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UV Nano-Lights - Nonlinear Quantum Dot-Plasmon Coupling

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Final Report**

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ABSTRACT

Optical properties of hybrid nanoparticles consisting of zinc oxide (ZnO) nanoparticles coupled to gold (Au) nanoparticles, were examined both theoretically and experimentally. This work was performed to establish if confined light fields in the form of the localised surface plasmon resonance of the gold component of nanoparticle hybrids could enhance nonlinear emission by several orders of magnitude from the Au-ZnO nanoparticle system. In order to study this, experimental advances in the synthesis of coupled Au-ZnO nanoparticles were necessary. We discovered that hybrid nanoparticles made by crystallising ZnO from gold-nanoparticle seeds attached at an interface formed between the Au (111) crystal facets possessing hexagonal symmetry, and the (000 $\bar{1}$) basal plane of the seeded, wurzite ZnO nanocrystals. Additionally, a distinct gold seed size-effect was discovered. Au particle size played a crucial role in determining the structure and morphology of newly forming crystallites. Small (~4 nm) Au seeds promoted nucleation and growth of 1-to-1 Au-ZnO nanoparticle dimers. The large lattice mismatch between the Au seed crystal facet and the seeded-ZnO appeared to lead to a thermodynamically unfavourable situation that caused the 4nm diameter Au-seeds to detach, making them available to re-seed new ZnO nanocrystal growth at their surfaces. These small Au nanoparticle seeds thereby behaved as crystallisation 'catalysts'. Large Au seeds (~9 nm and ~11 nm) provided stable ZnO-nucleation sites and generated multi-crystalline Au₂ZnO trimers, tetramers and oligomers instead. Our published study confirmed a prediction for crystallisation promotion predicted by hard-sphere modelling of seeded crystal growth. By controlling gold seed-size, our study provided a synthetic method to control the number of ZnO nanoparticles attached to a gold nanoparticle [Fernando, ACS Crystal Growth and Design, 15, 4324, 2015]. The aim to control numbers of Au nanoparticles attached to individual ZnO nanoparticles was then accomplished after studying Au photodeposition on ZnO nanoparticles. We established that the rate of interfacial electron transfer from photoexcited ZnO nanoparticles to metastable, photolytically-prepared AuCl₂⁻ precursor ions in solution proved to be an essential parameter that

controlled the Au photodeposition, and thereby the form of the final Au-ZnO product. In this context, the solvent dielectric constant and dissolved oxygen in the solvent determined whether separate, individual Au nanoparticles attached to ZnO, or whether Au nanoparticle cluster (aggregate) growth occurred in these hybrid systems. The attachment of photodeposited gold to the ZnO nanoparticle hosts was confirmed to be non-epitaxial [Fernando, ACS Applied Materials & Interfaces, **8**, 14271, 2016]. z-Scan nonlinear absorption measurements were performed on the Au-ZnO hybrid nanoparticle systems to determine if Au nanoparticles significantly enhance optical nonlinearity in the hybrid nanoparticles through the intense electric fields generated by the localised surface plasmon absorption at the Au nanoparticle interface. When measured, it was found that a significant improvement in 2-photon absorption (2PA) properties of ZnO nanoparticles occurred when attached to plasmonic Au nanoparticles. Au-ZnO hybrids exhibited an enhancement in the 2PA coefficient (β) of up to 3-orders-of-magnitude. The 2PA absorption appeared to be independent of the size and the number of Au nanoparticles (NPs) attached to the ZnO NPs. An increase in saturable absorption was also observed when the ZnO NPs were covered with small Au NPs – this was attributed to a greater overall surface area coverage by the small Au NPs, compared to larger Au NPs, at the same mass fraction of Au. [Walden, Advanced Optical Materials - submitted, 2016]. Our studies have therefore proved that localised surface plasmon resonance absorption of visible light by Au NPs can enhance nonlinear absorption in ZnO by up to 3 orders of magnitude (for the case of excited state absorption) when the Au NPs are directly attached to ZnO in the hybrid.

INTRODUCTION

The project **aim was to discover new excitation pathways that enable visible-to-UV light up-conversion** using extremely compact, well defined coupled-nanoparticle systems. By understanding the manner and degree to which NPs might enhance nonlinear processes in QDs, the project aimed to uncover principles that could have application in future novel QD-based UV light sources. With this system, emission properties could be designed by the user and energized with visible light harvested by the attached NPs.

Summary of Specific Aims

The research team's plan was to investigate up-conversion of Au nanoparticle-ZnO nanoparticle hybrid composites by

1. *Modelling of Au-ZnO NP interactions*: to establish and validate an effective theoretical model of electromagnetic energy coupling between localized surface plasmons in Au NPs and light emission from ZnO in the hybrids, with an emphasis on visible to UV light up-conversion. Such nonlinear energy exchange still has not been explored deeply on a theoretical level.
2. *Fabrication Experiments*: controlled deposition of coupled Au-ZnO nanoparticle structures and
3. *Proof-of-concept study*: experimental demonstration that nanoscale Au-ZnO NP hybrids can perform as UV light sources that could be energized through visible light absorption and efficiently emit through coupling with the gold NP-supported plasmons. Spectroscopic investigations of the physical parameters that influence visible light absorption and UV emission in the coupled systems were examined. The composite nanoparticle system studied 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 project goals were to discover how coupled-NPs can perform as nonlinear optical materials and so ultimately, to create novel UV light sources, with emission properties designed by the user, which could be energized by visible light harvested by the attached

Au NPs. The scientific significance of this proposal lies in the improved level of understanding of energy exchange processes between plasmonic NPs and optically active colloid media. We set our experimental task to see how confined light fields might drive non-linear visible UV light up-conversion. Confined light fields in the form of localised surface 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 and 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.¹ The outcomes of this research project should 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.

PROJECT TIMELINE

The project timeline was segmented into 3 monthly intervals. The PhD students, assisted by the Research Associate, undertook the experimental component of the project under the supervision of EW and EJ with KV as the student's associate supervisor.

	Description	2014				2015			
1.	MODELLING OF QD-NP PLASMON COUPLING (KV and EJ)			X	X	X	X	X	X
2.	FABRICATION & CHARACTERIZATION OF COLLOIDAL QD-NP MATERIALS (EW)			X	X	X	X	X	X
3.	MEASUREMENT OF NONLINEAR OPTICAL PROPERTIES OF QD-NP HYBRID MEDIA (EJ)			X	X	X	X	X	X

RESEARCH OUTCOMES

(Grant Targets):

1. **Model Results** - Our plan was to develop a phenomenological quantum mechanical nonlinear optical model of the composite Au-ZnO hybrid nanoparticles, to perform numerical modelling on these and related systems. This has formed the training component of PhD student Morgana Longhorn's PhD. The modelling effort was initiated at the outset of the grant, with results communicated by thesis and journal papers throughout Morgana's PhD.

This study expanded quantum mechanical model previously developed in AOARD project FA2386-13-1-4016, to describe nonlinear effects composites.

Our 2014 z scan measurements revealed a significant change in the optical properties of the gold nanoparticle- ZnO quantum dot heterostructures that is dependent on the gold particle. Initial COMSOL modelling of the electromagnetic interaction shows significant plasmonic interaction at the interface between the gold and semiconductor particles as shown in Figure 1. This development ties in well with initial modelling that suggested that nonlinear effects, such as SHG, are produced in the binary nanostructure at the symmetry perturbation at the interface. The enhanced local electromagnetic field caused by plasmonic activity at the interface suggests a much greater nonlinear response could occur. In addition, we found that the change in optical properties caused by adding gold to the semiconductor dramatically reduces the laser damage threshold of the binary structure.

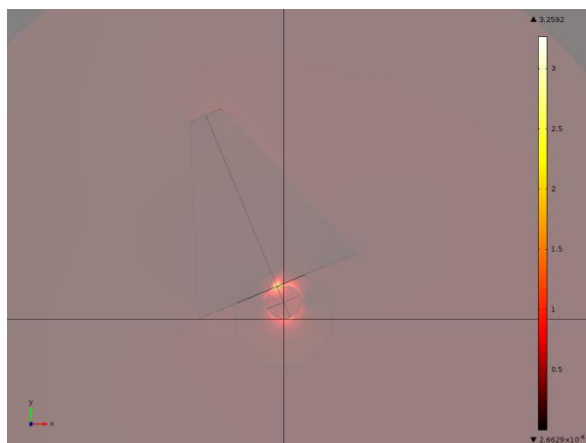


Figure 1: COMSOL model of the *EM*-field intensity for interaction between spherical gold nanoparticle and a truncated ZnO cone-shaped nanocrystal.

Unfortunately, COMSOL Multiphysics can only be used to simulate linear interaction of light with the hybrid. There are add ons to the model that can study nonlinear interactions, but the model must be 2D in nature for these add ons to be applicable. Hence numerical modelling of the NPs is being performed using an in-house 3D finite-difference time-domain code utilising absorbing boundary conditions written in MATLAB to simulate light striking the NPs. The permittivity of the metal NPs is simulated using the free electron model. The code was tested in the linear regime, allowing calculation of the near-field generated by the NP. The code was written in Cartesian co-ordinates to enable simulation of complex NP geometries likely to be encountered in experiment. Currently this code is being extended in 2 ways

1. Morgana (PhD student) worked on converting the code in spherical co-ordinates, to enable better meshing and smaller computational times
2. Scattering and absorption calculations are being written into the code

Once these linear codes have been completed, the calculations done by Moloney *et al.*² will be written into the codes to enable us to analyse nonlinear effects such as second harmonic generation.

2. **Experimental Results** - We identified the experimental parameter range necessary to perform measurements on the coupled QD-NP particle systems through the modelling of plasmonic effects as thin films. Measurements on the linear and nonlinear optical properties of the ZnO QD material in bulk and particle form in isolation from the gold NPs were performed in our previous study [AOARD project FA2386-13-1-4016]. To accomplish the Au-ZnO hybrid colloid synthesis, new synthetic experimental techniques were developed: **Synthetic Method (1)** The synthetic method to prepare pure, crystalline and monodisperse Au-ZnO nanocrystal hybrids for this project was perfected first. A crystal seeding approach was taken to produce 1-to-1 Au-ZnO NP hybrids and 1 Au NP-to-2,3,4&(more)-ZnO NPs in these hybrids, [Fernando, ACS Crystal Growth and Design, 15, 4324, 2015].

This study identified a significant size-effect on crystallisation parameters in this system. Judicious choice of gold nanoparticle seed size leads to a high yield of the sample type and shape we targeted at the outset of the grant (Figure 2 shows an excerpt from the manuscript in which we identified the lattice matching between gold and ZnO in this system)

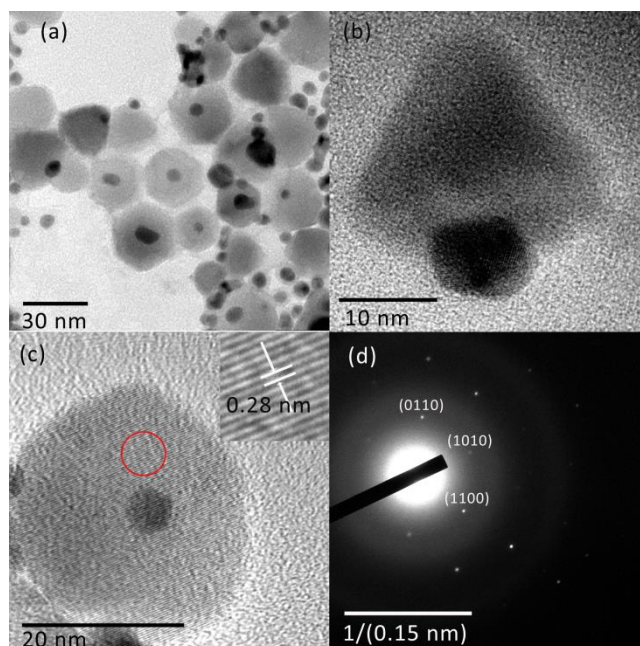


Figure 2: (a) TEM image of the as prepared Au-ZnO hybrid nanopyrramids product. (b) Magnified TEM image of the side-view of Au-ZnO hybrid single particle. (c) Magnified TEM image of the basal view of Au-ZnO hybrid single particle; the inset shows the HRTEM image of the marked area. (d) SAED pattern of Au-ZnO hybrid particle along [0001] axis.

Although some free gold nanoparticles can be observed in the TEM images of Figure 2(a), we have since shown that a simple centrifuge step at the end of the synthesis separates the product into hybrids-only. Precise control over the synthesis of these hybrids took a greater amount of research effort (and hence time) than was anticipated at the outset of the grant.

Synthetic method (2) Multiple Au NP attachment to individual ZnO nanoparticles was accomplished after investigating photodeposition approaches to their production [Fernando, ACS Applied Materials & Interfaces, **8**, 14271, 2016]. An excerpt from this manuscript provides a schematic representation of the photodeposition approach we used to accomplish this task is given in Figure 3. These studies measured the linear optical absorption and emission properties of these materials – thereby completing task 2 of the Project Timeline. During the course of these studies our team developed a new, simple technique to remove the scattering component of light from the fluorescence emission with commonly-used fluorimeters [Shortell, Optics Express - submitted, 2016].

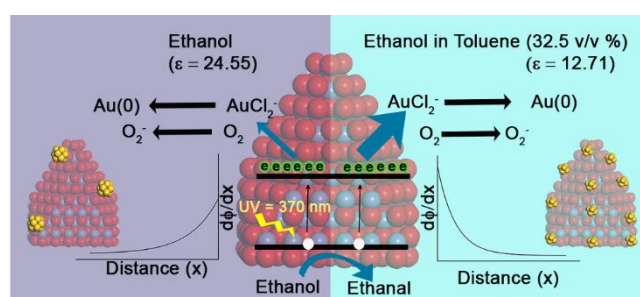


Figure 3. Schematic representation of the potential gradient at the excited ZnO NP-solution interphase, in two different solvent systems and the subsequent photodeposition product.

During 2014, our nonlinear optical measurement capability was significantly enhanced through a range of developments to our z scan measuring facility. The system was fully automated which allowed the nonlinear properties of a sample to be measured and calculated in a few minutes compared to the half an hour it previously took. This efficiency dividend allowed us to measure a much larger number of samples. This greatly improved our understanding of the nanostructure light interaction and also has helped understand and remove unwanted signal contamination through optical element interference effects as well as sample scatter. Following a refurbishment of the laser system with the addition of a new third harmonic unit, our laser output power was increased allowing us to probe samples with weaker optical nonlinearities. In-house z-scan nonlinear measurement on these hybrids was completed recently [Walden, Advanced Optical Materials - submitted, 2016].

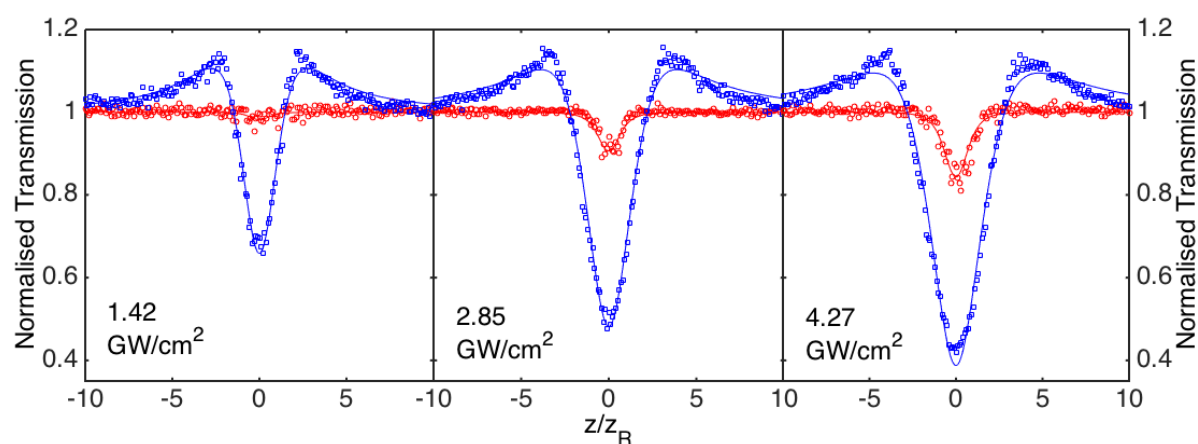


Figure 4. Open aperture zscan traces of ZnO (red circles) and ZnO-Au (blue squares) samples at peak intensities of 1.42, 2.85 and 4.27 GW/cm^2 . Solid lines show theoretical fits to Equations 1 and 2 for ZnO and Equations 1 and 3 for ZnO-Au.

List of Publications and Training Outcomes

Peer-Reviewed Journal Publications

3. J. F. S. Fernando, M. P. Shortell, C. J. Noble, J. R. Harmer, E. A. Jaatinen, E. R. Waclawik, "Controlling Au Photodeposition on Large ZnO Nanoparticles", *ACS Applied Materials & Interfaces*, **8**, 14271–14283, 2016.
4. C.S. Perera, A.M. Funston, H. Cheng, K.C. Vernon, "Mapping bound plasmon propagation on a nanoscale stripe waveguide using quantum dots: Effect of spacer layer thickness", *BJ Nano*, **6**, 2046-2051, 2015.
5. J.F.S. Fernando, M.P. Shortell, K.C. Vernon, E.A. Jaatinen, E.R. Waclawik, "Small gold nanoparticles as crystallization 'catalysts': Effect of Seed size and concentration on Au-ZnO Hetero Nanoparticles", *ACS Crystal Growth and Design*, **15 (9)**, 4324-4330, 2015.
6. C. Perera, K.C. Vernon, A.M. Funston, E. Cheng, F. Eftekhari, T.J. Davis, "Excitation of bound plasmons along nanoscale stripe waveguides: a comparison of edge and grating coupling techniques", *Optics Express*, **23 (8)**, 10188-10197, 2015.

Conference Publications and Proceedings

1. C. S. Hettiarachchige, K. Vernon, "Optimizing the quantum dot: Plasmon interaction in a nano gap waveguide", In Boardman, A. (Ed.) *Proceedings of SPIE 9163, Plasmonics: Metallic*

Nanostructures and Their Optical Properties XII, Society of Photo-Optical Instrumentation Engineers, San Diego, CA, 91632E-1-8 (2014).

Thesis Publications and Reports

1. Chamanei Sandamali Perera Hettiarachchige, *“The Interaction of Quantum Dots with Plasmons Supported by Metal Waveguides”* QUT PhD Thesis (2016)
Free available available online access: <http://eprints.qut.edu.au/92278/>
2. J. Davies, *“A Quantum Mechanical Model for the Inclusion of Intersubband Transitions in the Calculation of the Second Harmonic Generation from a ZnO/Au Quantum Dot - Nanoparticle Hybrid System”* Physics Honours Thesis, QUT (2015).
3. M. Shortell, *“Zinc Oxide Quantum Dot Nanostructures”*, QUT PhD Thesis (2014) Free available online access: <http://eprints.qut.edu.au/76335/>
4. M. Longhorn, *“Quantum mechanical model of second harmonic light from a quantum dot - nanoparticle hybrid nanostructure”*, Physics Honours thesis, QUT (2014)
5. L. Hegarty, *“Synthesis of hybridised metal-semiconductor nanoparticles for nonlinear applications”*, CVB304 Chemistry Research Project Report, QUT (2014).

Manuscripts in Preparation and Submitted Publications for Peer Review

1. J. F. S. Fernando, *“Engineering of Colloidal Gold-Zinc Oxide Hybrid Nanoparticles”* QUT PhD Thesis (Submitted for External Review, 2016)
2. M. P. Shortell, R. A. Hewins, J. F.S. Fernando, S. L. Walden, E. R. Waclawik, E. A. Jaatinen, *“Multi-angle fluorometer technique for the determination of absorption and scattering coefficients of nanoparticles”*, Manuscript Submitted to Optics Express, 1st June 2016.
3. S. L. Walden, J. F. S. Fernando, M. P. Shortell, E. R. Waclawik, E. A. Jaatinen, *“Comparison of enhancements in nonlinear absorption and fluorescence in ZnO and Au-ZnO nanostructures”*, Manuscript Submitted to Advanced Optical Materials (Wiley VCH), 18th May 2016.
4. C.S Perera, K.C. Vernon, H. Cheng, J. Sathian, E.A. Jaatinen, T.J. Davis, *“Compact nanoscale refractive index sensors for lab-on-a-chip sensing”*, accepted 13th of May, 2016, BJ Nano.

Scientific Training

Higher Degree Research (HDR) Students:

PhD C. (Chani) S. Perera. Hettiarachchige Thesis: *“The Interaction of Quantum Dots with Plasmons Supported by Metal Waveguides”*, (2016). 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.

Chani fabricated stripe plasmon waveguides and excited long range plasmon modes. This work was published in Optics Express in 2015. She extended this experimental work to coupling between plasmons in the stripe waveguides and quantum dot films suspended above the waveguide and was able to show that the optimal distance for the QD film from the waveguide was 20 nm [see publication #4 & Thesis publication #1]. At this distance maximal coupling between the quantum dots and plasmon occurred. This value matched the theoretical predictions. It is hoped that this work could be extended, by future PhD students, to the coupling of quantum dots to lithographically fabricated nanoparticles. Lithography gives finer control over the particle geometries, allowing for the fabrication of interesting particle shapes. However it is much more expensive than synthesis methods (Supervisors: Kristy Vernon, Eric Waclawik and Esa Jaatinen)

PhD Matthew Paul Shortell Thesis: *“Zinc oxide quantum dot nanostructures”* (2014). The focus of Matt’s research was to fabricate suitable zinc oxide nanostructures, accurately characterize their geometrical properties, and measure the nonlinear optical properties. The findings presented in his

thesis (<http://eprints.qut.edu.au/76335/>) have advanced not only the understanding of zinc oxide nanoparticles, but also the methods used to characterize nanoparticles in general. The new techniques developed for core-shell nanoparticles using dynamic light scattering and experimentally distinguishing between various nonlinear optical processes are applicable to a wide range of nanoparticle samples [submitted publication #2 – Optics Express]. (Supervisors: A. Prof. Eric Waclawik, A. Prof Esa Jaatinen)

PhD Sarah Walden (January 2013 - current); Sarah became our chief measurement specialist of the nonlinear optical properties of the binary nanostructures. Her work has revealed that while the addition of gold nanoparticles does enhance the nonlinear emission from the heterostructure, it also dramatically reduces the damage threshold. Sarah is finalizing experiments and a quantitative model of the damage mechanism. In addition, Sarah built on our prior work in determining the various competing nonlinear optical processes that occur in the binary nanostructure for her experimentally-based PhD thesis [submitted publication #3].

PhD Joseph Fernando (July 2013 – current); Joe established new methods for controlling Au-ZnO nanoparticle hybrids. This work has been summarised journal articles published in ACS Applied Materials & Interfaces (#1) and ACS journal Crystal Growth & Design (#3). The significance of the work is that it established a gold seed particle size-dependency on heterogeneous, seeded-ZnO nanocrystal growth and he has also developed a method to control gold nanoparticle growth on ZnO nanocrystals. These are the test materials for the nonlinear measurements used by Sarah [submitted paper #3] (Supervisors: Eric Waclawik, Kristy Vernon and Esa Jaatinen)

PhD Morgana Longhorn (commenced February 2015); Morgana completed her physics honours thesis using quantum perturbation theory to investigate the enhancement in optical second harmonic generation in zinc oxide semiconductor quantum dots coupled with gold nanoparticles. This work complements prior work done by Sarah Walden (2012) and other students that investigated nonlinear effects in perturbed gold nanoparticles. Morgana's honours work found that the second harmonic emission decays exponentially with increasing band gap and that the emission from the quantum dot will always be less than from a gold nanoparticle of the same size.

As a result of Morgana's successful honours project she was awarded a scholarship and is now undertaking a PhD in Synergistic second harmonic enhancement in binary hybrid nanocrystal heterostructures. This work will attempt to accurately model the nonlinear light – nanostructure interaction using numerical methods such as the Finite Difference Time Domain (FDTD) method.

PhD Angus McLeod (July 2014 - current); Angus McLeod completed his masters in single particle spectroscopy of gold nanoparticles on glass. His PhD is devoted to the study of the optical coupling between single nanoparticles and exotic materials such as graphene and quantum dots. Angus worked with Joseph Fernando on studying the optical properties of gold-ZnO nanocone systems using single particle spectroscopy (Supervisors: Kristy Vernon, Nunzio Motta and Ken Ostrikov)

MSc Liam Hegarty (February 2015 – current); Following on from his undergraduate project in 2014, Liam started his SC80 Masters by Research degree on the synthesis of gold NP – semiconductor NP composites for the UV Nanolights AOARD Project in February 2015. (Supervisor: Eric Waclawik)

Undergraduate Students

Liam Hegarty (August – December 2014); PhD student, Joe Fernando directly trained and supervised Liam in our materials chemistry laboratories during Liam's final year chemistry project research unit, CVB304 Research Project. We used this opportunity to explore new materials for the UV Nanolights AOARD project. The undergraduate research project was entitled "*Synthesis of hybridised metal-semiconductor nanoparticles for nonlinear applications*". The project task was to explore synthesis of the efficient nonlinear optical material iron iodate ($\text{Fe}(\text{IO}_3)_3$) which is a known effective second-

harmonic generation material explored by Bell Labs in the 1970's. Attempts were made to couple gold nanoparticles to the iron iodate without the use of long-chain organic ligands. (Supervisors: Joseph Fernando & Eric Waclawik)

EXECUTIVE SUMMARY

By July 2016, this UV Nanolights project will have directly led to research training of four (4) PhD completions one (1) MSc completion, with communication of research outcomes by journal publications and by thesis, on each of the separate aspects of the project: synthesis, modelling and nonlinear optical measurements. In the course of this work, the coupled nanoparticle synthesis, nonlinear absorption measurements and theoretical modelling of the systems was performed. The hypothesis that confined light fields in the form of localised surface plasmon resonance supported by gold nanoparticles could absorb visible light and lead to enhanced nonlinear optical effects in Au-ZnO nanoparticle hybrids was confirmed. When measured, it was found that a significant improvement in 2-photon absorption (2PA) properties of ZnO nanoparticles occurred when attached to plasmonic Au nanoparticles. Au-ZnO hybrids exhibited an enhancement in the 2PA coefficient (β) of up to 3-orders-of-magnitude. The 2PA absorption appeared to be independent of the size and the number of Au nanoparticles (NPs) attached to the ZnO NPs. An increase in saturable absorption was also observed when the ZnO NPs were covered with small Au NPs – this was attributed to a greater overall surface area coverage by the small Au NPs, compared to larger Au NPs, at the same mass fraction of Au. [Walden, *Advanced Optical Materials* - submitted, 2016]. Our studies have therefore proved that localised surface plasmon resonance absorption of visible light by Au NPs can enhance nonlinear absorption in ZnO by up to 3 orders of magnitude (for the case of excited state absorption) when the Au NPs are directly attached to ZnO in the hybrid.

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