CONTROLLED SYNTHESIS TO PRODUCE UPCONVERSION MATERIALS WITH MULTICOLOUR LUMINESCENCE

By

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This thesis is presented for the degree of Doctor of Philosophy

April 2019

Certificate of Original Authorship

I, Ming Guan, declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mathematical and Physical Sciences, Faculty of Science, at the 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 literature used are indicated in the thesis.

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

This thesis is the result of a research candidature jointly delivered with China University of Geosciences (Beijing) as part of a Collaborative Doctoral Research Degree.

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

Production Note:
Signature: Signature removed prior to publication.

Date: 27. April. 2019

Acknowledgements

As a cotutelle PhD student at the University of Technology Sydney (UTS) and China University of Geosciences Beijing (CUGB), I have been assisted by many people over my doctoral period. I really appreciate all of them.

Firstly, I would like to thank my principal supervisor at UTS, Dr Jiajia Zhou, for her precious supervision and guidance through all the years I studied at UTS. 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.

Simultaneously, I am so grateful to my co-supervisor at UTS, distinguished Professor Dayong Jin. It is Professor Jin who provided me the opportunity to be a PhD candidate at UTS. He gave the greatest support to my research over my years at UTS. Professor Jin set an excellent example for me by never giving up, staying enthusiastic, enjoying science, loving life, learning and giving. I count myself so lucky to have been his student.

Next, I would like to thank my principal supervisor at CUGB (Professor Hong Zheng) and my co-supervisor at CUGB (Associate Professor Lefu Mei), as well as Professor Zhaohui Huang. Without them, I cannot imagine how I could have completed this undertaking. All of them are respected teachers and my friends. They provided me so much help in research, working and living. They supported and encouraged me to optimistically meet the challenges in my life. All the things they taught me are precious gifts to my life.

Thanks also to my dear friends and colleagues that I met at IBMD, who not only gave me academic help but also gave my life colour. These include Dr Xiaoxue Xu, Dr Fan Wang, Dr Shihui Wen, Dr Zhiguang Zhou, Dr Yinghui Chen, Dr Hien Dong, Mr Christian Clark, Dr Olga Shimoni, Dr Qian Peter Su, Mr Chaohao Chen, Mr Yong Tao Liu, Ms Du Li, and Dr Wenjing Zhang. Thanks to our international collaborators, Dr Li Wang and Dr Yi Du, and the staff of the XPS lab at the Australian Synchrotron. I sincerely appreciate the generous help from all these nice people. Furthermore, special acknowledgement is also given to all the staff of our MAPS school and MAU lab. All of them provided me with much guidance and help. In addition, thanks to Mr John who helped revising the thesis.

Deep appreciation should be given to Dr Wei Ren, Mr Hao He, Mr Chao Mi and Ms Jiayan Liao. Words can't express how much I appreciate you. Thanks also to my parents and my girlfriend, I love you all.

Finally, thanks to the China Scholarship Council and the Faculty of Science, UTS, who supported my tuition fees and my living expenses. I appreciate the support I received from both China and Australia. I hope that the friendship between these two great countries will last forever.

Format of the Thesis

This thesis follows the conventional format of six chapters. The relationship between these chapters is illustrated in the flowchart below.

Chapter 1 is the introductory chapter, which is composed of six sections. These sections describe the motivation and background knowledge relevant to developing multicolour luminescent upconversion (UC) materials, including the concepts of multicolour UC luminescence, the mechanism of UC luminescence, the compositions of UC materials, ways of synthesizing UC materials, and current progress on how to fine-tune multicolour UC luminescence. These sections provide the research inspiration and specific aims of this thesis, which were to study the controlled synthesis of UC materials with multicolour luminescence, high-throughput production and wide gamut.

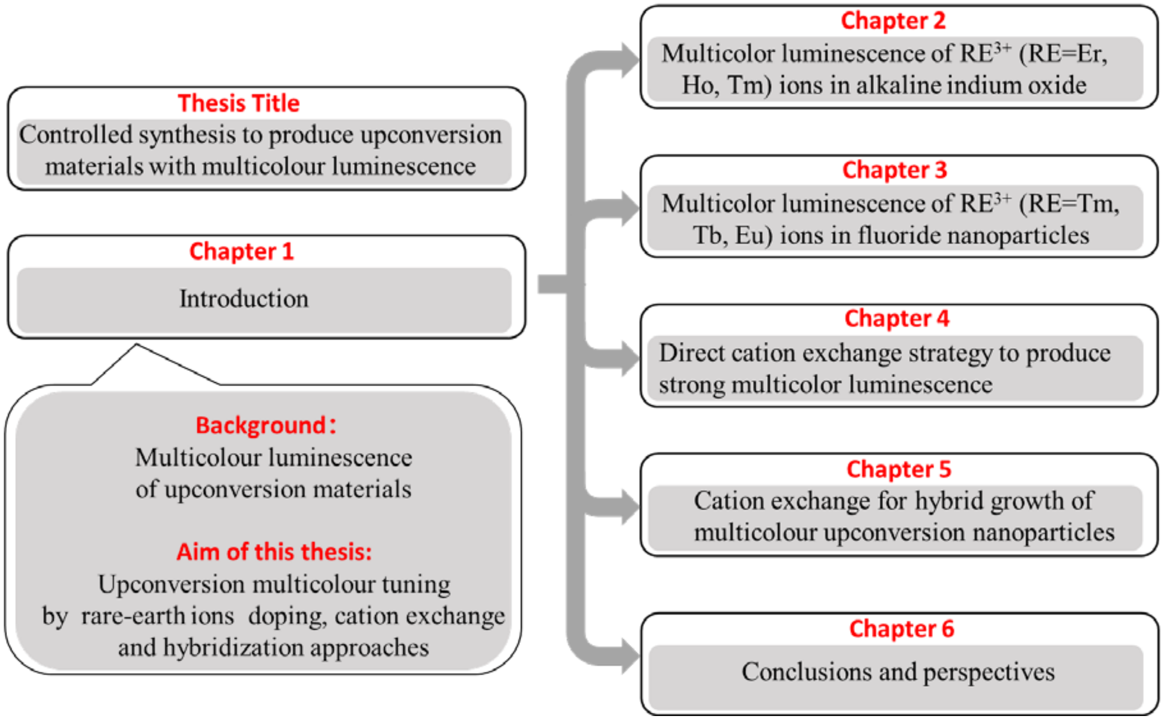
Chapter 2 is the first research chapter, which investigates the distribution and multicolour luminescence of RE^{3+} (RE=Er^{3+}, Ho^{3+}, Tm^{3+}) in alkaline indium oxide UC materials. It indicates that the strategy of doping various RE^{3+} ions is a simple and feasible route to achieving multicolour UC emission.

Chapter 3 is a parallel research chapter that investigates the distribution of RE^{3+} (RE=Tm^{3+}, Yb^{3+}) in fluoride UC nanoparticles. After that, multicolour luminescence was realized via the addition of new activators such as Tb^{3+} and Eu^{3+} by cation exchange.

Chapter 4 presents a novel method of direct cation exchange in surface ligand capped UC nanoparticles. This allows efficient, high-throughput production of strong, multi-coloured, luminescent nanoparticles.

Chapter 5 further applies the knowledge obtained in Chapter 4. Using the current cation exchange strategy, hybridization of UC nanoparticles and lead halide perovskite quantum dots (PQDs) is attempted to fine-tune the multicolour, wide gamut luminescence.

Finally, the key research outcomes of this thesis are summarized in Chapter 6. Potential future developments and prospects of multicolour luminescent UC materials are discussed.


Thesis Title
Controlled synthesis to produce upconversion materials with multicolour luminescence
Chapter 1
Introduction
Background:
Multicolour luminescence of upconversion materials
Aim of this thesis:
Upconversion multicolour tuning by rare-earth ions doping, cation exchange and hybridization approaches
Chapter 2
Multicolor luminescence of RE^{3+} (RE=Er, Ho, Tm) ions in alkaline indium oxide
Chapter 3
Multicolor luminescence of RE^{3+} (RE=Tm, Tb, Eu) ions in fluoride nanoparticles
Chapter 4
Direct cation exchange strategy to produce strong multicolor luminescence
Chapter 5
Cation exchange for hybrid growth of multicolour upconversion nanoparticles
Chapter 6
Conclusions and perspectives

List of Publications

Research Papers:

[1] **Ming Guan**, Zhiguang Zhou, Lefu Mei, Hong Zheng, Wei Ren, Li Wang, Yi Du, Dayong Jin and Jiajia Zhou, Direct cation exchange of surface ligand capped upconversion nanocrystals to produce strong luminescence, *Chemical Communications*, 2018, 54: 9587-9590.

[2] Xiaoxue Xu, Christian Clarke, Chenshuo Ma, Gilberto Casillas, Minakshi Das, **Ming Guan**, Deming Liu, Li Wang, Anton Tadich, Yi Du, Cuong Ton-That and Dayong Jin, Depth-Profiling of Yb^{3+} Sensitizer Ions in $NaYF_4$ Upconversion Nanoparticles, *Nanoscale*, 2017, 9: 7719-7726.

[3] **Ming Guan**, Hong Zheng, Lefu Mei, Maxim S. Molokeev, Jing Xie, Tao Yang, Xiaowen Wu, Saifang Huang, Zhaohui Huang, and A. Setlur, Preparation, Structure, and Up-conversion Luminescence of Yb^{3+}/Er^{3+} Codoped $SrIn_2O_4$ Phosphors, *Journal of the American Ceramic Society*, 2015, 98: 1182-87.

[4] **Ming Guan**, Hong Zheng, Zhaohui Huang, Bin Ma, Maxim S. Molokeev, Saifang Huang, and Lefu Mei, Ca/Sr Ratio Dependent Structure and Up-conversion Luminescence of $(Ca_{1-x}Sr_x)In_2O_4 : Yb^{3+}/Ho^{3+}$ Phosphors, *RSC Advances*, 2015, 5: 59403-07.

List of Acronyms

(in alphabetical order)

DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
EDS	Energy-dispersive X-ray spectroscopy
EMU	Energy migration mediated upconversion
ETU	Energy transfer upconversion
FRET	Fluorescence resonance energy transfer
FT-IR	Fourier transform infrared spectroscopy spectra
HCl	Hydrochloric acid
HRTEM	High-transmission electron microscopy
LRR	Luminescence radiative reabsorption
NIR(IR)	Near-infrared
OA	Oleic acid
ODE	1-octadecene
OM	Oleylamine
OSCE	Organic solvent allowing cation exchange
PQDs	Lead halide perovskite quantum dots
QDs	Quantum dots
RE	Rare earth

RGB	Red green blue
SEM	Scanning electron microscopy
STEM	Scanning transition electron microscopy
TEM	Transmission electron microscopy
TFA	Trifluoroacetate
THF	Tetrahydrofuran
UC	Upconversion
UCL	Upconversion luminescence
UCNPs	Upconversion nanoparticles
UV	Ultraviolet
WACE	Cation exchange in water
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Abstract

Significant development has been done in rare earth (RE^{3+}) ion-doped upconversion (UC) materials over the past few years, however one challenge remaining lies in the controlled synthesis of UC materials with tunable, wide-gamut, multicolour luminescence and high-throughput production. This thesis focuses on exploring the distribution of RE^{3+} ions, understanding the network of energy transfer systems within interior UC materials, and developing resource- and time-saving methods for fine-tuning UC materials with multicolour luminescence, high performance and wide colour gamuts.

Chapter 1 summarizes the motivations for the thesis and background knowledge relevant to the development of multicolour luminescent UC materials, as well as the specific aims of this thesis: controlled synthesis of multicolour luminescent UC materials and distribution study of RE^{3+} ions within them.

In Chapter 2, Rietveld refinement of X-ray powder diffraction (XRD) was employed to characterize the distribution of RE^{3+} ions in bulk UC materials. Different RE^{3+} ions produced distinct emission peaks. Therefore, multicolour luminescence of activators, such as Er^{3+}, Tm^{3+} and Ho^{3+}, was achieved in alkaline indium oxide UC materials.

In Chapter 3, synchrotron-based X-ray photoelectron spectroscopy (XPS) measurements were used to investigate the depth-resolved distribution of RE^{3+} within fluoride upconversion nanoparticles (UCNPs). The author proposed a natural Gd^{3+}-rich shell in Yb^{3+}/Tm^{3+} doped $NaGdF_4$ UCNPs, which can effectively bridge the gap of energy transfer between sensitizers and activators to realized multicolour luminescence via cation exchange.

Chapter 4 reports on a novel direct cation exchange method for UCNPs without removing surface ligands in organic solvent. It avoids the tedious pre-treatment of synthesized UCNPs, and the luminescent intensities using the new method are much stronger than those using conventional cation exchange in water. This facile and rapid cation exchange strategy opens a new path to the synthesis of multicolour-emitting nanoparticles expeditiously with high performance and high-throughput.

Chapter 5 further applies the knowledge obtained from Chapter 4. We attempted to develop hybrid heterostructures of UCNPs and lead halide perovskite quantum dots (PQDs), and to produce and fine-tune multicolour luminescence. The cation-exchanged ions were expected to bridge these two kinds of nanomaterials. However, it remains a great challenge.

Conclusions and perspectives are given in Chapter 6, which also summarizes the key achievements of the thesis. Controlled synthesis and fine-tuning of the spectral UC emission properties of UCNPs may open a path to more complex applications.

Keywords: Rare-earth ions, upconversion, cation exchange, multicolour luminescence

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