Title	Gold-coated silver nanowire-based Tip-Enhanced Raman Spectroscopy probe for long life and high enhancement [an abstract of dissertation and a summary of dissertation review]
Author(s)	文, 晗
Citation	北海道大学. 博士(情報科学) 甲第15544号
Issue Date	2023-03-23
Doc URL	http://hdl.handle.net/2115/89422
Rights(URL)	https://creativecommons.org/licenses/by/4.0/
Type	theses (doctoral - abstract and summary of review)
Additional Information	There are other files related to this item in HUSCAP. Check the above URL.
File Information	Han_Wen_abstract.pdf (論文内容の要旨)

学　位　論　文　内　容　の　要　旨

博士の専攻分野の名称　　博士（情報科学）　　氏名　Wen Han

学　位　論　文　題　名

Gold-coated silver nanowire-based Tip-Enhanced Raman Spectroscopy probe for long life and high enhancement

（金コート銀ナノワイヤを用いた探針増強ラマン散乱プローブの開発）

Optical spectroscopic techniques are key analytical tools in a wide range of fields, shaping our essential understanding of many fundamental phenomena. Among these, Raman spectroscopy is one important technique. In Raman scattering, the change of the frequency of light is only related to the vibrational modes of the molecular electronic ground state. Thus, each molecule has a unique Raman spectrum, which makes the Raman spectrum the "molecular fingerprint", enabling Raman scattering to precisely analyze the structure of a molecule and interaction between them. Besides the specificity, the Raman scattering technique possesses the following advantages: non-invasive measurement, simple preparation of the sample (i.e., label free), the ability to simultaneously detect different analytes, and the applicability to biological samples and so on. However, the intensity of Raman scattering is inherently weak, and the spatial resolution is restricted by the diffraction limit, hindering its further applications.

To overcome these drawbacks, Surface-Enhanced Raman Scattering (SERS) technique has been developed, which dramatically enhances the intensity of Raman signal. However, the SERS technique requires nanoparticle aggregations or substrate surface to be roughened or deposited with nanostructures made of noble metals, such as Ag, Au, or Cu. SERS is enhanced at positions that randomly located on these substrates, which makes it difficult to locate the SERS active position (hotspot) relative to the sample of interest. The resulting relatively poor spatial resolution achieved with these substrates often becomes a limiting factor in practical applications. To overcome this limitation, an innovative technique called tip-enhanced Raman spectroscopy (TERS) emerged as the times require.

Tip-enhanced Raman spectroscopy (TERS) is the combination of Raman spectroscopy with scanning probe microscopy (SPM). By using the electromagnetic field enhancement resulting from the localized surface plasmon resonances (LSPRs) of silver or gold SPM tips, the Raman signal can be enhanced and localized to the area beneath the tip, which allows TERS to give correlated Raman and topographic images at a nanoscale resolution. In a TERS system, the SPM part could be the scanning tunneling microscope (STM), shear force microscopy (SFM), and atomic force microscope (AFM), among which the AFM-based TERS is more widely used as being more stable, faster, and having no intrinsic substrate limitations. However, the widely used AFM-TERS probes fabricated with metal deposition suffer from relatively low reproductivity as well as their limited mapping and storage lifetime, which requires precise control over surface structure on the nanoscale.

Our research group previously developed the chemically synthesized silver nanowires (AgNW)-based AFM-TERS probe, which, thanks to the high homogeneity of the liquid-phase synthesis of AgNW,

can achieve high TERS performance with excellent probe reproductivity, but still presenting short lifetime due to probe oxidation. Besides, this fabrication method still suffers from the low control of the protruded length of AgNW. This thesis thus focused on solving the durability, length control and enhancement.

On the first section, a simple Au coating method is proposed to overcome the limited lifetime and improve the performance of the AgNW-based TERS probe. For the Au-coating, different [Au]/[Ag] molar ratios were investigated. The TERS performance was evaluated in terms of change in enhancement factor (EF) and signal-to-noise ratio through multiple mappings and the storage lifetime in air. The Au-coated AgNWs exhibited higher EF than pristine AgNW and galvanic-replaced AgNW with no remarkable difference between the two molar ratios tested. However, for longer scanning time and multiple mappings, the probes obtained with low Au concentration showed much longer-term stability with keeping high EF. Furthermore, the Au-coated AgNW probes were found to possess a longer storage lifetime in air, allowing for long and multiple TERS mappings with one single probe.

On the second section, a simple water-air interface electro-cutting method is proposed to achieve wide controllability of the length. This water-cut method was combined with the succedent Au coating on AgNW surface after cutting, which enabled to obtain high durability, impressive enhancement factor (EF) and excellent spatial resolution. The TERS performance was evaluated in terms of change in EF through multiple mappings and spatial resolution. The water-cut Au-coated AgNWs, with appropriated Au concentration and pH, achieved up to 100 times higher EF and two times smaller spatial resolution than pristine AgNW. Thanks to this excellent EF, the water-cut Au-coated AgNW probes were found to possess high TERS activity even in non-gap mode, allowing for broader applications.

In summary, this work offers solution to the issues of the durability, length control of the AgNW-based AFM-TERS probe, and achieved high Raman enhancement even can conduct non-gap mode TERS measurement, which significantly broadens the application of TERS and provides some promising development directions of TERS technique.