

Novel plasmonic probes for Tip- Enhanced Raman Spectroscopy

Valentinas Snitka¹, Lina Ramanauskaite¹, Huizhong Xu², Tomas Gadisauskas¹, Rasa Zukiene^{1,3}

¹Research Centre for Microsystems and Nanotechnology, Kaunas University of Technology, Studentu 65, LT-51369 Kaunas, Lithuania

² Physics Department, St. John's University, 8000 Utopia Parkway Queens, New York, 11439718-990-2000, USA

³ Department of Biochemistry, Vytautas Magnus University, K. Donelaicio 58, LT- 44248 Kaunas
vsnitka@ktu.lt

Abstract

Hybridization of Atomic force microscopy with plasmonic probes stimulated the development of the several new spectroscopic techniques. Tip-Enhanced Raman Scattering (TERS) is the technique utilizing a special AFM probe (nano-antenna) to localize light at the nanometer scale area near the probe apex. TERS has emerged as a potentially powerful nanochemical analysis tool [1]. However, questions about the reproducibility of TERS data still remain a challenge [2]. The TERS data of biomolecules obtained in liquid open even more questions. A deep integration of AFM with confocal Raman microscopy is required for successful TERS experiment. In this work we investigated the application of novel AFM plasmonic probes for TERS fingerprinting of proteins (α -synuclein) and monitoring the structural changes during the protein interaction with nanoparticles. We used a commercial novel AFM-TERS probes (NT-MDT Inc.) and home made AFM-TERS probes made by chemical silver deposition on so-called “Top Visual” AFM Si cantilevers (NT-MDT Inc.). Top-illumination AFM-Tip-enhanced Raman scattering system adapted on an upright optical microscope have been used in our experiments. Simulation of localized plasmon electromagnetic field distribution between the tip and substrate was done using COMSOL software EM package. We evaluated the Raman enhancement spectra as a function of experimental variables such as excitation power, acquisition time, molecules type and substrate. Based on the spectra obtained, the peak positions, number of bands, peak intensity ratios, and comparability to reference micro-Raman data are discussed. This study demonstrated the suitability of investigated cantilevers to be used for biological TERS applications.

References

[1] Hacksung Kim, Kathryn M. Kosuda, Richard P. Van Duyne^a and Peter C. Stair, *Chem. Soc. Rev.*, 2010,39, 4820-4844

[2] Carolin Blum, Lothar Opilik, Joanna M. Atkin, Kai Braun, et all, *J. Raman Spectrosc.* 2014, 45, 22–31

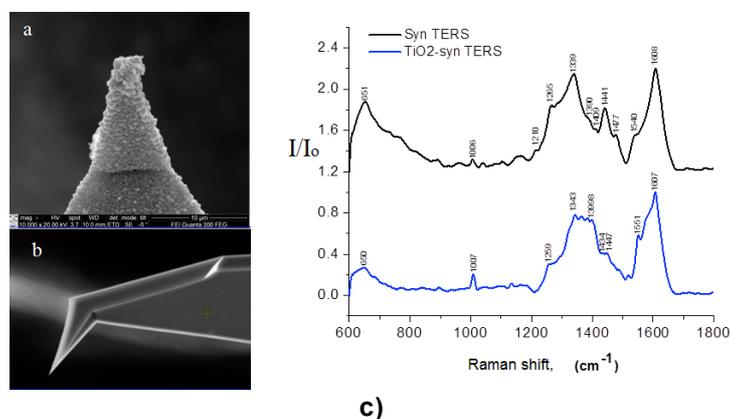


Figure 1. AFM-TERS probes used in experiment: a) silver chemically decorated apex of the probe, b) NT-MDT probe based on so-called “Top Visual” AFM Si cantilevers. TERS spectra of α -synuclein (c).