Declaration

The work presented in this thesis was carried out at the Nanophotonics Group in the Cavendish Laboratory, University of Cambridge between October 2011 and July 2015. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically indicated in the text. It has not been submitted in whole or in part for any degree at this or any other university, and is less than sixty thousand words long.

Alan Sanders

List of Talks, Posters and Publications

Publications

- A. Sanders et al., Particle & Particle Systems Characterization **32**, 182–187 (2015)
- F. Benz et al., Nano letters **15**, 669–674 (2014)

Conference Presentations

- A. Sanders et al., in Quantum plasmonics 15 (Mar. 2015)
- A. Sanders et al., in Photon14 (Sept. 2014)
- A. Sanders et al., in Cavendish graduate student conference (Dec. 2013)
- A. Sanders et al., in SPP6 (May 2013)
- A. Sanders et al., in Cavendish graduate student conference (Dec. 2012)

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Abstract

On the Plasmonic Properties and Dynamic Interactions of Nanostructured AFM Tips

Alan Sanders

Plasmonics, the confinement of light to nanometric dimensions in the form of optically-driven collective oscillations of conduction electrons, enables strong, local field enhancements, which can be exploited to realise nano-optics and nano-spectroscopy. However, the onset of quantum mechanical effects serves as a fundamental limit to plasmonic confinement in what has recently become known as the quantum regime of plasmonics.

In the present work, a dual AFM tip approach to form sub-nm plasmonic cavities is adopted to investigate the quantum regime of plasmonics and to determine, in particular, the relationship between conductance and plasmonics, a theme of great interest in the field. The technology required to reliably form sub-nm plasmonic cavities between AFM tips is further developed. A custom optical microscope with an ultra-stable nanopositioning platform has been entirely designed and optimised to facilitate experiments. Light scattering from both single and gap-coupled nanostructures can be measured over a broad wavelength range using a novel dark-field spectroscopy technique utilising a supercontinuum white-light laser.

This experimental system has been exploited to fully characterise the optical response of both sharp and spherically nanostructured Au AFM tips in order to understand their plasmonic properties. Additional spherical Au nanoparticle-tipped AFM probes are fabricated using apex-selective pulsed electrodeposition to demonstrate a simple method for introducing localised surface plasmons into a robust tip geometry. Hyperspectral imaging is utilised to optically characterise single nanostructures and identify localised surface plasmons. Spherical Au tips, with their nanoparticle-like apex geometry, are found to exhibit a radiative plasmon resonance between 600–700 nm, not present in sharp Au tips, leading to a 30× improvement in Raman scattering efficiency compared with sharp Au tips.

Finally, plasmonic interactions between two AFM tips are studied and the transition between coupled and charge transfer plasmons is dynamically observed. Simultaneous measurement of the d.c. current, applied force and optical scattering as tips come together is used to determine the effects of an optical conductance in a plasmonic nano-gap. Critical conductances are experimentally identified for the first time, determining the points at which quantum tunnelling and conductive charge transport begin to influence plasmon coupling. This is a step towards fully understanding the relationship between conduction and plasmonics and the fundamental, quantum mechanical limitations of conventional plasmonic coupling.