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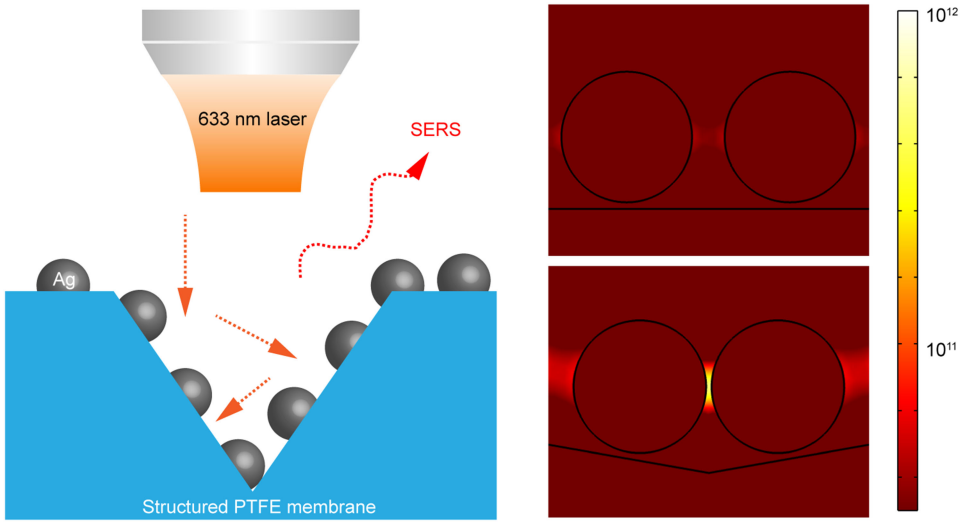

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Femtosecond Laser Structuring for Flexible Surface-Enhanced Raman Spectroscopy Substrates

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Abstract: Surface-enhanced Raman spectroscopy (SERS) is an optical technique for molecule identification. However, fabrication of flexible and structured SERS substrates for performance improvement in a facile and cost-effective manner is challenging. In this work, we reported a polytetrafluoroethylene (PTFE)-based flexible SERS substrate by femtosecond laser direct writing (FsLDW) technology. The femtosecond laser-treated PTFE surface is 3D hierarchical micro-/nano-structures, and the structured PTFE-based SERS chip shows excellent performance enhancement. As a result, 10^{-7} M can be detected, which shows excellent potentials in developing flexible SERS for wearable electronics.

Index Terms: Raman spectroscopy, ultrafast lasers, ultrafast nonlinear processes.

1. Introduction

Surface-enhanced Raman spectroscopy (SERS) is an optical technique for molecule identification [1]–[5] and shows distinguished advantages in chemical and biological analytics [6]–[10]. Particularly, SERS can obtain a molecular fingerprint with high selectivity and sensitivity in a non-destructive manner [11]–[15]. Typically, SERS substrates show strong Raman scattering because electromagnetic (EM) field is significantly enhanced on the tip of plasmonic materials (*e.g.,* Au, Ag) [16]–[20]. Recently, to improve SERS performance, various SERS substrates with micro-/nano-structures have been developed based on EM field enhancement mechanism. The improvement of SERS performance is attributed to creating interparticle nanogaps, localized surface plasmon resonance (LSPR) effect, incident light standing wave effect, the increasing interaction time between exciting light and matter [21]–[25]. As a result, there have been developed various SERS substrates with micro-/nano-structures for performance improvement [26]–[31]. Up

to now, there are successful approaches (*e.g.,* metal colloid self-assembly, soft lithography, uniaxial stretching) and materials (*e.g.,* biocompatible poly(ε-caprolactone) film, PMMA) for the fabrication of flexible SERS substrates [32]–[37]. For example, Sharma *et al.* proposed "nano-fingers" on silicon nanowire arrays as SERS substrate, in which the silicon nanowire arrays are fabricated by using deep-ultraviolet lithography [38]. Li *et al.* prepared superhydrophobic-superhydrophilic silicon plate for SERS trace detection by metal-assist chemical etching and selectively electrochemical deposition [39]. Wang *et al.* fabricated porous silicon photonic crystals for SERS by electrochemical anodization [40]. Tian *et al.* demonstrated 3D SiO_2 nano-grids for SERS substrates with maximizing multiple coupling effects by using electron-beam lithography [41]. Choi *et al.* developed periodic MgF_2 nanopillar arrays on a silicon wafer for highly reliable SERS substrates by combining nanoimprint lithography and electron beam evaporation [42]. Nevertheless, it is still urgent to develop new enhancing substrates with hierarchical micro-/nano-structures in a facile and cost-effective manner despite the big success.

Laser processing has become an emerging cutting-edge technology for the preparation of hierarchical micro-/nano-structures in simple, high-speed, large area manners [43]–[48]. Recently, few SERS substrates have been fabricated by laser technologies [49]–[54]. For example, silica, sapphire, and polymethylmethacrylate polymer-based SERS substrates have been successfully demonstrated by femtosecond laser ablations [51], [52]. Bai *et al.* prepared periodic surface structures for SERS chip by femtosecond laser (Fs) assisted wet etching [53]. Lao *et al.* successfully developed nanogap plasmonic structures for localized SERS sensing by laser printing and capillary force-driven self-assembly [55]. Botta *et al.* demonstrated 3D structured aluminum sheets based on SERS substrate by laser engraving technology[56]. However, the fabrication of flexible and large SERS substrates by a femtosecond laser is rarely reported, especially for future wearable devices.

Herein, we proposed a polytetrafluoroethylene (PTFE) based flexible SERS substrates with hierarchical micro-/nano structures by Fs laser direct writing (FsLDW) technology. In addition, PTFE shows excellent heat, acid, and alkali resistance, having abroad applications in power, automotive, and aerospace industries [57]–[59].Flexible SERS chips were prepared by silver nanoparticles thermal evaporation on the structured PTFE substrates. Due to the flexibility of the PTFE membrane, the SERS chip can twine on a metal wire. In addition, because of the hybrid micro-/nano-structures on PTFE membranes, the SERS chip shows high performance by enhancing the internal light reflection and the LSPR.

2. Experimental Details

2.1 Fabrication of SERS Substrates

The flexible and structured PTFE SERS substrate was fabricated by Fs laser technology. Firstly, PTFE membranes (thickness, $\sim$100 μm) were cleaned with ethanol and deionized water. A Roban Nano System (Jicheng Ultrafast Equipment, Ltd) was employed for laser structuring PTFE membranes (L-PTFE). As for the relationship between laser processing parameters and PTFE structure, the wider the pulse width and the higher the Fs laser's repetition frequency, the wider the resulted linewidth of the L-PTFE surface [60]–[62]. As for the period, when the period is too small, the laser scanning will repeatedly destroy the structure before fabricated. When the period is too large, the micro-/nano-structure is not enough. Therefore, an appropriate period is needed [63]–[65]. As a result, the detailed Fs laser processing parameters are as follows: λ = 1030 nm, the pulse duration = 290 fs, the repetition rate = 200 kHz, the laser power $\approx$ 1500 mW, respectively. SD400B-Multisource Organic Molecular Vapor Deposition System conducts the thermal evaporation.

2.2 Characterization and Measurement

The confocal laser scanning microscopy (CLSM) images were obtained by LEXT 3D measuring laser microscope (OLS4100). The scanning electron microscopy (SEM) images were collected by

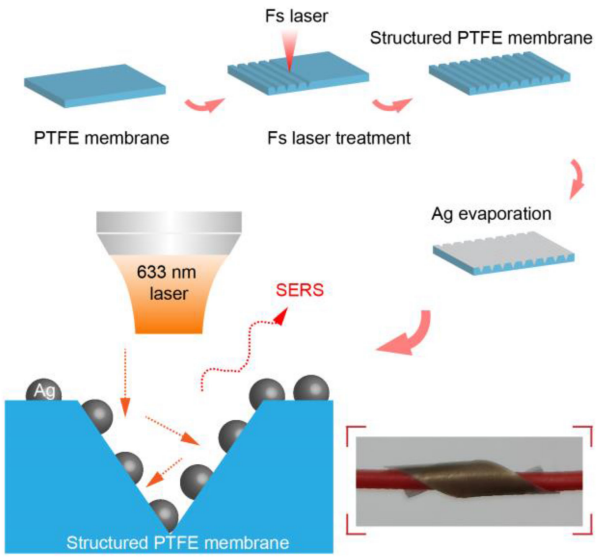

Fig. 1. Schematic Illustration of Fs laser micro-/nano-fabrication technology for flexible and structured SERS substrates based on PTFE membranes. The inset is a photograph of a flexible L-PTFE-Ag based SERS substrate twining on a metal wire.

a JEOL field-emission scanning electron microscope (JSM-7500). The Raman signals were taken by LabRAM HR Evolution (HOARIBA).

3. Results

After laser treatment, flatten PTFE membranes become rough. Silver was coated on the rough PTFE membranes by thermal evaporation (L-PTFE-Ag); flexible L-PTFE-Ag SERS substrates were designed and fabricated. As shown in the inset of Fig. 1, the flexible L-PTFE-Ag SERS substrates are capable of twining on a metal wire (diameter, $\sim$1.17 mm), which demonstrated outstanding flexibility. Additionally, instead of the outstanding flexibility, the L-PTFE-Ag membrane can be used to develop high-performance SERS substrates because of the LSPR effect and 3D micro-/nano-structures. The 3D micro-/nano-structures are helpful to enhance the internal light reflection, leading to the improvement of SERS performance [66]–[71].

In order to characterize microstructures of samples, CLSM was used to examine the surface morphology of PTFE, L-PTFE, and L-PTFE-Ag (Fig. 2). The pristine PTFE surface is flat, and there are some wrinkles on the surface (Fig. 2(a)). The wrinkles may be introduced in the PTFE preparation process by mold pressing. The wrinkles are inapparent, which may limit the PTFE membrane in the fabrication of high-performance SERS substrates. After the laser treatment, gratings (T $\approx$ 25 μm) could be observed (Fig. 2(b)). Simultaneously, there are micro-/nano-structures on the edge of the grating and the untreated PTFE surface. The micro-/nano-structures on the grating edge may be attributed to the instantaneous high energy interaction between Fs laser and PTFE. The micro-/nano-structures on the untreated PTFE surface maybe originate from debris that splashed on untreated areas during the interaction between Fs laser and PTFE. When it comes to the L-PTFE-Ag surface, the L-PTFE-Ag surface shows distinct bright gray due to Ag film's color (Fig. 2(c)). Ag film thickness is $\sim$18 nm, which is precisely controlled by the thermal evaporation equipment. Compared with the micro-/nano-structures of L-PTFE, Ag film's nanoscale thickness has nearly no effect on the microscale surface morphology between L-PTFE and L-PTFE-Ag. As shown in Fig. 2(d), each grating's width and height can be extracted from L-PTFE-Ag's 3D perspective. The average width is $\sim$4 μm, and the average height is $\sim$7.6 μm.

To investigate the micro-/nano-structures of samples, SEM has been adopted to reveal the surface morphology of PTFE, L-PTFE, and L-PTFE-Ag (Fig. 3). Not surprisingly, the PTFE surface

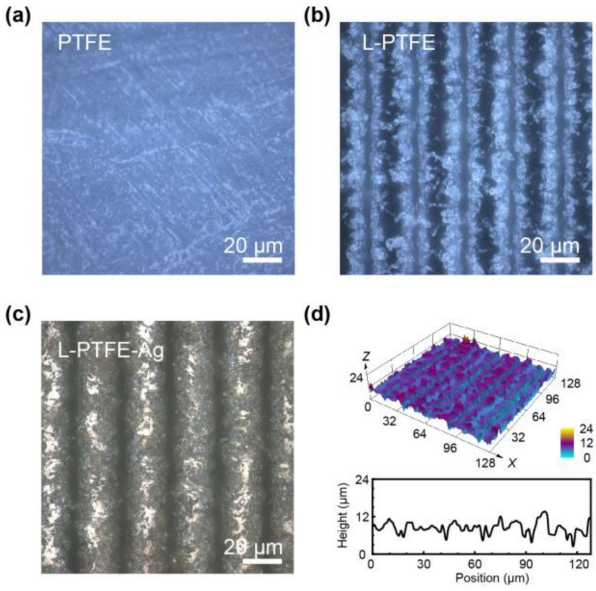

Fig. 2. Top-view CLSM images of (a) PTFE, (b) L-PTFE, and (c) L-PTFE-Ag surfaces. (d) 3D view and corresponding sectional profile of the L-PTFE-Ag surface.

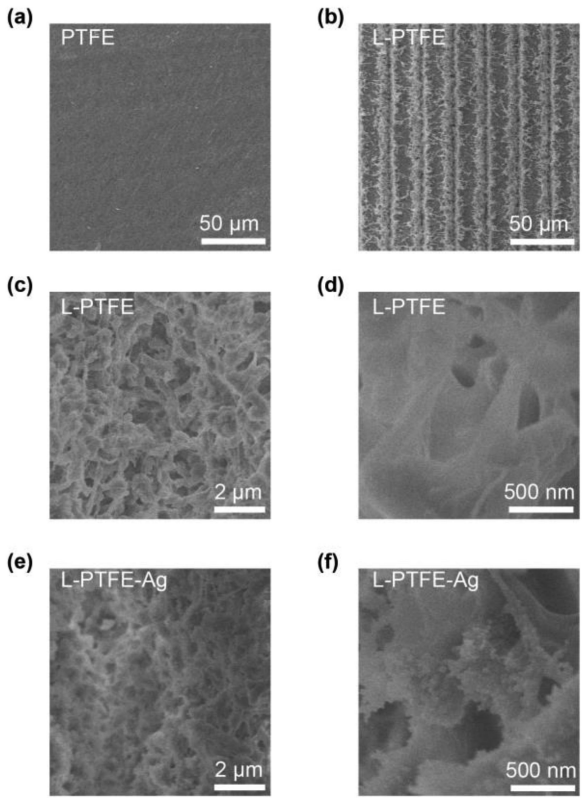

Fig. 3. SEM images of (a) PTFE and (b) L-PTFE. The enlarged SEM images of (c), (d) L-PTFE and (e), (f) L-PTFE-Ag surfaces.

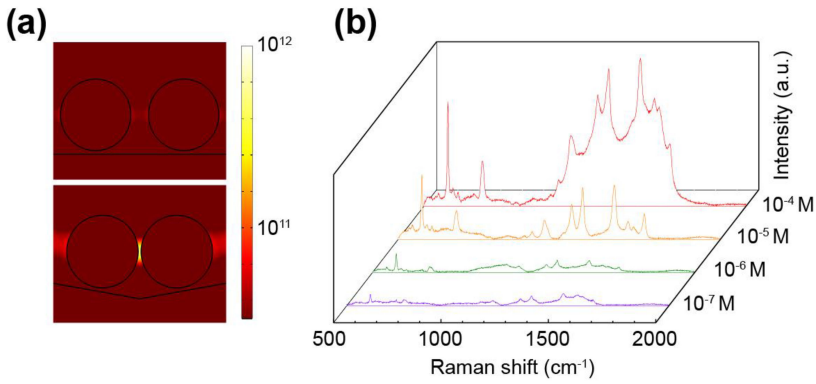

Fig. 4. (a) COMSOL simulations of local electrical field distribution on flatten and structured L-PTFE-Ag surfaces. (b) SERS spectra of R6G molecules.

is flat. Besides, the L-PTFE surface is rough and has grating micro-structures (Fig. 3(a), (b)). It worth mentioning that there are many nanoporous structures on the surface L-PTFE (Fig. 3(c), (d)). The focused Fs laser shows a high temperature at the focus point. Then PTFE decomposes in the form of gas when the Fs laser interacts with PTFE. As a result, the gas escaped from PTFE materials, leading to nanoporous structures. After Ag-coating, compared with the L-PTFE surface, there are many silver nanoislands on the L-PTFE surface (Fig. 3(e), f). After the Ag-coating, there are two advantages: (1) The Ag nanoislands help further enhance the internal light reflection. (2) The Ag nanoislands provide hot pots by the LSPR. The combination of these two advantages mentioned above plays a vital role in developing PTFE-based SERS substrates. Appropriate diameter and spacing of silver nanoparticles (AgNPs) will help to improve the SERS performance [1], [69], [72]. As a pioneer, Kumar *et al.* reported flexible SERS substrates with AgNPs on grating PDMS structures that combine LSP and surface plasmon polariton structures [73], [74]. Compared with this successful work, the laser-treated area shows much more hybrid micro-/nano-structures formation in a simple, high-speed, large-area way [75]–[80]. The porous PTFE structures enhance the interaction time between exciting light and matter, leading to the incident light reflection enhancement using the PTFE structure's porosity, which is significant for performance improvement. Besides, our methods' fabrication repeatability has been tested 100 times, which shows good repeatability.

COMSOL simulations of local electrical field distribution were employed to qualitatively analyze the enhancement effect by combining the LSPR and 3D micro-/nano-structures (Fig. 4(a)). Ag nanoislands on a structured substrate show two orders of magnitude electrical field distribution improvement. The electrical field distribution improvement between the adjacent silver nanoislands maybe because the structured substrate shortens the distance between two adjacent nanoislands. As shown in Fig. 4b, R6G probe molecule was chosen to evaluate SERS performances. The wavelength of the excitation source is 633 nm. The bands at 1360 and 1509 cm^{-1} are observed. Therefore, 10^{-4} $\sim$$10^{-7}$ M R6G were used to evaluate the L-PTFE-Ag SERS performance. The Raman signal intensity decreases with the concentration. Due to the advantages of the flexibility, flexible SERS substrates have been demonstrated for conformal rapid and non-invasive SERS detection [33], [34], [81]. Besides, we measured the sensing performance under repeated 100 cycling between different bending degrees, which shows stability without noticeable deterioration.

4. Conclusion

In conclusion, PTFE-based SERS substrates have been fabricated for developing a flexible SERS chip by FsLDW technology. After Fs laser treatment, the PTFE surface becomes rough with 3D hierarchical micro-/nano-structures. Then, The SERS chip was prepared by silver thermal evaporation

on the structured PTFE membrane. It worth mentioning that the structured PTFE-based SERS chip shows excellent performance enhancement by the LSPR effect and the increasing interaction time between exciting light and matter. The mentioned method shows excellent potentials in developing flexible SERS for wearable electronics.

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References

[1] X. Wang, S. C. Huang, S. Hu, S. Yan, and B. Ren, "Fundamental understanding and applications of plasmon-enhanced Raman spectroscopy," *Nat. Rev. Phys.*, vol. 2, no. 5, p. 253–271, 2020.
[2] J. Heo *et al.*, "Electro-inductive effect: Electrodes as functional groups with tunable electronic properties," *Science*, vol. 370, no. 6513, pp. 214–219, 2020.
[3] R. You, Y. Q. Liu, Y. L. Hao, D. D. Han, Y. L. Zhang, and Z. You, "Laser fabrication of graphene-based flexible electronics," *Adv. Mater.*, vol. 32, 2020, Art. no. 1901981.
[4] D. D. Han *et al.*, "Bioinspired graphene actuators prepared by unilateral UV irradiation of graphene oxide papers," *Adv. Funct. Mater.*, vol. 25, no. 28, pp. 4548–4557, 2015.
[5] X. Y. Fu, Z. D. Chen, D. D. Han, Y. L. Zhang, H. Xia, and H. B. Sun, "Laser fabrication of graphene-based supercapacitors," *Photon. Res.*, vol. 8, no. 4, pp. 577–588, 2020.
[6] L. Piatkowski, J. T. Hugall, and N. V. Hulst, "Raman spectroscopy: Watching a molecule breathe," *Nat. Photon.*, vol. 8, no. 8, pp. 589–591, 2014.
[7] E. D. Feng, T. T. Zheng, X. X. He, J. Q. Chen, and Y. Tian, "A novel ternary heterostructure with dramatic SERS activity for evaluation of PD-L1 expression at the single-cell level," *Sci. Adv.*, vol. 4, no. 11, p. eaau3494, 2018.
[8] Y. Zhu *et al.*, "Raman tensor of layered black phosphorus," *PhotoniX*, vol. 1, no. 1, p. 17, 2020.
[9] S. Xu *et al.*, "Cross-wavelength invisibility integrated with various invisibility tactics," *Sci. Adv.*, vol. 6, no. 39, p. eabb3755, 2020.
[10] Y. G. Bi *et al.*, "Broadband light extraction from white organic light-emitting devices by employing corrugated metallic electrodes with dual periodicity," *Adv. Mater.*, vol. 25, no. 48, pp. 6969–6974, 2013.
[11] X. Zhou *et al.*, "Bacteria detection: From powerful SERS to its advanced compatible techniques," *Adv. Sci.*, vol. 7, no. 23, p. 2001739, 2020.
[12] W. Yang and D. K. Lim, "Recent advances in the synthesis of intra-nanogap Au plasmonic nanostructures for bioanalytical applications," *Adv. Mater.*, vol. 32, no. 51, p. 2002219, 2020.
[13] Q. Ma, and T. J. Cui, "Information metamaterials: Bridging the physical world and digital world," *PhotoniX*, vol. 1, no. 1, p. 1, 2020.
[14] Y. Jin *et al.*, "Solving efficiency-stability tradeoff in top-emitting organic light-emitting devices by employing periodically corrugated metallic cathode," *Adv. Mater.*, vol. 24, no. 9, pp. 1187–1191, 2012.
[15] D. D. Han *et al.*, "Airflow enhanced solar evaporation based on janus graphene membranes with stable interfacial floatability," *ACS Appl. Mater. Interfaces*, vol. 12, pp. 25435–25443, 2020.
[16] D. D. Han, Y. L. Zhang, J. N. Ma, Y. Q. Liu, B. Han, and H. B. Sun, "Light-mediated manufacture and manipulation of actuators," *Adv. Mater.*, vol. 28, no. 38, pp. 8328–8343, 2016.
[17] S. Kasani, K. Curtin, and N. Q. Wu, "A review of 2D and 3D plasmonic nanostructure array patterns: Fabrication, light management, and sensing applications," *Nanophotonics*, vol. 8, no. 12, pp. 2065–2089, 2019.
[18] R. H. Siddique, J. Mertens, H. Holscher, and S. Vignolini, "Scalable and controlled self-assembly of aluminum-based random plasmonic metasurfaces," *Light Sci. Appl.*, vol. 6, p. e17015, 2017.
[19] Z. G. Dai *et al.*, "Plasmon-driven reaction controlled by the number of graphene layers and localized surface plasmon distribution during optical excitation," *Light Sci. Appl.*, vol. 4, p. e342, 2015.
[20] Y. L. Zhang *et al.*, "A 'Yin'-'Yang' complementarity strategy for design and fabrication of dual-responsive bimorph actuators," *Nano Energy*, vol. 68, p. 104302, 2020.
[21] S. Yang *et al.*, "Monitoring the charge-transfer process in a Nd-doped semiconductor based on photoluminescence and SERS technology," *Light Sci. Appl.*, vol. 9, no. 1, p. 117, 2020.
[22] P. K. Kannan, P. Shankar, C. Blackman, and C. H. Chung, "Recent advances in 2D inorganic nanomaterials for SERS sensing," *Adv. Mater.*, vol. 31, no. 34, p. 1803432, 2019.
[23] Y. Q. Liu *et al.*, "Bioinspired soft robots based on the moisture-responsive graphene oxide," *Adv. Sci.*, 2021, doi: 10.1002/advs.202002464.
[24] Y. Q. Liu *et al.*, "Three-dimensional micropatterning of graphene by femtosecond laser direct writing technology," *Opt. Lett.*, vol. 45, no. 1, pp. 113–116, 2020.
[25] Y. L. Zhang *et al.*, "Quantum-confined-superfluidics-enabled moisture actuation based on unilaterally structured graphene oxide papers," *Adv. Mater.*, vol. 31, no. 32, p. 1901585, 2019.
[26] Z. Zhu, B. Bai, O. You, Q. Li, and S. Fan, "Fano resonance boosted cascaded optical field enhancement in a plasmonic nanoparticle-in-cavity nanoantenna array and its SERS application," *Light Sci. Appl.*, vol. 4, p. e296, 2015.
[27] Y. Q. Liu, Z. D. Chen, J. W. Mao, D. D. Han, and X. Y. Sun, "Laser fabrication of graphene-based electronic skin," *Front. Chem.*, vol. 7, p. 461, 2019.
[28] J. A. Huang, Y. L. Zhang, Y. Q. Zhao, X. L. Zhang, M. L. Sun, and W. J. Zhang, "Superhydrophobic SERS chip based on a Ag coated natural taro-leaf," *Nanoscale*, vol. 8, no. 22, p. 11487–11493, 2016.

[29] J. A. Huang, Y. L. Zhang, H. Ding, and H. B. Sun, "SERS-enabled lab-on-a-chip systems," *Adv. Opt. Mater.*, vol. 3, no. 5, pp. 618–633, 2015.
[30] Y. Q. Zhao, Y. L. Zhang, J. A. Huang, Z. Y. Zhang, X. F. Chen, and W. J. Zhang, "Plasmonic nanopillar array embedded microfluidic chips: An in situ SERS monitoring platform," *J. Mater. Chem. A*, vol. 3, no. 12, pp. 6408–6413, 2015.
[31] B. B. Xu *et al.*, "Silver-coated rose petal: Green, facile, low-cost, and sustainable fabrication of a SERS substrate with unique superhydrophobicity and high efficiency," *Adv. Opt. Mater.*, vol. 1, no. 1, pp. 56–60, 2013.
[32] K. C. Xu *et al.*, "Uniaxially stretched flexible surface plasmon resonance film for versatile surface enhanced Raman scattering diagnostics," *ACS Appl. Mater. Interfaces*, vol. 9, no. 31, pp. 26341–26349, 2017.
[33] J. E. George, V. K. Unnikrishnan, D. Mathur, S. Chidangil, and S. D. George, "Flexible superhydrophobic SERS substrates fabricated by in situ reduction of Ag on femtosecond laser-written hierarchical surfaces," *Sensors Actuators B-Chem.*, vol. 272, pp. 485–493, 2018.
[34] K. C. Xu, R. Zhou, K. Takei, and M. H. Hong, "Toward flexible surface-enhanced Raman scattering (SERS) sensors for point-of-care diagnostics," *Adv. Sci.*, vol. 6, no. 16, p. 1900925, 2019.
[35] S. Kumar, M. Kanagawa, K. Namura, T. Fukuoka, and M. Suzuki, "Multilayer thin-film flake dispersion gel for surface-enhanced Raman spectroscopy," *Appl. Nanosci.*, 2021, doi: 10.1007/s13204-020-01562-0.
[36] R. Zhao, L. Huang, and Y. Wang, "Recent advances in multi-dimensional metasurfaces holographic technologies," PhotoniX, vol. 1, no. 1, p. 20, 2020.
[37] H. K. Lee *et al.*, "Designing surface-enhanced Raman scattering (SERS) platforms beyond hotspot engineering: Emerging opportunities in analyte manipulations and hybrid materials," *Chem. Soc. Rev.*, vol. 48, no. 3, pp. 731–756, 2019.
[38] Y. Sharma, and A. Dhawan, "Plasmonic 'nano-fingers on nanowires' as SERS substrates," *Opt. Lett.*, vol. 41, no. 9, pp. 2085–2088, 2016.
[39] H. Z. Li, Q. Yang, J. Hou, Y. A. Li, M. Z. Li, and Y. L. Song, "Bioinspired micropatterned superhydrophilic Au-areoles for surface-enhanced Raman scattering (SERS) trace detection," *Adv. Funct. Mater.*, vol. 28, no. 21, p. 1800448, 2018.
[40] J. J. Wang, Z. H. Jia, and Y. J. Liu, "Improvement of SERS by the optical modulation of photonic crystal," *IEEE Sensors J.*, vol. 19, no. 23, pp. 11221–11227, 2019.
[41] Y. Tian *et al.*, "A generalized methodology of designing 3D SERS probes with superior detection limit and uniformity by maximizing multiple coupling effects," *Adv. Sci.*, vol. 6, no. 11, p. 1900177, 2019.
[42] M. Choi, S. Kim, S. H. Choi, H. H. Park, and K. M. Byun, "Highly reliable SERS substrate based on plasmonic hybrid coupling between gold nanoislands and periodic nanopillar arrays," *Opt. Exp.*, vol. 28, no. 3, pp. 3598–3606, 2020.
[43] Z. Z. Li *et al.*, "O-FIB: Far-field-induced near-field breakdown for direct nanowriting in an atmospheric environment," *Light Sci. Appl.*, vol. 9, no. 1, p. 41, 2020.
[44] P. S. Salter, and M. J. Booth, "Adaptive optics in laser processing," *Light Sci. Appl.*, vol. 8, p. 110, 2019.
[45] D. D. Han *et al.*, "Moisture-responsive graphene paper prepared by self-controlled photoreduction," *Adv. Mater.*, vol. 27, no. 2, pp. 332–338, 2015.
[46] M. Sakakura, Y. H. Lei, L. Wang, Y. H. Yu, and P. G. Kazansky, "Ultralow-loss geometric phase and polarization shaping by ultrafast laser writing in silica glass," *Light Sci. Appl.*, vol. 9, no. 1, p. 15, 2020.
[47] X. B. Li, N. K. Chen, X. P. Wang, and H. B. Sun, "Phase-change superlattice materials toward low power consumption and high density data storage: Microscopic picture, working principles, and optimization," *Adv. Funct. Mater.*, vol. 28, no. 44, p. 1803380, 2018.
[48] T. T. Zou *et al.*, "High-speed femtosecond laser plasmonic lithography and reduction of graphene oxide for anisotropic photoresponse," *Light Sci. Appl.*, vol. 9, no. 1, p. 69, 2020,.
[49] D. Yin *et al.*, "Efficient and mechanically robust stretchable organic light-emitting devices by a laser-programmable buckling process," *Nat. Commun.*, vol. 7, p. 11573, 2016.
[50] Y. L. Sun *et al.*, "Dynamically tunable protein microlenses," *Angewandte Chemie-Int. Ed.*, vol. 51, no. 7, pp. 1558–1562, 2012.
[51] L. Yuan, X. W. Lan, J. Huang, H. Z. Wang, L. Jiang, and H. Xiao, "Comparison of silica and sapphire fiber SERS probes fabricated by a femtosecond laser," *IEEE Photon. Technol. Lett.*, vol. 26, no. 13, pp. 1299–1302, 2014.
[52] Y. Geng, Z. Yin, X. Tan, Y. Du, X. Hong, and X. Li, "Femtosecond laser ablated polymer SERS fiber probe with photoreduced deposition of silver nanoparticles," *IEEE Photon. J.*, vol. 8, no. 5, p. 4502006, 2016.
[53] S. Bai, D. Serien, A. M. Hu, and K. Sugioka, "3D microfluidic surface-enhanced Raman spectroscopy (SERS) chips fabricated by all-femtosecond-laser-processing for real-time sensing of toxic substances," *Adv. Funct. Mater.*, vol. 28, no. 23, p. 1706262, 2018.
[54] Z. X. Yan *et al.*, "Superhydrophobic SERS substrates based on silver-coated reduced graphene oxide gratings prepared by two-beam laser interference," *ACS Appl. Mater. Interfaces*, vol. 7, no. 49, pp. 27059–27065, 2015.
[55] Z. X. Lao *et al.*, "Nanogap plasmonic structures fabricated by switchable capillary-force driven self-assembly for localized sensing of anticancer medicines with microfluidic SERS," *Adv. Funct. Mater.*, vol. 30, no. 15, p. 1909467, 2020.
[56] R. Botta *et al.*, "3D structured laser engraves decorated with gold nanoparticle SERS chips for paraquat herbicide detection in environments," *Sensors Actuators B: Chem.*, vol. 304, p. 127327, 2020.
[57] E. Dhanumalayan, and G. M. Joshi, "Performance properties and applications of polytetrafluoroethylene (PTFE)-A review," *Adv. Composites Hybrid Mater.*, vol. 1, no. 2, pp. 247–268, 2018.
[58] B. H. Kim *et al.*, "Mussel-inspired block copolymer lithography for low surface energy materials of teflon, graphene, and gold," *Adv. Mater.*, vol. 23, no. 47, pp. 5618–5622, 2011.
[59] K. Ren, W. Dai, J. Zhou, J. Su, and H. Wu, "Whole-teflon microfluidic chips," *Proc. Nat. Acad. Sci. USA*, vol. 108, no. 20, pp. 8162–8166, 2011.
[60] C. H. Li, J. H. Zhao, X. Y. Yu, Q. D. Chen, J. Feng, and H. B. Sun, "Fabrication of black silicon with thermostable infrared absorption by femtosecond laser," *IEEE Photon. J.*, vol. 8, no. 6, p. 6805809, 2016.

[61] W. N. Han, D. F. Li, F. R. Liu, Y. P. Yuan, and X. W. Li, "Controllable formation of Si nanostructures based on quasi-plasmonic planar nanostructures formed by annular-shaped femtosecond laser pulse," *IEEE Photon. J.*, vol. 11, no. 4, p. 2400208, 2019.
[62] Y. C. Zhang *et al.*, "Localized self- growth of reconfigurable architectures induced by a femtosecond laser on a shape-memory polymer," *Adv. Mater.*, vol. 30, no. 49, p. 1803072, 2018.
[63] X. Q. Liu, B. F. Bai, Q. D. Chen, and H. B. Sun, "Etching-assisted femtosecond laser modification of hard materials," *Opto-Electron. Adv.*, vol. 2, no. 9, p. 190021, 2019.
[64] L. Jiang, A. D. Wang, B. Li, T. H. Cui, and Y. F. Lu, "Electrons dynamics control by shaping femtosecond laser pulses in micro/nanofabrication: Modeling, method, measurement and application," *Light Sci. Appl.*, vol. 7, p. 17134, 2018.
[65] F. Sima, K. Sugioka, R. M. Vazquez, R. Osellame, L. Kelemen, and P. Ormos, "Three-dimensional femtosecond laser processing for lab-on-a-chip applications," *Nanophotonics*, vol. 7, no. 3, pp. 613–634, 2018.
[66] S. Kumar *et al.*, "Highly stable and reproducible Au nanorod arrays for near-infrared optofluidic SERS sensor," *Mater. Lett.*, vol. 286, p. 129106, 2021.
[67] S. Kumar, K. Tokunaga, K. Namura, T. Fukuoka, and M. Suzuki, "Experimental evidence of a twofold electromagnetic enhancement mechanism of surface-enhanced Raman scattering," *J. Phys. Chem. C*, vol. 124, no. 38, pp. 21215–21222, 2020.
[68] A. Rajput, S. Kumar, and J. P. Singh, "Vertically standing nanoporous Al-Ag zig-zag silver nanorod arrays for highly active SERS substrates," *Analyst*, vol. 142, no. 20, pp. 3959–3966, 2017.
[69] V. Shvalya, G. Filipic, J. Zavasnik, I. Abdulhalim, and U. Cvelbar, "Surface-enhanced Raman spectroscopy for chemical and biological sensing using nanoplasmonics: The relevance of interparticle spacing and surface morphology," *Appl. Phys. Rev.*, vol. 7, no. 3, p. 031307, 2020.
[70] Y. J. Kim, G. R. Lee, E. N. Cho, and Y. S. Jung, "Fabrication and applications of 3D nanoarchitectures for advanced electrocatalysts and sensors," *Adv. Mater.*, vol. 32, no. 35, p. 1907500, 2020.
[71] S. Bai, Y. J. Du, C. Y. Wang, J. Wu, and K. Sugioka, "Reusable surface-enhanced Raman spectroscopy substrates made of silicon nanowire array coated with silver nanoparticles fabricated by metal-assisted chemical etching and photonic reduction," *Nanomaterials*, vol. 9, no. 11, p. 1531, 2019.
[72] O. Pryshchepa, P. Pomastowski, and B. Buszewski, "Silver nanoparticles: Synthesis, investigation techniques, and properties," *Adv. Colloid Interface Sci.*, vol. 284, p. 102246, 2020.
[73] S. Kumar, Y. Doi, K. Namura, and M. Suzuki, "Plasmonic nanoslit arrays fabricated by serial bideposition: Optical and surface-enhanced Raman scattering study," *ACS Appl. Bio Mater.*, vol. 3, no. 5, pp. 3226–3235, 2020.
[74] S. Kumar, D. K. Lodhi, P. Goel, Neeti, P. M., and J. P. Singh, "A facile method for fabrication of buckled PDMS silver nanorod arrays as active 3D SERS cages for bacterial sensing," *Chem. Commun.*, vol. 51, no. 62, pp. 12411–12414, 2015.
[75] D. Serien, and K. Sugioka, "Fabrication of three-dimensional proteinaceous micro- and nano-structures by femtosecond laser cross-linking," *Opto-Electron. Adv.*, vol. 3, no. 1, p. 180008, 2019.
[76] J. Yang, J. B. Li, Z. R. Du, Q. H. Gong, J. H. Teng, and M. H. Hong, "Laser hybrid micro/nano-structuring of si surfaces in air and its applications for SERS detection," *Sci. Rep.*, vol. 4, p. 6657, 2014.
[77] K. C. Xu, C. T. Zhang, R. Zhou, R. Ji, and M. H. Hong, "Hybrid micro/nano-structure formation by angular laser texturing of si surface for surface enhanced Raman scattering," *Opt. Exp.*, vol. 24, no. 10, pp. 10352–10358, 2016.
[78] S. Bai, D. Serien, Y. Ma, K. Obata, and K. Sugioka, "Attomolar sensing based on liquid interface-assisted surface-enhanced Raman scattering in microfluidic chip by femtosecond laser processing," *ACS Appl. Mater. Interfaces*, vol. 12, no. 37, pp. 42328–42338, 2020.
[79] L. Jia, W. Zheng, and F. Huang, "Vacuum-ultraviolet photodetectors," *PhotoniX*, vol. 1, no. 1, p. 22, 2020.
[80] Z. Qiao, Z. Wan, G. Xie, J. Wang, L. Qian, and D. Fan, "Multi-vortex laser enabling spatial and temporal encoding," *PhotoniX*, vol. 1, no. 1, p. 13, 2020.
[81] S. Kumar, P. Goel, and J. P. Singh, "Flexible and robust SERS active substrates for conformal rapid detection of pesticide residues from fruits," *Sensors Actuators B-Chem.*, vol. 241, pp. 577–583, 2017.