Electronic Supplementary Information

Surface-enhanced optical-mid-infrared photothermal microscopy using shortened colloidal silver nanowires: A noble approach for mid-infrared surface sensing

Naoki Baden,[a] Hirohmi Watanabe,[b] Masaru Aoyagi,[b] Hiroshi Ujii [c,d,e] and Yasuhiko Fujita*[b]

a. Nihon Thermal Consulting, Co., Ltd., 3-9-2 Nishishinjuku, Sinjuku-ku, Tokyo 160-0023, Japan

b. Research Institute for Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Kagamiyama 3-11-32, Higashihiroshima, Hiroshima, 739-0046 Japan

c. Research Institute for Electronic Science (RIES), Hokkaido University, N20W10, Sapporo, 001–0020 Japan

d. Department of Chemistry, Division of Molecular Imaging and Photonics, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.

e. Institute for Integrated Cell-Material Science (WPI-iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan.

Sample preparation

All chemicals were used without further purification.

Short silver nanowires: A silver nanowire solution, purchased from Sigma Aldrich (product# 778095-25 mL, diameter 120-150 nm, length 20-50 μm), was diluted 16-32 times with isopropanol and sonicated using an ultrasonic cleaner (Branson, model 1510) in a 0.5 mL Eppendorf tube. Sonication was continued until the desired nanowire lengths were obtained (typically 3 h under our experimental conditions).

Silver nanowires on Low-e glass: 20 μL of the shortened silver nanowire solution was spin-cast onto cleaned Low-e glass (MirrIR, Kevley) at 2500 rpm for 60 s.

Silver nanowires on PS/glass: PS pellets (MW=2000) were dissolved in toluene and then 50 μL of PS/toluene solution was spin-cast on a cleaned glass substrate at 2000 rpm for 60 s. The PS film thickness was controlled by the PS concentration. In particular, PS concentration of 1, 3, 5, 8, 10 wt% resulted in PS thickness of about 40, 160, 320, 710, 1000 nm, respectively. Finally, 20 μL of the shortened silver nanowire solution was spin-cast on the PS-coated glass at 2500 rpm for 60 s.

Silver nanowires on PAA/PI: Polyimide (PI) film (Kapton 100H (thickness 25 μm), Toray Dupont) was cut into 10 x 20 mm and soaked into 20 mL of 0.5 M KOH solution for the target time 't'. During the reaction, the temperature of the solution was kept at 30 °C. After the reaction was completed, the PI film was removed from the solution, immediately washed with an excess amount of milliQ water, and blow-dried with N_2 gas. Finally, the film was attached to a glass slide with double-sided adhesive tape, and the shortened silver nanowire solution was spin-casted at 2500 rpm for 60 s.

Measurements/Analysis

Structural analysis: Structural characterization (i.e. nanowire width/length, coating layer thickness, etc) was performed using a scanning electron microscope/EDX (SU9000, Hitachi), a digital microscope (VH-X7000, Keyence), a laser microscope (VK-X3000, Keyence), an ultramicrotome (EM-FC7, Leica), an ion-beam slicer (IB-09060CIS, JEOL), an imaging FT-IR (Hyperion, Bruker), and an atomic force microscope (Dimension IconIR, Bruker).

FDTD simulation: 3D-FDTD simulation was performed using a commercial FDTD software (Lumerical FDTD, Ansys). The silver nanowire was modeled as a cylindrical structure with rounded ends. The optical constants, nanowire diameter, mesh size, and incident beam were set to Ag (Palik, 1-10 μm), 100 nm (end radius 50 nm), 2.5

nm, and Gauss (N.A. 0.6), respectively. The E-field distribution image of the surface normal plane was obtained to analyze the antenna responses (E-field intensity, width, mode, etc.).

Optical-MIP measurements: A commercial MIP (O-PTIR) system (mIRage™, Photothermal Spectroscopy Corp., Santa Barbara, CA, USA) was used for optical-MIP measurements. Briefly, pulsed mid-infrared laser light (=pump) from a quantum cascade laser and 532 nm laser light (=probe) from a diode laser were co-focused onto sample surface by a Cassegrain objective lens (Pike, 40x 0.78 N.A.). The irradiated area of the pump and probe is around 10 um and sub-um, respectively. The pulse width of the pump laser was set to 500 ns with the duty cycle of 5% (pulse rate 100 kHz) unless otherwise stated. This measures the thermally diffused photothermal response and allows for the detection of enhanced MIP signals at the center of the nanowire. The laser power of the pump and probe light was adjusted in the range of 2-6 mW/cm^2. The pulse width (duty cycle) was occasionally changed to 160 ns (1.5 %) to reduce the thermally-diffused components and to minimize laser-induced sample damage. The reflectance change of the probe laser upon pump-irradiation was lock-in detected by a Si photodetector (Gain: x10) and plotted against the pump IR laser frequency to obtain an optical MIP spectrum. Background was measured on Low-e glass with >30 times averaging. The MIP spectrum was obtained with a QCL scan speed of 100 cm^{-1}/s (2 cm^{-1} step) with >5 times averaging. The length of the nanowire was estimated from a bright field optical microscope image with an accuracy of 100 nm.

Software: ImageJ 1.54d and IgorPro 9.05 were used additionally to the software equipped to the instruments.

Supplementary figures

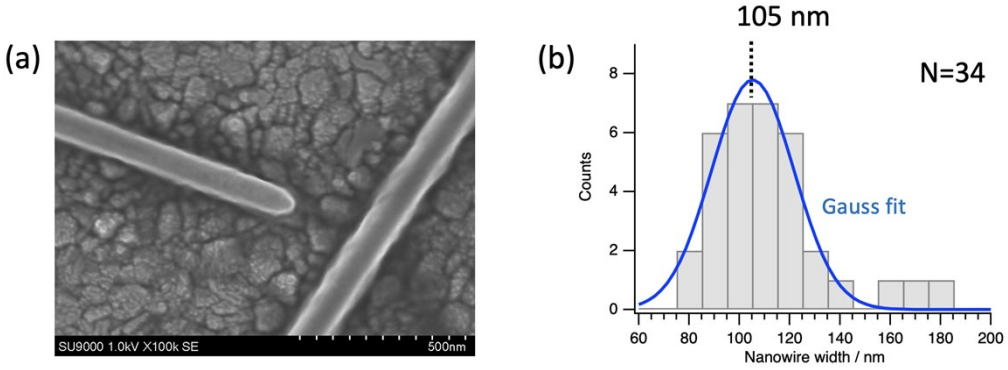


Figure S1. SEM image and width histograms of original silver nanowires before the sonication process. 34 silver nanowires spin-cast on an ITO substrate were measured by SEM and subjected to width-histogram analysis.

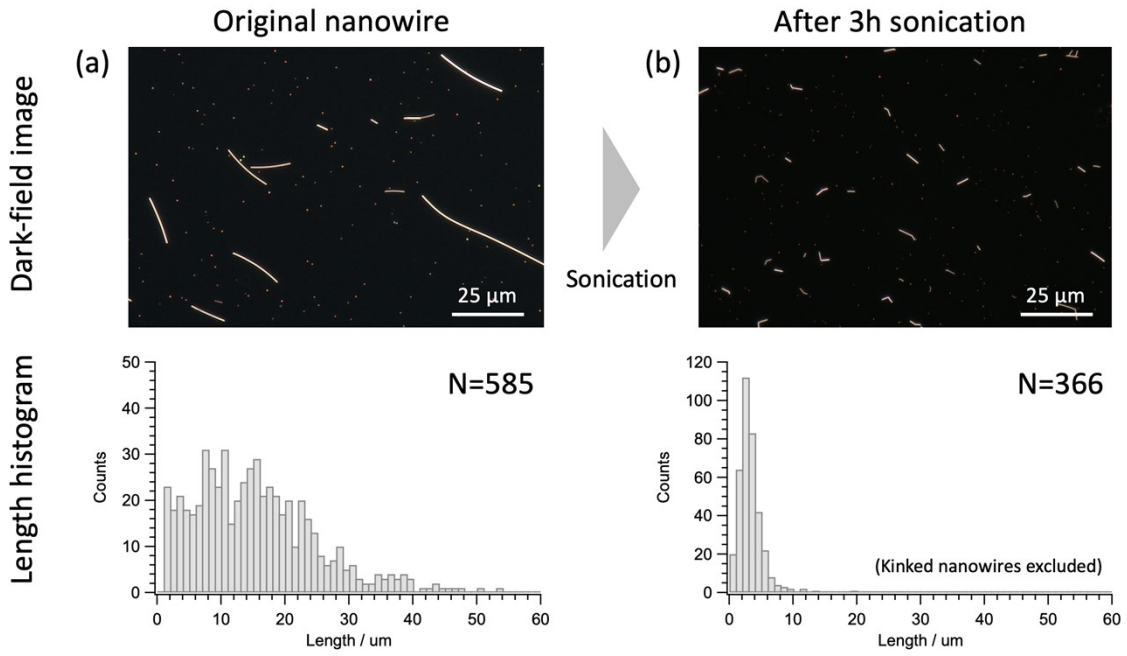


Figure S2. Dark-field optical image and length histogram of silver nanowires before (a) and after (b) the sonication process. In both cases, 10 dark-field images (view size: 303 x 227 μm) were randomly obtained and the length of the nanowires was statistically analyzed by particle analysis using ImageJ software. The number of nanowires subjected to the histogram analysis are N=585 (before sonication) and N=366 (after sonication). Note that kinked nanowires observed after the sonication were excluded from the histogram analysis.

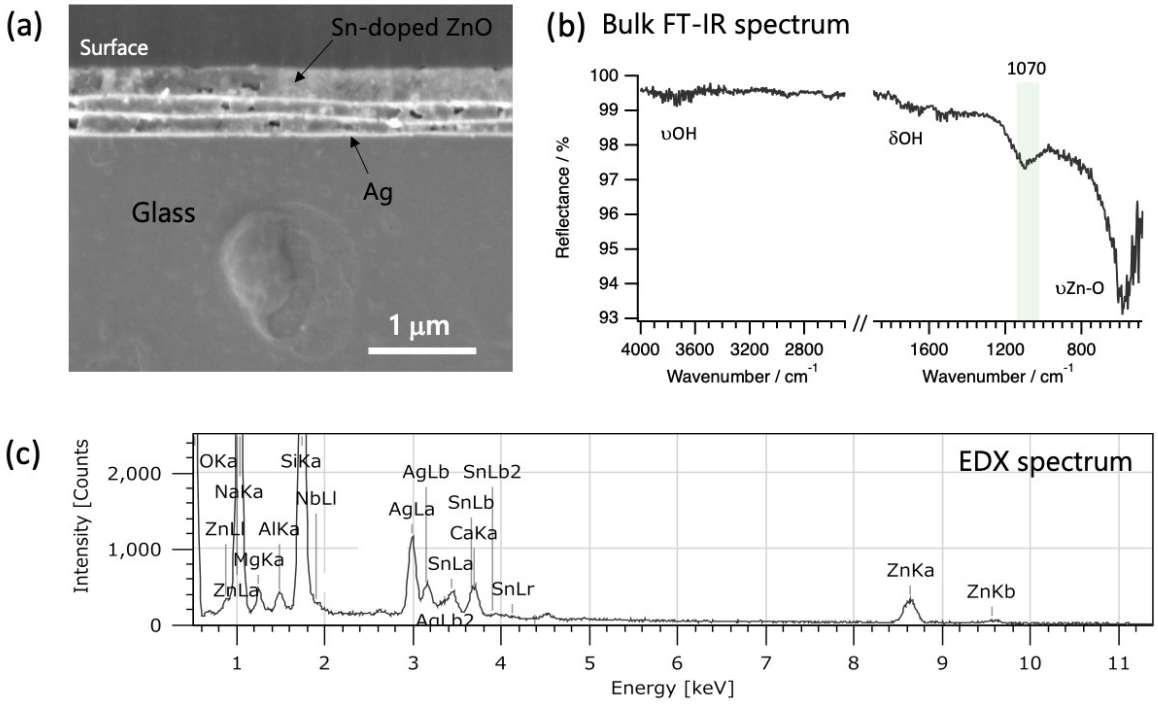


Figure S3. Structural analysis of Low-e glass. (a-c) Cross-sectional SEM image (a), mid infrared reflectance spectrum (b), and EDX spectrum (c) of Low-emissivity (Low-e) glass.

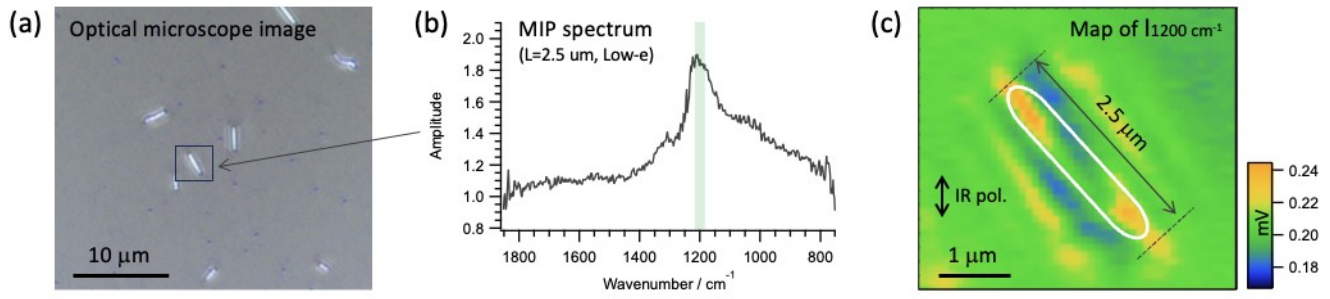


Figure S4. Plasmonic mode assignment of the cavity resonance. (a) A bright-field optical microscope image of silver nanowires on a Low-e substrate. (b) MIP spectrum of the silver nanowire (L=2.5 um) marked as a square in (a). (c) IR mapping image at the cavity resonance wavenumber of 1200 cm^{-1}. Note that the QCL pulse width was reduced to 100 ns to improve image contrast by suppressing thermally-diffused IR components. The direction of IR polarization is indicated by an arrow in (c). On the nanowire, higher intensity was observed at both distal ends of the nanowire, representing the cavity resonance of a fundamental mode (m=1).

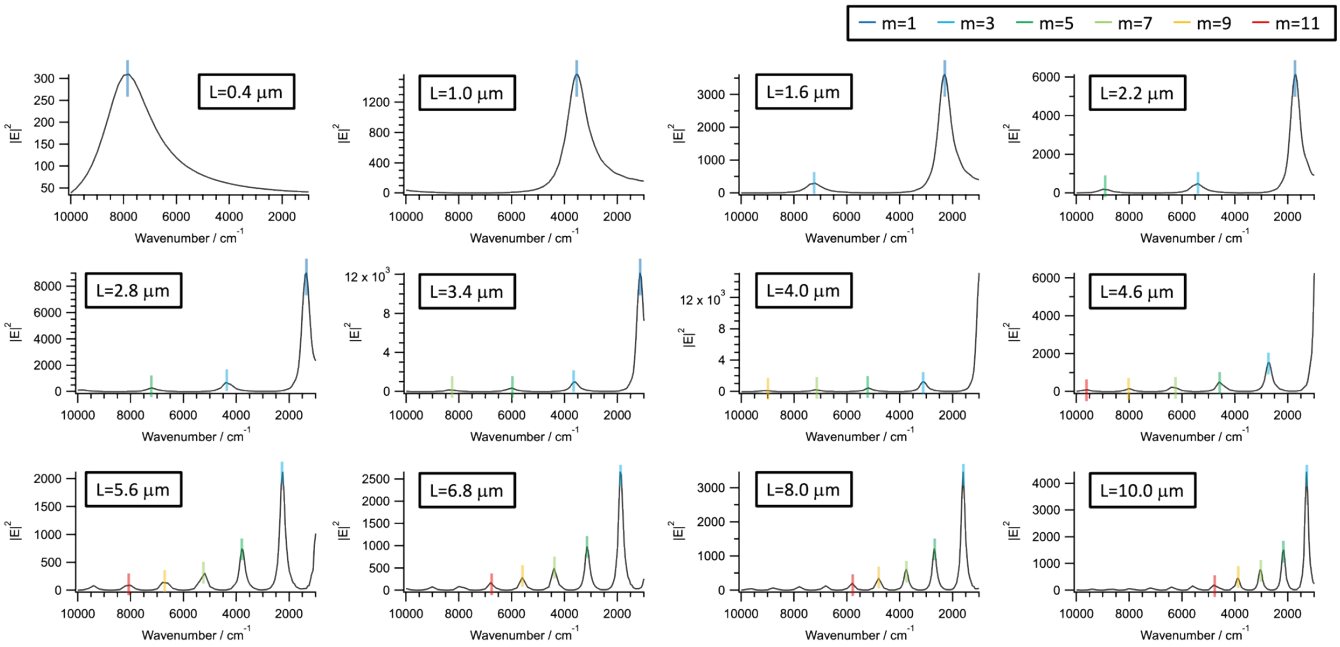


Figure S5. Simulated $|E|^2$ spectrum of silver nanowire (diameter: 100 nm) with different wire length.

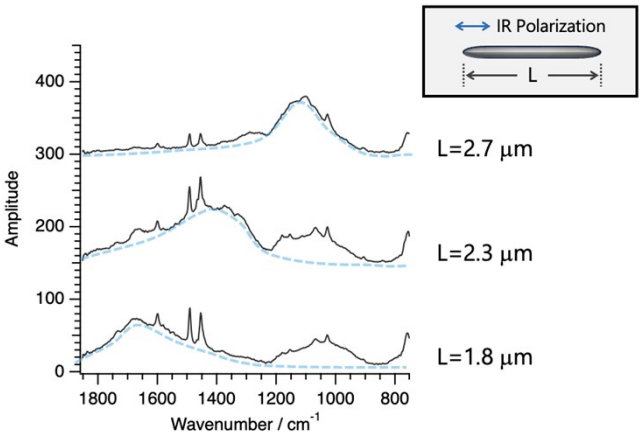
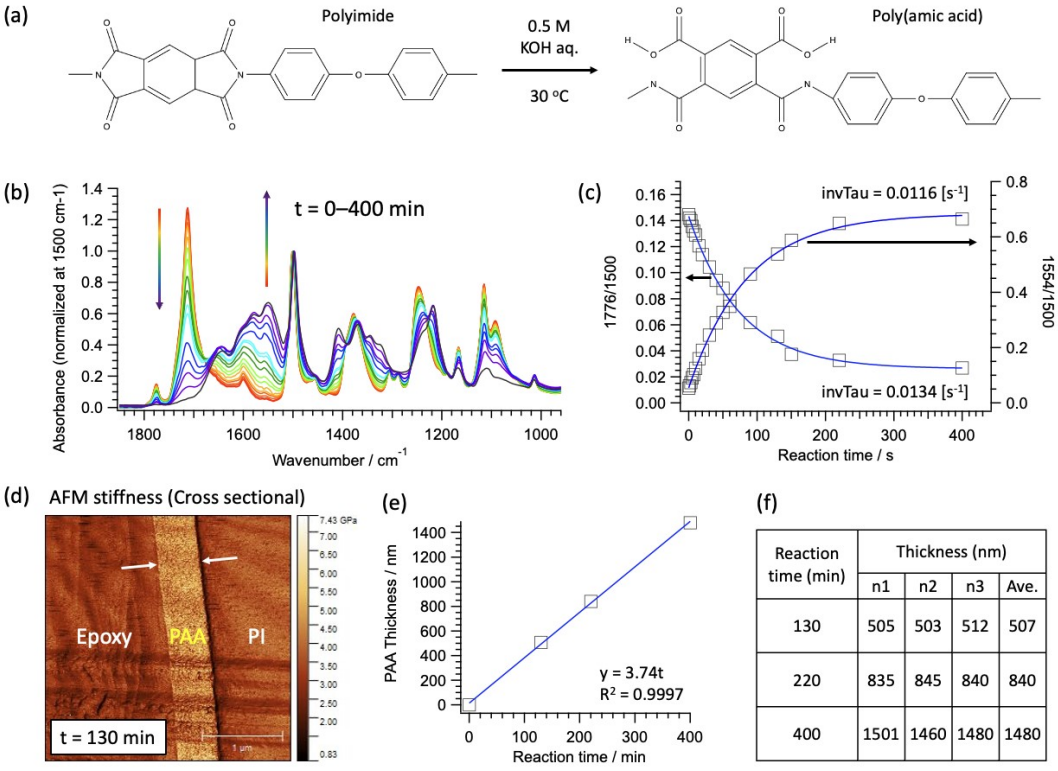


Figure S6. Optical-MIP spectrum of PS/glass (PS thickness: 1000 nm) obtained on silver nanowire with different lengths (L=1.8, 2.3, 2.7 um). The blue dotted lines correspond to the background increase due to the cavity resonance of the nanowire.



Reaction time (min)	Thickness (nm)			
	n1	n2	n3	Ave.
130	505	503	512	507
220	835	845	840	840
400	1501	1460	1480	1480

Figure S7. Structural characterization of PAA/PI films. (a) Reaction scheme of alkaline-treatment of polyimide (PI). (b) ATR-FTIR spectra of PI films with the reaction time of t = 0-400 min. A Ge prism with a liquid N_2-cooled MCT detector was used for the ATR-FTIR measurements. (c) A plot of I_{1776}/I_{1500} (for PI) and I_{1554}/I_{1500} (for PAA) as a function of the reaction time. Blue lines represent the result of a single exponential fit. (d) Cross-sectional AFM stiffness image of the etched film (t=130 min). PI films were embedded in epoxy resin and cross-sectional specimens were prepared using an ultramicrotome. AFM stiffness measurements were performed using a peak-force quantitative nanomechanical mapping (PF-QNM) mode with a tip-view Si cantilever (OMCL-AC160TS, Olympus). (e) A plot of AFM-measured PAA thickness (average of n=3) as a function of the reaction time. The AFM-measured PAA thickness is summarized in table (f).

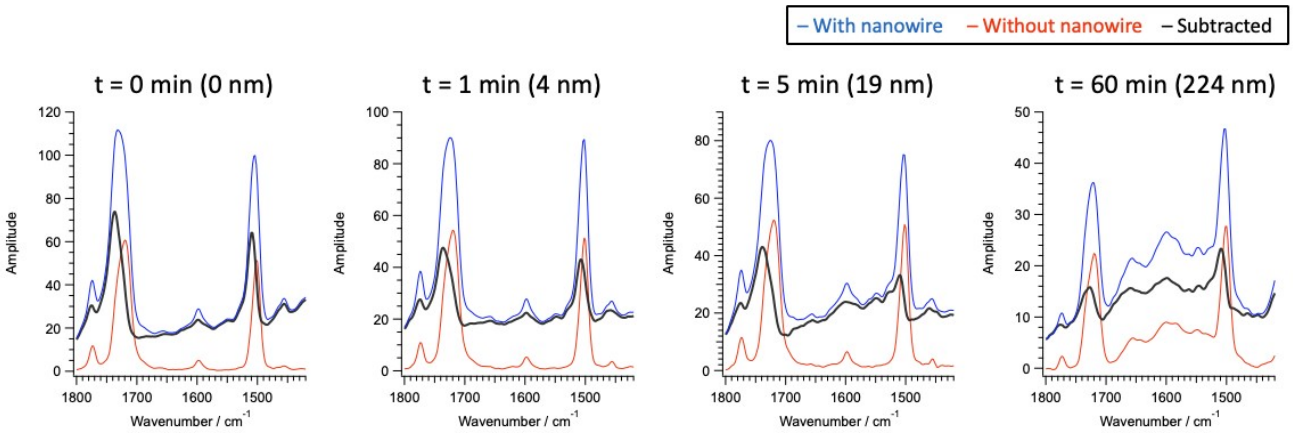


Figure S8. Optical MIP spectra of PI films with the reaction time of 0, 1, 5, and 60 min. Blue, red, and black curves represent the spectrum obtained with nanowire, without nanowire, and by subtraction of these two spectra. The peak position difference around 1720 cm^{-1} between with and without nanowire is commented in the main text.