

Biophotonics characterization of upconversion nanoparticles

by Lei DING

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the degree of

Doctor of Philosophy

under the supervision of Prof. Igor Aharonovich, Dr. Fan Wang

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Certificate of Original Authorship

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

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

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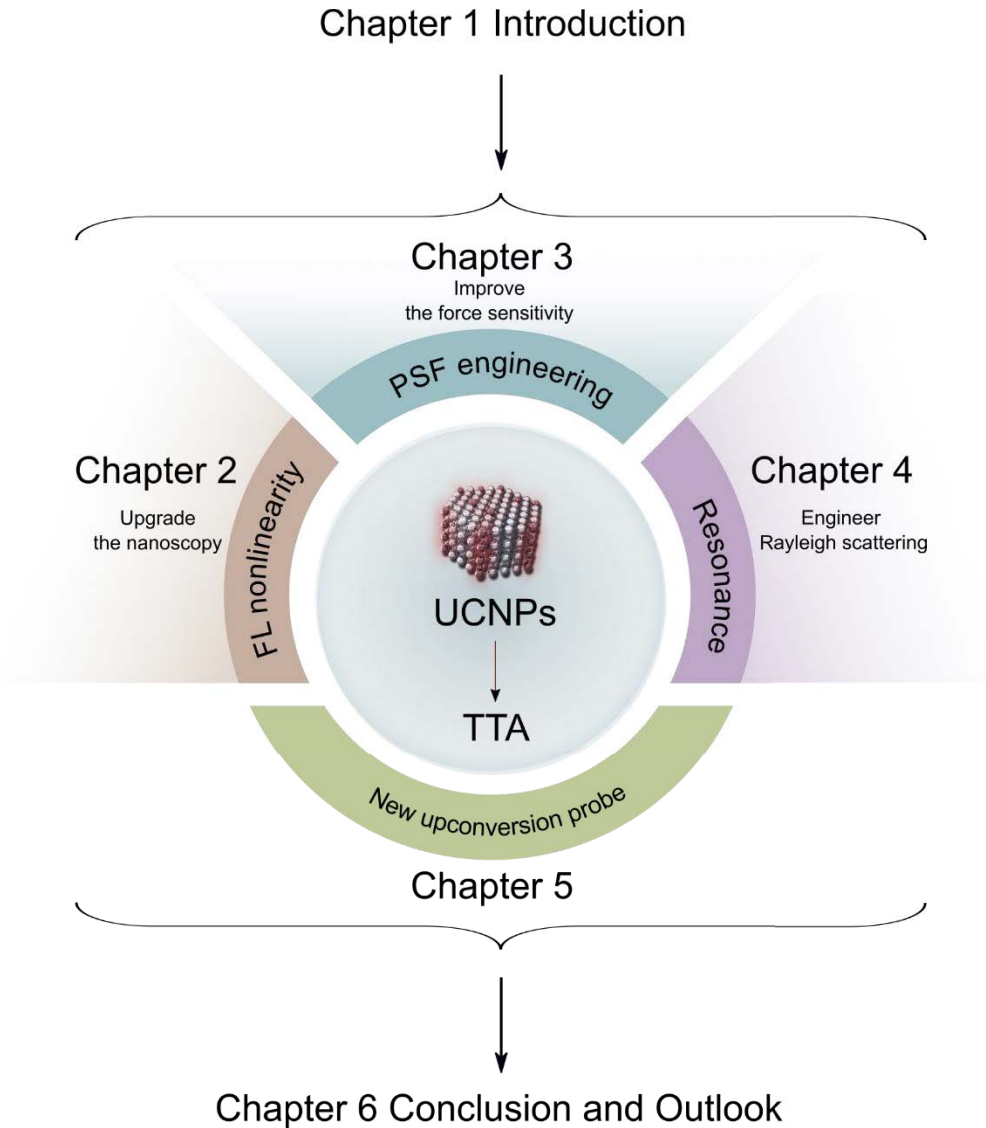
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Format of Thesis

This thesis is composed of six chapters. Chapter 1 is the introduction. Chapters 2-5 refer to the research results for the four goals (to see, sense, modulate, and develop new upconversion probes) in my PhD study. Chapter 6 gives the conclusion and perspective.



List of Publications

➤ Articles

1. **L. Ding**[†], X. Shan[†], P. Reece, I. Aharonovich and F. Wang*. Controlling Rayleigh scattering from lanthanide ion-doped nanoparticles. (*under review*)
2. X. Shan[†], **L. Ding**[†] (co-first), S. Wen, J. Lu, J. Chennupati, X. Zhong*, D. Jin* and F. Wang*. Atto-Newton Force Sensitivity of Machine Learning Empowered Astigmatism Optical Tweezers. (*to be submitted*)
3. C. Chen[†], **L. Ding**[†] (co-first), B. Liu and F. Wang*. Exploiting The Tunable Nonlinearity in Upconversion Nanoparticles for Super-resolution Imaging. (*under review*)
4. **L. Ding***, Q. Fu*, I. Aharonovich and F. Wang. Breaking Oxygen Quenching of Triplet–Triplet Annihilation Upconversion by Multidimensional Structures. (*to be submitted*)
5. **L. Ding**, J. Zhou*, Q. Fu, G. Bao, Y. Liu and D. Jin. Triplet-fusion Upconversion with Oxygen Resistance in Aqueous Media. *Anal. Chem.*, 2021, 93, 4641–4646.
6. B. Liu, J. Liao, Y. Song, C. Chen, **L. Ding**, J. Lu, J. Zhou* and F. Wang*. Multiplexed Structured Illumination Super-Resolution Imaging with Lifetime-engineered Upconversion Nanoparticles. *Nanoscale Adv.*, 2022.
7. X. Shan[†], F. Wang^{†*}, D. Wang, S. Wen, C. Chen, X. Di, P. Nie, J. Liao, Y. Liu, **L. Ding**, P. J. Reece* and D. Jin*. Optical Trapping Beyond Refractive Index Mismatch Using Highly Doped Nanoparticles. *Nat. Nanotechnol.*, 2021, 1-7.
8. L. Zhang, K. Cook, A. Szmalenberg, B. Liu, **L. Ding**, F. Wang, D. McGloin*. Dual beam optical fiber traps for aerosols with angular deviation. *Complex Light and Optical Forces XVI 12017*, 2022, 126-132.

Table of Symbols

λ	laser wavelength	k_B	Boltzmann's constant
n	Refractive index	T	Temperature
σ_{sat}	Scattering cross-section	k	Stiffness
α	Polarizability	F_{ex}	Restoring force
ε	Permittivity	δ_{eq}	Position shift
φ	Phase difference	SD_{eq}	Standard deviation of position shift
I_r	Reflect light intensity	σ_k	Possibility variance of position
I_s	Scattering intensity	σ_p	Localisation accuracy
E_r	Reflect filed	ω	Angular frequency
E_s	Scattering field	k_m	Wavenumber
c_i	Energy transfer ratio	σ_i	Damping coefficient
k_{ij}	Cross-relaxation coefficient	ϕ_{UC}	UC quantum efficienc
a_{ij}	Branching ratio from energy level	η	Refraction coefficient
n_i	Population of photons	S_r	Sensitivity
w_i	Intrinsic decay rate	Q	Integral upconversion intensity
$F_i(x)$	Fluorescence intensities	$U(x)$	Potential energy
N_0	Fluorophore concentration	$g(x)$	Components of spatial information
k_B	Boltzmann's constant		

Abbreviations

UCNP	upconversion nanoparticle
HAADF-STEM	high-angle annular dark-field scanning transmission electron microscopy
Ln-NPs	lanthanide-doped nanoparticles
TEM	transmission electron microscopy
PSF	point spread function
TTA	triplet-triplet annihilation
ISC	intersystem crossing
NA	numerical aperture
STORM	stochastic optical reconstruction microscopy
PALM	photoactivated localisation microscopy
SIM	structured illumination microscopy
STED	stimulated emission depletion
SLM	spatial light modulator
QPD	quadrant photodiode detector
CCD	Charge-Coupled Device
CMOS	Complementary Metal Oxide Semiconductor
3D	three-dimensional
aN	attoNewton
iSCAT	interferometric scattering
SPAD	single-photon counting avalanche photodiode
FWHM	full width at half maximum
OA-VT	astigmatism video tracking
DNN	deep neural network

fN	femtoNewton
2D	two-dimensional
CL	cylindrical lens
PS	polystyrene sphere
M-iSCAT	multiplexed iSCAT
OA	oleic acid
ODE	1-octadecene
BF	bright-field
FL	fluorescence
PdTCPP	Pd(II) meso-Tetra(4-carboxyphenyl)porphine
QCDDPA	5,5'-(9,10-anthracenediyl)diisophthalic acid
DMF	dimethyl formamide
NMR	nuclear magnetic resonance

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Abstract

Upconversion materials have attracted enormous attention for a broad range of applications in biological imaging, energy-related light harvesting, and sensing, due to their unique physicochemical properties. However, the comprehensive understanding and characterization of upconversion nanoparticles for novel applications remain challenging. In this thesis, we set four goals to refresh the present characterization and provide a wider and deeper cognition of these upconversion nanoparticles. After the delicate design of optical setups and nanomaterials, we realized the super resolution enhancement, optical force sensitivity improvement, Rayleigh scattering modulation, and a new water-soluble molecular upconversion probe.

Experimentally and theoretically, we upgrade the nanoscopy by exploiting the unique nonlinearity of upconversion nanoparticles using conventional confocal microscopy. We realize three-dimensional attoNewton-level optical force of optical via revolutionizing the configuration, data collection and accuracy analysis based on the property of upconversion nanoparticles. We refresh the morphology-independent method of engineering Rayleigh scattering at the nanoscale level based on the resonance effect of upconversion nanoparticles. We develop water-soluble molecular upconversion materials based on the ionic equilibrium of upconversion dyes. Based on the improved characterization of upconversion materials, as well as the technologies, we anticipate the potential applications in future, such as, deep tissue imaging, monitoring the interaction in the limit region (e.g., attoNewton level), and multiplexed scattering microscopy of cell dynamics.