Highly Reproducible Gap-Mode Tip-Enhanced Raman Spectroscopy with One-Side Metal-Coated Cantilever Tips

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Gap-mode tip-enhanced Raman spectroscopy (TERS) is a powerful nano-analytical technique, in which the plasmonically enhanced light field at the junction between a metallic tip and a metallic substrate excites Raman scattering from a tiny volume of a sample, which reflects chemical information of the sample at nanoscale. A scanning tunneling microscopy (STM) is usually used for the gap-mode TERS since STM requires a metallic substrate to tunnel current, which makes STM-based TERS inherently work in the gap-mode configuration and constantly produce high signal enhancement. In contrast, the cantilever-based atomic force microscopy(AFM) approach has different advantages over STM-based TERS, such as less intrinsic sample limitations and versatile imaging modes, for example force curve mapping and Kelvin force imaging. It could also easily work in vacuum, air or even liquid environment, so that a unique and correlative analysis is accessible with AFM-TERS. Nevertheless, AFM-based TERS is still not very common because granular plasmonic tips used in AFM-based TERS, prepared by conventional methods, do not provide reproducible enhancement because of random arrangement of metallic grains on tips. Although some other methods, such as employing electrodeposition[1] and attaching a silver nanowire[2] produce plasmonically active TERS tips in a reproducible way, they require optimal procedures to fabricate tips, which is still not feasible for everyone.

In this talk, a simplistic and cost-effective fabrication method of reproducible metal-coated cantilever tips for gap-mode TERS measurement will be discussed. We took advantages of our previous work, in which we reported an efficient fabrication method for a tapered metallic structure on the body of an AFM cantilever tip, aimed for plasmon nanofocusing, which is a type of plasmonic waveguide, on the cantilever tip[3]. Figure 1(a) shows schematic illustration of our tip design, which we called a "one-side metal coated tip" placed on the gold thin film. The one-side metal coated tip consists of an oxidized silicon body structure in a pyramidal shape and a smooth silver layer on one surface of the pyramidal structure. The plasmonic hot-spot is generated at the junction between the plasmonic tip and the gold thin film.

Our plasmonic tips can be reproducibly fabricated via only thermal evaporation, in which a high-speed evaporation rate (>3 nm s^{-1}) was adopted. In addition, the evaporation angle was set perpendicular to the evaporated tip surface, which gives only one side of the pyramid a silver coating. Figure 1(b) shows a scanning electron microscope (SEM) image of a representative plasmonic tip, where a smooth silver layer is always formed on the tip body. We demonstrated that fabricated plasmonics tips provided signal enhancement of the Raman signal from standard samples on a gold thin film in the gap-mode configuration with virtually 100% reproducibility (Fig. 1(c)). In this talk, we will also discuss AFM performance of our tips and other advantages of our plasmonic tips compared to conventionally used granular tips, such as less possibilities of suffering from contamination from molecular fragments desorbed from the sample surface.

Our simple and reliable plasmonic tips hold promise for rendering TERS as a powerful analytical technique in a broad range of fields.

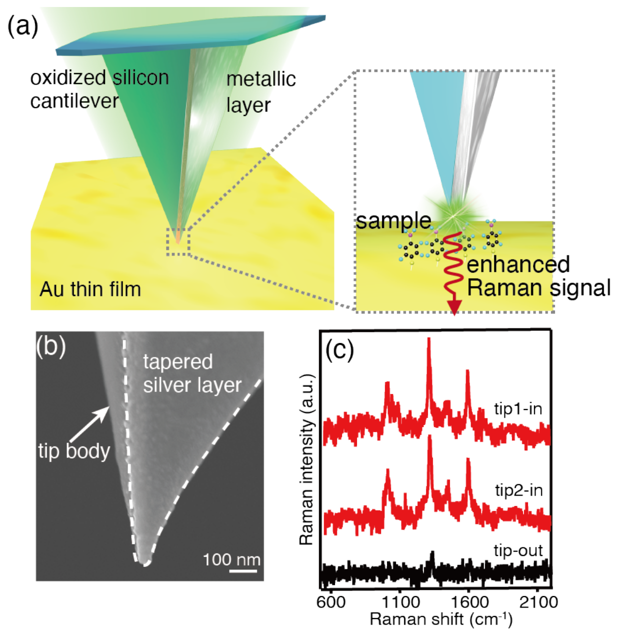

Figure 1(a) Schematic illustration of our tip design, composed of a pyramidal AFM cantilever tip and a metallic thin layer on one surface.
(b) SEM image of the silver-coated oxidized silicon tip (c) Representative TERS (tip-in) and normal Raman (tip-out) spectra of 4-nitrobenzenthiol

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References

[1] Teng-Xiang Huang et al., *Nanoscale* (2018), **10**, 4398-4405
[2] Peter Walke et al., *Nanoscale* (2018), **10**, 7556-7565
[3] Takayuki Umakoshi et al., *Sci. Adv.* (2020), **6**, 4179