RATIOMETRIC NANOTHERMOMETRY BASED ON THE PHONON ASSISTED ANTI-STOKES LUMINESCENT MATERIALS

By

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Certificate of Original Authorship

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

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literatures used are indicated in the thesis.

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

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Format of Thesis

This thesis has a conventional format with six chapters as illustrated by the flow chart below.

Chapter 1 is an introduction chapter based on a comprehensive literature review. The classifications, thermometric properties of nanothermometers, and the advantages of RE doped luminescent nanothermometers are discussed in details.

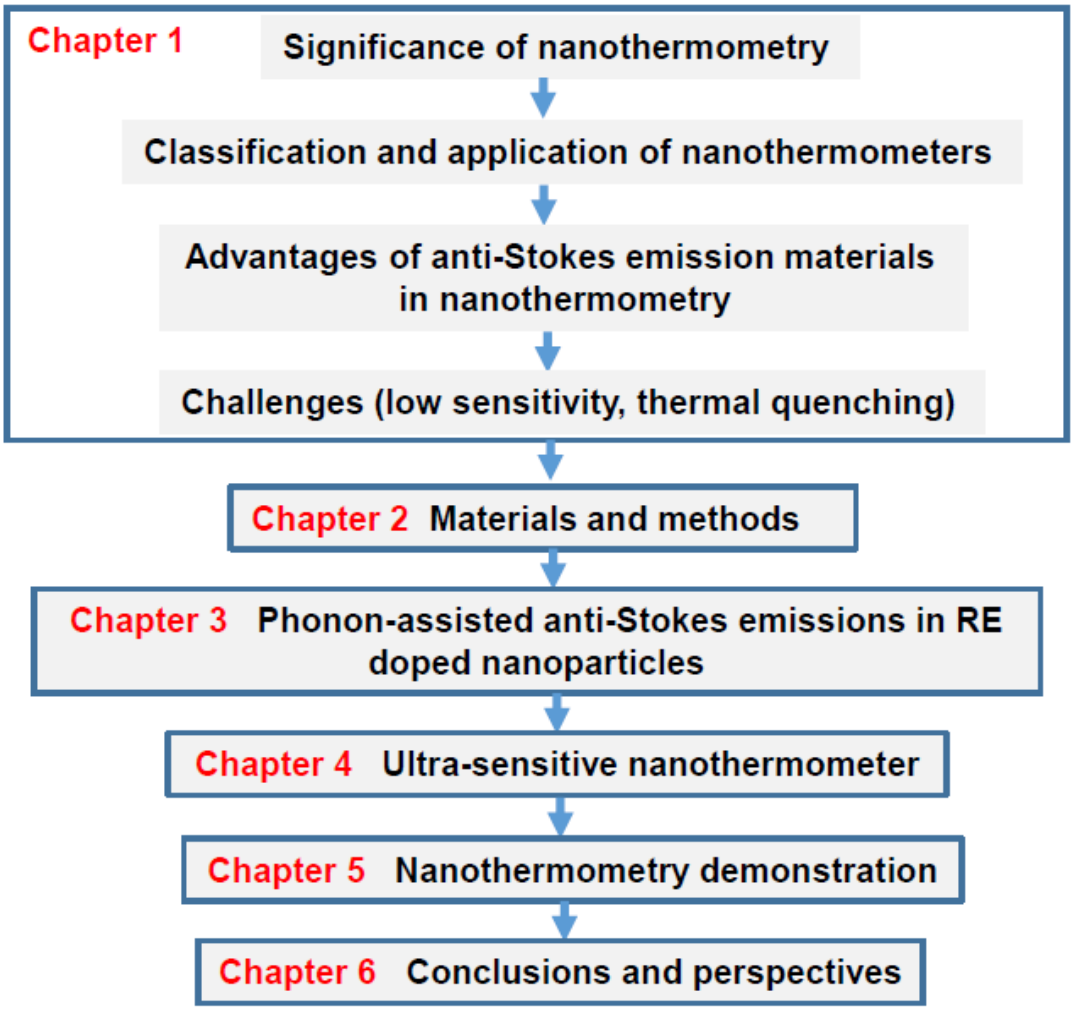
Chapter 2 provides detailed methods of the materials synthesis and sample characterizations used in the result chapters.

Chapter 3 investigates the thermal induced emission enhancement in RE doped anti-Stokes luminescent nanoparticles and proposes the surface-phonon-assistance behind this phenomenon, which provides the experimental foundation for the following chapters.

Chapter 4 describes the strategy to create ultra-sensitive nanothermemeters based on the phonon-assisted anti-Stokes emissions in RE doped nanoparticles.

Chapter 5 gives the nanothermometry demonstration results on two different applications to show the ability of the created nanothermometers.

Chapter 6 summarizes the main research results of this project and future research work based on the current progress described in this thesis.



The flow chart outlines the thesis structure.

List of Publications

Research papers:

[1] Chao Mi, Jiajia Zhou*, Fan Wang and Dayong Jin, Anti-Stokes emission enhancement of near infrared nanothermometry probes, ***Nanoscale***, 2019, 11, 12547.

[2] Chao Mi, Jiajia Zhou*, Fan Wang, Gungun Lin and Dayong Jin, Ultra-sensitive ratiometric nanothermometer with large dynamic range and photostability, ***Submitted.***

[3] Jiajia Zhou*, Shihui Wen, Jiayan Liao, Christian Clarke, Sherif Abdulkader Tawfik, Wei Ren, Chao Mi, Fan Wang and Dayong Jin*, Activation of the surface dark-layer to enhance upconversion in a thermal field, ***Nature Photonics***, 2018, 12, 154-158.

[4] Yinghui Chen, Hien T. T. Duong, Shihui Wen, Chao Mi, Yingzhu Zhou, Olga Shimoni, Stella M. Valenzuela, and Dayong Jin*, Exonuclease III-assisted upconversion resonance energy transfer in a wash-free suspension DNA assay, ***Analytical Chemistry***, 2018, 90 (1), 663–668.

[5] Juan Xie, Xiaoji Xie, Chao Mi, Ziyu Gao, Yue Pan, Quli Fan, Haiquan Su, Dayong Jin*, Ling Huang*, and Wei Huang*, Controlled Synthesis, Evolution Mechanisms, and Luminescent Properties of ScFx:Ln (x = 2.76, 3) Nanocrystals, ***Chemistry of Materials***, 2017, 29 (22), 9758–9766.

[6] Deming Liu, Xiaoxue Xu*, Fan Wang, Jiajia Zhou, Chao Mi, Lixin Zhang, Yiqing Lu, Chenshuo Ma, Ewa Goldys, Jun Lin and Dayong Jin*, Emission stability and reversibility of upconversion nanocrystals, ***Journal of Materials Chemistry C***, 2016, 4, 9227-9234.

List of Acronyms (in alphabetic order)

3D	3 Dimensional
AC	Alternating Current
AFM	Atomic Force Microscope
AuNCs	Gold Nanoclusters
CCD	Charge-Coupled Device
CT	Computed Tomography
DC	Direct Current
DNA	Deoxyribonucleic Acid
EMCCD	Electron Multiplying Charge Coupled Device
ESA	Excited State Absorption
ETU	Energy Transfer Upconversion
FCCP	4-(trifluoromethoxy)phenylhydrazone
FTIR	Fourier Transform Infrared Spectroscopy
h-BN	Hexagonal Boron Nitrid
IR	Near Infrared
Mito-RTP	Ratiometric Fluorescent Molecular Probe
MR,	Magnetic Resonance
NIR	Near Infrared
OA	Oleic Acid
OA^-	Oleate Anions
OAH	Oleate Molecules
ODE	1-Octadecene
PET	Positron Emission Tomography

PMT	Photomultiplier Tube
QD	Quantum Dot
RE	Rear Earth
RNA	Ribonucleic Acid
SPA	Ionic Potassium 3-Sulfopropyl Acrylate
SPECT	Single-Photon Emission Computed Tomography
SThM	Scanning Thermal Microscopy
STM	Scanning Tunneling Microscope
TCSPC	Time-Correlated Single-Photon Counting
TEM	Transmission Electron Microscope

Abstract

Thermometers working at nanoscale provide new approaches of non-invasive temperature sensing with high spatial resolution to break the limitations in conventional methods. Over the past few decades, the developing of nanothermometry has been accelerated by the numerous challenging requests arising from the advanced areas like microelectronics, and nanomedicine. As nanothermometry can give the basic information on the temperature distribution of micrometric and nanostructured systems whose dynamic state is determined by temperature, the comprehensive studying on the performance of such small systems can be carried out in this way.

Based on the current literatures, the most studied nanothermometers can be grouped in two major categories: luminescent and non-luminescent nanothermometers. Luminescent thermometers is due to their temperature-dependent optical properties, which widely exist in luminescent nanomaterials including QDs, RE doped nanoparticles, artificial biomolecules, organic dyes, as well as hybrid polymeric nanomaterials and organic–inorganic hybrid materials. Non-luminescent thermometers contains the scanning thermal microscopy that combines the techniques of probe scanning microscope with nanoscale thermocouples or thermal resistance, while the temperature is determined by the electrical signal change of the nanoscale thermal sensors as scanning probes.

This thesis summarizes different kinds of luminescent nanothermometers and their unique thermometric properties including temperature induced spectra position shift, emission intensity change and luminescent lifetime change. Also, the development of probe scanning microscope is introduced in the first section. In the second section, on one hand, the advantages of RE doped anti-Stokes luminescent materials working as nanothermometers are described based on the literature review, and on the other hand the aim of this thesis is

established to solve the current problems in the developing of ultra-sensitive RE doped anti-Stokes luminescent nanothermometers. By developing the thermal induced emission enhancement in RE doped nanoparticles, the performance of luminescent nanothermometers at high temperature have been largely improved. Based on this investigation, a new generation of ratiometric nanothermometers is created with a high sensitivity. More significantly, the luminescence nanothermometry demonstration shows the high spatial resolution and high accuracy in the temperature sensing by the created RE doped anti-Stokes luminescent nanothermometers.

Key words: nanothermometry, anti-Stokes luminescence, phonon assistance, rear earth doped nanomaterials, upconversion,

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