

# Length controlled AFM-AgNW probes for tip-enhanced Raman Scattering

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## 1. Introduction

Tip-enhanced Raman scattering (TERS) is a unique analytical tool to provide complementary chemical and topographic information of surfaces with nanometric resolution. Due to the high resolution and sensitivity, TERS is suitable for the investigation of nanoscale heterogeneity of nanomaterials. Despite the promising performance of TERS in nanoscopic spectroscopy, the fabrication of reliable TERS probe is still difficult. In that context, we developed the method to attach silver nanowires (AgNW) on atomic force microscopy (AFM) cantilever, denoted as AFM-AgNW TERS probe. The AFM-AgNW TERS probe shows high reproducibility and TERS activity. Due to the shifting and deviation of the nanowire, TERS signals from AFM-AgNW probe in which AgNW longer than 5  $\mu\text{m}$  is extended from the top of AFM cantilever, is unstable. In other words, the length of AgNWs is vital to obtain stable TERS signals; however, their length is uncontrollable in chemical synthesis. Thus, we developed the method to control the length of AgNW attached to AFM cantilever to fabricate the promising AFM-AgNW TERS probe.

## 2. Experimental

The silver nanowires (AgNW) were attached to an AFM cantilever by following the reported method<sup>1</sup>. Then, the part of the AgNW was cut by applying a voltage, similar to our previous work.<sup>2</sup> TERS mapping of carbon nanotube (CNTs) was obtained by using the AFM-AgNW TERS probe. 633 nm laser was used for the excitation ( $\sim 1.0$  mW).

## 3. Results and discussion

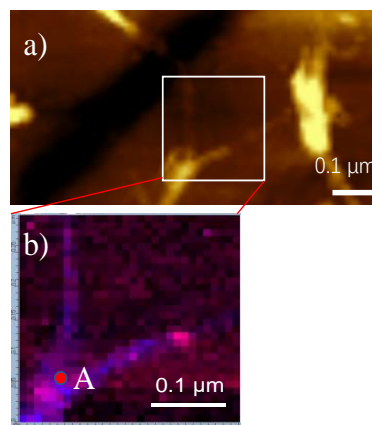
The nanowire length over the apex of AFM cantilever was tuned to be about 2.5  $\mu\text{m}$ , which is suitable for AFM scanning operations. **Figure 1a** shows an AFM image of a CNT used cut probe. The clear image shows that high-quality AFM image was obtained. **Figure 1b** shows a CNT TERS mapping image (200 nm  $\times$  200 nm). The image was merged with intensity maps of D- (red) and G-bands (blue), respectively. The resolution of TERS mapping is better than the diffraction limits. According to the profile, the spatial resolution is estimated to be better than 10 nm. Furthermore, we also tested the lifetime of cut probe. Compared with untreated probes, the lifetime of cut probe is shorter. This phenomenon may be because of the quick oxidation at the apex of AgNW.

## 4. Conclusion

We successfully obtained the length-controlled AFM-AgNW TERS probes. The cutting of AFM-AgNW TERS probes showed a good TERS activity and high special resolution. The lifetime of our probes is longer than several hours and several TERS mapping is possible with one TERS probe, which is often challenging with commercial TERS probes. The lifetime of the cut probe becomes shorter than that of untreated AgNW probes. This is most likely due to the quick oxidation at an apex of AgNW.

## 5. References

- [1] Walke, P.; Fujita, Y.; Peeters, W.; Toyouchi, S.; Frederickx, W.; De Feyter, S.; Uji-i, H. *Nanoscale* 2018, 10, 7556–7565.
- [2] Walke, P.; Toyouchi, S.; Wolf, M.; Peeters, W.; Prabhu, S.; Inose, T.; De Feyter, S.; Fujita, Y.; Uji-i, H. *J. Phys. Chem. Lett.* 2018, 9, 7117–7122.



**Fig. 1** a) AFM mapping image of carbon nanotubes (CNTs) dispersed on an Au(111) substrate with a cut tip under tapping-mode AFM feedback. b) TERS mapping image of CNTs (200 nm  $\times$  200 nm) obtained with a cut tip. The acquisition time of each pixel was 0.2 s. The image was merged with D-, G-band maps with red and blue, respectively, with arbitrary intensity.