Photo-induced growth of silver nanoparticles for *in-situ* preparation of tips for near-field Raman spectroscopy

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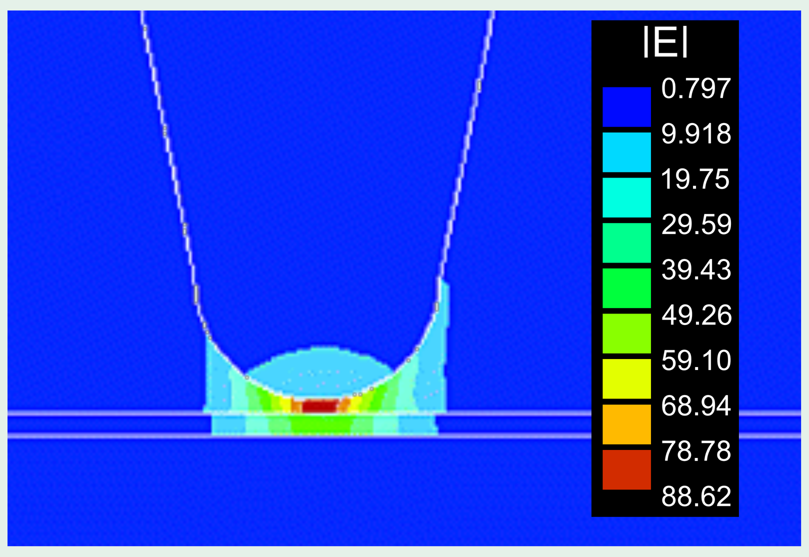
Introduction

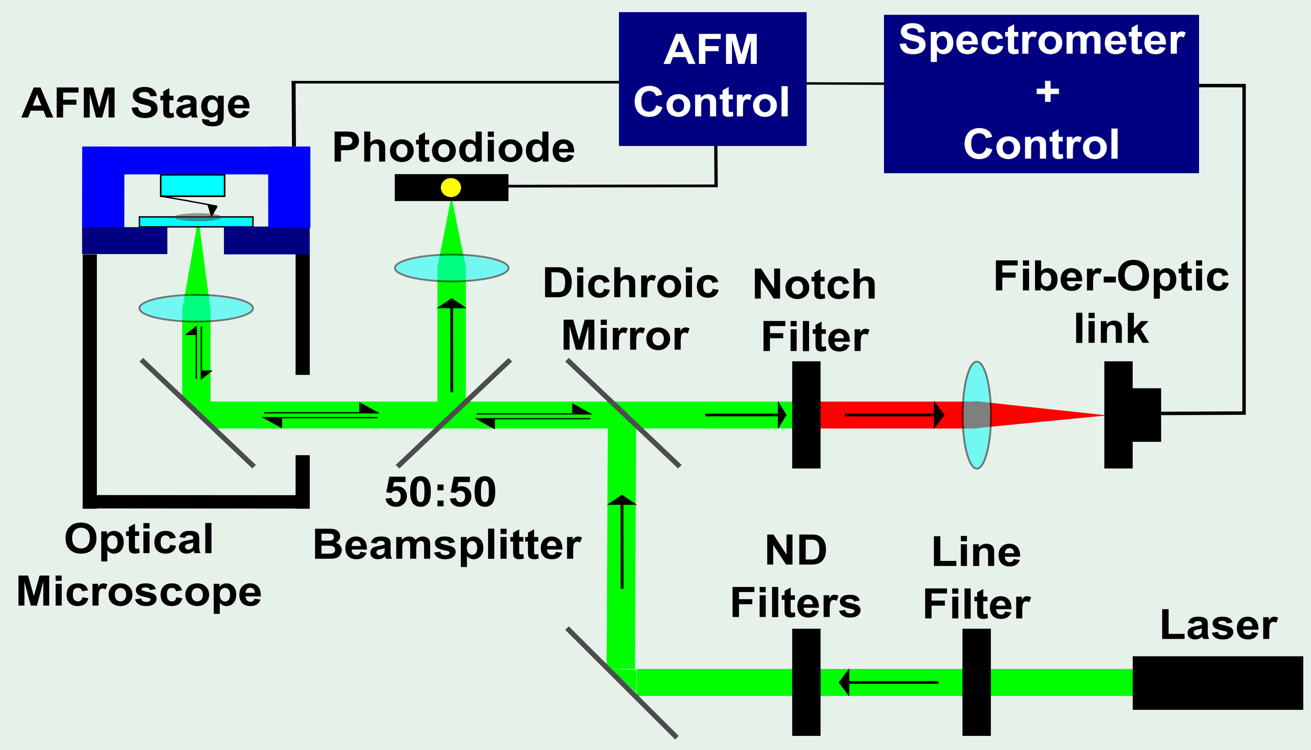
The Raman effect is an inelastic process whereby scattered light can gain or lose energy corresponding to particular vibrational transitions in molecules.
Raman spectra contain a wealth of information regarding the composition of the sample, and can be used as unique chemical "fingerprints".

The maximum spatial resolution of Raman microspectroscopy is limited by microscope resolution, i.e. the diffraction limit. However this limit is not fundamental and can be bypassed when considering near-field optics, and the use of a nanoscale probe. An analogy to this is a doctor's stethoscope, which can be used to locate the position of the heart to within a few centimeters, even though the typical wavelength of the sound is tens of meters.



Early instruments consisted of a small fiber probe with a small aperture to collect light from the near-field. For Raman spectroscopy this is not sufficient as scattering is very weak. For tip-enhanced Raman spectroscopy (TERS), an apertureless probe is used, with a metallic nanoparticle at the apex which acts as an optical antenna and enhances the Raman scattering (see above image from simulation, modified from [1]).

Instrumentation



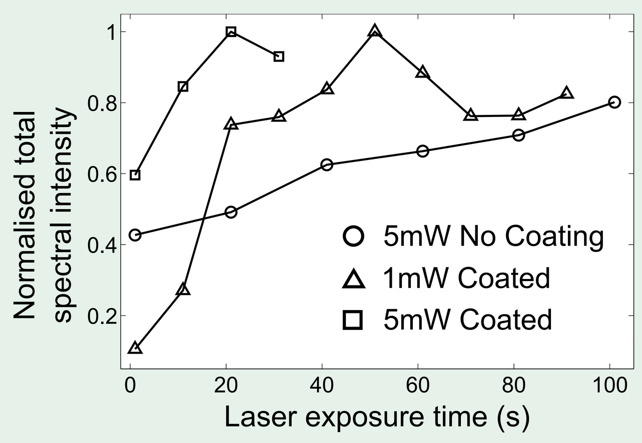
Our equipment consists of an atomic force microscope (AFM) mounted on an inverted optical microscope coupled to a Raman spectrometer. Such a setup is versatile for investigating a range of samples with each technique separately or simultaneously.

TERS fully utilises such a combination, but requires modification to the tip probe. This is typically done by etching wire or metal vapor deposition onto AFM tips [2]. Below we present a new method which has many advantages over the established techniques.

A Novel Tip-Preparation Method

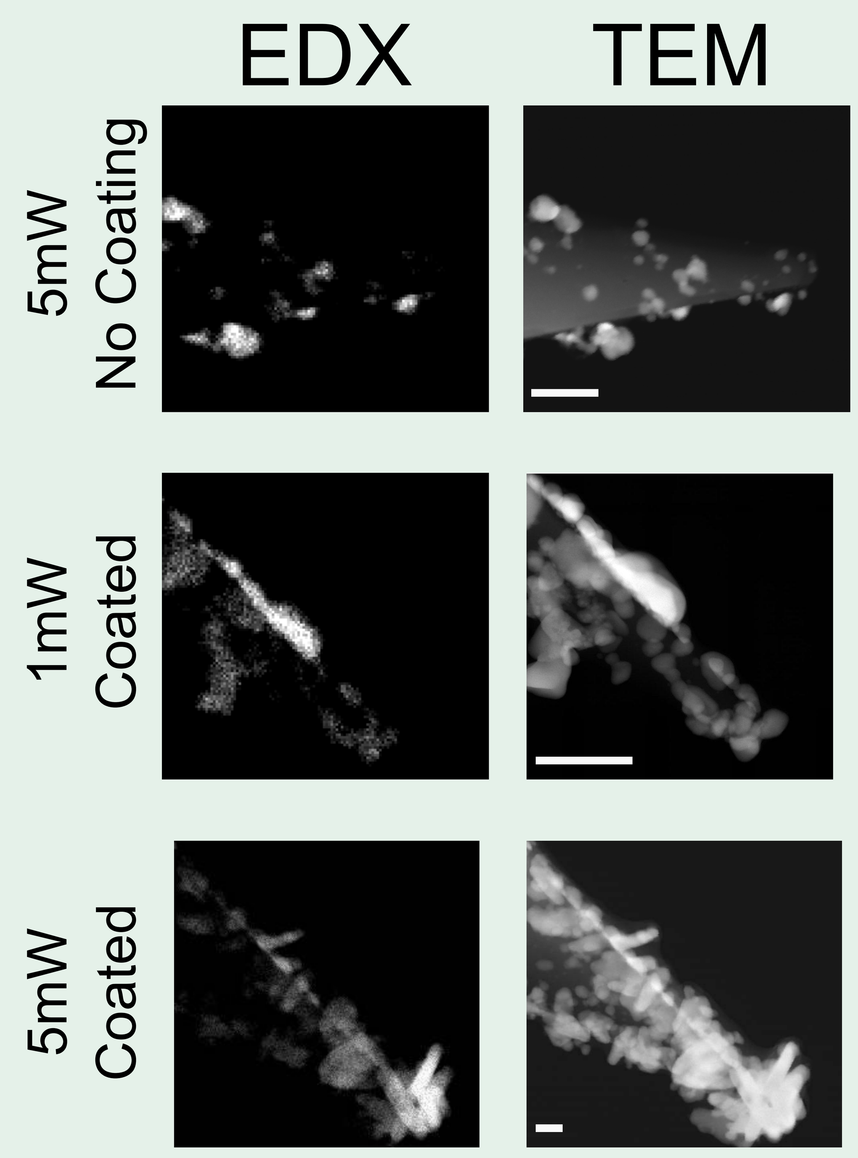
Nanoparticle aggregates have been shown to form at an interface between a dilute solution of silver nitrate ($AgNO_3$) and sodium citrate under light exposure, where they can subsequently be used as SERS substrates [3].

This method was tested on standard silicon AFM tips for different incident laser powers. A coating of 3-amino-triethoxysilane (APTES) was used on some tips so that silver particles would preferentially bind to the surface.



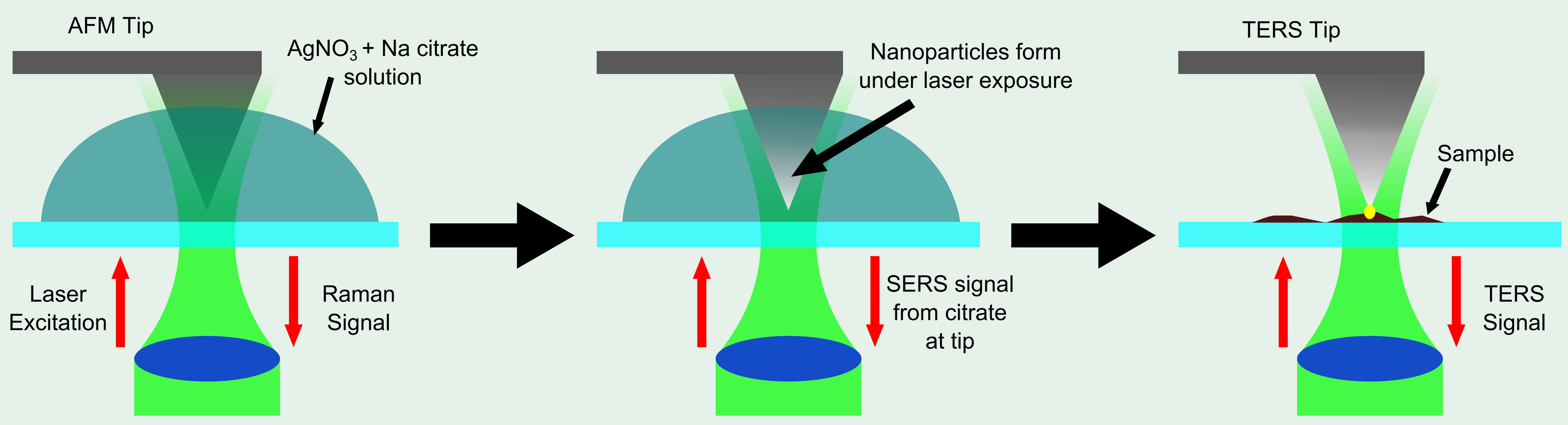
Left: Comparison of growth rates for tips prepared under different conditions.

Right: Transmission electron microscopy (TEM) and energy dispersive X-Ray (EDX) analysis of nanoparticles on tips grown under different conditions.



(Scale bars: 200nm)

Right: Protocol
- Align tip and submerge in growth solution
- Expose laser to begin growth, simultaneously collect Raman scattering
- Clean tip and use for TERS experiment



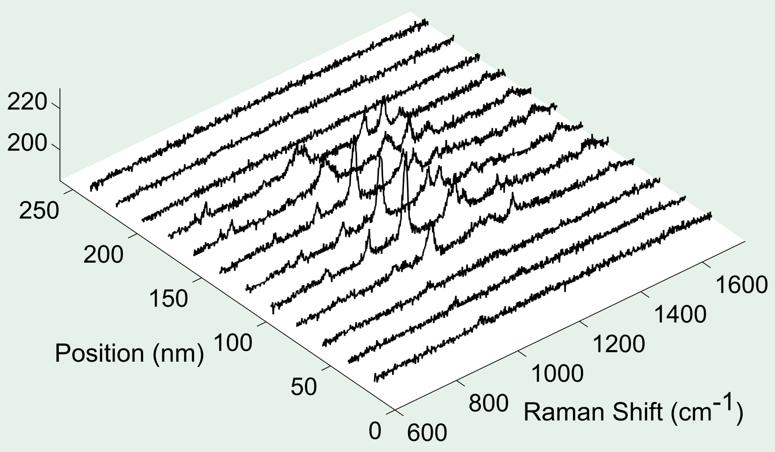
Testing on Self-Assembled Diphenylalanine Peptide Nanotubes (FFNT)

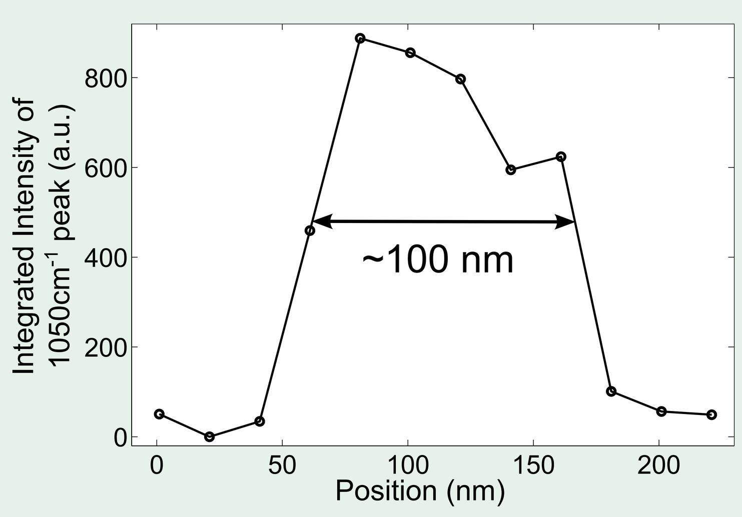
Self-assembled peptide nanotubes were used to assess the capabilities of the *in-situ* prepared tips as these structures are biologically relevant and have nanoscale features which can be used to test spatial resolution.

TERS experiments were most successful when using tips coated in APTES, particularly those prepared at lower laser power.

Below Left: TERS spectra taken along the cross section of a FFNT with diameter of 80nm.

Below Right: Peak intensity line profile. Deconvolution with the AFM profile suggests a Raman spatial resolution between 20-30nm.





Summary and Future Work

The photo-induced process for *in-situ* preparation of TERS tips has been successfully demonstrated to give spectral information at a spatial resolution below the diffraction limit.

The growth mechanism is not well understood, thus future work will involve finding parameters that control the shape and size of the resulting nanoparticles and comparing with simulations. Parameters currently being considered include:

- Incident Power
- Wavelength
- Polarization
- Solution concentration
- Temperature
- Coating

Once this growth process is understood, and reproducible TERS tips can be fabricated using this method, it will be possible to investigate a plethora of biological and material nanostructures with chemical information at nanoscale resolution.

References

[1] I. Notingher and A. Elfick, *J. Phys. Chem. B*, **2005**, 109, 15699-15706

[2] B.S. Yeo et. al., *Chem. Phys. Lett.*, **2009**, 472, 1-13

[3] E.J. Bjerneld et. al., *Nano Lett.*, **2003**, Vol. 3, No. 5, 593-596