Synthesis of rare-earth oxide/titanate for upconversion luminescence with an ultra-high power efficiency

Wu, Mingda

2019

Wu, M. (2019). Synthesis of rare-earth oxide/titanate for upconversion luminescence with an ultra-high power efficiency. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/89870>

<https://doi.org/10.32657/10220/47727>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**SYNTHESIS OF RARE-EARTH OXIDE / TITANATE FOR
UPCONVERSION LUMINESCENCE WITH AN ULTRA-HIGH
POWER EFFICIENCY**

WU MINGDA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

**SYNTHESIS OF RARE-EARTH OXIDE / TITANATE FOR
UPCONVERSION LUMINESCENCE WITH AN ULTRA-HIGH
POWER EFFICIENCY**

WU MINGDA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

August 3rd, 2018

.....
Date

Wu Mingda 吴鸣达

.....

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

August 3rd, 2018

.....

Date

.....

Authorship Attribution Statement

This thesis contains material from a paper will publish in a following peer-reviewed journal where I was the first and corresponding author.

Chapter 6 will publish as M.D. Wu, Y.S. TEE, B.Q. Yao, S.H Liu, G.J. Guan, C.P. Teng, Z.L. Dong and M.Y. HAN. Bright upconversion luminescence from lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$. *In preparation*.

The contributions of the co-authors are as follows:

- A/Prof Dong and Dr. HAN provided the initial orientation, guided the experiment performance, and edited the manuscript drafts.
- I performed all the materials synthesis, collected X-ray diffraction patterns and visible light spectra, carried transmission electron microscopy, and prepared the manuscript drafts.
- Ms. Yao Bingqing carried transmission electron microscopy and scanning eletron microscopy.
- Dr. TEE Si Yin, Dr Guan Guijian and Dr. Liu Shuhua provide guidance in experimental optimization.
- Dr TENG Choon Peng assisted in the cell culture.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.

August 3rd, 2018

.....
Date

Wu Mingda 吴明达

.....

Abstract

In the last decade, lanthanide-doped upconversion(UC) materials have become a shining star and been focused by a growing number of researchers all over the world, due to its unique and fascinating NIR-to-visible light conversion. Effective upconversion materials (e.g. β -NaYF₄:Yb³⁺,Er³⁺ and β -NaYF₄:Yb³⁺,Tm³⁺) have been demonstrated to be promising in a wide range of bio-medical and luminescent applications. However, such lanthanide-doped fluorides are found structurally instable in ambient conditions and sensitive to aqueous solutions, leaving shadows in the further development and promotion of upconversion luminescence. Compared with fluorides, their oxide counterparts possess higher binding energies, more stable structures, and a better tolerance to aqueous solutions, while being limited by difficulties in synthesizing nanocrystals and achieving effect upconversion luminescence. Hence, it's of great promising to synthesize oxides-based upconversion materials in nanoscale and with high upconversion efficiency.

In the first part, a systematic study in both controlled synthesis and enhanced luminescence of lanthanide-doped gadolinium oxides was performed. To start with, uniform and size-tunable gadolinium hydroxide rods were prepared through surfactant-free hydrothermal synthesis and could further transform into corresponding oxides through calcination treatment. The upconversion luminescence of as-prepared lanthanide-doped gadolinium oxide (Gd₂O₃:Ln³⁺) was substantially enhanced through a thermal treatment, being accompanied with the improvement of crystallinity. As a sequence, Gd₂O₃:Yb³⁺,Er³⁺ (10/1 mol%) nanorods with an upconversion efficiency comparable to fluoride counterparts were successfully obtained.

To achieve a better understanding of energy transfer and upconversion luminescence, an investigation of host matrix-sensitized upconversion material (erbium-doped ytterbium oxide, denoted as Yb₂O₃:Er³⁺) was performed. By using ytterbium oxide powder and erbium chloride solution as precursors, Yb₂O₃:Er³⁺ with three-dimensional porous structure were prepared through hydrothermal synthesis followed by calcination treatment. The retention of the three-dimensional porous structure was demonstrated critical to

overcome quenching effect. Such work proved a potential platform to study the short-term energy transfer between sensitizers and activators.

Subsequently, oxide perovskite crystals with tunable cavities, in which doped cations were immobilized, were synthesized and used as host matrices for upconversion luminescence. To make it specific, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ nanocubes were found promising for flexible lanthanide-doping and tunable upconversion luminescence. Markedly, through a further structural improvement and compositional optimization, effective upconversion luminescence with an ultrahigh power efficiency of 40.7 % was achieved on $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ (20/2 mol%) nanocubes.

Admittedly, effective upconversion nanoparticles could be potentially utilized in a plenty of applications. As a proof of concept, a $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ -based phosphor chip was fabricated to generate a combinational RGB-emission, achieving bright white-light emission consequently. Similarly, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanocubes were demonstrated eligible for light emitting and security pattern drawing. Furthermore, the dispersibility, stability, and bio-compatibility of rare-earth oxide and titanate (e.g. Gd_2O_3 and $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$) were assessed and demonstrated by cellular imaging. Taken together, rare-earth oxide/titanate nanocrystals were versatile and promising candidates for upconversion applications.

Lay Summary

Photon upconversion (UC) is a phenomenon that photons with lower energy are absorbed, converted, and emitted as photons with higher energy. In the past few years, numerous exploitations and progresses have been achieved in such research field, among which lanthanide-doped upconversion nanoparticles that convert near infrared (NIR) irradiation into visible emission is a shining star. Effective upconversion phosphors, e.g. β -NaYF₄:Yb³⁺,Er³⁺ and β -NaYF₄:Yb³⁺,Tm³⁺, have been demonstrated to be feasible, by researchers all over the world, in a variety of bio-medical and luminescent applications.

Benefitting from abundant f electrons, lanthanide ions possess characteristic ladder-like energy levels, endowing them promising candidate for energy absorption and conversion. Lanthanide-based down-conversion, also known as fluorescence, has been widely achieved in commercial and industrial applications. However, lanthanide-based upconversion materials, on the contrary, is still far from practicality. Though the unique and fascinating anti-stock shift emission had been demonstrated feasible and promising in a variety of applications, the proactivity of upconversion materials is still limited by the inherent poor power efficiency.

In this thesis, a series of rare-earth oxide and rare-earth titanate-based upconversion materials had been developed and assessed, in order to investigate principles to achieve an effective upconversion luminescence. The hydrothermal synthesis, calcination treatment, and annealing treatment were studied systematically, to generate oxide host matrix with desired morphology and structures. Then the flexible lanthanide-doping into these host matrices was performed and the corresponding upconversion luminescent properties were evaluated parallely. As a consequence, a series of effect upconversion materials, including Gd₂O₃:Ln³⁺ for white-light emission, Yb₂O₃:Er³⁺ for host-sensitized emission, and Na_{1/2}Y_{1/2}TiO₃:Yb³⁺,Er³⁺ for upconversion luminescence with high-efficiency, were obtained successfully. Finally, as a proof of concept, such upconversion materials developed in this work were utilized in a series of applications under practical conditions, demonstrating the feasibility and practicality of such upconversion materials.

Acknowledgements

First and foremost, I would like to express my deep gratitude to my supervisors Prof. Dong Zhili and Dr. HAN Ming Yong, for their patient and invaluable guidance on the research, as well as their encouragement during my whole Ph.D. candidature. Also, thanks to my TAC members, Prof. Li Shuzhou and Prof. Jason Xu Zhichuan, for their instructions on my thesis.

I would like to thank to all my lab colleagues in both NTU and IMRE, Dr. Xia Jing, Ms. Yao Bingqing, Ms. Yin Danlei, Dr. Zhang Shuanyuan, Dr. ICE Tee Si Yin, Dr. Liu Shuhua, Dr. Guan Guijian, Dr. Teng Choon Peng, and Dr. Wee-Jun Ong. All of them gave me a lot of help and suggestions to my research work.

I also would like to express my gratitude to my cooperators in other groups: Dr. Zeng Deqian (XMU), Dr. BAI Shiqiang (IMRE), Dr. CHUA Chin Sheng (IMRE), Dr. Liang Liangliang (NUS), Ms. Yuki Tanaka (NUS), Mr. Siarhei Zhuk (NTU), and Mr. Fu Qundong (NTU). I thank these experienced researchers for their timely help on the experience performance.

My special thanks should go to my wife, Ms. Wei Chen, who is the most important person in my life. Thanks for her support, never-ending patience, and encouragement.

Last but not least, I am also deeply indebted to my parents, for their faith in me all the time and their support for me to pursue the doctoral degree in Singapore.

Table of Contents

Abstract.....	i
Lay Summary	iii
Acknowledgements.....	v
Table of Contents	vii
Table Caption	xi
Figure Captions	xiii
Abbreviations	xxi
Chapter 1 Introduction	1
1.1 Problem Statement and Hypothesis	2
1.1.1 Problem Statement.....	2
1.1.2 Hypothesis	3
1.2 Objective and Scope.....	3
1.3 Dissertation Overview.....	4
1.4 Findings and Outcomes.....	6
References	6
Chapter 2 Literature Review	9
2.1 Introduction of Upconversion Luminescence	10
2.2 Upconversion Materials	12
2.2.1 Host Matrix.....	12
2.2.1.1 Oxide Matrix	12
2.2.1.2 Fluoride Matrix	14
2.2.2 Activators and Sensitizers	16
2.2.2.1 Activators for ESA Process	16
2.2.2.2 Activators for ETU process	17
2.2.2.3 Activators for EMU Process	18
2.2.2.4 Sensitizers	18
2.3 Optical Properties of Upconversion Materials.....	20

2.3.1 Color-Manipulation	20
2.3.2 Enhancement of Upconversion Luminescence.....	22
2.3.2.1 Surface-Manipulation	22
2.3.2.2 Plasmonics	24
2.4 Applications of Upconversion Materials	26
2.4.1 Biomedical Applications	26
2.4.1.1 Cell / Tissue Imaging	27
2.4.1.2 Monitored/Stimulated Drug Delivery System	28
2.4.2 Light-emitting and Display Applications	30
2.4.2.1 White-Light Emitting.....	30
2.4.2.2 Single-particle Imaging.....	30
2.4.2.3 Security Patterns	31
2.4.2.4 Three-Dimensional (3D) Display	31
References	33
Chapter 3 Experimental Methodology	39
3.1 Hydrothermal Synthesis.....	40
3.2 Characterization Techniques.....	41
3.2.1 X-Ray Diffraction Crystallography	41
3.2.2 Transmission Electron Microscopy	42
3.2.3 Scanning Electron Microscopy.....	43
3.3 Power Efficiency Measurement	45
References	47
Chapter 4 Tunable Upconversion Luminescence from Gd₂O₃:Ln³⁺ (Ln = Yb, Er, and Tm) nanorods.....	49
4. 1 Introduction.....	50
4.2 Experimental Section	52
4.2.1 Materials	52
4.2.2 Synthesis of Uniform RE ₂ O ₃ Nanorods	53
4.2.3 Sample Preparation for Characterization.....	54
4.3 Results and Discussion.....	55

4.3.1 Hydrothermal Synthesis of $\text{Gd}(\text{OH})_3$ Nanorods	55
4.3.2 Thermal Decomposition of $\text{Gd}(\text{OH})_3$ Nanocrystals	62
4.3.3 Synthesis of Rare-earth Hydroxides and Corresponding Oxides	63
4.3.4 Lanthanide-doping into Gd_2O_3 Crystals	65
4.3.5 Luminescent Enhancement of Lanthanide-doped Gd_2O_3 Crystals	68
4.3.5 Color-tuning of Lanthanide-doped Gd_2O_3 Crystals to Achieve White-light Emission	70
4.4 Summary	74
References	75
Chapter 5 Host-sensitized Upconversion Luminescence from $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) Microrods	77
5.1 Introduction	78
5.2 Experimental Section	80
5.2.1 Materials	80
5.2.2 Synthesis of Yb_2O_3 Precursors	80
5.2.3 Synthesis of Er^{3+} -Doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ through Solid-Liquid Interfacial Reaction of Porous Yb_2O_3 with Erbium (III) Aqueous Solution	80
5.2.4. Calcination of Er^{3+} -Doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ to Generate $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$	81
5.2.5 Sample Preparation for Characterization	81
5.3 Result and Discussion	81
5.3.1 Structures and Porosity of Yb_2O_3 Precursors	81
5.3.2 Solid-Liquid Interfacial Reaction	84
5.3.3 Structure and Luminescence of Er^{3+} -Doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods ..	85
5.3.4 Structure and Luminescence of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods	92
5.3.5 Efficiency of Upconversion Microrods	99
5.3.6 Collapse of Upconversion Luminescence	100
5.4 Summary	102
References	103
Chapter 6 Highly Efficient Upconversion Luminescence from Lanthanide-Doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ Nanocubes	105

6.1 Introduction	106
6.2 Experiment section.....	107
6.2.1 Materials	107
6.2.2 One-pot Synthesis of Lanthanide-doped Metal Titanates	108
6.2.2.1 Synthesis of Lanthanide-doped Alkaline Earth Titanates.....	108
6.2.2.2 Synthesis of $\text{Ca}_{n-1/2}(\text{NaY})_{1-n}\text{TiO}_3$ ($n = 0 - 1$)	108
6.2.2.3 Synthesis of Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$	109
6.2.3 Annealing Treatment of Samples	109
6.2.4 Sample Preparation for Characterization.....	109
6.3 Results and Discussion.....	110
6.3.1 Structure and Luminescence of Lanthanide-doped Alkaline Earth Titanates	110
6.3.2 Structure and Luminescence of Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$	116
6.3.3 Mechanism Study of the Formation of Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$	
Nanocubes	117
6.3.4 Manipulation of Upconversion luminescent Properties of Lanthanide-doped	
$\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$	122
6.3.4.1 Manipulation of Luminescence Properties Achieved by Tuning Dopants	
.....	122
6.3.4.2 Enhancement of Luminescence Achieved by Annealing	125
6.3.4.3 Power Efficiency of Upconversion Nanocubes.....	129
6.3.5 Applications of Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ Nanocubes	132
6.3.5.1 Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ Nanocubes for Cell-labeling	133
6.3.5.2 Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ for Display	135
6.3.5.3 Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ Nanocubes for Illumination	135
6.4 Summary	136
References	137
Chapter 7 Conclusions and Future Work	139
7.1 Conclusions	140
7.2 Future work	142

Table Caption

Table 6.1 Ionic radii of various ions with a coordination number of VIII 115

Figure Captions

- Figure 2.1** Schematic representations of UC processes, where upward (red) and downward (blue) full arrows stand for direct excitation processes and radiative emission processes, respectively. Dashed arrows (green) represent energy transfer processes. 12
- Figure 2.2** A series of oxide nano- and micro-crystals utilized as matrix for upconversion applications. 14
- Figure 2.3** A series of fluoride nanocrystals utilized as matrix for upconversion applications. ... 16
- Figure 2.4** Typical sensitizers and activators for an effective upconversion process. 20
- Figure 2.5** Typical works focus on manipulation of color of emission. a) Schematic diagram and emission spectra of dye-modified UCNPs used for coding applications.⁵⁰ b) Schematic diagram of dye-based single band-UCNP fabrication.¹¹ c) Single-band emission of $\text{KMnF}_3\text{:Yb,Ln}$ ($\text{Ln} = \text{Er, Ho, Tm, respectively}$).⁴¹ d) Design of UCNPs capable of emitting three primary colors from one single particle with a pulsed NIR laser.⁸ e) Luminescence (up) and integrated intensities (down) of RGB emissions under tunable irradiation power density.¹⁰ 22
- Figure 2.6** a) Core-shell structured UCNPs for enhanced upconversion luminescence.⁵¹ b) Schematic illustration (up), HRTEM image and FFT pattern (down) of selective cation exchange remediated dissimilar structure for the growth of $\beta\text{-NaLnF}_4\text{@CaF}_2$ nanoparticles.⁵² c) Schematic illustration (left) and the emission spectra (right) of the size-dependent surface-phonon-enhanced upconversion process.⁹ 24
- Figure 2.7** a) $\text{Ag@SiO}_2\text{:Y}_2\text{O}_3\text{:Er}$ core-shell nanoparticles for tunable upconversion luminescence.⁵⁵ b) Au nanocrystals-UCNPs clusters for upconversion luminescence.⁵⁴ c) UCNPs-AuNPs core-shell nanostructures for plasmonic modulation of upconversion luminescence.⁵³ d) “Islands” Au-Ag alloy/UCNPs composite film for large enhanced upconversion luminescence.⁵⁶ e) UCNPs-Ag nanograting for plasmonic enhanced upconversion luminescence.⁵⁷ 25
- Figure 2.8** Surface-modification of UCNPs prior to bio-applications. a) TEM images of $\text{UCNP@d}_1\text{-SiO}_2$ (left), $\text{UCNP@d}_1\text{-SiO}_2\text{@d}_2\text{-SiO}_2$ (middle), and yolk-shell structured UCSNs (right), respectively.⁶⁴ b) TEM images of concentric- (left) and eccentric- (right) UCNR@SiO_2 core-shell structures.⁶² c) SEM (left) and TEM (right) images of UCNPs@ SiO_2 fibers (up), UCNPs@ SiO_2 tubes (middle), and UCNPs@m SiO_2 @fibers (down), respectively.^{59,65} 27
- Figure 2.9** UCNPs for bio-applications. a) *In vivo* up-conversion luminescence imaging of subcutaneous HeLa tumor-bearing athymic nude mice.⁷⁰ b) Optical, upconversional, and fluorescent imaging of blood vessels in the mouse ear.⁶⁹ c) Experimental scheme (left) and relative

DA signals (right) for transcranial NIR stimulation of the VTA in anesthetized mice.¹⁶ d) Therapeutic and imaging bi-functional DOX-loaded UCNPs@mSiO₂ nanoparticles.⁷¹ e) NIR light-triggered drug delivery systems.⁷⁷ 29

Figure 2.10 UCNPs for luminescence and display applications. a) schematic (left) and luminescence (right) of upconversional white-light-emitting nanocrystals.¹⁰ b) White light generated by combining three sets of upconversion nanoparticles featuring monochromatic RGB emission.⁸ c) Luminescent image of a monochromatic 3D-display generated in the UCNPs-embedded PDMS disk via computer-controlled near-infrared laser scanning.⁵ d) Luminescent image of multi-color 3D-display generated in UCNPs/PDMS composite using computer-controlled laser scanning.⁸ e) Luminescence intensity (left) and confocal luminescence images (right) of single 8 nm UCNPs. f) Demonstrations of super resolution by comparing conventional confocal images (left) with as-established nanoscopy images (right) of the Tm-based UCNPs.¹⁵ g) Demonstrations of security inks using the power-dependent optimal Tm³⁺ concentration.¹³ h) Demonstration of time-resolved scanning shows desired patterns based on the lifetime components of every pixel.¹⁴ 32

Figure 3.1 Two typical autoclaves used for hydrothermal synthesis. 40

Figure 3.2 The refraction of a wave-train by successive lattice planes.⁷ 42

Figure 3.3 a) Bright field, b) dark field TEM images, c) electron diffraction pattern and d) HRTEM image.^{8,9} 43

Figure 3.4 Figure An overview of information obtained by SEM technique.⁷ 45

Figure 3.5 Schematic (up) and digital (down) images of a power meter-based set-up for power efficiency measurement. 46

Figure 4.1 Change of pH value as gadolinium chloride aqueous solution is titrated against NH₃ H₂O or NaOH solution. 56

Figure 4.2 Structural information of as-prepared Gd(OH)₃ white powders..... 57

Figure 4.3 Characterization of Gd(OH)₃ crystals prepared through ammonia-assisted hydrothermal synthesis. (a) FESEM image of as-prepared Gd(OH)₃ hexanol prisms. (b-d) TEM images of as-prepared Gd(OH)₃ crystals..... 58

Figure 4.4 TEM images of Gd(OH)₃ micro-crystals synthesized at 120 °C (a), 160 °C (b), and 200 °C (c), respectively. 59

Figure 4.5 Initial pH value-induced morphology evolution. a) Z-potential of Gd(OH)₃^{+(3-x)} sol at various pH values. b) TEM images of Gd(OH)₃ crystals prepared at pH values ranging from 9.0 to 11.5. c) Length values and length-to-diameter ratio of Gd(OH)₃ crystals prepared at various initial pH value. 61

Figure 4.6 Thermal decompose of $\text{Gd}(\text{OH})_3$ to form corresponding Gd_2O_3 crystals. a) TGA and TGA derivative curve of $\text{Gd}(\text{OH})_3$ crystals, two thermal decomposition peaks could be found at 320 and 420, respectively. b) XRD pattern of samples calcined at various temperature.....	62
Figure 4.7 a) XRD pattern of Gd_2O_3 microrods obtained through thermal decomposition of $\text{Gd}(\text{OH})_3$. b) TEM image of Gd_2O_3 uniform microrods.....	63
Figure 4.8 TEM image (a) and SAED pattern (b) of Gd_2O_3 obtained through thermal decomposition.....	63
Figure 4.9 XRD patterns of rare-earth hydroxide crystals prepared through ammonia-assisted hydrothermal synthesis.....	64
Figure 4.10 TEM images of typical rare-earth hydroxide crystals.....	64
Figure 4.11 XRD patterns of rare-earth oxide crystals fabricated by the calcination treatment...	65
Figure 4.12 a) Emission spectra of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ (10/1 mol%) phosphors. b) Proposed energy transfer diagram between sensitizer Yb^{3+} and activator Er^{3+}	66
Figure 4.13 Comparison between the aqueous suspension of (a) $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ (10/1 mol%) nanorods and (b) $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ (10/1 mol%) microrods.....	68
Figure 4.14 Annealing-induced enhancement of upconversion luminescence.....	69
Figure 4.15 a) c) SEM image and SAED pattern of a poly-crystalline $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorod annealed at 600 °C. b) d) The SEM image and SAED pattern of a single-crystalline $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorod annealed at 1,000 °C.....	70
Figure 4.16 a) Emission spectra of $\text{Gd}_2\text{O}_3:10\% \text{Yb}, 0.2\% \text{Tm}$ crystals. b) Proposed energy transfer diagram between sensitizer Yb^{3+} and activator Tm^{3+}	71
Figure 4.17 Emission spectra of $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ ($\text{Ln} = \text{Yb}, \text{Er}, \text{Tm}$) with varied doping ratio. (a,b) $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ phosphors could generate output light with green-to-red varied color. (c,d) $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ phosphors could generate monochromatic blue-light emission and the output intensity reaches the peak at a doping ratio of 0.2 mol%.....	72
Figure 4.18 CIE chromaticity diagram of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ and $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanoparticles. A rational combination between $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ phosphors and $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ phosphors could generate emissions with tunable colors located within the triangle drawn on the CIE chromaticity diagram.....	73
Figure 4.19 Emission spectra (a) and digital images (b) of a white-light emitting chip made from Gd_2O_3 -based upconversion nanoparticles.....	74
 Figure 5.1 Characterization of amorphous ytterbium oxide microrods fabricated by hydrothermal synthesis-calcination strategy. a) b) TEM images of uniform ytterbium oxide microrods, showing the well-dispersity and porous structure of them. c) SEM image of uniform ytterbium oxide microrods. d) XRD pattern of ytterbium oxide microrods, indicating amorphous structure of them.....	82
Figure 5.2 Characterization of three-dimensional nanoporous architecture of Yb_2O_3 microrods. a) b) TEM and SEM images of porous Yb_2O_3 microrods, showing that the cracks and cavities in nanoscale exist on the surface and in the body of the microrods. c) BET test of porous Yb_2O_3 nanorods.....	84

Figure 5.3 Schematic illustration of stirring-assisted hydrothermal synthesis set-up. The sands-bath and stirring are utilized to achieve a 200 °C homogenous hydrothermal reaction.	85
Figure 5.4 Erbium-doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ crystals prepared by the hydrothermal reaction possess three-dimensional frames with one-dimensional channels.	86
Figure 5.5 SEM (a) and TEM (b,c) images of as-prepared $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ micro-crystals.	87
Figure 5.6 X-ray photoelectron spectroscopy (XPS) spectra of as-prepared $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ micro-rods.....	88
Figure 5.7 Elemental mapping obtained through EDX scanning of erbium-doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ micro-rods.	89
Figure 5.8 TEM and HRTEM images of as-prepared Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods. The one-dimensional morphology corresponds to the one-dimensional growth along [001] direction.	89
Figure 5.9 SAED pattern of Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods fabricated through hydrothermal synthesis. The diffraction spots correspond to (200) plane and (-101) plane could be indexed on the SAED pattern, suggesting Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods fabricated through hydrothermal synthesis are single-crystals.	90
Figure 5.10 Thermal gravity analysis (TGA) of as prepared Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$. The removal of hydrate molecules, hydroxide ions, and chloride ions are achieved below 250 °C, between 250 °C to 380°C, and above 380 °C, sequentially.....	91
Figure 5.11 XRD pattern reveals the structural evolution from Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ to $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ during the calcination treatment.....	92
Figure 5.12 Upconversion emission spectra of sample calcined at various temperature. Samples calcined at 300 °C and below generate extreme weak upconversion luminescence. When the calcination temperature rises to 400 °C and above, the intensity of upconversion emission increases dramatically.	93
Figure 5.13 XRD pattern of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ fabricated by thermal decomposition of framework-structured $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$	94
Figure 5.14 SEM images of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods. The uniform rod-in-shape morphology is preserved after the calcination treatment.	95
Figure 5.15 a) X-ray photoelectron spectroscopy (XPS) spectra of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods. b) High-resolution XPS scan of Yb 4d and Er 4d electrons.	96
Figure 5.16 Elemental analysis of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods. (left) STEM image and EDX line-scan profile of a single $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrod, the blue line and red line represent the content of Yb^{3+} and Er^{3+} , respectively. (right) Element mapping of the same $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrod.	97
Figure 5.17 a) Emission spectra of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) microrods. b) Proposed energy transfer diagram between sensitizer Yb^{3+} and activator Er^{3+}	98
Figure 5.18 Decay time of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) microrods.....	99
Figure 5.19 a) Digital photograph of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphors dispersed in DI water. Bright green-light upconversion emission could be observed under the irradiation of 980 nm laser beam. b) $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphors possess a quantum yield of 0.42 %.	100

Figure 5. 20 Emission spectra of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods calcined at various temperature.....	101
Figure 5. 21 TEM images (a,b) and XRD patterns (c) of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods calcined at various temperature.	102
Figure 6.1 SEM image and XRD pattern of $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ micro-crystals prepared through hydrothermal synthesis. The insert figure shows the size distribution measured by DLS analysis.	111
Figure 6.2 Elemental analysis of rare-earth doped calcium titanate crystals, suggesting that sodium ions are co-doped with rare-earth ions to balance the charging.....	112
Figure 6.3 A structural (a) and upconversion-luminescent (b) comparison between $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$, $\text{SrTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$, and $\text{BaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ crystals, among which $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ generates the most effective upconversion luminescence.	113
Figure 6.4 The structural (a) and upconversion luminescent (b) comparison between hydrothermal products using various bases.....	114
Figure 6.5 Structure evolution from CaTiO_3 to $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals.....	115
Figure 6.6 XRD pattern of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ crystals.....	116
Figure 6.7 Evolution of upconversion luminescent properties between $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ to $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$. a) Emission spectra of various $\text{Ca}_n\text{1/2}(\text{NaY})_{1-n}\text{TiO}_3$ ($n = 0 - 1$) phosphors. b) A comparison of the intensity of green-light emissions (545 nm) between various phosphors.	117
Figure 6.8 XRD patterns (a), TEM images and corresponding SAED patterns (b-e) of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ prepared for 2 hours, 3 hours, 4 hours, and 6 hours.....	119
Figure 6.9 (top) The heating curve and the reaction progress of hydrothermal synthesis. (down) TEM images (from left to right) corresponds to the amorphous precursors, crystalline fragments, fragment assemblies, and crystalline cubes, respectively. The scale bar represents 200 nm.....	120
Figure 6.10 (a-c) TEM images of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ nano- and micro- crystals with various sizes through hydrothermal synthesis. (d) DLS analysis of the suspension of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals, the average size of the crystals shown in (a)-(c) are 240 nm, 1.15 μm , and 4.5 μm , respectively. ...	121
Figure 6.11 Structural analysis of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ with a perovskite structure.	122
Figure 6.12 (a) Emission spectra of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ (20/2 mol%) samples. The insert is the digital image of upconversion luminescent “Er” pattern drawn by $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles. The scale bar corresponds to 5 mm. (b) The ETU energy transition process between Yb^{3+} to Er^{3+}	123
Figure 6.13 Emission spectra of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles with various doping ratio of Yb^{3+} and Er^{3+} . The sample doped with Yb^{3+} and Er^{3+} with a concentration of 20 mol% and 2	

mol%, respectively, possesses the most effective and efficient upconversion luminescent capacity.	
.....	124
Figure 6.14 Emission spectra (a,c) and corresponding energy transition process (b,d) of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Ho}^{3+}$ (20/1 mol%) and $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ upconversion nanoparticles (UCNPs). The inserts are the digital image of “Ho” and “Tm” pattern drawn by using corresponding UCNPs ink. The scale bar represents a length of 5 mm.....	125
Figure 6.15 Annealing-induced enhancement of upconversion luminescence. a) emission spectra of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ (20/2 mol%) film sample annealed at various temperature for two hours. b) Comparison of emission intensity at 544 nm between samples annealed at various temperature.	
.....	126
Figure 6.16 a) TGA curve of the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals. The 2 % weight losses between 400 °C and 600 °C corresponds to the purge out of impurities and defects trapped in the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals. b) XRD pattern of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals before and after annealing treatment indicates that only pure orthorhombic phase of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ exists during the whole procedure.	127
Figure 6.17 Decay time (a) and Raman shift (b) of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanocrystals before and after annealing treatment.....	128
Figure 6.18 Measurement of relative upconversion luminescent efficiency of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles generated in this work by using conversional $\beta\text{-NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles as reference.	130
Figure 6.19 Measurement of absolute upconversion luminescent efficiency of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles generated in this work by using a power-meter set-up. ..	131
Figure 6.20 Aqueous dispersity of 200 nm $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles. a) Z-potential measurement of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles at various pH values. b) Digital images of 100 $\mu\text{g/ml}$ $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ aqueous dispersion under visible light (left) and 980 nm laser (right).	132
Figure 6.21 a) In vitro cell viability of CCD-112CoN cells cultured with $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ upconversion nanoparticles (UCNPs) at various concentrations for periods of 24 hours. (b-e) Confocal upconversion luminescent images of CCD-112CoN cells labeled with $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ UCNPs, taken under the identical instrumental condition and the cell nucleus are labeled with DAPI.	134
Figure 6.22 Information written with security ink could only be read under the irradiation of 980 nm laser (scale bar, 5 mm). The power density is 2 W cm^{-2}	135

Figure 6.23 $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3\text{:Yb}^{3+}, \text{Er}^{3+}$ powders used for illumination (scale bar, 2 cm). The total power of 980 nm beam is 1.2 W, and the power density is around 6 W cm^{-2} 136

Abbreviations

UC	Upconversion
UCNPs	Upconversion nanoparticles
UV	Ultraviolet
IR	Infrared radiation
NIR	Near-infrared
ETU	Energy transfer upconversion
PA	Photon avalanche
ESA	Excited state absorption
EMU	Energy migration-mediated upconversion
CET	Cooperative energy transfer
RE	Rare earth
Ln	Lanthanide
SEM	Scanning electron microscope
TEM	Transmission electron microscope
STEM	Scanning transmission electron microscopy
HRTEM	High-resolution transmission electron microscope
SAED	Selected area electron diffraction
FFT	Fast Fourier transform
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
EDX	Energy-dispersive X-ray spectroscopy
TGA	Thermal gravity analysis
DLS	Dynamic light scattering
LED	Light-emitting diode
CIE	International Commission on Illumination
RGB	Red, green, blue
α -NaYF ₄	Cubic phase sodium yttrium fluoride
β -NaYF ₄	Hexagonal phase sodium yttrium fluoride

AuNP	Gold nanoparticles
CTAB	Cetyltrimethylammonium bromide
PEG	Polyethylene glycol
PDMS	Polydimethylsiloxane
PVP	Polyvinylpyrrolidone
DAPI	4',6-diamidino-2-phenylindole

Chapter 1

Introduction

In this chapter, the background of photon upconversion is presented. Photon upconversion refers to a nonlinear optical procedure in which photons with lower energy are converted into those with higher energy. The potential of upconversion luminescent materials has been demonstrated by researchers all over the world, while the application is seriously limited by the poor energy efficiency. Hence, it is of great significance to fabricate novel materials to achieve an effective and efficient upconversion luminescence.

1.1 Problem Statement and Hypothesis

1.1.1 Problem Statement

Photon upconversion (UC) is a phenomenon that photons with lower energy are absorbed, converted, and emitted as photons with higher energy. Due to the unique anti-Stokes shift, upconversion has been focused by a growing body of research for more than half of a century.^{1,2} A series of progresses has been carried out, among which the lanthanide-doped upconversion nanoparticles (UCNPs) are the most effective and versatile ones.^{1,3-6} Benefitting from the abundant 4f electrons, lanthanide ions possess character ladder-like energy levels, endowing them eligible platforms for energy conversion. Pioneer works like lanthanide-doped Y_2O_3 , YAlO_3 , CaF_2 , and NaYF_4 crystals are successfully fabricated to generate effective visible emission with the excitation of NIR light.⁷⁻⁹ Recently, as the studies of lanthanide-doped nanoparticles get aggressive, the practical applications of upconversion luminescent material has marched on.^{10,11} Particularly, solvothermal synthesized $\beta\text{-NaYF}_4\text{:Yb}^{3+},\text{Er}^{3+}$ nanoparticles with a quantum yield of 1 % – 3 % have been demonstrated eligible for a variety of bio-medical and luminescent applications.¹²⁻¹⁹ However, a luminescent quantum yield of 3 % is far from enough. Such inherent poor upconversion efficiency, as well as the consequential undesired heating effects, lay restraints in the promoting of upconversion materials.²⁰ Hence, it is urgent and of great importance to develop a promising substitute, with sufficient external UC efficiency, comparable versatility, and moderate preparation strategy, to promote the further development of lanthanide-doped upconversion nanoparticles.

Despite from the well-established lanthanide-doped fluorides (e.g. CaF_2 and NaYF_4), alternative candidates, lanthanide-doped oxides, are promising while lack of investigation. Benefitting from the simplicity in composition and easy access of O^{2-} ions, most oxides could be generated through sol-gel methods, hydrothermal synthesis, and solid phase reactions. Such easily performed and low-cost fabrication strategies are conducive to promoting the commercialization of upconversion luminescence. More significantly, lanthanide-doped oxides, also known as lanthanide-doped ceramics, are capable to bear high temperature annealing treatment and extreme application circumstances, achieving a

more effective photon upconversion. Recently, an amazing 16 % of power efficiency is achieved in $\text{ZrO}_2\text{:Yb}^{3+}$ (28 mol%) powders at 2850 K by C. H. Yan *et al.*, through a thermal radiation process.²¹ Another NIR-to-NIR photon upconversion with an external efficiency of 15.1 % is achieved in $\text{Gd}_2\text{O}_3\text{:Er}^{3+}$ (25 mol%) powders by S. Fischer *et al.*,²² which is better than erbium-doped fluorides. Hence, it is reasonably to propose that, lanthanide-doped oxides possess great potential in generating an effective and efficient upconversion luminescence.

1.1.2 Hypothesis

1. Gadolinium cations, which possess a half-filling electron configuration of $4f_7$, has been demonstrated feasible as a mediate for energy migration in rare-earth fluorides. Hence, it could reasonably propose that efficient energy migration, as well as an effective upconversion emission, could be achieved from gadolinium oxide-based upconversion luminescent materials.
2. The introducing of sensitized host matrix with moderate structural confinement might overcome the concentration quenching effect, to generate an effective ETU process-based upconversion luminescence.
3. Rare-earth titanate with perovskite structures, which possess unique cavities formed by TiO_6 octahedral, could provide adequate structural confinement to achieve a homogeneous lanthanide-doping with desired chemical circumstance.

1.2 Objective and Scope

The objective of this thesis is to study the principles for an efficient photon upconversion process, as well as to develop eligible oxides host matrixes to achieve effective upconversion luminescence for practical applications.

To achieve such objective, the research work was carried out as follows:

1. Develop a facile and effective strategy to fabricate lanthanide-doped rare-earth oxide and rare-earth titanate, with controllable morphology and stable structures. Meanwhile study the inherent structural information of host matrixes and lanthanide dopants.
2. Investigate the energy transfer between lanthanide dopants within the gadolinium oxide host matrix. Tuning the structural and doping conditions to study the manipulation of upconversion luminescent properties.
3. Fabricate lanthanide rare-earth oxides with desired frameworks, overcoming concentration quenching effect and generating effective upconversion luminescence.
4. Develop a general hydrothermal strategy to Fabricate lanthanide-doped metal titanates with varied structures and doping status, to study the role of lattice accordance and co-embedding in the case of effective upconversion emission generation.
5. Study the tuning of structures, the morphology, and the luminescent properties of lanthanide-doped perovskite oxides, to fabricate novel upconversion nanoparticles with ultrahigh power efficiency and feasibility for practical applications.

1.3 Dissertation Overview

There are six chapters in this thesis with this introduction as Chapter 1.

Chapter 2 is a brief literature review. First, energy upconversion processes are summarized and discussed, for a general illustration of photon upconversion phenomena. Then the three-essential part of an upconversion phosphor, host matrix, activators, and sensitizers are sequentially discussed. Also, the energy transfer diagram and manipulation of upconversion emissions are summarized for a better understanding of the photon upconversion procedure. Finally, the potential applications of upconversion luminescent materials are discussed.

Chapter 3 summarizes experimental methodologies and characterization methodologies utilized in this work.

Chapter 4 is the first part of the whole work, focusing on the controlled synthesis of rare-earth hydroxides and corresponding oxides with ammonia-assisted hydrothermal synthesis. The as-prepared rare-earth oxide nanorods are uniform and highly crystallized. The feasibility for the upconversion luminescence is demonstrated on lanthanide-doped Gd_2O_3 nanorods, from which a bright combinational white-light emission is achieved.

Chapter 5 focuses on the host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods. Admittedly, sensitizers that capture the pump photons and transfer absorbed energy to activators are essential for an effective photon upconversion. However, the high concentration of sensitizers always results in concentration quenching effect and a poor upconversion efficiency. In this part of work, $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods, derived from $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ with three-dimensional frameworks, are fabricated and demonstrated feasible for generating efficient upconversion luminescence. Such high in photon upconversion efficiency is due to the partial preservation of the three-dimensional frameworks.

In Chapter 6, a novel rare-earth titanate, namely $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$, with perovskite structure, is proposed and successfully fabricated. The neighbored TiO_6 octagonal forms moderate cavities, which are alternatively occupied by the rare-earth cations and sodium cations. The as-prepared lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ could generate bright upconversion luminescence, which could be further enhanced by an annealing treatment. The power efficiency of such perovskite-structured nanoparticles is measured to be 37 %, by both relative method and directive measurement. Finally, such high-efficient upconversion phosphors are demonstrated feasible for biological and luminescent applications.

Finally, in Chapter 7, the summary and conclusion of works on lanthanide-doped oxides for effective upconversion luminescence are drawn majorly, together with the recommendation of future works.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Development of a facile and general one-step hydrothermal synthesis to fabricate uniform rare-earth hydroxide with desired morphologies.
2. Achievement of an effective energy transfer within lanthanide-doped gadolinium oxide to generate tunable luminescent properties.
3. Demonstration of the structural confinement generated by inner frameworks could contribute to an upconversion luminescence with high efficiency.
4. Novel perovskite-type lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ for upconversion luminescence with ultra-high power efficiency.

References

- (1) Liu, X.; Yan, C.-H.; Capobianco, J. A. *Chemical Society Reviews* **2015**, *44*, 1299.
- (2) Auzel, F. *Chemical reviews* **2004**, *104*, 139.
- (3) Sun, L.-D.; Dong, H.; Zhang, P.-Z.; Yan, C.-H. *Annual review of physical chemistry* **2015**, *66*, 619.
- (4) Chen, X.; Peng, D.; Ju, Q.; Wang, F. *Chemical Society Reviews* **2015**, *44*, 1318.
- (5) Gnach, A.; Lipinski, T.; Bednarkiewicz, A.; Rybka, J.; Capobianco, J. A. *Chemical Society Reviews* **2015**, *44*, 1561.
- (6) Yang, D.; Hou, Z.; Cheng, Z.; Li, C.; Lin, J. *Chemical Society Reviews* **2015**, *44*, 1416.
- (7) Huang, S.; Xu, J.; Zhang, Z.; Zhang, X.; Wang, L.; Gai, S.; He, F.; Niu, N.; Zhang, M.; Yang, P. *Journal of Materials Chemistry* **2012**, *22*, 16136.
- (8) Li, Z.; Zhang, Y. *Angewandte Chemie International Edition* **2006**, *45*, 7732.
- (9) Zheng, W.; Zhou, S.; Chen, Z.; Hu, P.; Liu, Y.; Tu, D.; Zhu, H.; Li, R.; Huang, M.;

Chen, X. *Angewandte Chemie* **2013**, *125*, 6803.

(10) Mai, H.-X.; Zhang, Y.-W.; Si, R.; Yan, Z.-G.; Sun, L.-d.; You, L.-P.; Yan, C.-H. *Journal of the American Chemical Society* **2006**, *128*, 6426.

(11) Mai, H.-X.; Zhang, Y.-W.; Sun, L.-D.; Yan, C.-H. *The Journal of Physical Chemistry C* **2007**, *111*, 13721.

(12) Wang, Y.-F.; Liu, G.-Y.; Sun, L.-D.; Xiao, J.-W.; Zhou, J.-C.; Yan, C.-H. *ACS nano* **2013**, *7*, 7200.

(13) Sun, Y.; Zhu, X.; Peng, J.; Li, F. *ACS nano* **2013**, *7*, 11290.

(14) Chen, S.; Weitemier, A. Z.; Zeng, X.; He, L.; Wang, X.; Tao, Y.; Huang, A. J.; Hashimoto, Y.; Kano, M.; Iwasaki, H. *Science* **2018**, *359*, 679.

(15) Zhao, J.; Jin, D.; Scharfner, E. P.; Lu, Y.; Liu, Y.; Zvyagin, A. V.; Zhang, L.; Dawes, J. M.; Xi, P.; Piper, J. A. *Nature nanotechnology* **2013**, *8*, 729.

(16) Lu, Y.; Zhao, J.; Zhang, R.; Liu, Y.; Liu, D.; Goldys, E. M.; Yang, X.; Xi, P.; Sunna, A.; Lu, J. *Nature Photonics* **2014**, *8*, 32.

(17) Wang, F.; Han, Y.; Lim, C. S.; Lu, Y.; Wang, J.; Xu, J.; Chen, H.; Zhang, C.; Hong, M.; Liu, X. *nature* **2010**, *463*, 1061.

(18) Zhang, C.; Yang, L.; Zhao, J.; Liu, B.; Han, M. Y.; Zhang, Z. *Angewandte Chemie International Edition* **2015**, *54*, 11531.

(19) Liu, Y.; Lu, Y.; Yang, X.; Zheng, X.; Wen, S.; Wang, F.; Vidal, X.; Zhao, J.; Liu, D.; Zhou, Z. *Nature* **2017**, *543*, 229.

(20) Wolfbeis, O. S. *Chemical Society Reviews* **2015**, *44*, 4743.

(21) Wang, J.; Ming, T.; Jin, Z.; Wang, J.; Sun, L.-D.; Yan, C.-H. *Nature communications* **2014**, *5*, 5669.

(22) Fischer, S.; Martín-Rodríguez, R.; Fröhlich, B.; Krämer, K. W.; Meijerink, A.; Goldschmidt, J. C. *Journal of luminescence* **2014**, *153*, 281.

Chapter 2

Literature Review

This chapter presents the current research progress on upconversion luminescent materials. It starts with a brief introduction of the concept, as well as the mechanism of a photon upconversion procedure. Then, three-principle compositions, the host matrix, the activators, and the sensitizers are discussed. Subsequently, several well-established manipulation methods for upconversion luminescence are briefly reviewed. Finally, the applications, for both bio-medical and luminescent, are summarized systematically.

2.1 Introduction of Upconversion Luminescence

Upconversion luminescence is a phenomenon that converts photons with lower energy into photons with higher energy.¹ In the past half a century, numerous exploitations and progresses had been achieved in such research field, among which lanthanide-doped upconversion nanoparticles that convert near infrared (NIR) excitation into visible emission are the most successful and effective ones.²

Benefit from abundant f electrons, lanthanide ions possess characteristic ladder-like energy levels, endowing them promising candidate for energy absorption and conversion. Lanthanide-doped upconversion nanoparticles possess unique advantages, e.g. unique anti-stoke shift, excellent photo-stability, and sharp emission peak.² Particularly, as the preparation of lanthanide-doped NaYF₄ nanoparticles get aggressive,^{3,4} various structural and luminescent manipulating strategies⁵⁻¹², as well as diverse fascinating application concepts¹³⁻¹⁶ have been achieved on lanthanide-doped upconversion nanoparticles. Literally speaking, lanthanide-doped upconversion nanoparticles have been grown into a competitive challenger against two conventional giants, organic fluorophores and semiconductor nanocrystals, in the field of bio-imaging^{17,18}, anti-counterfeiting^{13,14}, three-dimensional display^{5,10}, and super-resolution microscopy¹⁵.

In general, upconversion emission is derived from five different mechanisms: excited state absorption (ESA), photon avalanche (PA), energy transfer upconversion (ETU), cooperative energy transfer (CET), and energy migration-mediated upconversion (EMU).^{1,19}

An excited state absorption (ESA) process refers to a sequential absorption of two pump photons by a single ion which is possessed of multiple energy levels. Therefore, the adequate and stable intermediate energy level of the dopant ion, with adequate electron populations, is essential for an efficient upconversion. In the case of the energy gap does not match the energy of the pump photon, upconversion luminescence can be generated by a photon avalanche (PA) process. In such a case, an unstable super-excited stage of

activator ion is generated by the absorption of two mismatched pump photons. Then a cross-relaxation between such super-excited ion and a neighbor ground-state ion, namely avalanche transition, occurs, resulting in two intermediate-state excited ions. The repeating of such process generates fully-excited activator ions and the following upconversion emission.²⁰ Among all process, the ESA and PA are the simplest ones since only one dopant ion is required. Thus, the efficiency of ESA/PA process-based upconversion luminescence is extremely low, due to the difficulties lying in energy accumulation and transition.

As a comparison, Energy transfer upconversion (ETU) process is much more efficient in generating upconversion luminescence, as well as being deepest studied one. In a typical ETU-related upconversion system, two dopant ions, namely sensitizer and activator respectively, are imbedded within one upconversion crystal. Two different types of ions, namely a sensitizer and an activator, are employed in the same matrix lattice. Upon excitation, both the sensitizer and the activator could be pumped to their excited states. Subsequently, the energy absorbed by sensitizer is non-radiatively transferred to the activator via a dipole–dipole resonant interaction. Benefiting from the large absorption cross-sections of the sensitizers and their efficient energy transferring to activators, an effective upconversion emission is consequently generated. Similar to the ETU process, a cooperative energy transfer (CET)-based UC process requires a combination of sensitizers and activators. In such case, two sensitizers are cooperatively activated to a virtual excited state to fulfill a simultaneous energy transfer to a neighboring activator. A CET-based upconversion is usually observed in bulk materials, like glasses and polymers, under the irradiation of high excitation power.^{21,22} Ascribing to the critical requirement of ladder-like energy levels and moderate energy gaps, the candidate list of activators is restricted. To address such a problem, a sequential energy transition process, absorption-accumulation-transfer-emission, namely energy migration upconversion (EMU) process, is proposed by Liu et al. recently.¹² In a typical EMU process, an ETU process is first conducted between sensitizer and accumulator, resulting in the higher excited state of the accumulator. Subsequently, a migration of energy from the accumulator to activator via the mediate of migrator occurs. The energy is released by activated activator and generate characteristic emissions of the activators. Such designation enriches the list of activators and broadens

the potential applications of upconversion dramatically.

Figure 2.1 Schematic representations of UC processes, where upward (red) and downward (blue) full arrows stand for direct excitation processes and radiative emission processes, respectively. Dashed arrows (green) represent energy transfer processes.

2.2 Upconversion Materials

2.2.1 Host Matrix

Host matrix acted as a key role in the field of upconversion. On the one hand, matrix materials were supposed to provide an adequate chemical environment that maximized the energy transfer efficiency and minimized the energy loss simultaneously. On the other hand, only materials that were high in stability and facile in manipulation were capable to fulfill the complicated requirements of various applications. More specifically, an ideal candidate of host material needs to meet such requirements, (i) high tolerance for luminescent centers, (ii) low phonon energy to minimize undesirable nonradiative relaxations, (iii) high transparency for free migration of NIR photons in the lattice and (iv) excellent chemical and thermal stabilities to retain the original crystal structures.¹⁹ Till now, a series of oxide, sulfide, and fluoride compounds has been generated for upconversion applications, among which oxide and fluoride were most effective and efficient.

2.2.1.1 Oxide Matrix

As one of the simplest compounds, metal oxides are easy in prepared, high in stability, and

ordered in structure, which making them eligible candidates for upconversion applications. Taking yttrium oxide (Y_2O_3) as an example. Benefiting from the similar ion radius shared by yttrium and heavy rare-earth ions, which are usually used as activators and emitters, it is easy to introduce dopants into crystal Y_2O_3 matrix, resulting in an effective upconversion platform. Other oxides, like aluminum oxide²³, bismuth oxide²⁴, lanthanum oxide²⁵, cerium oxide, have also been prepared recently.

Besides simple monometallic oxide, another composite oxide has attracted increasingly attentions, due to the possibilities in complex structure control. A series of ceramic oxides, e.g. YVO_4 ,²⁶ $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$,²⁷ CaTiO_3 ,²⁸ BaTiO_3 ,²⁹ SrAl_2O_4 ,³⁰ and $\text{Yb}_3\text{Al}_5\text{O}_{12}$ (YbAG)³¹ had been successfully prepared (Fig. 2.2 bottom), and upconversion luminescence was also achieved on these matrixes. Benefitting from the high thermal stability and low phonon energy of the ceramic materials, the upconversion luminescence from these matrixes were attractively high, and could be utilized as an indicator for the temperature.^{27,30,31}

Oxides host matrix had been widely studied in the field of upconversion luminescence. However, compared to the fluoride nanocrystals, e.g. NaYF_4 , NaGdF_4 , GdF_3 etc., the difficulties lying in the controlled synthesis, as well as a comparable low upconversion efficiency, restrict the further investigation and application of the oxide-based upconversion nanomaterials. Conventionally, rare-earth oxides (RE_2O_3) are synthesized by thermal decomposition of either organometallic compounds (e.g. RE-oleate, RE-acetate, etc.) or RE-containing precursors (e.g. gel, $\text{RE}_2\text{O}(\text{CO}_3)_2$, $\text{RE}(\text{OH})_3$, etc.) prepared by sol-gel, coprecipitation and hydrothermal methods. Thermal decomposition of organometallic compounds results in homogeneous nanoparticles, while the crystallinity is poor, and the lanthanide-doping is hardly to achieve. Synthesis of lanthanide-doped precursors prior to thermal decomposition, on the contrary, generates homogeneously doped products with poor size-control and undesired aggregations. To date, only a few of rare-earth oxide micro-crystals with efficient upconversion luminescence properties are successfully prepared, which are ineligible for in-depth fundamental study and practical applications like cell-labeling and optical therapy. Moreover, the challenge exists in achieving highly

crystalline RE_2O_3 nanoparticles, Hence, only by overcoming such challenges lying in preparation and modification, can oxide-based upconversion materials be revived as promising candidates and further applied in the field of upconversion luminescence.

Figure 2.2 A series of oxide nano- and micro-crystals utilized as matrix for upconversion applications.²²⁻³¹

2.2.1.2 Fluoride Matrix

Fluoride matrixes were an alternative, meanwhile the most popular, candidates for upconversion applications. Till now, a series of fluoride, e.g. CaF_2 ,³² YF_3 ,³³ YOF ,³⁴ LiYF_4 ,³⁵ NaGdF_4 ,³⁶ NaYF_4 ,^{3,37,38} NaBiF_4 ,³⁹ KYb_2F_7 ,⁷ BaLuF_5 ,⁴⁰ and KMnF_3 ⁴¹ (Fig. 2.3) had been synthesized and assessed systematically, among which NaREF_4 nanoparticles, like NaYF_4 , were the most effective and well-studied ones. NaREF_4 processes two different phases, namely cubic phase (α) and hexagonal phase (β), Generally, cubic phase NaREF_4

(usually noted as α -NaREF₄) could be obtained at lower preparation temperature, while hexagonal ones(noted as β -NaREF₄) are synthesized at higher temperature and longer reaction time.⁵

Though both α - and β -NaREF₄ are similar in both component and synthesis method, β -NaREF₄-based upconversion materials show their paces due to their unique structures⁴² during the last decade. On the one hand, the solvothermal synthesis method carried out by Zhang et al.³⁸ and the solvothermal decomposition method carried by Yan et al.³ simplify and standardize the synthesis procedure, resulting in the enhancement of the reliability and reproducibility of upconversion works. On the other hand, the lanthanide-doping strategy proposed by Liu et al.⁵ solves the problem in phase and size control. As a consequence, bright green light emitter β -NaYF₄:Yb,Er, one of the most effective and efficient upconversion materials till now, has been synthesized and utilized in various applications, including but not limited to bio-imaging, 3D display, coding, anti-counterfeit, and white light emitting. What's more, by adjusting the doping reagent and doping ratio, a series of upconversion emitters, with various color of light, various decay time, and even various absorbed wavelength could be obtained.

Figure 2.3 A series of fluoride nanocrystals utilized as matrix for upconversion applications.³²⁻⁴¹

2.2.2 Activators and Sensitizers

The activator is the luminescent center imbedded homogeneously in matrix and is required by all kinds of upconversion phosphors. Owing to the characteristic and abundant energy levels, various lanthanide ions could generate effective upconversion emission with or without the assist of sensitizers in different energy transfer processes. The sensitizers, on the contrary, have nothing to do with the final emission, but it is still essential for some upconversion processes due to the assistant in capturing of pump photons.

2.2.2.1 Activators for ESA Process

In the case of excited state absorption (ESA) process, erbium (Er) is one of seldom candidates, due to the accordance of energy gaps ($^4I_{15/2} \rightarrow ^4I_{11/2} \rightarrow ^2F_{7/2}$) to the energy of pump photons. What's more, a recent work has demonstrated that Nd-doped materials

could generate ESA-based upconversion luminescence, though the efficiency is extremely low.⁴³ Overall, such rigorous requirements and lack of activators restrict the further development of ESA-based upconversion.

2.2.2.2 Activators for ETU process

Unlike ESA process, an energy transfer upconversion (ETU) process is much more effective due to the involvement of sensitizers, resulting in the enrichment of candidate list. A valid ETU process could employ one or more activators from these commonly used candidates, erbium (Er), thulium (Tm), and holmium (Ho).

Among all ETU activators, Er^{3+} is most popular due to the highest upconversion efficiency. Such excellent optical property also attributes to the accordance of energy gaps ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$, $^4\text{I}_{11/2} \rightarrow ^2\text{F}_{7/2}$, $^4\text{I}_{13/2} \rightarrow ^4\text{F}_{9/2}$) to the energy of pump photons. To make it more detailed, a continuous two-step excitation ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2} \rightarrow ^2\text{F}_{7/2}$, “ $\rightarrow$ ” represents energy transition) results in an intermediate energy level of $^2\text{F}_{7/2}$ and the accumulated doubled electron energy, generating green light emission (521 nm corresponds to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transition, and 541 nm corresponds to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition). Meanwhile, an interval two-step excitation ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2} \Rightarrow ^4\text{I}_{13/2} \rightarrow ^4\text{F}_{9/2}$, “ $\Rightarrow$ ” represents nonradiative relaxation) results in an intermediate energy level of $^2\text{F}_{9/2}$, generating red light emission (652 nm corresponds to $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition). By adjusting the matrix structure, the doping ratio, or even the pump power density, the dominant excitation process varies, resulting in a tunable emission color, from red to yellow and then green. Such phenomenon could be utilized either generating white light by coupling yellow light emitter with another blue light emitter, or as an indicator for detect.

Similar to Er^{3+} , Tm^{3+} and Ho^{3+} also possess ladder-like energy levels and moderate energy gaps, endowing them the capacity of energy accumulation during ETU process. Specifically, Tm^{3+} could generate near IR light of 808 nm and visible light of 694 nm through two-photon process, visible light of 475 nm from three-photon process, and UV light of 362nm/345nm from four-photon or five-photon process, alternatively.

Analogously, Ho^{3+} could generate visible light of 655 nm / 542 nm through two-photo or three-photon process. However, the energy gaps of Tm^{3+} ($^3\text{H}_6 \rightarrow ^3\text{H}_5$, $^3\text{F}_4 \rightarrow ^3\text{F}_2$, $^3\text{H}_4 \rightarrow ^1\text{G}_4$) and Ho^{3+} ($^5\text{I}_8 \rightarrow ^5\text{I}_6$, $^5\text{I}_6 \rightarrow ^5\text{F}_4$, $^5\text{I}_7 \rightarrow ^5\text{F}_5$, $^5\text{I}_5 \rightarrow ^8\text{K}_3$) are lower than the energy of pump photons, thus energy loss will occur during every single transition. Therefore, in most cases, the upconversion efficiency of Tm^{3+} and Ho^{3+} is much lower than that of Er^{3+} .

Besides these three superstar activators, some other rare earth ions, like dysprosium (Dy^{3+}), samarium (Sm^{3+}), and praseodymium (Pr^{3+}) could also generate upconversion emission through ETU process.⁴⁴⁻⁴⁶ However, due to the discordance of energy gaps and the prominent of nonradiative relaxation, the upconversion efficiency is rather low when compare with those well-established superstar activators.

2.2.2.3 Activators for EMU Process

Benefiting from the structure of isolated energy absorbing layer and energy emitting layer, more activators could be successfully involved on the candidate list of upconversion activators. Among which europium ion (Eu^{3+}) and terbium ion (Tb^{3+}) are the most attractive ones. The energy of pump photons is collected and accumulated in the core, into higher energy level, like $^1\text{I}_6$ of the thulium ion. Then the energy could “migrate” to the outer layer through the mediate of gadolinium ions, and finally arrive at activators like europium ion (Eu^{3+}) and terbium ion (Tb^{3+}), resulting in the characteristic red emission (for Eu^{3+}) and green emission (for Tb^{3+}), respectively. Other rare earth ions, like dysprosium (Dy^{3+}) and samarium (Sm^{3+}), are also able to generate upconversion emissions through EMU process, though the intensity of emission is extremely weak.

2.2.2.4 Sensitizers

As mentioned before, the sensitizers act as an assistant in upconversion process, assisting activators make full use of pump photons in energy transfer upconversion process (ETU), cooperate energy transfer process (CET) and energy migration upconversion process (EMU). Hence, large absorption cross-section and moderate energy levels accordant to

activators are essential for an ideal sensitizer. To date, the ytterbium ion (Yb^{3+}) is the best choice.

The absorption cross-section of the Yb^{3+} is measured to be $9.11 \times 10^{-21} \text{ cm}^2$ (976 nm , $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$),¹⁹ which is relatively large among all rare earth ions. Besides, the energy gap between ground state and excited state (976 nm , or $10.25 \times 10^3 \text{ cm}^{-1}$) was accordant to the that of commonly used activators (Er^{3+} , Tm^{3+} , and Ho^{3+}). Most importantly, the excited state of $^2\text{F}_{5/2}$ and the ground state of $^2\text{F}_{7/2}$ were the only two states of Yb^{3+} , such simple energy level diagram endowed Yb^{3+} an ideal energy donor. These advantages coordinately made Yb^{3+} an excellent sensitizer to donate energy to activators.

Another well-studied sensitizer is the neodymium ion (Nd^{3+}).^{17,47} As was known to us, Yb^{3+} -sensitized upconversion materials respond to the 978 nm or 980 nm excitation, which coincides the strong absorption of the water. As a comparison, Nd^{3+} has multiple NIR excitation bands at 730 nm ($^4\text{I}_{9/2} \rightarrow ^4\text{F}_{7/2}$), 808 nm ($^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}$), and 865 nm ($^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}$). Moreover, the energy transfer between Nd^{3+} and Yb^{3+} is demonstrated feasible.⁴⁸ Thus, a series of Nd^{3+} - Yb^{3+} co-sensitized upconversion materials has been developed, generating upconversion materials responding to excitations other than 978 nm or 980 nm , for example, NIR of 808 nm . In a typical work of Nd^{3+} -sensitized UCNPs,¹⁷ a core-shell structured UCNP ($\text{NaGdF}_4:\text{Yb,Er}@\text{NaGdF}_4:\text{Yb,Nd}$) was prepared, with Nd^{3+} doped in the shell layer as sensitizer, Er^{3+} doped in the core layer as activator, and Yb^{3+} doped in both shell layer and core layer as energy mediate. Under the irradiation of an 808 nm laser, the energy of pump photon was absorbed by Nd^{3+} ($^4\text{I}_{9/2} \rightarrow ^4\text{F}_{5/2}$), transferred through Yb^{3+} ($^2\text{F}_{5/2}$), accumulated at Er^{3+} ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2} \rightarrow ^2\text{F}_{7/2}$), and finally emitted visible green light ($^2\text{H}_{11/2}, ^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$).

Besides lanthanide elements, organic dyes possesses moderate absorption band could also be utilized as sensitizers for upconversion luminescence. Han and coworkers⁴⁹ had demonstrated such concept with the IR-806-dye-sensitized UCNPs. IR-806 dye that absorbing light with wavelength of 806 nm was modified on the surface of UCNPs, endowing the UCNPs being capable to emit visible light under the excitation of 806 nm

laser. When a barrier layer with an increasing thickness was employed between the dye molecule and the UCNPs, the intensity of the upconversion emission decreased accordingly. Such phenomenon confirms that the energy transfers between dye molecules and activators embedded in UCNPs.

Figure 2.4 Typical sensitizers and activators for an effective upconversion process.

2.3 Optical Properties of Upconversion Materials

Though the luminescent property of upconversion luminescent materials is mainly correlated to the characteristic energy levels of dopants and intrinsic properties of the matrix, the endeavors toward a further and precisely manipulated upconversion luminescence never stopped their pace.

2.3.1 Color-Manipulation

As mentioned above, most upconversion activators possess more than one emission peak, making it significant to tune the chromatic color or mixed colors. In a typical work,⁵⁰ organic dyes were used to tune the selective one of the dual emission bands. Based on the same concept, a strategy that generated single-band upconversion emission was carried out by Zhang and co-workers.¹¹ In their work, the dye molecule-upconversion nanoparticle conjunctions were fabricated systematically. The dye molecules were selected carefully, that totally absorbed one single band of dual upconversion emission while did not affect

another one. Moreover, by varying dye molecules and upconversion activators, the emission of the nanocomplexes could be tuned precisely, endowing such technique promising for next-generation optical multiplexing applications. Another single-band emission concept was demonstrated by Liu and co-workers.⁴¹ By introducing Mn^{2+} as host matrix, the energy transition in activators was strongly confined, resulting in the single-band upconversion emissions.

In another pioneer work, Liu and co-workers⁸ discovered a novel phenomenon, namely non-steady-state upconversion, in which the color of emitting light corresponded to the duration of the pulsed laser. To be specific, the authors found that the deactivation of excitation energy and the energy transfer process occurred at different rates. Hence, when exposed to a pulsed laser with a moderate irradiation duration, the activators would bear a non-steady-state process. The dominant energy levels correlated to the duration of pulsed laser, resulting in the variable of emission peaks. Such proposal was demonstrated by a UCNP embedded with Yb^{3+} as sensitizer, Ho^{3+} as activator, and Ce^{3+} as assistant. Furthermore, the addition of Nd^{3+} -sensitized Tm^{3+} -containing layer, three beams of light with three primary colors could be generated from one single UCNP.

Similarly, the power density of the 980 nm laser was utilized, by Zhang and co-workers,¹⁰ to tune the emission color of UCNPs. It had been demonstrated that the total emission intensity was linear to the irradiation intensity, however, the ratio between different emission bands was not constant during such process. Thus, by tuning the irradiation power density, a series of colors varying from cyan to violet could be generated gradually.

Figure 2.5 Typical works focus on manipulation of color of emission. a) Schematic diagram and emission spectra of dye-modified UCNP used for coding applications.⁵⁰ b) Schematic diagram of dye-based single band-UCNP fabrication.¹¹ c) Single-band emission of KMnF₃:Yb,Ln (Ln = Er, Ho, Tm, respectively).⁴¹ d) Design of UCNP capable of emitting three primary colors from one single particle with a pulsed NIR laser.⁸ e) Luminescence (up) and integrated intensities (down) of RGB emissions under tunable irradiation power density.¹⁰

2.3.2 Enhancement of Upconversion Luminescence

An upconversion luminescence consisted three steps, which are photon absorption, energy transfer/migration, and photon emission. Maximizing the photon absorption and energy transition efficiency, as well as minimizing the quenching effects and nonradiative relaxation, are effective methods to achieve an effective upconversion.

2.3.2.1 Surface-Manipulation

Due to the large surface-to-volume ratio of UCNPs, the surface quenching effect influences the total upconversion efficiency dramatically. To address such drawback, numerous endeavors had been devoted in the surface manipulation to enhance the upconversion efficiency. A pioneer work, in which NaYF₄:Yb,Er@NaYF₄ core-shell nanoparticles were prepared, was carried out by Chow and co-workers.⁵¹ The inert shell of NaYF₄ did inhibit surface quenching effect, resulting the enhancement of upconversion luminescence. Another work conducted by Liu and co-workers³⁶ studied the effect of particle size and the content of water molecules, conforming the size-dependent surface-quenching effect caused by water molecules. Recently, a novel progress proposed by Yan and co-workers⁵² successfully coated UCNPs with a dissimilar structured shell, to achieve a large enhancement of upconversion luminescence.

Besides the surface-coating achievements mentioned above, an art-of-the-state approach was recently proposed by Jin and co-workers,⁹ by utilizing phonons generated at the surface of UCNPs to enhance the photon accumulation of the activators embedded in UCNPs. In detailed, a chelate was applied to form [Yb--O] complexes, which could act as phonon centers upon heating. When increasing the temperature, [Yb--O] complexes assisted the transfer of trapped energy to the Tm³⁺ activators, eventually generating a 2000-fold enhancement in blue emission at temperature of 453K.

Figure 2.6 a) Core-shell structured UCNP for enhanced upconversion luminescence.⁵¹ b) Schematic illustration (up), HRTEM image and FFT pattern (down) of selective cation exchange remediated dissimilar structure for the growth of β -NaLnF₄@CaF₂ nanoparticles.⁵² c) Schematic illustration (left) and the emission spectra (right) of the size-dependent surface-phonon-enhanced upconversion process.⁹

2.3.2.2 Plasmonics

To generate plasmonic modulation for upconversion materials, the core-shell structured Ag@SiO₂@Y₂O₃:Er and UCNP@AuNPs nanocomplex, as well as heterogeneous AuNP-UCNP nanoclusters, were prepared by Zhao *et al.*, Duan *et al.*, and Cha *et al.*, respectively.⁵³⁻⁵⁵ The heterogeneous structures, electric field amplitude, and luminescent properties were studied systematically. In another work, large upconversion enhancement was achieved in the “islands” Au-Ag alloy/UCNPs composite film, by Song and co-workers.⁵⁶ In such work, the Au-Ag alloy was deposited on the subject to form an

inhomogeneous film, on which alloy-rich “islands” were separated by alloy-poor “valleys”. UCNPs deposited on the surface of alloy “islands” showed bright green emission, compared with those deposited on the bare glass. After a systematical analysis, the authors owed such 180-fold enhancement of upconversion luminescence to the coupling of Au–Ag alloys SP with the excitation electromagnetic field of the UCNPs. In a similar work, Park and co-workers⁵⁷ fabricated a UCNPs-Ag nanograting of which the surface plasmon resonance matched the excitation wavelength of UCNPs. The plasmonic enhancement was also achieved on such structure.

Figure 2.7 a) Ag@SiO₂@Y₂O₃:Er core-shell nanoparticles for tunable upconversion luminescence.⁵⁵ b) Au nanocrystals-UCNPs clusters for upconversion luminescence.⁵⁴ c) UCNPs-AuNPs core-shell nanostructures for plasmonic modulation of upconversion luminescence.⁵³ d) “Islands” Au-Ag alloy/UCNPs composite film for large enhanced upconversion luminescence.⁵⁶ e) UCNPs-Ag nanograting for plasmonic enhanced upconversion luminescence.⁵⁷

2.4 Applications of Upconversion Materials

2.4.1 Biomedical Applications

As it's known to us, the upconversion nanoparticles (UCNPs) possess the advantages of high photostability, narrow emission bands, and unique anti-stoke shift. Moreover, the excitation wavelengths for upconversion materials (e.g., 980 nm or 808 nm) locate within the “optical transparency window” (700 – 1100 nm).^{58,59} Thus upconversion materials are suitable for cell labelling, monitored or triggered drug delivery, *in vivo* deep tissue imaging, and other biomedical applications. Ytterbium and erbium co-doped β -NaYF₄ (β -NaYF₄:Yb³⁺,Er³⁺) nanoparticles or nanorods are the most popular module platforms that have been deeply studied.

Due to the usage of organic solvent in the solvothermal synthesis of β -NaYF₄, a surface modification is essential for UCNPs before the application in bio-system. Among all strategies, coating UCNPs with a thin layer of silica (SiO₂) is the most representative and successful one. As an instance, Lin et. al.⁶⁰ have proposed a strategy in which these as-prepared hydrophobic UCNPs (β -NaYF₄:Yb,Er) were mixed with surfactant cetyltrimethylammonium bromide (CTAB) to form CTAB-capped UCNPs. By doing this, water-dispersible UCNPs were generated. Then a well-established sol-gel process⁶¹ was applied to coat these water-dispersible UCNPs with a mesoporous silica (mSiO₂) shell with tunable thickness. Finally, the obtained UCNP@mSiO₂ nanospheres were modified with polyethylene glycol (PEG) to enhance the dispersion and bio-compatibility. Similarly, eccentric-UCNP@SiO₂,⁶² UCNP@SiO₂@mSiO₂,⁶³ yolk-shell UCNP@SiO₂,⁶⁴ and UCNP@SiO₂ fiber⁶⁵ have been successfully prepared.

Figure 2.8 Surface-modification of UCNPs prior to bio-applications. a) TEM images of UCNP@d₁-SiO₂ (left), UCNP@d₁-SiO₂@d₂-SiO₂ (middle), and yolk-shell structured UCSNs (right), respectively.⁶⁴ b) TEM images of concentric- (left) and eccentric- (right) UCNR@SiO₂ core-shell structures.⁶² c) SEM (left) and TEM (right) images of UCNPs@SiO₂ fibers (up), UCNPs@SiO₂ tubes (middle), and UCNPs@mSiO₂@fibers (down), respectively.^{59,65}

2.4.1.1 Cell / Tissue Imaging

In vitro cell culture is the primary test prior to the practical usage of upconversion nanoparticles (UCNPs) in biomedical applications. Numerous pioneer works had been carried out by various groups to verify the bio-compatibility and photo-stability of the UCNPs.⁶⁶⁻⁶⁸

Subsequently, a series of wonderful *in vivo* cellular and tissue imaging applications were achieved. In a typical work, Hilderbrand *et al.*⁶⁹ synthesized polyethylene glycol-modified Y₂O₃:Yb,Er nanoparticles which possessed the upconversion luminescence centered at 660 nm for blood pool imaging *in vivo*. The nanoparticles could be firstly visualized by a whole-field-illumination upconversion microscope (Fig. 2.9b). In another work, Li *et al.*⁷⁰ prepared FA-modified UCNPs used for *in vitro* tumor imaging. After the injection of such tumor-targeted imaging agent into the Hela tumor-bearing mouse for 24 hours, significant

upconversion luminescent signal could be observed in the tumor tissue, under the irradiation of NIR light of 120 mW/cm². (Fig. 2.9a)

As the *in vitro* usage of UCNPs becomes various, increasingly therapeutic applications had been proposed recently. Among these proposals, an art-of-the-state UCNPs-mediated optogenetics carried out by Chen and co-workers was of most remarkable.¹⁶ In such work, high-penetrative NIR light and high-stimulative blue light were used jointly. To make it more specific, UCNPs@SiO₂ nanoparticles were injected to the specific part of the brain of mice, under the irradiation of NIR light, high energy blue/green light could be emitted in situ, stimulating the acceptors (ChR2 for activation and NpHR/Arch for inhibition) located on the membrane of neuron cells and generating neural activation/inhibition. Furthermore, such NIR-mediate optogenetics could be utilized to alter the behavior of an awake animal by targeted activation/inhibition specific regions of the brain. (Fig. 2.9c) Such work was a milestone of the UCNPs in the field of biomedicine, it could be expectable for the clinical applications of UCNPs soon.

2.4.1.2 Monitored/Stimulated Drug Delivery System

As promising photoluminescence (PL) materials, the combination of upconversion nanoparticles (UCNPs) could be combined with drug delivery systems to generate luminescence-monitored drug delivery systems.⁷¹⁻⁷³ In a typical work,⁷¹ β -NaYF₄@m-SiO₂-PEG was prepared successfully, and the antitumor drug doxorubicin (DOX) was loaded within the mesoporous silica layer. After a certain period of drug-carrier uptake and tissue culture, the uptake of DOX-loaded NaYF₄@m-SiO₂-PEG nanoparticles was monitored by upconversion luminescence, and the efficacy of antitumor function was verified by the decrease of tumor weight. (Fig. 2.9d)

Besides the application of tracking, the visible light emitted by UCNPs could also be applied to trigger the release of drug. Light-response drug delivery platforms were promising for the delivery of highly toxic or targeted drugs. Conventional drug delivery systems were based on high energy UV or visible light, resulting in side-effects like cellular

photodamage and insufficient tissue penetration depth. Alternatively, the application of NIR-response UCNPs could endow those photolysis/photo-switching/photo-activation processes triggered by visible light with the capacity that responds to NIR light.⁷⁴⁻⁷⁶ Following such concept, Shi and co-workers⁷⁷ have reported a work in which UCNP@mSiO₂-azobenzene nanoparticles were successfully synthesized. The irradiation of NIR light (980 nm) could be converted into UV or visible light, triggering the trans–cis photoisomerization of azobenzene group, resulting in the release of drugs from the mSiO₂ layer.

Figure 2.9 UCNPs for bio-applications. a) *In vivo* up-conversion luminescence imaging of subcutaneous HeLa tumor-bearing athymic nude mice.⁷⁰ b) Optical, upconversional, and fluorescent imaging of blood vessels in the mouse ear.⁶⁹ c) Experimental scheme (left) and relative DA signals (right) for transcranial NIR stimulation of the VTA in anesthetized mice.¹⁶ d) Therapeutic and imaging bi-functional DOX-loaded UCNPs@mSiO₂ nanoparticles.⁷¹ e) NIR light-triggered drug delivery systems.⁷⁷

2.4.2 Light-emitting and Display Applications

2.4.2.1 White-Light Emitting

The white backlight, which is the combination of three primary colors, is essential for the display applications. Color pixels are usually generated or isolated from a full-wavelength backlight, thus the rapid development of display industry calls for novel white-light phosphors all the way. Benefiting from the abundant energy levels of various members in lanthanide family, corresponding assorted emissions could be obtained simultaneously. Zhang and co-workers¹⁰ prepared a multi-shell upconversion luminescent platform, from which emission with tunable colors, involving white color, could be achieved. Such white-light emitting UCNPs consisted two lanthanide-functionalized layers, the outer one consisted Eu^{3+} generating red emission, and the inner one consisted Er^{3+} and Tm^{3+} to generate green and blue emissions. Under the irradiation of 980 nm laser with a power density of 15 W/cm^2 , bright white light emitted and lighted up surroundings. (Fig. 2.10a)

2.4.2.2 Single-particle Imaging

Differing from organic dyes and quantum dots, upconversion nanoparticles are size-tunable clusters or nanoparticles of which the emission centers could be tuned precisely. Such advantage makes it possible to achieve imaging at single particle-level or even nanoscopy that exceeded the limitation of light wavelength. P. James Schuck and coworkers conducted a pioneer work in the year of 2014, in which the surface-related non-radiative recombination was revealed and overcome by tuning the doping ratio of activators. Under the irradiation of 980 nm with high intensity (10^5 - 10^6 W/cm^2), 20 mol% Er^{3+} -doped UCNPs possess sufficient emission intensity that could achieve single-particle imaging. (Fig. 2.10e)

Based on the single-particle imaging mentioned above, recently, a super-resolution microscopy (or so-called “nanoscopy”) was carried out by Jin and co-workers¹⁵ via the amplified stimulated emission from UCNPs. Through tuning the doping ratio of Tm^{3+} in a

single UCNP, the respond of such UCNP to 980 nm and 808 nm laser varied. 980 nm laser was employed as excitation light and the power intensity was fixed at 0.66 MW/cm^2 , meanwhile 808 nm laser was employed as depletion and the power intensity varied from 0 to 9.75 MW/cm^2 . The combination of excitation and depletion improved the resolution dramatically and finally resulted in a stimulated emission depletion microscopy with a resolution of $\sim 28 \text{ nm}$. (Fig. 2.10f)

2.4.2.3 Security Patterns

Owing to the unique upconversion luminescence, the security information written with UCNP could only be read under the irradiation of NIR lasers (e.g. 980 nm). Moreover, benefitting from the energy transfer during the upconversion process, the emission intensity and decay time vary simultaneously. Based on such concept, Tanya M. Monro and co-workers developed a series of power density-depended upconversion security ink, with which various information could be read under the irradiation of various laser power density. (Fig. 2.10g) Similarly, Jin and co-workers¹⁴ developed a series of decay time-depended upconversion security ink, written by which various information could be displayed at various capture time points. (Fig. 2.10h)

2.4.2.4 Three-Dimensional (3D) Display

As the crystal phase, size, and emission color of UCNP could be precisely tuned. For instance, a transparent PDMS sample embedded with ultra-small UCNP was prepared by Liu and co-workers. Under a computer-controlled NIR laser scanning, visible green three-dimension images could be displayed as desired.⁵ (Fig. 2.10c) Later, benefitting from the non-steady-state upconversion, researchers from the same group⁸ achieved a progress in which unable full-color emission could be generated from one single UCNP. The UCNP fabricated in this work consisted of five or more layers, in which activators like $\text{Ho}^{3+}/\text{Ce}^{3+}/\text{Tm}^{3+}$ and sensitizers like $\text{Yb}^{3+}/\text{Nd}^{3+}$ were doped separately. A PDMS sample imbedded with such full-color UCNP could generate a volumetric three-dimensional full-

color display with the irradiation of three dimension-scanning pulsed laser system. (Fig. 2.10d)

Figure 2.10 UCNPs for luminescence and display applications. a) schematic (left) and luminescence (right) of upconversional white-light-emitting nanocrystals.¹⁰ b) White light generated by combining three sets of upconversion nanoparticles featuring monochromatic RGB emission.⁸ c) Luminescent image of a monochromatic 3D-display generated in the UCNPs-embedded PDMS disk via computer-controlled near-infrared laser scanning.⁵ d) Luminescent image of multi-color 3D-display generated in UCNPs/PDMS composite using computer-controlled laser scanning.⁸ e) Luminescence intensity (left) and confocal luminescence images (right) of single 8 nm UCNPs. f) Demonstrations of super resolution by comparing conventional confocal images (left) with as-established nanoscopy images (right) of the Tm-based UCNPs.¹⁵ g) Demonstrations of security inks using the power-dependent optimal Tm³⁺ concentration.¹³ h) Demonstration of time-resolved scanning shows desired patterns based on the lifetime components of every pixel.¹⁴

References

- (1) Auzel, F. Chemical reviews 2004, 104, 139.
- (2) Liu, X.; Yan, C.-H.; Capobianco, J. A. Chemical Society Reviews 2015, 44, 1299.
- (3) Mai, H.-X.; Zhang, Y.-W.; Si, R.; Yan, Z.-G.; Sun, L.-d.; You, L.-P.; Yan, C.-H. Journal of the American Chemical Society 2006, 128, 6426.
- (4) Mai, H.-X.; Zhang, Y.-W.; Sun, L.-D.; Yan, C.-H. The Journal of Physical Chemistry C 2007, 111, 13721.
- (5) Wang, F.; Han, Y.; Lim, C. S.; Lu, Y.; Wang, J.; Xu, J.; Chen, H.; Zhang, C.; Hong, M.; Liu, X. nature 2010, 463, 1061.
- (6) Gargas, D. J.; Chan, E. M.; Ostrowski, A. D.; Aloni, S.; Altoe, M. V. P.; Barnard, E. S.; Sanii, B.; Urban, J. J.; Milliron, D. J.; Cohen, B. E. Nature nanotechnology 2014, 9, 300.
- (7) Wang, J.; Deng, R.; MacDonald, M. A.; Chen, B.; Yuan, J.; Wang, F.; Chi, D.; Hor, T. S. A.; Zhang, P.; Liu, G. Nature materials 2014, 13, 157.
- (8) Deng, R.; Qin, F.; Chen, R.; Huang, W.; Hong, M.; Liu, X. Nature nanotechnology 2015, 10, 237.
- (9) Zhou, J.; Wen, S.; Liao, J.; Clarke, C.; Tawfik, S. A.; Ren, W.; Mi, C.; Wang, F.; Jin, D. Nature Photonics 2018, 1.
- (10) Zhang, C.; Yang, L.; Zhao, J.; Liu, B.; Han, M. Y.; Zhang, Z. Angewandte Chemie International Edition 2015, 54, 11531.
- (11) Zhou, L.; Wang, R.; Yao, C.; Li, X.; Wang, C.; Zhang, X.; Xu, C.; Zeng, A.; Zhao, D.; Zhang, F. Nature communications 2015, 6.
- (12) Wang, F.; Deng, R.; Wang, J.; Wang, Q.; Han, Y.; Zhu, H.; Chen, X.; Liu, X. Nature Materials 2011, 10, 968.
- (13) Zhao, J.; Jin, D.; Schartner, E. P.; Lu, Y.; Liu, Y.; Zvyagin, A. V.; Zhang, L.; Dawes, J. M.; Xi, P.; Piper, J. A. Nature nanotechnology 2013, 8, 729.
- (14) Lu, Y.; Zhao, J.; Zhang, R.; Liu, Y.; Liu, D.; Goldys, E. M.; Yang, X.; Xi, P.; Sunna, A.; Lu, J. Nature Photonics 2014, 8, 32.
- (15) Liu, Y.; Lu, Y.; Yang, X.; Zheng, X.; Wen, S.; Wang, F.; Vidal, X.; Zhao, J.; Liu, D.; Zhou, Z. Nature 2017, 543, 229.

- (16) Chen, S.; Weitemier, A. Z.; Zeng, X.; He, L.; Wang, X.; Tao, Y.; Huang, A. J.; Hashimoto, Y.; Kano, M.; Iwasaki, H. *Science* 2018, 359, 679.
- (17) Wang, Y.-F.; Liu, G.-Y.; Sun, L.-D.; Xiao, J.-W.; Zhou, J.-C.; Yan, C.-H. *ACS nano* 2013, 7, 7200.
- (18) Sun, Y.; Zhu, X.; Peng, J.; Li, F. *ACS nano* 2013, 7, 11290.
- (19) Dong, H.; Sun, L.-D.; Yan, C.-H. *Chemical Society Reviews* 2015, 44, 1608.
- (20) Deng, H.; Yang, S.; Xiao, S.; Gong, H.-M.; Wang, Q.-Q. *Journal of the American Chemical Society* 2008, 130, 2032.
- (21) Hernández, I.; Pathumakanthar, N.; Wyatt, P. B.; Gillin, W. P. *Advanced Materials* 2010, 22, 5356.
- (22) Arai, Y.; Yamashita, T.; Suzuki, T.; Ohishi, Y. *Journal of Applied Physics* 2009, 105, 083105.
- (23) Singh, V.; Rai, V.; Ledoux-Rak, I.; Badie, L.; Kwak, H.-Y. *Applied Physics B* 2009, 97, 805.
- (24) Lei, P.; Liu, X.; Dong, L.; Wang, Z.; Song, S.; Xu, X.; Su, Y.; Feng, J.; Zhang, H. *Dalton Transactions* 2016, 45, 2686.
- (25) Xu, Z.; Zhao, Q.; Sun, Y.; Ren, B.; You, L.; Wang, S.; Ding, F. *RSC Advances* 2013, 3, 8407.
- (26) Nguyen, V.; Tran, T. K. C.; Van Nguyen, D. *Advances in Natural Sciences: Nanoscience and Nanotechnology* 2011, 2, 045011.
- (27) Du, P.; Luo, L.; Li, W.; Yue, Q. *Journal of Applied Physics* 2014, 116, 014102.
- (28) Fu, Y.; Liu, H.; Ren, Z.; Li, X.; Huang, J.; Best, S.; Han, G. *Journal of Materials Chemistry B* 2017, 5, 5128.
- (29) Hao, J.; Zhang, Y.; Wei, X. *Angewandte Chemie* 2011, 123, 7008.
- (30) Tang, M.; Wang, X.; Peng, D.; Wang, W.; Sun, H.; Yao, X. *Journal of Alloys and Compounds* 2012, 529, 49.
- (31) Dong, B.; Cao, B.; He, Y.; Liu, Z.; Li, Z.; Feng, Z. *Advanced Materials* 2012, 24, 1987.
- (32) Zheng, W.; Zhou, S.; Chen, Z.; Hu, P.; Liu, Y.; Tu, D.; Zhu, H.; Li, R.; Huang, M.; Chen, X. *Angewandte Chemie* 2013, 125, 6803.
- (33) Chen, G.; Qiu, H.; Fan, R.; Hao, S.; Tan, S.; Yang, C.; Han, G. *Journal of Materials*

Chemistry 2012, 22, 20190.

(34) Yi, G.; Peng, Y.; Gao, Z. Chemistry of Materials 2011, 23, 2729.

(35) Mahalingam, V.; Vetrone, F.; Naccache, R.; Speghini, A.; Capobianco, J. A. Advanced Materials 2009, 21, 4025.

(36) Wang, F.; Wang, J.; Liu, X. Angewandte Chemie 2010, 122, 7618.

(37) Yi, G. S.; Chow, G. M. Advanced Functional Materials 2006, 16, 2324.

(38) Li, Z.; Zhang, Y.; Jiang, S. Advanced Materials 2008, 20, 4765.

(39) Lei, P.; An, R.; Yao, S.; Wang, Q.; Dong, L.; Xu, X.; Du, K.; Feng, J.; Zhang, H. Advanced Materials 2017, 29.

(40) Sarkar, S.; Meesaragandla, B.; Hazra, C.; Mahalingam, V. Advanced Materials 2013, 25, 856.

(41) Wang, J.; Wang, F.; Wang, C.; Liu, Z.; Liu, X. Angewandte Chemie International Edition 2011, 50, 10369.

(42) Krämer, K. W.; Biner, D.; Frei, G.; Güdel, H. U.; Hehlen, M. P.; Lüthi, S. R. Chemistry of Materials 2004, 16, 1244.

(43) Ramakrishna, P.; Pammi, S.; Samatha, K. Solid State Communications 2013, 155, 21.

(44) Wang, X.; Yan, X.; Kan, C. Journal of Luminescence 2011, 131, 2325.

(45) Balda, R.; Fernández, J.; Mendioroz, A.; Voda, M.; Al-Saleh, M. Physical Review B 2003, 68, 165101.

(46) Dwivedi, Y.; Rai, S. Optical Materials 2009, 31, 1472.

(47) Li, X.; Wang, R.; Zhang, F.; Zhou, L.; Shen, D.; Yao, C.; Zhao, D. Scientific reports 2013, 3, 3536.

(48) Weber, M. J. Physical Review B 1971, 4, 3153.

(49) Wu, X.; Zhang, Y.; Takle, K.; Bilsel, O.; Li, Z.; Lee, H.; Zhang, Z.; Li, D.; Fan, W.; Duan, C. ACS nano 2016, 10, 1060.

(50) Gorris, H. H.; Ali, R.; Saleh, S. M.; Wolfbeis, O. S. Advanced Materials 2011, 23, 1652.

(51) Yi, G.-S.; Chow, G.-M. Chemistry of Materials 2007, 19, 341.

(52) Dong, H.; Sun, L.-D.; Li, L.-D.; Si, R.; Liu, R.; Yan, C.-H. Journal of the American Chemical Society 2017.

- (53) Zhang, H.; Li, Y.; Ivanov, I. A.; Qu, Y.; Huang, Y.; Duan, X. *Angewandte Chemie* 2010, 122, 2927.
- (54) He, L.; Mao, C.; Cho, S.; Ma, K.; Xi, W.; Bowman, C. N.; Park, W.; Cha, J. N. *Nanoscale* 2015, 7, 17254.
- (55) Zhang, F.; Braun, G. B.; Shi, Y.; Zhang, Y.; Sun, X.; Reich, N. O.; Zhao, D.; Stucky, G. *Journal of the American Chemical Society* 2010, 132, 2850.
- (56) Chen, X.; Xu, W.; Zhang, L.; Bai, X.; Cui, S.; Zhou, D.; Yin, Z.; Song, H.; Kim, D. H. *Advanced Functional Materials* 2015, 25, 5462.
- (57) Lu, D.; Cho, S. K.; Ahn, S.; Brun, L.; Summers, C. J.; Park, W. *ACS nano* 2014, 8, 7780.
- (58) Zhan, Q.; Qian, J.; Liang, H.; Somesfalean, G.; Wang, D.; He, S.; Zhang, Z.; Andersson-Engels, S. *ACS nano* 2011, 5, 3744.
- (59) Yang, D.; Hou, Z.; Cheng, Z.; Li, C.; Lin, J. *Chemical Society Reviews* 2015, 44, 1416.
- (60) Li, C.; Hou, Z.; Dai, Y.; Yang, D.; Cheng, Z.; Lin, J. *Biomaterials Science* 2013, 1, 213.
- (61) Kim, J.; Lee, J. E.; Lee, J.; Yu, J. H.; Kim, B. C.; An, K.; Hwang, Y.; Shin, C.-H.; Park, J.-G.; Kim, J. *Journal of the American Chemical Society* 2006, 128, 688.
- (62) Chen, L.; Li, L.; Zhang, L.; Xing, S.; Wang, T.; Wang, Y. A.; Wang, C.; Su, Z. *ACS applied materials & interfaces* 2013, 5, 7282.
- (63) Liu, B.; Li, C.; Yang, D.; Hou, Z.; Ma, P. a.; Cheng, Z.; Lian, H.; Huang, S.; Lin, J. *European Journal of Inorganic Chemistry* 2014, 2014, 1906.
- (64) Fan, W.; Shen, B.; Bu, W.; Chen, F.; Zhao, K.; Zhang, S.; Zhou, L.; Peng, W.; Xiao, Q.; Xing, H. *Journal of the American Chemical Society* 2013, 135, 6494.
- (65) Hou, Z.; Li, C.; Ma, P. a.; Cheng, Z.; Li, X.; Zhang, X.; Dai, Y.; Yang, D.; Lian, H.; Lin, J. *Advanced Functional Materials* 2012, 22, 2713.
- (66) Wu, S.; Han, G.; Milliron, D. J.; Aloni, S.; Altoe, V.; Talapin, D. V.; Cohen, B. E.; Schuck, P. J. *Proceedings of the National Academy of Sciences* 2009, 106, 10917.
- (67) Yu, M.; Li, F.; Chen, Z.; Hu, H.; Zhan, C.; Yang, H.; Huang, C. *Analytical Chemistry* 2009, 81, 930.
- (68) Xiong, L.; Chen, Z.; Tian, Q.; Cao, T.; Xu, C.; Li, F. *Analytical chemistry* 2009,

81, 8687.

(69) Hilderbrand, S. A.; Shao, F.; Salthouse, C.; Mahmood, U.; Weissleder, R. *Chemical communications* 2009, 4188.

(70) Xiong, L.-Q.; Chen, Z.-G.; Yu, M.-X.; Li, F.-Y.; Liu, C.; Huang, C.-H. *Biomaterials* 2009, 30, 5592.

(71) Li, C.; Yang, D.; Ma, P. a.; Chen, Y.; Wu, Y.; Hou, Z.; Dai, Y.; Zhao, J.; Sui, C.; Lin, J. *Small* 2013, 9, 4150.

(72) Hou, Z.; Li, C.; Ma, P.; Li, G.; Cheng, Z.; Peng, C.; Yang, D.; Yang, P.; Lin, J. *Advanced functional materials* 2011, 21, 2356.

(73) Kang, X.; Cheng, Z.; Li, C.; Yang, D.; Shang, M.; Ma, P. a.; Li, G.; Liu, N.; Lin, J. *The Journal of Physical Chemistry C* 2011, 115, 15801.

(74) Zhao, L.; Peng, J.; Huang, Q.; Li, C.; Chen, M.; Sun, Y.; Lin, Q.; Zhu, L.; Li, F. *Advanced Functional Materials* 2014, 24, 363.

(75) Chien, Y.-H.; Chou, Y.-L.; Wang, S.-W.; Hung, S.-T.; Liao, M.-C.; Chao, Y.-J.; Su, C.-H.; Yeh, C.-S. *Acs Nano* 2013, 7, 8516.

(76) Min, Y.; Li, J.; Liu, F.; Yeow, E. K.; Xing, B. *Angewandte Chemie International Edition* 2014, 53, 1012.

(77) Liu, J.; Bu, W.; Pan, L.; Shi, J. *Angewandte Chemie* 2013, 125, 4471.

Chapter 3

Experimental Methodology

This chapter describes the experience methodology and characterization methodology used in this work. The hydrothermal synthesis strategy is introduced in detail. Subsequently, the principles and the roles of characterization techniques employed in this project including transmission electron microscopy, scanning electron microscopy and X-ray diffraction are discussed. Finally, a power meter set-up for power efficiency measurement is described.

3.1 Hydrothermal Synthesis

Hydrothermal synthesis refers to a variety of strategies, in which high-temperature aqueous solutions at high vapor pressures serve as dispersant or reagent. After a systematical development for more than half a century, a series of products, including oxides, hydroxides, sulfites, halides, phosphates, carbonates, zeolites, MOF, and perovskite, have been successfully fabricated through hydrothermal synthesis.¹⁻⁶

Figure 3.1 Two typical autoclaves used for hydrothermal synthesis.

Usually, the products of a hydrothermal synthesis are single-crystals, ranging from several nanometers to millimeters. The crystal-growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave, in which a nutrient is supplied along with water. Either gradient heating or homogeneous heating is applied, to generate crystals with desired composition and morphology.

Recently, several novel methods have been carried out, endowing the hydrothermal synthesis with a variety of advantages as follows:

1. Widely used for both researches and industries. Due to the ease in performance and low-cost of the equipment, hydrothermal synthesis could be easily achieved both in lab and in factory.
2. Mild condition and soft chemistry. A hydrothermal synthesis is usually performed under a comparably low temperature, while generating a highly ordered structure.
3. Particularly condense material. The high pressure of hydrothermal synthesis could result in the condensed materials.
4. Perfect crystal, high crystallinity and equilibrium defect. The hydrothermal synthesis possesses a stage in which a dynamic balance between precursors and products is generated. Hence, the products of a hydrothermal synthesis are thermodynamically stable, as well as perfect crystals with high crystallinity.
5. Homogeneous doping. The products of hydrothermal synthesis are thermodynamically equilibrated, which means both hosts and dopants are homogeneously allocated. Such advantage of hydrothermal synthesis is particularly for preparation of luminescent materials.

3.2 Characterization Techniques

3.2.1 X-Ray Diffraction Crystallography

X-ray Diffraction (XRD) is a tool which is used for characterizing the atomic or molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays being diffracted into many specific orientations. By measuring the angles and intensities of these diffracted beams, the crystal structure information like lattice distance and crystal surface

parameters could be described. Based on this structure information, the crystal can be determined, as well as their chemical bonds, their composition and various other information.⁷

Admittedly, crystals are regular arrays of atoms, and X-rays can be considered as waves of electromagnetic radiation. An X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron (or lighthouse) is known as the scatterer. A regular array of scatterer produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, which is determined by Bragg's law:

$$2d\sin\theta = \lambda$$

Figure 3.2 The refraction of a wave-train by successive lattice planes.⁷

3.2.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) can characterize the inner structure of materials. Differing from optical microscopy used for observation of items from several millimeters to less than one micrometers, Transmission Electron Microscopy substitute visible light with electron beam, achieving a better resolution reaching sub-angstrom level. When the parallel electron beam transmits an ultrathin or ultrafine sample, some of electrons are either absorbed or diffracted by the sample, resulting in the intensity differences which

could be recorded by CCD. Hence, the brightness on a TEM image corresponds to the inner structure of the sample be recorded.

A general TEM equipment consists of electron gun, a series of lenses with different functions, specimen stage and imaging system are included in a TEM.^{8,9}

Figure 3.3 a) Bright field, b) dark field TEM images, c) electron diffraction pattern and d) HRTEM image.^{8,9}

3.2.3 Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the

detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Usually the specimens should be observed in high vacuum.⁷

By performing electron scanning, a series of signals could be collected:⁷

1. Secondary Electron Detection (SE). Secondary electron imaging (SEI) is the most widely used imaging mode. Secondary electrons with low-energy are generated by inelastic scattering interactions between specimen atoms and beam electrons. Due to their low energy, these electrons can only be collected within a few nanometers from the sample surface. The intensity of the signal depends on the distance between the surface of the specimen and the fixed detector. Hence, a clear and easy-to-read information of the morphology could be achieved. Furthermore, by increasing the angle of incidence, the images with a well-defined, three-dimensional appearance.

2. Backscattered Electron Detection (BE). Backscattered electrons consist of high-energy electrons originating in the electron beam, which are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms. Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear to be brighter in the image, BSE are used to detect contrast between areas with different chemical compositions.

3. Characteristic X-ray Detection. Also known as energy-dispersive X-ray spectroscopy (EDX). Incident of electrons ionize atomic shell electrons to create vacancies. The rapid re-population of these electrons from higher energy shells to lower shells could release the energy in the form of X-rays. Due to the quantization of shell energies, the energy of the generated from each element are unique and could be utilized to characterize the element composition.

Figure 3.4 Figure An overview of information obtained by SEM technique.⁷

3.3 Power Efficiency Measurement

To evaluate the external efficiency of the upconversion luminescent nanoparticles fabricated in this work, a power meter-based setup is carried out to measure the power efficiency of upconversion luminescence.

To make it more specific, the detector of power-meter, which possesses a testing cavity on the top of the surface, is set on the bench. The detector film locates at the bottom of the testing chamber, which guarantees only light emitting towards to this film can be recorded and measured. The precise output power of laser-fiber combination is measured step-by-step by using the same power-meter. Prior to the placing of sample film, an IR / UV cut-off filter is first placed upon the detector film. Any could be filter out. The filter is adjusted

according to the round-shape and the 19 mm-in-diameter detector film, totally matching the testing cavity. A thin-film sample with a certain thickness is placed upon the filter and is covered with a reflector. The reflector is fabricated by polymer through 3-D printing. The inner curve of reflector is well designed and coated with an aluminum film to collect all emissions parallelly towards the detector. Through the hole located at the center of the reflector, 980 nm laser beam is irradiated to the sample film, and the total power of light generated within the detector chamber, of which IR and UV parts are filtered, is recorded by the power meter.

Figure 3.5 Schematic (up) and digital (down) images of a power meter-based set-up for power efficiency measurement.

References

- (1) Barrer, R. M. *Hydrothermal chemistry of zeolites*; Academic press, 1982.
- (2) Yaghi, O.; Li, H. *Journal of the American Chemical Society* **1995**, *117*, 10401.
- (3) Liu, B.; Zeng, H. C. *Journal of the American Chemical Society* **2003**, *125*, 4430.
- (4) Wiff, J. P.; Fuenzalida, V.; Arias, J.; Fernandez, M. *Materials Letters* **2007**, *61*, 2739.
- (5) Xing, G.; Guo, Q.; Liu, Q.; Li, Y.; Wang, Y.; Wu, Z.; Wu, G. *Ceramics International* **2014**, *40*, 6569.
- (6) Zhang, H.; Sheng, Y.; Zheng, K.; Zhou, X.; Shi, Z.; Xu, X.; Zou, H. *European Journal of Inorganic Chemistry* **2014**, *2014*, 3305.
- (7) Leng, Y. *Materials characterization: introduction to microscopic and spectroscopic methods*; John Wiley & Sons, 2009.
- (8) Thirunavukkarasu, G.; Ward, M. R.; Gai, P. L.; Boyes, E. D. In *European Microscopy Congress 2016: Proceedings*; Wiley Online Library: 2016, p 69.
- (9) Niu, J.; Wang, D.; Qin, H.; Xiong, X.; Tan, P.; Li, Y.; Liu, R.; Lu, X.; Wu, J.; Zhang, T. *Nature Communications* **2014**, *5*, 3313.

Chapter 4

Tunable Upconversion Luminescence from $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ (Ln = Yb, Er, and Tm) nanorods

This chapter presents controlled synthesis of rare-earth hydroxides and corresponding oxides with ammonia-assisted hydrothermal strategy. The as-prepared rare-earth oxide nanorods are uniform and highly crystalized. The feasibility for the upconversion luminescence is demonstrated on lanthanide-doped Gd_2O_3 nanorods, from which the bright monochromatic emission, as well as combinational white-light emission, is successfully achieved.

4. 1 Introduction

Lanthanide-doped upconversion materials possess unique anti-Stokes shift, inherent high photostability and low cytotoxicity, as well as the potential for the luminescent manipulation, endowing it a promising candidate in the fields of bio-labelling, bioimaging, analytical sensing, light-emitting, and energy conversion.¹⁻⁵ A typical upconversion process includes at least three steps, 1) the absorption of pump energy, 2) the accumulation and/or the transfer of the absorbed energy, and 3) the release of accumulated energy through radiative/nonradiative relaxation. Such complicated and time-consuming process requires a stable and moderate host matrix, which consists a large amount of candidates, e.g. oxides, sulfides, fluorides, and their composites. Among them, rare earth oxides-based ones, from our perspective, possess a promising prospect.

High in thermal stability, easy in preparation, and low in expense, rare earth oxides and their derivatives, though simple in composition, are ideal selection for the luminescent applications. Fluorescence oxide powers $\text{Y}_2\text{O}_3:\text{Eu}$, $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (also known as YAG), $\text{Y}_2\text{SiO}_5:\text{Ce}$, $\text{YVO}_4:\text{Eu}$, and $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$ are already commercially available and are widely utilized in the fields of display and luminescence. In the specific field of upconversion, pioneer works like Yb^{3+} and $\text{Er}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$ co-doped Y_2O_3 ,⁶⁻⁹ Gd_2O_3 ,^{10,11} La_2O_3 ,¹² $\text{Y}_2\text{O}_2\text{S}$,^{13,14} and YOF ^{15,16} had emerged successively.

The synthesis strategy of rare-earth oxide could be divided into two types. One is the one-step synthesis of RE_2O_3 with certain component through solvothermal reaction or solid-state reaction; another is to prepare the rare-earth precursors with desired morphology and component through sol-gel method or hydrothermal synthesis, after which thermal decompose precursors to generate corresponding RE_2O_3 product. One-step solvothermal synthesis generates uniform and ultra-small rare-earth oxide nanoplates or nanorods. However, the requirement of the toxic and expensive organic solvent, as well as the complicated oxygen-free technique, restricts their promoting and applications. Solid-state method, on the opposite, is easy to perform but difficult to achieve the size and morphology tuning. In terms of the hydrothermal-calcination method, by firstly forming and then

calcining the corresponding crystalline rare-earth precursors, uniform rare-earth oxide crystals can be generated.

However, when being utilized in practical applications, like bio-systems, those crude rare-earth oxide crystals are far from eligible. For instance, only uniform rare-earth oxide micro-crystals with effective upconversion luminescence capacity are successfully prepared, which is too large for bio-system applications. Worse more, an efficient upconversion procedure calls for a highly crystalline and highly ordered structure, requiring an annealing treatment of the oxide particles. It's still a challenge to achieve such highly crystalline oxide matrix with well-dispersity. Hence, only by overcoming such challenges lying during the preparation and modification, can oxide-based upconversion materials be further applied and commercially expanded.

As a comparison, benefiting from the morphology control through lanthanide-doping, β - NaYF_4 -based upconversion nanoparticles have achieved an outbreak development during the last decade,^{1,2,17-19} The synthesis of NaYF_4 requires expensive organic solvent and complicated oxide-free conditions, meanwhile a post-modification is required for these hydrophobic nanoparticles before any further applications. However, the expanding requirement for effective upconversion nanoparticles, from both bio-medical and luminescent researches, still impels the commercialization of such fluoride-based upconversion materials enormously. Moreover, as a promising candidate for luminescence applications, inexpensive and effective white-light emitting upconversion materials possess a promising future due to the unique anti-stoke shift properties. Hence, it will be promising to develop a size-tunable and highly-effective upconversional rare-earth oxide materials, for both bio-medical and luminescent applications.

In this work, a series of uniform $\text{Gd}(\text{OH})_3$ hexagonal prism-in-shape crystals with the size ranging from hundreds of nanometers in length and tens of nanometers in diameter, to several micrometers in length and hundreds of nanometers in diameter has been successfully prepared. After a thermal decomposition treatment, corresponding Gd_2O_3 single-crystals with the preserved morphology, uniformity, and dispersibility are achieved.

Such ammonia-assisted hydrothermal synthesis could be applied to fabricate other rare-earth hydroxide crystals and corresponding rare-earth oxide single crystals. To study the luminescent capacity of such rare-earth oxide nanocrystals, lanthanide-doped Gd_2O_3 nanorods (noted as $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$, $\text{Ln} = \text{Yb}$, Er , and Tm) with various size and doping ratio were prepared and luminescent properties were studied. Through a further annealing treatment, $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ single-crystals with excellent upconversion luminescent capacity are fabricated. Benefiting from the pH-dependent morphology-evolution, $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ with various sizes are prepared. Compared with larger ones, small nanorods show comparable luminescent capacity, but better light-transmission when dispersed in water. Moreover, by combining the green-red-light emitting $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanocrystals and blue-light emitting $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ nanocrystals, white-light emitting upconversional phosphors, with high efficiency, are achieved.

4.2 Experimental Section

4.2.1 Materials

Yttrium(III) chloride hexahydrate ($\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, 99.99 %), gadolinium(III) chloride hexahydrate ($\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, 99%), europium(III) chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %), terbium(III) chloride hexahydrate ($\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %), erbium(III) chloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %), ytterbium(III) chloride hexahydrate ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %), lanthanum(III) acetate hydrate ($\text{La}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, 99.9 %), cerium(III) acetate hydrate ($\text{Ce}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, 99.9 %), neodymium(III) acetate hydrate ($\text{Nd}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, 99.9%), samarium(III) acetate hydrate ($\text{Sm}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, 99.9 %), praseodymium(III) acetate hydrate ($\text{Pr}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, 99.9 %), thulium(III) acetate hydrate ($\text{Tm}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, 99.9 %), lutetium(III) acetate hydrate ($\text{Lu}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$, 99.9 %), Sodium hydroxide (NaOH , 99%) was purchased from Merch. Ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt%) and hydrochloride acid (HCl , 37 wt%) were purchased from Honey well. All chemicals were used as received without further purification. Double distilled water was used in all the experiments.

4.2.2 Synthesis of Uniform Gd_2O_3 Nanorods

In this work, uniform $\text{Gd}(\text{OH})_3$ nanorods were synthesized through hydrothermal strategy, followed by thermal transformation into corresponding Gd_2O_3 through calcination treatment. In a typical synthesis of Gd_2O_3 , $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.6 mmol) was dissolved in 60 mL of deionized water, followed by slowly adding 0.6 mL ammonia (28 wt%) under vigorous stirring. The mixture was continuously stirred for sufficient time to form semi-transparent colloidal. Then the resulting mixture was transferred to a Teflon-lined stainless-steel autoclave and incubated at 120, 160 and 200 °C for 6 h. After cooling down to room temperature naturally, the resulting $\text{Gd}(\text{OH})_3$ precipitates were collected through centrifugation, washed with deionized water thrice and dried at 60 °C overnight. To further increase or decrease the pH value of the reaction system, sodium hydroxide aqueous solution (5 M) or hydrochloride acid (37 wt%) were used, adjusting the pH value to 10.0, 11.0, 12.0, 12.5 and 9.5, 9.0, 8.0.

To synthesis lanthanide-doped $\text{Gd}(\text{OH})_3$ ($\text{Gd}(\text{OH})_3:\text{Ln}^{3+}$, $\text{Ln} = \text{Yb}, \text{Er}$ or Tm), corresponding lanthanide precursors were used. Taking $\text{Gd}(\text{OH})_3:10\%\text{Yb}, 1\%\text{Er}$ as an example, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.534 mmol), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (0.06 mmol) and $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (0.006 mmol) were dissolved in water and mixed with 0.82 mL of ammonia (28 wt%), forming a mixture with a total concentration of 10 mM RE^{3+} and 200 mM ammonia. After the pH value was adjust to 12.5 by adding 0.75 mL of 5M NaOH solution, the mixture was transferred to a Teflon-lined stainless-steel autoclave and incubated at 160 °C for 6 h. The products were collected and washed with water for three times after cooling down naturally.

The thermal decomposition of $\text{Gd}(\text{OH})_3$ and $\text{Gd}(\text{OH})_3:\text{Ln}^{3+}$ rods were performed at 400, 500, and 600 °C for two hours, with a ramp rate of 10 °C/min. To study the thermal treatment-induced enhancement of upconversion luminescence, a further annealing treatment of $\text{Gd}_2\text{O}_3:\text{Yb}, \text{Er}$ nanorods were performed at 800 and 1,000 °C for two hours, with a ramp rate of 10 °C/min.

4.2.3 Sample Preparation for Characterization

TEM images were recorded on a Carl Zeiss Libra 120Plus transmission electron microscope operating at accelerating voltages of 120 kV. HRTEM images were recorded on a JEOL-2100F (200 kV) equipped with GATAN filter. TEM samples were prepared by depositing a drop of diluted colloidal nanoparticles in di-water on copper grids and dried under ambient conditions. TGA data was collected on TA instruments Q500. XRD of samples on glass substrates was performed with a Shimadzu XRD-6000 system using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Emission spectra were recorded by Shimadzu RF-5301 PC fluorometer linked with a 980 nm laser.

4.3 Results and Discussion

4.3.1 Hydrothermal Synthesis of $\text{Gd}(\text{OH})_3$ Nanorods

In this study, the $\text{Gd}(\text{OH})_3$ nanorods are synthesized via a standard hydrothermal synthetic process. All precursors are directly mixed in the Teflon-liner under virous stirring. A semi-transparent sol mixture could be observed after the ammonia is added, indicating the formation of positive charged $\text{Gd}(\text{OH})_x^{+(3-x)}$.

The changes of pH value as gadolinium solution is titrated against two base solutions, ammonia and sodium hydroxide, are shown in Fig 4.1. It could be concluded that Gd^{3+} ions (10 mM) were stable when pH value was lower than 6.9. When the pH value reached 6.9, the extra OH^- ions would combine with Gd^{3+} to form $\text{Gd}(\text{OH})_x$ complexes. When gradually adding NaOH to Gd^{3+} solution, the pH value kept unchanged before the concentration of NaOH reaches three times of the concentration of Gd^{3+} ions, and then increases dramatically. It could be concluded that all Gd^{3+} ions transform into $\text{Gd}(\text{OH})_3$ precipitates immediately as the addition of NaOH. On the contrary, the usage of ammonia results in a continuous increase of pH value, indicating the co-existence of Gd-OH complexes. Moreover, the $\text{NH}_3\text{-NH}_4\text{Cl}$ pair served as buffer, to provide a proper pH value ranging for the formation of uniform $\text{Gd}(\text{OH})_3$ crystals under hydrothermal condition. The dynamic balance between such Gd-OH complexes and $\text{Gd}(\text{OH})_3$ precipitates during hydrothermal synthesis would finally result in uniform $\text{Gd}(\text{OH})_3$ micro- or nano-crystals.

Figure 4.1 Change of pH value as gadolinium chloride aqueous solution is titrated against $\text{NH}_3 \cdot \text{H}_2\text{O}$ or NaOH solution.

The complex formed by mixing 10 mM Gd^{3+} with 200 mM ammonia, with a pH value of 9.7, were transferred to an autoclave and undergone a hydrothermal synthesis at 600 °C for 6 h. The obtained products were collected, washed, and dried prior to the further characterization. As shown in Figure 4.2, the X-ray diffraction (XRD) pattern of hydrothermal synthesized products can be readily indexed to be the pure hexanal phase ($a = b = 6.35 \text{ \AA}$, $c = 3.63 \text{ \AA}$) of $\text{Gd}(\text{OH})_3$ crystals.

Figure 4.2 Structural information of as-prepared $\text{Gd}(\text{OH})_3$ white powders.

The morphology of as-prepared $\text{Gd}(\text{OH})_3$ crystals obtained through hydrothermal synthesis are characterized by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) (Fig. 4.3). It could be observed that $\text{Gd}(\text{OH})_3$ powders are hexagonal micro-prisms with two concave end faces. All prisms are around 2 μm in length and 400 nm in diameter. The prisms are uniform in scale and could be well-dispersed in aqueous solution. Such uniformity is attributed to the employment of the ammonia, which will form complexes with RE^{3+} ions. The chelate function of ammonia reduce the reactive activity of gadolinium ions to hydroxide ions, resulting in a dynamic balance in the hydrothermal system. As the growing rate slows down, more uniform hexagonal prisms with lower surface energies are obtained. A further structural study is carried out by HRTEM (Fig. 4.3d), from which plane (10-11) with a d-spacing of 3.0 Å could be observed, revealing the one-dimensional growth along [0001] direction. Such one-dimensional growth leads to the one-dimensional prism-in-shape of $\text{Gd}(\text{OH})_3$ crystals, which agrees to the works conducted on other rare earth hydroxide crystals.^{8,20,21}

Figure 4.3 Characterization of $\text{Gd}(\text{OH})_3$ crystals prepared through ammonia-assisted hydrothermal synthesis. (a) FESEM image of as-prepared $\text{Gd}(\text{OH})_3$ hexanol prisms. (b-d) TEM images of as-prepared $\text{Gd}(\text{OH})_3$ crystals.

Fig. 4.4 depicts the TEM images of $\text{Gd}(\text{OH})_3$ micro-prisms obtained at various temperature. It is worth noting that, when the reacting temperature rises, the shape of main body keeps constant while concave terminal faces are “filled up”. It is due to the higher activity of Gd^{3+} precursors at higher temperature. A hydrolysis synthesis procedure consists of three stages, which are nucleation, growth, and termination. At lower reacting temperature, the activity of Gd^{3+} precursors are relatively low, tending to attach and deposit on the outer surface of the micro-prism along the $[0001]$ direction. Such inhomogeneous terminating results in the formation of a “crater”-like terminal (Fig. 4.4 a bottom). When the temperature rises, the activation of Gd^{3+} precursors increases associatedly, resulting in the homogeneous growth

along the [0001] direction and a “filled” terminal (Fig. 4.4 c bottom). Such phenomenon agrees with the observation from a previous work of our group, in which ZnO nanotubes and ZnO nano-prisms are formed respectively at various reaction temperature.²²

Figure 4.4 TEM images of $\text{Gd}(\text{OH})_3$ micro-crystals synthesized at 120 °C (a), 160 °C (b), and 200 °C (c), respectively.

As mentioned above, the formation of crystal $\text{Gd}(\text{OH})_3$ crystals are driven by the dynamic balance between Gd^{3+} -ammonia sol and crystalline $\text{Gd}(\text{OH})_3$ precipitates. Therefore, the concentration of hydroxide ions, which is correlated to the initial pH value, is supposed to

be an influential factor to the reaction. Hence, series of hydrothermal synthesis, with the same concentration of Gd^{3+} , the same usage of ammonia, and various initial pH values are carried out.

Concentrated hydrochloride acid (37 wt%) and sodium hydroxide aqueous solution (5 M) are employed to adjust the initial pH value of the hydrothermal system, with a small amount of usage. The products prepared with various initial pH values are characterized by TEM technique (Fig. 4.5b), followed by quantitatively measuring by ImageJ software (Fig. 4.5c). It can be reasonably concluded that, as the pH value increases, the length of $\text{Gd}(\text{OH})_3$ decreases, and the length-to-diameter ratio increases simultaneously.

To study the mechanism of such pH value-induced morphology evolution, the zeta-potential of the sol formed by mixing Gd^{3+} and ammonia was measured (Fig. 4.5a). It could be concluded that, as the pH increase from 9.0 to 12.0, the zeta-potential of the sol decreases from +40 mV to +6 mV. Such decrease in surface charging lead to the formation of more nuclei at the initial stage of the hydrothermal synthesis. Meanwhile, a higher pH value corresponds to higher concentration of OH^- , which the growth of $\text{Gd}(\text{OH})_3$ crystals along [0001] direction is accelerated, resulting in the increasement of length-to-diameter ratio (Fig. 4.5c). When the initial pH value is adjusted lower, the nuclei are minimized and the growth of $\text{Gd}(\text{OH})_3$ crystals is slowed down simultaneously, larger, and comparably shorter $\text{Gd}(\text{OH})_3$ crystals with well-grown hexagonal prism-in-shape are generated. Significantly, if we compare $\text{Gd}(\text{OH})_3$ crystals obtained at pH 9.5 with those obtained at pH 9.0, though the length increases from two micrometers to around three micrometers, the length-to-diameter ratio preserves, suggesting the thermal balance of a fully grown $\text{Gd}(\text{OH})_3$ crystal is with a length-to-diameter ratio of four. To make it short, the pH value is the predominately influential factor in the determination of size and morphology of the final products, and the precise relationship between pH value and the length of $\text{Gd}(\text{OH})_3$ rods are summarized in Fig. 4.5c.

Figure 4.5 Initial pH value-induced size evolution. a) Z-potential of $\text{Gd}(\text{OH})_x^{+(3-x)}$ sol at various pH values. b) TEM images of $\text{Gd}(\text{OH})_3$ crystals prepared at pH values ranging from 9.0 to 11.5. c) Length values and length-to-diameter ratio of $\text{Gd}(\text{OH})_3$ crystals prepared at various initial pH value.

4.3.2 Thermal Decomposition of $\text{Gd}(\text{OH})_3$ Nanocrystals

Subsequently, we study the thermal-decomposition behavior of the $\text{Gd}(\text{OH})_3$ hexagonal prism through thermal gravity analysis (TGA) and X-ray diffraction (XRD) techniques. From the TGA profile (Fig. 4.6a), two rapid weight losses could be identified during heating. The first weight loss occurring at 300 °C to 320 °C corresponds to the dehydration of $\text{Gd}(\text{OH})_3$ to generate $\text{GdO}(\text{OH})$; and the second weight loss around 420 °C corresponds to the further dehydration of $\text{GdO}(\text{OH})$ to generate thermal stable Gd_2O_3 crystals. XRD analysis of samples calcined at various temperature agrees with such two-step thermal decomposition process (Fig. 4.6b).

Figure 4.6 Thermal decompose of $\text{Gd}(\text{OH})_3$ to form corresponding Gd_2O_3 crystals. a) TGA and TGA derivative curve of $\text{Gd}(\text{OH})_3$ crystals, two thermal decomposition peaks could be found at 320 and 420, respectively. b) XRD pattern of samples calcined at various temperature.

The structures of Gd_2O_3 obtained at 600 °C for 2h is further characterized by TEM. (Fig. 4.7) It could be concluded that all products inherit their shapes and dispersibility after thermal decomposition. The morphologies are maintained during thermal treatment is due to the higher activation energies needed for the collapse of such structures^{6,20}. Fig 4.8 shows the corresponding HRTEM image and SAED pattern of a fraction of Gd_2O_3 crystals. The d-spacing of 0.77 nm between the adjacent lattice fringes corresponds to the (110) plane of cubic phase Gd_2O_3 .

Figure 4.7 a) XRD pattern of Gd_2O_3 microrods obtained through thermal decomposition of $\text{Gd}(\text{OH})_3$. b) TEM image of Gd_2O_3 uniform microrods.

Figure 4.8 TEM image (a) and SAED pattern (b) of Gd_2O_3 obtained through thermal decomposition.

4.3.3 Synthesis of Rare-earth Hydroxides and Corresponding Oxides

Benefitting from the similar physicochemical properties, various rare-earth hydroxide crystals could be successfully prepared through the ammonia-assisted hydrothermal synthesis (Fig. 4.9). And, some typical rare-earth hydroxide nanorods are characterized by TEM (Fig. 4.10). It is worth noting that cerium (III) ions are not stable in hydrothermal conditions, generating cerium (IV) dioxide directly.

Figure 4.9 XRD patterns of rare-earth hydroxide crystals prepared through ammonia-assisted hydrothermal synthesis.

Figure 4. 10 TEM images of typical rare-earth hydroxide crystals.

Subsequently, the corresponding rare-earth oxide crystals could be generated by calcination treatment of the hydroxide crystals (Fig 4.11). It is worth noting that among these oxide crystals fabricated through thermal-treatment, $\alpha\text{-La}_2\text{O}_3$ and $\alpha\text{-Nd}_2\text{O}_3$ are trigonal phase, while others are all cubic phase. Meanwhile, cerium (IV) dioxide and praseodymium (IV) dioxide crystals are more thermal-stable when compared with their trivalent compounds.

Figure 4.11 XRD patterns of rare-earth oxide crystals fabricated by the calcination treatment.

4.3.4 Lanthanide-doping into Gd_2O_3 Crystals

Rare-earth oxides have been utilized in a variety of luminescent applications by doping corresponding lanthanide dopants.^{8,23-27} Among these works, effective upconversion luminescence materials are still challenging. In the following part of this work, we focus

on investigating the upconversion luminescent properties of lanthanide-doped Gd_2O_3 nanocrystals, to generate white-light phosphors. Certain amount of sensitizer ytterbium (Yb^{3+}) and activator erbium (Er^{3+}) are co-doped in the $\text{Gd}(\text{OH})_3$ matrix through hydrothermal synthesis. After a calcination treatment, white ultrafine powers of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ crystals are obtained. Under the irradiation of 980 nm NIR laser, bright green-yellow visible light is emitted from the powder. It is worth noting that $\text{Gd}(\text{OH})_3:\text{Yb}^{3+}, \text{Er}^{3+}$ crystals show no upconversion luminescent capacity, which is reasonably due to the quenching effect of OH^- group.

The emission spectra of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ (10/1 mol%) is recorded by fluorescence spectrometer. Three characterized emissions could be recognized. Ultraviolet light with wavelength of 410 nm corresponds to $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} , while green-light emission with wavelength between 520 nm to 560 nm corresponds to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} , and red-light with wavelength between 650 nm to 680 nm corresponds to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} . (Fig. 4.12a) Such effective upconversion emission suggests the successful generation of ETU process between sensitizer Yb^{3+} and activator Er^{3+} , within the host matrix of Gd_2O_3 crystal (Fig. 4.12b).

Figure 4.12 a) Emission spectra of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ (10/1 mol%) phosphors ($\lambda_{\text{EX}} = 980 \text{ nm}$). b) Proposed energy transfer diagram between sensitizer Yb^{3+} and activator Er^{3+} .

As mentioned in the introduction part, the upconversion nanoparticles are promising in the fields of bio-medical applications. On the one hand, small-size particles could be easily dispersed in aqueous solution and be utilized in bio-systems. On the other hand, the tiny volume could minimize the stimulation to the target cells. More significantly, micrometer-scale particles could cause several light scatterings, interfering the imaging of the target bio-systems. Hence, it is of great importance to fabricate effective Gd_2O_3 -based upconversion nanocrystals.

Based on the pH value-induced morphology evolution, Yb^{3+} and Er^{3+} co-doped Gd_2O_3 crystals with various sizes could be generated. To make the comparison more apparent, $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ crystals with two differential sizes are fabricated. The larger ones are 2 μm in length and 0.5 μm in diameter while the smaller ones are 300 nm in length and 40 nm in diameter. Benefiting from the inherent properties of the metal oxide, all two samples could be dispersed in DI water. Due to the small-in-size of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorods, its aqueous solution is clear and much more transparent than the aqueous suspension of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ micro-rods. Under the irradiation of 980 nm, such comparison is more apparent. It is worth noting that, after a 30-minute of measurement, large amount of precipitates occurs at the bottom of suspension of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ micro-rods, while no precipitate for $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorods. It could be reasonably concluded that the $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorods possess a comparable effective upconversion luminescence capacity, as well as minimized light-scattering effects and aggregations effects, making them promising candidates for bio-applications.

Figure 4.13 Comparison between the aqueous suspension of (a) $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ (10/1 mol%) nanorods and (b) $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ (10/1 mol%) microrods.

4.3.5 Luminescent Enhancement of Lanthanide-doped Gd_2O_3 Crystals

Based on the thermal decomposition behavior of rare earth hydroxide, crystalline Gd_2O_3 could be achieved at 500 °C and the higher temperature results in the higher degree of crystallization. Thus, a further annealing treatment at higher temperature (600 °C to 1,000 °C) is utilized to study the relationship between the crystallization and the upconversion efficiency. The emission spectra of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorods annealed at various temperature are recorded and compared in Fig 4.14. A significant 15-folds enhancement of upconversion luminescence is achieved through annealing treatment. And, it's worth noting that, the $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ crystals annealed at 600 °C emit weak red light, while those annealed at 1,000 °C emit bright green-yellow light.

Figure 4.14 Annealing-induced enhancement of upconversion luminescence.

To study such annealing-induced enhancement, the $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorods annealed at 600 °C and 1,000 °C are characterized by using TEM. It could be observed that $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorods annealed at 600 °C are more transparent to electrons, while those annealed at 1,000 °C are more compacted. By comparing the selected area electron diffraction (SAED) pattern of them, it could be clearly observed that the $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorods annealed at 600 °C are poly-crystals, while those annealed at 1000 °C are single-crystals. It could be reasonably concluded that multiple crystalline clusters exist at the early stage of the annealing treatment. As the annealing temperature rises, the clusters are activated to merge with each other to form a single-crystal.

The annealing treatment contribute to the enhancement of upconversion luminescence from two aspects. On the one hand, the refinement of the lattice structure contributed to an improved energy transfer efficiency from Yb^{3+} to Er^{3+} , meanwhile, on the other hand, the purging out of the defects minimized undesired energy losses. Taken together, a substantially enhanced UC luminescence was successfully achieved in $\text{Gd}_2\text{O}_3: \text{Yb}, \text{Er}$. As revealed by the XRD, SAED and TEM characterization of the products, a 1,000 °C

calcination contributes to the improvement of crystallinity, as well as the formation of monocrystalline structure of Gd_2O_3 , hence an optimized annealing treatment at $1,000^\circ\text{C}$ is used in the rest of the experiment.

Figure 4.15 a) c) SEM image and SAED pattern of a poly-crystalline $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorod annealed at 600°C . b) d) The SEM image and SAED pattern of a single-crystalline $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanorod annealed at $1,000^\circ\text{C}$.

4.3.5 Color-tuning of Lanthanide-doped Gd_2O_3 Crystals to Achieve White-light Emission

The white-light emission, which arises from the rational combination of RGB emissions, is essential for display and LED applications. In the previous part of our work, an effective green-to-red upconversion phosphor $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ has been fabricated successfully.

Thus, it will be promising to fabricate a blue-light phosphor, to achieve a combinatorial white-light. Hence, another activator thulium (Tm^{3+}), which is capable to generate blue light through upconversion luminescence, is introduced.

By using the hydrothermal-calcination method mentioned above, uniform $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$, Tm^{3+} crystals are successfully fabricated. After a further annealing treatment, bright blue-light emission could be generated under the irradiation of 980 nm NIR laser. The emission spectra of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$, Tm^{3+} (10/0.2 mol%) is recorded by fluorescence spectrometer. (Fig 4.16a) One characterized emission peak located between 470 nm to 495 nm corresponding to $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transition of Tm^{3+} . The effective upconversion emission suggests the successful generation of ETU process between sensitizer Yb^{3+} and activator Tm^{3+} , within the host matrix of Gd_2O_3 crystals. (Fig 4.16b)

Figure 4.16 a) Emission spectra of $\text{Gd}_2\text{O}_3:10\% \text{Yb}$, $0.2\% \text{Tm}$ crystals. b) Proposed energy transfer diagram between sensitizer Yb^{3+} and activator Tm^{3+} .

A further study of tuning the luminescent properties of phosphors with various doping ratio, a series of $\text{Gd}_2\text{O}_3: 10\% \text{Yb}^{3+}$, $x\% \text{Er}^{3+}$ ($x = 0.5 - 20$) and $\text{Gd}_2\text{O}_3:10\% \text{Yb}^{3+}$, $x\% \text{Tm}^{3+}$ ($x = 0.1 - 10$) nanoparticles have been prepared. The emission spectra are summarized in Fig. 4.17. It could be concluded that, as the doping ratio of Er^{3+} increases, the intensity of red-light emission (656 nm) keeps constant while the green-light emission (554 nm) reaches its peak at 1 mol% and then decreases gradually. Such phenomenon results in the green-to-red varying of the output light. In terms of thulium ions-doped phosphors, the

monochromaticity of blue-light emission (488 nm) keeps constant, while the intensity reaches a peak at 0.2 mol% and then decreases rapidly.

Figure 4.17 Emission spectra of $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ ($\text{Ln} = \text{Yb}, \text{Er}, \text{Tm}$) with varied doping ratio. (a,b) $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ phosphors could generate output light with green-to-red varied color. (c,d) $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ phosphors could generate monochromatic blue-light emission and the output intensity reaches the peak at a doping ratio of 0.2 mol%.

Through the chromatic analysis of the emission spectra, it could reasonably indicate that, a rational combination between $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ phosphors and $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}, \text{Tm}^{3+}$ phosphors with various content ratio and various Er^{3+} doping ratio, could generate emissions with tunable colors located within the triangle drawn on the CIE chromaticity diagram (Fig 4.18), including the white-light located at the center of it.

Figure 4.18 CIE chromaticity diagram of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$, Er^{3+} and $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$, Tm^{3+} nanoparticles. A rational combination between $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$, Er^{3+} phosphors and $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$, Tm^{3+} phosphors could generate emissions with tunable colors located within the triangle drawn on the CIE chromaticity diagram.

To generate a combinatorial white-light phosphor, green-red light phosphor $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$, Er^{3+} (10/10 mol%) and blue light phosphor $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}$, Tm^{3+} (10/0.2 mol%) are mixed with a weight ratio of 1 to 2 and milled thoroughly. The mixture is casted on the glass substrate to form a square-in-shape chip ($5 \times 5 \text{ mm}^2$). Under the irradiation of 980 nm laser with a power density of 5 W cm^{-2} , bright white-light could be emitted from the luminescent chip (Fig. 4.19).

Figure 4.19 Emission spectra (a) and digital images (b) of a white-light emitting chip made from Gd_2O_3 -based upconversion nanoparticles.

4.4 Summary

A general ammonia-assisted hydrothermal synthesis strategy to prepare uniform rare-earth hydroxide with tunable size and morphology is reported. The introducing of ammonia decreases the hydrolysis rate of the rare-earth ions, resulting in the uniform rare-earth hydroxide prisms grown along the [0001] direction. The size evolution could be achieved through pH adjustment. Such hydroxide crystals could be utilized to generate corresponding rare-earth oxide crystals with uniform morphology and excellent dispersity through a calcination treatment.

Subsequently, using Gd_2O_3 as host matrix, a series of lanthanide-doped upconversion phosphors are fabricated. The upconversion luminescent efficiency of these $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ phosphors could be significantly enhanced through annealing treatment, due to the improvement in crystallization. By tuning the dopant ratio, green-to-red light emission and monochromatic blue light emission could be generated from $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+}, x\%\text{Er}^{3+}$ phosphors and $\text{Gd}_2\text{O}_3:10\%\text{Yb}^{3+}, 0.2\%\text{Tm}^{3+}$ phosphors, respectively. Hence, effective upconversional white-light emission, which derives from a combination of RGB, is successfully achieved from a $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ -based luminescent chip.

References

- (1) Auzel, F. Chemical reviews 2004, 104, 139.
- (2) Liu, X.; Yan, C.-H.; Capobianco, J. A. Chemical Society Reviews 2015, 44, 1299.
- (3) Sun, L.-D.; Dong, H.; Zhang, P.-Z.; Yan, C.-H. Annual review of physical chemistry 2015, 66, 619.
- (4) Chen, X.; Peng, D.; Ju, Q.; Wang, F. Chemical Society Reviews 2015, 44, 1318.
- (5) Gnach, A.; Lipinski, T.; Bednarkiewicz, A.; Rybka, J.; Capobianco, J. A. Chemical Society Reviews 2015, 44, 1561.
- (6) Das, G. K.; Tan, T. T. Y. The Journal of Physical Chemistry C 2008, 112, 11211.
- (7) Zong, L.; Xu, P.; Ding, Y.; Zhao, K.; Wang, Z.; Yan, X.; Yu, R.; Chen, J.; Xing, X. Small 2015, 11, 2768.
- (8) Huang, S.; Xu, J.; Zhang, Z.; Zhang, X.; Wang, L.; Gai, S.; He, F.; Niu, N.; Zhang, M.; Yang, P. Journal of Materials Chemistry 2012, 22, 16136.
- (9) Zhao, X.; Suo, H.; Zhang, Z.; Zhang, L.; Guo, C. Dyes and Pigments 2017, 146, 119.
- (10) Guo, H.; Dong, N.; Yin, M.; Zhang, W.; Lou, L.; Xia, S. The Journal of Physical Chemistry B 2004, 108, 19205.
- (11) Tian, G.; Gu, Z.; Liu, X.; Zhou, L.; Yin, W.; Yan, L.; Jin, S.; Ren, W.; Xing, G.; Li, S. The Journal of Physical Chemistry C 2011, 115, 23790.
- (12) Xu, Z.; Zhao, Q.; Sun, Y.; Ren, B.; You, L.; Wang, S.; Ding, F. RSC Advances 2013, 3, 8407.
- (13) Kumar, G.; Pokhrel, M.; Martinez, A.; Dennis, R.; Villegas, I.; Sardar, D. Journal of Alloys and Compounds 2012, 513, 559.
- (14) Wang, H.; Xing, M.; Luo, X.; Zhou, X.; Fu, Y.; Jiang, T.; Peng, Y.; Ma, Y.; Duan, X. Journal of Alloys and Compounds 2014, 587, 344.
- (15) Shao, B.; Zhao, Q.; Lv, W.; Jiao, M.; Lü, W.; You, H. Advanced Optical Materials 2015, 3, 583.
- (16) Sun, L.; Pan, J.; Zhang, X.; Wang, H.; Li, L.; Yu, Y. RSC Advances 2015, 5, 77673.
- (17) Wang, F.; Han, Y.; Lim, C. S.; Lu, Y.; Wang, J.; Xu, J.; Chen, H.; Zhang, C.; Hong, M.; Liu, X. nature 2010, 463, 1061.

- (18) Liu, Y.; Lu, Y.; Yang, X.; Zheng, X.; Wen, S.; Wang, F.; Vidal, X.; Zhao, J.; Liu, D.; Zhou, Z. *Nature* 2017, 543, 229.
- (19) Chen, S.; Weitemier, A. Z.; Zeng, X.; He, L.; Wang, X.; Tao, Y.; Huang, A. J.; Hashimoto, Y.; Kano, M.; Iwasaki, H. *Science* 2018, 359, 679.
- (20) Liu, Y.; Ruan, Y.; Song, L.; Dong, W.; Li, C. *Journal of Alloys and Compounds* 2013, 581, 590.
- (21) Tang, Q.; Liu, Z.; Li, S.; Zhang, S.; Liu, X.; Qian, Y. *Journal of Crystal Growth* 2003, 259, 208.
- (22) Yu, H.; Zhang, Z.; Han, M.; Hao, X.; Zhu, F. *Journal of the American Chemical Society* 2005, 127, 2378.
- (23) Fischer, S.; Martín-Rodríguez, R.; Fröhlich, B.; Krämer, K. W.; Meijerink, A.; Goldschmidt, J. C. *Journal of luminescence* 2014, 153, 281.
- (24) Sotiriou, G. A.; Schneider, M.; Pratsinis, S. E. *The Journal of Physical Chemistry C* 2012, 116, 4493.
- (25) Zhang, L.; Hou, X.; Liu, M.; Lv, Y.; Hou, X. *Chemistry-A European Journal* 2011, 17, 7105.
- (26) Hu, L.; Ma, R.; Ozawa, T. C.; Sasaki, T. *Angewandte Chemie International Edition* 2009, 48, 3846.
- (27) Hu, Z.; Åhrén, M.; Selegård, L.; Skoglund, C.; Söderlind, F.; Engström, M.; Zhang, X.; Uvdal, K. *Chemistry-A European Journal* 2013, 19, 12658.

Chapter 5

Host-sensitized Upconversion Luminescence from $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) Microrods

In this chapter, the host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods, derived from Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ with three-dimensional frameworks, are fabricated and demonstrated feasible for generating efficient upconversion luminescence. The overcoming of concentration quenching effect, which is due to the partial preservation of the three-dimensional frameworks, consequently results in an effective upconversion emission.

5.1 Introduction

Energy transfer between sensitizers and activators is essential for an effective upconversion luminescence.¹ In a typical and effective ETU process-based upconversion luminescence, sensitizer Yb^{3+} capture the pump photons and transfer the absorbed energy to co-doped activator Er^{3+} , generating upconversion emission as a consequence. Such process has been demonstrated feasible in various host matrix, e.g. Y_2O_3 , Gd_2O_3 , CaTiO_3 , CaF_2 , and NaYF_4 .^{2,3} However, the direct combination of ytterbium and erbium is still unsuccessful. When a novel host matrix is proposed and carried out successfully, the optimization of doping ratio is always performed simultaneously, indicating that the highest upconversion luminescence can only be achieved at a doping ratio of 20 mol% or below. The higher in doping ratio of sensitizers, though increasing the absorption efficiency, usually causes concentrated quenching effect.

Taking rare-earth oxide like Y_2O_3 and Gd_2O_3 as an example,^{4,7} as the concentration of Yb^{3+} increases, the emission intensity decreases dramatically. Particularly, only extremely weak upconversion emission could be generated when the matrix cation is totally substituted by Yb^{3+} , forming $\text{Yb}_2\text{O}_3:\text{Ln}^{3+}$ ($\text{Ln} = \text{Er}, \text{Ho}, \text{and Tm}$). In the case of rare-earth fluoride, $\text{NaYbF}_4:\text{Ln}^{3+}$ ($\text{Ln} = \text{Er}, \text{Ho}, \text{Tm}$) nanoparticles have also been studied and demonstrated ineffective by various researchers.⁸⁻¹⁰ In a state-of-the-art achievement carried out by Prof. Paras N. Prasad and coworkers,¹¹ CaF_2 modified $\alpha\text{-NaYbF}_4:\text{Tm}^{3+}$ nanoparticles (cubic phase) were successfully fabricated, from which NIR emission with a wavelength of 800 nm could be generated under the excitation of NIR with a wavelength of 980 nm. Such NIR-to-NIR upconversion, though being the most effective till now, is still incomparable to those fractional doped nanoparticles. Hence, it is of great significance to study the upconversion luminescent materials in which activators are directly doped in sensitizers as host, to achieve a better understanding of energy transfer between them.

Materials that adopt framework structures have been the focus of attentions in the last few years, due to the potential applications in a diverse range of fields, including catalysis, recognition, separation, and storage. Numerous endeavors and achievements have been

carried out by researchers all around the world. Examples of such materials includes zeolites,¹² gallophosphates,¹³ metal-organic frameworks (MOFs),¹⁴ covalent organic frameworks (COFs),¹⁵ and layered double hydroxides (LDHs).¹⁶ Among them, cationic lanthanide hydroxide frameworks, which initiate from the layered double hydroxides, are rare but attractive, due to the unique cationic frameworks, exchangeable anions, as well as lanthanide-enabled properties.

Cationic lanthanide hydroxide is a small family, among which two-dimensional layer-structured $[\text{Ln}_2(\text{OH})_5]\text{X} \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Sm} - \text{Lu}$, $\text{X} = \text{NO}_3, \text{Cl}, \text{Br}$),¹⁷⁻¹⁹ as well as three-dimensional framework-structured $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$,²⁰ are typical and successfully reported ones. Such hydroxides possess long-range ordered two-dimensional or three-dimensional structures, immobilizing and confining the lanthanide cations within the desired frameworks and generating unique luminescent capacities. Significantly, the enhanced fluorescent properties enabled by lanthanide-doping have been demonstrated feasible in these hydroxide frameworks and their derivations.^{17,21,22} Hence, it is great promise to study the host-sensitized upconversion luminescent properties in such framework-structured hydroxides and the corresponding derivations.

In this work, erbium-doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods with framework structures are generated through hydrothermal synthesis. Particularly, a stirring-assisted solid-liquid interfacial reaction is induced to achieve a homogeneous doping. The as-prepared $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ crystals possess weak upconversion luminescence, due to the quenching effect of hydrate molecules and hydroxide ions. After a calcination treatment, $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ phosphors with effective upconversion luminescent capacities could be successfully generated. The luminescent properties of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphors are further characterized and studied.

5.2 Experimental Section

5.2.1 Materials

Ytterbium (III) chloride hexahydrate ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %) and erbium (III) chloride hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH , 99%) was purchased from Merch. Ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt%) was purchased from Honey well. All chemicals were used as received without further purification. Double distilled water was used in all the experiments.

5.2.2 Synthesis of Yb_2O_3 Precursors

The crystalline ytterbium hydroxide nanorods were synthesized through a simple ammonia-assisted hydrothermal method. In a typical synthesis, 760 mg of $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (2 mmol) was dissolved in 65 mL of DI water, then 2 mL of 28 wt% $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous solution was added under vigorous stirring. After the pH value was adjusted to 9.5 through addition of chloride acid solution, the mixture was transferred to a 100 mL sealed Teflon-lined autoclave and incubated at 200 °C over night. After cooling down naturally, white powders were collected through centrifugation, washed with DI water three times, and dried in oven at 60 °C overnight. The totally-dried powders were place in a pre-heated, performing rapid thermal decomposition at 600 °C for 30 min. Finally, white fine powders were collected and stored in dry oven for further usage.

5.2.3 Synthesis of Er^{3+} -Doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ through Solid-Liquid Interfacial Reaction of Porous Yb_2O_3 with Erbium (III) Aqueous Solution

The porous Yb_2O_3 obtained at 600 °C were used as precursors for the synthesis of Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$. To start with dispersed in DI water and mixed with a certain volume of ErCl_3 aqueous solution under sonication. Then the suspension was placed in a vacuum oven in order to purge out air contained in the pores and get solution refilling them. Then the mixture was transferred to a 20 mL sealed Teflon-lined autoclave and incubated

at 200 °C for 6 hours. After the autoclave cooled down naturally, white precipitates were collected and washed with DI water for three times.

5.2.4. Calcination of Er^{3+} -Doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ to Generate $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$

The thermal decomposition of Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ was performed at 250 °C – 1000 °C for two hours, with a ramp rate of 10 °C min^{-1} .

5.2.5 Sample Preparation for Characterization

TEM images were recorded on a Carl Zeiss Libra 120Plus transmission electron microscope operating at accelerating voltages of 120 kV. HRTEM images were recorded on a JOEL-2100F (200 kV) equipped with GATAN filter. TEM samples were prepared by depositing a drop of diluted colloidal nanoparticles in di-water on copper grids and dried under ambient conditions. TGA data was collected on TA instruments Q500. XRD of samples on glass substrates was performed with a Shimadzu XRD-6000 system using Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Emission spectra were recorded by Shimadzu RF-5301 PC fluorometer equipped with a 980 nm laser.

5.3 Result and Discussion

5.3.1 Structures and Porosity of Yb_2O_3 Precursors

In this work, porous Yb_2O_3 micro-rods are fabricated through a hydrothermal-calcination strategy developed in the previous part of the work. To make it more specific, microrod-in-shape ytterbium hydroxide precursors are synthesized through ammonia-assisted hydrothermal synthesis method. The white precipitates of ytterbium hydroxide are collected, purified and dried thoroughly. Subsequently, such white ytterbium hydroxide powders are placed in a furnace, which is pre-heated to 600 °C, in order to perform rapid thermal decomposition. The thermal decomposition treatment finishes within half an hour, then the calcined products are taken out of the furnace, getting rid of the further crystallization of the Yb^{3+} and O^{2-} ions.

The calcined products are characterized by using X-ray diffraction (XRD) technique, from which it could be concluded that the crystalline structure of ytterbium hydroxide crashed. Meanwhile the crystalline structure of ytterbium oxide corresponding to the diffraction peaks located at 29° and 34.5° , still unfinished. Such amorphous-in-structure powders possess high surface energy and instable structure, being eligible for the further reactions.

The size and the morphology of as-fabricated amorphous Yb_2O_3 micro-rods are illustrated by using SEM and TEM techniques. The Yb_2O_3 micro-rods obtained through hydrothermal-calcination strategy are uniform and well-dispersed, with a length of three to five micrometers and a diameter of less than 100 nanometers. The rapid thermal decomposition at the temperature of 600°C preserves the microrod-in-shape, while leaves surface with porosity and roughness. (Fig. 5.1).

Figure 5.1 Characterization of amorphous ytterbium oxide microrods fabricated by hydrothermal synthesis-calcination strategy. a) b) TEM images of uniform ytterbium oxide microrods, showing

the well dispersibility and porous structures. c) SEM image of uniform ytterbium oxide microrods. d) XRD pattern of ytterbium oxide microrods, indicating amorphous structure of them.

The porosity of as-fabricated ytterbium oxide microrods is assessed. The TEM and SEM images show the rough surface, as well as the porous inner structure of the ytterbium oxide microrods. It is worth noting that, the hexagonal prism-in-shape is preserved after the thermal decomposition treatment, while cracks and holes emerge on the surface and the inner of the micro-rods, respectively. Such three-dimensional porous architecture stems from the inherent structural contraction during thermal decomposition, as well as the inhomogeneous rapid heating process. As it is known to us, a temperature gradient exists during the calcination treatment, according to thermal diffusion rate of the sample. And also, calcining samples in a pre-heated furnace could amplify the temperature variety between the surface and inner part. Hence, the removal of hydroxide ions by forming water vapor are performed rapidly and sequentially, from the surface to the inner part. The water vapor formed at inner part is continually heated and kept expanding, leaving holes with several nanometers in the inner part and cracks with the same scale on the surface of the microrods. Such top-down fabrication of nanoporous architecture has been proposed and demonstrated feasible in previous works of our group.^{23,24} Subsequently, the BET analysis is performed to quantitatively characterize the porosity. The surface area of such nanoporous ytterbium oxide microrods is $26 \text{ m}^2 \text{ g}^{-1}$, and the average pore diameter is measured to be 8 to 10 nanometers. The combination of nanoporous architecture and amorphous structure endow such microrods with sufficiently large surficial area and thermodynamically unstable ions, making them eligible precursors for further chemical reactions.

Figure 5.2 Characterization of three-dimensional nanoporous architecture of Yb_2O_3 microrods. a) b) TEM and SEM images of porous Yb_2O_3 microrods, showing that the cracks and cavities in nanoscale exist on the surface and in the body of the microrods. c) BET test of porous Yb_2O_3 nanorods.

5.3.2 Solid-Liquid Interfacial Reaction

The porous Yb_2O_3 microrods are utilized as precursors for solid-liquid hydrothermal reaction. Firstly, the Yb_2O_3 powders are mixed with erbium chloride (ErCl_3) aqueous solution under sonication treatment. The mixture is placed in a vacuum oven, purging out

the air contained in the pores and activating the whole body of ytterbium oxide microrods. Then the mixture is transferred to a sealed Teflon-lined autoclave, heated up to 200 °C with a sands-bath. Vigorously magnetic stirring is applied to achieve a homogeneous solid-liquid interfacial hydrothermal reaction. After incubating for six hours, the autoclave is cooled down naturally, and the white precipitates are collected by centrifugation and washed with DI water three times.

Figure 5.3 Schematic illustration of stirring-assisted hydrothermal synthesis set-up. The sands-bath and stirring are utilized to achieve a 200 °C homogenous hydrothermal reaction.

5.3.3 Structure and Luminescence of Er^{3+} -Doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods

The white powders generated through solid-liquid hydrothermal synthesis are firstly characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM) techniques (Fig. 5.4). The XRD pattern of the products can be readily indexed to a pure orthorhombic phase ($a = 12.86 \text{ \AA}$, $b = 19.26 \text{ \AA}$, $c = 3.596 \text{ \AA}$) of $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ crystals. differing from other rare-earth hydroxide possessing layered structures, $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ could form a cationic framework with exchangeable anions. The structure consists of oxide-centered Yb_4O tetrahedra linked by hydroxide groups, creating a three-dimensional framework structure that contains one-dimensional channels. The oxide ions therefore act as nodes in the structure around which

the framework can form, overcoming the strong preference of the hydroxides to form layered phases. The hydroxides form the hydrophilic surface of the channels, storing chloride ions and hydrate molecules within the channels along the crystal.

Figure 5.4 Erbium-doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ crystals prepared by the hydrothermal reaction possess three-dimensional frames with one-dimensional channels.

The morphologies of as-prepared $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ crystals are studied by using SEM and TEM techniques. It could be observed that $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ crystals are one-dimensional microrod in morphology, with a length of several micrometers and a diameter of about 100 nanometers. (Fig. 5.5)

Figure 5.5 SEM (a) and TEM (b,c) images of as-prepared $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ micro-rods.

To investigate the composition and chemical states of element elements in the sample, X-ray photoelectron spectroscopy (XPS) spectra of the as-prepared $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ microrods are investigated and analyzed. The results strongly suggest that the XPS information is recorded at the surface of material. The spectrum in Fig. 4.6 indicates that

the surface of the samples is composed of ytterbium and oxygen elements with chloride contamination. Particularly, the peak at 185 eV, 201 eV and 348 eV are attributed to Yb 4d_{5/2}, Yb 4d_{3/2}, and Yb 4p electron, respectively. And, the peaks at 271 eV and 530 eV correspond to Cl 2s electron and O 1s electron, respectively. As mentioned before, the Cl⁻ ions occupy the one-dimensional channels formed by inward hydroxide ions. The strong signal of Cl⁻ ions detected by XPS technique strongly suggests that the one-dimensional channels are homogeneously distributed along the microrods.

Figure 5.6 X-ray photoelectron spectroscopy (XPS) spectra of as-prepared Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ micro-rods.

An EDX scanning is performed to study the element component of $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ microrods (Fig. 5.7). The elemental mapping majorly proves that the successfully imbedding of Er^{3+} in the whole-body of $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods. It is worth noting that, the signals collected through EDX analysis are generated from the deep part of the samples, representing the average condition of the whole sample. Meanwhile, the chloride ions, which occupy the one-dimensional channels of along the microrod, are also homogeneously imbedded.

Figure 5.7 Elemental mapping obtained through EDX scanning of erbium-doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ micro-rods.

The crystal-structure of Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ micro-rods are further studied by using HRTEM. From the HRTEM image (Fig. 5.8b) of Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$, the (131) plane with a d-spacing of 3.0 Å and the (001) plane with a d-spacing of 3.6 Å can be identified, indicating that the rod-in-shape morphology derives from the one-dimensional growth along [001] direction.

Figure 5.8 TEM and HRTEM images of as-prepared Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods. The one-dimensional morphology corresponds to the one-dimensional growth along [001] direction.

The selected area electron diffraction (SAED) pattern is shown in Fig. 5.9. The diffraction spots correspond to (200) plane and $(\bar{1}01)$ plane could be indexed on the SAED pattern, and the zone axis is $[010]$. It could be concluded that the Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods prepared through hydrothermal synthesis were fully-grown crystals with a growth preference along $[001]$ direction.

Figure 5.9 SAED pattern of Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods fabricated through hydrothermal synthesis. The diffraction spots correspond to (200) plane and $(\bar{1}01)$ plane could be indexed on the SAED pattern, suggesting Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods fabricated through hydrothermal synthesis are single-crystals.

It is worthy to note that the as-prepared $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ crystals possess extreme weak upconversion luminescence, which is due to the quenching effect of OH^- groups and hydrate molecules in the channels. Thus, a further thermal decomposition is applied to remove the undesired molecules.

The thermal gravity analysis (TGA) is performed prior to the calcination. The TGA curve (Fig. 5.10) reveals the thermal decomposition behavior of $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ crystals, which is consisted of three-stages. Firstly, 2.5 % weight loss occurs at below 200

$^{\circ}\text{C}$, corresponding to the removal of one hydrate molecule out of total two molecules. Then another 2.5 % of weight loss occurs rapidly at around 220°C , corresponding to the removal of another hydrate molecule. When continuously heating the sample, a further weight loss of 6 % occurs from 220°C to 370°C , corresponding to the removal of the hydroxide ions. The last weight loss occurs at 370°C and above, indicating the gradual removal of Cl^- and the formation $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$.

Figure 5.10 Thermal gravity analysis (TGA) of as prepared Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$. The removal of hydrate molecules, hydroxide ions, and chloride ions are achieved below 220°C , from 220°C to 370°C , and above 370°C , sequentially.

XRD pattern (Fig. 5.11) reveals the structural evolution from $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ to $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ during the calcination treatment. According to the TGA curve, the hydrate molecules stored in the channels are released when heated up to 250°C , while the crystal structure is preserved. As the temperature raises, the hydroxide ions are gradually dehydrated, transforming into oxide ions. The crystal structure collapses simultaneously, which strongly suggests that the crystal structure of $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ is supported and confined by the ordered arrangement of hydroxide ions. When the microrods are heated to 400°C and above, the crystal structure of Yb_2O_3 emerges and become increasingly ordered. Differing from hexagonal rare-earth hydroxide which can generate intermediate

rare-earth oxide hydroxide, the thermal decomposition of orthorhombic $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ could generate the thermal stable oxide crystals directly, minimizing the structural shifting during the thermal treatment.

Figure 5.11 XRD pattern reveals the structural evolution from Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ to $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ during the calcination treatment.

5.3.4 Structure and Luminescence of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods

The upconversion luminescent properties of samples, which are calcined at various temperatures, are recorded and compared in Fig. 5.12. It is worthy to note that samples calcined at 300 °C and below generate extreme weak upconversion luminescence. When the calcination temperature rises to 400 °C and above, the intensity of upconversion emission increases dramatically. Based on the TGA curve of the sample, such enhancement in upconversion luminescence correlates to the removal of hydroxide ions. Such phenomenon strongly suggests that, the erbium ions imbedded in the $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ crystals are well-dispersed, possessing inherent potential for upconversion luminescence. The upconversion luminescence is quenched off by hydroxide anions consisted in the crystals. By removal of hydroxide anions, the more effective and efficient upconversion luminescence could be achieved. Furthermore, the samples calcined at 600 °C for 2 hours

are more effective in upconversion luminescence, generating bright green-light emission with the excellent monochromaticity, under the irradiation of 980 nm laser beam.

Figure 5.12 Upconversion emission spectra of sample calcined at various temperature. Samples calcined at 300 °C and below generate extreme weak upconversion luminescence. When the calcination temperature rises to 400 °C and above, the intensity of upconversion emission increases dramatically.

The structure of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ generated through calcination is studied by X-ray diffraction (XRD) technique (Fig. 5.13). It could be indexed to be a typical cubic phase Yb_2O_3 crystal ($a = 10.46 \text{ \AA}$).

Figure 5.13 XRD pattern of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ fabricated by thermal decomposition of framework-structured $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$.

The morphology of obtained $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ crystals is characterized by SEM (Fig. 5.14). It could be concluded that one-denominational rod-in-shape morphology is preserved during the calcination treatment procedure. Also, the well dispersibility of products is also remained after thermal decomposition. It is due to the higher activation energies needed for the collapse of such structures. Significantly, such $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods possess dense surfaces with a certain roughness, suggesting that the inner cavities and porosities are preserved within these upconversion microrods with a high efficiency.

Figure 5.14 SEM images of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods. The uniform rod-in-shape morphology is preserved after the calcination treatment.

The composition and chemical states of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ upconversion luminescent micro-rods are analyzed by X-ray photoelectron spectroscopy (XPS). By compared with the XPS spectra of $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$, the signal peaks located at 170 eV, 185 eV, 348 eV and 530 eV are preserved, which is attributed by Er 4d, Yb 4d, Yb 4p, and O 1s electrons, respectively. It is worth noting that, the peak at 271 eV, corresponding to Cl 2s electron, is partially preserved as well. Combining with the XRD data, in which only pure cubic phase Yb_2O_3 crystals could be identified, it could be reasonably concluded that the Cl^- ions are partially preserved in the amorphous part of the microrods, suggesting the structure of one-dimensional channels occupied by Cl^- ions are partially preserved as well.

By analyzing the high-resolution Yb 4d and Er 4d XPS spectrum (Fig. 5.15b), it could be revealed that the ratio between signal peak Er 4d electrons, located at 168 eV, and that of Yb 4d electrons, located at 181 eV to 205 eV, is much lower than desired value. Such irregular phenomenon suggests that the Er^{3+} dopants are concentrated in the inner layer of the micro-rod. Moreover, the signal peaks of Yb 4d electrons could be resolved to multiple Gaussian function peaks (blue lines in Fig. 5.15b), which suggest the strong interaction between Yb imbedded in the cavity and surroundings.

Figure 5.15 a) X-ray photoelectron spectroscopy (XPS) spectra of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods. b) High-resolution XPS scan of Yb 4d and Er 4d electrons.

The element mapping of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ upconversion luminescent micro-rods are performed by using STEM-EDX technique (Fig. 5.16). The left part is the STEM image and EDX line-scan profile of a single of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrod. The red straight-line located in the middle of the microrod describe the EDX scanning pathway, and the blue curve and red curve represent the content of Yb^{3+} and Er^{3+} , respectively. It could be concluded that the Er^{3+} ions are successfully imbedded in the host matrix of Yb_2O_3 microrods.

Figure 5.16 Elemental analysis of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods. (left) STEM image and EDX line-scan profile of a single $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrod, the blue line and red line represent the content of Yb^{3+} and Er^{3+} , respectively. (right) Element mapping of the same $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrod.

The emission spectra of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphors fabricated through the calcination of $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ (10 mol%) is further studied. It could be concluded that, the emission spectra of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphors consist three identifiable emission peaks, 521 nm, 545 nm, and 662 nm. The green-light emission located at 521 nm and 545 nm corresponds to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transition and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition, respectively. It is worth noting that, both $^2\text{H}_{11/2}$ energy level and $^4\text{S}_{3/2}$ energy level consist large amount of sub-levels, resulting the multi-peak emission.^{25,26} Additionally, a weak red-light emission is recorded around 662 nm, corresponding $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition. Such emission spectra conform to the typical energy transfer between sensitizer Yb^{3+} and activator Er^{3+} through ETU progress, and the correlated energy level and energy transfer diagram is drawn in Fig. 5.17.

Figure 5.17 a) Emission spectra of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) microrods. b) Proposed energy transfer diagram between sensitizer Yb^{3+} and activator Er^{3+} .

The decay time of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphors fabricated through calcination treatment of $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ microrods. The measurement is performed by using an FLS920 Fluorescence Spectrometer equipped with an Integrating Sphere. Under the irradiation of 980 nm laser, the time evolution of green-light emission located at 521 nm to 545 nm, corresponding to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} , is recorded. The decay time of the emission is fitted to:

$$I(t) = I_0 e^{-t/\tau} \quad (1)$$

The decay time (τ) is fitted to be 81.3 μs , being agreed with the successfully achieved energy transfer upconversion (ETU) process.

Figure 5.18 Decay time of host-sensitized $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) microrods

5.3.5 Efficiency of Upconversion Microrods

Finally, the quantum yield of upconversion luminescence is measured, by using the same FLS920 Fluorescence Spectrometer, equipped with an Integrating Sphere. The integrating sphere is mounted on the fluorimeter with the entry and output ports of the sphere located in 90° geometry from each other in the plane of the spectrometer. The standard measurement procedure has been described by Frank C. J. M. van Veggel and coworkers.²⁷ To make it more specific, the background is firstly recorded. Then samples are placed at the center of the integrating sphere, and the emission spectra is recorded using the same settings. The spectra consist both emission peaks located at visible region and unabsorbed irradiation peak located at NIR region. The quantum yield could be defined as:

$$\text{QY} = \frac{\# \text{ photons emitted}}{\# \text{ photons absorbed}} = \frac{Em_{\text{sample}}}{Ex_{\text{reference}} - Ex_{\text{sample}}} \quad (2)$$

Fig. 5.19 shows the digital photograph of upconversion luminescence of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphors dispersed in DI water. Such dispersion possesses a quantum yield of 0.42 %.

Figure 5.19 a) Digital photograph of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphors dispersed in DI water. Bright green-light upconversion emission could be observed under the irradiation of 980 nm laser beam. b) $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphors possess a quantum yield of 0.42 %.

5.3.6 Collapse of Upconversion Luminescence

The $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods are further calcined to study the structure-induced enhancement of upconversion luminescence. Significantly, as the calcination temperature rises from 600 °C to 1,000 °C, the emission intensity decreases dramatically (Fig. 5.20). To make it more specific, as the calcination temperature rises, the green-emission located around 550 nm decreases, while the red-emission located around 660 nm increases slightly. The bright green color emission transforms into weak red color emission. Such phenomenon is different from those activators/sensitizers co-doped inert matrixes, of which higher calcination temperature usually results in higher upconversion efficiency.

Figure 5. 20 Emission spectra of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods calcined at various temperature.

The XRD pattern and TEM image of the $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods calcined at 600 °C, of the upconversion luminescence is efficient, and those calcined at 1000 °C, of which upconversion luminescence is seriously quenched, are compared in Fig. 5.21. It could be clearly revealed that, no phase change occurs during the further calcination, while the porous structure collapses. To make it more specific, the $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods calcined at 600 °C possess regular rod-in-shape morphologies and granular surfaces. On the contrary, the $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods calcined at 1,000 °C possess irregular and twisted-in-shape morphologies, as well as smooth surfaces. Hence, it could be reasonably concluded that, highly efficient upconversion luminescence of the further calcination causes the collapse of the porous structure of the $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods calcined at 600 °C derives from the specific porous structures, which could be collapsed by calcination at 1,000 °C and above, resulting in the quenching of the upconversion luminescence.

Figure 5. 21 TEM images (a,b) and XRD patterns (c) of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods calcined at various temperature.

5.4 Summary

In this work, amorphous Yb_2O_3 powders with porous architectures are fabricated by the rapid thermal decomposition of the ytterbium hydroxide rods. Such powders possess large surface area and thermodynamic instability, endowing them eligible as precursors for further reaction. Subsequently, such Yb_2O_3 powders are dispersed in ErCl_3 aqueous solution, performing the solid-liquid interfacial hydrothermal reaction. The reaction system is placed in the sands bath and applied stirring during the reaction, to achieve a

homogeneous reaction. By doing so, erbium homogeneously-doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ microrods with framework structures are successfully fabricated. As-prepared Er^{3+} -doped $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}$ crystals possess weak upconversion luminescence, due to the quenching effect of hydrate molecules and hydroxide ions. Hence, a calcination treatment is applied, which releases hydrate molecules and hydroxide groups while preserves the framework structures. After the calcination treatment, $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ phosphors with effective upconversion luminescent capacities are generated. The inherent decay time of $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ (10 mol%) phosphor is 83 μs and the quantum yield of it reaches to 0.42 %. The high in quantum yield stems from the confinement of preserved porous structure. If the samples are further calcined, the porous structures are collapsed, resulting in the quenching of luminescence.

References

- (1) Dong, H.; Sun, L.-D.; Yan, C.-H. *Chemical Society Reviews* 2015, 44, 1608.
- (2) Liu, X.; Yan, C.-H.; Capobianco, J. A. *Chemical Society Reviews* 2015, 44, 1299.
- (3) Chen, X.; Peng, D.; Ju, Q.; Wang, F. *Chemical Society Reviews* 2015, 44, 1318.
- (4) Zong, L.; Xu, P.; Ding, Y.; Zhao, K.; Wang, Z.; Yan, X.; Yu, R.; Chen, J.; Xing, X. *Small* 2015, 11, 2768.
- (5) Huang, S.; Xu, J.; Zhang, Z.; Zhang, X.; Wang, L.; Gai, S.; He, F.; Niu, N.; Zhang, M.; Yang, P. *Journal of Materials Chemistry* 2012, 22, 16136.
- (6) Guo, H.; Dong, N.; Yin, M.; Zhang, W.; Lou, L.; Xia, S. *The Journal of Physical Chemistry B* 2004, 108, 19205.
- (7) Suo, H.; Guo, C.; Li, L. *Ceramics International* 2015, 41, 7017.
- (8) Zhan, Q.; Qian, J.; Liang, H.; Somesfalean, G.; Wang, D.; He, S.; Zhang, Z.; Andersson-Engels, S. *ACS nano* 2011, 5, 3744.
- (9) Chen, G.; Ohulchanskyy, T. Y.; Law, W. C.; Ågren, H.; Prasad, P. N. *Nanoscale* 2011, 3, 2003.
- (10) Xing, H.; Bu, W.; Ren, Q.; Zheng, X.; Li, M.; Zhang, S.; Qu, H.; Wang, Z.; Hua, Y.; Zhao, K. *Biomaterials* 2012, 33, 5384.
- (11) Chen, G.; Shen, J.; Ohulchanskyy, T. Y.; Patel, N. J.; Kutikov, A.; Li, Z.; Song, J.; Pandey, R. K.; Ågren, H.; Prasad, P. N. *ACS nano* 2012, 6, 8280.

- (12) Feng, G.; Cheng, P.; Yan, W.; Boronat, M.; Li, X.; Su, J.-H.; Wang, J.; Li, Y.; Corma, A.; Xu, R. *Science* 2016, 351, 1188.
- (13) Estermann, M.; McCusker, L.; Baerlocher, C.; Merrouche, A.; Kessler, H. *Nature* 1991, 352, 320.
- (14) Jagadeesh, R. V.; Murugesan, K.; Alshammari, A. S.; Neumann, H.; Pohl, M.-M.; Radnik, J.; Beller, M. *Science* 2017, 358, 326.
- (15) Diercks, C. S.; Yaghi, O. M. *Science* 2017, 355, eaal1585.
- (16) Wang, Q.; O'Hare, D. *Chemical reviews* 2012, 112, 4124.
- (17) Geng, F.; Ma, R.; Sasaki, T. *Accounts of chemical research* 2010, 43, 1177.
- (18) Liang, J.; Ma, R.; Geng, F.; Ebina, Y.; Sasaki, T. *Chemistry of Materials* 2010, 22, 6001.
- (19) Gándara, F.; Perles, J.; Snejko, N.; Iglesias, M.; Gómez - Lor, B.; Gutiérrez - Puebla, E.; Monge, M. *Angewandte Chemie International Edition* 2006, 45, 7998.
- (20) Goulding, H. V.; Hulse, S. E.; Clegg, W.; Harrington, R. W.; Playford, H. Y.; Walton, R. I.; Fogg, A. M. *Journal of the American Chemical Society* 2010, 132, 13618.
- (21) Liu, L.; Yu, M.; Zhang, J.; Wang, B.; Liu, W.; Tang, Y. *Journal of Materials Chemistry C* 2015, 3, 2326.
- (22) Hu, L.; Ma, R.; Ozawa, T. C.; Sasaki, T. *Angewandte Chemie International Edition* 2009, 48, 3846.
- (23) Yu, H.; Wang, D.; Han, M.-Y. *Journal of the American Chemical Society* 2007, 129, 2333.
- (24) Yu, H.; Wang, D.; Han, M. Y. *Advanced Materials* 2008, 20, 2276.
- (25) Kaczmarek, F.; Malak, H. *Acta Physica Polonica-Series A General Physics* 1996, 89, 669.
- (26) Wybourne, B. *The Journal of Chemical Physics* 1960, 32, 639.
- (27) Boyer, J.-C.; Van Veggel, F. C. *Nanoscale* 2010, 2, 1417.

Chapter 6

Highly Efficient Upconversion Luminescence from Lanthanide-Doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ Nanocubes

In this chapter, a novel oxide perovskite host matrix for photon upconversion, namely $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$, is proposed and successfully fabricated. The neighbored TiO_6 octagonal forms moderate cavities, which are alternatively occupied by the rare-earth cations and sodium cations. The lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ nanoparticles could generate bright upconversion luminescence, of which the energy efficiency reaches 37 %. With such ultra-high efficiency, the lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ upconversion phosphors are demonstrated feasible for biological and luminescent applications.

6.1 Introduction

In the previous chapters, it is introduced that rare-earth oxide-based upconversion luminescent materials with various emission properties have been successfully developed. Meanwhile, the crystallinity of the host matrix and the homogeneity of doping are demonstrated to be essential for effective and efficient upconversion luminescence. However, such simply rare-earth oxide matrixes are still unsatisfiable, due to the structural discordance among RE_2O_3 (i.e. Y_2O_3 $a = 10.60 \text{ \AA}$, Yb_2O_3 $a = 10.45 \text{ \AA}$, and Er_2O_3 $a = 10.54 \text{ \AA}$). On the one hand, it could generate large structural reformation and defect-trapping during calcination treatment, due to the inherent structural variance between rare earth hydroxide (hexagonal or orthorhombic phase with three-dimensional structure) and oxide (cubic phase). On the other hand, the homogeneous doping and effective energy level-coupling are difficult to be achieved in rare-earth oxide systems, due to the inherent radii distinction caused by lanthanide contraction. Hence, it is urgent and of great significance to develop a novel host matrix, eliminating the lattice discordance between lanthanide dopants and preserving the distinct energy levels of them.

Perovskite, a structure derived from calcium titanate, refers a series of compounds sharing the same formula of ABX_3 and excellent electronic and photonic properties.¹⁻⁴ Organic-inorganic hybrid perovskite, which undergoes an unprecedentedly rapid emergence during the past six years, has been demonstrated to be profoundly potential in photovoltaics.⁵⁻¹¹ Subsequently, perovskite, especially all inorganic perovskite with a better thermal stability, has been transited to be regarded as distinguished semiconductor material for LED and laser application.¹²⁻¹⁵ Being a superstar, meanwhile accomplishing enormous breakthroughs and surpassing giant rivals (e.g. silicon, III-V semiconductors, and quantum dots) in short time, halide perovskites possess supreme optical properties and easily performed processing, owing to their unique structures. For a typical AMX_3 halide perovskite, cation A occupies the cavity formed by MX_6 metal halide octahedra. Such 3D network structure can tolerate various ions with similar ionic radii, enriching the component diversity.^{4,16} Particularly, The A cations immobilized in the cavities and the M

cations at the center of the octahedra, are all confined and regulated within a long-range-order crystal lattice, resulting in an amplification of the desired properties and capacities.

Similarly, oxide perovskites, sharing the general formula of ABO_3 , possess the comparable diverse component and versatile capacities. Taking metal titanate as an example, the structure consists Ti-centered TiO_6 octahedra forming the cubic frame, with the cavities in between occupied by metal cations. The asymmetric perovskite structure of metal titanate can strongly confine the imbedded metal cations and effectively prohibit the undesired shifting. Particularly, metal titanate, e.g. calcium titanate and barium titanate, possesses instinctive excellent bio-compatibility and thermal stability, endowing them as promising host candidates for lanthanide doping in wide range of bio-medical and luminescent applications.¹⁷⁻²³ However, the regulations for lanthanide-doping in oxide perovskite, as well as the principles for effective luminescence generation, are still lack of investigation. Moreover, the controllable synthesis of such ceramics with uniform morphology and homogeneous doping remains challenges as well.

In this work, a series of metal titanate with perovskite structure, as well as the lanthanide-doping within these host matrixes, are studied systematically. Based on the concluded regulations, a novel host matrix with perovskite structure, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$, for lanthanide doping and upconversion luminescent applications is successfully developed. The synthesis strategy, structural information, upconversion luminescent properties, and luminescent enhancement are studied sequentially. Finally, as a proof-of-concept, such high effective upconversion luminescent nanoparticles are utilized in several scenarios, demonstrating the great potential for practical applications.

6.2 Experiment section

6.2.1 Materials

Titanium(IV) chloride (TiCl_4 , $\geq 99.0\%$), Yttrium(III) chloride hexahydrate ($\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, 99.99 %), ytterbium(III) chloride hexahydrate ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %), erbium(III) chloride

hexahydrate ($\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %), holmium(III) chloride hexahydrate ($\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %), thulium(III) chloride hexahydrate ($\text{TmCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9 %), sodium chloride (NaCl , $\geq 99\%$), magnesium chloride (99 %), calcium chloride (99%), barium acetate (99 %), strontium oxide (99.9 %), citric acid ($\geq 99.5\%$), and Tetrachlorotitanium (TiCl_4 , 99.7%) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH , 99 %) and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28 wt%) were purchased from Merck and Honey Well, respectively. All chemicals were used as received without further purification. Double distilled water was used in all the experiments.

6.2.2 One-pot Synthesis of Lanthanide-doped Metal Titanates

6.2.2.1 Synthesis of Lanthanide-doped Alkaline Earth Titanates.

In a typical synthesis of $\text{CaTiO}_3:\text{Yb,Er}$, CaCl_2 (86.6 mg, 0.78 mmol), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (38.8 mg, 0.1 mmol), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (3.8 mg, 0.01 mmol), and citric acid (576 mg, 3 mmol) were firstly dissolved in 20 mL of DI water, then 0.5 mL of 2 M TiCl_4 solution (1 mmol) was added. The mixture was incubated in an ice-water bath for 10 minutes, then 4 mL of chilled NaOH solution (5 M) was added dropwise under vigorous stirring. The resulting mixture was continuously stirred for several minutes, until the clear solution turned into turbid, indicating the hydrolysis reaction was initiated. Then such semi-transparent solution was transferred to a 45-mL sealed Teflon-lined autoclave and incubated at a preset temperature overnight. After the autoclave was cooled down naturally, white powders were collected, washed with DI water for 3 times and thoroughly dried before further treatment. For other metal titanate matrix, corresponding metal chloride were used.

6.2.2.2 Synthesis of $\text{Ca}_n\text{-1/2}(\text{NaY})_{1-n}\text{TiO}_3$ ($n = 0 - 1$)

The structural evolution and the luminescent properties of a series of matrix had been studied by synthesis of a series of $\text{Ca}_n\text{-1/2}(\text{NaY})_{1-n}\text{TiO}_3$ ($n = 0 - 1$). TiCl_4 (1 mmol), CaCl_2 (n mmol) and $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ ($(1-n)/2$ mmol) and citric acid (3 mmol) were mixed and dissolved in 20 mL of DI water in an ice-bath, then 4 mL of chilled NaOH solution (5 M)

was added dropwisely under vigorous stirring. Then the mixture was transferred to a 45-mL sealed Teflon-lined autoclave and incubated at a preset temperature overnight. After the autoclave was cooled down naturally, white powders were collected, washed with DI water for 3 times and thoroughly dried before further treatment. For other metal titanate matrix, corresponding metal chloride was used.

6.2.2.3 Synthesis of Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$

In a typical procedure, 0.5 mL of 2M TiCl_4 (1 mmol) solution was mixed with an aqueous solution (5.5 mL) of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (118.3 mg, 0.39 mmol), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (38.8 mg, 0.1 mmol), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (3.8 mg, 0.01 mmol) and citric acid (576 mg, 3 mmol) in an ice bath. After incubating in ice-bath for several minutes, 4 mL of NaOH solution (5 M) was added dropwise under vigorous stirring. The resulting mixture was continuously stirred for a while, until the clear solution turned into turbid, indicating the hydrolysis reaction was initiated. Then such semi-transparent solution was transferred to a 20-mL sealed Teflon-lined autoclave and incubated at 240 °C for 6 h. After the autoclave was cooled down naturally, white powders were collected, followed by washed with DI water for 3 times and thoroughly dried before further usage.

6.2.3 Annealing Treatment of Samples

To achieve highly crystalized and highly luminescent upconversion phosphors, all dried powders were annealed at a certain temperature (600 – 1,000 °C) for 2 hours with a ramp rate of 10 °C min⁻¹. Benefitting from the excellent thermal stability of titanate, the uniform morphology and well dispersibility were remained after annealing treatment.

6.2.4 Sample Preparation for Characterization

TEM images were recorded on a Carl Zeiss Libra 120Plus transmission electron microscope operating at accelerating voltages of 120 kV. HRTEM images and EDX-STEM scanning were recorded on a JEOL-2100F (200 kV) equipped with GATAN filter. TEM

samples were prepared by depositing a drop of diluted colloidal nanoparticles in di-water on copper grids and dried under ambient conditions. SEM images and EDX-SEM scanning were recorded on a JEOL-7600F scanning electron microscope equipped with EDX detector, at accelerating voltage of 20 kV. TGA data was collected on TA instruments Q500. XRD of samples on glass substrates was performed with a Shimadzu XRD-6000 system using Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Emission spectra were recorded by Shimadzu RF-5301 PC fluorometer linked with a 980 nm laser. Dynamic light scattering (DLS) and Z-potential measurement were performed at 25 °C using Malvern Zetasizer. The power of the laser beam and the emission light were measured by using COHERENT PowerMax[®]-PM10 power meter.

6.3 Results and Discussion

6.3.1 Structure and Luminescence of Lanthanide-doped Alkaline Earth Titanates

In this work, a series of rare-earth doped metal titanate crystals with perovskite structures are synthesized through hydrothermal strategy. Taking $\text{Yb}^{3+}, \text{Er}^{3+}$ doped calcium titanate ($\text{CaTiO}_3\text{:Yb}^{3+}, \text{Er}^{3+}$) as an example, the precursors calcium chloride, ytterbium chloride, erbium chloride, titanium chloride, citric acid, and sodium hydroxide are mixed within a Teflon liner directly, in an ice-bath. It is worth noting that sodium hydroxide pills are pre-dissolved in DI water and chilled prior to the final mixing. The citric acid is utilized to stabilize metal ions and slow down the hydrolysis rate, which is confirmed by the forming of clear solution after sodium hydroxide is added. The hydrolysis reaction is initiated by removal of the ice-bath and accelerated with thermal treatment. Semi-transparent homogeneous sol is generated when the system warms up to room temperature (25 °C). Then the system is sealed with an autoclave and placed in a pre-heated oven, incubating at 240 °C overnight.

The as-prepared $\text{CaTiO}_3\text{:Yb}^{3+}, \text{Er}^{3+}$ micro-crystals are characterized with XRD analysis and SEM imaging (Fig 6.1). The XRD pattern of the products can be readily indexed to a pure

cubic phase ($a = 3.795 \text{ \AA}$) of CaTiO_3 crystals. Such CaTiO_3 micro-crystals are uniform in morphology, with a diameter of about $1.1 \mu\text{m}$.

Figure 6.1 SEM image (a) and XRD pattern (b) of $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ micro-crystals prepared through hydrothermal synthesis. The inset shows the size distribution measured by DLS analysis.

The as-prepared $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ micro-crystals are further characterized through EDX scanning. It could be concluded that both ytterbium (III) ions and erbium (III) ions are homogenously doped within the CaTiO_3 host matrix. Meanwhile, to our surprise, sodium ions are also introduced into the CaTiO_3 host lattice, accompanied with rare-earth ions. It could be reasonable, due to the imbalance of charging caused by the one extra positive charge of a rare-earth ion comparing to a calcium ion. Hence, the introduce of sodium ion could balance the total charges within a single crystal.

Figure 6.2 Elemental analysis of rare-earth doped calcium titanate crystals, suggesting that sodium ions are co-doped with lanthanide cations, taking the A position of perovskite.

Other lanthanide-doped alkaline earth titanate with perovskite structure, $\text{SrTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$, and $\text{BaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ are prepared through the same one-pot hydrothermal strategy. XRD analysis reveals that an expanding tendency exists in lattice parameters between CaTiO_3 , SrTiO_3 , and BaTiO_3 , which is confirmed by the decrease in 2θ values of the (101) faces. And the emission spectra of these lanthanide-doped micro-crystals are recorded and compared (Fig 6.3b). It is obvious that the ytterbium and erbium co-doped calcium titanate ($\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$) micro-crystals possess the most effective upconversion luminescent capacity.

Figure 6.3 A structural (a) and upconversion-luminescent (b) comparison between $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$, $\text{SrTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$, and $\text{BaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ crystals, among which $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ generates the most effective upconversion luminescence.

A further study of the role of sodium hydroxide (NaOH) is carried out subsequently. Calcium and rare-earth precursors are preserved, while alternative bases like lithium hydroxide (LiOH) and potassium hydroxide (KOH) are utilized. The obtained hydrothermal products, with various bases, are characterized by XRD analysis and emission spectra (Fig. 6.4). It could be concluded, cubic phase of CTO could be obtained by using NaOH and KOH, while a mixture of lithium titanate, ytterbium oxide hydroxide, and calcium di-titanate is generated. And, only NaOH could generate effective upconversion phosphors. It is worthy to note that the phosphors synthesized with the assistance of KOH emit yellow-color light, indicating the unfavorable state of the dopants.

Figure 6.4 The structural (a) and upconversion luminescent (b) comparison between hydrothermal products using various bases.

Based on such facts, it could be reasonably concluded that the perovskite structure of CaTiO_3 with moderate lattice parameters, as well as the introducing of sodium ions as charge balancer, are essential for the fabrication of effective and efficient upconversion phosphors.

The ionic radii of corresponding ions are summarized in the Table 6.1. It could be concluded that the calcium ion and sodium ion share the accordant radii (112 pm and 118 pm, respectively). Hence the substitution of Ca^{2+} by Na^+ could be achieved due to the size accordance, especially when the Na^+ is excess. Subsequently, the rare-earth ions with a

smaller ionic radius (about 100 pm) could be introduced into the CaTiO_3 host matrix as a charge balancer to achieve a homogeneous doping. Thus, we propose that based on the principle of charge balance and scale-accordance, one sodium ion and one rare-earth ion could substitute two neighbor calcium ions, without any structural varying.

Table 6.1 Ionic radii of various ions with a coordination number of VIII

Ca^{2+}	112 pm	Na^+	118 pm	Yb^{3+}	98.5 pm
Sr^{2+}	126 pm	Li^+	92 pm	Er^{3+}	100.4 pm
Ba^{2+}	142 pm	K^+	151 pm	Y^{3+}	102 pm

To verify our proposal, a series of $\text{CaTiO}_3:\text{Na}^+,\text{Y}^{3+}$ with doping ratio from 0 (pure phase of CaTiO_3) to 100 (pure phase of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$) are synthesized successfully. The XRD analysis of these crystals confirms that, the perovskite structure of CaTiO_3 preserves during such content tuning. Slight expansion of (101) face, which corresponds to the X-ray diffraction peak located at 33.2 degree, suggests the slight shrink in lattice spacing to fit smaller rare-earth ions. (Fig. 6.5)

Figure 6.5 Structure evolution from CaTiO_3 to $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals.

6.3.2 Compositional and Luminescent Study of Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$

The structure of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ crystals are further studied by labelling XRD pattern with standard PDF document. The XRD pattern of the as-prepared $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ powders can be readily indexed to a pure orthorhombic phase ($a = 5.44 \text{ \AA}$, $b = 7.62 \text{ \AA}$, and $c = 5.33 \text{ \AA}$) of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals. The structure of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ derives from the cubic phase of CaTiO_3 , while electrostatic interaction between two neighbor calcium ions and that between a pair of neighbor sodium ion and yttrium ion are different, leading to the expansion along a and c axis and the shrink along b axis. The splitting between the diffraction peak of (200) plane and that of (002) plane (located at around 33.5°), as well as the splitting between the diffraction peak of (321) plane and that of (123) plane (located at around 59°), confirm such structural expansion. Meanwhile, the EDS analysis (Fig. 6.6b) of the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:20\%\text{Yb}^{3+},2\%\text{Er}^{3+}$ matches the proposed formula perfectly, demonstrating the occupation of A site by rare-earth and sodium ions.

Figure 6.6 XRD (a) and EDS (b) analysis of as-prepared $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:20\%\text{Yb}^{3+},2\%\text{Er}^{3+}$.

The upconversion luminescent capacity of such evolutionary matrixes has also been studied. Fig 6.7 concludes the emission spectra of as-prepared from $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ to $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ crystals. As the calcium ions are replaced by sodium ions and yttrium ions, the upconversion emission intensity first decreases and then increases gradually. It could be concluded that the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ crystals possess the most effective upconversion luminescent capacity among all.

Figure 6.7 Evolution of upconversion luminescent properties between $\text{CaTiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ to $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$. a) Emission spectra of various $\text{Ca}_{n-1/2}(\text{NaY})_{1-n}\text{TiO}_3$ ($n = 0 - 1$) phosphors. b) A comparison of the intensity of green-light emissions (545 nm) between various phosphors. By the end of this moment, a novel and promising host matrix with a perovskite structure, namely $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$, is successfully generated for effective upconversion luminescence.

6.3.3 Mechanism Study of the Formation of Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ Nanocubes

The growth mechanism of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ is studied by using XRD and TEM techniques. To generate the samples at various reacting point, a series of parallel prepared hydrothermal system is placed in a pre-heated oven simultaneously. The autoclaves are taken out sequentially at desired time point and cooled down immediately. After totally cooled down, the autoclaves are unfolded, and the suspension is collected, washed, and prepared as XRD and TEM samples.

According to the result in Fig. 6.7, it could be reasonably concluded that after a two-hours hydrothermal reaction, only amorphous irregular particles and films emerge. Selected area electron diffraction (SAED) pattern confirms the amorphous structure of these intermediate products. When the reaction period is prolonged to three hours, crystalline $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ appears. The XRD and SAED pattern reveal that these parallelogram-in-shape plates are crystalline $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ fragments, meanwhile, amorphous intermediate products are not totally consumed at this point of time. One hour later, samples hydrothermal reacting for four hours is achieved. The signal of amorphous intermediate products disappears on the XRD pattern, indicating the reaction comes into the second step, which is the assembly. From TEM illumination, fractions, irregular assemblies, and ordered cubes / cuboids co-exist in the system. Particularly, the existence of cube-in-shape assembling with unfinished edges demonstrates the fact that the formation of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ cubes / cuboids derives from the assembly of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ fragments. Subsequently, the samples taken at 6 hours and 12 hours are also characterized by XRD and TEM techniques. As the reaction time is prolonged, the content of ordered cubic crystals increases, while the intensity of XRD signal keeps unchanged, confirming that the crystalline fragment is the intermediate state while the cube is the final state. The only difference between the 12-hour sample and the 6-hour one is that the content of fragments is further reduced to be rarely observed.

Figure 6.8 XRD patterns (a), TEM images and corresponding SAED patterns (b-e) of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ prepared for 2 hours, 3 hours, 4 hours, and 6 hours.

A further study of the reaction mechanism is carried out by quantitatively analysis of the XRD signal and TEM patterns. To make it more specific, the contents of amorphous and crystalline products are established by the integration of the peak area, and the contents of crystalline fragments and assemblies are established by the area proportion measured from TEM images. Moreover, the effect of the heating rate of the reaction system is also taken into consideration (Fig 6.9 left axis). It could be clearly concluded that, the formation of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals is initiated when temperature reaches 210 °C and higher. Such critical temperature point is also confirmed by the fact that reaction conducted at 200 °C for sufficient time only generates amorphous gel. When the reaction time reaches to 3 hours,

and the temperature reaches 220 °C and above, the amorphous intermediate products are consumed rapidly, where no amorphous part could be observed after a four-hour reaction from both XRD signal and TEM illustration. As the amorphous part decreases, the crystalline parts, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ fragment and $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ cubes, appear simultaneously. At the beginning, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ fragments predominate the content. Seldom cubes could be found in the reaction whose time is shorter than 4 hours. With the prolonging of reaction period, the content of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ cubes could be observed more frequently, and gradually these assemblies predominate in the products until a reaction period reaches to six hours. It is worth noting that, some of intermediate products exhibit un-finished edges and faces, strongly suggesting the assembly of the fragments.

Figure 6.9 (top) The heating curve and the reaction progress of hydrothermal synthesis. (bottom) TEM images (from left to right) corresponds to the amorphous precursors, crystalline fragments, cubes with unfinished edges, and crystalline cubes, respectively. The scale bar represents 200 nm.

Benefitting from the advantages of hydrothermal synthesis, the morphology of the products could be easily tuned by adjusting reaction conditions. As the formation of cubes derives from the assembly of fragments, the concentration of sodium hydroxide is adjusted to tune the morphology of the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ cubes. Moreover, as we discovered in the first part of

work, ammonia molecules possess the capacity of chelating with rare-earth ions, thus a certain amount of ammonia solution is introduced to achieve a better size-control. The TEM images and the DLS analysis of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ nano- and micro- cubes with various sizes are showed in Fig 6.10. It could be concluded that by adjusting the usage of the sodium hydroxide and ammonia solution, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals ranges from 200 nm to 5 μm could be prepared successfully.

Figure 6.10 (a-c) TEM images of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ nano- and micro- crystals with various sizes through hydrothermal synthesis. (d) DLS analysis of the suspension of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals, the average size of the crystals shown in (a)-(c) is 4.5 μm , 1.2 μm , and 240 nm, respectively.

A further study of the structure of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ is performed by using HRTEM technique. Fig. 6.11 shows a single crystal unit of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ and the HRTEM images of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$. Viewing down from the [101] direction, a crisscross alternative occupation of titanium ions and sodium / yttrium ions could be observed (Fig 6.11b). When tilting the sample and viewing down from the [210] direction, titanium ions, sodium ions, and yttrium ions are overlaid to form a honeycomb-like lattice (Fig 6.11c).

Figure 6.11 Structural analysis of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ with a perovskite structure.

6.3.4 Manipulation of Upconversion luminescent Properties of Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$

6.3.4.1 Manipulation of Luminescence Properties Achieved by Tuning Dopants

Based on the one-step hydrothermal synthesis strategy developed in our work, a series of lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ cubic crystals are prepared successfully. Using $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals as an example, under the irradiation of the NIR laser with a wavelength of 980 nm, bright green light could be observed from it. The emission spectra of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ (20/2 mol%) is recorded by fluorescence spectrometer. Three characterized emissions could be recognized. Green light with wavelength of 521 and 544 nm corresponds to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} , as well as the red

light with wavelength between 650 to 680 nm corresponds to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} , among which the green-light emission predominates. Such effective upconversion emission suggests the successful generation of ETU process between sensitizer Yb^{3+} and activator Er^{3+} , within the host matrix of perovskite-structured $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$. It is worth noting that the insert figure of the spectra is drawn by using the suspension of corresponding upconversion nanoparticles as inks. And the emission brightness of each pattern is clear and visible under sunlight.

Figure 6.12 (a) Emission spectra of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ (20/2 mol%) samples. The insert is the digital image of upconversion luminescent “Er” pattern drawn by $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles. The scale bar corresponds to 5 mm. (b) The ETU energy transition process between Yb^{3+} to Er^{3+} .

To study the influence on luminescence of doping ratio, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles with various Yb^{3+} and Er^{3+} content have been prepared and annealed (Fig. 6.13). To start with, the content of activator Er^{3+} is kept constant as 2 mol%, and the content of sensitizer Yb^{3+} is tuned from 0 to 98 mol%. It could be concluded that the sample doped with Yb^{3+} with a concentration of 20 mol% possesses the highest energy absorption and energy transfer capacity. Subsequently, the content of sensitizer Yb^{3+} is kept constant as 20 mol%, and the content of activator Er^{3+} is tuned from 0.5 to 20 mol%. Finally, it could be concluded that the sample doped with a content of 20 mol% of sensitizer Yb^{3+} and a content of 2 mol% of activator Er^{3+} , possesses the highest upconversion luminescent intensity. It is worth noting that when tailoring the content of dopants, the intensity of the emission varies while the chromaticity remains, which majorly suggests that the energy

transfer process is stable while the possibility of effective energy transfer varies according to the content of dopants.

Figure 6.13 Emission spectra of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles with various doping ratio of Yb^{3+} and Er^{3+} . The sample doped with Yb^{3+} and Er^{3+} with a concentration of 20 mol% and 2 mol%, respectively, possesses the most effective and efficient upconversion luminescent capacity.

Another two alternative upconversion activators, Ho^{3+} and Tm^{3+} are utilized to study the universality of the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ host matrix. By utilizing corresponding precursors, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ and $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Ho}^{3+}$ nanoparticles are fabricated successfully through the hydrothermal synthesis strategy.

Fig. 6.14 shows the upconversion emission spectra of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ (20/0.5 mol%) and $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Ho}^{3+}$ (20/1 mol%). For Ho^{3+} -doped samples, characteristic green-light emission located at 545 nm and red-light emission at 652 nm could be recorded under the excitation of 980 nm laser, corresponding to $^5\text{F}_4 \rightarrow ^5\text{I}_8$, $^5\text{S}_2 \rightarrow ^5\text{I}_8$, and $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transitions, respectively. For Tm -doped sample, characterized blue-light emission, corresponding to $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transition, could be identified. Also, the ETU process is successfully achieved between sensitizer Yb^{3+} and activators $\text{Ho}^{3+}/\text{Tm}^{3+}$. It is worth noting that though each of activators possess more than one characteristic emission peaks, only one of them is predominant. Thus, these upconversion nanoparticles show excellent monochromaticity. The insert figures of each spectra are drawn by corresponding upconversion nanoparticles, and the scale bar represents 5 mm. The emission brightness of each pattern is clear and visible even under sunlight.

Figure 6.14 Emission spectra (a,c) and corresponding energy transition process (b,d) of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Ho}^{3+}$ (20/1 mol%) and $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ upconversion nanoparticles (UCNPs). The inserts are the digital image of “Ho” and “Tm” pattern drawn by using corresponding UCNPs ink. The scale bar represents a length of 5 mm.

6.3.4.2 Enhancement of Luminescence Achieved by Annealing

Due to the uniform crystalline cubes deriving from the self-assembly of fragments, it is inevitable to trap impurities and defects within the assemblies. Thus, an annealing treatment is applied to purge out the impurities and defects, as well as to improve the crystallization and luminescent capacity of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ cubes.

The thermal stability of as-prepared $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ cubic assemblies is firstly studied by thermal gravity analysis (TGA). The TGA curve shows that no obvious thermal decomposition occurs during the thermal treatment, only a slight weight lost (about 2 %) occurs. Such weight loss corresponds to the release of impurities and defects trapped within

the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ cubic assemblies. By comparing the XRD patterns of as-prepared $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals and annealed ones, no phase varying occurs during the annealing treatment, confirming the excellent thermal stability of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals. Moreover, the good dispersibility and uniform morphology also remain after annealing treatment.

Based on such excellent thermal stability, the $\text{Yb}^{3+}/\text{Er}^{3+}$ co-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals are annealed at various temperature, ranging from 300 °C to 1,000 °C, in order to study the upconversion luminescent capacity. The upconversion emission intensities are summarized in Fig.6.15. All samples are prepared by depositing a film on the glass substrate. The thickness of each sample is controlled uniformly by depositing the same amount of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals on the substrate with the same area. To measure the upconversion emission, incident 980 nm laser beam is set perpendicular to the detector pathway, and the film samples are settled at central position, inclining 45° to both. An IR-cutoff filter is placed before the detector to eliminate the influence of reflected incident beam. It is amazing that the emission is enhanced dramatically as the annealing temperature increases, even achieving a more than 15-fold of upconversion enhancement of samples annealed at 1,000 °C. Based on the TGA and XRD results, it is reasonably to attribute such dramatical improvement in upconversion luminescence to the purge out of defects by annealing treatment. It is worthy to note that the improvement mainly occurs during 400 °C to 800 °C, whereas the weight loss occurs simultaneously.

Figure 6.15 Annealing-induced enhancement of upconversion luminescence. a) emission spectra of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ (20/2 mol%) film sample annealed at various temperature for two hours. b) Comparison of emission intensity at 544 nm between samples annealed at various temperature.

To study the thermal behavior of the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals, a thermal gravity analysis (TGA) is performed. It could be concluded from the TGA curve of the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals that, about 2 % of the total weight losses between 400 °C and 600 °C (Fig 6.16a). However, the XRD analysis reveals that only pure phase of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals exist during the whole procedure (Fig. 6.16b). As it has been mentioned before, the formation of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ nanocubes derives from the assembly of the crystalline fragments, and a part of such intermediate fragments are preserved after a sufficient long duration of reaction. Hence, it is reasonable to owe such slight weight loss to the purge of impurities both trapped within nanocubes and absorbed on the surface of fragments. And, the purge out of impurities and defects result in the improvement of the crystallization of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ nanocubes, which is confirmed by the XRD analysis and contributes to the annealing-induced upconversion enhancement.

Figure 6.16 a) TGA curve of the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals. The 2 % weight losses between 400 °C and 600 °C corresponds to the purge out of impurities and defects trapped in the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals. b) XRD pattern of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals before and after annealing treatment indicates that only pure orthorhombic phase of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ exists during the whole procedure.

To further study the annealing-induced enhancement, the luminescent lifetime and Raman spectra of as-prepared sample and annealed $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ are comparably measured (Fig. 6.17a). It could be observed that the decay time of emission (544 nm) of as-prepared $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ sample is just 9.8 μs , quite short for an upconversion emission. As it is known to us, the upconversion luminescence involves the complicated energy transfer between sensitizers and activators. Thus, a stable intermediate stage of activators and a comparable long decay time are essential for an effective and efficient

upconversion phosphor. The decay time of emission (544 nm) from an annealed $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ sample is much longer, increasing to about 102 μs , suggesting that the intermediate states of dopants are more stable. And hence, the energy transfer is more efficient. The Raman spectra of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ phosphors before and after annealing are recorded under the excitation of 532 nm (Fig. 6.17b). Raman shift located at $600 - 1,000 \text{ cm}^{-1}$ and $3,500 - 4,200 \text{ cm}^{-1}$ corresponds to the $^4\text{F}_{5/2} \rightarrow ^4\text{F}_{3/2}$ and the $^4\text{F}_{7/2} \rightarrow ^4\text{F}_{5/2}$ transition of Er^{3+} , respectively. The enhancement of these transition after annealing strongly suggests the activator Er^{3+} doped in the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ host matrix possess a more favorable surrounding after the annealing treatment, contributing to the enhancement of upconversion luminescence significantly.

Figure 6.17 Decay time (a) and Raman shift (b) of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanocrystals before and after annealing treatment.

6.3.4.3 Power Efficiency of Upconversion Nanocubes

To study the upconversion efficiency of our $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3\text{:Yb}^{3+}, \text{Er}^{3+}$ cubic crystals, two methods, involving a relative measurement and an absolute measurement, are utilized.

Firstly, conventional $\beta\text{-NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ (20/2 mol%) nanoparticles with a diameter of 20 nm are prepared by an oxygen-free solvothermal strategy at 320 °C. Such well-studied and widely-applied upconversion nanoparticles possess a upconversion efficiency about 2-3 %. Then certain amount of the hexane solution of $\beta\text{-NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ nanoparticles are casted on a glass substrate to form a flat film, with the same thickness with $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3\text{:Yb}^{3+}, \text{Er}^{3+}$ (20/2 mol%) film. Under the excitation of same power density, the emission intensity of these two film samples are recorded by using a fluorescence spectrometer equipped with a 980 laser, and the summarized integral of emission intensity are showed in the Fig. 6.17. It could be concluded that the under the excitation of a moderate power density range (0.2 – 4 W cm^{-2}), $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3\text{:Yb}^{3+}, \text{Er}^{3+}$ (20/2 mol%) nanoparticles prepared in our work possess a 12-fold enhancement in upconversion luminescence, compared with conventional $\beta\text{-NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ (20/2 mol%) upconversion nanoparticles. To make it clearer, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3\text{:Yb}^{3+}, \text{Er}^{3+}$ dispersion and $\beta\text{-NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ dispersion with same weight concentration are used as ink, to draw two straight parallel lines on a commercial A4 printing paper. The digital photos of the upconversion luminescent images are recorded by a digital camera, equipped with a NIR-cutoff filter, using a fixed camera setting. Under the excitation of 980 nm laser with a power intensity ranges from 0.2 to 4 W cm^{-2} , significant and visible differences in brightness could be observed and recorded, which strongly agrees to the disparities of emission spectra.

Figure 6.18 Measurement of relative upconversion luminescent efficiency of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}$, Er^{3+} nanoparticles generated in this work by using conversional $\beta\text{-NaYF}_4:\text{Yb}^{3+}$, Er^{3+} nanoparticles as reference.

Subsequently, a power-meter set-up is assembled to measure the absolute upconversion luminescent efficiency (Fig. 6.19). To make it more specific, the detector of power-meter, which possesses a testing chamber on the top of the surface, is set on the bench. The

detector film locates at the bottom of the testing chamber, which guarantees only light emitting towards to this film can be recorded and measured. The precise output power of laser-fiber combination is measured step-by-step by using the same power-meter. Prior to the placing of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ sample, an IR/UV cut-off filter is first placed upon the detector film. Any could be filter out. The filter is adjusted according to the round-shape and the 19 mm-in-diameter detector film, totally filtering out unabsorbed excitation irradiations. A thin-film sample with a certain thickness is placed upon the filter and is covered with a reflector. The reflector is fabricated by polymer through 3-D printing. The inner curve of reflector is well designed and coated with an aluminum film to collect all emissions parallelly towards detector. Through the hole located at the center of the reflector, 980 nm laser beam is irradiated to the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ film-sample, and the total power of light generated within the detector chamber, of which IR and UV parts are filtered, is recorded by the power meter. It could be found that the thinner $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ film-samples cannot make the full usage of the irradiation. The highest external power efficiency of 37% is achieved with a $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ film-sample with a weight concentration of 2 mg/cm^2 . (Fig. 6.19)

Figure 6.19 Measurement of absolute upconversion luminescent efficiency of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles generated in this work by using a power-meter set-up.

6.3.5 Applications of Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ Nanocubes

The annealed green-luminescent $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles are dispersed the aqueous solution first. The annealing treatment in air results in the hydrophobic surface of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles. Thus, a hydrothermal treatment is carried out to improve the hydrophilicity and dispersibility in aqueous solution of the upconversion nanoparticles (UCNPs). To make it more specific, certain amount of UCNPs, with a size of about 200 nm, are mixed with DI water in a Teflon-lined autoclave and incubated at 160 °C for 4 hours. After cooled down naturally, a stable UCNPs aqueous dispersion is achieved. The Z-potential measurement reveals that these $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles are negative charged, possessing a Z-potential of -30 mV to -40 mV at physiological pH ranges (Fig. 6.20a). Such moderate surface charging assists the well dispersion of the UCNPs. The digital images of UCNPs aqueous dispersion and corresponding luminescence under the irradiation of 980 nm laser are recorded. The concentration is 200 $\mu\text{g}/\text{ml}$. Benefitting from the tiny-in-size and efficient-in-luminescence, the aqueous dispersion shows excellency in transparency for both observation and luminescence (Fig. 6.20b).

Figure 6.20 Aqueous dispersibility of 200 nm $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles. a) Z-potential measurement of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles at various pH values. b) Digital images of 100 $\mu\text{g}/\text{ml}$ $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ aqueous dispersion under visible light (left) and 980 nm laser (right).

To verify whether such $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles are nontoxic and biocompatible, a cytotoxicity study of CCD-112CoN are performed using alamar blue assay. The CCD-112CoN cells are cultured with various concentration of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles for 24 hours. And then, the cellular viabilities are assessed with alamar blue assay using a standard method. The viability of the untreated cells is used as negative reference and is assumed to be 100%. For those cells cultured with $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles with a concentration up to 200 $\mu\text{g}/\text{ml}$, it could be concluded that, more than 98 % of cellular viability remains. Such excellency of biocompatibility derives from the stable skeleton formed by TiO_6 octahedral, as well as the intrinsic low toxicity of the rare-earth ions.

6.3.5.1 Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ Nanocubes for Cell-labeling

Such biocompatible $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles are utilized for practical cell imaging in a biological system. It is confirmed by conducting analogous experiments using CCD-112CoN cells. Upon incubation, incorporation of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanoparticles into CCD-112CoN cells were confirmed by confocal fluorescence microscopy. Specifically, after incubation with 150 $\mu\text{g}\cdot\text{mL}^{-1}$ of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanoparticles for 2 hours at 37 °C, an intense intracellular luminescence was observed, under the excitation of 980 nm laser, as shown in Fig. 6.21. These lanthanide-loaded nanoparticles clearly retained their intrinsic upconversion fluorescent properties upon cellular internalization.

Figure 6.21 a) In vitro cell viability of CCD-112CoN cells cultured with $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ upconversion nanoparticles (UCNPs) at various concentrations for periods of 24 hours. (b-e) Confocal upconversion luminescent images of CCD-112CoN cells labeled with $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ UCNPs, taken under the identical instrumental condition and the cell nucleus are labeled with DAPI.

6.3.5.2 Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ for Display

The colorless aqueous suspension of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles are subsequently utilized as security ink. As a proof of concept, letters of “NTU” and “IMRE” are hand-written onto a piece of standard A4 paper with the security ink, using the aqueous suspension of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles. Subsequently, letters of “present” are written with a signing pen. Under the irradiation of 980 nm laser with a power density of 2 W cm^{-2} , the letters written with security ink could be clearly observed by naked eyes, showing the complete information. When the laser is removed, the photo-luminescence disappears immediately, and the key information is hidden. (Fig. 6.22)

Figure 6.22 Information written with security ink could only be read under the irradiation of 980 nm laser (scale bar, 5 mm). The power density is 2 W cm^{-2} .

6.3.5.3 Lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ Nanocubes for Illumination

Due to the ultrahigh upconversion efficiency, the $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles could possibly serve as phosphors, illuminating surroundings under the irradiation of 980 nm beam. To study the illumination capacity of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles, 2 mg of dried powders are packed with transparent tape, forming a $0.5 \times 0.5\text{ cm}^2$ phosphor chip. Under the irradiation of a divergent 980 nm beam, the whole chip is covered,

generating bright green-color emission and lightening up the the surroundings. The information on paper could be easily read, and even the whole fume hood could be illuminated to a certain extent, confirming the potential application of such $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ powders in the field of illumination (Fig. 6.23). The total power of 980 nm beam is 1.2 W, and the power density is around 6 W cm^{-2} .

Figure 6.23 $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ powders used for illumination (scale bar, 2 cm). The total power of 980 nm beam is 1.2 W, and the power density is around 6 W cm^{-2} .

6.4 Summary

In this work, the optical properties of a series of perovskite-type upconversion luminescent materials are studied systematically, suggesting that scale-accordant cavities and co-embedded sodium ions are essential for an efficient and effective upconversion luminescence. Hence, a novel perovskite-type host matrix, namely $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$, is proposed and successfully achieved.

Subsequently, the synthesis mechanism, luminescent properties, and crystal structures of lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals are studied. At the same time, the upconversion efficiency of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanoparticles are measured to be as high as 37 %. Such $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ upconversion nanoparticles (UCNPs) are able to be utilized for various applications. Firstly, benefiting from the inherent low toxicity and excellent water dispersibility, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+}, \text{Er}^{3+}$ nanoparticles are super bio-compatible and

are successfully used for bio-labelling. Secondly, the aqueous suspension of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3\text{:Yb}^{3+}$, Er^{3+} nanoparticles could be potentially utilized as security ink for information recording, which can only be accessed with the assist of NIR light. Last but not least, $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3\text{:Yb}^{3+}$, Er^{3+} powders can serve as specific photoluminescence materials, for widely purposes of illumination.

To draw a conclusion, lanthanide-doped $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ crystals fabricated in this study are effective in upconversion luminescence and promising in broad applications. Though challenges like one-step fabrication and luminescent manipulation still exist, such perovskite-type upconversion nanoparticles are confidentially versatile and possess huge potential for the practical upconversion applications in the future.

References

- (1) Zener, C. *Physical Review* 1951, 82, 403.
- (2) Demirors, A. F.; Imhof, A. *Chemistry of Materials* 2009, 21, 3002.
- (3) Sutherland, B. R.; Sargent, E. H. *Nature Photonics* 2016, 10, 295.
- (4) Wang, H.; Kim, D. H. *Chemical Society Reviews* 2017.
- (5) Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. *Science* 2013, 342, 344.
- (6) Heo, J. H.; Im, S. H.; Noh, J. H.; Mandal, T. N.; Lim, C.-S.; Chang, J. A.; Lee, Y. H.; Kim, H.-j.; Sarkar, A.; Nazeeruddin, M. K. *Nature photonics* 2013, 7, 486.
- (7) Liu, D.; Kelly, T. L. *Nature photonics* 2014, 8, 133.
- (8) Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. *Nature* 2013, 499, 316.
- (9) Zhou, H.; Chen, Q.; Li, G.; Luo, S.; Song, T.-b.; Duan, H.-S.; Hong, Z.; You, J.; Liu, Y.; Yang, Y. *Science* 2014, 345, 542.
- (10) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. *Nature Photonics* 2014, 8, nphoton.2014.134.
- (11) Grätzel, M. *Nature materials* 2014, 13, 838.
- (12) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C.

- H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. *Nano letters* 2015, 15, 3692.
- (13) Xing, G.; Mathews, N.; Lim, S. S.; Yantara, N.; Liu, X.; Sabba, D.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C. *Nature materials* 2014, 13, 476.
- (14) Stranks, S. D.; Snaith, H. J. *Nature nanotechnology* 2015, 10, 391.
- (15) Zhang, L.; Yang, X.; Jiang, Q.; Wang, P.; Yin, Z.; Zhang, X.; Tan, H.; Yang, Y. M.; Wei, M.; Sutherland, B. R. *Nature communications* 2017, 8, 15640.
- (16) Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G. *Advanced Materials* 2016, 28, 6804.
- (17) Fu, Y.; Liu, H.; Ren, Z.; Li, X.; Huang, J.; Best, S.; Han, G. *Journal of Materials Chemistry B* 2017, 5, 5128.
- (18) Wiff, J. P.; Fuenzalida, V.; Arias, J.; Fernandez, M. *Materials Letters* 2007, 61, 2739.
- (19) Eduardo, A. C.; de Figueiredo, A. T.; Li, M. S.; Longo, E. *Ceramics International* 2014, 40, 15981.
- (20) Rabuffetti, F. A.; Culver, S. P.; Lee, J. S.; Brutchey, R. L. *Nanoscale* 2014, 6, 2909.
- (21) Mahata, M. K.; Koppe, T.; Mondal, T.; Brüsewitz, C.; Kumar, K.; Rai, V. K.; Hofsäss, H.; Vetter, U. *Physical Chemistry Chemical Physics* 2015, 17, 20741.
- (22) Yang, P.; Tai, B.; Wu, W.; Zhang, J.-M.; Wang, F.; Guan, S.; Guo, W.; Lu, Y.; Yang, S. *Physical Chemistry Chemical Physics* 2017.
- (23) Takashima, H.; Shimada, K.; Miura, N.; Katsumata, T.; Inaguma, Y.; Ueda, K.; Itoh, M. *Advanced Materials* 2009, 21, 3699.

Chapter 7

Conclusions and Future Work

This chapter draws together the threads of the thesis. The whole works are briefly summarized. Three well-designed upconversion luminescent materials are successfully fabricated, which are demonstrated feasible for practical applications. Furthermore, the recommendation for future works are discussed and proposed.

7.1 Conclusions

Lanthanide-doped upconversion (UC) materials have attracted an increasingly interests from researchers all over the world and have been demonstrated feasible in a variety of bio-medical and luminescent applications, due to the unique and fascinating anti-stock shift and energy conversion. Achieving effective and sufficient upconversion efficiency is of great significance to promote the practicality and commercialization of upconversion techniques. Among all designations, exploiting eligible host matrix with accordant lattice structure to luminescent centers, low phonon energy, high transparency, and excellent thermal and chemical stability is of most promise.

In the present work, oxides matrix like rare-earth oxide and rare-earth titanate were fabricated through facile and low-cost hydrothermal synthesis and thermal treatment. Such materials are eligible for lanthanide-doping to generate effective and bright upconversion luminescence under the irradiation of 980 nm laser beam. The synthesis strategy, structural analysis, energy transfer process, and the luminescent tuning of each system were studied in detail.

The results in this thesis, as well as the main contribution are summarized as follows:

1. Uniform rare-earth hydroxides were fabricated by a general ammonia-assisted hydrothermal synthesis strategy. Taking gadolinium hydroxide as an example, by adjusting the reaction conditions, gadolinium hydroxide crystals with a continuous evolution in morphology, from nanorods to microrods with various terminals, could be achieved. After a calcination treatment, gadolinium oxide crystals with preserved morphology and dispersibility were fabricated. Such strategy could be successfully applied to fabricate a series of rare-earth hydroxide and oxide crystals, with predictable morphologies.
2. Based on strategy mentioned above, a series of lanthanide-doped Gd_2O_3 ($\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$) upconversion nanorods were generated. The effective ETU process could be achieved in single-crystalline $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ nanorods, generating bright upconversion

luminescence under the irradiation of 980 nm laser beam. Moreover, by tuning the dopant ratio, green-to-red light emission and monochromatic blue light emission could be generated from $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Er}^{3+}$ crystals and $\text{Gd}_2\text{O}_3:\text{Yb}^{3+},\text{Tm}^{3+}$ crystals, respectively. Hence, a combinational white-light upconversion emission was successfully generated from a $\text{Gd}_2\text{O}_3:\text{Ln}^{3+}$ -based luminescent chip.

3. Some of the lanthanide cations were difficult to be co-imbedded directly, due to the cationic discordance caused by lanthanide contraction. Thus, a solid-liquid interfacial hydrothermal reaction was utilized to achieve a homogeneous doping. To make it more specific, Er^{3+} aqueous solution and Yb_2O_3 powders with nanoporous architecture were utilized as precursors, to generate $\text{Yb}_3\text{O}(\text{OH})_6\text{Cl} \cdot 2\text{H}_2\text{O}:\text{Er}^{3+}$ crystals with three-dimensional frameworks. After a calcination treatment, effective $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ phosphors were successfully fabricated, from which bright upconversion emissions with a quantum yield of 0.42 % could be generated.

4. Oxide perovskites like metal titanate possessed unique optical and electric properties, being eligible for lanthanide-based luminescent applications. A general hydrothermal strategy was carried out to fabricate a series of lanthanide-doped metal titanates with varied structures and doping status, from which the accordant lattice parameters and the co-imbedding of sodium cations were discovered to be essential for an effective upconversion luminescence. Consequently, lanthanide-doped sodium yttrium titanate ($\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Ln}^{3+}$) cubes with effective and efficient upconversion luminescence were fabricated successfully.

5. The synthetical mechanism, morphological control, crystal structure, optical properties, and the annealing-induced enhancement of $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Ln}^{3+}$ were studied sequentially, after which effective $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3:\text{Yb}^{3+},\text{Er}^{3+}$ upconversion nanoparticles (UCNPs) with an ultrahigh external efficiency reaching 37 % were fabricated. Benefitting from the inherent tolerance to water, such upconversion nanoparticles could be dispersed in water directly, being utilized for bio-labeling, information display, and illumination applications.

7.2 Future work

Based on the results of present works, future efforts could be focused on such aspects as follows:

1. Crystalline Gd_2O_3 powders with a cubic phase are commonly used for generation of transparent ceramic. In the first part of my work, lanthanide-doped Gd_2O_3 nano- and micro-rods, it will be promising to fabricate transparent ceramic bulk material, with upconversion luminescent properties. Hence, a series of sintering studies will be performed on lanthanide-doped Gd_2O_3 nano- and micro-rods, in the first part of the future works.
2. The further investigation of the framework-structures involved in $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods. The Cl^- anions and frameworks partially preserved $\text{Yb}_2\text{O}_3:\text{Er}^{3+}$ microrods possess effective upconversion luminescent properties, while the emission from calcined one is seriously quenched. Such phenomenon demands a further and deeper investigation, in order to generate a better understanding for energy transfer within the upconversion nanoparticles.
3. A deeply and progressive study in the electron status of lanthanide cations imbedded in perovskite-structured $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ nanoparticles should be taken into a well consideration. The cavities formed by TiO_6 octahedral are moderate to accommodate lanthanide dopants and could generate dimensional confinement for dopants as well. An in-depth study in the electron status of the lanthanide cations imbedded in $\text{Na}_{1/2}\text{Y}_{1/2}\text{TiO}_3$ nanoparticles could help generating a better understanding of emitting centers.