

# Plasmonic Silver Nanowire Structures for Two-Dimensional Multiple-Digit Molecular Data Storage Application

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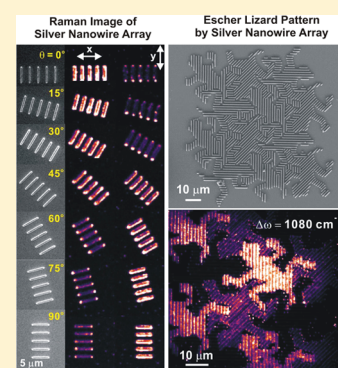
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## S Supporting Information

**ABSTRACT:** The surface-enhanced Raman scattering (SERS) spectrum exhibits huge potential as an alternative data storage element. Using plasmonic nanostructures as the physical building blocks where probe molecules are adsorbed, their corresponding structural and SERS information are stored within a finite volume of plasmonic nanostructures. However, the current SERS development is hampered by the difficulty in fabricating quantitative and homogeneous SERS platforms. Here, we introduce the concept of “plasmonic molecular data storage” using SERS intensity as the basic data storage element (or digit). SERS signal is quantitatively tunable by manipulating the orientation (hence the localized surface plasmon modes) of the respective nanowire nanostructures to achieve multiple-digit SERS intensity data storage. We address the reproducibility problem by fabricating homogeneous plasmonic nanowire structures using two-photon lithography and thermal evaporation. Silver (Ag) nanowires of different orientations carrying different digits of molecular information can be combined to form sophisticated 2D geometrical structures, such as geometrical patterns, letters in the alphabet, and complex tessellated reptiles to impart multiple-digit-per-microstructure data storage. In particular, a 7-digit SERS information storage system has been achieved by tuning the Ag nanowires' orientation from 0° to 90° at 15° intervals. Spatial data, especially the coordinates and topology, brought about by the predefined Ag nanowire structures create an additional level of information to the plasmonic data storage system. Using 1 byte (8 binary digits) as the basis of comparison, our 7-digit platform is able to store 22 500-fold denser information than the binary system. In addition, our plasmonic nanowire data storage system also provides unique physical morphology and chemical Raman information. It is analogous to optical data storage, but it acquires richer multidimensional information and exhibits higher spectral resolution than the broader-band response of conventional optical spectroscopic techniques.

**KEYWORDS:** polarization-dependent surface-enhanced Raman spectroscopy (SERS), gray-scale Raman image, silver nanowire, multiple-digit molecular data storage



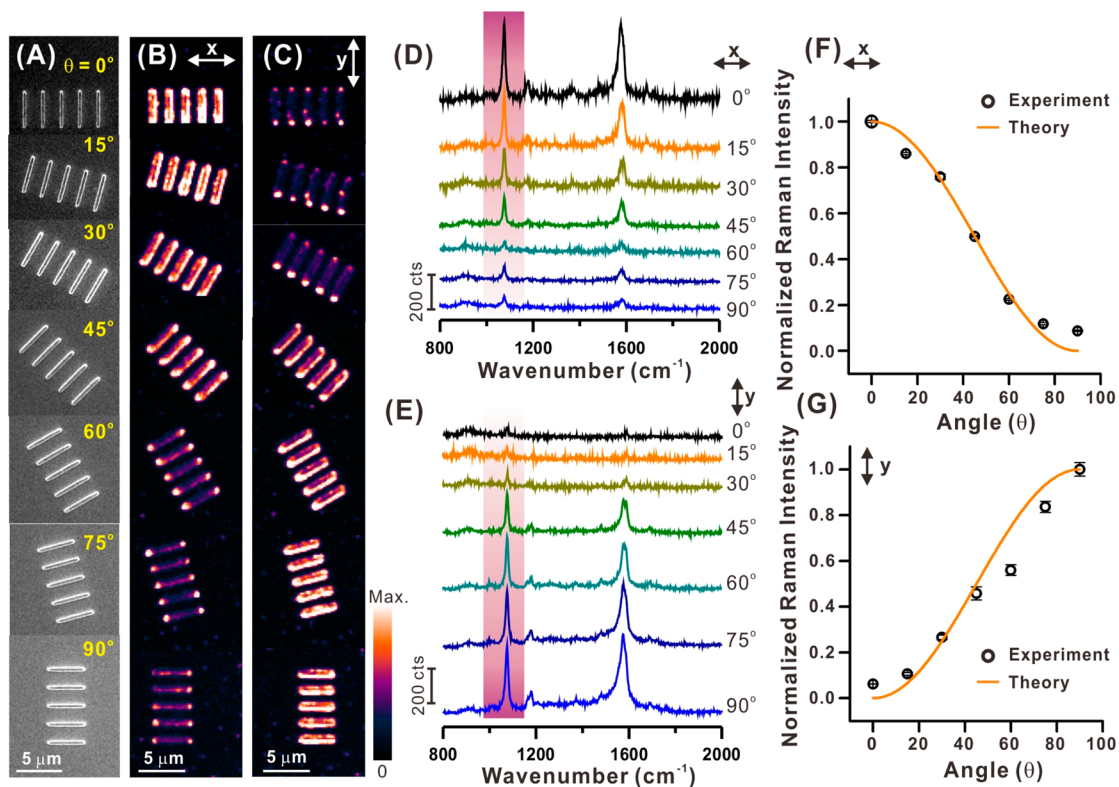
Surface-enhanced Raman scattering (SERS) platforms made from noble metallic nanoparticles and/or nanostructures, such as self-assembled Ag/Au nanoparticles, nanoprism-over-mirror structures, enhance the Raman scattering signal of probe molecules in their close proximity by orders of magnitude owing to the localized surface plasmon resonances (LSPRs) from the metallic nanostructures.<sup>1–7</sup> The molecular spectra in SERS are highly specific to the probe molecules, with spectral bandwidth much narrower than most optical-based systems. Such a molecular vibration spectrum in SERS can be used as the data storage element that is analogous to conventional optical data storage systems. While conventional data storage systems use the change in physical or optical properties, such as electric charge, or magnetism of the data storage materials to store information,<sup>8–11</sup> the same principle can be applied to plasmonic data storage.<sup>12–17</sup> Raman scattering from molecules coated on plasmonic structures can function as an alternative data storage element that provides both structural and chemical composition information stored within a finite volume of

plasmonic nanostructures. However, unlike conventional data storage based on the binary system with only two possible data input/output, SERS has the potential to create multiple-digit storage systems.

To obtain a multiple-digit molecular information storage system with large information capacity, a gradient of SERS signal intensity that gives rise to different digits of information is a prerequisite. Theoretically, SERS signals can be tuned quantitatively by manipulating the LSPR mode of the respective nanostructures to achieve multiple-digit SERS intensity. However, difficulties in fabricating a SERS platform with quantitative and homogeneous SERS response over large areas have hindered the development of SERS platforms for data storage. Thus far, most of the SERS studies are still limited to the fabrication of hot spots at localized junctions or gaps

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**Figure 1.** (A) SEM images; (B, C) *x*- and *y*-polarized 2D SERS images of Ag nanowires at orientation angles of  $\theta = 0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ,$  and  $90^\circ$ . (D, E) Respective *x*- and *y*-polarized SERS spectra collected from Ag nanowires with orientation angles in the range  $\theta = 0-90^\circ$ . (F, G) Plots of simulated and normalized experimental SERS intensity versus Ag nanowire orientation angle when polarized in the *x*- and *y*-directions, respectively. All scale bars are 5  $\mu\text{m}$ .

between nanostructures to increase SERS intensity at these highly localized regions.<sup>18–22</sup> The signal distribution of such a SERS substrate is generally heterogeneous; that is, the number of SERS hot spots is relatively small, but these small numbers of hot spots dominate the overall SERS signal.<sup>23</sup> Hence, SERS platforms that yield quantitative and homogeneous intensity and reasonable SERS enhancement factors are highly desirable for developing plasmonic molecular information data storage systems. In particular, careful control over the nanostructure fabrication to generate a homogeneous SERS response in a predictable way over a large area is essential.

Recently, our group reported plasmonic nanowire structures that are embedded with binary chemical SERS images. By tuning the polarization of the incident light along the *x*- or *y*-direction, we can selectively excite the LSPR modes of metallic nanowires, therefore giving rise to “bright” and “dark” SERS signals.<sup>24</sup> Such a binary SERS response is still rudimentary when compared with multiple-digit optical data storage systems.<sup>13,25,26</sup> Hence, a quantitative SERS intensity must be developed to achieve a multiple-digit SERS response.

Here we demonstrate multiple-digit 2D “plasmonic molecular information storage” using a highly tunable gradient of SERS intensities obtained in nanowire structures as the basic data storage element (or digit). We exploit the directional light–matter interaction between the plasmonic nanowire’s structural orientations with respect to incident light to achieve a dynamic range of gray-scale SERS intensities. Predesigned Ag nanowire structures with different orientations are fabricated by combining two-photon lithography and metal evaporation and are homogeneously functionalized with probe molecules (4-methylbenzenethiol, 4-MBT) prior to SERS imaging. We will

first demonstrate that the SERS intensity of a single Ag nanowire can be tuned by the orientation of the nanowire along *x*- or *y*-polarization. Although Ag nanowires are homogeneously coated with probe molecules, different digits (or shades) of SERS intensity can be generated by tuning the nanowires’ structural orientation with respect to the incident light. Using more complicated two-dimensional Ag nanowire structures, we will demonstrate that multiple digits of SERS information can be stored within a microstructure with precise control over spatial and spectral resolution as well as the resulting SERS intensity. Our plasmonic nanowire system possesses distinct physical morphology and chemical Raman information with narrow spatial and spectral resolution. Such plasmonic molecular data storage is analogous to optical data storage, but it acquires richer multidimensional information and exhibits higher spectral resolution than the broad-band response from other optical spectroscopic techniques.

We first explore the potential of using the SERS spectrum as a data storage element. Ag nanowires function as the physical building blocks, where probe molecules are adsorbed and their corresponding SERS signals are stored and read out in a 2D *x*–*y* SERS image. The concept of such plasmonic data storage is based on exploiting the unique polarization-dependent and directional interactions of plasmonic nanowires with incident light,<sup>24,27</sup> to quantitatively manipulate the SERS response over a defined range of intensity. The resulting gray-scale SERS intensity represents “digits” of molecular SERS information. This read-out from a 2D SERS image provides both morphological information and multiple shades of gray-scale SERS intensities within a finite volume, thus giving rise to a

multidimensional and quantitative plasmonic data storage system.

We design and fabricate Ag nanowires with different orientation angles with respect to the vertical axis ( $\theta$ ), where  $\theta = 0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ$ , and  $90^\circ$  (Figure 1A). Plasmonic Ag nanowires are tailor-made using two-photon lithography followed by Ag deposition, as described previously.<sup>24</sup> In brief, polymeric nanowires of 500 nm in diameter and 4  $\mu\text{m}$  in length are first fabricated using two-photon polymerization. A piezo-stage with  $x$ -,  $y$ -, and  $z$ -axis manipulation is used to obtain the resulting nanostructures. A uniform layer of a 150 nm Ag film is subsequently thermally evaporated over the substrate, on both the polymeric nanowires and the flat areas. Only the areas with nanowire structures are endowed plasmonic behaviors and show SERS activity (Figure 1B, C; see Figure S1 for a discussion on the plasmonic behavior of Ag nanowires). The relatively smooth Ag film with no distinct features does not give rise to strong enhancement in local electromagnetic fields to generate significant SERS signals.<sup>24</sup>

The 2D SERS image is read out using 2D  $x$ - $y$  SERS mapping of the Ag nanowire structures. 4-MBT is used as our probe molecules, as a strong Ag-S coordination bond is expected to form a well-packed homogeneous self-assembled monolayer of probe molecules on the Ag nanowire.<sup>28</sup> In addition, 4-MBT molecules are more photostable in prolonged measurements compared to most fluorescent dyes. As 4-MBT yields strong SERS signals at 1080 and 1584  $\text{cm}^{-1}$  (Figure 1D),<sup>24</sup> we use the SERS intensity at the 1080  $\text{cm}^{-1}$  peak as the reference peak ("digit") to construct SERS molecular images for the rest of this article.

The 2D SERS image collected at  $x$ -polarization and the respective Raman spectra of Ag nanowire arrays at various orientation angles are demonstrated in Figure 1B and D, respectively. The SERS image of 4-MBT molecules gradually changes from the brightest to very dim when the orientation of the Ag nanowires is systematically tuned from  $\theta = 0^\circ$  to  $\theta = 90^\circ$ . This indicates a progressive reduction in SERS intensity from its maximum ( $I_{\text{max}}$ ) to near zero (Figure 1D,F). By normalizing the SERS intensity against  $I_{\text{max}}$ , a gradient of discrete SERS values of 1.00, 0.84, 0.73, 0.45, 0.15, 0.04, and 0.00 are obtained when the orientation of the Ag nanowires is aligned at  $0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ$ , and  $90^\circ$  with respect to the vertical axis, respectively. This is a presentation of 7 digits of SERS information by tuning the Ag nanowires' orientation. The plot of normalized Raman intensity against the nanowires' orientation angle ( $\theta$ ) demonstrates a good fit to a  $\cos^2 \theta$  function (Figure 1F). The SERS signal tunability is manipulated by directional coupling of Ag nanowires with incident light. At  $x$ -polarization, the transverse LSPR modes of the vertical nanowires are coupled to the incident light, resulting in strong electromagnetic fields and SERS intensities at the edges of the nanostructures. However, with an increase in the nanowire's orientation angle, the LSPR's strength that is coupled to the incident light decreases (in relationship to  $\cos^2 \theta$ ) correspondingly, therefore reducing the SERS intensity. At  $90^\circ$ , there is negligible coupling between incident light and the longitudinal mode of the Ag nanowires owing to the momentum mismatch between the incident photon and the propagating plasmons. Consequently, this leads to the weakest SERS intensity observed at  $90^\circ$ . It is also noted that, owing to the highly reproducible and precise fabrication method used, these Ag nanowires exhibit quantitative and uniform SERS intensities. Such quantitative regulation of SERS intensities with

respect to Ag nanowires' orientation can be potentially useful for storing multiple-digit molecular information in nanostructures.

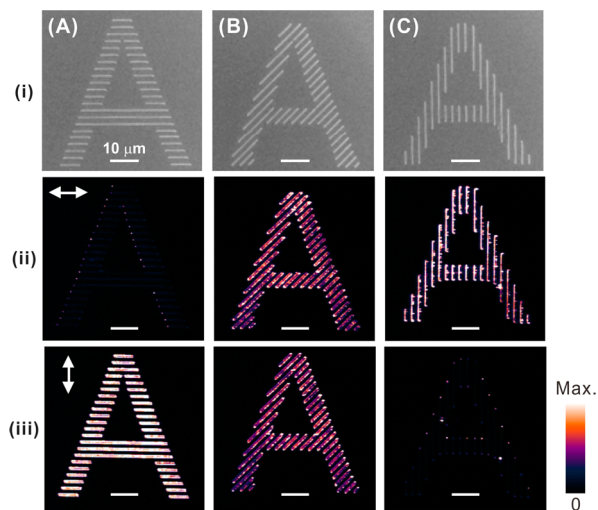
In addition, when the polarization of the incident laser is tuned to  $y$ -polarization, the trend of SERS intensity with respect to nanowire orientation is reversed (Figure 1C,E). Normalized SERS values of 0.00, 0.05, 0.22, 0.42, 0.53, 0.82, and 1.00 are obtained when the orientation of the Ag nanowires is aligned at  $0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ$ , and  $90^\circ$  with respect to the vertical axis, respectively (Figure 1G). A  $\sin^2 \theta$  relationship is observed for the plot of normalized SERS intensity and the nanowires' orientation angle.

The experimentally observed dependence of the SERS signal on the orientation of the plasmonic nanowire long axis with respect to the incident electric field corroborates well both with earlier experimental observations and with the fundamental theory of SERS. SERS intensity is generally attributable to  $I_{\text{SERS}} \propto |E(\omega)/E_0(\omega)|^2 |E(\omega_s)/E_0(\omega_s)|^2$ , where  $E(\omega)$  and  $E(\omega_s)$  are the enhanced local fields at the excitation and scattering frequencies respectively, and  $E_0$  is the incident field.<sup>29,30</sup> The first term of the SERS intensity approximation is primarily associated with the excitation process and is due to the local electromagnetic (EM) field enhancement arising from the incident light. Since the first term discusses the effect of incident light on SERS intensity, the local electric field is more accurately described as  $E(\omega, \theta) = E(\omega) \cos(\theta)$  for  $x$ -polarization, and  $E(\omega, \theta) = E(\omega) \sin(\theta)$  for  $y$ -polarization, respectively. This is because the incident light can be unpolarized or polarized with half-wave plates. The second term is related to the emission process at the Raman scattering frequency and factors in the Raman emission enhancement caused by the antenna of the metal nanostructures as well as other molecular parameters of the probe molecule. The Raman scattering is taken to be isotropic, as it is a complicated process to model, and this gives rise to a polarization-independent  $E(\omega_s)$ .<sup>30</sup> Therefore, we anticipate the SERS intensity to follow a  $\cos^2 \theta$  and  $\sin^2 \theta$  relationship as we change the orientation of the nanostructure at  $x$ - and  $y$ -polarizations, respectively. For example, at polarization angle  $\theta = 0^\circ$  (Figure 1F), the SERS intensity when incident light is polarized at the  $x$ -axis is  $I_{\theta=0^\circ} = I_x \cos^2(0^\circ) = I_x$ , which is the maximum SERS intensity at  $x$ -polarization, whereas at  $\theta = 30^\circ$ ,  $I_{\theta=30^\circ} = I_x \cos^2(30^\circ) = 0.74I_x$ . Conversely, when incident light is polarized at the  $y$ -axis, the SERS intensity follows  $I_{\theta=0^\circ} = I_y \sin^2(\theta)$ .

The polarization dependence of the SERS intensity from the Ag nanowires gives rise to a dynamic gradient of normalized SERS intensities, ranging from "1" to "0" at both polarization angles (theoretical predictions are shown in orange curve in Figure 1F,G). The experimental results are in good agreement with the theoretical  $\cos^2 \theta$  and  $\sin^2 \theta$  relationship (Figure 1F,G, orange curve). The results highlight that, despite having similar physical morphology and being homogeneously coated with a monolayer of probe molecules, Ag nanowires of different orientations exhibit different defined "digits" of SERS intensities that are dependent on their orientation angle and polarization of the incident light. Hence, a SERS molecular image with a total of seven shades of SERS intensities can be obtained simply by exploiting their polarization-dependent SERS responses. In general, units with  $N$  well-defined states can provide up to  $N^P$  combinations in a sequence of  $P$  digits. For an 8-digit (1 byte) code in the binary system, the total possible combinations are 256 ( $2^8$ ). In contrast, for an 8-digit code in our 7-digit system, the total possible combinations are 5 764

801 ( $7^8$ ). This translates to nearly 22 500-fold denser information storage capability for just 8 digits (1 byte) for our system ( $2^8$  vs  $7^8$ ). A comparison with the conventional bit (binary digit) system having two defined states per digit also highlights that our system can carry 3.5-fold denser information per digit with seven defined states.

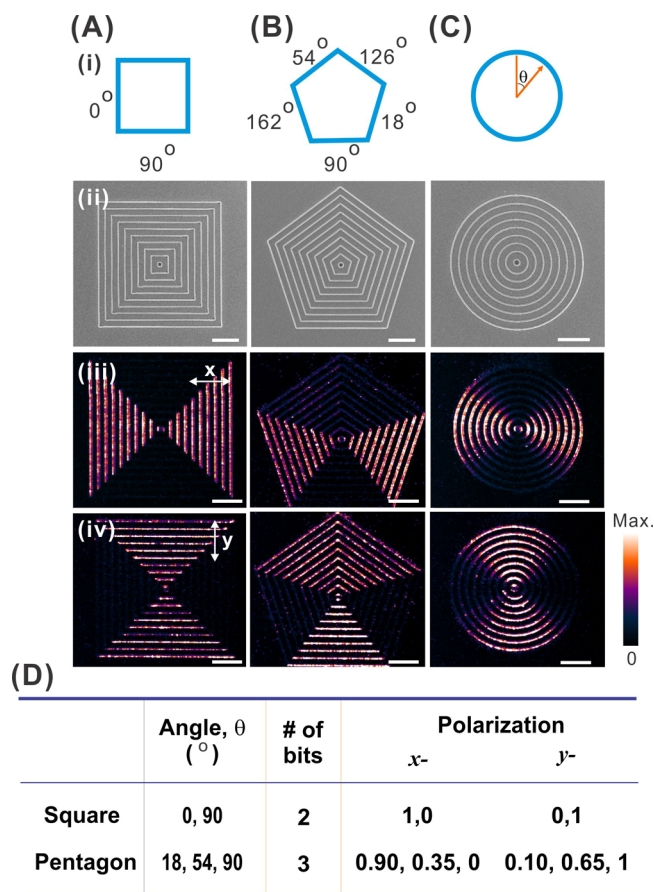
In the following section, plasmonic microstructures with similar macroscopic appearance are fabricated and stored with different digits of SERS information. We design and fabricate three letter “A” structures formed entirely by horizontal nanowires ( $\theta = 0^\circ$ ), nanowires oriented at  $45^\circ$ , and vertical nanowires ( $\theta = 90^\circ$ ), respectively. The SEM images (Figure 2A–C, (i)) reveal that these A’s have a similar physical



**Figure 2.** (i) SEM image of the alphabets “A” fabricated entirely by (A) horizontal nanowires, (B) nanowires oriented at  $45^\circ$ , and (C) vertical nanowires. (ii)  $x$ -polarized 2D SERS images of the respective letter “A”s. (iii)  $y$ -polarized 2D SERS images of the respective letter “A”s. All scale bars are  $10\ \mu\text{m}$ .

appearance. However, their respective  $x$ -polarized SERS images are totally different. Three shades of SERS images, in black, gray, and white, are obtained. The quantitative intensity of the SERS images demonstrates that 0,  $0.5I_{\text{max}}$ , and  $I_{\text{max}}$  corresponding to three digits of SERS information per  $x$ -polarization, are stored by manipulating the orientation of our Ag nanowires to  $0^\circ$ ,  $45^\circ$ , and  $90^\circ$ , respectively (Figure 2 (ii)). However, the molecular information is reversed when  $y$ -polarized SERS imaging is performed, corresponding to  $I_{\text{max}}$ ,  $0.5I_{\text{max}}$  and 0 digits of SERS information at  $0^\circ$ ,  $45^\circ$ , and  $90^\circ$  (Figure 2 (iii)). This is a demonstration of storing 6 distinct digits of SERS information within a microstructure by combining the  $x$ - and  $y$ -polarized data, where the molecular intensity information is manipulated by the orientation of our Ag nanowires and/or the polarization of the SERS imaging process.

Ag nanowires of various orientations carrying different digits of molecular intensity information can be combined to form sophisticated 2D geometrical structures to impart multiple-digits-per-microstructure data storage. The spatial data, especially the coordinates and topology, brought about by the predefined Ag nanowire structures create an additional level of information to the plasmonic data storage system. The as-fabricated Ag nanostructured squares, pentagons, and rings are demonstrated in the SEM images in Figure 3(ii) (information

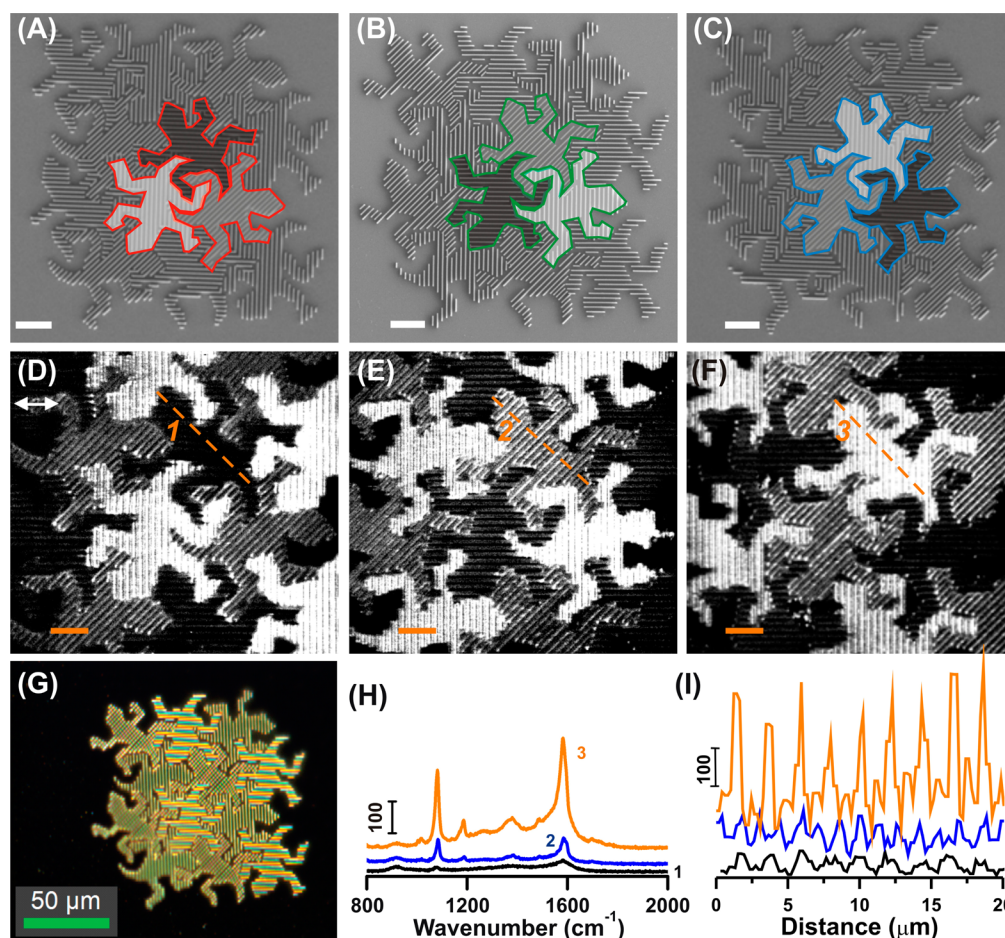


**Figure 3.** (i) Schematics of Ag nanowires oriented at different angles to form concentric structures of (A) squares, (B) pentagons, and (C) rings. The respective orientation angles ( $\theta$ ) of the Ag nanowires are indicated in the respective schemes. (ii) SEM images; (iii, iv)  $x$ - and  $y$ -polarized 2D SERS images of concentric structures. All scale bars are  $10\ \mu\text{m}$ . (D) Table of the nanowires with different orientation angles decomposed into squares and pentagons, the represented multiple digits per structure, and the theoretical quantitative SERS intensity.

on triangles, hexagons, and octagons is available in Supporting Information Figure S2). Such complicated nanostructures can be easily fabricated using two-photon lithography but is challenging using nanoparticle wet chemical synthesis and assembly techniques. Note that the width and the periodicity of the nanowires are intentionally set at  $\sim 500\ \text{nm}$  and  $\sim 2\ \mu\text{m}$  to minimize plasmonic coupling between nanowires.

The 2D SERS images of square, pentagonal, and ring structures collected at  $x$ - and  $y$ -polarization are shown in Figure 3(iii and iv). The square structure can be decomposed into two nanowire components with orientation angles of  $0^\circ$  and  $90^\circ$ , respectively (Figure 3A), representing a 2-digit-per-structure SERS information. The  $x$ -polarized SERS image indicates that only the nanowires at  $0^\circ$  exhibit strong SERS intensity, whereas the nanowires oriented at  $90^\circ$  exhibit undetectable SERS responses (Figure 3A, iii). The quantitative SERS intensity profile (Figure 3D) validates that maximum normalized Raman intensities ( $I_{\text{max}}$ ) are obtained when nanowires are oriented at  $0^\circ$ , which is in good agreement with the theoretical calculation of  $I = I_{\text{max}} \cos^2(0^\circ) = I_{\text{max}}$ .

Further increasing the number of sides of a polygon increases the number of digits available for information storage in the nanowire structures. A pentagonal structure (Figure 3B) is composed of nanowire components aligned at  $18^\circ$ ,  $54^\circ$ ,  $90^\circ$ ,



**Figure 4.** (A–C) SEM images and (D–F) their corresponding  $x$ -polarized gray-scale 2D SERS images of an Escher lizard pattern with different nanowire orientations, respectively. The orientation of the nanowires used to draw the individual lizards is rotated  $45^\circ$  from (A) to (B) and a further  $45^\circ$  from (B) to (C) to create different gray-scale images. All scale bars are  $10\ \mu\text{m}$  in (A)–(F). (G) Optical image of the corresponding gray-scale Escher lizard pattern (B). Average SERS spectra (H) and the intensity profile (I) across the lizards with different gray scales in (D)–(F).

$126^\circ$ , and  $162^\circ$ , respectively. The total orientation angles can be categorized into three groups, i.e.,  $18^\circ$  ( $18^\circ$  and  $162^\circ$ ),  $54^\circ$  ( $54^\circ$  and  $126^\circ$ ), and  $90^\circ$ . Hence, three digits of SERS intensities,  $\sim 0.91I_{\text{max}}$ ,  $\sim 0.34I_{\text{max}}$ , and 0, are stored in a pentagon at  $x$ -polarization (Figure 3B, iii). Conversely, at  $y$ -polarization,  $\sim 0.096I_{\text{max}}$ ,  $\sim 0.65I_{\text{max}}$ , and  $I_{\text{max}}$  are obtained at the  $18^\circ$  ( $18^\circ$  and  $162^\circ$ ),  $54^\circ$  ( $54^\circ$  and  $216^\circ$ ), and  $90^\circ$  oriented nanowires (Figure 3B, iv).

For a concentric ring structure consisting of continuous nanowires with an angle change from  $0^\circ$  to  $360^\circ$ , this results in a continuous change in SERS intensity across the ring that gives rise to a “dumbbell”-shaped SERS distribution (Figure S3), with the strongest SERS intensities ( $I_{\text{max}}$ ) observed at  $\sim 0^\circ$  and  $180^\circ$  (Figure 3C, iii) at  $x$ -polarization. This is a clear demonstration of a microstructure stored with multiple-digit SERS information. Such a simple yet elegant technique has yet to be extensively explored until now.

To demonstrate the flexibility of plasmonic nanostructures for multiple-digit data storage with enhanced spatial information, we fabricated a tessellated pattern consisting of 12 Escher lizards using a combination of Ag nanowires oriented at  $\theta = 0^\circ$ ,  $45^\circ$ , and  $90^\circ$  (Figure 4). Both the SEM image and dark-field optical micrograph (Figure 4A,G) of the tessellated pattern yield indistinguishable images with no physical features and are not able to reveal the distinct molecular information stored within the structures. Using SERS imaging, a microstructure

with rich molecular and spatial information is revealed. The tessellated microstructure can be decoded into three categories of lizards carrying different digits of SERS intensities; that is, the lizards fabricated using vertical,  $45^\circ$ -oriented, and horizontal nanowires exhibit  $I_{\text{max}}$ ,  $0.5I_{\text{max}}$ , and 0 SERS signals, respectively (Figure 4D).

Furthermore, by simply switching the orientation of nanowires in the same tessellated microstructure (Figures 4B,C), completely different SERS images carrying different digits of SERS intensities and spatial information can be obtained (Figures 4E,F). This highlights the flexibility and reproducibility of our two-photon lithography tool to fabricate different micro/nanostructures over a large area for molecular information storage. In addition, the seemingly similar physical appearance of tessellated microstructures encoded with different molecular information can be potentially useful for anticounterfeiting applications.

In conclusion, we have introduced a 2D SERS-based plasmonic molecular data storage capable of encoding multiple-digit molecular SERS intensity information per unit structure. We have successfully applied the quantitative SERS intensity as the basic data storage element (or digit). Highly quantifiable and tunable SERS intensity (digit) is manipulated by the orientation of Ag nanowire structures, which can be routinely reproduced using two-photon lithography and thermal evaporation. Our plasmonic nanowire system possesses

distinct physical morphology and chemical Raman information with narrow spatial and spectral resolution. Such plasmonic molecular data storage is analogous to optical data storage but acquires richer multidimensional information (with large-area 2D geometrical patterns) and exhibits higher spectral resolution than broad-band response from optical response. In addition, as demonstrated in the tessellated lizards, despite having similar physical appearance, different digits of molecular intensity information with enhanced spatial information can be stored simultaneously. This opens up a brand new horizon with huge potential for multiplex data storage. This unique data storage system with emphasis on molecular information storage bridges the gap between existing optical data storage and molecular memory.

## METHODS

**Materials.** IP-L 780 photoresist (Nanoscribe Inc., Germany) that contains pentaerythritol triacrylate (>95%) and 7-(diethylamino)-3-(2-thienylcarbonyl)-2H-1-benzopyran 2-one (<5%) was used as a negative photoresist for two-photon lithography. 4-Methylbenzenethiol (98%), propylene glycol, monomethyl ether acetate, isopropyl alcohol, and ethanol were purchased from Sigma-Aldrich. All chemicals were used without further purification, unless otherwise stated. Milli-Q water (>18.0 M $\Omega$ -cm) was purified with a Sartorius Arium 611 UV ultrapure water system.

**Fabrication of Well-Defined Plasmonic Structures.** The fabrication method consists of two parts: the fabrication of polymeric nanowires and the deposition of Ag film. To begin, polymeric nano- and/or microstructures were fabricated using a direct laser writing system (Nanoscribe Inc., Germany). In brief, a droplet of IP-L 780 monomer drop-casted on a glass substrate was polymerized by a computer-assisted femtosecond pulsed fiber laser with a center wavelength of 780 nm to form a polymer structure predefined by a graphics program. The direct laser writing was performed using inverted microscopy with an oil immersion lens (100 $\times$ , NA 1.4) and a computer-controlled piezoelectric stage. The average laser power was around 12 mW. A writing speed of 30  $\mu$ m/s was used. After writing, unexposed IP-L 780 was removed in propylene glycol and monomethyl ether acetate for 30 min and then washed with isopropyl alcohol for another 30 min. The polymeric structures were subsequently thermal evaporated with 2 nm Cr and 150 nm Ag using the thermal evaporation method.

**High-Speed Slit-Scanning Confocal Raman Spectroscopy Measurements.** The plasmonic structures were incubated in 10 mM 4-MBT in ethanol solution overnight. After that, samples were removed and rinsed with copious ethanol and dried in nitrogen gas. Owing to a strong Ag-S coordination bond, 4-MBT is expected to form a self-assembled monolayer on the Ag nanostructures. SERS spectra and SERS mapping were obtained with the sample mounted on a Ramantouch microspectrometer (Nanophoton Inc., Osaka, Japan). A 532 nm laser was used as an excitation laser. The excitation laser light was focused into a line on a sample through a cylindrical lens and an air objective lens (LU Plan Fluor 100 $\times$ , NA 0.9). The backscattered Raman signal from the line illuminated site was collected with the same objective lens, and a one-dimensional Raman image (1D space and Raman spectra) was obtained with a two-dimensional image sensor (Princeton Instrument, PIXIS 400 BR, -70  $^{\circ}$ C, 1340  $\times$  400 pixels) at once. At a single acquisition, line-shaped illumination is shone on the sample, where 400 Raman scattering points are

then collected simultaneously in the  $x$ -direction. Two-dimensional (2D) Raman spectral images were obtained by scanning the line-shaped laser focus in a single direction. The line illumination drastically reduces the acquisition time for  $x$ - $y$ -axis Raman mapping to less than half an hour for a 6400  $\mu$ m<sup>2</sup> area, as compared to the few hours required when using a conventional Raman system. The excitation laser power was 0.09 mW on the sample plane. The exposure time for each line and slit width of the spectrometer were 2 s and 50  $\mu$ m for 2D Raman imaging. The line scan mode with a resolution of the  $y$ -direction around 300 nm was used for  $x$ - $y$  imaging. A half-wave plate and a polarizer were used to change the polarization direction of the laser from initially the  $y$ -direction to the  $x$ -direction. The SERS intensities are obtained from the longitudinal body of nanowires at different orientation angles (excluding the Raman intensity from the respective tips).

**Characterization.** Scanning electron microscopy (SEM) was performed using a JEOL-JSM-7600F with an accelerate voltage of 5 kV. Pt (10 nm) was sputtered onto the substrates to increase their conductivity for SEM imaging.

## ASSOCIATED CONTENT

### Supporting Information

Details of photoluminescence map and spectra of the Ag nanowire and Raman controls of Ag nanowires oriented at different angles to form concentric structures are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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