From 1D to 3D: Tunable Sub-10 nm Gaps in Large Area Devices

Ziwei Zhou, Zhiyuan Zhao, Ye Yu, Bin Ai, Helmuth Möhwald, Ryan C. Chiechi, Joel K. W. Yang, and Gang Zhang*

The fabrication of nanostructures for large electric-field enhancements has become increasingly attractive over the last several years due to outstanding performance in applications of sensing and imaging.[1] In particular, nanometric gaps between noble metals constitute one of the most explored structures. Especially for sub-10 nm gaps, squeezing light through them can generate extreme subwavelength confinement of electromagnetic energy.[2] Thus subwavelength “hot spots” with highly confined energy are easily generated in the gaps, leading to dramatically enhanced signals from adsorbates. This intriguing capability was essential to enable applications in nonlinear optics, optical trapping, and surface-enhanced spectroscopies.[1] In view of the remarkable advantages and broad application prospects, many efforts have been made to fabricate various nanogaps. Gap-separated gold nanoparticle chains in silica nanoapods, self-aligned sub-1 nm gaps between gold electrodes, and nanostar dimers with a sub-10-nm gap were fabricated and exhibit hallmarks of exceedingly high Raman sensitivity.[3] Plasmonic nanogaps have been fabricated by aggregates of nanoparticles, electromigration, electron-beam lithography (EBL), focused ion beam (FIB) bombardment, nanosphere lithography, and on-wire lithography.[4] However, simple and efficient manufacturing of sub-10 nm gaps remains a challenge. For broader dissemination, improved sensitivity, higher reproducibility, and relaxed requirements on intense sources for spectroscopies, it is, however, necessary to fabricate large-area nanogaps in parallel and at low cost.

Z. Zhou, Z. Zhao, Dr. Y. Yu, B. Ai, Prof. G. Zhang
State Key Lab of Supramolecular Structure and Materials
College of Chemistry
Jilin University
Changchun 130012, P. R. China
E-mail: gang@jlu.edu.cn
Z. Zhao, Prof. R. C. Chiechi
Stratingh Institute for Chemistry, and Zernike Institute for Advanced Materials
University of Groningen
Nijenborgh 4, 9747 AG, Groningen, The Netherlands
Dr. Y. Yu, Prof. J. K. W. Yang
Engineering Product Development
Singapore University of Technology and Design
8 Somapah Road, Singapore 487372, Singapore
Prof. H. Möhwald
Max Planck Institute of Colloids and Interfaces
D-14424 Potsdam, Germany

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An approach based on nanoskiving provides a feasible strategy to meet these criteria.[6] It combines the deposition of thin films on a flat or topographically patterned polymeric substrate with sectioning of the sample into slabs (20–1000 nm) by an ultramicrotome.[6a] The resulting slabs are free-standing and can be transferred to flat or curved surfaces and various kinds of substrates, solving the substrate-dependence problem of nanofabrication in conventional techniques. Recently, nanoskiving has been utilized to fabricate linear nanogaps with ultrasmall stationary gap-widths by Chiechi and Lipomi using, respectively, self-assembled monolayers (SAM) and single layer graphene as templates.[7] Fabricating width-tunable ultrathin nanogaps is imperative to systematically investigate the gap-width dependence of the nanogaps.

Moreover, with the rapid development of nano-optics and nanoelectronics, devices with a high level of integration are in great demand.[8] Nevertheless, the conventional point-like nanogaps only provide a few dominant “hot spots” contributing to the overall signal, in which the field distribution varies with position.[9] In addition, the amount of light that can be coupled into these gaps is limited due to the mismatch with optical wavelengths.[3] In contrast, for those 1D nanogaps composed of two close flat-sided metals, it is straightforward to generate well-defined, high-density hotspots along the entire length.[10] Thus, 1D nanogaps are robust against local defects or impurities, enabling more reliable and reproducible surface-enhanced Raman spectroscopy (SERS). Further, fabricating a 2D array on a plane will largely increase the throughput and gap density.[11] This approach can integrate nanogap devices with required geometries over a large area that is suitable for modern planar technology.[12] Likewise, 3D nanogap arrays with high integration by adequately utilizing stereoscopic space, which are hard to realize through conventional methods, will be of great significance in the future.

In this work, we demonstrate a scalable nanofabrication approach based on nanoskiving to create a series of 1D millimeter-long nanogaps with tunable sub-10 nm gap-widths, and these structures are optimum to relate simulations and experiments to obtain the strongest plasmonic coupling with 5 nm gap-width, enabling a 250 times greater enhancement compared with an individual gold nanowire. We provide a mechanistic explanation to the nonmonotonic electric-field dependence on gap-width. Further, we generated 2D nanogap arrays rapidly by introducing surface patterning techniques. Notably, we successively built novel 3D nanogap arrays that are hard to achieve by conventional nanofabrication via a unique stacking procedure, possessing higher
integration, and much enhanced electric-field driven by adiabatic nanofocusing.

As illustrated in Figure 1a, to build the basic 1D linear nanogaps, gold (90 nm thick)/aluminum (nanometric)/gold (90 nm thick) sandwich films \(^{[13]}\) were successively deposited on a flat epoxy substrate (the small roughness of the films are illustrated in Figure S1, Supporting Information). With sectioning, ultrathin epoxy slabs with the thickness of 150 nm were generated and then transferred onto a silicon wafer bearing a gold mirror. After the removal of aluminum template and epoxy each individual 1D nanogap, consisting of two parallel gold nanowires with sub-10 nm spacing, was formed. The gap-width can be tuned by the thickness of the sacrificial aluminum layer; it is well known that techniques of thin film deposition such as physical/chemical vapor deposition can provide a level of nanometric precision. Here, thermally deposited aluminum was used as a spacer to template the nanogap because aluminum tends to form precise, ultrathin films and its etching process is fast and highly uniform. Moreover, the gap-width can be continuously tuned by controlling the evaporation amount of aluminum. The average yield of the 1D nanogaps could reach up to 70%–80%. In addition, using this method, insulators (e.g., silica, alumina) could also be deposited between gold films without etching to construct metal–insulator–metal (MIM) waveguides.

As the gap-width is one of the crucial parameters that determines the magnitude of the local electromagnetic field,\(^{[14]}\) we first demonstrate that 1D nanogaps with well-controlled gap-widths were successfully fabricated. Figure 2a illustrates the geometric parameters of the final 1D nanogap structure, where the wire width (W) = 90 nm, height (H) = 150 nm, length (L) = 2 mm, and gap-width (G) are varied from 2 to 8 nm (the gap-heights characterized in Figure S2, Supporting Information). The wire width is determined by the thickness of deposited gold. The height is determined by the thickness of every slab programmed on the ultramicrotome, while the length is determined by the rough sectioning process of cutting the film sample into 2–2.5 mm wide stripes, which is limited by the width of the diamond knife (3.0 mm wide in this work). By controlling the deposition thickness of aluminum, the gap-width can be precisely tuned. Figure 2b–f shows scanning electron microscopy (SEM) images of the linear nanogaps with different gap-widths. The gaps can be clearly seen in the SEM images indicating that the aluminum spacers have been etched. Also the gap-widths differ from each other, commensurate with the thickness of the respective aluminum templates, demonstrating that the evaporated aluminum is a suitable spacer material for nanogaps to tune the gap-width with nanometer precision. The intact spans of the 1D nanogaps could be millimetric depending on the width of the diamond knife. Corresponding voltage-current curve of a 5 nm gap behaving as nano-electrodes \(^{[7a]}\) indicates the intactness of the nanogap with no short-out or broken points (Figure S3a, see more details of measurement in the Supporting Information). For smaller gap-width (e.g., 2 or 3 nm), it may be difficult to keep the two nanowires completely separated along their entire length. The wires maintain gaps for several microns, and maybe touch at points.
(more than 90% of the gaps are intact, Figure S3b, Supporting Information).

A gap at sub-10 nm scale provides a strongly coupled plasmonic device, which is an attractive candidate for sensing and imaging. As the gap-widths are precisely tuned, we can systematically investigate the gap-width dependence of the nanogaps. We used finite-difference time-domain (FDTD) simulations to calculate the near-field distribution of the nanogaps with varied gap-width from 2 to 8 nm, while keeping the wire width and height constant (W = 90 nm, H = 150 nm) and all wires residing on a gold mirror (Figure 2b–f). The excitation wavelength was set at 633 nm with the electric field polarized along the x-axis (FDTD simulation with y-polarized light is depicted in Figure S4, Supporting Information, showing nearly no coupling). If two parallel gold nanowires are close enough, a prominent near-field interaction occurs between the nanowires, owing to the strong coupling of the localized surface plasmon resonance (LSPR) supported by each nanowire. From the calculations a 2 nm gap results in a slight field enhancement and localization in the gap, comparable with that induced by the outside edges of the wires (Figure 2b–f). The gap plasmon plays a more important role than that of the corners of the wire, enabling strong confinement of the optical field to the nanometric gap. Notably, while the gap-width increases, the electric-field intensity in the nanogap approaches the maximum compared with nanogaps of other sizes (Figure 2g), at which the surface plasmon polaritons (SPPs) tend to form a strong standing wave (see simulation movie of a 5 nm gap in the Supporting Information). However, the electric-field intensity begins to weaken with the further increase of the gap-width (Figure 2g). The maximum of calculated electric-field intensity also shows a nonmonotonic dependence on gap-width (Figure S5, Supporting Information). In comparison, from the simulation for a single 90 nm wide nanowire (G → ∞) on a gold mirror (Figure S6, Supporting Information), weak electric-field intensity induced just by the outside edges of the wires is observed, which can be regarded as two gold nanowires separated too far to establish plasmonic coupling. The electric-field dependence on gap-height was also simulated, showing very weak sensitivity on plasmonic response compared with the change of gap-width (Figure S7, Supporting Information).

We acquired SERS spectra on the 1D nanogaps with different gap-widths to experimentally investigate the signal enhancements. A schematic diagram of this SERS workbench principle for a 1D nanogap is illustrated in Figure 3a. The nonresonant molecule p-aminothiophenol (PATP) was used as the analyte due to its capability of forming a self-assembled monolayer on gold surfaces. Figure 3b shows SERS spectra in the range of 800–1800 cm⁻¹ for a self-assembled monolayer of PATP molecules, which were deposited on the 1D nanogap structures with different gap-widths and a single gold nanowire (W = 90 nm, H = 150 nm, L ≈ 2 mm) by means of chemisorption. The incident laser was nonpolarized with 633 nm wavelength. Distinct features of PATP are clearly identifiable as strong bands center at 1077 and 1590 cm⁻¹ and many other low-intensity bands can be observed in the spectra (see detailed Raman spectra in Figure S8, Supporting Information).

We used the SERS intensities of the C–S stretch at 1077 cm⁻¹ to illustrate the impact of the gap-width on the enhancement of
As the gap-width increases from 2 to 5 nm, the SERS intensity increases sharply and reaches its maximum at a 5 nm gap-width. However, if the gap continues enlarging, the SERS intensity begins to drop. The maximum intensity of the signal originating from PATP, obtained with the 5 nm nanogap (as the blue line plotted in Figure 3b), is 250 times greater compared with that obtained with the single gold nanowire 90 nm wide (Figure 3d) under the same test conditions. As a reference, compared with the nanogap structures, the Raman spectrum recorded on the sandwich nanowires without removal of aluminum spacer shows a weak Raman signal similar to that of the single gold nanowire (Figure S9, Supporting Information), indicating the necessity of the gap in generating strong plasmonic coupling. The reference Raman spectrum recorded from PATP on a flat gold film is shown in Figure S9 of the Supporting Information, with a weak signal of the Raman bands at 1077 and 1590 cm\(^{-1}\), only slightly above the noise level. These experimental results are highly consistent with the simulations. Precise control over all dimensions, particularly by tuning the gap-width, allows us to obtain superb near-field generation. From these observations, we conclude that the nanometric gap between two spaced gold nanowires is the dominant cause of the strong enhancement of the Raman signal; gold cuboid nanowire only yields a weak enhancement resulting from the outside edges. Interestingly, among the sub-10 nm gap-widths, the enhancement reaches the maximum at the 5 nm gap-width due to the formation of a strong standing wave of SPPs, in accord with simulations and experiments.

Unlike conventional nanogaps which are usually "flat", having a short gap-height, our nanogaps are relatively "tall" and uniform with a tunable height-to-width ratio (H/W) of more than 18. Thus, the propagation of SPP waves along the long-narrow gaps cannot be ignored. To confirm the nonmonotonic electric-field dependence on gap-width, we investigated the formation of a strong standing wave produced by the 5 nm gaps, which reduces the loss of waves and enhances the plasmonic coupling. This standing wave is formed by the resonance of the SPP waves generated by the two closed edges of the gold nanowires and the SPPs reflected by the gold mirror on the substrate. The standing wave cannot form if the gap resides directly on the silicon substrate without a gold mirror due to lack of a strong reflected waves (Figure S10, Supporting Information). The first requirement for forming a standing wave is two sufficiently strong waves with the same wavelength and speed, but opposite directions. The second requirement is that the wave path (the gap-height, H = 150 nm here) fits the equation

$$H = n \frac{\lambda}{2} \quad n \in N$$  

(1)

When 633 nm light impinges on a nanogap, a strong SPR is excited. This generates SPPs propagating along the long-narrow gaps with much smaller wavelengths than the excitation wavelength.\(^{[15]}\) The decreased wavelength may satisfy the equation above for the gap-height (H = 150 nm). Smaller gap-widths contribute to stronger coupling,\(^{[5c]}\) while large gap-widths which lead to weak coupling may also result to a weak resonance with the reflected SPPs and low field enhancement in the gap. However, for much smaller gap-widths, even though it can excite a stronger coupling, a significant amount of light is reflected by the upper surface of the two gold nanowires. Thus, the amount of light that can interact with the two closed edges of gold is insufficient to excite strong SPP waves. The SPPs that can reach the gold mirror is then too little to form a standing wave. This relationship explains why neither a smaller gap nor a larger gap can form effective standing waves, why the maximum is obtained with a 5 nm gap-width and enables a mechanistic study of the electric-field dependence on gap-width for the high-ratio nanogaps.

Based on the individual 1D nanogap, in order to integrate nanogap devices with required geometries over a large area,
we introduce a surface patterning technique to produce 2D patterned nanogap arrays in the horizontal plane. We invoke standard photolithography as an example because of its low cost and universality. As illustrated in Figure 1b, the patterned epoxy substrate was replicated from a photoresist template via soft lithography (schematic in Figure S11, Supporting Information). We successively deposited gold/aluminum/gold at a glancing angle on the unilateral sides of the shaped epoxy replica and then embedded the entire structure in more epoxy for sectioning. Due to the low adhesion between gold and the epoxy substrate, they tended to separate by the shear force during sectioning. However, we used angular deposition to fabricate discrete “L” shaped sandwich films, so that the epoxy on both sides of the films can interconnect and thus weakened the effect of the shear force caused by the diamond knife during sectioning. The epoxy block was sectioned parallel to the substrate into 150 nm thick slabs containing arrays of gold/aluminum/gold sandwich nanowires. The slabs were transferred onto a silicon wafer bearing a gold mirror. After removal of aluminum and epoxy, a 2D linear nanogap array was constructed (Figure 1b) with a higher level of integration than that of a single nanogap. The average yield of the 2D nanogap array was about 50%–60%. Using this method, different lithographic masks will provide a wide variety of design freedom for making 2D patterned plasmonic and electric devices with required geometries over a large area. The packing density of the 2D nanogap array is increased along the horizontal direction compared with 1D linear nanogap. In general, a closer array leads to a larger hot spot density and a higher throughput. In practice, the resolution of conventional lithography techniques limits the period of stripes. Therefore, it remains a challenge to integrate more nanogaps on the same area with a higher throughput and improve their electric-field enhancement without resorting to costly direct-writing techniques.

To address this challenge, we explored the construction of 3D nanogaps along the vertical direction analogous to multi-story construction, which is difficult for conventional nanogaps made by planar lithography. Likewise, nanoskiving is a process that usually focuses on the 1D or 2D nanostructures contained in one individual slab,[12] thus it might constrain the fabrication of 3D nanostructures. Nevertheless, different from most nanofabrication strategies, which usually yield a fixed structure on a substrate, the sectioned slabs are quasi-copies with free-standing and transferrable properties, thus we can position a second slab onto the original one using a “Perfect Loop” tool (Electron Microscope Sciences) to guide the second nanogap array over the first nanogap array in desired orientation and position as illustrated in Figure 1c. The alignment of the two nanogap-arrays varying with the stacking angle (\(\alpha\)) defines the shape of the nanogrids. After removal of the sacrificial spacer and epoxy, 3D packed nanogap grids were constructed (illustrated in Figure 1c). For the 3D nanogap arrays, the average yield was about 40%–50% based on the yield of the 2D nanogap arrays. In this way, we are able to pack more nanogaps on the same area by occupying the vertical space, only requiring a simple stacking process with no special infrastructure. Moreover, the linear nanogaps in the 3D structures are able to interlock with each other into a highly stable 3D woodpile configuration in comparison with loosely packed 2D structures assembled by metallic nanoparticles.[16] To our knowledge this is the first report on the stacking of nanogap arrays along the vertical direction. In the 2D nanogap array (Figure 4a) the gap density is largely increased, but the electric-field intensity remains unchanged compared with the 1D nanogap, because the individual nanogaps are too far from each other to couple. Nevertheless, in the 3D nanogap grids, two types of hotspots were acquired.

![Figure 4.](https://www.advmat.de/)

**Figure 4.** a) SEM images of a linear nanogap array. b,c) SEM images of a nanogap grid array with different stacking angles. Scale bar: 20 µm. Insets show magnified images. Scale bar: 100 nm. d) SERS spectra obtained from the linear gap and the crossing point of (b) and (c).
One is the linear gap as mentioned above; the other is the “two-story” gap at the crossing point where upper and lower linear nanogaps are stacked angularly. Manipulating the position of the second slab generates differently shaped nanogap grids, such as a square grid and a diamond grid (Figure 4b,c). To explore the electric-field enhancements in these unconventional plasmonic structures, SERS measurements were performed on linear nanogaps and crossing points of the nanogrids with different $\alpha$ (Figure 4d). The black dotted line shows the Raman spectra of PATP taken from the linear gap in the nanogap grid, and the intensity from the crossing point of $\alpha = 90^\circ$ shown by the black solid line is a factor of 2.5 greater than that from the linear gaps (C–S stretch at 1077 cm$^{-1}$ was used for comparison). Notably, the crossing point of $\alpha = 45^\circ$ generates a signal, plotted by the red line, stronger by a factor of 4.5 compared with that from the linear gaps. This observation suggests that 3D packed nanogap grids not only enlarge the gap density by extending into the vertical space, but also improve the electric-field intensity, which may originate from a strong and intense localized electromagnetic field (hot spots) at the crossing point. To a certain extent, smaller angle crossing points may generate the stronger electric-field enhancement according to the corresponding SERS measurements.

The 3D nanogaps are composed of two 1D nanogaps with different $\alpha$, which may range from 0$^\circ$ to 90$^\circ$. Without consideration of the interaction of the two gaps, under nonpolarized light (whose beam spot is 1 µm, which is much larger than the crossing point region, corresponding sketch in Figure S12, Supporting Information), the total Raman intensity ($I_{3D}$) at the crossing point region is approximately the sum of either gap intensity ($I_{1D}$) because of the doubled coupling region, which remains unchanged no matter what the stacking angle is ($I_{1D} = 2I_{1D}$). However, according to the corresponding SERS experiments, the crossing points in the 3D orthogonal nanogaps generated a more enhanced signal, $I_{3D,90^\circ} = 2.5I_{1D}$; the crossing point of $\alpha = 45^\circ$ generates a much stronger signal, $I_{3D,45^\circ} = 4.5I_{1D}$. The additional enhancement should be attributed to the interaction of the two linear gaps as

$$I_{3D,90^\circ} = 2.5I_{1D} - 2I_{1D} = 0.5I_{1D}$$
$$I_{3D,45^\circ} = 4.5I_{1D} - 2I_{1D} = 2.5I_{1D}$$

(2)

FDTD simulations were performed upon the differently angled 3D nanogaps (Figure 5a–c). The excitation wavelength was set at 633 nm with the electric field polarized along the x-axis (same with the simulations for the 1D nanogaps). The strongest electric-field enhancement happens at the outside corners of the crossing points; the lower nanogap residing on the gold mirror also generates a strong electric-field enhancement which is weaker than the corners but much stronger than the corresponding 1D gap. However, the upper nanogap performs really slight electric-field enhancement. For the orthogonal 3D gaps, the local highest electric-field intensity is approximately 700; the local highest electric-field

![Figure 5. a–c) FDTD simulations of the electric-field distribution in the 3D stacked nanogaps with different $\alpha$. d) FDTD simulation of two 30$^\circ$-stacked nanowires with doubled wire-width but no inset gaps. The scale represents the normalized electric-field intensity.](image-url)
item intensity for 45° case reaches up to 6000, comparing with the local highest electric-field intensity for the corresponding 1D nanogaps of nearly 400. These comparisons could corroborate the experimental data interpretation. Moreover, when \( \alpha \) decreased to 30°, the electric field enhances extremely sharply with a local highest electric-field intensity of approximately 20 000, indicating that decreasing the intersection angle will tremendously enhance the electric field at the crossing points. The huge field enhancement could be attributed to the adiabatic nanofocusing caused by the SPP propagation toward the tapered tip (acute-angled region of the crossing point).\(^{[17]}\) This propagation causes accumulation of the SPP energy at the tip and giant increase of the local fields. Sharper tips generate stronger accumulation of the energy, thus smaller \( \alpha \) contributes to stronger electric field. As a reference, a simulation for two 30°-stacked nanowires with doubled wire-width but no inset gaps shows a strong field enhancement at the acute corners of the crossing point with a local highest electric-field intensity of about 2000, which is still much weaker than the homological ones with nanogaps inset. We infer that the presences of nanogaps and the smaller \( \alpha \) are both vital to the huge field enhancement. The sub-10 nm gaps provide strong SPPs which could propagate toward the sharp tip to accumulate energy and enormously enhance the local field. When \( \alpha \) is definitely 0°, which means the upper and lower nanogaps completely overlapped (i.e., a 1D nanogap with doubled-height), the sharp tip disappears and SPPs could not accumulate, lowering the electric field to a common level (Figure S13, Supporting Information).

In summary, we have utilized nanoskiving to produce 1D, 2D, and 3D plasmonic gaps with tunable, sub-10 nm gap-widths. These gap-widths can be controlled with nanometer precision via the thickness of sacrificial spacer films. As the hot spots of each nanogap extend uniformly along macroscopic lengths, our nanogaps are robust to local defects or contaminants, facilitating more reproducible SERS spectroscopy. This enables a systematic investigation of the dependence of electric-field enhancement on gap-width, with the surprising result that it is nonmonotonic in the range between 2 and 8 nm with a maximum at 5 nm, which we attribute to the formation of a strong standing wave. In agreement with FDTD simulations, the maximum SERS signal is obtained for this gap width. The surface patterning technique could be extended to fabricate a 2D patterned nanogap array on a horizontal plane with a higher integration. Furthermore, we stacked nanogaps along the vertical direction, and 3D nanogap grids were easily constructed. The construction of 3D nanogap grids not only enlarges the gap density, but also improves the electric-field intensity at the crossing points. For a smaller stacking angle, the electric field is tremendously enhanced, which result from the adiabatic nanofocusing caused by the SPP propagation toward the crossing tip. Such structures will facilitate the control of plasmonic interactions and contribute to applications in nano-optics as well as nanoelectronics.\(^{[18]}\) We also expect that the 3D nanogap arrays based on nanoskiving and stacking of nanogaps along the vertical direction will broaden the scope of fabricating 3D complex nanostructures in a simple and efficient way and improve our understanding of local electric fields.

**Experimental Section**

**Fabrication of Tunable 1D Nanogaps:** A flat epoxy substrate was cured from the template of monocrystalline silicon. Successive deposition of Au/Al/Au films on the substrate was performed in a commercial thermal evaporation system (KYKY Technology Development Co.). The deposition for nanometric aluminum was basically the same as gold. The epoxy substrate bearing sandwich films were cut into a jeweler’s saw (into \( \approx 2 \times 10 \text{ mm}^2 \) pieces) and placed into separate wells in a polyethylene microtome mold (Electron Microscopy Sciences), which was then filled with epoxy prepolymer, and cured. The epoxy blocks were mounted in the sample chuck of the ultramicrometer (Leica EM UC 7) and cut to define an area of \( \approx 4 \text{ mm}^2 \) around the embedded structure with a razor blade. The blocks were sectioned at a speed of 0.8 mm s\(^{-1}\) with a set thickness of 150 nm. After skiving, the slabs were collected by a silicon wafer (0.5 \( \times \) 0.5 \( \text{ mm}^2 \), bearing a gold mirror) beneath the slabs. After removal of sandwiched aluminum by immersion in hydrochloric acid (2 mol L\(^{-1}\), with some ethanol added), the thin epoxy film was etched by slight oxygen reactive ion etching (RIE). An inductively coupled plasma (ICP) power (200 W) was applied for 2 min, which was performed with a Plasmalab Oxford 80 plus system (Oxford Instrument Co.). After these procedures, the 1D nanogap was formed.

**Fabrication of 2D and 3D Nanogap Arrays:** For a 2D nanogap array: successive deposition of Au/Al/Au was performed at a glancing angle on the unilateral sides of the shaped epoxy replica. The shaped substrate bearing disconnected sandwich films was cut into \( \approx 2 \times 2 \text{ mm}^2 \) pieces. These pieces were embedded in more epoxy according to the previous method to make the metal structure parallel to the epoxy substrate.\(^{[16]}\) Parallel sectioning to the substrate using an ultramicrometer generated 150 nm thick slabs. After removal of Al and epoxy, 2D nanogap arrays were obtained. For a 3D nanogap array: Based on the 2D nanogap arrays another slab was collected by surface tension in a loop tool and placed angularly on the first one with a hair-clip. After removal of Al and epoxy, a 3D nanogap array was obtained.

**Finite-Difference Time-Domain Simulations:** A commercial software package (FDTD Solutions v8.12.590, Lumerical Solutions Inc.) was used to perform simulations of electromagnetic fields with the same structural dimensions as extracted from the actual fabricated gap samples. The structure was excited by a normally incident, unit magnitude total-field scattered-field propagating in the \( z \) direction with an electric-field polarization along the \( x \)-axis. Monitors were placed to calculate the distributions of 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 handbook.

**Characterization:** SEM images were taken with a Nova Nano (FEI) scanning electron microscope (SEM) 450 field emission scanning electron microscope with primary electron energy of 15 kV. In the Raman spectroscopy analysis, we used a solution of PATP (Sigma-Aldrich), with 97% purity diluted to 1 \( \times \) 10\(^{-3}\) M in ethanol. The nanogap samples 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 with 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 \( \mu \)m beam spot was used to measure the SERS spectra. The exposure time was set to 15 s.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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