Facile and Reproducible Fabrication of Ag-Coated AFM Probes for Tip-Enhanced Raman Spectroscopy

<u>V. Kesava Rao</u>, K. Kanishka H. De Silva and M. Yoshimura Surface Science Laboratory, Toyota Technological Institute, Nagoya, 468-8511, Japan. <u>Email : kesava2123@toyota-ti.ac.jp</u>

Development of simple fabrication of plasmonic probes with tip-enhanced Raman scattering (TERS) efficiency and identifying optimal requirements for maximizing the enhancement factor (EF) and long lifetime are essential in terms of both application and fundamental aspects of TERS.¹⁻³ In the present work, Ag-based atomic force microscopy-TERS probes with rough morphology are fabricated by a simple three-stage protocol (Figure a), which are based on solid-state dewetting (SSD) of Ag-coated AFM-probes employing UV-ozone (UVO) treatment and hydrazine vapor exposure. The nanoscale roughness induced on probes by different UVO irradiation periods on the TERS efficiency is investigated by employing them in TERS experiments (Figure b). We investigated the reproducibility of TERS probes fabrication by comparing the TERS contrast with 20 rough Ag probes (obtained using 30 min UVO irradiation and 30 min hydrazine exposure) (Figure c). The highest TERS contrast (~172) and EF (~10⁵) are observed with the probe obtained using 30 min UVO exposure and 30 min hydrazine treatment. TERS map investigation of SWCNTs coated on Au substrate indicated an optical resolution is down to below ~10 nm (Figure d). Importantly, we present a simple and efficient method to restore oxidized TERS tips as a result of exposure to ambient atmosphere (Figure e), which can be implemented to all Ag-based TERS tips, rendering the method applicable for a broad community.⁴



Figure (a) Schematic representation of rough Ag-based AFM tips fabrication in three-stages, (b) Effect of different UVO exposure times on TERS contrast, (c) TERS contrast histograms and fitted Gaussian profiles for rough probes, (d) Higher resolution G-band mapping image of SWCNT on Au substrate and (e) The effect of areal oxidation and reversal of TERS efficiency.

References:

- 1. R. M. Stöckle, Y. D. Suh, V. Deckert and R. Zenobi, Chem. Phys. Lett., 2000, 318, 131-136.
- 2. M. Richard-LacroiChem. Phys. Lett., x, Y. Zhang, Z. Dong and V. Deckert, *Chem. Soc. Rev.*, **2017**, 46, 3922-3944.
- 3. A. Taguchi, J. Yu, P. Verma and S. Kawata, Nanoscale, 2015, 7, 17424-17433.
- 4. V. Kesava Rao, K. Kanishka H. De Silva, M. Yoshimura, Appl. Surf. Sci., 2022, 577, 151937.