OPTICAL FINGERPRINTS OF UPCONVERSION NANOPARTICLES FOR SUPER-CAPACITY MULTIPLEXING

By

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Certificate of Original Authorship

I, Jiayan Liao declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledged.

In addition, I certify that all information sources and literatures used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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List of Publications

Research papers:

[1] **Jiayan Liao,** Dayong Jin, Chaohao Chen, Yiming Li, Jiajia Zhou, "Helix shape power-dependent properties of single UCNPs", The Journal of Physical Chemistry Letters, 11 (8), 2883-2890

[2] **Jiayan Liao,** Baolei Liu, Yiliao Song, Fan Wang, Chaohao Chen, Jiajia Zhou, Jie Lu, Dayong Jin, "Optical Fingerprints of Single Nanoparticles for Deep Learning Aided Super-Capacity Optical Multiplexing", revised, Nature Communications.

[3] Jiajia Zhou, Shihui Wen, **Jiayan Liao,** Christian Clarke, Sherif Abdulkader Tawfik, Wei Ren, Chao Mi, Fan Wang, Dayong Jin, "Activation of the surface dark-layer to enhance upconversion in a thermal field", Nature Photonics, 2018, 12, 154.

[4] Baolei Liu, Chaohao Chen, Xiangjun Di, **Jiayan Liao,** Shihui Wen, Qian Peter Su, Xuchen Shan, Zai-Quan Xu, Lining Arnold Ju, Fan Wang, Dayong Jin, "Upconversion nonlinear structured illumination microscopy", Nano Letters, 2020, 20, 7, 4775–4781.

[5] Chaohao Chen, Baolei Liu, Yongtao Liu, **Jiayan Liao,** Xuchen Shan, Dayong Jin, "Fourier domain heterochromatic fusion for single beam scanning super-resolution microscopy" revised, Nature Communication.

[6] Xuchen Shan, Fan Wang, Dejiang Wang, Shihui Wen, Chaohao Chen, Xiangjun Di, Peng Nie, **Jiayan Liao,** Yongtao Liu, Peter Reece, Dayong Jin, "Optical trapping beyond refractive index mismatch using ion resonance", revised, Nature Nanotechnology.

[7] Hao He, Baolei Liu, Shihui Wen, **Jiayan Liao,** Gungun Lin, Jiajia Zhou, Dayong Jin, "Quantitative Lateral Flow Strip Sensor Using Highly Doped UCNPs", Analytical Chemistry, 2018, 90, 12356-12360.

[8] Yingzhu Zhou, Yinghui Chen, Hao He, **Jiayan Liao,** Hien TT Duong, Maryam Parviz, Dayong Jin, "Activation of the surface dark-layer to enhance upconversion in a thermal field", Journal of Rare Earths, 2018, 37, 11-18.

[9] **Jiayan Liao,** Zhengwen Yang, Bo Shao, Jun Li, Jianbei Qiu, Zhiguo Song, Yong Yang, "Significant Suppression of Photoluminescence of $NaGdF_4$: Eu^{3+} Nanocrystals in the Crystalline Colloidal Arrays." Science of Advanced Materials, 2016, 8, 697-702.

([1] – [8] are closely related to my Ph.D. program)

Conference papers:

2020 Oral presentation, Institute for Biomedical Materials and Devices (IBMD), UTS Research Week (Sydney, Australia)

2020 Oral presentation, International Conference on Nanoscience and Nanotechnology, ICONN 2020, (Brisbane, Australia)

2020 Poster presentation, Three Wise Men Winter School on Luminescent Nanothermometry for Biomedical Applications (Madrid, Spain)

2019 Poster presentation, International Symposium on Luminescent Materials, Phosphor Safari 2019 (Xiamen, China)

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Abstract

This thesis includes six chapters.

Chapter 1 outlines the background knowledge and motivation relevant to the development of luminescence materials for optical multiplexing. The materials include fluorescence dyes, quantum dots, metal particles and upconversion nanoparticles (UCNPs). This thesis introduces different optical dimensions of UCNPs. The challenges associated with luminescence materials for multiplexing are approached. These sections detail the motivation for and the specific aims of the current study—that is, to tune the energy-transfer process in the core-shell UCNPs and to achieve the optical multiplexing of UCNPs in the spectral and lifetime orthogonal dimensions.

Chapter 2 provides detailed information on the materials, instruments and equipment, preparation and characterization methods.

Chapter 3 is the first research chapter, and it investigates the peak tuning of the excited state population of powder samples in Nd-Yb-Tm core-shell UCNPs. For the take-off of upconversion emissions, the duration can be extended from 100 μs to 900 μs after the 808 nm excitation is switched off. This strategy creates a set of time-resolved emission profiles over a large dynamic range, where they can be tuned from either the time of rising or decay.

Chapter 4 synthesizes two groups of UCNPs: Yb^{3+}-Nd^{3+}-Er^{3+} and Yb^{3+}-Tm^{3+} core-shell UCNPs. This chapter outlines the systematic analysis (via the confocal microscope system) of the emission intensity/spectra and lifetimes of single UCNPs. Strategies to control the energy migration process and to arbitrarily tune the rising and decay times and the plateau moment are presented, where it is suggested a unique time-domain optical fingerprint can be assigned to each type of nanoparticles.

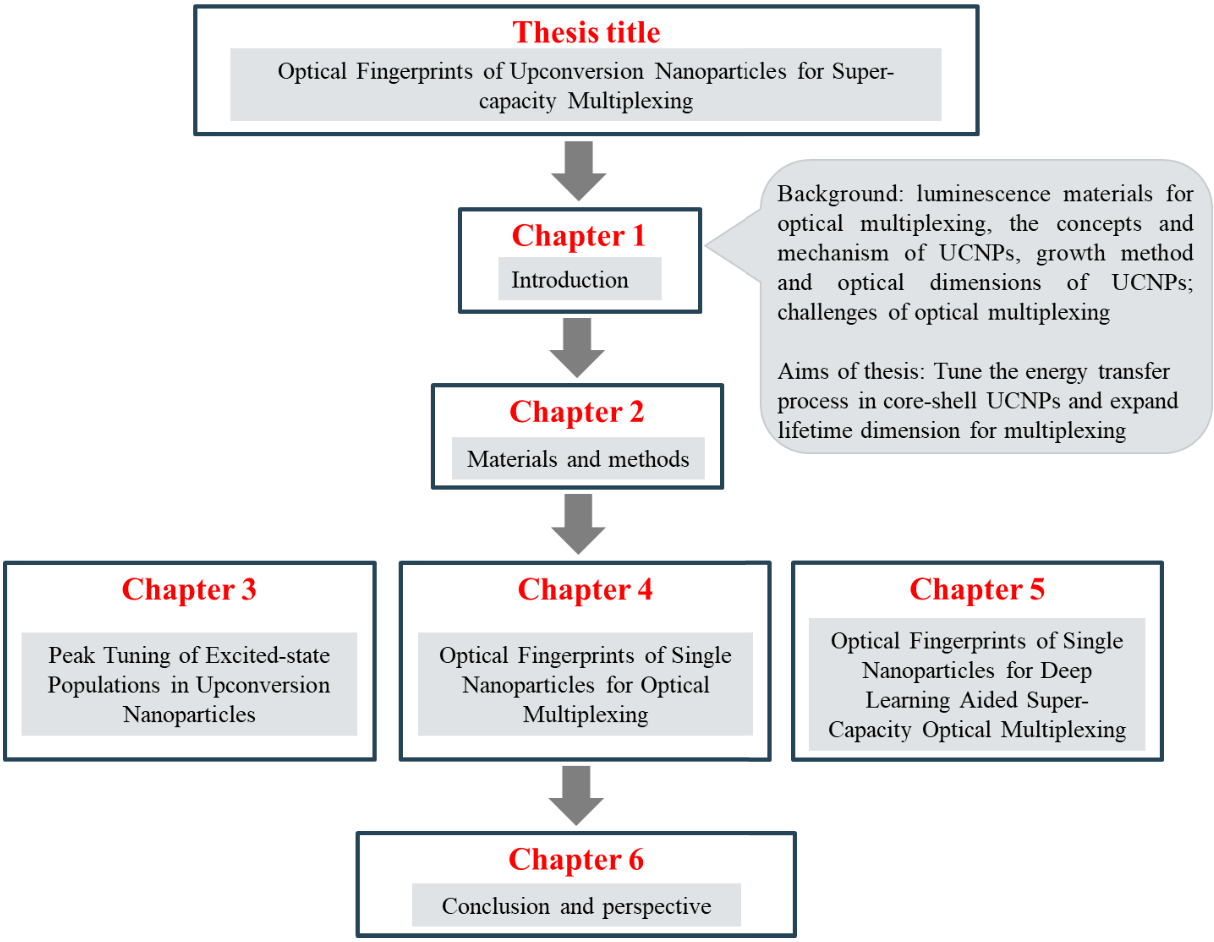
Chapter 5 outlines the finding that the nanoparticles show a unique lifetime signature under wide-field systems upon 976 nm (Yb^{3+}-Tm^{3+} doped UCNPs) and 808 nm (Yb^{3+}-Nd^{3+}-Er^{3+} doped UCNPs) excitation. To achieve high-throughput multiplexing, the lifetime profiles can

be detected under a wide-field microscope system. A novel method is also introduced here (i.e., deep learning) to decode the lifetime fingerprints of 14 batches of UCNPs. Through deep learning, the large amount of optical data from different batches of UCNPs allows the classification of each single UCNPs for the untapped opportunity to decode these nanoscale lifetime barcodes. The classification capability associated with deep learning allows all 14 kinds of UCNPs to achieve accuracies of over 90%.

Finally, the research results of this thesis are summarised in Chapter 6. Potential future developments and prospects regarding the multidimensional optical properties of UCNPs are discussed.

Keywords: rare earth doped nanomaterials, upconversion, optical multiplexing, wide-field microscope, machining learning, DNA conjugation.

The relationship between these chapters is shown in the flowchart given below.



List of Acronyms (in alphabetic order)

BET	Back Energy Transfer
CR	Cross-Relaxation
DNA	Deoxyribonucleic Acid
EMCCD	Electron Multiplying Charge Coupled Device
ESA	Excited State Absorption
ETU	Energy Transfer Upconversion
ET	Energy Transfer
EDC	N-(3-Dimethylaminopropyl)-N′-ethyl carbodiimide hydrochloride
ESP	Excited-state Populations
HCl	Hydrochloric Acid
IEM	Interfacial Energy Migration
NIR	Near-Infrared
NaOH	Sodium Hydroxide
NH_4F	Ammonium Fluoride
OA	Oleic Acid
ODE	1-Octadecene
QDs	Quantum Dots
RE	Rare Rarth
SEM	Scanning Electron Microscopy

STEM	Scanning Transition Electron Microscopy
SERS	Surface-enhanced Raman Spectroscopy
SHG	Second-harmonic Generation
TEM	Transmission Electron Microscopy
TPA	Two-photon Absorption
THF	Tetrahydrofuran
UCNPs	Upconversion Nanoparticles
UV	Ultraviolet
XRD	X-ray Diffraction