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Published in:
Nanoscale

DOI:
[10.1039/c8nr08946a](https://doi.org/10.1039/c8nr08946a)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Gu, P., Zhou, Z., Zhao, Z., Möhwald, H., Li, C., Chiechi, R. C., Shi, Z., & Zhang, G. (2019). 3D zig-zag nanogaps based on nanoskiving for plasmonic nanofocusing. *Nanoscale*, 11(8), 3583-3590.
<https://doi.org/10.1039/c8nr08946a>

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Cite this: *Nanoscale*, 2019, **11**, 3583

3D zig-zag nanogaps based on nanoskiving for plasmonic nanofocusing†

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We combine anisotropic wet etching and nanoskiving to create a novel three-dimensional (3D) nano-antenna for plasmonic nanofocusing, vertically aligned zig-zag nanogaps, constituted of nanogaps with defined angles. Instead of conventional lithography, we used the thickness of a self-assembled monolayer (SAM) to define nanogaps with high throughput, and anisotropic etching of Si V-grooves to naturally define ultra-sharp tips. Both nanogaps and sharp tips can synergistically squeeze the electro-magnetic (EM) field and excite 3D nanofocusing, enabling great potential applications in chemical sensing and plasmonic devices. The dependence of the EM field enhancement on structural features is systematically investigated and optimized. We found that the field enhancement and confinement are stronger at the tipped-nanogap compared to what standalone tips or nanogaps produce. The intensity of surface-enhanced Raman spectroscopy (SERS) recorded on the 70.5° tipped-nanogaps is 45 times higher than that recorded with linear nanogaps and 5 times higher than that recorded with tip-only nanowires, which is attributed to the integration of the tip and gap in plasmonic nanostructures. This proposed nanofabrication technique and the resulting structures equipped with a strongly enhanced EM field will promote broad applications for nanophotonics and surface-enhanced spectroscopy.

Received 6th November 2018,
Accepted 20th January 2019

DOI: 10.1039/c8nr08946a

rsc.li/nanoscale

Introduction

Nanometer-scale gaps and sharp tips made from noble metals are key building blocks for plasmonic devices,^{1,2} heat-assisted magnetic recording systems,³ metamaterials,^{4,5} and optical antennae.^{6,7} On the one hand, nanogaps between two plasmonic structures can squeeze light through them, leading to large electro-magnetic (EM) field enhancement,^{8,9} which has attracted attention in terms of non-linear optics,¹⁰ sensing^{11,12} and surface-enhanced spectroscopy.^{13–15} Many reports have focused on gap structures with various materials and topologies fabricated by several methods, including electron-beam lithography,¹⁶ focused ion beam lithography¹⁷ and electromi-

gration.¹⁸ On the other hand, as an alternative way to generate optical hot spots, nanotips can readily confine optical energy and lead to local EM field enhancement *via* plasmonic nanofocusing.^{19–21} For this reason, three-dimensional metallic nanotips have been used for nano-imaging,^{19,22} nonlinear spectroscopy^{20,21} and particle trapping.^{23,24} Researchers have made great efforts to create such nanotips through metallization of fiber tips,²⁵ nanosphere lithography,²⁶ and complex multistep processes.²⁷

So it could be rationally inferred that when a nano-structure is equipped with nanogaps and nanotips, both of them will promote localization and boosting of optical fields, showing much potential for plasmonic field confinement compared to a single plasmonic structure. However, there were only a few research studies on fabricating composite nanostructures combining nanogaps and sharp nanotips,^{17,28–30} because of difficulties in preparing these structures reproducibly with nanometric precision. Either their fabrication process is too complex, time-consuming and with low throughput, or the resulting nanogaps and nanotips are mostly in-plane and thus limited to excite strong plasmonic enhancement with normally incident light. Therefore, it is desirable to develop the fabrication of advanced optical nanostructures with vertically-oriented nanogaps and sharp tips for dual enhancement of the EM field, especially using a simple technique.

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†Electronic supplementary information (ESI) available: Details of methods and characterization; additional SEM images, Raman spectra and FDTD simulations of the electric-field. See DOI: 10.1039/c8nr08946a

A relatively young nanotechnology named “nanoskiving” can be leveraged to solve this problem. It involves the deposition of a thin film on a flat or topographically patterned polymeric substrate and then sectioning using an ultra-microtome.^{31–33} Compared with conventional nanofabrication, nanoskiving is of low-cost and simple with high resolution, requiring no sophisticated lithographic tools or clean rooms.

In this paper, we introduce novel 3D vertically aligned zig-zag plasmonic nanogaps based on nanoskiving. This nanostructure is endowed with both sub-5 nm vertically-oriented gaps and sharp tips. This configuration is achieved by a sacrificial self-assembled monolayer between two Au films providing sub-1 nm precision. The coupling of gap plasmons and tip-induced nanofocusing throughout propagation synergistically leads to enormous EM field enhancement, when light is focused on the zig-zag nanogaps. This plasmonic device is characterized optically *via* SERS, confirming that the field enhancement at the tipped-nanogaps is orders of magnitude stronger than that from either the linear nanogaps or the tip-only nanowires, which opens exciting perspectives for practical applications in near-field fluorescence imaging and detection of a single or a few molecules in near-field Raman scattering.

Results and discussion

Fabrication of 3D zig-zag plasmonic nanogaps

The fabrication procedure of the zig-zag nanogaps, briefly described in Fig. 1, consists of two key steps: (1) fabrication of a V-grooved silicon template and (2) sectioning of the gold/self-assembled monolayer (SAM)/gold sandwich films using an ultra-microtome. The V-grooved silicon template was created

via standard photolithography and anisotropic wet etching techniques (Fig. 1a, see more details of the fabrication procedure in Fig. S1, ESI†).^{34,35} Then soft templating was used to replicate the V-grooved epoxy substrate (Fig. 1b).³⁶ After vertical deposition of the gold film on the V-grooved epoxy substrate, a self-assembled monolayer (SAM) is formed by submerging this gold-on-epoxy substrate in 1,16-hexadecanedithiol (C16) in ethanol overnight.^{37,38} Then, a second layer of the gold film is vertically deposited on the substrate to form a gold/SAM/gold sandwich topological structure (Fig. 1c). As both heads of the molecular chain can form Au–S bonds with the gold film, the stability of the structure was much increased in sectioning. The sandwich topological structure is embedded in epoxy, and then sliced into ultrathin sections along the direction perpendicular to the substrate through nanoskiving (Fig. 1d and e). The slabs can be placed onto arbitrary substrates. Here we transferred one of the skived slabs onto a gold film supported by a silicon substrate (Fig. 1f). The slab was then dried at 60 °C to improve adhesion to the substrate. The free-standing structures containing two laterally zig-zag nanowires separated by nanometer-scale gaps were fabricated after removing epoxy and SAM using reactive ion etching (RIE) (Fig. 1g).³⁹ The gap width can be tuned by the carbon chain length of the SAM or using other alternative sacrificial spacer materials like insulators (*e.g.* silica, aluminum).

As the angle of the nanotips is a crucial parameter that determines the magnitude of the local EM field intensity,⁴⁰ we first demonstrate that 3D zig-zag nanogaps with different geometries were successfully fabricated (Fig. 2). Fig. 2a is a schematic of the as-prepared zig-zag nanogaps, showing the geometric parameters, where the width ($W = 100$ nm) is determined by the thickness of the deposited metal film; the height

Fig. 1 Schematic illustration of the procedure used to fabricate the zig-zag plasmonic nanogaps. (a) A silicon (100) wafer is patterned *via* anisotropic KOH etching with a chromium mask. (b) A V-grooved epoxy replicate is peeled from the V-grooved silicon template through soft templating. (c) Successive deposition of gold (thickness: 100 nm)/SAM (nanometric)/gold (thickness: 100 nm) films on the V-grooved epoxy substrate. (d) Embedding the sandwich topological structure film in more epoxy. (e) Perpendicular sectioning by using an ultra-microtome. (f) Transfer one of the sections onto a gold film. (g) Removal of SAM and epoxy by RIE.

Fig. 2 (a) Sketch of the zig-zag nanogaps and primary structural parameters. (b) A 45°-tilted SEM image of a V-grooved silicon template. Top width of the trapezoid unit is 10 μm , with a periodicity of 20 μm . The bright line is due to the higher electron emission of Au. (c) SEM image of the zig-zag nanogaps in low magnification. (d) Enlarged SEM image of (c). The SEM images of (e–h) indicate the magnified regions of (d) in red, green, yellow, and blue circles, respectively. The brighter lines are from the surfaces of the Au films, and the dark line in the center is from the nanogap. The scale bars: 10 μm in (b, c, d) and 100 nm in (e, f, g, h).

($H = 150\text{ nm}$) is determined by the set parameter on the ultramicrotome; the length ($L \approx 2\text{ mm}$) is restricted by the width of the diamond knife (the width of the diamond knife we used is 3 mm); and the gap-width ($G = 2.5\text{ nm}$) is determined by the thickness of the SAM.³⁷ Taking advantage of crystalline-orientation-dependent wet etching of the silicon (100) template, the etched V-grooved silicon template exhibits high quality with sharp tips, and smooth side-walls could be readily obtained without using high-resolution lithography (Fig. 2b).

The base width of each groove is 10 μm , and the distance between two adjacent tips is 20 μm .

The tapered angle of the V-grooves is 70.5° and the radius of curvature is about 10 nm, consistent with previous reports.^{34,35} The periodicity can be controlled by the initial standard photolithography step, in which the technical limit for narrow periodicity can be resolved using electron beam lithography or focused ion beam lithography. Moreover, the sharper-angled zig-zag nanogaps could be fabricated by an additional oxidation step.³⁴

The SEM image in Fig. 2c demonstrates that the as-prepared 3D zig-zag nanostructures with tipped-nanogaps are uniform and large area. From the magnified image (Fig. 2d), the integrity of the zig-zag nanogaps can be seen clearly. Each typical area of the zig-zag nanogaps possesses uniform 2.5 nm gaps as shown in Fig. 2e–h corresponding to the red, green, yellow, and blue circles in Fig. 2d. However, a short circuit is likely to occur in the zig-zag nanogaps. The short-circuit is caused by the gold penetrating through defects in the SAM during deposition. For dithiols, these defects may arise from the molecules forming loops where both thiol groups of one molecule are attached to the same gold substrate, which can be mitigated by fine-tuning the concentration of dithiol solu-

tion and soak time during the formation of the SAM.^{37,38} Fortunately, the short-circuit doesn't affect the SERS measurements.⁴⁰ The measured curvature radius of the nanowire in Fig. 2e is slightly larger than 10 nm, because the metal layer deposited in a sharp V-groove can smoothen the tip edge⁴¹ and the mechanical stress during nanoskiving also leads to slight deformation of the tip. The Au nanowire in the horizontal linear nanogaps is thicker than that in the oblique linear nanogaps (Fig. 2f), because in the deposition step a quartz crystal microbalance was used to monitor only the vertical thickness,⁴² which is illustrated in the inset of Fig. 2f. Also, from the magnified SEM images of the oblique linear nanogap (Fig. 2g) and the horizontal linear nanogap (Fig. 2h), we could clearly observe the thickness deviation between nanowires. We found it possible, but difficult, to achieve perfect nanowires with the same width; however, the thickness had a negligible impact on the subsequent experiments. The gap widths, which vitally influence the plasmonic effects,⁴⁰ were uniform along the whole nanowires despite the different topologies, due to the uniformly-formed SAM layer.

Finite-difference time-domain (FDTD) simulations

The core point of our nanostructure for plasmonic nanofocusing is integrating both the nanogap and sharp tip into one nanostructure. To illustrate the EM field distribution on the zig-zag nanogaps, we performed 3D finite-difference time-domain (FDTD) modeling for a zig-zag nanogap with different tip-angles (Fig. 3). The non-polarized incident light was set to 633 nm and focused on the tip-gap interface perpendicularly (Fig. 3a). We calculated the EM field in a cross-section ($x \times z$) for the 2.5 nm linear nanogap, and only a slight field enhancement in the nanogap and the outside edge of each nanowire is

Fig. 3 (a) Simulated schematic of a non-polarized light beam illuminating the tip-gap interface of the zig-zag nanogaps from above. (b–d) FDTD simulations of the electric-field $|E|^2$ distribution on a zig-zag nanogap with 180°, 125.2°, 70.5° tip-angles, respectively. The dashed line in (b) represents the EM field distribution in the nanogap. The scale represents the normalized electric-field intensity.

observed, and the EM field enhancement in the nanogap is weaker than that at the outside edge of each nanowire (Fig. 3b, the dashed line represents the EM field distribution in the nanogap). More details are shown in Fig. S2.† Furthermore, the plasmons propagating in the x -directions along the metal-dielectric interface can be clearly seen in Fig. 3b. It demonstrates that the vertical excitation of the nanostructures lead to not only the localized surface plasmon but also the propagating plasmon mode. As shown in Fig. 3c, the outside of the 125.2° tip angle has much stronger field enhancements than the inside, and the EM field enhancement in the nanogap is weaker than the outside edge of the nanowire.

The reason is that the tip angle is too large to cause the propagating plasmon to be focused on the tips. Notably, when the tip angle is 70.5° (Fig. 3d), the strong electromagnetic field enhancement is located at both the outside and inside of the tip, and the nanogap also generates obvious EM field enhancement. The maximum EM field intensity in the 70.5° tip angle zig-zag nanogap has a factor of 38 compared with the linear nanogaps (the maximum of the calculated electric-field intensity as a function of tip-angle is shown in Fig. S3, ESI†). The huge field intensity at the tip and nanogap could be attributed to adiabatic nanofocusing caused by surface plasmon polaritons (SPPs) propagating toward the tapered tip,¹⁹ the confinement of the optical field to the nanogap, and also by the strong coupling of the gap plasmons with tip-induced nanofocusing. It is worth mentioning that if the nanogaps come into contact with the bulk Si substrate directly, the local electric field will spread broadly, and the final EM field would be

greatly weakened.¹⁴ So here we placed the zig-zag nanogaps on a gold film supported by a silicon substrate to confine and amplify the electric field, and the benefit of using a reflective gold substrate is clearly demonstrated in Fig. S4, ESI.† By introducing a reflective gold mirror, the field enhancement is increased by a factor of 9. The additional enhancement is due to the constructive interference between the incident and reflected light.⁴⁰ It is noted that a 0 nm radius tip was modeled in the analytical model, but under our experimental conditions the radius was 10 nm, and the slight increase in the radius of curvature has little effect on the EM field.²³ The 3D simulations demonstrate that the smaller tip-angle nanogap tends to increase the field enhancement and that the field is tightly confined to within a few nanometers of the tip and nanogap (Fig. 3d). Notably, the non-negligible EM field enhancement at the nanogap of the 70.5° tip angle leads to a larger total EM field than that at the spot with maximum enhancement; thereby the zig-zag nanogaps have much potential for nanophotonics and surface-enhanced spectroscopy. We also simulated the EM field illustrated by polarized light. For polarized light irradiation, the EM field intensity will be stronger (Fig. S5, ESI†), which has a great application in single molecule detection. The simulated EM field distribution by polarized light irradiation further proves that the enhancement of the EM field is caused by surface plasmon polaritons (SPP) propagating toward the tapered tip, the strong coupling of the gap plasmons, and the tip-induced nanofocusing. As a reference, simulations for the laterally zig-zag nanowire with different tip angles were performed (Fig. S6, ESI†). They demonstrate that a smaller tip angle in the lateral zig-zag nanowire without a nanogap tends to increase the EM field enhancement (Fig. S6a–c†), consistent with the zig-zag nanogaps. But the EM field enhancement is obviously fainter than that at the zig-zag nanogaps. The maximum EM field intensity in the 70.5° tip angle zig-zag nanogap has a factor of 7 compared with the 70.5° tip angle tip-only nanowire. Thus, the presence of both nanogaps and smaller tip-angle is vital to effectively excite huge field enhancement. In order to quantitatively prove that the zig-zag nanogap has strong electromagnetic field enhancement, we simulated the electromagnetic field of the nanocube under the same structural parameters, and the electric field of the zig-zag nanogap is 4 times than that of the nanocube (Fig. S7, ESI†). This indicates that the optical properties of zig-zag nanogaps are superior to those of nanocubes.

Surface-enhanced Raman scattering (SERS) enhancement by the zig-zag nanogaps

As mentioned above, the zig-zag nanostructure with tipped-nanogaps leads to stronger EM field enhancement, which can be used as a coupled plasmonic device. To demonstrate the intense optical near-fields of zig-zag nanogaps experimentally, we acquired Raman spectra after coating the gold surfaces with Raman-active molecules. A schematic diagram of this SERS workbench principle for a zig-zag nanogap is illustrated in Fig. 4a. Non-resonant *p*-aminothiophenol (PATP) molecules

Fig. 4 (a) Illustration of the SERS workbench principle for the zig-zag nanogaps. $h\nu_i$ and $h\nu_s$ represent the incoming and scattered photon energy, respectively. The molecule is smaller than the gap width, so it can also reside inside the gap. (b) Experimentally recorded dependence of the SERS intensity versus tip-angle from 70.5° to 180°. (c) SERS intensity at 1077 cm^{-1} for different tip-angles in (b). (d) Raman spectra produced by an individual gold nanowire on a gold mirror.

were used as the analyte due to their capability of forming a SAM on the exposed gold surfaces and the internal gap.⁴⁰ Fig. 4b shows Raman spectra in the range of 800–1800 cm^{-1} for the SAM of PATP molecules, which were deposited on the zig-zag nanogaps with different tip angles by means of chemisorption. The incident laser was non-polarized with 633 nm wavelength. Distinct features of PATP are clearly identifiable as strong bands centering at 1077 and 1590 cm^{-1} , and many other low-intensity bands can be observed in the spectra (see detailed Raman spectra in Fig. S8, ESI†). The blue line in Fig. 4b shows the Raman spectrum of PATP taken from the linear nanogap in the zig-zag nanogaps, and the Raman spectrum recorded from the 125.2° tip angle was plotted by the green line, whose intensity is 13 times greater than that from the linear nanogap. Notably, the Raman spectrum recorded on the 70.5° tip angle nanogap is indicated by the red line, whose signal is stronger by a factor of 45 compared with that from the linear nanogap.

Here, we used the SERS intensities of the C–S stretch at 1077 cm^{-1} to illustrate the impact of the tip-angle on the enhancement of the EM field (Fig. 4c). It demonstrates that the smaller tip angle tends to increase the SERS intensity. To a certain extent a smaller tip angle generated the stronger EM field enhancement according to the corresponding SERS measurements. These experimental results are highly consistent with the simulations. In addition, the tendency of SERS change is expected to be greater than that of the EM field, as the SERS intensity depends on $|E|^4$.⁴³ These results demonstrate that the zig-zag nanogaps have great potential application in SERS. In addition, comparing the 70.5° tip angle nanogaps with the linear nanogap, the SERS enhancement factor (45) is less than the $|E|_{\text{max}}^4$ enhancement (38^2), which is

due to the fact that the probe molecules can attach anywhere along the y-axis in the nanogap and that the Raman signal is a weighted average. As a reference, compared with the zig-zag nanogaps, the Raman spectra recorded on the corresponding zig-zag nanowires without nanogaps show much weaker Raman signals (Fig. S9, ESI†), and the SERS intensity of the 70.5° tip angle zig-zag nanogap is 5 times higher than that in the 70.5° tip-only zig-zag nanowire, indicating the necessity of the nanometer-scale gaps for generating strong plasmonic coupling. Notably, under the same test conditions, the Raman spectra recorded from the 70.5° tip angle in the zig-zag nanogaps is greater than that from the single linear nanowires by a factor of 280. The reference Raman spectrum recorded from PATP on a single linear nanowire is shown in Fig. 3d, with a weak signal of the Raman bands at 1077 and 1590 cm^{-1} , only slightly above the noise level. From these observations, we conclude that the nanometer-scale gap and tip-angle in the zig-zag nanogaps are the two dominant causes of the strong enhancement of the Raman signal; a gold cuboid nanowire only yields a weak enhancement resulting from the outside edges.

Additionally, other sophisticated nanogaps could also be readily fabricated just by changing the skiving direction, providing various potentials for optical devices. When the skiving direction is parallel to the substrate (Fig. S10a, ESI†), a large-area equidistant linear nanogap array was obtained (Fig. S10b†). More interestingly, we slightly tilted the skiving direction (Fig. S10c†), and a nanogap array with gradient spacings from nanometer to micrometer was successfully prepared (Fig. S10d†). This method can potentially solve the problem of limited resolution of standard photolithography. Another interesting aspect is that, just like a single zig-zag nanogap structure with different tip angles (70.5°, 125.2°, 180°), the nanostructures obtained by parallel skiving have gradient gap spacing (from nanometer to micrometer), which can be used for side-by-side comparison of Raman enhancement factors.

Experimental section

Materials

Silicon (100) wafers used as substrates were cleaned and wetted by immersion in piranha solution (7:3 concentrated H_2SO_4 /30% H_2O_2) for 1.5 h at 100 °C, to create a hydrophilic surface, and then washed repeatedly with Millipore water (18.2 MΩ cm) and absolute ethanol. The substrates were dried in a nitrogen stream before use. Positive photoresist (PR, BP212-37) was purchased from Kempur Microelectronics, Inc. Potassium hydroxide (KOH), chromium etchants, trichloro-(1H,1H,2H,2H-perfluorooctyl)silane (PFS), 1,16-alkanedithiols (C16) and PATP were purchased from Aldrich. Polydimethylsiloxane (PDMS) was purchased from Dow Corning. Epoxy resin and hardener and polyethylene microtome mold were purchased from Electron Microscopy Sciences. Ethanol was purchased from Beijing Chemical Works and used as received.

Preparation of the chromium stripe mask

First, the patterned photoresist stripes were prepared onto a conventional (100) silicon wafer by photolithography, where the stripes were aligned parallel to the (110) direction. Briefly, the photoresist was spin-coated on the cleaned silicon wafer at a spinning speed of 3000 rpm for 1 min, and the thickness of the resulting resist film is about 2 μm . The resist film was then patterned using conventional photolithography techniques with a stripe pattern mask (10 $\mu\text{m} \times 10 \mu\text{m}$). After that, a chromium (Cr) film with a thickness of 20 nm was vertically deposited on the substrate by using a commercial thermal evaporation system (KYKY Technology Development Co. Ltd China). Next, we removed the Cr-covered photoresist with ethanol. The residual Cr stripes will act as mask in the following anisotropic wet etching process.

Fabrication of V-grooved silicon template

Prior to silicon wet etching, the native oxide on the exposed silicon regions was removed by immersion in 1% hydrofluoric acid solution for 1 min and subsequently rinsing with de-ionized water. Then the patterned Cr-stripe silicon substrate was wet etched in a 40% KOH solution at 50 $^{\circ}\text{C}$. The wet etching process lasted for 48 min. Soft ultra-sonication was employed during the wet etching process to accelerate the etching rate. Subsequently, the Cr mask was removed by a commercial chromium etchant and the V-grooved silicon template was prepared successfully.

Fabrication of V-grooved epoxy substrate

The V-grooved silicon template was modified by trichloro-(1H,1H,2H,2H-perfluorooctyl) silane (PFS). Then the polydimethylsiloxane (PDMS) pre-polymer was cast onto the V-grooved silicon mold; after the PDMS pre-polymer was cured in a drying oven at 60 $^{\circ}\text{C}$ for 6 hours, the PDMS inversed mold was peeled off from the V-grooved silicon mold. Next, the epoxy pre-polymer (volume ratio of resin and hardener 15:2) was cast onto the PDMS inversed mold for ~ 2 mm thickness and then cured in a drying oven at 60 $^{\circ}\text{C}$ for 6 hours. After curing and peeling off, an epoxy replica of the V-grooved silicon template mold was obtained.

Fabrication of the zig-zag nanogaps

Gold deposition on the V-grooved epoxy template was performed in a commercial thermal evaporation system. The deposition rate was 1.0–1.5 $\text{\AA} \text{ s}^{-1}$, and the thickness of the gold film was 100 nm. Then the gold-on-epoxy substrate was immersed in a 30 mM concentration of 1,16-hexadecanedithiol (C16) in ethanol overnight, to form a self-assembled monolayer on the exposed Au surfaces. The samples were then rinsed with ethanol spraying for 2 min to remove the excess C16 molecules and dried in a nitrogen stream. Another gold film of 100 nm thick was then again deposited on the sample. The V-grooved epoxy substrate bearing the sandwich films was cut out using a jeweler's saw (into $\approx 2 \times 10 \text{ mm}^2$ pieces) and placed into separate wells in a polyethylene microtome mold,

which was then filled with the epoxy pre-polymer, and cured. Then the epoxy blocks were mounted in the sample chuck of the ultra-microtome (Leica EM UC 7) and cut to define an area of $\approx 4 \text{ mm}^2$ around the embedded structure using a razor blade. The blocks were sectioned at a speed of 0.6 mm s^{-1} with a set thickness of 150 nm. After slicing, the slabs were collected by a gold film ($0.5 \times 0.5 \text{ mm}^2$) beneath the slabs. The slabs were then dried at 60 $^{\circ}\text{C}$ to improve adhesion to the substrate. The self-assembled monolayer and thin epoxy film were etched by slight oxygen reactive ion etching (RIE). An inductively coupled plasma (ICP) power (200 W) was applied for 15 min, which was performed with a Plasmalab Oxford 80 Plus system (Oxford Instruments Co.). After these procedures, the zig-zag nanogaps were formed. The Raman spectra show that the nanogaps are free of epoxy and C16.

Finite-difference time-domain simulations

A commercial software package (FDTD Solutions v8.12.590, Lumerical Solutions Inc.) was used to perform simulations of electro-magnetic fields with the same structural dimensions as those extracted from the actual fabricated zig-zag nanogaps. The structure was excited by a normally incident light, and unit magnitude total-field scattered-field propagating in the z direction with an un-polarized electric field. Monitors of a frequency-domain field profile were placed to calculate the distribution of the surface plasmon (SP) energy. The magnitude of the incident electric fields was taken to be unity. The optical parameters of Au and Si were taken from Palik's hand book.⁴⁴

Characterization

Scanning electron microscopy images were obtained with a JEOL JSM 6700F field emission scanning electron microscope with a primary electron energy of 3 kV. In Raman spectroscopy analysis, we used a solution of PATP, with 97% purity diluted to $1 \times 10^{-3} \text{ M}$ in ethanol. The zig-zag nanogaps were soaked in the solution for 12 h to allow PATP monolayer formation on the metal surface and on the sidewall inside the gap. Before measurement, the samples were cleaned under a flow of ethanol for 2 min to remove excess PATP molecules. A Raman microscope (LabRAM HR Evolution) with a 633 nm excitation source (5% transmittance) and a 1 μm beam spot was used to measure the SERS spectra. The exposure time was set to 15 s.

Conclusions

In summary, we have prepared the 3D vertically oriented zig-zag nanogaps in a low-cost and scalable way. Both the linear nanogaps and the sharp tips can localize and boost electro-magnetic fields, so this integrated nanostructure exhibits great optical field enhancement, which was further proved by FDTD simulations in agreement with SERS experiments. The SERS intensity recorded on the 70.5 $^{\circ}$ tipped-nanogap is 45 times higher than that of the linear nanogaps and 5 times than that of the tip-only nanowire. Also, since nanoskiving can create thousands of sections in one time and requires no sophisti-

cated equipment or clean room, it provides a new cost-effective and reproducible route for a wide range of applications including non-linear plasmonics, particle trapping, high-throughput sensing and surface enhanced infrared absorption (SEIRA).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51673085, 51873078 and 51373066). We would like to thank Prof. Helmuth Möhwald for scientific discussions. When we revised this article, Prof. Helmuth Möhwald left us forever. We have lost a great scientist and a wonderful person. We will remember Prof. Helmuth Möhwald as a generous and open-minded person, who always kept a clear view of the bigger picture. Our sincere thoughts and prayers are with Prof. Helmuth Möhwald and his family.

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