Aluminum nanostructures with strong visible-range SERS activity for versatile micropatterning of molecular security labels

Lay, Chee Leng; Koh, Charlynn Sher Lin; Wang, Jing; Lee, Yih Hong; Jiang, Ruibin; Yang, Yijie; Yang, Zhe; Phang, In Yee; Ling, Xing Yi

2017

Lay, C. L., Koh, C. S. L., Wang, J., Lee, Y. H., Jiang, R., Yang, Y., . . . Ling, X. Y. (2018). Aluminum nanostructures with strong visible-range SERS activity for versatile micropatterning of molecular security labels. *Nanoscale*, 10(2), 575-581. doi:10.1039/C7NR07793A

<https://hdl.handle.net/10356/90091>

<https://doi.org/10.1039/C7NR07793A>

© 2018 The Royal Society of Chemistry. All rights reserved. This paper was published in *Nanoscale* and is made available with permission of The Royal Society of Chemistry.

Downloaded on 26 Apr 2023 16:40:54 SGT

Aluminum Nanostructures with Strong Visible-range SERS Activity for Versatile Micropatterning of Molecular Security Labels[†]

Chee Leng Lay,^{a,b} Charlynn Sher Lin Koh,^a Jing Wang,^c Yih Hong Lee,^a Ruibin Jiang,^c Yijie Yang,^a Zhe Yang,^a In Yee Phang,^{b,*} Xing Yi Ling^{a,*}

The application of aluminum (Al)-based nanostructures for visible-range plasmonics, especially for surface-enhanced Raman scattering (SERS), currently suffers from inconsistent local electromagnetic field distributions and/or inhomogeneous distribution of probe molecules. Herein, we lithographically fabricate structurally uniform Al nanostructures which enable homogeneous adsorption of various probe molecules. Individual Al nanostructures exhibit strong local electromagnetic field enhancements, in turn leading to intense SERS activity. The average SERS enhancement factor (EF) for individual nanostructures exceeds 10^4 for non-resonant probe molecules in the visible. These Al nanostructures also retain more than 70 % of their original SERS intensities after one-month storage, displaying superb stability under ambient conditions. We further achieve tunable polarization-dependent SERS responses using anisotropic Al nanostructures, facilitating the design of sophisticated SERS-based security labels. Our micron-sized security label comprises two-tier security features, including a machine-readable hybrid quick-response (QR) code overlaid with a set of ciphertexts. Our work demonstrates the versatility of Al-based structures in low-cost modern chemical nano-analytics and forgery protection.

1. Introduction

Aluminum (Al) is a promising substitute for gold (Au) and silver (Ag) in plasmonics research due to its lower cost and higher abundance on Earth's crust.¹⁻³ More importantly, Al nanostructures support tunable localized surface plasmon resonances (LSPRs) across the UV-visible range, arising from the large negative real component and small positive imaginary component of Al's dielectric constant throughout this spectral region.^{3, 4} Visible-range electric field enhancement between two Al nanoparticles has also been simulated to reach 10^5 to 10^6 .⁵ Al nanostructures are also passivated by an ultrathin native oxide layer (Al_2O_3), protecting the nanostructures against corrosion while enabling versatile surface modification with various chemical functionalities.^{5, 6} Consequently, Al nanostructures have given rise to applications in plasmonic colors,⁷⁻⁹ photocatalysis,^{10, 11} surface-enhanced Raman scattering (SERS)^{5, 12-14} and metal-enhanced fluorescence.¹⁵

Despite these numerous advantages, several unresolved challenges limit the use of Al nanostructures for practical SERS applications in the visible. SERS signal inhomogeneity is a significant issue, typically arising from inconsistent electromagnetic field distribution on aggregated Al nanocrystals,⁵ or uncontrolled distribution of probe molecules on various Al-based SERS substrates.^{13, 16} Furthermore, the conventional positioning of Al nanostructures on substrates for SERS applications is stereotyped to random,^{4, 5, 12, 13, 16} square^{14, 17} or hexagonal^{18, 19} orientations. Fabricating large-area sophisticated Al nanostructures with versatile micropatterning capabilities for SERS applications remains unexplored, thus restricting their potential applications in fingerprint anti-counterfeiting labels or microchannels for integrated sensors.

Here, we demonstrate the on-demand micropatterning of Al nanostructure arrays to generate homogeneous SERS signals in the visible, and highlight the capability of our platform as promising anti-counterfeiting security labels. The ultrathin Al_2O_3 layer on our Al nanostructures further enables homogeneous adsorption of various chemical functionalities to serve as SERS probe molecules. Average SERS enhancement

factors (EF) for non-resonant probe molecules on single Al nanodots exceed 10^4 . The Al_2O_3 layer also aids in retaining more than 70 % SERS intensity after one-month storage. We further demonstrate the polarization-dependent SERS response of our arrays using elongated Al nanostructures. To develop a proof-of-concept Al-based security label, we design an array with two-tier encoded information which comprises a micron-sized machine-readable SERS-based quick-response (QR) code and a set of ciphertexts. Our work establishes the potential of Al-based platforms as visible-range security labels.

2. Experimental Section

2.1 Materials. IP-L 780 photoresist was purchased from Nanoscribe Inc, Germany. Triethoxyphenylsilane (TEPS, > 98 %), naphthalene (NAP, 99 %), propylene glycol monomethyl ether acetate (PGMEA, > 99.5 %), acetic acid (≥ 99.7 %), isopropyl alcohol and ethanol were purchased from Sigma-Aldrich. Aluminum (Al) target (99.99 %) was purchased from Zhongnuo Advanced Material (Beijing) Technology Co. Ltd, China. All chemicals were used without further purification, unless otherwise stated. Milli-Q water (> 18.0 M Ω .cm) was purified with a Sartorius Arium® 611 UV ultrapure water system.

2.2 Fabrication of polymeric nanostructures. Polymeric nanostructures were fabricated using the Nanoscribe® Photonic Professional (Nanoscribe Inc., Germany). The system is equipped with an erbium-doped, femtosecond laser source with a centre wavelength of 780 nm, pulse repetition rate of 80 MHz and pulse length of 100 fs. IP-L 780 nanostructures were designed using computer-aided design (CAD) software, 3ds Max®. Dimensions of the structures were defined by the Nanoslicer and DeScribe softwares. All structures were written on square glass substrates (width = 22 mm and thickness $\approx$ 0.13 to 0.16 mm). The direct laser writing (DLW) processes were performed using an inverted microscope with an oil immersion lens (Zeiss Plan Apochromat, 100 $\times$, NA 1.4), and a computer controlled piezoelectric stage. The average laser power was around 10 mW and writing speed was 20 $\mu\text{m/s}$.

After writing, sample substrates were developed in PGMEA, followed by isopropyl alcohol for 30 min each. The substrate was then blow-dried using nitrogen gas.

2.3 Generation of QR code. To create Version 1 quick response (QR) code (21 × 21 modules) for the Singapore government's official website (www.gov.sg), we used a QR code generator software offered by QRStuff, QR Code Generator, Inc. Lines and dots of specific length and spacing were then arranged according to the QR code pattern using 3ds Max® software.

2.4 Metallization of the polymeric structures. Good-quality Al film was deposited on the substrates at a rate of 15 Å/s with a thermal evaporator system (Syskey, Taiwan) operating under high vacuum of 2.7×10^{-7} mbar.

2.5 Deposition of TEPS on Al-coated nanostructures. The substrate with Al-coated nanostructures was submerged in 3 mL of ethanol for 30 minutes. TEPS solution (approx. pH 5) containing 300 µL TEPS, 50 µL acetic acid, 500 µL Milli-Q water and 7 mL ethanol was prepared and left for 5 minutes. The substrate was then added to the TEPS solution and immersed for 3 hrs at room temperature. The substrate was subsequently washed with copious of ethanol to remove excess silane compounds. Next, the substrates were dried under low vacuum at room temperature for 6 hrs to aid the removal of water and ethanol, as well as to promote the formation of siloxane bonds.²⁰

2.6 Deposition of NAP on Al-coated nanostructures. 20 mg of NAP suspension (1mL water and 0.5 mL ethanol) was frozen and then deposited on the Al-coated polymeric structures via sublimation at – 82 °C and under vacuum of 0.010 mbar.

2.7 Surface-enhanced Raman scattering (SERS). SERS measurements were conducted using a Ramantouch microspectrometer (Nanophoton, Osaka, Japan) and a uRaman microscopy module (uRaman-532-TEC-Ci, Technospex Pte. Ltd, Singapore). SERS spectra of NAP and TEPS adsorbed on the surface of Al nanodots were generated by using excitation wavelength of 532 nm, a 100 × objective lens (Nikon TU Plan ELWD, NA 0.8), excitation power of 40 mW and integration time of 20 s. For normal Raman evaluation of solution containing 1 M TEPS or 1 M NAP in ethyl acetate, Raman spectra were collected using the 100 × objective lens (Nikon TU Plan ELWD, NA 0.8) at laser power of 40 mW with 20 s exposure time. For polarized Raman measurements, polarizer and half-wave plate were used to adjust the laser travelling pathway emitted from the Ramantouch microspectrometer. Raman intensities and spectra were obtained by averaging at least 50 individual spectrum. Baseline subtract treatment on spectra were processed using OriginPro software.

2.8 Materials characterization. To prepare samples for scanning electron microscopy (SEM) imaging, samples attached on glass substrates (with or without Al coating) were sputter-coated with platinum particles at 40 mV for 40 s using a JEOL JFC-1600 Auto Fine Coater. Coated surfaces were viewed using a JEOL

7600F SEM operating at accelerating voltage of 5.0 kV and beam current of 5 in SEI mode. AFM was used to determine actual width and height of the Al-coated polymeric structures using a Bruker Multimode 8 with NanoScope V controller from Bruker. ScanAsyst® mode (a PeakForce Tapping® based image optimization technique) image was acquired using a pyrex-nitride cantilever from Nanoworld (PNP-TR, force constant: 0.32 N/m and, resonance frequency: 67 kHz) in ambient condition. Data analysis was carried out using Bruker NanoScope Software 8.10. Static contact angles were measured with a 4 µL ultrapure water droplet using an Attension Theta Lite tensiometer equipped with a USB 2.0 digital camera. Average contact angle and standard deviation were calculated from five measurements at each of at least three locations across a substrate. Angle-resolved X-ray photoelectron spectroscopy (AR-XPS; SPECS Phoibos 100 spectrometer equipped with a monochromatic Mg X-ray radiation source) was employed to determine thickness of aluminum oxide layer formed on surfaces of the structures. Anode voltage and emission current used were 12.5 kV and 16.1 mA, respectively. For XPS calibration, 284.5 eV for C 1s binding energy peak was used. Presented results based on XPS measurements were average data taken from total 5 different regions of 3 substrates. 2D SERS image of the micron-sized plasmonic QR code was decoded using a QR code reader application (QR Scanner, Honestly App) on a smartphone (Xperia C3, Sony Mobile Communications Inc. or iPhone 6, Apple Inc.).

2.9 Dark-field scattering measurements. The scattering from the individual microstructures was measured on a dark field microscope (Nikon Eclipse Ti-U) that was integrated with a halogen lamp (12V, 100 W), a flat field imaging spectrograph (Andor Shamrock SR-303i-B), and a charge-coupled device camera (Andor iDus DU401A BR-DD). The camera was thermoelectrically cooled to – 60 °C during measurement. A dark-field objective (Nikon LU Plan Fluor EPI P 100×, NA 0.9) was employed for exciting and measuring the scattering from the individual microstructures. Andor-Einst software was used to control the detector, spectrograph and motorized systems. The obtained scattering spectra were calibrated based on Equation 1. $Q(\lambda)$ represents the scattering spectrum, $I_{Mea}(\lambda)$ is the recorded spectrum of the microstructures, $I_{Bckgrd}(\lambda)$ is the scattering spectrum collected from the blank region, $I_{Silica}(\lambda)$ is the spectrum collected from a glass substrate covered by a condensed film of silica nanoparticles, and $I_{Peak}(\lambda)$ is the peak value of the spectrum collected from the condensed silica film. The term, $I_{Mea}(\lambda) - I_{Bckgrd}(\lambda)$, eliminates the background scattering. The term, $1/(I_{Silica}(\lambda)/I_{Peak}(\lambda))$, removes nonuniformity of the source spectrum and the response of the entire optical system.

$$Q(\lambda) = \frac{I_{Mea}(\lambda) - I_{Bckgrd}(\lambda)}{I_{Silica}(\lambda)/I_{Peak}(\lambda)}$$

2.10 Electromagnetic simulations. All electrodynamic simulations were performed using finite-difference time-domain (FDTD) Solutions v8.6 (Lumerical Solutions). During the simulations, an electromagnetic pulse from 300 to 1600 nm

was launched into a box containing the target Al nanostructure. The Al nanostructure and its surrounding medium were divided into meshes of 0.5 nm in size. The model of the Al nanostructure was built according to the experimental parameters (Fig. S1C). The simulated Al nanostructure consisted of a truncated cone with a hemisphere on top. The truncated cone was 37 nm in height, while its top and bottom bases had radii of 87 nm and 97 nm, respectively. Radius of the hemisphere was 87 nm. The surface of the Al nanostructure was covered with 3-nm thick Al_2O_3 layer. The Al nanostructure was set on a polymeric truncated cone (IP-L 780) with radii of 97 nm and 150 nm for its top and bottom bases, respectively. The refractive index of the polymer was fixed at 1.4.²¹ The surrounding medium was set to 1. The dielectric function of Al and Al_2O_3 was taken from previously measured values.²² The electric field intensity at wavelength of 398 nm, 532 nm and 583 nm was monitored at the surface of Al.

2.11 Density functional theory (DFT) calculations. We used the Gaussian 09 computational chemistry package to determine theoretical molecular occupying area of NAP and TEPS molecules on Al. Geometric optimization of both NAP- and TEPS-adsorbed Al was carried out using the unrestricted B3LYP exchange-correlation functional. And the 6-311g (d p) basis set was used for all atoms.

2.12 Data analysis. Measurements of dimensions of the as-fabricated Al-coated IP-L 780 nanostructures were conducted using ImageJ. All data for the physical characterization of Al-coated polymeric nanostructures were averaged using at least 10 measurements.

3. Results and Discussion

We employ two-photon lithography and thermal evaporation to fabricate arrays of structurally tailored SERS-active Al nanostructures. A femtosecond pulse laser raster-scans through an acrylate-based photoresist (IP-L 780) to generate uniform polymeric nanodots (Fig. 1A(i)). These polymeric nanodots are then coated with (115 ± 8) -nm thick Al films via thermal evaporation (Fig. 1A(ii), Fig. S1). The fabricated Al nanodots have uniform average diameters of (196 ± 20) nm and heights of (300 ± 25) nm (Fig. 1B).

Fig. 1 (A) Fabricating Al nanostructure using (i) two-photon lithography, followed by (ii) Al thermal evaporation. (B) (i) Tilted SEM micrographs of Al nanodots array and their close-up views (inset). (ii) AFM height profile of the Al nanodots. (C) Angle-resolved XPS measurements to determine Al_2O_3 thickness on our Al nanostructures. Tilt angle-dependent (i) distribution of Al and Al_2O_3 , and (ii) Al_2O_3 thickness. (iii) Illustration of tilt angle during XPS measurements. (D) Darkfield image of Al nanodots. (E) Simulated (pink curve) and experimental (blue curve) scattering spectra of individual Al nanodots. Local electric field distribution of an Al nanodot at (F) 398 nm, (G) 583 nm, and (H) 532 nm.

Next, we use angle-resolved X-ray photoelectron spectroscopy (XPS) to quantify the thickness of aluminum oxide (Al_2O_3) on our Al nanostructures, which are typically exposed to ambient conditions (25 °C, 65% relative humidity) for 24 hours. XPS measurements unveil a very thin Al_2O_3 layer on the Al nanostructures' surfaces. Decreasing tilt angle increases the surface sensitivity of the XPS measurements, in turn giving rise to higher oxide content (Fig. 1C(i)). The estimated Al_2O_3 thickness on our Al nanostructures is around 3 nm (Fig. 1C, Fig. S2, Equation S1), in good agreement with reported values.²³⁻²⁵

Darkfield optical characterization elucidates a yellowish-green appearance for the Al nanodots, suggesting that their plasmon bands are in the visible (Fig. 1D). Indeed, the darkfield scattering spectrum of individual Al nanodot exhibits two plasmon resonance bands at 450 nm and 583 nm (Fig. 1E, blue line). The dominant scattering band at 583 nm corresponds well with the observed colors of these Al nanodots. Additionally, our darkfield scattering measurements match well with the scattering spectrum simulated using the finite-

difference time-domain (FDTD) approach (Fig. 1E, pink line). However, there is slight peak shift in the higher energy scattering resonance. The experimental resonance centers at 450 nm while the simulated resonance centers at 398 nm. We attribute this difference to the significant reduction in quantum yield of our CCD camera, decreasing from 52 % at 450 nm to 32 % at 398 nm.²⁶ With a lower photon collection efficiency and hence lower sensitivity for measurements below 450 nm, we observe an apparent cut-off peak at around 450 nm.

We also perform electric field calculations to elucidate the nature of plasmon resonance modes on the Al nanodots (Fig. 1F and 1G). The resonance at 398 nm corresponds to an electric quadrupole with field enhancement at the top and bottom of the Al nanodots (Fig. 1F). The resonance at 583 nm is an electric dipole with field enhancement only at the bottom of the Al nanodots (Fig. 1G). Moreover, we observe a similar field distribution pattern at our 532-nm laser excitation as the field distribution at 583 nm (Fig. 1H), indicating that the dipolar resonance is excited in our subsequent SERS experiments. Our results indicate that Al nanostructures are promising candidates for visible frequency plasmonics.

Next, we demonstrate that the native Al_2O_3 layer on our Al nanostructures provides a versatile platform to introduce probe molecules with various chemical functionalities. We graft naphthalene (NAP) and triethoxyphenylsilane (TEPS) as model molecules onto the Al nanostructures (Fig. 2A and B). NAP is physically adsorbed onto the Al nanostructures via sublimation (Fig. 2A(i)). The water contact angle of NAP-functionalized Al substrates is $(97 \pm 3)^\circ$ (Fig. 2A(ii)), while that of bare Al substrate is $(50 \pm 2)^\circ$ (Fig. S3). This contact angle increase after functionalization arises from the introduction of hydrophobic flat benzene rings on the Al nanostructures (Fig. 2A(i)).²⁷ For TEPS, we covalently bind the molecules to the Al nanodot surfaces via a condensation reaction between the silanol groups on hydrolyzed TEPS and Al_2O_3 (Fig. 2B(i)).²⁰ The water contact angle of TEPS-functionalized Al substrates is $(65 \pm 1)^\circ$ (Fig. 2B(ii)). The presence of residual ethoxy silane groups renders our TEPS-coated Al substrate slightly more hydrophilic than the NAP-functionalized one.²⁸ Such versatility in functionalizing Al nanodots implies that we can expand beyond the conventional amine- or thiol-terminated molecules which are used in Au- or Ag-based systems, thereby increasing our selection of probe molecules for subsequent anti-counterfeiting applications.

Fig. 2 Schematic illustrations of grafting (A) naphthalene (NAP) and (B) triethoxyphenylsilane (TEPS) molecules to Al-coated surfaces. (C) SERS spectra of NAP and TEPS adsorbed on Al nanodots. (D) Stability of NAP intensity over 1 month. 2D SERS images of Al nanodots functionalized with (E) NAP and (F) TEPS generated using the 1330 cm^{-1} fingerprint. Consistent SERS signals measured across a row of (G) NAP- and (H) TEPS-coated Al nanodots (yellow lines in (E) and (F)).

We proceed to investigate the SERS capabilities of our Al nanostructures in the visible, using both NAP and TEPS as the non-resonant Raman probes at 532-nm excitation. The SERS spectra of NAP and TEPS show common fingerprints at 1090 cm^{-1} and 1330 cm^{-1} (Fig. 2C, Fig. S4). Additionally, NAP displays another vibrational mode at 1590 cm^{-1} while TEPS exhibits a broad fingerprint at 1700 cm^{-1} , both with negligible SERS background from the substrate (Fig. S5). Density functional theory (DFT) simulations show that for both NAP and TEPS, the vibrations near 1090 cm^{-1} arises from CCC symmetric phenyl ring stretching, while the band at 1330 cm^{-1} represents the in-plane phenyl ring asymmetric stretching (Fig. S6 and S7).²⁹ The narrow band of NAP centered at 1590 cm^{-1} represents the in-plane phenyl ring asymmetric stretching mode (Fig. S6), while the broad fingerprint of TEPS at 1700 cm^{-1} comprises multiple in-plane and out-of-plane phenyl-ring stretching modes (Fig. S7). The SERS intensity of the 1330 cm^{-1} mode for NAP-adsorbed Al nanodots remains stable, decreasing by less than 30 % after one month storage under nitrogen environment (Fig. 2D). Furthermore, the native oxide

layer remains at around 3 nm thick on the as-fabricated Al nanodots (Fig. S2). Consequently, the stable SERS signals imply that the Al₂O₃ layer is sufficiently dense to prevent corrosion towards the Al core, preserving the SERS activity of our platform.¹⁸ Notably, analyses of the 1330 cm⁻¹ mode over 50 Al nanodots show uniform SERS signals of (7656 ± 467) counts and (7163 ± 319) counts for NAP and TEPS respectively (Fig. 2E – 2H). Such consistent SERS signals, with low relative standard deviation of < 10 %, imply homogeneous adsorption of the Raman probe molecules on the Al nanodots. Our work is the first report to showcase practical SERS performance of individual Al nanostructures in the visible.

We estimate the average SERS enhancement factors (EF) of NAP and TEPS to be 7.0×10^4 and 1.7×10^4 , respectively, based on the 1330 cm⁻¹ mode (Equation S2). The strong SERS EFs observed from our Al nanodots arises predominantly from electromagnetic enhancement. The electric field enhancement ($(|E|/|E_0|)^2$) is approximately 72.4 at 532 nm (Fig. S8), clearly demonstrating that the Al nanodots can proficiently enhance SERS signals. The high SERS EFs of our Al nanodots in the visible indicate that SERS EFs of 10^3 to 10^6 are not limited to deep-UV/UV excitation.^{17, 30, 31} In fact, the SERS EFs measured in this work is the highest recorded for single Al nanostructures in the visible. Our results thus affirm the capability of individual Al nanostructures as high-performance SERS platform in the visible.

Besides nanodots, we demonstrate polarization-dependent SERS responses using concentric rings of continuous circular Al nanowires functionalized with NAP (Fig. 3A, S9). Such tunable SERS intensities are essential for the subsequent creation of complex SERS-based security labels. Our setup enables continuous measurements of the polarization-dependent SERS response between 0° to 360° along the circular Al nanowires, where the angle between the polarized laser excitation and nanowire orientation (θ) is defined with respect to the vertical y-axis (Fig. 3A). At x-polarization, the SERS image generated using the 1330 cm⁻¹ mode depict signals changing from bright to dim as θ shifts from 0° to 90° (Fig. 3B, 3D). A reverse gradient of SERS intensities is observed at y-polarization (Fig. 3C). By normalizing the SERS intensity at various θ against the measured I_{max} at $\theta = 0^\circ$, we obtain a gradient of discrete SERS values ranging from 1.00, 0.90, 0.69, 0.40, 0.19, 0.02 to 0.00 when the orientation of the Al nanowires is aligned at 0°, 15°, 30°, 45°, 60°, 75°, and 90°, respectively. A plot of normalized SERS intensity against θ further demonstrates a good fit to a $\cos^2\theta$ function (Fig. 3E). Moreover, a regular “dumbbell”-shaped SERS intensity distribution can be observed in the θ -dependent SERS-intensity plot (Fig. 3F), illustrating a continuous polarization-dependent variation in the experimental SERS intensity across the concentric ring.

This polarization-dependent tunability of SERS signals arises from the directional coupling of Al nanowires with incident light.³² The anisotropic morphology of nanowires allows these structures to support longitudinal and transverse LSPRs. At x-polarization ($\theta = 0^\circ$), the transverse LSPR mode couples efficiently with incident light to result in strong

electromagnetic fields along the nanowires, generating the strongest SERS intensities. Increasing θ reduces the coupling strength and thus leads to progressively weaker SERS intensity following a $\cos^2\theta$ relationship. At $\theta = 90^\circ$, momentum mismatch between the incident photon and the propagating plasmons significantly reduces the coupling strength and generates the weakest SERS intensity (Fig. 3B, D). Compared to current works which focus on using polarization to study the fundamental optical response of Al nanostructures³ or for use in color display,⁷⁻⁹ our work extends the application of Al nanostructures to create a dynamic range of gray-scale polarization-dependent SERS intensities. Such consistent polarization-dependent SERS signals suggest that Al nanostructures can be applied to multi-digit data storage and anti-counterfeiting platforms.³²

Fig. 3 (A) SEM micrograph of Al concentric rings. (B) X- and (C) y-polarized 2D SERS images of the Al concentric rings generated using the 1330 cm⁻¹ fingerprint of NAP. (D) X-polarized SERS spectra of the Al concentric circles collected at different angles ($\theta = 0^\circ$ – 90°). (E) Plot of normalized SERS intensity against θ at x-polarization. (F) “Dumbbell”-shaped distribution of simulated (dotted purple line) and normalized experimental (red circles) SERS intensity against θ at x-polarization for (B).

To design a proof-of-concept AI-based security label, we proceed to develop a steganograph comprising two tiers of covert information (Fig. 4A). A steganograph hides a secret message within an ordinary image.³³ The first tier of security feature is a microscale SERS quick-response (QR) code, which conventionally is a square two-dimensional (2D) barcode with black dots strategically arranged on a white background (Fig. 4B). The second tier of security feature consists of two ciphertexts “ntu” and “cbc”, which are embedded at the top and bottom position markers of the QR code, respectively (Fig. 4C).

Our designed steganograph can only be fully decoded utilizing the unique polarization-dependent SERS response of our Al nanostructures. Our SERS QR code comprises an array of vertically-oriented Al nanorods and nanodots which can be directed to the Singapore government’s website (www.gov.sg) (Fig. 4D). The ciphertexts are fabricated using Al nanodots and horizontally-oriented Al nanorods (Fig. 4E). Physical characterization using scanning electron microscopy (SEM)

Fig. 4 (A) SEM micrograph of our two-tier security label comprising a QR code overlaid with ciphertexts. (B) QR code for the official website of the Singapore government. (C) Embedded ciphertext within (B). (D) x- and (E) y-polarized 2D SERS images depicting the encrypted QR code and ciphertexts, respectively. Images are generated using the 1330 cm^{-1} fingerprint of NAP. (F) SERS spectrum of NAP extracted from the square region in (E). (G) (i) Reading the QR code in (D) using a smartphone directs the reader to the (ii) Singapore government's official website.

reveals only a complex pattern with neither visible ciphertexts nor decodable QR code (Fig. 4A). In contrast, the QR code and ciphertexts can be discerned in the respective x- and y-polarized SERS images generated using the 1330 cm^{-1} fingerprint of NAP (Fig. 4D – F). More importantly, scanning the QR code in the x-polarized SERS image (Fig. 4D) immediately directs the scanner to the coded website (Fig. 4G). There is no signal cross-talk between the two polarizations. Our microscale steganograph is therefore an ideal candidate for providing advanced security, possessing images which are readable and trackable using commercial imaging scanners and multiple security features on protection against forgery. Current visible-range plasmonic security labels do not have any source tracking function.^{32, 34, 35} Moreover, we are the first to overlay ciphertexts with QR codes to achieve a highly sophisticated two-tier security system. This achievement has thus far remained challenging to attain via optofluidic maskless lithography.³⁶ Our approach is also more practical as compared to fluorescence based double-layered QR codes fabricated within single silver zeolite microcarrier via two-photon activation.³⁷

Conclusions

In summary, we establish Al nanostructures as promising SERS-based security labels in the visible. Uniform Al nanostructures fabricated lithographically enable homogeneous adsorption of various probe molecules. Single Al nanostructures generate strong average SERS EF above 10^4 , and their SERS intensities also remain stable up to a month. By incorporating nanodots

with nanorods/wires, we successfully fabricate micron-sized security labels featuring polarization-tunable two-tier security. Our security label comprises a machine-readable 2D QR code and a set of ciphertexts at x- and y-polarization, respectively. The feasibility of our approach to create highly complex and affordable plasmonic authentication codes will drive the continuous development of new anti-counterfeiting labels against forgery. Micro-patterns with Al nanostructures also provide opportunities for cost-effective multiplex data storage and label-free plasmonic nanosensors.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

X.Y.L. thanks the financial support Singapore Ministry of Education for Tier 1 (RG21/16) and Tier 2 (MOE2016-T2-1-043 (S)) grants, and Nanyang Technological University. C.L.L. thanks the support from A*STAR Graduate Scholarship, Singapore. C.S.L.K. acknowledges support from Nanyang Presidential Graduate Scholarship.

References

1. J. Martin and J. Plain, *J. Phys. D Appl. Phys.*, 2015, **48**, 184002.
2. C. J. DeSantis, M. J. McClain and N. J. Halas, *ACS Nano*, 2016, **10**, 9772-9775.
3. D. Gerard and S. K. Gray, *J. Phys. D Appl. Phys.*, 2015, **48**, 184001.
4. C. Langhammer, M. Schwind, B. Kasemo and I. Zorić, *Nano Lett.*, 2008, **8**, 1461-1471.
5. S. Tian, O. Neumann, M. J. McClain, X. Yang, L. Zhou, C. Zhang, P. Nordlander and N. J. Halas, *Nano Lett.*, 2017, **17**, 5071-5077.
6. I. Liaskuciene, M. Steffenhagen, S. J. Asadauskas, J.-F. Lambert and J. Landoulsi, *Langmuir*, 2014, **30**, 5797-5807.
7. X. M. Goh, Y. Zheng, S. J. Tan, L. Zhang, K. Kumar, C.-W. Qiu and J. K. W. Yang, *Nat. Commun.*, 2014, **5**, 5361-5369.
8. J. S. Clausen, E. Højlund-Nielsen, A. B. Christiansen, S. Yazdi, M. Grajower, H. Taha, U. Levy, A. Kristensen and N. A. Mortensen, *Nano Lett.*, 2014, **14**, 4499-4504.
9. J. Olson, A. Manjavacas, L. Liu, W.-S. Chang, B. Foerster, N. S. King, M. W. Knight, P. Nordlander, N. J. Halas and S. Link, *Proc. Natl. Acad. Sci. U.S.A.*, 2014, **111**, 14348-14353.
10. M. Lee, J. U. Kim, K. J. Lee, S. Ahn, Y.-B. Shin, J. Shin and C. B. Park, *ACS Nano*, 2015, **9**, 6206-6213.
11. L. Zhou, Y. Tan, J. Wang, W. Xu, Y. Yuan, W. Cai, S. Zhu and J. Zhu, *Nat Photon*, 2016, **10**, 393-398.
12. B. Sharma, M. F. Cardinal, M. B. Ross, A. B. Zrimsek, S. V. Bykov, D. Punihaoale, S. A. Asher, G. C. Schatz and R. P. Van Duyne, *Nano Lett.*, 2016, **16**, 7968-7973.
13. K. B. Mogensen, M. Guhlke, J. Kneipp, S. Kadkhodazadeh, J. B. Wagner, M. Espina Palanco, H. Kneipp and K. Kneipp, *Chem. Commun.*, 2014, **50**, 3744-3746.
14. Z.-L. Yang, Q.-H. Li, B. Ren and Z.-Q. Tian, *Chem. Commun.*, 2011, **47**, 3909-3911.
15. M. Bauch, K. Toma, M. Toma, Q. Zhang and J. Dostalek, *Plasmonics*, 2014, **9**, 781-799.

16. C. Zhang, A. I. Smirnov, D. Hahn and H. Grebel, *Chem. Phys. Lett.*, 2007, **440**, 239-243.
17. S. K. Jha, Z. Ahmed, M. Agio, Y. Ekinici and J. F. Löffler, *J. Am. Chem. Soc.*, 2012, **134**, 1966-1969.
18. G. H. Chan, J. Zhao, G. C. Schatz and R. P. Van Duyne, *J. Phys. Chem. C*, 2008, **112**, 13958-13963.
19. A. Taguchi, Y. Saito, K. Watanabe, S. Yijian and S. Kawata, *Appl. Phys. Lett.*, 2012, **101**, 081110.
20. G. T. Hermanson, in *Bioconjugate Techniques (Third edition)*, Academic Press, Boston, 2013, DOI: <https://doi.org/10.1016/B978-0-12-382239-0.00013-3>, pp. 535-548.
21. Y. Cui, I. Y. Phang, Y. H. Lee, M. R. Lee, Q. Zhang and X. Y. Ling, *Chem. Commun.*, 2015, **51**, 5363-5366.
22. D. Y. Smith, E. Shiles and M. Inokuti, in *Handbook of Optical Constants of Solids*, Academic Press, Burlington, 1997, DOI: <https://doi.org/10.1016/B978-012544415-6.50016-9>, pp. 369-406.
23. B. R. Strohmeier, *Surf. Interface Anal.*, 1990, **15**, 51-56.
24. M. R. Alexander, G. E. Thompson, X. Zhou, G. Beamson and N. Fairley, *Surf. Interface Anal.*, 2002, **34**, 485-489.
25. M. W. Knight, N. S. King, L. Liu, H. O. Everitt, P. Nordlander and N. J. Halas, *ACS Nano*, 2014, **8**, 834-840.
26. iDus DU401A BR-DD: "USB Camera for Spectroscopy" Andor™ Technology.
27. R. Duschek, F. Mittendorfer, R. I. R. Blyth, F. P. Netzer, J. Hafner and M. G. Ramsey, *Chem. Phys. Lett.*, 2000, **318**, 43-48.
28. D. G. Kurth and T. Bein, *Langmuir*, 1995, **11**, 3061-3067.
29. D. W. Mayo, in *Course Notes on the Interpretation of Infrared and Raman Spectra*, John Wiley & Sons, Inc., 2004, DOI: [10.1002/0471690082.ch5](https://doi.org/10.1002/0471690082.ch5), pp. 101-140.
30. X.-M. Li, M.-H. Bi, L. Cui, Y.-Z. Zhou, X.-W. Du, S.-Z. Qiao and J. Yang, *Adv. Funct. Mater.*, 2017, **27**, 1605703.
31. T. Ding, D. O. Sigle, L. O. Herrmann, D. Wolverson and J. J. Baumberg, *ACS Appl. Mater. Interfaces*, 2014, **6**, 17358-17363.
32. Y. Cui, I. Y. Phang, R. S. Hegde, Y. H. Lee and X. Y. Ling, *ACS Photonics*, 2014, **1**, 631-637.
33. S. Islam, M. R. Modi and P. Gupta, *EURASIP J. on Info. Security*, 2014, **2014**, 8-14.
34. Y. Cui, R. S. Hegde, I. Y. Phang, H. K. Lee and X. Y. Ling, *Nanoscale*, 2014, **6**, 282-288.
35. Y. Liu, Y. H. Lee, Q. Zhang, Y. Cui and X. Y. Ling, *J. Mater. Chem. C*, 2016, **4**, 4312-4319.
36. S. Han, H. J. Bae, J. Kim, S. Shin, S.-E. Choi, S. H. Lee, S. Kwon and W. Park, *Adv. Mater.*, 2012, **24**, 5924-5929.
37. G. De Cremer, B. F. Sels, J.-i. Hotta, M. B. J. Roeflaers, E. Bartholomeeusen, E. Coutiño-Gonzalez, V. Valtchev, D. E. De Vos, T. Vosch and J. Hofkens, *Adv. Mater.*, 2010, **22**, 957-960.

Nanoscale

ARTICLE

Supporting Information

Aluminum Nanostructures with Strong Visible-range SERS Activity for Versatile Micropatterning of Molecular Security Labels[†]

Chee Leng Lay,^{a,b} Charlynn Sher Lin Koh,^a Jing Wang,^c Yih Hong Lee,^a Ruibin Jiang,^c Yijie Yang,^a Zhe Yang,^a In Yee Phang,^b Xing Yi Ling^{*,a}

^a. Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371.

Email: xyling@ntu.edu.sg

^b. Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634.

^c. Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, China 710119.

Nanoscale

ARTICLE

Fig. S1 (A) TEM micrographs of Al layers on silver nanocubes. (B) SEM cross-sectional view of Al layer coated on a silicon wafer. Average thickness of the Al layer is (115 ± 8) nm. (C) Model of Al-coated IP-L 780 nanostructure used for FDTD simulations.

Fig. S2 We investigate the stability of Al₂O₃ layer on Al-coated substrates (A) 1 day after Al deposition, (B) 1 day after Al deposition and 4 hour after immersion in TEPS ethanolic solution, and (C) 1 month after Al deposition and 4 hour after immersion in TEPS ethanolic solution. (i) Dependence of XPS spectra on tilt angle for 100-nm thin Al film which was evaporated under the same conditions as in fabrication of Al nanostructures. (Inset) Schematic depiction on tilt angle, defined as the angle between the plane of the sample surface and the entrance to the analyzer. The low energy (~ 72.9 eV) and high energy (~ 74.4 eV) shoulders correspond to the Al 2p line from Al and Al₂O₃, respectively. (ii) Calculated elemental distribution of Al and Al₂O₃ as a function of tilt angle based on angle dependence of ratio between the area under the curves of the Al metal peak and Al 2p oxide peak. (iii) Calculated thickness of Al₂O₃ layer against tilt angles.

Using angle-resolved X-ray photoelectron spectroscopy (XPS), we quantify the thickness of aluminum oxide (Al₂O₃) on our Al nanostructures by varying the angle between the detector and the Al samples from 90° to 30° (Fig. 1C, Fig. S2). It is observed that Al₂O₃ content increases as more near-surface compositions are measured at lower tilt angles (Fig. 1C(i)), verifying formation of very thin Al₂O₃ layer at the surface of Al samples. The thickness of the homogenous native oxide layer after 24 h of exposure to ambient conditions (25 °C, 65% relative humidity) is approximately 3 nm (Fig. S2, Equation S1). The 3-nm thick oxide layer is fairly dense and stable in preventing oxygen diffusion which dramatically slows down the oxidation process.^{1,2} After keeping in nitrogen box for a month, the Al nanodots remain stable and provide consistent SERS performance after molecular adsorption (Fig. 2D, Fig. S2). Moreover, Raman peak recorded at 1330 cm⁻¹ for NAP adsorbed Al nanodots after 1-month storage only experiences less than 30 % drop in SERS intensity (Fig. 2D). Consequently, the stable SERS signals imply that the oxide layer is sufficiently dense to prevent oxygen diffusion towards the Al core, in turn dramatically slowing down the corrosion of the Al nanodots to preserve the SERS-activity of our platform.^{1,2}

Nanoscale

ARTICLE

Characterization of the aluminum oxide layer using XPS

Thickness of aluminum oxide layer is calculated using Equation S1:³

$$d_{Oxide} = \lambda_{Oxide} \sin \theta \ln \left(\frac{\rho_{Al} \lambda_{Al} A_{Oxide}}{\rho_{Oxide} \lambda_{Oxide} A_{Al}} + 1 \right) \quad \text{----- Equation S1}$$

ρ_{Al} = Volume density of aluminum = 0.1 mol/cm⁻³

ρ_{Oxide} = Volume density of aluminum oxide = 0.0777 mol/cm⁻³

λ_{Al} = Inelastic mean free path of electrons in aluminum = 2.8 nm

λ_{Oxide} = Inelastic mean free path of electrons in aluminum oxide = 2.6 nm

A_{Al} and A_{Oxide} = Area under the curve of fit curves to the experimental results

θ = Tilt angle of the substrate with respect to the XPS detector. This angle corresponds to the take-off angle of photoelectrons from the substrate's surface.

Nanoscale

ARTICLE

(A) Al-coated glass

$50 \pm 2^\circ$

(B) TEPS

$65 \pm 1^\circ$

(C) NAP

$97 \pm 3^\circ$

Fig. S3 Water contact angle measurements for (A) Al-coated glass substrate, (B) TEPS- and (C) NAP-adsorbed Al-coated substrate.

Fig. S4 (A)(i) top view of DFT-simulated structural configuration of NAP molecules, and (ii) geometry calculation on theoretical molecular occupying area of NAP molecules on Al. (B)(i) Side view and (ii) top view of simulated structural configuration of TEPS molecules, respectively. Geometry calculation on theoretical molecular occupying area of TEPS molecules on Al based on (iii) distance between O atoms and (iv) size of phenyl ring on TEPS, respectively. (C) SERS spectrum of NAP molecules adsorbed on Al-coated IP-L 780 nanodots (orange), normal Raman spectrum of 1 M NAP in ethyl acetate (blue), DFT simulated graph for NAP (pink) and normal Raman spectrum of ethyl acetate (violet). (D) SERS spectrum of TEPS molecules adsorbed on Al-coated IP-L 780 nanodots (orange), normal Raman spectrum of 1 M TEPS in ethyl acetate (blue), DFT simulated graph for TEPS (pink) and normal Raman spectrum of ethanol (violet). Intensity at $\sim 1330 \text{ cm}^{-1}$ Raman band from both molecules is used for calculating SERS EF. (E) Optical resolutions of 532 nm laser passing through Nikon TU Plan ELWD 100x objective lens (NA 0.8) for (i) x-, (ii) y- and (iii) z-axis, respectively.

Nanoscale

ARTICLE

The simulated distance between H atoms for phenyl rings and O atoms on the probe molecules are listed in Fig. S4A and S4B. From calculations, the theoretical molecular occupying area of a NAP molecule on Al is 0.348 nm^2 (Fig. S4A(ii)). On the other hand, the estimated molecular area of a TEPS molecule based on O atoms on silane is 0.062 nm^2 (Fig. S4B(iii)) and the area becomes 0.181 nm^2 when phenyl group (Fig. S4B(iv)) is considered. Our calculated molecular areas of NAP and TEPS molecule are much smaller than the reported molecular areas of NAP and benzene, which are 0.65 nm^2 , and 0.30 to 0.43 nm^2 , respectively.⁴⁻⁶ Therefore, our calculated molecular areas assume the closest packing of probe molecules on the Al surfaces. The estimated SERS EFs are thus underestimated.

We observe that the experimental Raman peaks of NAP at 1090 cm^{-1} , 1330 cm^{-1} and 1590 cm^{-1} are respectively shifted to 1055 cm^{-1} , 1411 cm^{-1} and 1624 cm^{-1} in the simulated results (Fig. S4C). On the other hand, Raman peaks of TEPS at 1090 cm^{-1} , 1330 cm^{-1} and 1700 cm^{-1} are shifted to 1050 cm^{-1} , 1310 cm^{-1} and 1642 cm^{-1} respectively in the simulated results (Fig. S4D). The main reason for the blue/red shift in the Raman peaks is the difference in structure between the compact passivating Al_2O_3 layer and the simulated Al_2O_3 -molecules model. Moreover, the DFT simulation with single molecule neglects the neighbouring effects of close-packed molecules grafted on surface which deviate the experimental SERS bands.^{7, 8} Nevertheless, the presence of aforementioned Raman characteristic peaks provides strong evidence on the adsorption of NAP and TEPS molecules onto Al surfaces.

Nanoscale

ARTICLE

Calculation of SERS enhancement factor

To calculate SERS enhancement factor (EF) of the fabricated Al-coated IP-L 780 nanostructures, Equation S2 is used. To simplify SERS EF calculation, Al-coated IP-L 780 nanodots with diameter of (196 ± 20) nm and thickness of (115 ± 8) nm are used for SERS measurements. Both SERS and normal Raman measurements are conducted using point mode with laser power of 40 mW and exposure time of 20 s. By using Equation S2 and the theoretical molecular occupying area of a NAP or a TEPS molecule, it is assumed that a monolayer of NAP or TEPS molecules with the closest molecular packing is adsorbed on surfaces of the Al-coated IP-L 780 nanostructures.

$$EF = \frac{I_{SERS}}{N_{SERS}} / \frac{I_{Normal}}{N_{Normal}} \quad \text{-----Equation S2}$$

(A) NAP

I_{SERS} = Intensity of the 1330 cm^{-1} Raman band from NAP adsorbed on Al-coated IP-L 780 microstructures

$$= 7656 \text{ counts}$$

N_{SERS} = Number of NAP molecules contributing to I_{SERS}

= Surface area of the deposited Al film / molecular occupying area of a NAP molecule

The deposited Al film on IP-L 780 micro-dot is assumed as a hemisphere, so

$$\begin{aligned} \text{Surface area} &= 2\pi r^2 \\ &= 60344 \text{ nm}^2 \end{aligned}$$

Therefore,

$$\begin{aligned} N_{SERS} &= 60344 / 0.348 \\ &= 173402 \text{ molecules} \end{aligned}$$

I_{Normal} = Intensity of the 1330 cm^{-1} Raman band from 1 M NAP – ethyl acetate solution (same laser power and acquisition time as for I_{SERS} measurements)

$$= 1134 \text{ counts}$$

N_{Normal} = Number of NAP molecules that yield I_{Normal} .

$$= \text{Volume of laser spot} \times \text{Concentration of NAP} \times \text{Avogadro's number}$$

To determine volume of laser spot, the lateral spot size of the focus beam is measured from the displayed laser spot that gives the highest sample signal. The axial size of the laser is determined by adjusting the stage position along the z-axis (optical path) to get the z-distance from maximum signal intensity to zero intensity. The lateral and axial spot sizes are used to get optical resolutions of the 532 nm laser, which are: $x = (914 \pm 110)$ nm; $y = (850 \pm 55)$ nm; and $z = (4880 \pm 247)$ nm. And,

$$\begin{aligned} \text{Volume of laser spot} &= [\pi \times (x / 2) \times (y / 2) \times z] / 10^{21} \\ &= 2.978 \times 10^{-12} \text{ cm}^3 \end{aligned}$$

Nanoscale

ARTICLE

Therefore,

$$N_{\text{Normal}} = 2.978 \times 10^{-12} \times 1 \times 6.023 \times 10^{23} \times 0.001$$

$$= 1.794 \times 10^9 \text{ molecules}$$

$$\text{SERS EF} = (7656 / 173402) / (1134 / 1.794 \times 10^9)$$

$$= 7.0 \times 10^4$$

(B) TEPS

$$I_{\text{SERS}} = \text{Intensity of the } 1330 \text{ cm}^{-1} \text{ Raman band from TEPS adsorbed on aluminum-coated IP-L 780 microstructures}$$

$$= 7163 \text{ counts}$$

The theoretical molecular occupying area of a TEPS molecule on aluminum is 0.062 nm^2 , so

$$N_{\text{SERS}} = \text{Number of TEPS molecules contributing to } I_{\text{SERS}}$$

$$= 60344 / 0.062$$

$$= 973290 \text{ molecules}$$

$$I_{\text{Normal}} = \text{Intensity of the } 1330 \text{ cm}^{-1} \text{ Raman band from 1 M TEPS – ethyl acetate solution}$$

$$= 779.65 \text{ counts}$$

$$N_{\text{Normal}} = \text{Number of TEPS molecules that yield } I_{\text{Normal}}$$

$$= 2.978 \times 10^{-12} \times 1 \times 6.023 \times 10^{23} \times 0.001$$

$$= 1.794 \times 10^9 \text{ molecules}$$

$$\text{SERS EF} = (7163.39 / 973290) / (779.65 / 1.794 \times 10^9)$$

$$= 1.7 \times 10^4$$

Fig. S5 Comparison of SERS intensity of (A) NAP adsorbed Al nanodots, (B) NAP adsorbed flat Al-coated glass substrate, (C) Al nanodots without probe molecules, (D) IP-L 780 polymeric nanodots and (E) blank cover slip only. As observed, there is no interference from background signals on SERS intensity of NAP adsorbed Al nanodots.

Fig. S6 Schematic representatives for DFT-simulated vibrational modes of the NAP molecules adsorbed on Al surfaces at Raman shift (A) 1090 cm^{-1} , (B) 1330 cm^{-1} and (C) 1590 cm^{-1} .

To understand types of vibration in TEPS molecules adsorbed on Al surfaces upon 532-nm excitation, we capture the molecular vibration animations obtained from the DFT simulation at Raman shifts of (A) 1090 cm^{-1} , (B) 1330 cm^{-1} and (C) 1590 cm^{-1} . These three Raman peak positions are the dominant peaks observed from our measured SERS spectra (Fig. 2C and Fig. S4C). Fig. S6 illustrates that vibrations of the phenyl rings on the TEPS molecules give rise to the major SERS signals. The peak at 1090 cm^{-1} represents the phenyl ring CCC symmetric stretching vibration mode. On the other hand, the peaks at 1330 cm^{-1} and 1590 cm^{-1} represent the in-plane phenyl ring asymmetric stretching mode.^{9,10} The presence of aforementioned vibrational modes provides strong evidence on the physisorption of NAP molecules onto Al surfaces.

Fig. S7 Schematic representatives for DFT-simulated vibrational modes of the TEPS molecules adsorbed on Al surfaces at Raman shift (A) 1090 cm^{-1} , (B) 1330 cm^{-1} and (C) 1700 cm^{-1} .

To understand types of vibration in TEPS molecules adsorbed on Al surfaces upon 532-nm excitation, we capture molecular vibrations animations displayed in DFT simulation at Raman shifts of (A) 1090 cm^{-1} , (B) 1330 cm^{-1} and (C) 1700 cm^{-1} . These three Raman peak positions are the dominant peaks observed from our measured SERS spectra (Fig. 2C and Fig. S4D). Fig. S7 illustrates that vibrations of the phenyl rings on the TEPS molecules give rise to the major SERS signals. From the simulation, the peak at 1090 cm^{-1} represents the phenyl ring CCC symmetric stretching vibration mode. On the other hand, the peak at 1330 cm^{-1} is due to the in-plane phenyl ring asymmetric stretching mode, while out-of-plane phenyl-ring stretching mode is observed at peak 1700 cm^{-1} .^{9, 10} The presence of aforementioned vibrational modes provides strong evidence on the chemisorption of TEPS molecules onto Al surfaces.

Fig. S8 Electric field intensity $(|E|/|E_0|)^2$ of an Al nanodot simulated at excitation wavelength of 532 nm.

Nanoscale

ARTICLE

Fig. S9 SEM micrographs of concentric ring structure consisting of continuous Al nanowires at different magnifications.

The width and periodicity of the Al nanowires are set at (170 ± 20) nm and 2 μm to minimize plasmonic coupling between neighboring nanowires (Fig. 3A, Fig. S9).¹¹

Nanoscale

ARTICLE

References

1. G. H. Chan, J. Zhao, G. C. Schatz and R. P. Van Duyne, *J. Phys. Chem. C*, 2008, **112**, 13958-13963.
2. W. M. Haynes, *CRC Handbook of Chemistry and Physics*, 95th Edition, CRC Press, 2014.
3. S. Ayas, A. E. Topal, A. Cupallari, H. Güner, G. Bakan and A. Dana, *ACS Photonics*, 2014, **1**, 1313-1321.
4. K. K. Qian, S. L. Suib and R. H. Bogner, *J. Pharm. Sci.*, 2011, **100**, 4674-4686.
5. A. L. McClellan and H. F. Harnsberger, *J. Colloid. Interface Sci.*, 1967, **23**, 577-599.
6. A. Nonaka, *Colloids Surf.*, 1992, **62**, 207-213.
7. L. Laurentius, S. R. Stoyanov, S. Gusarov, A. Kovalenko, R. Du, G. P. Lopinski and M. T. McDermott, *ACS Nano*, 2011, **5**, 4219-4227.
8. X. Han, H. K. Lee, Y. H. Lee, W. Hao, Y. Liu, I. Y. Phang, S. Li and X. Y. Ling, *J. Phys. Chem. Lett.*, 2016, **7**, 1501-1506.
9. T. Shimanouchi, *J. Phys. Chem. Ref. Data*, 1972, **1**, 189-216.
10. D. W. Mayo, in *Course Notes on the Interpretation of Infrared and Raman Spectra*, John Wiley & Sons, Inc., 2004, DOI: 10.1002/0471690082.ch5, pp. 101-140.
11. Y. Cui, I. Y. Phang, R. S. Hegde, Y. H. Lee and X. Y. Ling, *ACS Photonics*, 2014, **1**, 631-637.