

**OPTICAL FINGERPRINTS OF UPCONVERSION
NANOPARTICLES FOR SUPER-CAPACITY
MULTIPLEXING**

By

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This thesis is presented for the degree of Doctor of Philosophy

September 2020

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.

This research is supported by China Scholarship Council Scholarships (Jiayan Liao: No. 201508530231) and University of Technology Sydney Ph.D. Scholarship.

This research is supported by an Australian Government Research Training Program.

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Signature: Signature removed prior to publication.

Date: 07-09-2020

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Acknowledgments

After 4 years' study at the University of Technology Sydney (UTS), I have completed my Ph.D. thesis with the help of people in our group. Firstly, I would like to thank my supervisor, Prof. Dayong Jin, for the valuable opportunity of the Ph.D. study in Australia. Dr. Jin is a professor of great personal charisma, always considerate, patient and encouraging. From the beginning of my study, Prof. Jin has paid much energy and time to my research plan development. I respect very much his diligence in research and kindness in person. I learned a lot from Jin's self-motivated and optimistic attitude to life, aspiring, energetic and collaborative research style. He has insights to foresee the trend of the related research area and provided great ideas and suggestions for my research. I could not imagine how to complete my research without his guidance. Moreover, supervised by Prof. Jin, I have improved my ability on how to conduct the research project logically. I feel very lucky to have such great mentors and very grateful to them for their enormous efforts in guiding me throughout my Ph.D. study to reach the completion of this thesis.

Meanwhile, I also would like to express my heartfelt thanks to my supervisor Dr. Jiajia Zhou, for her precious supervision and guidance through all the years I studied at UTS. Although Dr. Zhou has been my principal supervisor in the last year of my Ph.D. study, she started to support my research since 2017 as my research project is closely connected to her research area. Dr. Zhou helped me a lot with my experimental design, discussion and we overcame the challenges in my research together. I learned how to undertake a research project logically, solve problems and overcome challenges. She is my idol. Her tender care and warm encouragement were of vital importance to my growth.

I acknowledge our group members and lab colleagues. I am proud that our lab is a place full of the atmosphere of sharing and support. Greatly, thanks a lot to our group members and collaborators who contributed to my research. Thanks to Dr. Fan Wang, Baolei Liu and Chaohao Chen for teaching me on the optical test systems. As my background is optical

material synthesis, I learned a lot of new knowledge on the optical instrument operation from them, and my research benefits a lot from this. Also, I would like to thank Dr. Shihui Wen, Dr. Chao Mi, Dr. Deming Liu and Dr. Helen Xu for help with upconversion nanoparticle synthesis. Thanks to Prof. Jie Lu and Dr. Yiliao Song from the Faculty of Engineering and IT, the University of Technology Sydney for providing deep learning algorithm support. Thanks for Dr. Lin Zhang from the University of New South Wales for providing the polymer used in my research, Dr. Yinghui Chen for the DNA conjugation, Dr. Mark Lockrey for STEM characterization and Dr. Hongwei Liu in the University of Sydney for his assistance on TEM characterization.

Next, I would like to acknowledge all my colleagues who have given me help over the last several years. Thanks to the optics group including Zhiguang Zhou, Yongtao Liu, Xuchen Shan, and Yuan Liu. And my office mates, Hao He, Wei Ren, Ming Guan, Dejiang Wang, Lei Ding, Xiangjun Di, Guochen Bao, Guochen Fang. I cherish interactions with Dr. Gungun Lin, Dr. Qian Peter Su, Dr. Hongxu Lu, Dr. Joris Goudsmits, Dr. Olga Shimoni. Thank you for a lot of beneficial discussions and helps in both my study and life, and I appreciate your supports and friendship very much.

I give my deep appreciation to my family. I thank my parents for their moral support to my oversea Ph.D. study, understanding and sincere company. Words can't express how much I love all of you.

Special thanks to our school manager Elizabeth Gurung Tamang, lab manager Katie McBean, scientific officer Mark Lockrey and Ronald Shimmon for their technical support.

Finally, I would like to acknowledge the China Scholarship Council Scholarships and UTS for providing me with Ph.D. scholarship and research opportunities.

Table of Contents

Certificate of Original Authorship	II
Acknowledgments.....	IV
List of Publications	X
Abstract.....	XII
List of Acronyms (in alphabetic order).....	XV
Chapter 1 Introduction.....	1
1.1 Luminescence materials for optical multiplexing	1
1.1.1 Fluorescence dyes.....	2
1.1.2 Quantum dots.....	4
1.1.3 Metal particles	6
1.1.4 Rare-earth doped nanoparticles	8
1.2 Fundamentals and development of UCNPs	10
1.2.1 Lanthanides-doped UCNPs	11
1.2.2 Mechanism of UC luminescence	14
1.2.3 Core-shell structure strategy of UCNPs	18
1.2.4 Excitation wavelength design in core-shell UCNPs.....	23
1.3 Optical parameters of UCNPs	29
1.3.1 Wavelength characteristics of UCNPs.....	30
1.3.2 Emission ratio characteristics of UCNPs.....	31
1.3.3 Polarization characteristics of UCNPs	34
1.3.4 Lifetime characteristics of UCNPs	36
1.4 Challenges of luminescence materials for super-capacity optical multiplexing	38
1.4.1 Limitations for spectral multiplexing	38
1.4.2 Micro-sized information carriers	39
1.5 Thesis aims and outline	39
1.6 Reference.....	42
Chapter 2 Materials and methods	64
2.1 Chemicals and reagents.....	64

2.2 Instruments and equipment	67
2.3 Characterisation methods and home-built optical instruments	68
2.3.1 Characterisation methods	68
2.3.2 Spectra measurement system.....	70
2.3.3 Confocal microscope for single nanoparticles.....	70
2.3.4 Wide-field microscope for spectra and lifetime measurement	72
2.4 General NaREF ₄ nanocrystals and polymer synthesis	75
2.4.1 General NaREF ₄ nanocrystals synthesis methods	75
2.4.2 Synthesis protocols of UCNPs	76
2.4.3 Synthesis protocols of PEGMEMA-b-EGMP polymer.....	80
2.5 PEGMEMA-b-EGMP polymer-modified UCNPs	82
2.6 Detection of DNA based on UCNPs assay	84
2.6.1 Conjugation of carboxyl-UCNPs with NH ₂ -DNA	84
2.6.2 Detection of DNA target based on UCNPs assay.....	85
2.7 Data processing and networks for deep learning	86
2.7.1 Data processing to select single nanoparticles	87
2.7.2 Determining the network architecture	88
2.7.3 Network architecture	89
2.8 Reference.....	90
Chapter 3 Peak Tuning of Excited-state Populations in Upconversion Nanoparticles ...	93
3.1 Preamble.....	93
3.2 Introduction	93
3.3 Experimental section.....	95
3.3.1 Synthesis of NaYF ₄ :18%Yb, 0.5%Nd, 0.2%Tm core nanoparticles.....	95
3.3.2 Synthesis of core-shell nanoparticles	96
3.4 Results and discussion.....	96
3.4.1 Materials characterization and the lifetime peak tailoring in core-shell ensemble nanoparticles.....	96
3.4.2 Lifetime peak tailoring in core-shell-shell ensemble nanoparticles.	101
3.4.3 Cross-relaxation in core-shell-shell ensemble nanoparticles.....	104
3.4.4 The library of time-resolved profiles in core-shell-shell ensemble nanoparticles.	106

3.5 Conclusion.....	109
3.6 Reference.....	109
Chapter 4 Optical Fingerprints of Single Nanoparticles for Optical Multiplexing.....	113
4.1 Preamble.....	113
4.2 Introduction.....	114
4.3 Experimental section.....	115
4.3.1 Synthesis of NaYF ₄ : Yb, Er/Tm core nanoparticles.....	115
4.3.2 Synthesis of core-shell nanoparticles.....	116
4.4 Results and discussion.....	118
4.4.1 Materials characterization of two groups of nanoparticles.....	118
4.4.2 Optical fingerprints of Yb ³⁺ -Nd ³⁺ -Er ³⁺ doped single nanoparticles under confocal microscope system.....	126
4.4.3 Lifetime property of two groups of single nanoparticles under confocal microscope system.....	133
4.5 Conclusion.....	140
4.6 Reference.....	140
Chapter 5 Optical Fingerprints of Single Nanoparticles for Deep Learning Aided Super-Capacity Optical Multiplexing.....	144
5.1 Preamble.....	144
5.2 Introduction.....	145
5.3 Experimental section.....	147
5.3.1 Synthesis of NaYF ₄ : Yb ³⁺ , Tm ³⁺ / Er ³⁺ core nanoparticles.....	147
5.3.2 Synthesis of core-shell nanoparticles.....	148
5.4 Results and Discussion.....	149
5.4.1 Optical system setup and material characterization of single nanoparticles.....	149
5.4.2 Optical signatures of fourteen kinds of τ^2 -dots nanoparticles under the wide-field microscope system.....	154
5.4.3 Deep learning aided single nanoparticles classification.....	161
5.4.4 DNA conjugation with Yb ³⁺ -Tm ³⁺ doped single nanoparticles.....	170
5.5 Conclusion.....	173
5.6 Reference.....	174
Chapter 6 Conclusion and Perspective.....	177

6.1 Conclusion.....	177
6.2 Perspective	180
6.3 Reference.....	182

List of Publications

Research papers:

- [1] **Jiayan Liao**, Dayong Jin, Chao hao 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, Chao hao 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, Chao hao 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] Chao hao 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, Chao hao 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 NaGdF₄: Eu³⁺ 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)

Awards:

Vice Chancellor’s Postgraduate Research Student Conference fund, 2019

CSC-UTS Ph.D. scholarship, 2016-2020

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: $\text{Yb}^{3+}\text{-Nd}^{3+}\text{-Er}^{3+}$ and $\text{Yb}^{3+}\text{-Tm}^{3+}$ 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.

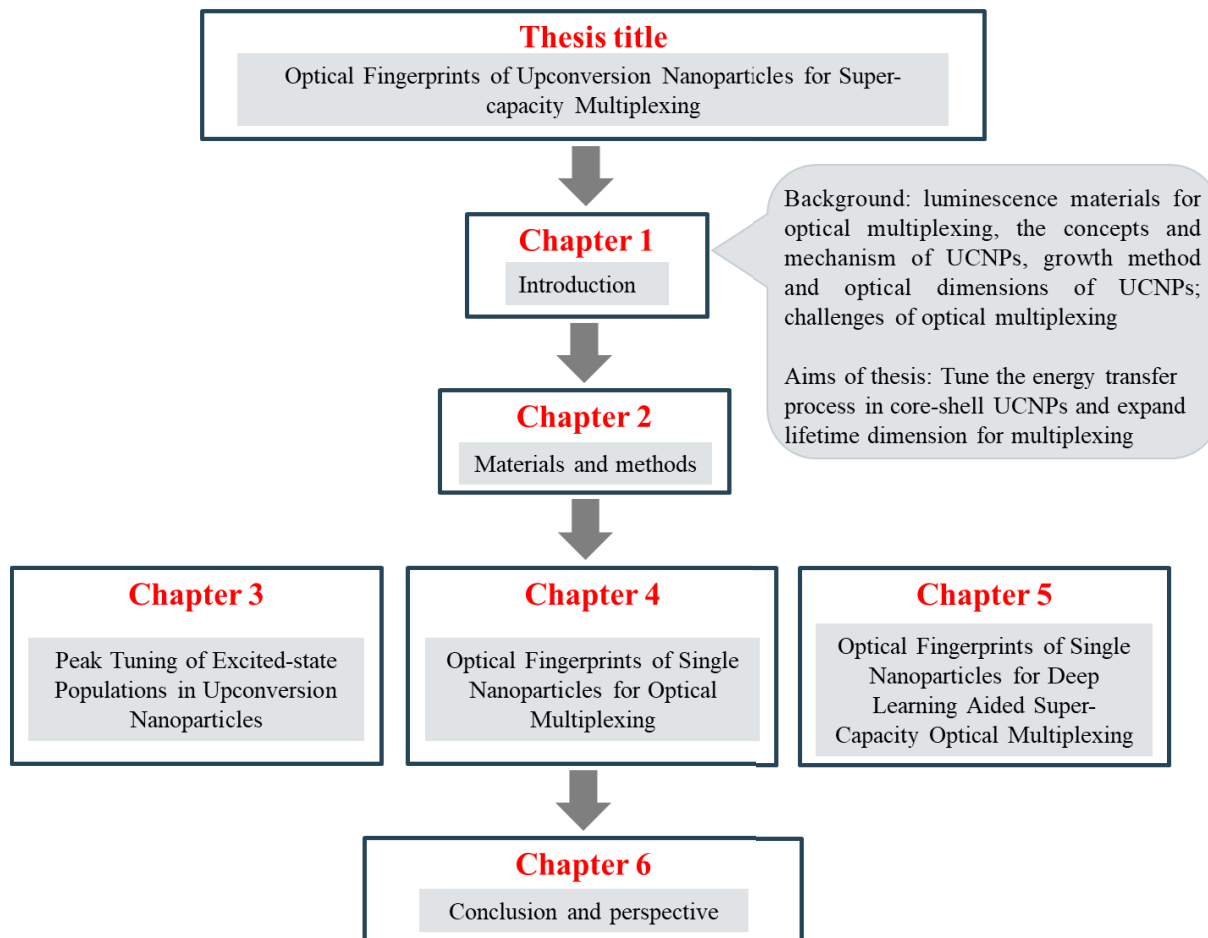
Chapter 5 outlines the finding that the nanoparticles show a unique lifetime signature under wide-field systems upon 976 nm ($\text{Yb}^{3+}\text{-Tm}^{3+}$ doped UCNPs) and 808 nm ($\text{Yb}^{3+}\text{-Nd}^{3+}\text{-Er}^{3+}$ doped UCNPs) excitation. To achieve high-throughput multiplexing, the lifetime 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, machine 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 ₄ F	Ammonium Fluoride
OA	Oleic Acid
ODE	1-Octadecene
QDs	Quantum Dots
RE	Rare Earth
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