the peaks at 34.73 eV and 32.59 eV correspond to the W 4f_{7/2} and W 4f_{5/2} orbitals of 2H-WS₂, respectively, while the peaks at 163.28 eV and 162.08 eV correspond to the S 2p_{3/2} and S 2p_{5/2} orbitals of 2H-WS₂, respectively. In the processed region, the W 4f_{7/2} and W 4f_{5/2} peaks appear at 34.71 eV and 32.55 eV, and the S 2p_{5/2} and S 2p_{3/2} peaks appear at 163.26 eV and 162.07 eV, respectively. These results indicate that there is no significant shift in the XPS peak

positions between the NGA region and the unprocessed region, confirming that femtosecond laser-induced nanostructure does not cause structural damage to the surrounding unprocessed 2H-WS₂ regions.

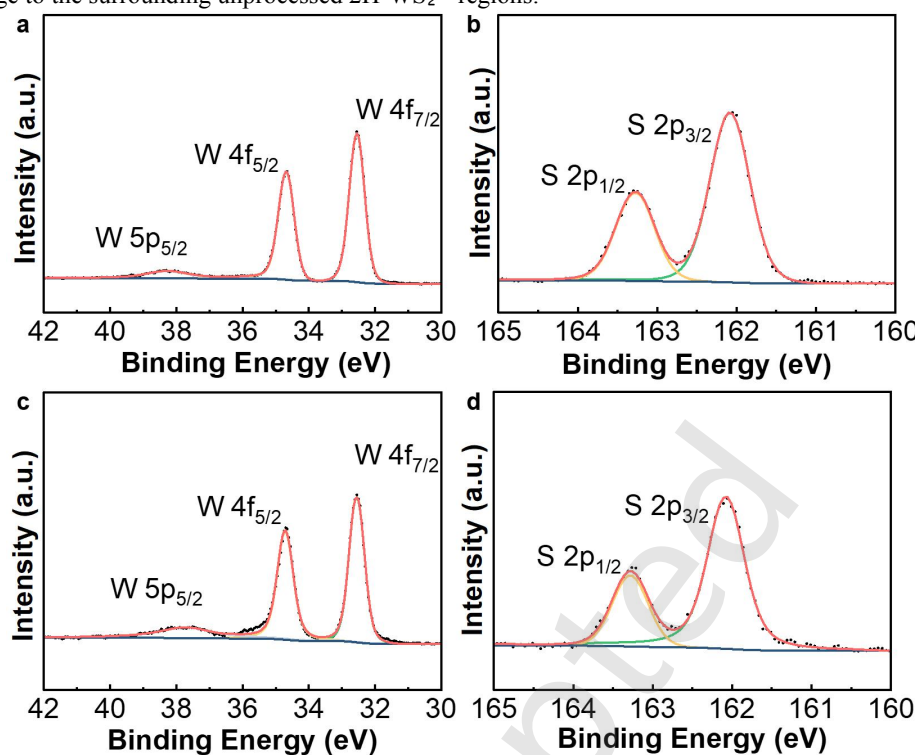


Fig S8. Comparison of XPS spectra with and without NGA structures. (a) W element XPS spectrum of the unprocessed region. (b) S element XPS spectrum of the unprocessed region. (c) W element XPS spectrum of the NGA region. (d) S element XPS spectrum of the NGA region

3. Characterization of SERS Properties

The conventional P-2H-WS₂ exhibits a limited detection performance for CV molecules, being effective only at concentrations down to 10^{-5} M, with very weak signal intensity.

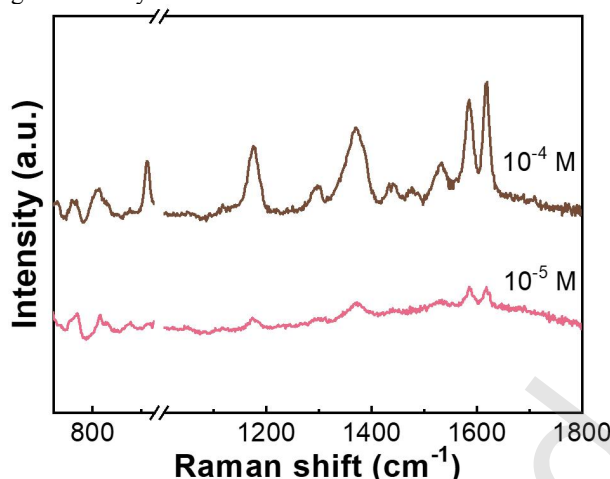


Fig. S9. SERS performance of P-2H-WS₂ for detecting CV molecules.

To evaluate the SERS enhancement capability of the NGA structures for CV molecule detection, their performance was compared with that of multilayer P-2H-WS₂. To ensure a detectable SERS signal from P-2H-WS₂, CV molecules at a concentration of 10^{-5} M were used as the analyte. As shown in Supplementary Fig. 10, the NGA structures exhibit a significant enhancement in SERS performance, with the detection intensity of CV molecules increasing by approximately 12–53 times compared to that of P-2H-WS₂.

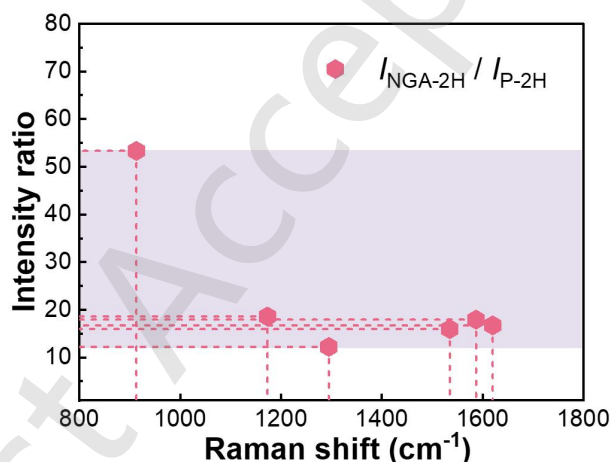


Fig S10. Comparison of SERS performance of multilayer 2H-WS₂ nanostructures and P-2H-WS₂ for CV (10^{-5} mol/L).

To evaluate the reproducibility, Raman spectra of 10^{-6} M CV molecules were randomly collected 30 times on a single-track 2H-WS₂ NGA. The results show that only minor variations were observed among the 30 SERS spectra (Supplementary Fig. 11(a)–(b)). Furthermore, the histogram of Raman intensities at the 1620 cm^{-1} peak of CV molecules indicates a relative standard deviation (RSD) of 9.54%, confirming that the NGA surfaces maintain uniform SERS detection performance. This consistency can be attributed to the femtosecond laser fabrication process, which does not cause significant structural ablation or extensive nanoparticle ejection on the NGA surfaces.

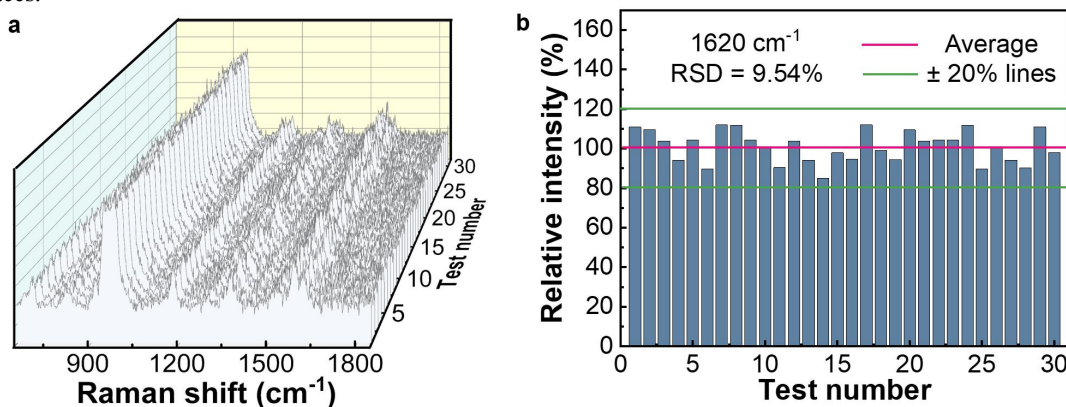


Fig S11. Reproducibility test of multilayer 2H-WS₂ nanostructures for CV (10⁻⁶ mol/L). (a) Raman spectra collected from 30 random points. (b) Intensity statistics at the 1620 cm⁻¹ peak

The stability of the SERS performance of the 2H-WS₂ NGA regions was evaluated by placing the nanogroove-containing nanosheets under ambient conditions for one month and then performing comparative measurements. As shown in Supplementary Fig. 12, the SERS response toward 10⁻⁶ M CV molecules remains consistent even after one month, confirming the excellent long-term SERS stability of the 2H-WS₂ NGA structures.

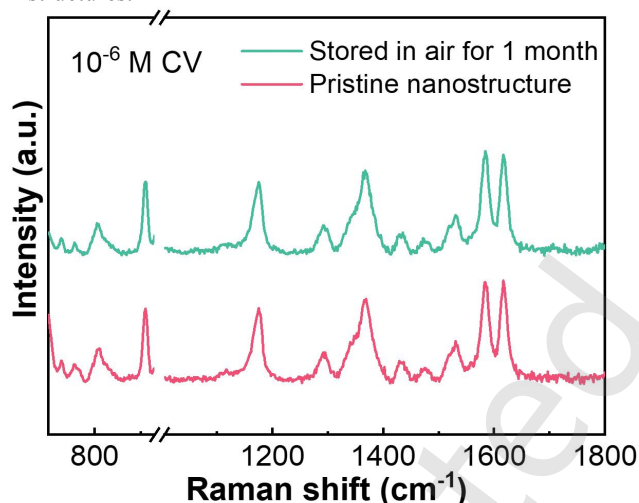


Fig 12. Stability of the SERS performance of 2H-WS₂ NGA structures

To further demonstrate the universality of the NGA structures for molecular detection, their SERS performance was additionally investigated using a broader range of target molecules, including MB, BCB, and Eosin. First, taking MB molecules as an example, Raman area and point scans were performed on the red dashed box region indicated in Fig. S13(a). The spatial distribution mapping based on the characteristic Raman peak of MB at 1621 cm⁻¹ (Fig. S13(b)) confirms that the NGA structures exhibit significant, spatially localized SERS enhancement. Furthermore, concentration-dependent Raman spectra revealed that the NGA regions enable the detection of MB molecules at concentrations as low as 10⁻⁹ M (Fig. S13(c, d)). To solidify the proof of universality, we extended the SERS evaluation to BCB and Eosin molecules, as presented in Fig. S14. The NGA substrates achieved an impressive limit of detection of 10⁻⁸ M for both BCB (Fig. S14(a)) and Eosin (Fig. S14(c)). Notably, the Raman signals obtained from the NGA-2H-WS₂ at an ultra-low concentration of 10⁻⁸ M were still significantly stronger than those from the untreated 2H-WS₂ substrate even at a much higher concentration of 10⁻⁵ M (Fig. S14(b, d)). Together, these comprehensive results solidly demonstrate the outstanding capability and robust universality of the NGA structures for highly sensitive detection of various large organic molecules.

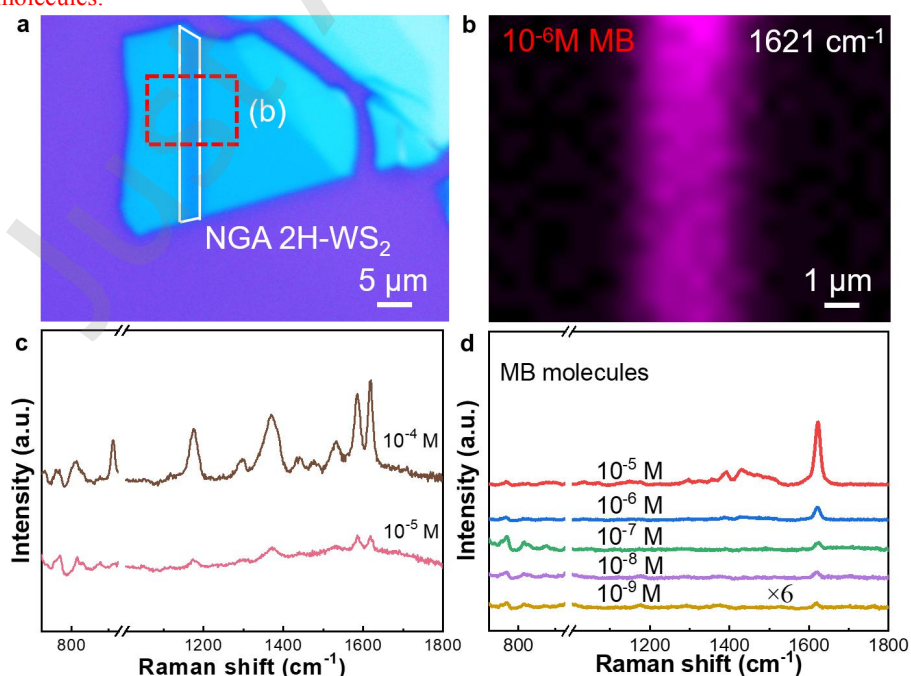


Fig S13. SERS performance of multilayer 2H-WS₂ NGA structures for MB molecules. (a) Optical image. (b) Raman mapping of 10⁻⁶ mol/L MB molecules. (c) SERS detection range of MB molecules

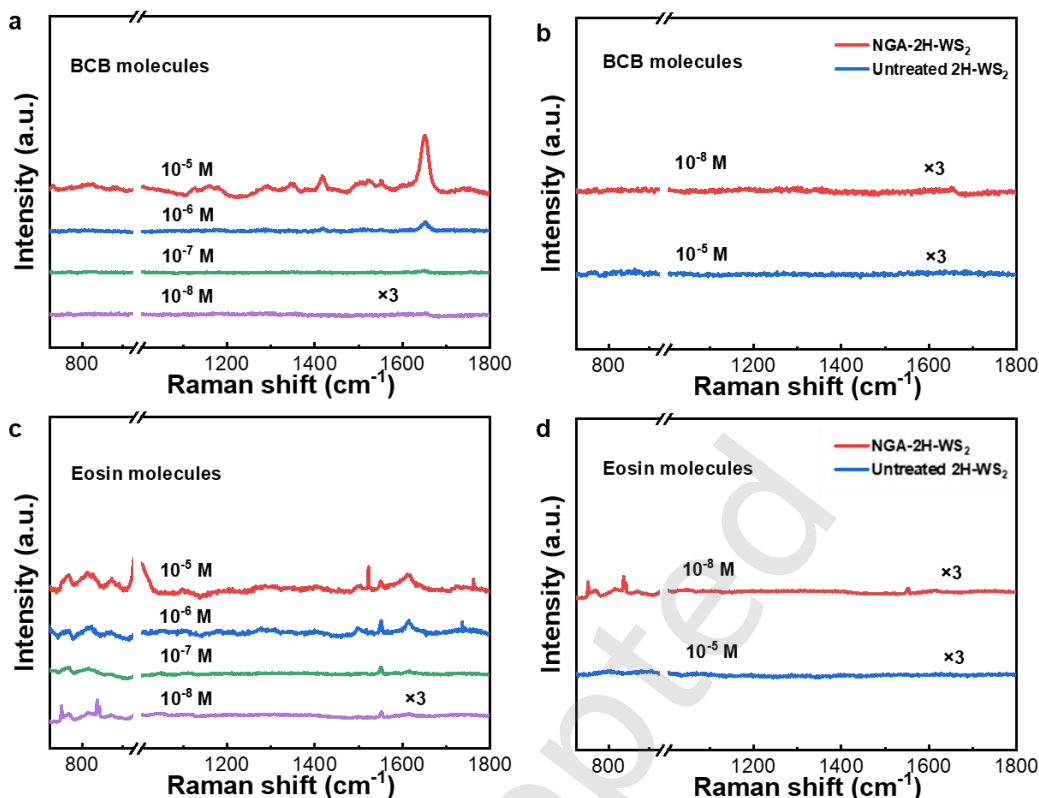


Fig S14. SERS performance of multilayer 2H-WS₂ NGA structures for BCB and Eosin molecules. (a) SERS spectra of BCB molecules on the multilayer 2H-WS₂ NGA structures at different concentrations. (b) Comparison of SERS signals between the untreated 2H-WS₂ (at a BCB concentration of 10⁻⁵ M) and the NGA-2H-WS₂ (at 10⁻⁸ M). (c) SERS spectra of Eosin molecules on the multilayer 2H-WS₂ NGA structures at different concentrations. (d) Comparison of SERS signals between the untreated 2H-WS₂ (at an Eosin concentration of 10⁻⁵ M) and the NGA-2H-WS₂ (at 10⁻⁸ M).

Table S1. Summary of detection limits of CV and MB molecules for reported 2D materials.

2D Materials	CV Detection limit	MB Detection limit	BCB Detection limit	Eosin Detection limit	Ref.
Ultrathin n-WO ₃	10 ⁻⁵	10 ⁻⁷	/	/	1
Few-layer 2H-TaS ₂	10 ⁻⁵	10 ⁻⁶	/	/	2
SnSe ₂	10 ⁻⁷	/	/	/	3
2D BCN	10 ⁻⁷	10 ⁻⁶	10 ⁻⁶	10 ⁻⁶	4
Monolayer PdSe ₂	10 ⁻⁸	10 ⁻⁴	/	/	5
Multilayer Ti ₃ CN	10 ⁻⁸	/	/	/	6
Multilayer Mo ₄ /3B ₂ MBene	10 ⁻⁸	10 ⁻⁶	/	/	7
Ti ₃ C ₂ T _x MXene	2×10 ⁻⁶	10 ⁻⁶	/	/	8
Monolayer ReS ₂	10 ⁻⁹	/	/	/	9
MoS ₂ /Au nanocomposites	2.1×10 ⁻⁹	/	/	/	10
GO/Au nanostars	10 ⁻¹¹	/	/	/	11
Multilayer 2H-WS ₂	10 ⁻⁹	10 ⁻⁹	10 ⁻⁸	10 ⁻⁸	This work

To quantitatively evaluate the chemical interaction and charge transfer dynamics contributing to the SERS performance, Density Functional Theory (DFT) calculations were conducted. The theoretical model was constructed to simulate a CV molecule adsorbing onto the exposed edge of a 2H-WS₂ lattice, closely representing the highly active "artificial sharp edges" generated within our NGA structures. As shown in the differential charge density map (Fig S15), a significant charge transfer is observed between the CV molecule and the 2H-WS₂ edge, confirming a strong interaction. Quantitatively, the calculated adsorption energy of CV on the 2H-WS₂ edge is -0.72 eV, accompanied by a substantial charge transfer of 0.88 e⁻.

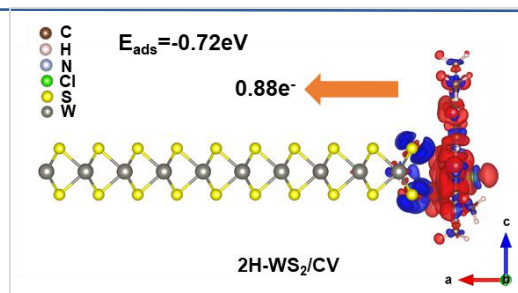


Fig S15. Charge density difference between the 2H-WS₂ edge and CV molecules, along with calculated adsorption energies and charge transfer.

To quantitatively evaluate the potential electromagnetic (EM) contribution to the SERS performance, Finite-Difference Time-Domain (FDTD) simulations were conducted (Fig S16). The geometric model of the 2H-WS₂-NGA was constructed strictly based on the experimental parameters: a periodic array with a periodicity of 260 nm, a groove gap width of 40 nm, and a groove length of 2 μ m, patterned on a 10-nm-thick 2H-WS₂ flake. The structure was irradiated using a simulated Raman excitation light source. As illustrated in Figure S13, the resulting local electric field enhancement ($|E/E_0|$) around the nanogrooves is exceptionally weak. Given that the geometric EM enhancement factor in SERS typically scales with the fourth power of the local electric field ($|E/E_0|^4$), such a marginal field enhancement is virtually negligible and cannot account for the massive, orders-of-magnitude SERS sensitivity observed experimentally. This simulation conclusively corroborates that geometrically induced EM "hotspots" are absent in our semiconducting system, and the remarkable SERS enhancement is overwhelmingly dominated by the chemical mechanism (CM) originating from the highly active artificial sharp edges.

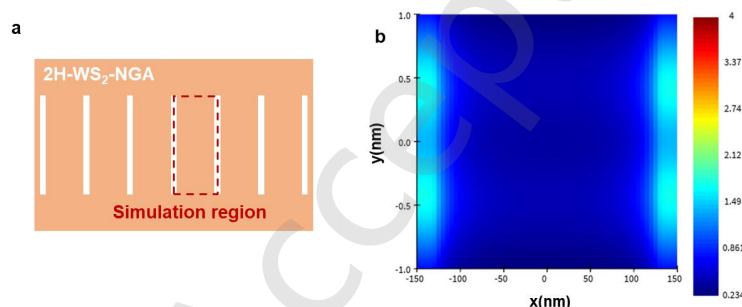


Fig S16. FDTD simulation of the local electric field distribution for the 2H-WS₂ nanogroove arrays (NGA) under Raman excitation. (a) Geometric schematic of the 2H-WS₂ NGA. The red dashed box indicates the specific simulation region selected for the FDTD calculations. (b) The calculated local electric field distribution map corresponding to the simulated region under Raman excitation.

Three 2H-WS₂ nanosheets with NGA structures of different periods were fabricated on Si₃N₄ substrates using varying laser fluences, as shown in Supplementary Fig. 14. Low-resolution TEM dark-field images reveal that femtosecond laser processing produces high-quality, clean-surfaced NGA with different periodicities on the 2H-WS₂ nanosheets. Notably, the groove widths remain largely unchanged despite variations in the array periodicity. High-resolution TEM imaging of the edges and the basal lattice structures of the three periodic structures shows that the unprocessed regions of 2H-WS₂ retain excellent crystalline lattice quality, with no observable structural damage or degradation. Additionally, no significant material residues are detected in the nanogroove regions, indicating complete ablation of the NGA across all periodicities. SAED characterization further confirms that the NGA structures retain a pristine single-crystalline 2H-WS₂ phase, with no disordered or amorphous diffraction spots observed, verifying the excellent preservation of the single-crystalline structure in the NGA. These results demonstrate that fabrication of NGA with different periodicities via laser modulation does not alter the structural state of the nanosheets, ensuring that the basal nanosheet maintains its pure single-crystalline 2H-WS₂ state, while the nanogroove edges remain sharp. This provides a solid foundation for subsequent structural modulation and performance characterization in molecular sensing applications using the NGA structures.

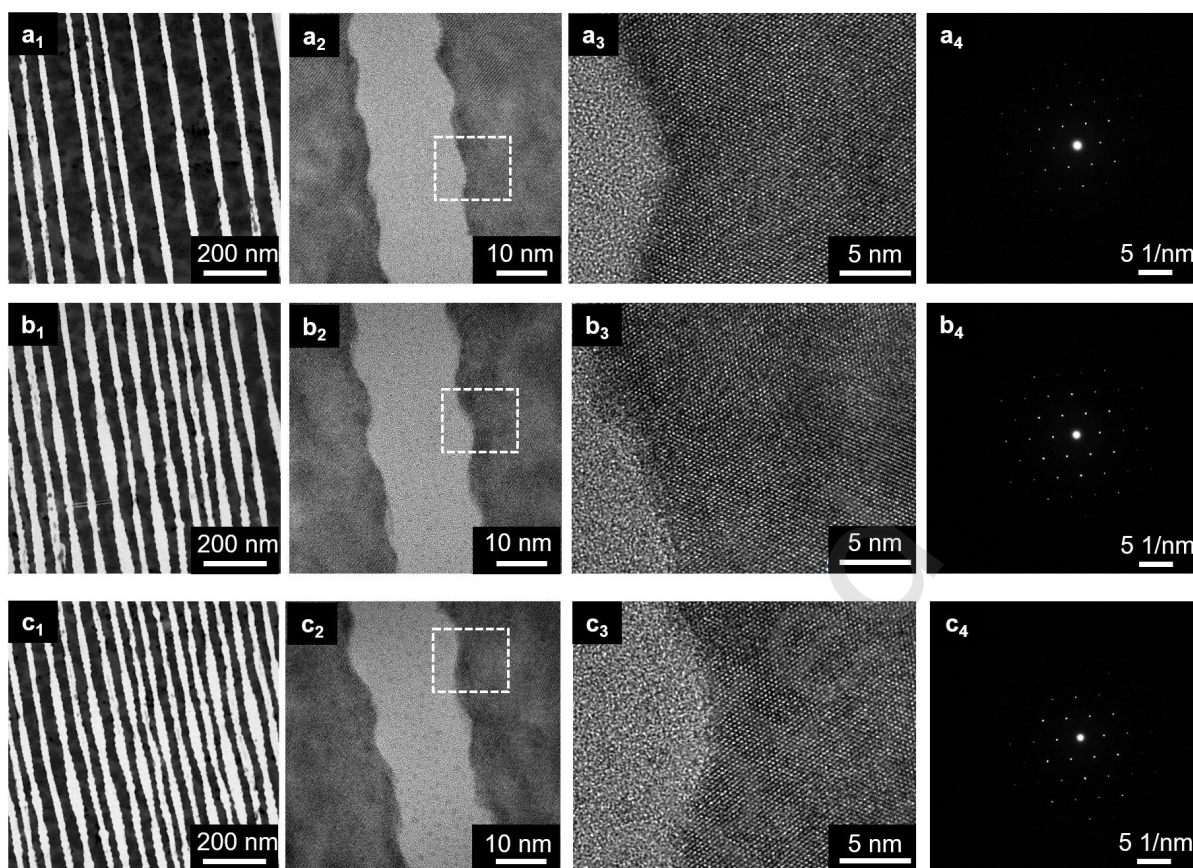


Fig S17. TEM characterization of NGA structures with different periods. (a1–a4) TEM images and corresponding SAED patterns of Period 1. (b1–b4) TEM images and corresponding SAED patterns of Period 2. (c1–c4) TEM images and corresponding SAED patterns of Period 3.

References

- (1) Song, G.; Gong, W.; Cong, S.; Zhao, Z. Ultrathin Two - Dimensional Nanostructures: Surface Defects for Morphology - Driven Enhanced Semiconductor SERS. *Angew. Chem. Int. Ed.* 2021, 60 (10), 5505–5511.
- (2) Lan, L.; Fan, X.; Zhao, C.; Gao, J.; Qu, Z.; Song, W.; Yao, H.; Li, M.; Qiu, T. Two-Dimensional MBenes with Ordered Metal Vacancies for Surface-Enhanced Raman Scattering. *Nanoscale* 2023, 15 (6), 2779–2787.
- (3) Liu, M.; Shi, Y.; Wu, M.; Tian, Y.; Wei, H.; Sun, Q.; Shafi, M.; Man, B. UV Surface - Enhanced Raman Scattering Properties of SnSe₂ Nanoflakes. *J. Raman Spectrosc.* 2020, 51 (5), 750–755.
- (4) Liang, C.; Lu, Z.-A.; Zheng, M.; Chen, M.; Zhang, Y.; Zhang, B.; Zhang, J.; Xu, P. Band Structure Engineering within Two-Dimensional Borocarbonitride Nanosheets for Surface-Enhanced Raman Scattering. *Nano Lett.* 2022, 22 (16), 6590–6598.
- (5) Jena, T.; Hossain, M. T.; Nath, U.; Sarma, M.; Sugimoto, H.; Fujii, M.; Giri, P. K. Evidence for Intrinsic Defects and Nanopores as Hotspots in 2D PdSe₂ Dendrites for Plasmon-Free SERS Substrate with a High Enhancement Factor. *npj 2D Mater. Appl.* 2023, 7, 8.
- (6) Lan, L.; Zhao, C.; Tang, X.; Gao, J.; Li, G.; Cai, H.; Yang, S.; Liu, J.; Qu, Z.; Fan, X.; Qiu, T. Charge-Transfer-Driven Ultrasensitive SERS Sensing in a Two-Dimensional Titanium Carbonitride MXene. *Opt. Lett.* 2024, 49 (9), 2405–2408.
- (7) Hu, M.; Li, K.; Dang, X.; Yang, C.; Li, X.; Wang, Z.; Li, K.; Cao, L.; Hu, X.; Li, Y.; Wu, N.; Huang, Z.; Meng, G. Phase-Tunable Molybdenum Boride Ceramics as an Emerging Sensitive and Reliable SERS Platform in Harsh Environments. *Small* 2024, 20 (31), e2308690.
- (8) Limbu, T. B.; Chitara, B.; Orlando, J. D.; Garcia Cervantes, M. Y.; Kumari, S.; Li, Q.; Tang, Y.; Yan, F. Green Synthesis of Reduced Ti₃ C₂ Tx MXene Nanosheets with Enhanced Conductivity, Oxidation Stability, and SERS Activity. *J. Mater. Chem. C* 2020, 8 (14), 4722–4731.
- (9) Zhang, X.; Zou, J.; Zhang, X.; Wei, A.; Luo, N.; Liu, Z.; Xu, J.; Zhao, Y. Controllable Growth of 2D ReS₂ Flakes and Their Surface Raman Enhancement Effects. *J. Alloys Compd.* 2023, 963, 171207.
- (10) Yu, H.; Sun, H.; Ma, J.; Han, B.; Wang, R.; Ma, Y.; Lou, G.; Song, Y. Resonance-Assisted Surface-Enhanced Raman Spectroscopy Amplification on Hierarchical Rose-Shaped MoS₂ /Au Nanocomposites. *Langmuir* 2024, 40 (1), 380–388.
- (11) Krishnan, S. K.; Chipatecua Godoy, Y. Deep Eutectic Solvent-Assisted Synthesis of Au Nanostars Supported on Graphene Oxide as an Efficient Substrate for SERS-Based Molecular Sensing. *ACS Omega* 2020, 5 (3), 1384–1393.