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Supporting information

Silver nanowire-based tip suitable for STM tip-enhanced Raman scattering

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Experimental

Materials. Silver nitrate ($AgNO_3$), gold(III) chloride trihydrate ($HAuCl_4$), sodium citrate, polyvinylpyrrolidone (PVP), copper(II) chloride ($CuCl_2$), ethylene glycol (EG), potassium hydroxide (KOH), and ethanol were purchased from Sigma-Aldrich and used without further purifications.

Synthesis of AgNWs . The AgNWs were synthesized using the polyol method as reported before.[1] Briefly, after heating up 5 mL of 0.15 M PVP solution in EG at 150 ˚C for 15 min, 40 μL of $CuCl_2$ (4 mM) solution in EG was injected, followed by adding 2.5 mL of $AgNO_3$ EG solution drop-wisely under magnetic stirring (600 rpm). Then the solution was kept at 150 ˚C for another 1.5 h, obtaining high-yield AgNWs. These AgNWs were then washed with ethanol for three times. Average diameter and length of AgNWs are 90±10 nm and 10±2 μm, respectively.

Attachment of the AgNWs onto W tip. W tips were fabricated by applying AC 10 V between W wire (ø 0.25 mm, Nilaco) and carbon rod in 1 M KOH solution,[2] Afterwards, the W tips were rinsed with ethanol and Milli Q water (18 MΩ, Millipore) and immediately subjected to the AC-DEP process. AC-DEP process was performed using ring-shaped Pt/Ir (=9:1) wire (ø 0.2mm, Nilaco) as a counter electrode. A W tip was immersed inside the counter Pt/Ir ring filled with AgNWs ethanol/water solution. AC-DEP was carried out for about 1 second with an operating voltage of 10 Vp-p at 1 MHz. The AgNWs-attached W tip was slightly heat up with a hot plate (100~200 ˚C) for several minutes and gently rinsed with ethanol solution and then dried with N_2 gas. Optical microscope or scanning electron microscope (SEM) (Hitachi, S-4300) was used to confirm the attachment of AgNWs on the W tip.

Preparation of gold nanoplates on graphite. Gold nanoplates were synthesized using citrate reduction method.[3] Briefly, 1.14 mL of 25 mM $HAuCl_4$ solution and 11 mg of citric acid were added to 96.2 mL milli Q water. The solution was kept at 3 ˚C for 3 days. These Au nanoplates were deposited onto a graphite surface from the solution using centrifugation.[3,4] This sample was used to estimate the tip radius.

Preparation of Au(111) substrate for TERS measurements. Au(111) substrate (Alliance Biosystems) was annealed with bunzene flame and rinsed with milli Q water several times, and then chemically modified by immerging it into an ethanol solution of 1 mM benzene thiol for 3 hours. Afterwards, this modified Au(111) substrate was rinsed with ethanol and water carefully and blow dried with N_2 gas. This substrate was used as a standard sample to evaluate the TERS activity of the AgNWs tip.

STM and TERS measurements. Atomically resolved STM imaging and TERS measurement were performed with SOLVER P-47 (NT-MDT) and NTEGRA (NT-MDT), respectively, or both simultaneously with OmegaScope™ 1000 (AIST-NT). TERS tip was approached to sample surface with an angle of 45˚. 632.8 nm light from a He-Ne laser (Research Electro-Optics) was focused onto the apex of the AgNW-tip from top side through an objective (MITUTOYO, BD Plan Apo 100x, N.A. 0.7). Power density at the tip apex was about 150 kW/cm^2. Raman scattering was collected with the same objective and directed to a Raman spectrograph (SolarTII, MS-3501I) equipped with a cooled-charge coupled device (CCD) camera operated at -85 ˚C (Andor technology, DU420) through a dichroic mirror (Semrock, LPD01-633RU) and long pass filter (Semrock, LP02-633RU). Accumulation time for each spectrum was 10 s. All the measurements were carried out under ambient conditions and at room temperature.

Supporting figures

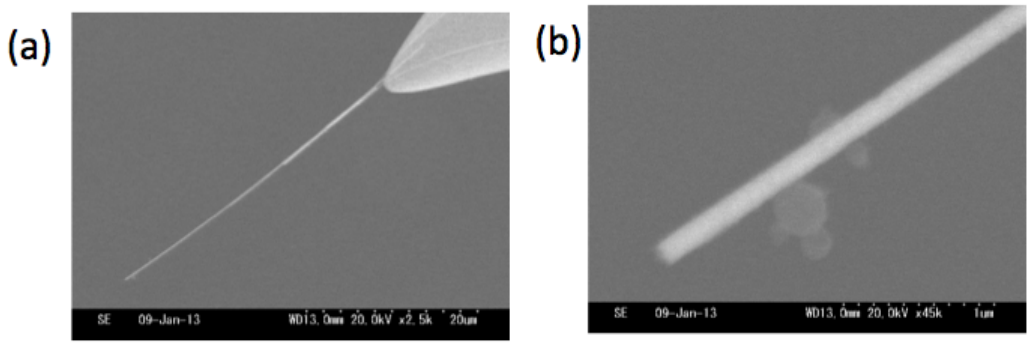

Fig. S1 SEM images of the AgNW-tip shown in Fig. 1 after STM scanning

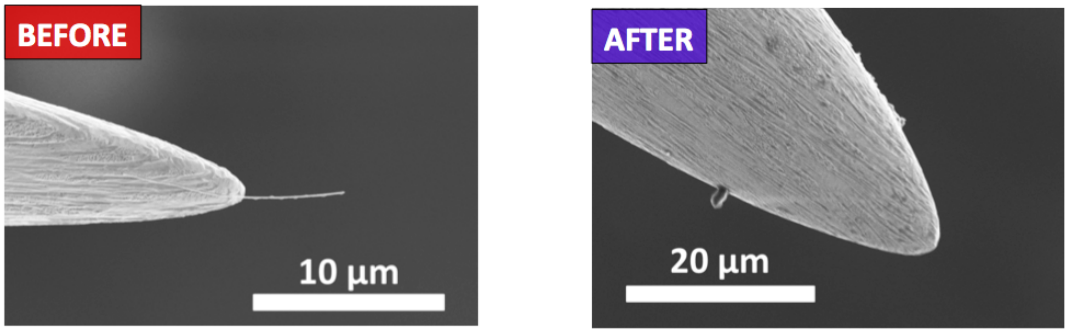

Fig. S2 SEM images of the AgNW-tip, that is attached with only single NW, before (left) and after (right) STM scanning.

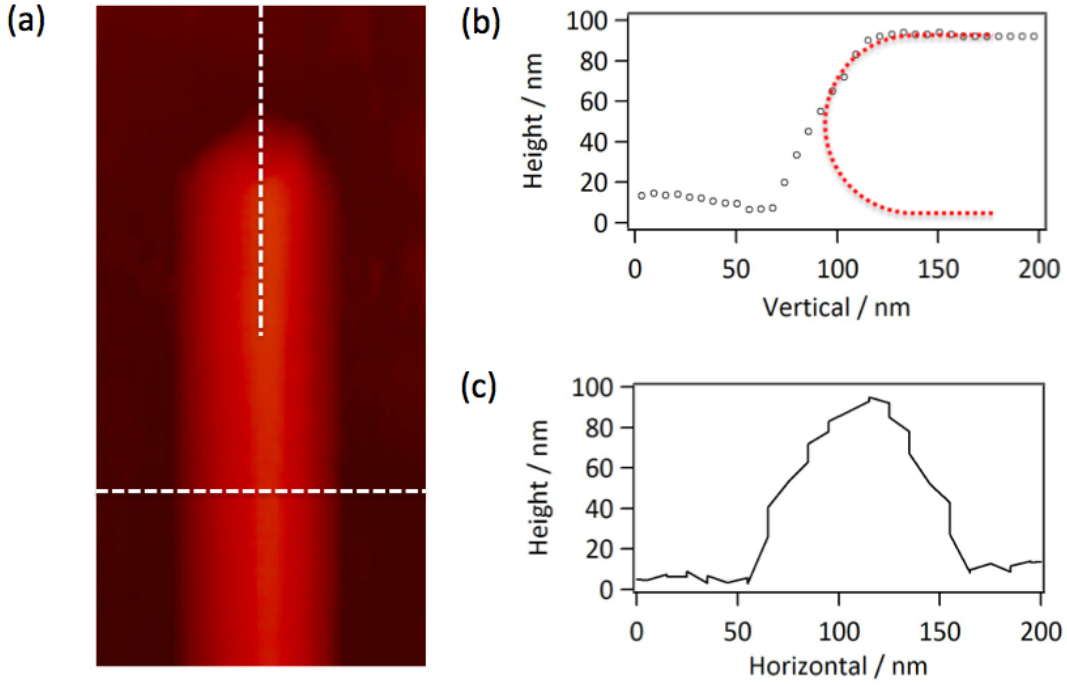

Fig. S3 (a) Typical STM topographic image of the AgNWs used in this study; (b) line profile at the end of the NW along the vertical white dashed line in (a); (c) Line cross section of the NW along the horizontal white dashed line in (a).

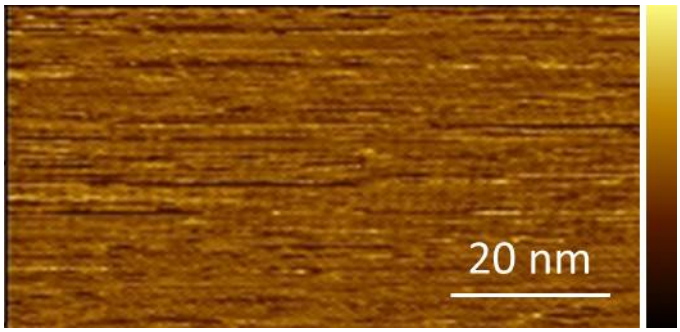

Fig. S4 Typical STM image of benzenethiol-modified Au(111) taken by the AgNW-tip. The colour bar: 0 – 4 nm (constant current mode at 1 nA and 0.1 V).

References:

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