Tip Preparation for STM Tip Enhanced Raman Experiment

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1. Introduction

TERS (tip enhanced Raman spectroscopy) has great potential for nanoscale characterization. However, how to make high quality and reproducible tips is a main problem since the invention of TERS. For our experiment, we fabricate tips for STM-TERS by electrochemical etching. The requirement of tips for STM operation is less than TERS measurement. For TERS, there are two main issues about tips; First, the geometry of tip apex and second, the contamination residue on the tip

2. Fabrication and the geometry of tip apex

Usually, sharp gold tips are made by single step electrochemical etching in a mixed solution of HCl: H_2O=1: 2. This mix ratio give the best tip curvature among all kinds of HCl: H_2O mixture. We inspect these tips under optical microscope. Sometimes we would etch them again under the view of microscope when the tips are not sharp enough. Representative optical and SEM images of a sharp tip are shown in below.

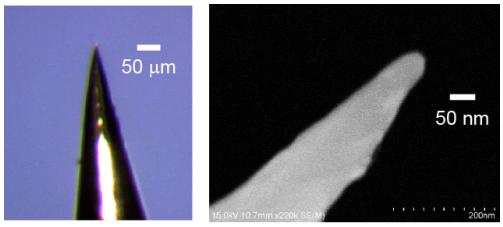

Fig. 1. (Left) Optical and (Right) STM images of one tip for STM-TERS. The surface of tip cone is shinny which avoids the possible disturbance of SERS signal. The diameter of the tip apex is about 40 nm.

3. Contamination issue

The main reason for using gold as tip material is because of the plasmon resonance in the visible light region. Even though silver has stronger plasmonic enhancement, the surface of etched silver tip is usually too rough and show abundant blinking Raman signal (SERS) from its surface contamination. Eventually we only use gold for tip material. Still there is some possibility to get a rough gold tip after etching and such tip would be excluded for further TERS experiment since it gives annoying photoluminescence and SERS background as shown in Fig. 2. On the other hand, contamination source could be also from anywhere in the ambient environment. To avoid the further contamination adsorption and also improving tunneling junction stability, a stainless steel chamber for dry nitrogen purge was added to the system. This environmental chamber is proved to help the overall stability as well as reduce the contamination issue.

While STM scanning, sometimes it would get sample molecules attaching to the tip. Use such molecules modified tip brought some interesting results showing reversed TERS contrast. Such reversed contrast also shows good spatial resolution around 3 nm. The modified tip could be considered as confined nanoscale light source and we can use it to explore the unknown optical and spectroscopic properties in nanoscale.

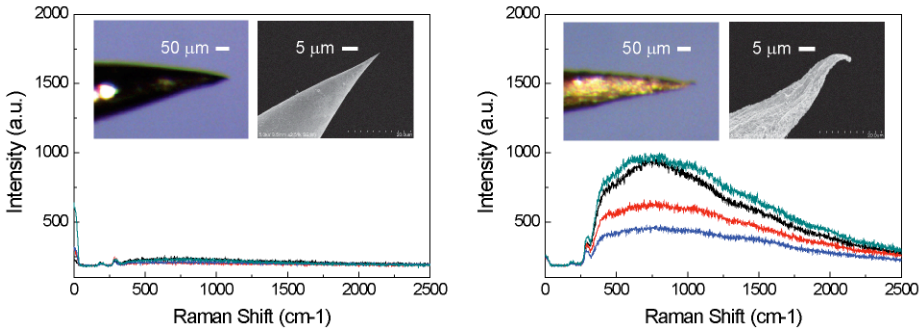

Fig. 2. Optical images, SEM images, background emission from (left) smooth and (right) rough surface tips. The photoluminescence from rough Au tip surface would disturb the TERS measurement. Spectra in different colors are taken at different position at the tip apex.