

Tuning optical properties in random arrays of plasmon resonant nanoparticles

by

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CERTIFICATE OF ORIGINALITY

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text. I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Preface

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- S. Schelm and G.B. Smith “Dilute LaB6 nanoparticles in polymer as optimized clear solar control glazing”, *Applied Physics Letters* **82** (24), 4346-4348 (2003)

Abstract

Small conductive particles show a resonant behaviour at wavelengths where bulk or thin film samples have no features. This resonance is caused by the collective oscillation of the free electrons in the particle and is called localised surface plasmon resonance. It is influenced by the shape of the particle, the surrounding medium and particle interaction.

I studied shape, matrix and interaction effects of metallic and metal-like particles in various systems with the aim to rationally tune the resonance to specific wavelengths for different applications.

Dilute samples of small LaB₆ particles were studied with regard to their NIR blocking performance. My analysis showed that they are more efficient than the alternative materials ITO and ATO. This is mainly due to the position of the LaB₆ particle resonance, which lies precisely in the spectral region which needs to be blocked (around 1 μm). I was able to model the optical properties of the window samples, using a dilute quasi-static approach for anisotropic particles.

Different embedding matrices and particle interaction have also an influence on the localised surface plasmon resonance. An example for a combination of matrix and interaction effects is a self-assembled gold particle film with organic linkers. Structural effects were especially important in these films, as was verified by electron microscopy. The optical properties were successfully modeled, using a two level effective medium approximation.

A different way to tune the resonance is to change the shell thickness to core size ratio in metallic nanoshells. The resulting spectral shift, though, is limited by

experimental realities for the metal coating and the onset of scattering for larger particles. The shell has two resonances, of which the low energy one can be tuned by the ratio mentioned above. This resonance also shows a different electric field profile to the normal dipole (and high energy shell) resonance. The field pattern also highlights a strong field gradient across the external shell interface and along the incident polarisation direction. The properties were calculated using Mie theory and the quasi-static approximation.

Finally, the far and near-field optical properties of thin silver films with randomly distributed holes were studied. They showed an enhanced absorption, due to coupling of the incident light into surface plasmon polaritons by the holes. Whereas the films did not show the enhanced transmission, which occurs in regular hole arrays, they still might provide some insight in the processes involved by helping to exclude some possible explanations.

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Glossary

AFM	Atomic Force Microscope
BR	Bruggeman EMA Scheme
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DDA	Discrete Dipole Approximation
EMA	Effective Medium Approximation
LBL	Layer-by-Layer deposition
LSP	Localised Surface Plasmon
MG	Maxwell Garnett EMA Scheme
NP	Nanoparticle
NF	Near-field
PDF	Probability Density Function
SAM	Self-Assembled Monolayer
SEM	Scanning Electron Microscope
SERS	Surface Enhanced Raman Scattering
SHGC	Solar heat gain coefficient
SNOM	Scanning Near-Field Optical Microscope
SPP	Surface Plasmon Polariton
SPR	Surface Plasmon Resonance