

SILVER NANOWIRE-BASED TIP FOR TIP-ENHANCED RAMAN SCATTERING MICROSCOPY

Yasuhiko Fujita¹, Tomoko Inose², and Hiroshi Uji-i^{2,3}

¹Toray Research Center Inc. 3-3-7 Sonoyama Otsu, Shiga, 520-8567, Japan

²KU Leuven, Department of Chemistry, Celestijnenlaan 200G-F, B-3001 Heverlee, Belgium

³N20W10, Kita-Ward Sapporo 001-0020 JAPAN

E-mail: hiroshi.uji@es.hokudai.ac.jp

Tip-enhanced Raman scattering (TERS) microscopy is a powerful variant of surface enhanced Raman scattering (SERS) spectroscopy combined with scanning probe microscopy (SPM), such as scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). This technique allows us to obtain both chemical and topographical information simultaneously with nanometre resolution. TERS activity is attributed to the excitation of the localized surface plasmons at an apex of a metalized SPM tip upon light illumination. Therefore, control of tip shape is a key issue for efficient TERS microscopy. In STM-based TERS, electrochemically-etched gold/silver tips have often been used. The apex shapes of such tips differ from tip to tip, causing low reproducibility in TERS measurements. In this sense, wet-chemically synthesized silver nanowires (AgNWs) are promising candidates as a TERS tip material because of the structural uniformity and good crystallinity. To our best knowledge, however, STM/AFM operation using AgNW-tip under feedback control has not been reported. Attaching a number of AgNWs attached on a W tip apex using electrophoresis (Fig.1a), we successfully obtained atomic resolution graphite lattice image (Fig.1b). Thanks to the quality of wet-chemically synthesized Ag NWs, nearly 100 % of AgNW-tips exhibit TERS activity, revealing excellent reproducible TERS measurements (Fig. 2). [1][2]

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 (Fig. 2a). When adsorbed metal nanoparticles or nanowires junction exists very close to the tip end, less excitation polarization effect was found (Fig. 2b). 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,[3] for TERS excitation that could drastically improve signal to noise ratio.[1]

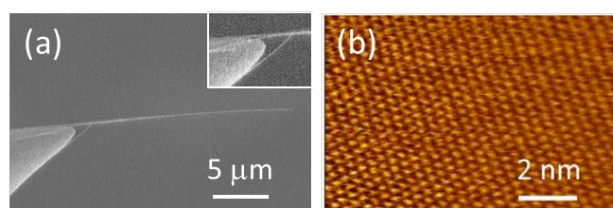


Fig. 1 (a) SEM image of typical AgNW-tip. (b) STM image of atomic resolution graphite lattice image

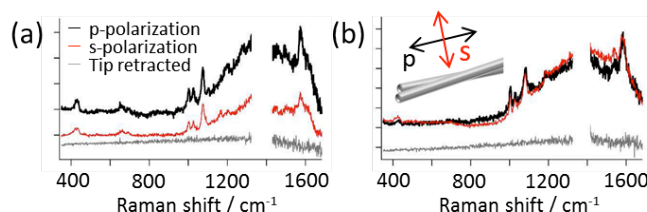


Fig. 2 Polarization dependence of TERS spectra of single AgNW (a) and bundled AgNW (b) at the end.

[1] Y. Fujita, P. Walke, S. De Feyter, H. Uji-i, Jpn. J. Appl. Phys. 55, 08NB03 (2016).

[2] Y. Fujita, R. Chiba, G. Lu, N. Horimoto, S. Kajimoto, H. Fukumura, H. Uji-i. Chem. Commun. 2014, 50, 9839-9841.

[3] J. A. Hutchison, S. P. Centeno, H. Odaka, H. Fukumura, J. Hofkens, H. Uji-i, Nano Lett. 2009, 9, 1002.