SUPPORTING INFORMATION:

Fabrication of the Funnel-Shaped Three-Dimensional Plasmonic Tip Arrays by Directional Photofluidization Lithography

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1. Uniformity of photo-reconfigured azopolymer focal conic arrays

The uniformity of photo-reconfigured nanofunnel arrays is clearly discerned by moiré fringe, as shown in Figure S1.

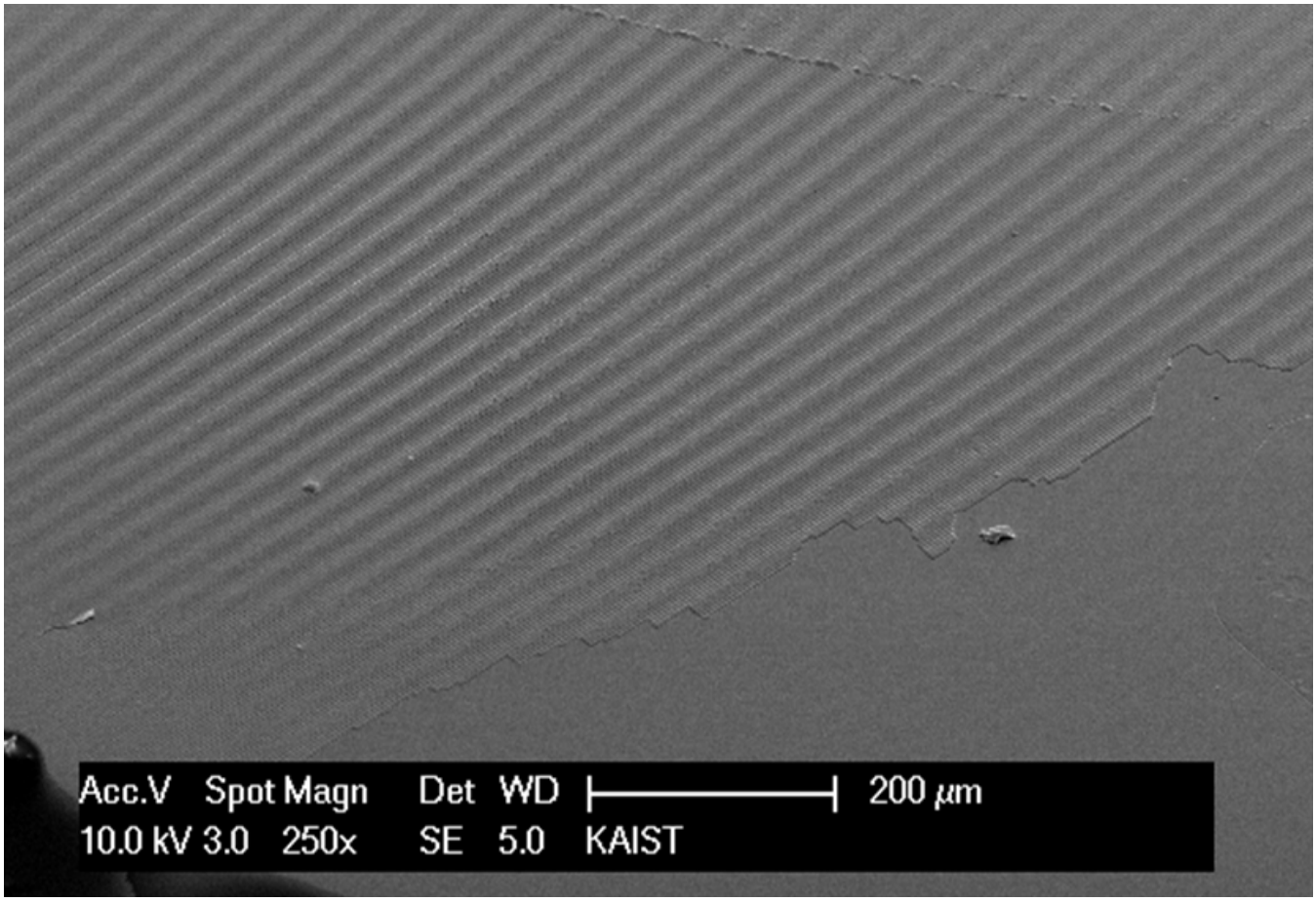

Figure S1. Low magnification SEM image of photo-reconfigured azopolymer hole array. The moiré fringe confirms that the uniformity of obtained structure.

2. Finite-Difference Time-Domain (FDTD) simulation: Theoretical analysis of electrical field enhancement at the surface of plasmonic nanofunnel

To rationalize the electrical field enhancement at the surface of gold-coated plasmonic nanofunnel, a numerical simulation was performed by using finite-difference time-domain (FDTD) method with Yee's discretization scheme.[S1,S2] To obtain the three-dimensional geometry to be simulated, the weighted-average revolution from the AFM profile was performed (see Figure S2). Permittivity data of the gold coated onto the reproduced nanofunnel array was obtained from Palik's book.[S3] Perfectly matched layer

terminates the domain in the vertical direction (z) at 1500 nm, in the horizontal direction (x, y) at 4000 nm.[S4] The computational domain is discretized in 6 nm in the x and y directions and in 4 nm in z direction. Excitation was induced by the irradiation of plane wave, linearly polarized in y direction.

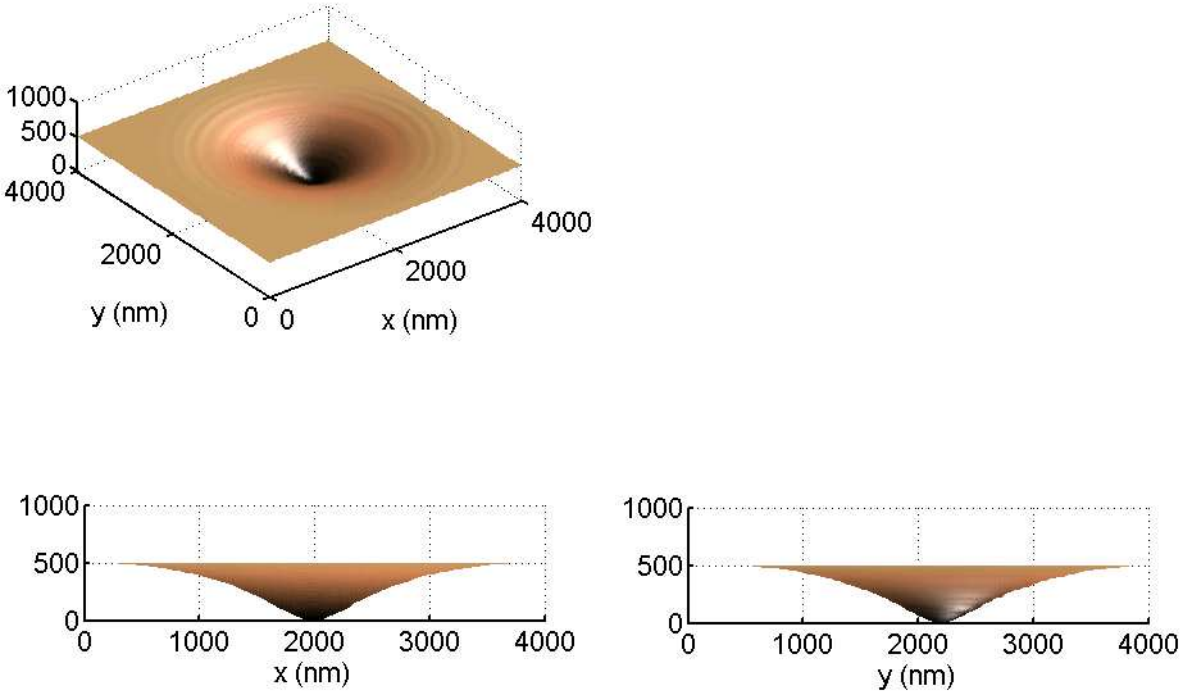

Figure S2. Example of simulated geometry of plasmonic nanofunnel (110 nm tip diameter): three-dimensional geometry (the upper part) was obtained by the weighted-average revolution from the AFM profiles in the x and y directions (the bottom part).

3. Dark-field OM image of methylene blue adsorbed plasmonic nanofunnel array

Methylene blue (MB, Sigma-Aldrich) was adsorbed onto Au-coated (20-nm thickness) plasmonic nanofunnel arrays by incubating in 1 mM ethanolic solution for 4 hr, subsequent rinsing with copious ethanol, and drying under N_2 gas for 2 days. After incubating, the structural integrity of Au-coated plasmonic nanofunnel arrays remained intact, as shown in Figure S3, and they exhibited little fluorescence.

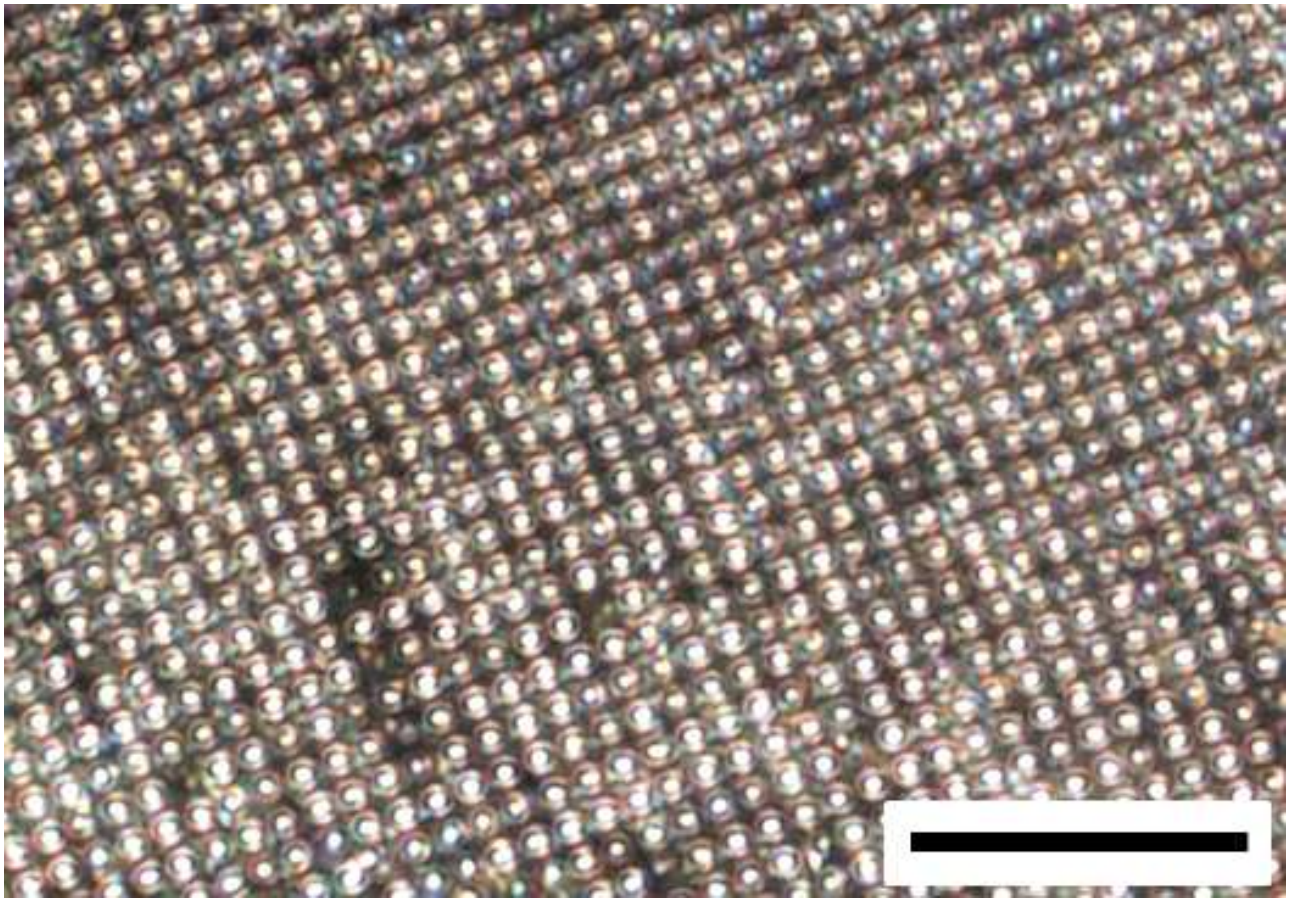

Figure S3. Dark-field OM image of MB adsorbed plasmonic nanofunnel arrays (8 min irradiated, 110-diameter tip). Scale bar is 40 μm.

4. Calculation of SERS enhancement factors (EFs)

Enhancement factors (EFs) were calculated using the intense C-C ring stretch mode approximately at 1628 cm^{-1} shift from both liquid and surface-adsorbed methylene blue (MB) after baseline subtraction, and the equation:

$$EF = \frac{N_{bulk}}{N_{MB,nanofunnel}} \times \frac{I_{MB,nanofunnel}}{I_{bulk}}$$

where N_{bulk} is the number of MB molecules contributing to the bulk liquid (1.0 M) Raman scattering signal, $N_{MB,nanofunnel}$ is the number of MB molecules contributing to the SERS signal; $I_{nanofunnel}$ and I_{bulk} (non-SERS) are the intensities of the scattering band of interest at 1628 cm^{-1} in the SERS and normal

Raman spectra, respectively. The molecular footprint of MB in terms of lateral dimension is around 1.35 nm^2: the size of MB molecule is 1.5 nm in length and 0.9 nm in width.[S5] Thus, the greatest packing density of MB monolayer could be 7.4×10^{13} molecules/cm^2. However, the actual packing density reported in the literature is 1.50×10^{10} molecules/cm^2 (sulfur modified polycrystalline gold deposited by sputter) or 2.55×10^{11} molecules/cm^2 (crystalline (111) gold).[S5,S6] The sulfur-modification of gold can enhance the chemisorption of the MB molecules, but the plasmonic nanofunnel is fabricated by e-beam deposition of bare gold (polycrystalline) onto polymer structure. In line with this, we assume that the greatest amount of MB monolayer contributing to the SERS signal will be 1.50×10^{10} molecules/cm^2. Additionally, the SERS enhancement factors were calculated by considering the surface area defined by the hotspots (~ 0.55 μm^2). To get the $N_{MB,nanofunnel}$ the surface area of plasmonic nanofunnel tip where the electric field is strongly enhanced by plasmonic resonance was obtained from the geometry of the weight-average evolution of two-axis AFM profile data (see Figure S2). Especially, as the incident beam diameter was 1 μm, the surface area was subtracted from the single plasmonic nanofunnel (2 μm in width). The total volume of electric field-enhanced region by surface plasmonic resonance and constructive interference between incident and reflected beams was roughly 5.5 μm^3: this value was calculated from FDTD electric field mapping, used to get N_{bulk}. SERS EFs from plasmonic nanofunnel are determined to be 10^8-10^9.

$$EF = \frac{N_{bulk}}{N_{MB,nanofunnel}} \times \frac{I_{MB,nanofunnel}}{I_{bulk}} = \frac{3.311 \times 10^9}{82} \times \frac{1240}{13} = 3.85 \times 10^9$$

$$N_{bulk} = 1M \times 5.5\ \mu m^2 \times 6.02 \times 10^{23} = 3.311 \times 10^9$$

$$N_{MB,nanofunnel} = 1.5 \times 10^{10}\ (molecules\ cm^{-2}) \times 0.55\ \mu m^2 = 82$$

5. Experimental details

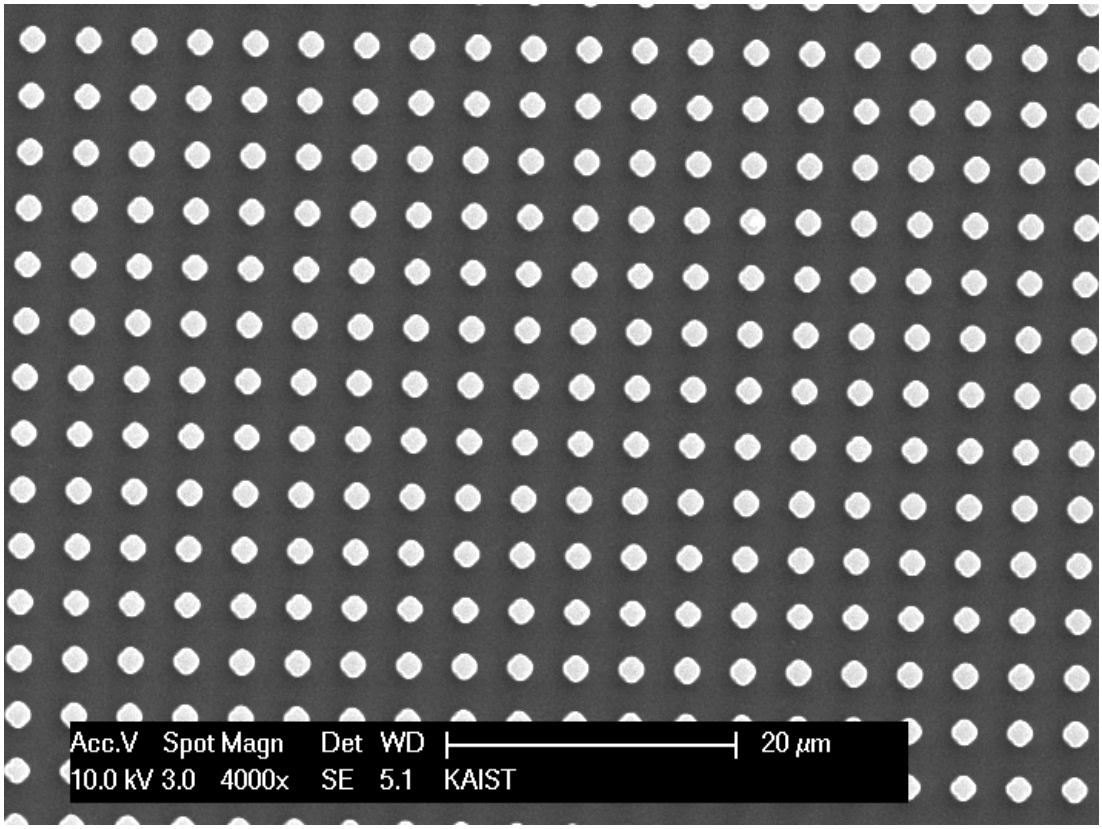

Figure S4. Scanning electron microscope (SEM) image of PDMS molds used in this study.

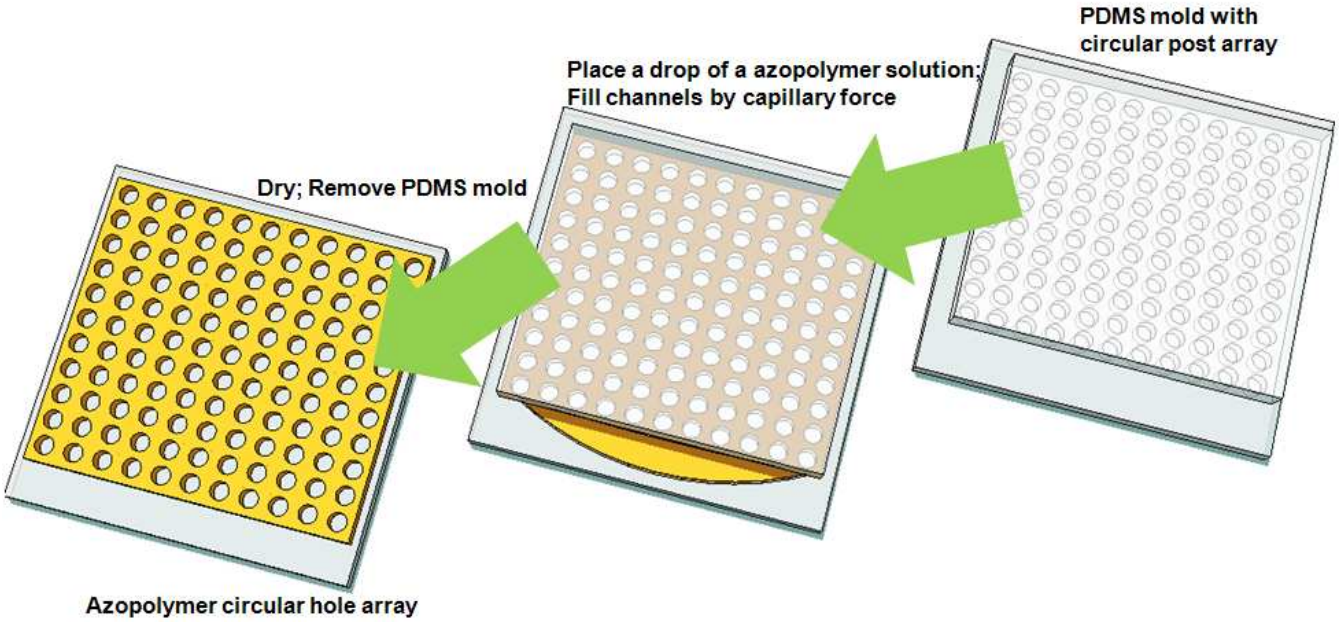

Figure S5. Schematic diagrams of MIMIC using a solvent for the fabrication of the pristine azopolymer

hole arrays.

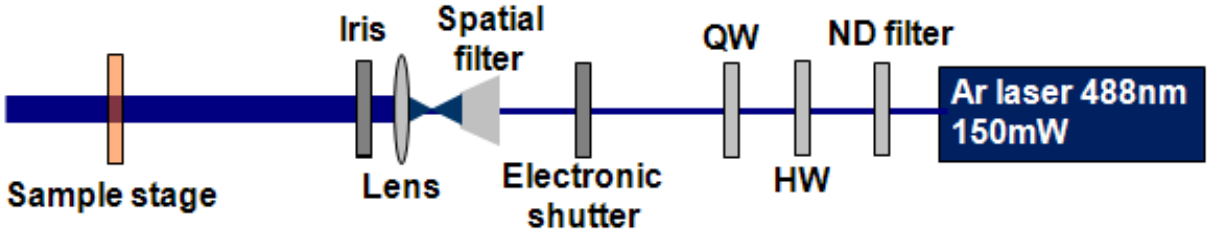

Figure S6. Schematic illustration of optical setup for one-beam irradiation: ND filter – Neutral density filter; HW – Half-wave plate; QW-Quarter-wave plate.

6. Analysis of dark-field OM images and extinction spectra

Measurement of dark-field OM images and extinction spectra

The experimental setup for measuring the dark-field OM images and corresponding extinction spectra is based on that reported by Whitesides et al.[S7] The micro-reflectance system was built on a standard optical microscope (OM, Olympus, BX51): a thermo-electrically cooled CCD detector (DV401A-BC, iDUS CCD detector, Andor technology) was equipped. An unpolarized, spatially filtered 100 W halogen light source (Fiber Illuminator OSL1) was irradiated at an incident angle of 70° (dark-field illumination); this slant irradiation can maximize the optical scattering of the plasmonic nanofunnel arrays.[S7,S8] The scattered light was collected by a 20× microscopic objective lens (Mitutoyo NIR M plan APO, numerical aperture (NA) = 0.42). Finally, the collected light arrived at the spectrometer and CCD. This experimental setup is schematically described in Figure S7.

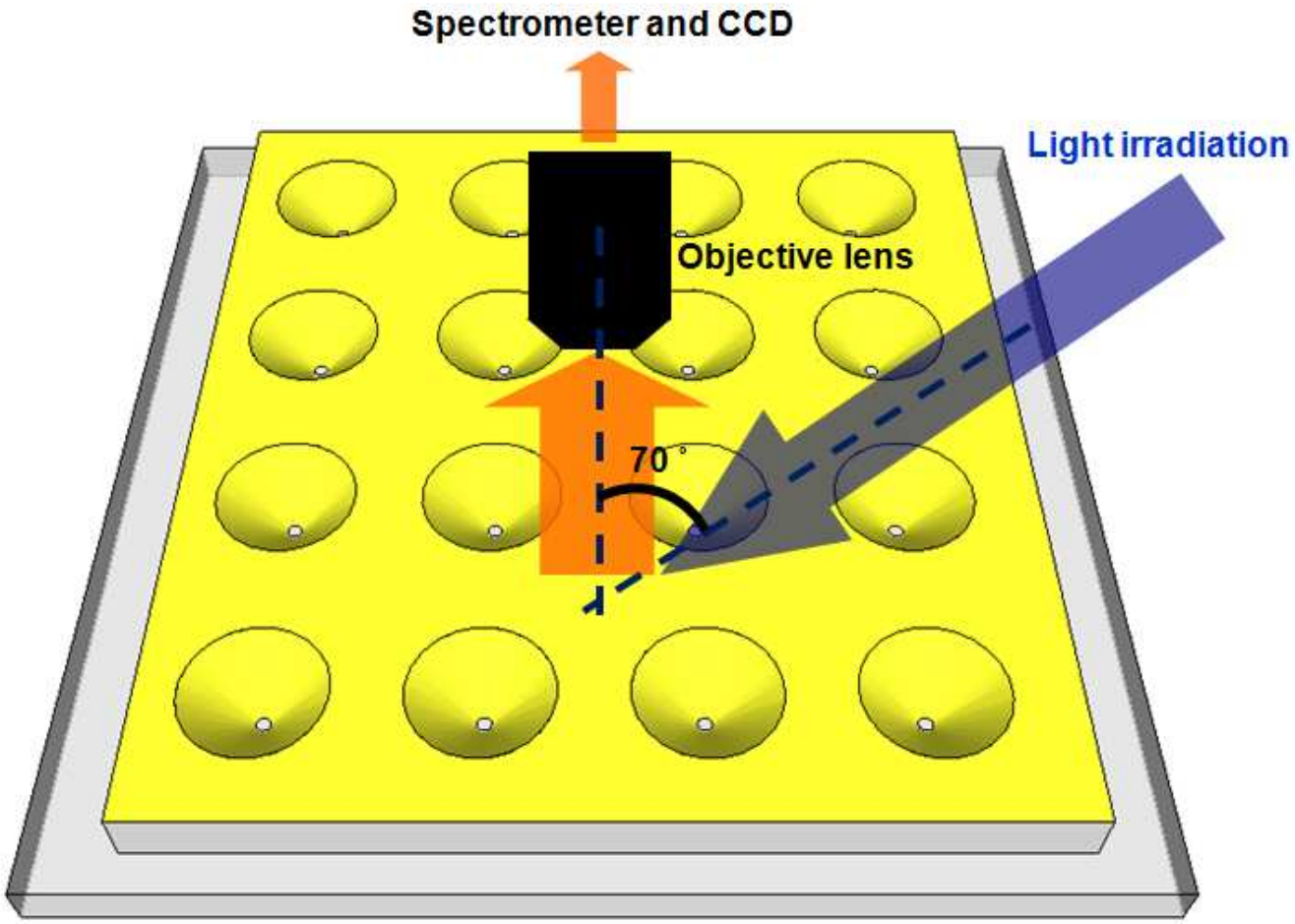

Figure S7. Schematic illustration of the experimental setup used to measure the dark-field optical microscope images and extinction spectra: The incident angle of light was 70° with respect to the normal direction of the substrate.

Measurement of Raman spectra: The experimental setup for measuring Raman spectra is based on epi-illumination as shown in Figure S8. The spectra were obtained by using a linearly polarized 632.8 nm, 50 μW diode laser (Melles Griot) implemented in a home-built micro-Raman system (Ramboss, Dongwoo Optron Co., Ltd) equipped with a thermo-electrically cooled CCD detector: focused beam diameter was 1 μm; the integration time was 3 min. The scattered light was collected by a 100× microscopic objective lens (Mitutoyo, numerical aperture (NA) = 0.9)

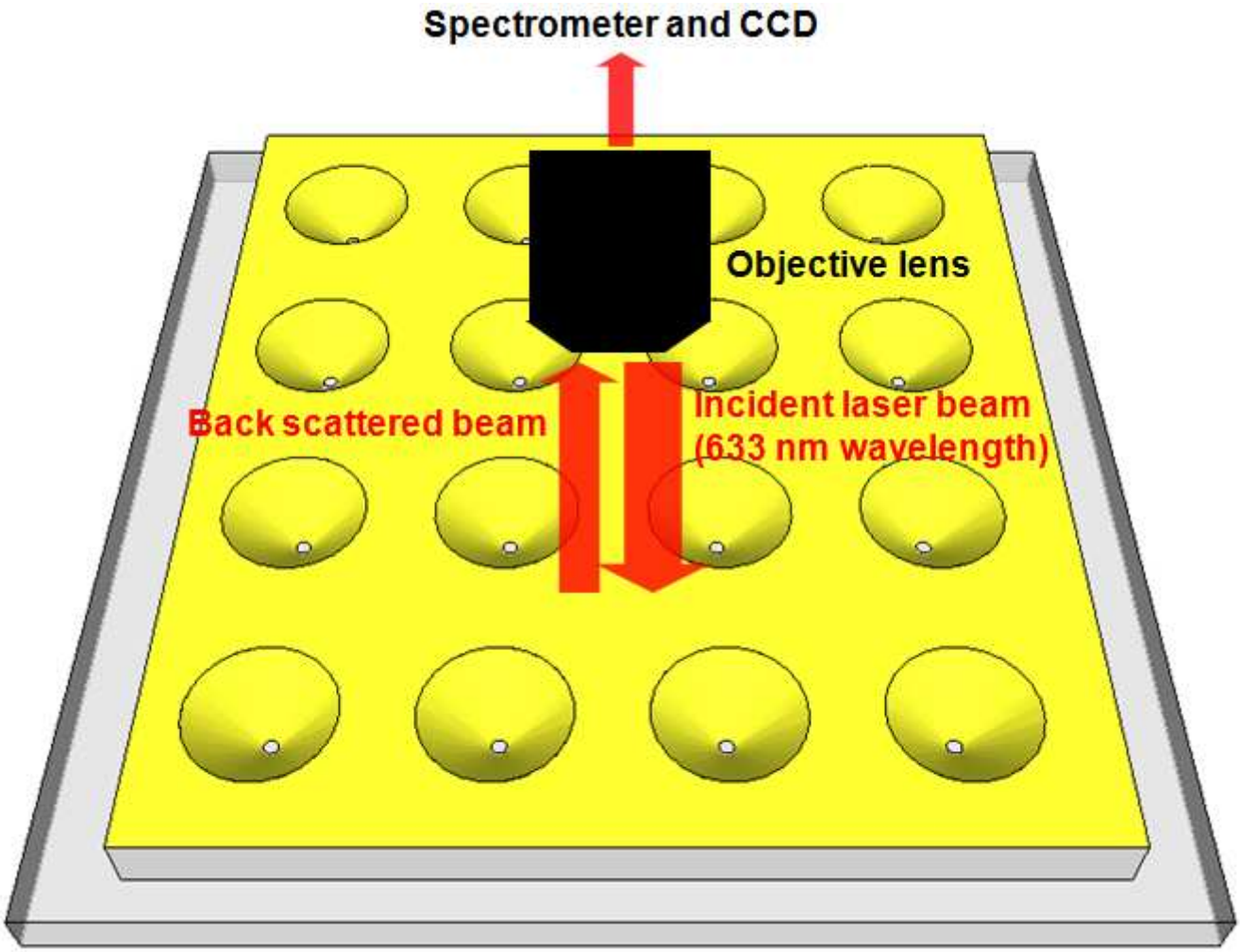

Figure S8. Schematic illustration of the experimental setup used to measure Raman spectroscopy. Our experimental setup is based on back scattering (epi-illumination).

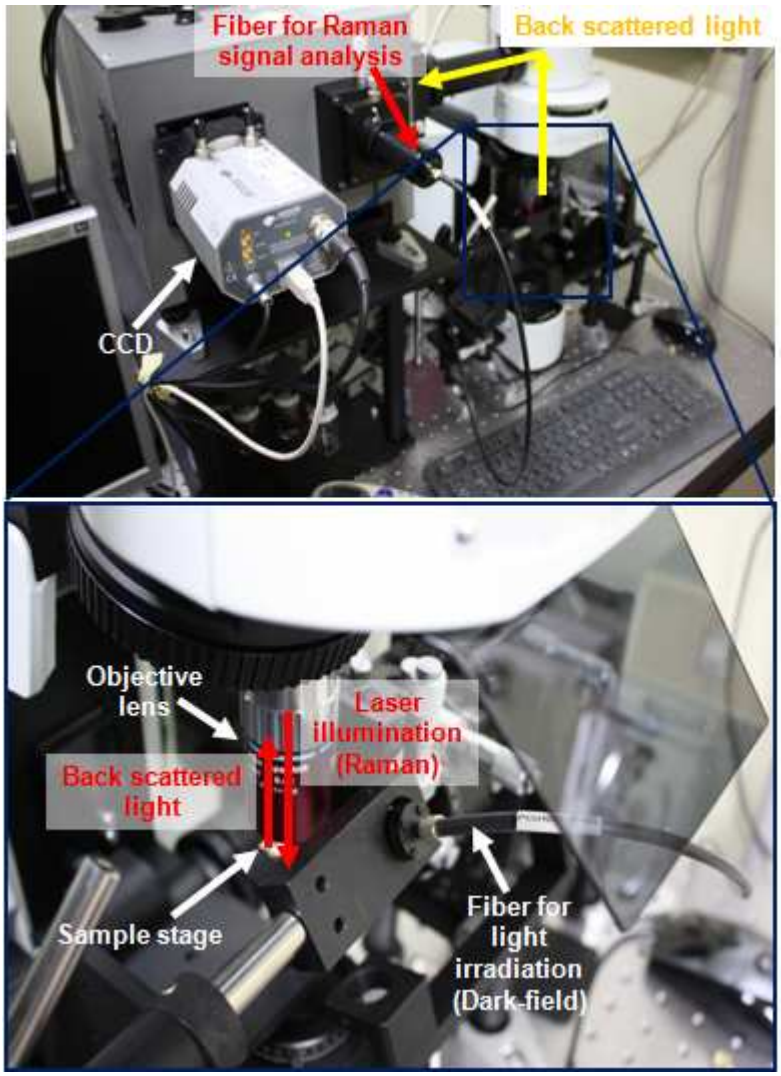

Figure S9. Digital photographs of the home-built experimental setup used to measure the dark-field optical microscope images and their extinction spectra; Raman spectroscopy

Supporting Information References.

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