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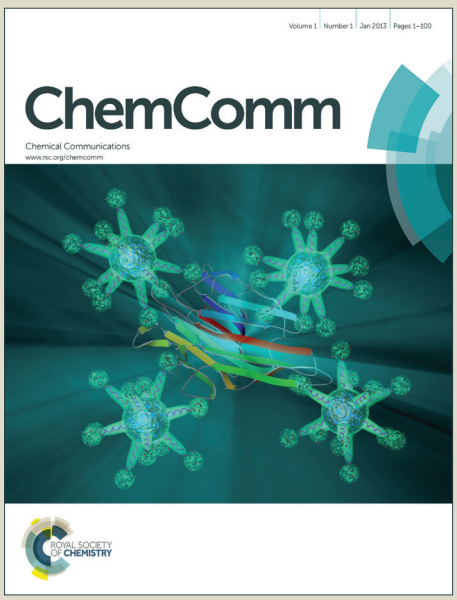

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Silver nanowire-based tip suitable for STM tip-enhanced Raman scattering

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Chemically synthesized silver nanowire was used for atomic-resolution STM imaging and tip-enhanced Raman scattering (TERS) spectroscopy, yielding excellent reproducibility. This TERS tip will open a new venue to surface analysis, such as molecular finger printing at nanoscale.

Obtaining both of chemical and morphological information at nanometre scale is of vital importance in nano-science and nanotechnology. Tip-enhanced Raman scattering (TERS) microscopy[1] is a promising surface sensitive technique that combines two concepts, i.e. chemical finger printing by surface enhanced Raman scattering (SERS)[2] and high spatial resolution atomic/molecular imaging of scanning probe microscopy (SPM), such as scanning tunnelling microscopy (STM) and atomic force microscopy (AFM).[3] In TERS measurement, a laser beam is focused onto a sharpened metal or metal-coated tip. Excitation of surface plasmon polaritons (SPPs) at the apex causes confinement and localization of electromagnetic field, resulting in a massive enhancement of Raman scattering (c.a. SERS effect). As a result, chemical information of a surface can be obtained underneath the tip end at nanometre scales.

Since the reproducibility of TERS mainly depends on the tip, the tip shape needs to be carefully controlled. On one hand for AFM-based TERS, deposition of noble metals on top of AFM tips or direct fabrication of AFM probes using nanolithography, such as electron beam lithography, are often employed.[4] On the other hand, electrochemically etched gold or silver wires have been widely used in STM-based TERS spectroscopy.[5] In these methods, however, precise control of the shape and the crystallinity of the metal(ized) tips still remain difficult, causing the low reproducibility of TERS experiments. Especially, chemically etched tips are often rough and even contain metal clusters on their surface, which lead to Raman hot-spots at undesired positions[6] and/or introduce additional background emission that often obscures Raman signals.[7]

Wet-chemically synthesized silver nanowires (AgNWs) are promising candidates as a TERS tip material because of their good crystallinity and atomically flat surface.[8] Y. You *et. al.* recently reported a method to attach AgNWs on a tungsten (W) tip (referred as to AgNW-tip) and performed SERS using the tip.[9] To the best of our knowledge, however, SPM operation using AgNW-tip with a feedback loop to maintain tip-sample distance has not been reported, which is most likely due to the poor conductivity and the low mechanical strength of the attached AgNWs on the W-tip, leading to unstable STM/AFM operation.

In this contribution, we report a modified You's method, suitable for stable STM imaging and TERS spectroscopy. By increasing the number of AgNWs at the connecting point on a W tip apex, the electric contact and the mechanical strength have been improved, which made it possible to perform atomic-resolution imaging and topographic imaging with less pronounced tip-sample convolution effects. TERS activity remained on the modified AgNW-tips, which is promising for TERS imaging applications.

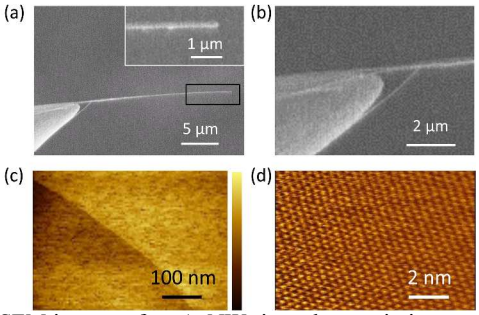

Fig. 1 (a) SEM images of an AgNW-tip and zoom in images of its end (inset). (b) The multiple AgNWs attachment on a W tip apex. (c) An STM image of graphite step edge (the colour bar: 0 - 2.5 nm). (d)

Atomic-resolution image of graphite lattice (constant height mode, tunnelling current: 2 nA, bias voltage: 0.1 V).

AgNWs were attached on an electrochemically etched W-tip by using the alternating current-dielectrophoresis (AC-DEP) method[10] in ethanol/water solution of AgNWs. Addition of water in the solution increased the success rate of AgNW attachment up to nearly 100 % and eventually strengthened the attachment[11]. The fabricated tip was occasionally annealed at 100 - 200 ˚C. AC-DEP[12] at silver concentration of ~0.04 g/L in NW synthesis (~2.5 x 10^{10} NW/L) led to attachment of multiple NWs at a W-tip apex (Fig. 1b). Note that a single AgNW could be exposed at a distal end by quickly lifting up the tip form the solution during the AC-DEP (Fig.1a and the inset).

Figure 1c and 1d display STM images of graphite step edges and atomically resolved graphite lattice measured with the AgNW-tip shown in Figure 1a, respectively. Note that all the experiments in this paper were performed at the solid-air interface in ambient condition. The multiple AgNWs attachment at the W-tip apex seems to be a key to the stable STM operation as the conductivity and mechanical strength at the joint increase. Importantly, unlike electrochemically etched Ag or Au tip, atomic resolution can be easily achieved using the AgNW-tip with a relatively high yield (> 30% of tips provided atomic resolution). After scanning surface, no obvious damage of the AgNW-tip apex was confirmed (Fig. S1), implying enough electric conductivity to maintain the tunnelling current.

In contrast, AC-DEP fabrication at low concentration of Ag NWs (~0.004 g/L) often resulted in a single AgNW attachment (Fig. S2a). Such a tip did not provide stable STM operation and often lost the AgNW during scanning implying the low conductivity and/or the low mechanical strength (Fig. S2b).

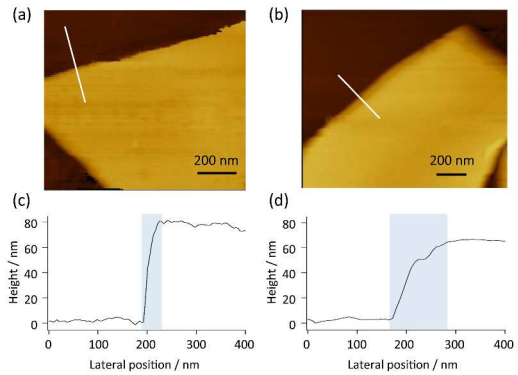

Fig. 2 (a) STM image of Au nanoplates fixed on graphite scanned with AgNW-tip (a) and chemically etched W conical tip (b) (constant current mode at 0.1 nA and 0.5 V). The line profiles along the white lines in (a) and (b) are shown in (c) and (d), respectively. The light blue regions indicate the region of the tip-convolution effect.

Another advantage of metal nanowire is its simple dimension. Topographic images of SPM always include effect of tip-sample convolution, which gives rise to artefactual images especially of large objects. Since the apex shape of etched metal tips differs from tip to tip and is not always symmetric, the tip effects become complicated. Since the AgNWs have a simple 1D pentagonal cross section,[8] the artefact must be less pronounced.

Fig. 2a represents an STM topographic image of ~80 nm-height gold nanoplates[13] scanned with an AgNW-tip. Since the basal plane of the plate is {111} facets and the sides consist of {110} facets, the nanoplates have steep edges.[14] The STM image taken with the AgNW-tip yields an edge width of ~ 40 nm (Fig. 2c), which well corresponds to the radius of the AgNWs used in this study (Fig. S3). Note that the tip effect is rather simple, as the edge appears to be a linear slope. As a comparison, the gold plates were imaged using a conical W tip (Fig. 2b). The tip effect is much larger (> 100 nm edge width in Fig. 2d) and yields a complex convolution; the slope at the edge is no longer straight but consists of multiple steps (c.a. ghost image).

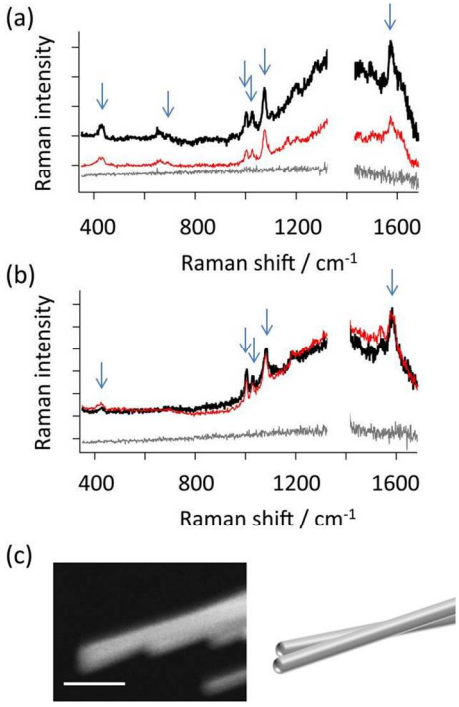

Fig. 3 TERS spectra excited at p-polarization (black line) and polarization (red line) taken with a single NW (a) and a bundle of two NWs (b) at the tip end. The weakest spectra plotted with grey lines in (a) and (b) represent Raman spectra of benzenethiol on Au(111) without the AgNW-tips. Vertical lines represent Raman peaks which assigned to benzenethiol. (c) A SEM image of the bundled AgNWs-tip (scale bar: 250 nm) (left) and a schematic drawing of the end structure (right).

TERS activity of the AgNW-tip was evaluated on a benzenethiol-modified Au(111) surface (typical STM image is shown in Fig. S4). Reproducibility is indeed excellent in the sense of TERS activity, as almost all the AgNW-tips yield TERS activity (Fig. 3), which is not the case for chemically etched Au or Ag tips. The Raman peaks at 420, 700, 999, 1023, 1072, 1572 cm^{-1} are clearly resolved in the spectra, which can be assigned to the vibrational modes of C-S stretching, C-H out-of-plane deformation, a mixture of S-H bending and in-plain ring deformation, in-plane ring deformation, a mixture of C-S stretching and in-plane ring deformation, and C-C stretching of benzenethiol, respectively. Other peaks may be due to Raman scattering from polyvinylpyrrolidone which absorbed on the AgNW surface or carbon contamination.

The excitation polarization dependence, however, differ from tip to tip. Fig. 3a and 3b displays a set of TERS spectra taken with two different AgNW-tips at p- and s-polarized excitation (p-polarization is defined as the light polarization parallel to the longitudinal axis of the NW). In any cases, Raman intensity drastically increases by factor of over 10 when the tip is approached to the surface (a few nm gap between the tip and the gold surface), clearly indicating the TERS activity.

A tip with a single AgNW at the distal end, which is the most of case, exhibits typical polarization dependence, i.e. stronger Raman signal at p-polarization rather than at s-polarization (Fig. 3a. A SEM image of such tip is shown in Fig. 1b). Occasionally, we found tips showing less sensitivity to the polarization (Fig. 3b). These tips are a bundle of more than two AgNWs (Fig. 3c) or having nanoparticles adsorbed very close to the distal end (within the laser focus spot ~ 600nm). SPPs can be usually excited only at an end of AgNW and not at the middle of the NW due to the larger in-plane momentum of SPPs than the momentum of free-propagating photons of same energy.[15] However, SPPs can be excited at the middle of NW with s-polarized light when light was focused on NPs adsorbed on the middle of a NW caused by the local scattering effect of the NPs.[16] The observed less response to the polarization is therefore likely due to the SPPs excitation at s-polarization through the "defect", while p-polarized light excite the gap-mode plasmon between the tip and the gold surface. Note that such "defect" usually does not disturb atomic resolution of STM for flat samples, while it could introduce complex tip-sample convolution effects for large objects.

In summary, we performed atomic-resolution STM imaging of graphite lattice and topographic imaging of large metal nanoparticles with reduced tip-artefacts using STM tips based on chemically synthesized silver nanowires. Excellent reproducibility of TERS activity was confirmed on the tips. Most of the nanowire-based TERS tips show typical excitation polarization dependence on the enhancement, that is, higher Raman signals at the excitation polarization parallel to the longitudinal axis of the nanowire. When adsorbed metal nanoparticles or nanowires junction exists very close to the tip end, less excitation polarization effect was found. In this case, s-polarized light could be coupled into SPPs at the defect and the excited plasmons propagate to the tip-sample gap, exciting Raman scattering. This result implies the possibility to use the remote excitation of SERS, which the authors recently proposed,[17] for TERS excitation that could drastically improve signal to noise ratio.

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Notes and references

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10 W tips were fabricated by applying AC 10 V between W wire (ø ~ 0.25 mm) and carbon rod in 1 M KOH solution.

11 The AgNWs were synthesized using the polyol method.[8] After heating 5 mL of 0.15 M PVP solution in ethyleneglycol (EG) at 150 ˚C for 15 min, 40 µL of $CuCl_2$ (4 mM) EG solution was injected, followed by adding 2.5 mL of $AgNO_3$ EG solution drop-wisely under magnetic stirring. Then the solution was kept at 150 ˚C for another 1.5 h. The AgNWs were then washed with ethanol for three times.

12 AC-DEP was performed using ring-shaped Pt/Ir (=9:1) wire (0.2mm, Nilaco) as a counter electrode. A fresh W tip was immersed inside the 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 AgNW-tip was gently soaked in ethanol solution after gentle annealing at 200 ˚C and dried with N_2 gas.

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