# CONTROLLED SYNTHESIS TO PRODUCE UPCONVERSION MATERIALS WITH MULTICOLOUR LUMINESCENCE

By

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# **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.

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## **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<sup>3+</sup> (RE=Er<sup>3+</sup>, Ho<sup>3+</sup>, Tm<sup>3+</sup>) in alkaline indium oxide UC materials. It indicates that the strategy of doping various RE<sup>3+</sup> 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<sup>3+</sup> (RE=Tm<sup>3+</sup>, Yb<sup>3+</sup>) in fluoride UC nanoparticles. After that, multicolour luminescence was realized via the addition of new activators such as Tb<sup>3+</sup> and Eu<sup>3+</sup> 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<sup>3+</sup> (RE=Er, Ho, Tm) ions in alkaline indium oxide

#### Chapter 3

Multicolor luminescence of RE<sup>3+</sup> (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<sup>3+</sup> Sensitizer Ions in NaYF<sub>4</sub> 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 Upconversion Luminescence of Yb<sup>3+</sup>/Er<sup>3+</sup> Codoped SrIn<sub>2</sub>O<sub>4</sub> 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<sub>1-x</sub>Sr<sub>x</sub>)In<sub>2</sub>O<sub>4</sub>: Yb<sup>3+</sup>/Ho<sup>3+</sup> 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<sup>3+</sup>) 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<sup>3+</sup> 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<sup>3+</sup> ions within them.

In Chapter 2, Rietveld refinement of X-ray powder diffraction (XRD) was employed to characterize the distribution of RE<sup>3+</sup> ions in bulk UC materials. Different RE<sup>3+</sup> ions produced distinct emission peaks. Therefore, multicolour luminescence of activators, such as Er<sup>3+</sup>, Tm<sup>3+</sup> and Ho<sup>3+</sup>, 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<sup>3+</sup> within fluoride upconversion nanoparticles (UCNPs). The author proposed a natural Gd<sup>3+</sup>-rich shell in Yb<sup>3+</sup>/Tm<sup>3+</sup> doped NaGdF<sub>4</sub> 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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