Electronic Supplementary Materials for

Multiplex Plasmonic Anti-counterfeiting Security Labels Based on Surface-enhanced Raman Scattering

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Materials and Methods:

Materials. IP-L 780 photoresist with refractive index, n≈1.485 and IP-Dip resist with n≈1.52 (Nanoscribe Inc, Germany) were used as a negative photoresist for two photon lithography in direct laser writing (DLW) and dip-in laser lithography (DiLL) configuration, separately. 4-methylbenzenethiol (4-MBT, 98%), rhodamine B isotheocyanate (RhBITC), propylene glycol monomethyl ether acetate, isopropyl alcohol, ethanol were purchased from Sigma-Aldrich chemical company. All chemicals were used without further purification, unless otherwise stated. Milli-Q water (> 18.0 MΩ.cm) was purified with a Sartorius Arium® 611 UV ultrapure water system.

Fabrication of plasmonic anticounterfeiting structures. The fabrication method consists of two parts – the fabrication of a polymeric template, and the deposition of Ag film. To begin, polymeric nano and/or microstructures were fabricated using direct laser writing system (Nanoscribe Inc., Germany). In brief, a droplet of IP-L 780 or IP-Dip monomer drop-casted on a glass substrate was polymerized by a computer-assisted femto second pulsed fiber laser with a center wavelength of 780 nm to form a polymer structure pre-defined by graphic program. The direct laser writing (DLW) and Dip-in Laser Lithography (DiLL) processes were performed using an inverted microscope with an oil immersion lens (100×, NA 1.4), and a computer-controlled piezoelectric stage. The average laser power was around 9 mW for DLW and 6 mW for DiLL. A writing speed of 30 μm/s was used. After writing, unexposed IP-L 780 was removed in propylene glycol monomethyl ether acetate for 30 min, and then washed with isopropyl alcohol for another 30 min.

Metallization of the nanowire arrays. Ag film was deposited on the substrates using a home-built thermal evaporator deposition system. The deposition rate Ag was 0.5 Å/s, which was monitored in-situ by a quartz crystal microbalance. Ag target with 99.99% purity was purchased from Advent Research Materials, UK.

Ligand exchange reactions. Formation of the 4-MBT self-assembled monolayer was performed by incubating the substrates in 100 mM 4-MBT ethanol solution for 6 hours. After that, samples
were removed and rinsed with copious amounts of ethanol, and dried in nitrogen gas. RhBITC functionalization was carried out by immersing the substrates into $10^{-5}$ RhBITC solution for 6 hours and then rinsing with Milli-Q water. The isothiocyanate group (N=C=S) also exhibits affinity for the Ag surface and can be used to prepare a self-assembled monolayer of RhBITC on the second Ag layer with the formation of the Ag-S bond.

**High speed slit-scanning confocal Raman spectroscopy measurements.** SERS spectra and images were obtained with the sample mounted on the 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× NA 0.9). The back-scattered 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 °C, 1340× 400 pixels) at once. At a single acquisition, line-shaped illumination was shone on the sample, where 400 Raman scattering points were 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 reduced the acquisition time for x-y axis Raman mapping to less than half an hour for a 6400 μm² area, as compared to the few hours required when using 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 5 s and 50 μm for 2D Raman imaging. The line scan mode with the resolution of 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 laser from initial y direction to 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 accelerating voltage of 5 kV. 10-nm Pt was sputtered onto substrates to increase their conductivity for SEM imaging.