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UV nanolights: Enhancing nonlinear emission from Quantum Dots through Plasmon Coupling

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ABSTRACT

A new approach to measure nonlinear absorption using the single beam Z-scan technique was developed.¹ By measuring the delay or advance of a light pulse reaching the detector, the nonlinear absorption could be identified as either instantaneous or transient. It was demonstrated that with this modification of the Z-scan technique, discrimination of excited state absorption (ESA) from two and three photon nonlinear absorption could be achieved. A colloidal suspension of ZnO nanocones in ethanol was the model system used to test the efficacy of this technique, where it was shown that when irradiated by high fluence 532 nm nanosecond pulses, nonlinear absorption that was 5 orders of magnitude larger than in bulk media occurred, mostly due to ESA not two photon absorption. Importantly this shows that by control of size and shape that the nonlinear optical properties of ZnO can be dramatically increased and that a new measurement technique was developed that can separate multi-photon nonlinear absorption processes.

Another important outcome of the work was development of a method to accurately measure the thickness of a thin organic molecule layer coating on small inorganic quantum dot particle cores using dynamic light scattering (DLS).² We demonstrated that a simple correction formula accurately yields hydrodynamic size in both the volume- and number-weighted size distributions, from which a precise determination of molecular shell thickness by DLS can be obtained. Small (core size < 5 nm) nanoparticles of ZnO and Au, coated with a layer of dodecanethiol were used to demonstrate this. The method can be widely applied to many systems. It can be used to find the capping thickness of different ligand coatings, or if capping thickness is known, this technique can be used to find particle size distributions using DLS alone. The method is also applicable to bare nanoparticles in polar solvents.

INTRODUCTION

Semiconductor QDs and nanocrystals show great potential as versatile light emitters. QD optoelectronic properties are often significantly different compared to their bulk form due to quantum confinement effects and thus depend on the dimensions of the medium (QD diameter). Nanocrystals can now be grown with tailored geometries to achieve certain desired properties. Since photon absorption and emission occurs through electron excitation and de-excitation, respectively, light emitted and absorbed by the QD becomes size dependent.³ These properties make QDs highly desirable candidates for gain materials in microscale lasers and nanoscale light sources. Despite these advantages, QDs have so far failed to reach the performance predictions and high expectations of some researchers, due to effects such as their lower quantum efficiency in solid

form⁴ and unwanted transient effects such as random on/off emission (blinking).⁵ The low internal quantum efficiency arises from competing decay processes such as non-radiative decay and defect emission.

To address the efficiency problem, hybrid QD systems interacting with plasmons have now attracted attention.⁶ Plasmonic metal nanostructures are characterised by their strong interaction with resonant photons through excitation of the localised surface plasmons (LSPs). The LSP is the resonant photon-induced coherent oscillation of charge at the metal/dielectric interface, established when the photon frequency matches the natural frequency of metal surface electrons oscillating against the restoring force of their positive nuclei. In the small particle limit, a resonantly enhanced field builds up inside the particle which is homogeneous throughout its volume, producing a dipolar field outside the particle. This leads to enhanced absorption and scattering cross sections for electromagnetic waves, as well as to a strongly enhanced near field in the immediate vicinity of the particle surface. **It is this resonantly enhanced near field from which most of the promising applications of metal NPs stem.** Our aim was to harness this near-field to induce 2 photon nonlinear processes in the QD. Photo-excited plasmonic nanostructures essentially act to concentrate the light flux (the energy of incoming photons) in small volumes around the nanostructure producing strong electric fields that are orders of magnitude higher than the photons used to photo-excite the nanostructure. Enhancements in the intensity of electric fields compared with the field intensity of the incoming photon flux are anywhere from $\sim 10^3$ at the surface of an isolated NP to more than 10^6 for two NPs separated by ~ 1 nm.⁷

When metal nanostructures are placed sufficiently close to QDs, energy can be transferred from one material to the other and the combination can be treated as a coupled system.⁶ Theoretical frameworks for the QD-NP coupling exist for NPs with simple geometries e.g. spheres, rods, ellipsoids.⁸ In the linear regime, metallic NPs can enhance the emission from QDs with some authors reporting a fourfold enhancement of luminescence intensity.⁹ There are several pathways by which the NP can increase the probability of a photon being emitted by the QD (this probability is known as quantum yield). While the details are complex, the enhancement in efficiency can be simply interpreted as the NP acting as an efficient absorber of visible light energy, which is then rapidly transferred to the QD. In doing so, there is an accompanying increase in the spontaneous emission rate of the QD, reducing the probability of competing decay processes and increasing the quantum yield.¹⁰ While efficient, a significant drawback of linear energy exchange processes is that the wavelength of the QD emission can be no shorter than that of the incident light. Therefore, the NPs must be bathed in UV incident light to generate UV QD emission via linear processes. An interesting possibility, and the focus of this proposal, is to use frequency mixing and other nonlinear optical processes to efficiently up convert visible light into the UV region of the spectrum.¹¹ Versatile, commercial solid state laser systems that utilise this phenomenon with bulk materials have been installed in research laboratories throughout the world. However, attention is now turning to exploration of nanotechnology pathways which would deliver cheap miniaturised alternatives to current UV light technology.¹² One example is to exploit nonlinear processes in disordered and nanostructured media to produce UV light.¹³ The enhanced optical fields near metal nanostructures are ideally suited for stimulating the nonlinear optical response of neighbouring materials, such as semiconductor QDs. The nonlinear response of any medium exposed to low intensity fields is typically much weaker than its linear response. However, exposure to high intensities dramatically increases the medium's nonlinear response because of its nonlinear dependence on local field strength. Therefore, while increasing the local field by a factor of 10^3 increases the linear response by the same factor, the nonlinear second-harmonic emission would increase by a factor of 10^6 . Commercial manufacturers of optical frequency up-converters made from bulk media harness this nonlinear dependence to achieve high conversion efficiencies ($\sim 50\%$) by generating high local field

amplitudes with intense ($\sim \text{MW/mm}^2$) laser radiation. In this project the heightened optical fields near metal NPs could be utilized to enhance frequency doubling processes in the particles.

The project **aim was to discover new excitation pathways for visible-to-UV light up-conversion** using extremely compact, well defined coupled-nanoparticle systems. Our hypothesis was that when noble metal nanoparticles (NPs) are coupled to semiconductor quantum dots (QDs), together they can effectively absorb visible light and generate UV light. Specifically that visible light can be harvested using gold NPs, by harnessing an effect called localised surface plasmon resonance, which can generate a large electromagnetic field to distort the optical susceptibilities of nearby quantum dots (QDs). Near-simultaneous energy transfer between the NP and QD would generate optical absorption and emission properties in the coupled system that could be designed by the user. By understanding the manner and degree to which NPs might enhance nonlinear processes in QDs, the project's goal was to uncover principles that could have application in future novel QD-based UV light sources. The novelty of this approach is our intention to use localised surface plasmons supported by the NPs to stimulate nonlinear interactions in a coupled NP-QD system.

Summary of Specific Aims

The research team's plan was to investigate up-conversion of nanoparticle/quantum dot composites by

1. *Modelling of NP-QD interactions:* to establish and validate an effective theoretical model of electromagnetic energy coupling between localized surface plasmons in noble metal NPs and light emitting QDs, with an emphasis on visible to UV light up-conversion. Such nonlinear energy exchange between NPs and QDs has not been explored deeply on a theoretical level.
2. *Fabrication Experiments:* controlled deposition of coupled QD - NP structures and
3. *Proof-of-concept study:* demonstrate that nanoscale QD light sources could energize and efficiently emit through coupling with the gold NP-supported plasmons by undertaking spectroscopic investigations of the physical parameters that influence visible light absorption and UV emission in the coupled systems. The composite quantum system proposed was considered an ideal platform to explore the quantum mechanical nature of nonlinear optical processes, allowing us to advance understanding of nonlinear optics.

By this approach the overarching goal was to discover the manner and degree to which NPs might enhance nonlinear processes in QDs and so ultimately, to create novel QD-based UV light sources, with emission properties designed by the user, which will be energized with visible light harvested by the attached NPs. However, the significance of this proposal ultimately lies in the better understanding of the energy exchange processes between plasmonic NPs and optically active QD media and how confined light fields can drive non-linear visible UV light up-conversion. Plasmons are considered the key to breaking down the diffraction limit of conventional optics because they enable the compact storage of optical energy in electron oscillations at the interfaces of metals and dielectrics. Accessing sub-optical wavelength length scales introduces the prospect of creating compact optical devices with new functionalities. Coupling electronic transitions directly to strongly localised optical modes is highly desirable because it would avoid the limitations of delivering light from a macroscopic external source to the nanometre scale.¹⁴ With new knowledge gained in this project, how to exploit these effects could not only be demonstrated, but also be applied more broadly and provide critical insight to help explain related phenomena. The outcomes of this

research project are likely to be of interest to both researchers in optical physics and spectroscopy and those interested in new methods to construct functional nanomaterials systems for nonlinear optics.

EXPERIMENT

Z-scan nonlinear absorption measurements¹

A full report on the approach we developed to discriminate ESA from two and three photon absorption, including details of the models used and the experimental set-up and parameters used, was communicated in Peer-Reviewed Publication #1 and is attached as Appendix #1.

Dynamic light scattering measurements²

A full report on the approach we developed to accurately measure molecular thickness of thin organic shells on inorganic ZnO QD and Au NP cores, including details of the model used and the experimental set-up and parameters used, was communicated in Peer-Reviewed Publication #2 and is attached as Appendix #2.

RESULTS and DISCUSSION

Theoretical Model verification

12 Month target: After the first year we planned to have developed a phenomenological quantum mechanical nonlinear optical model of the composite QD-NP particle. This was communicated as an honours thesis publication (see Non-Peer Reviewed Publication Section). While not quantitative, it allowed a conceptual understanding of nonlinear processes that are quantum mechanical in nature. Following on from this simplistic model a more rigorous numerical model will be developed to allow quantitative predictions of emissions we hope to experimentally measure in the future.

Final Project Outcomes:

The conceptual quantum mechanical model of the QD-NP composite particle aimed to answer the question, does the nonlinear optical properties of the composite particle result from the enhancement in the nonlinear optical properties of either the NP or QD due to the influence of the other? Or does the QD-NP composite need to be considered as a completely new quantum entity? With this in mind it became apparent that there are 3 possible pathways to nonlinear optical emission.

1. The QD perturbs the quantum mechanical system describing the metallic NP enhancing its nonlinear emission.
2. The NP perturbs the quantum mechanical system describing the semiconductor QD enhancing its nonlinear emission.
3. A completely new quantum mechanical system must be devised to describe the composite QD-NP particle and explain its nonlinear emission.

Under the right conditions, gold nanostructures are known to display nonlinear emission where the frequency of incident light is doubled through second harmonic generation (SHG). Therefore, of the 3 pathways listed we considered the first the more promising and investigated it through an honours student project. This project looked at determining what conditions must be satisfied in order for

gold particles to display SHG, since it is known that bulk gold does not. Our findings show that the gold NPs can exhibit SHG if the QD sufficiently perturbs the NPs dipole since this destroys the symmetry that prohibits SHG in bulk gold. Using time independent quantum perturbation theory we derived wavefunctions for the perturbed NP based on a free electron gas model. With these wavefunctions we then determined the SHG emission through second order time dependent quantum mechanical perturbation theory.

In 2013 we developed a conceptual quantum mechanical model of the metal nanoparticle system only to determine the properties and the environment required to optimize the nonlinear optical response. Besides the LSP effect, we considered it prudent to explore the extent to which noble metal NPs can contribute to nonlinear optical emission in a coupled system. The model focussed on the second harmonic generation (SHG) of light. The key findings of the study were:

1. Gold nanoparticle SHG emission will occur when a symmetry-breaking perturbation is introduced by the bonded semiconductor particle. Maximizing this perturbation increases the nonlinear response of the nanoparticle.
2. The incident light must have a component of field polarization aligned perpendicular to the interface between the gold nanoparticle and semiconductor in order for SHG to occur. This suggests self assembly with dipole alignment will improve the nonlinear light emission yield.
3. Increasing the gold nanoparticle radius increases the density of states resulting in a larger second order dipole moment and therefore more SHG.
4. Gold nanoparticle diameters of 20 nm or larger are preferable for optimal SHG output.
5. The SHG output from colloidal mixtures of gold nanoparticles is largely independent of nanoparticle radius for radii greater than 20 nm because any increase in SHG is counteracted by the corresponding fall off in nanoparticle concentration.

A full report on quantum mechanical model of second harmonic generation in NP-QD systems is provided as an attached in Appendix #3.

As an aside to the quantum mechanical model, a finite element numerical model was developed of a QD coupled to a gap plasmon waveguide (two rectangular strips of metal positioned nanometers apart). This was a simple model which approximated the QD as a dipole emitter, and calculated the spontaneous emission rate of the QD into plasmons supported by the gap plasmon waveguide. A full report on this model is attached in Appendix #4. We plan to improve upon this finite element model to simulate QD-NP systems.

Demonstration of nonlinear effects in QD-NP ordered and disordered media.

Target: After the first year we planned to have identified the experimental parameter range necessary to perform measurements on the coupled QD-NP particle systems. This involved measuring the linear and nonlinear optical properties of the ZnO QD material in bulk and particle form, in isolation from the gold NPs. This was necessary to determine what range of incident irradiance, pulse characteristics, and wavelengths the ZnO and gold could tolerate without damage.

This is crucial because nonlinear effects cannot be observed if the irradiance is too low, but too much absorbed light results in material vaporization.

Final Project Outcomes:

PhD candidate Susith Fernando was trained how to synthesise specific forms of ZnO colloid using an aminolysis method developed by a senior PhD student in Eric Waclawik's research group.¹⁵ He is now performing his own independent research on how to produce plasmonic gold nanoparticles suitable as a model experimental system for coupling to the ZnO quantum dots. During the 12 month project we developed the colloidal chemistry processes required to fabricate the gold and ZnO nanoparticle systems of interest both separately and as composites. This provided us with an excellent experimental platform to measure the nonlinear properties of the composite particles and compare to those of isolated nanocrystal control samples, thus revealing any enhancement. Susith's ZnO nanocrystal solutions were used to test the Z-scan system and refine the parameters suitable for nonlinear optical measurements. A major objective of this project was to uncover principles that can be applied to nonlinear optics. Our project's publications on pulse transit delay in Z-scan demonstrated that large nonlinear absorption occurs in ZnO hexagonal cone-shaped nanocrystals.¹

PhD candidate Matthew Shortell refined the experimental laser optical system, QUT's nanosecond Optical Parametric Oscillator, which we used to make the nonlinear optical absorption measurements. We are confident in the accuracy and reliability of this system. Matt demonstrated non-linear absorption with Susith's ZnO colloids.¹ The ZnO nanocone results indicated very high nonlinear absorption occurred with this material, even at low particle concentration. In addition, using our approach we were also able to determine whether there is any change in the nature of the nonlinearity and whether radiative emission from the system was enhanced or not. In terms of impact on the field, specifically, this simple method enables ESA to be identified using the Z-scan technique which does not require a large range of input laser fluencies or sophisticated pulse-probe experimental apparatus. As a follow on from this project, future work could be devoted to developing empirical relations between pulse delay and transmission measurements for different excited state absorption and refraction nonlinearities. Input pulses with a Gaussian beam profile would simplify this approach.

Finally a major indirect outcome of the research undertaken by these PhD students was the finding that current dynamic light scattering measurements can be inaccurate when the technique is expanded from homogeneous spherical nanoparticles to more complicated nanostructures (notably biological ones). Application of different diffusion models to account for vastly different complex structures has been the typical approach taken in DLS. We focussed on light-scattering properties. Our studies revealed that the diffusion models can result in conventional DLS analysis overestimating the hydrodynamic size in both volume- and number-weighted distributions, but that a correction to the formula used for scattering overcomes these short-comings. This insight is useful to anyone who would like to obtain accurate particle size information for organic ligand-coated nanoparticles using commercial dynamic light scattering instruments, such as the Malvern Zeta-sizer.²

LIST OF PUBLICATIONS AND SIGNIFICANT COLLABORATIONS THAT RESULTED FROM THE AOARD SUPPORTED PROJECT

Peer-Reviewed Journal Publications

1. M. P. Shortell, E. A. Jaatinen, J. Chang, E. R. Waclawik, "Using pulse transit delay in Z-scan to discriminate between excited-state absorption and other nonlinear processes in ZnO nanocones", *Optics Express*, **22** (6) (2014) 6222 - 6228.
2. M. Shortell, S. J. Fernando, E. A. Jaatinen, E. R. Waclawik, "Accurate Measurement of the Molecular Thickness of Thin Organic Shells on Small Inorganic Cores Using Dynamic Light Scattering", *Langmuir*, **30** (2) (2014) 470 - 476.
3. C. Perera, K.C. Vernon, A. Mcleod, "Simulations of the spontaneous emission of a quantum dot near a gap plasmon waveguide", *Journal of Applied Physics*, **115** (2014) 054314.

Non-Peer Reviewed Publications and Reports

1. S. Grunefeld, "Quantum Mechanical Model of Second Harmonic Generation in a NP-QD system", Honours Thesis, QUT (2013).

Submitted Publications for Peer Review

1. M. P. Shortell, "Zinc Oxide Quantum Dot Nanostructures", PhD Thesis, QUT, (Submitted for External Examination), March 2014.

Scientific Training

Higher Degree Research (HDR) Students:

Matthew Shortell; was supported directly by this grant, under Assoc. Prof. Jaatinen's guidance. He constructed and maintained the apparatus used to record nonlinear optical absorption. He performed the nonlinear measurements on nanocrystals and gold colloids and trained other students in this technique. The peer-reviewed publication outputs of this grant were achieved by Matt as the primary author, including his PhD thesis, which is now under review (Supervisors: Esa Jaatinen and Eric Waclawik).

Susith Fernando; Susith researched new methods for making and characterising the gold nanoparticle and quantum dot samples that are the focus of this work. Throughout the lifetime of the project, he collaborated with Matt Shortell (Supervisors: Eric Waclawik, Kristy Vernon and Esa Jaatinen)

Chamanei Perera; Chamanei developed the finite element model for QD-plasmon coupling for gap plasmon waveguides. She investigated the optimal positioning of the QD in relation to the waveguide to obtain maximal spontaneous emission of the QD into a plasmon mode. She also investigated the effect of waveguide geometrical parameters on the QD-NP coupling. (Supervisors: Kristy Vernon, Eric Waclawik and Esa Jaatinen)

Undergraduate Students

Johl Thorley (2013); Susith directly trained Johl in our laboratories for Johl's final year research unit. The undergraduate research project was entitled "*Langmuir-Blodgett Assembly of Nanoparticle SHG Films*". Susith trained Johl on how to characterise and produce gold colloid films suitable for testing in nonlinear optical films. (Supervisors: Susith Fernando & Eric Waclawik)

Swaantje Grunefeld (2013); Swaantje's 2013 honours research project involved the modelling of SHG in a coupled NP-QD system. Her thesis has provided a starting point where we can compare theory with experiment in order to refine the theoretical model and understand the QD-NP energy transfer and emission processes. (Undergraduate Honours Supervisor: Esa Jaatinen)

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