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**NON-STEADY STATE REGULATION OF LASER
EMISSION: APPLICATIONS TO LANTHANIDE-DOPED
GLASSES AND CARBON QUANTUM DOTS**

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**Non-Steady State Regulation of Laser Emission: Applications to
Lanthanide-Doped Glasses and Carbon Quantum Dots**

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A thesis submitted in partial fulfillment of the requirements for

the degree of Doctor of Philosophy

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Abstract

The precise control of laser emission properties in diverse gain media is a central challenge in modern photonics, underpinning applications ranging from optical communication and sensing to biomedical imaging and quantum information processing. Lanthanide-doped glasses and carbon quantum dots (CQDs) represent two distinct yet complementary classes of materials. Lanthanide-doped glasses offer high photochemical stability, sharp emission lines, and broad spectral coverage from ultraviolet (UV) to near-infrared (NIR) through multi-step energy transfer (ET) mechanisms, but their steady-state performance tuning is inherently constrained by fixed crystal-field environments and equilibrium population distributions. Conversely, CQDs offer broadband tunability, facile solution-processability, and strong environmental sensitivity due to their surface functionalization capabilities, yet suffer from lower optical gain coefficients and higher scattering losses compared to inorganic crystalline counterparts. The overarching theme of this dissertation is to develop, implement, and validate a non-steady state regulation framework—combining spatial and temporal control of energy transfer dynamics—to construct a universal method for regulating the laser performance of various gain materials and overcome their respective limitations.

Efficient near-infrared (NIR) to ultraviolet (UV) multiphoton upconversion is critical for applications in photocatalysis, sterilization, biomedicine, and compact lasers. However, inefficiencies from energy losses in intermediate states, including radiative

transitions, cross-relaxation (CR), nonradiative decay, and quenching, limit UV emission intensity. This thesis presents a novel approach to enhance NIR-to-UV upconversion in lanthanide (Ln^{3+})-doped fluoroaluminate glass-ceramics (GCs) through spatial and temporal control of energy transfer (ET), achieving significant UV emission enhancement and low-threshold UV random lasing. Using Förster-Dexter theory, we identified that ET rates depend on donor-acceptor distances, which are large in amorphous glasses, leading to low ET efficiency and defect quenching. Molecular dynamics (MD) simulations guided the design of glass compositions [$(30+x) \text{AlF}_3$ - $(54-x)(\text{Ca}, \text{Sr}, \text{Ba})\text{F}_2$ - 16YbF_3 , $x = 0$ -12 mol%] to precipitate nanocrystals with tunable $(\text{Ca}, \text{Sr}, \text{Ba})/\text{Yb}$ ratios. Higher AlF_3 content forms compact networks, reducing alkali-earth ion surroundings around $[\text{YbF}_x]$ polyhedra, enabling hexagonal $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}$ or cubic $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}$ nanocrystals via heat treatment. These nanocrystals enrich Ln^{3+} ions, shortening inter-ion distances (e.g., Tm^{3+} - Tm^{3+} from 42.7 Å in glass to 19.0 Å in hexagonal nanocrystals), thus increasing ET rates. $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Gd}^{3+}$ -tri-doped GCs were synthesized with optimized doping (10 mol% Yb^{3+} , 0.07 mol% Tm^{3+} , 5 mol% Gd^{3+}) to maximize ET upconversion (ETU) and CR while minimizing quenching. In GC-39Al (hexagonal $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$), UV emission at 311 nm ($\text{Gd}^{3+}: {}^6\text{P}_j \rightarrow {}^8\text{S}_{7/2}$) increased 267-fold compared to precursor glass, driven by enhanced ET rates (e.g., Yb^{3+} - Tm^{3+} ET from 352 s^{-1} to 950 s^{-1}). Power-dependent spectra confirmed efficient population of high-lying states ($\text{Tm}^{3+}: {}^1\text{D}_2, {}^1\text{I}_6$) via CR and ET to Gd^{3+} , enabling six- to seven-photon upconversion, including the first 205 nm emission in bulk materials. Temporal control further enhanced UV emission by

modulating excitation pulse widths (40 ms to 0.5 ms) at constant power (2.55×10^5 $\text{mJ} \cdot \text{cm}^{-2}$). Python-simulated rate equations showed that shorter pulses increase peak power, accelerating high-energy state population while suppressing mid-level accumulation and back ET. The UV emission ratio rose from 1.61% to 38.81%, with Gd^{3+} 's long lifetimes reserving UV photons. Room-temperature UV random lasing at 311 nm, 275 nm, and 253 nm was achieved in GC-39Al under 980 nm ns pulses, with a low threshold ($15 \text{ mJ} \cdot \text{cm}^{-2}$) and narrow linewidths (0.14–0.25 nm), outperforming nanocrystal systems. This thesis establishes a framework for efficient NIR-to-UV upconversion via MD-guided Ln^{3+} enrichment and pulse-compression kinetics, paving the way for compact UV lasers with applications in medical and industrial fields.

Carbon quantum dots (CQDs) are promising solution-processable nanomaterials for next-generation photonic devices due to their tunable emission from ultraviolet to near-infrared, enabled by surface functionalization and environmental sensitivity. However, their application in high-coherence lasers is limited by scattering losses and lower gain coefficients compared to colloidal quantum dots. This thesis introduces a novel framework for achieving tunable-wavelength broadband liquid-state CQD lasers, leveraging concentration-dependent Förster resonance energy transfer (FRET) and a gain-guided waveguide in a cuvette-based cavity, spanning 641–710 nm. O-phenylenediamine-based tunable CQDs (TCQDs) were synthesized via a solvothermal method, exhibiting uniform 4 nm spherical morphology with a 0.21 nm lattice spacing. Concentration-dependent photoluminescence (PL) and absorption spectra (2^{-5} to $1 \text{ g} \cdot \text{L}^{-1}$ in DMF) revealed FRET-induced redshifted emission (585–700 nm), deconvoluted

into stable luminescent centers at ~ 600 , ~ 630 , and ~ 700 nm. Time-resolved PL confirmed reduced fluorescence lifetimes (e.g., 3.05 to 1.74 ns at 700 nm) with increasing concentration, indicating efficient photon redistribution to lower energy states. This enabled tunable random lasing with thresholds rising from 1.91 to 27.85 $\text{mJ}\cdot\text{cm}^{-2}$ as concentration decreased, with Fourier transform analysis showing cavity lengths below 100 μm . A gain-guided waveguide was engineered by matching the solvent's refractive index (e.g., DMF, $n=1.450$) to the quartz cuvette, confining emission in a 200×500 μm channel. An external aluminum mirror facilitated optical feedback, enabling transitions from random lasing to Fabry–Pérot cavity multimode and single-mode lasing. Mode spacing increased from 0.71 to 4.66 nm as mirror spacing decreased from 485.23 to 38.04 μm , fitting the Fabry–Pérot model. The optical gain ($5.85\text{--}50.17$ cm^{-1}) exceeded cavity loss (4.773 cm^{-1}), supporting lasing emission. Refractive index mismatch in solvents like ethanol ($n = 1.38$) prevented lasing, highlighting index matching's role in coherence. Transient absorption spectroscopy revealed carrier dynamics, with ground-state bleaching at 515 nm and excited-state absorption at 600 nm within 1.09 – 6.14 ps, confirming rapid energy redistribution critical for population inversion. This work establishes a versatile platform for spectrally tunable liquid-state lasers, integrating FRET-optimized CQDs, index-matched cavities, and external feedback for modal control. The approach, applicable to other colloidal quantum dots, advances compact, low-cost photonic devices for integrated systems, with future improvements targeting precise cavity geometries for broader single-mode lasing.

List of Publications

1. **Xuezhe Dong**, Yu Siu Fung. Smoothing energy transfer pathway to enhance upconverted luminescence in the UVB region by introducing Gd^{3+} ions. In preparation.
2. **Xuezhe Dong**[#], Pengzhi WANG[#], Siu Fung Yu. Morphology controlled carbon quantum dots lasing. In Preparation.
3. Qunhuo Liu[#], **Xuezhe Dong**[#], Yujie Liu, Weilin Chen, Ting Wang, Xvsheng Qiao, Jincheng Du, Guodong Qian, Xianping Fan, Siu Fung Yu. Spatial and temporal control of energy transfer multiphoton upconversion in glass-ceramic for deep-ultraviolet enhancement. *Laser & Photonics Reviews*. (Accepted)
4. **Xuezhe Dong**, Pengzhi Wang, Wei Gao, Ting Wang, Luwei Zhou, Chen Yang, Shaofeng Zhang, Yimin Jiang, Mingjie Li, Siu Fung Yu. Tunable-Wavelength Broadband Liquid-State Carbon-Quantum-dot Lasers. *Advanced Optical Materials* (2025)
5. Yu Siu Fung, **Dong Xuezhe**, Wang Ting, Qiao Xusheng, Liu Qunhuo. CN202311222193. *Chinese Patent* (2023).
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List of Abbreviations

XRD	X-ray Diffraction
SAED	Selected Area Electron Diffraction
TEM	Transmission Electron Microscope
PL	Photoluminescence
PLQY	Photoluminescence Quantum Yields
CW	Continuous Wave
Ln^{3+}	Lanthanide Ions
GCs	Glass Ceramics
ET	Energy Transfer
ETU	Energy Transfer Upconversion
EBT	Energy Back Transfer
FFT	Fast Fourier transform
ESA	Excited State Absorption
EM	Energy Migration
CR	Cross Relaxation
QDs	Quantum Dots
CDs	Carbon Dots
CQDs	Carbon Quantum Dots
TCQDs	Tunable Carbon Quantum Dots
OCDs	Oxidized Carbon Dots
Crys	Crystals

XLVI

TA	Transient absorption
TRPL	Time-resolved Photoluminescent
Vis	Visible
UV	Ultraviolet
DUV	Deep Ultraviolet
UVA	Ultraviolet A
UVB	Ultraviolet B
UVC	Ultraviolet C
NIR	Near-infrared
Ns	Nanosecond
Ps	Picosecond
Fs	Femtosecond
FRET	Förster Resonance Energy Transfer
FP	Fabry–Pérot
WGM	Whispering Gallery Mode
FWHM	Full Width at Half Maximum
LED	Light-emitting Diode
MD	Molecular Dynamics
FDTD	Finite-Difference Time-Domain
DSC	Differential Scanning Calorimetry

Chapter 1 Introduction

1.1 Background

The invention of the laser (abbreviation for Light Amplification by Stimulated Emission of Radiation) in 1960 by Theodore H. Maiman using a ruby crystal has long been recognized as a watershed moment in modern physics and engineering.^[1-2] Before this breakthrough, light sources were largely limited to incoherent lamps and synchrotron radiation, all of which produced photons that were random in phase, broad in spectrum, and isotropic in spatial distribution. What made the ruby laser unique was not simply its narrow emission linewidth, but the underlying physical principle that enabled it: stimulated emission of radiation under conditions of population inversion (**Figure 1.1**). In spontaneous emission process, photosensitive materials in excited state relax to the ground state in an uncontrolled fashion, releasing photons with random direction, polarization, and phase after absorbing the incident photons. In contrast, laser action occurs when a photon stimulates another photon in an excited state to emit an identical photon. If this process is amplified within a resonant cavity to achieve effective net optical gain, a monochromatic, coherent, and directional beam can be obtained. Achieving this regime requires overcoming the balance between absorption and emission. Under thermal equilibrium conditions, the number of electronics in the ground state far exceeds that in the excited state, ensuring that absorption dominates over emission. Positive optical gain can only be achieved by inverting the particle distribution. Therefore, the generation, maintenance, and application of inverted

distributions have remained the core challenge in laser physics design for over six decades. In this context, it is worth noting why four-level or multi-level systems schemes are generally more favorable than three-level systems. In a three-level scheme, the lower energy level is the ground state of the material, which is heavily populated under thermal equilibrium, which means achieving population inversion requires pumping more than half of the atoms or ions into the excited state. By contrast, in a four-level system, the lower energy level lies above the ground state. This ensures that the lower energy levels remain largely unoccupied, while the higher laser excitation energy levels can be effectively occupied in an ultralow threshold. For this reason, most modern solid-state and semiconductor lasers adopt a four-level or quasi-four-level configuration.

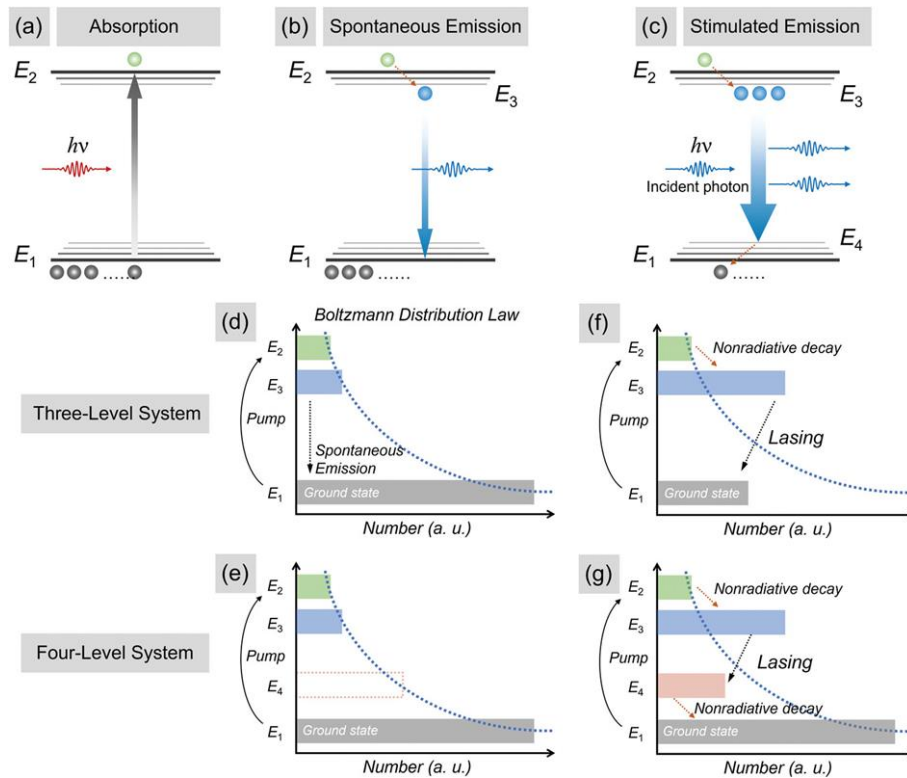


Figure 1.1. Fundamental principles for laser emission. a-c) difference among absorption,

spontaneous and stimulated emission. d-g) difference between spontaneous emission and stimulated emission in 3-level or 4-level systems.^[1]

The search for new gain media, like have moved far beyond the first ruby and Nd:YAG crystals toward a family of materials (lanthanide-doped upconverted materials, quantum dots (QDs), perovskite-based materials) whose key features is tunability—in composition, structure, and emission behavior.^[3-7] Lanthanide-doped glass-ceramics exemplify this principle at the atomic scale: their shielded 4f–4f transitions yield narrow emission lines and long-lived excited states, while the surrounding glass–crystal environment can be engineered to tailor phonon energies, and suppress nonradiative decay.^[8] Semiconductors or carbon quantum dots (CQDs) add another layer of control. Their emission wavelength depends sensitively on particle size, surface chemistry, and electronic coupling, enabling continuous tuning from the ultraviolet through the near-infrared simply by adjusting synthesis conditions or post-processing.^[9-10] Metal–halide perovskites (MHP) complement these systems by offering solution processability, high defect tolerance, and a flexible lattice that supports broad compositional substitution, allowing band-gap engineering and facile integration into diverse cavity geometries.^[11] Taken together, these materials illustrate a common theme: spectral and structural tunability as a design tool for lasers. By combining atomic-level control of electronic transitions (as in lanthanides), nanoscale quantum-confinement effects (as in QDs), and lattice-level band-gap engineering (as in perovskites), researchers can match emission properties to specific cavity designs and pumping schemes. This collective capability enables precise wavelength selection, low-threshold lasing output, and compatibility

with micro/nanophotonic platforms - attributes that are crucial for modern applications ranging from integrated photonic circuits to UV-visible light sources.

1.2 Objectives

The primary objective of this thesis is to examine how spatiotemporally controlled electronic energy transfer can drive the development of tunable laser sources, either wavelength or mode spacing. Adopting a collaborative optimization framework, we treat the electronic structure and excitation dynamics of each material as interdependent variables, exploiting their distinct advantages in a unified design strategy. This approach uncovers laser control mechanisms that strengthen population inversion and suppress nonradiative losses. Our investigation focuses on two representative gain media, lanthanide-doped glass-ceramics and CQDs, for their fundamentally different energy-transfer pathways. Finally, the general applicability of these control strategies across diverse material systems is critically evaluated.

First, for lanthanide-doped glass-ceramics, the objective is to manipulate multiphoton upconversion pathways by engineering the spatial distribution of Ln^{3+} ions within nanophases. Controlled enrichment of activators and sensitizers enables efficient inter-ion transfer while mitigating quenching effects. In parallel, temporal regulation via excitation pulse compression and modulation will be employed to match the lifetimes of long-lived intermediate states, ensuring that multiphoton absorption proceeds with minimal energy loss. Together, these spatial and temporal interventions are designed to amplify ultraviolet upconversion emission and achieve stable lasing

under non-steady-state conditions. For CQDs systems, the objective is to exploit their surface functionalization and aggregation-induced FRET effects as a means of regulating electronic energy transfer on ultrafast timescales. By tuning aggregation and solvent environments, broadband emission can be shifted and expanded across the visible range. To complement this, gain-guided cavity designs and optical feedback mechanisms will be integrated to counteract scattering losses and enable precise modal control, from multimode Fabry–Pérot behavior to single-mode lasing. This dual strategy not only broadens the accessible spectral window but also improves coherence and reduces lasing thresholds in solution-processed systems.

By pursuing these objectives, the thesis seeks to demonstrate the universality of electronic energy-transfer regulation as a guiding principle for laser design. Although the lanthanide and quantum dot platforms differ fundamentally in their emission physics and operational timescales, both reveal that carefully orchestrated spatial and temporal control leads to significant gains in efficiency, tunability, and stability. The expected outcome is the derivation of general design rules that transcend specific material classes, offering predictive guidance for compact, wavelength-adaptable, and durable ultraviolet-to-visible photonic devices.

1.2 Outline of Thesis

In chapter 2, the development history and evolution of non-steady-state control over laser output wavelength and mode spacing for various emerging optical gain materials, mainly on organic dyes, lanthanide-doped materials, QDs and perovskite-

based materials will be summarized.

For lanthanide-doped glass-ceramics in chapter 3, the objective is to manipulate multiphotons upconversion pathways by engineering the spatial distribution of Ln^{3+} ions within nanophases. In parallel, temporal regulation via excitation pulse compression and modulation will be employed to match the lifetimes of long-lived intermediate states, ensuring that multiphoton absorption proceeds with minimal energy loss. Together, these spatial and temporal interventions are designed to amplify ultraviolet upconversion emission and achieve stable lasing under non-steady-state conditions.

For CQDs systems, in chapter 4, the objective is to exploit their surface functionalization and aggregation-induced FRET effects as a means of regulating electronic energy transfer on ultrafast timescales. By tuning aggregation and solvent environments, broadband emission can be shifted and expanded across the visible range. To complement this, gain-guided cavity designs and optical feedback mechanisms will be integrated to counteract scattering losses and enable precise modal control, from multimode Fabry–Pérot behavior to single-mode lasing. This dual strategy not only broadens the accessible spectral window but also improves coherence and reduces lasing thresholds in solution-processed systems.

In chapter 5, the work done during my Ph.D. period is summarized, and the potential research work is proposed to be carried out in the future.

Chapter 2 Dynamic Engineering in Novel Optical Gain Materials from Conventional Media to Emerging Nanostructures

2.1 Introduction: From Laser Fundamentals to the Imperative for Tunability

The invention of the laser, an acronym for **L**ight **A**mplification by **S**timulated **E**mission of **R**adiation, stands as a pivotal achievement of twentieth-century physics, unleashing a technological revolution across communications, manufacturing, medicine, and scientific research.^[12] Albert Einstein set the basis in 1917. He described stimulated emission, where one photon makes an excited atom release another photon. The second photon is the same in phase, frequency, polarization, and direction. For a long time, this idea stayed only in theory. The reason was that light amplification needs population inversion, which means more atoms in a higher energy state than in a lower one. In 1960, Theodore H. Maiman made the first working laser. He used a ruby crystal ($\text{Cr}^{3+}:\text{Al}_2\text{O}_3$) and a flashlamp. This experiment turned the idea into reality.^[2] The core principles governing all lasers were thus established (**Figure 2.1a**): the necessity of a suitable gain medium (providing the atomic or molecular energy levels for inversion), a pumping mechanism (an external energy source to achieve this inversion), and an optical resonator (typically a pair of mirrors forming a cavity that provides positive feedback, where stimulated emission amplifies light during multiple passes, with one partially transparent mirror serving as the output coupler for the coherent beam). The

precise control of laser longitudinal and transverse modes is fundamental to unlocking their full application potential (**Figure 2.1b**). To use a laser with very high stability and clean frequency, it is important to control the longitudinal modes. This control makes it possible to run the laser at only one frequency. It is needed for things like high-resolution spectroscopy, sending signals in optical networks, and very accurate sensing with interferometers. To use a laser for sharp focusing of light, control of the transverse mode is key. Keeping the beam in the basic Gaussian shape allows focusing at the diffraction limit. This ability is needed for laser cutting and material processing, optical data storage, making circuits with photolithography, and for high-resolution LiDAR.^[13-17] Ultimately, the independent and synergistic engineering of these modes transforms a generic light source into a precision tool tailored for specific advanced scientific and industrial applications.

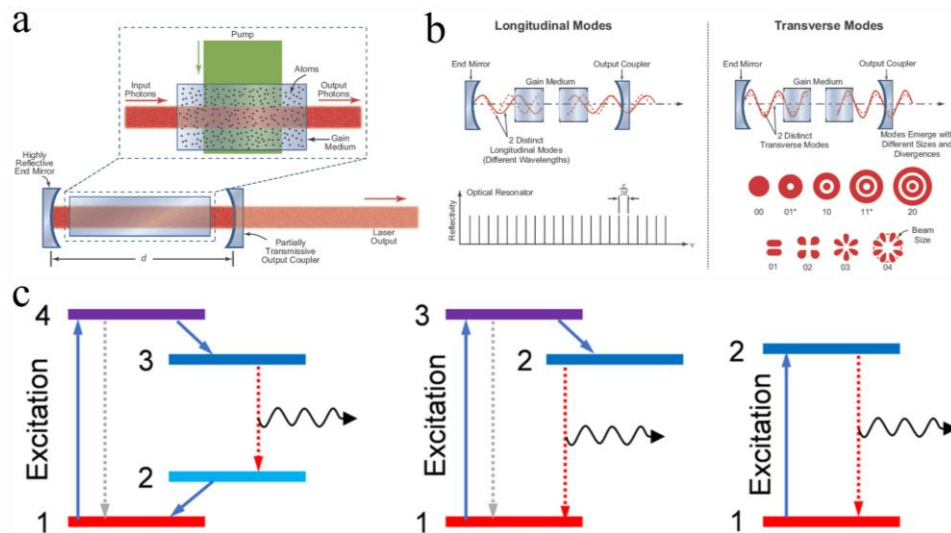


Figure 2.1 a) Simplified diagram of a laser, including the gain medium, pump source, and optical resonator mirrors with cavity length (d). b) Longitudinal and transverse modes generated by the optical cavity. c) Three models to achieve lasing.^[12]

The energy-level architecture of a gain medium fundamentally constrains laser performance shown in **Figure 2.1c**. In a three-level system, the laser transition terminates at the ground state, requiring over half of the particles to be excited to achieve population inversion. This results in high thresholds, low efficiency, and limited continuous-wave operation, as exemplified by ruby lasers. In contrast, four-level systems utilize a lower laser level situated above the ground state. Since this level remains largely unpopulated thermally and exhibits rapid depletion, population inversion occurs readily with minimal pumping. This leads to dramatically lower thresholds, higher efficiency, and robust continuous-wave output, as demonstrated by Nd:YAG. The profound performance gap between these systems highlights the critical importance of engineering multi-level energy structures for advanced laser control. By deliberately introducing intermediate energy levels or designing hybrid systems that combine advantageous features of both three- and four-level schemes, researchers can actively manipulate key laser parameters. Strategic energy-level engineering enables dynamic control over population inversion pathways, opening routes to power scaling, wavelength agility, and modal precision. This approach provides a fundamental materials-based strategy for achieving the tailored laser performance demanded by emerging applications in photonics, quantum technologies, and precision manufacturing.

2.1.1 Excited-state and Non-steady State Regulation on Lasing Output

Research on light-emitting materials shows that the way excited states are managed is as important as the material itself. When carriers move to higher energy levels and then relax, the steps they follow decide if light is emitted strongly or weakly. If we want low thresholds and tunable lasers, we must not only look at the material but also at how to control these excited states in time. Many studies have shown that several simple methods can guide this process.^[18-22]

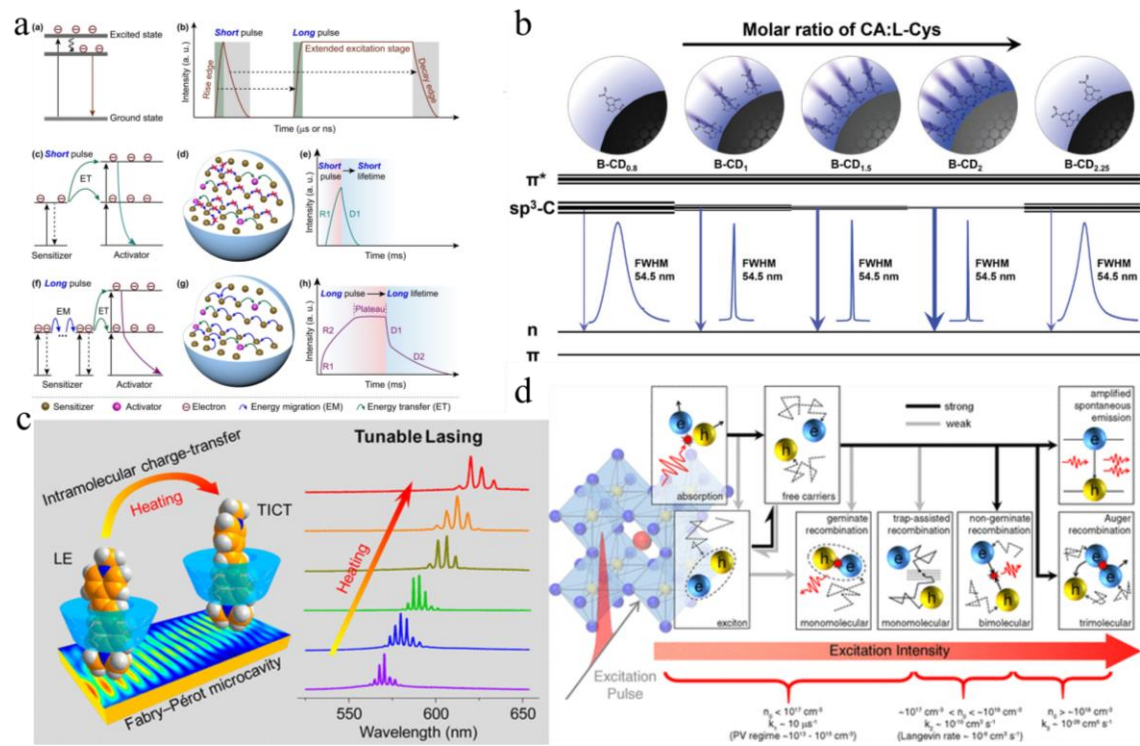


Figure 2.2 **a)** Temporal state-related regulation methods (taking lanthanide-doped materials for example) **b)** Surface groups-related regulation methods (taking CQDs for example). **c)** External stimuli-related regulation methods (taking organic dyes for example). **d)** Ultrafast timescale-related regulation methods (taking perovskites for example).^[19-22]

Another useful method is taking advantages of energy pathways (**Figure 2.2a**).^[20] When a material is surrounded by traps, interfaces, or solvents, the excited states may decay without light, which is derived from long-excited state lifetime of lanthanide ions. If surfaces are passivated, if spacers are used to separate layers, or if solvents are chosen to protect the structure, the emission efficiency rises. This shows that excited-state control is not only internal but also external, shaped by the environment. Another method is to change the chemical groups or structures in the material (**Figure 2.2b**).^[22] If functional groups are added or removed, the number and position of excited states can be shifted. When excited levels are centralized, electrons can move in and out faster, and this lowers the amount of energy needed for lasing. If molecules can twist or change shape under certain conditions, different excited states appear. That allows the system to move between them and makes the emission tunable across a wide range. This method shows that chemical design is not only about stability but also about shaping the excited state map. Another useful method is the use of external stimuli controls (**Figure 2.2c**).^[19] If temperature changes, the population of states can move from one level to another. If electric fields or strain are applied, the binding of excitons or the gap between states can shift. These changes directly affect how easy it is to reach inversion and how broad the emission becomes. Even simple changes in the way the material is excited, such as adjusting the pulse length, the pump power, or the excitation wavelength, can lead to large differences in emission color and lifetime. This means that control of the light source itself is a way to tune excited states without touching the material chemistry. A conventional method is time control at the ultrafast scale (**Figure**

2.2d).^[18<, >21] Carriers often relax through hot-phonon effects, band filling, or recombination. These are processes that happen in femtoseconds to nanoseconds. If such steps are slowed or sped up, the number of carriers available for emission changes. For example, if cooling is delayed, a non-equilibrium carrier pool stays longer, which helps light amplification. If recombination channels such as Auger or exciton-exciton annihilation is reduced, the emission can last longer and be stronger. So, the key is to manage how fast carriers leave or stay in excited states.

All these methods demonstrate that the focus is on the ways to manage transitions and lifetimes rather than only on finding a new type of material. Chemical changes, external inputs, ultrafast timing, and environmental design all give different paths to guide excited states and non-stationary processes. Each path is simple to describe but powerful in practice, because it allows us to move from fixed optical properties to flexible and tunable ones.

2.1.2 External Cavity Modulation

The introduction of an external optical cavity is one of the most effective strategies for controlling the mode behavior of semiconductor lasers.^[23-25] Both recent reports on quantum well and quantum dot gain chips in external cavities and earlier reviews of grating-coupled quantum dot devices emphasize that the cavity does much more than extend the optical path. It provides a flexible platform for mode selection, linewidth narrowing, wavelength tuning, and overall stability.

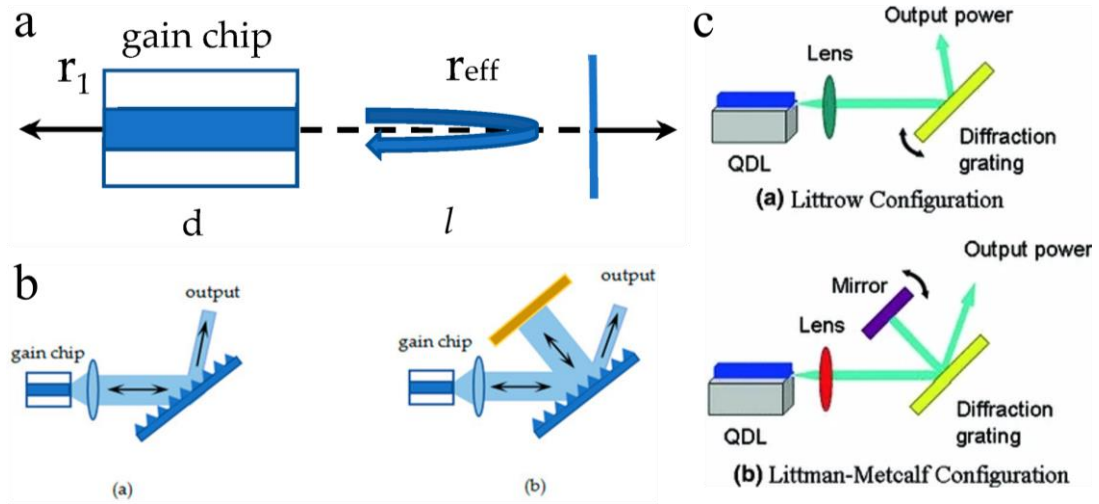


Figure 2.3 **a)** The basic structure of external cavity semiconductor laser. **b-c)** External cavity semiconductor configurations with diffraction grating. Littrow configuration and Littman configuration.^[23<, >25]

The central role of the external cavity is to enforce spectral purity.^[23<, >25-26] Free-running diode lasers typically exhibit multiple longitudinal modes and relatively broad linewidths. By adding an external resonator that incorporates mirrors, gratings, or filters, one can feed light back into the gain medium in a highly selective way. This suppresses unwanted Fabry-Perot modes from the internal chip cavity and supports single-mode operation. **Figure 2.3a** study shows that linewidths can be reduced to the kilohertz level with appropriate cavity design, while **Figure 2.3b and c** highlights the Littrow and Littman-Metcalf grating configurations as standard solutions for narrowing linewidth and enforcing stable single-frequency output. A second major significance is tunable emission across wide ranges. Internal cavities of semiconductor chips offer only limited wavelength flexibility. In contrast, when a grating or tunable filter is placed in the external cavity, the output wavelength can be adjusted continuously by changing the

grating angle or filter position. Quantum dot devices benefit further from their inhomogeneous size distribution, which naturally broadens the gain spectrum;^[26] combined with cavity feedback, this enables very wide, mode-hop-free tuning ranges. Reports describe tunability exceeding 40 nm with stable output, and reviews stress that external cavities routinely allow single-mode emission over large spectral windows.

A third contribution is the improvement of threshold and efficiency characteristics. The external cavity not only determines which mode lases but also modifies how efficiently the gain medium is used. By increasing effective feedback and coupling ground and excited states in quantum dots, threshold currents can be reduced, and slope efficiencies improved. These improvements are consistently observed in quantum dot external cavity lasers compared with quantum well systems, underscoring the synergy between gain medium properties and cavity design. Another important aspect is mode stability and suppression of mode hopping. Without external control, semiconductor lasers are prone to abrupt changes in lasing wavelength due to thermal drift or injection fluctuations. The external cavity, with carefully chosen feedback elements, can stabilize emission and suppress these unwanted jumps. This stability is vital in applications like high-resolution spectroscopy and coherent communication, where long-term frequency control is essential. Finally, the external cavity concept supports new functional architectures. Dual-wavelength configurations, integration with etalons or interference filters, and retro-reflective designs all expand the scope of possible outputs. Such architecture allows devices to operate simultaneously at two stable wavelengths, to deliver terahertz difference-frequency signals, or to provide agile sources for optical

sensing. The literature shows that by modifying the external cavity components, a single gain chip can serve diverse roles without fundamental re-design. In summary, across both contemporary and earlier studies, the external cavity emerges as the key enabler of practical semiconductor lasers with narrow linewidth, broad tunability, reduced threshold, and enhanced stability. It transforms basic diode structures into precision photonic sources suitable for advanced scientific and industrial applications.

2.2 Novel Optical Gain Materials: Properties and Prospects for Lasing Modulation

2.2.1 Organic Semiconductor Materials (OSCs)

Organic lasers are increasingly studied as candidates for compact, flexible, and versatile light sources, and a central research goal has been the achievement of reliable wavelength tunability.^[3<, >27-30] Related literatures demonstrate that tunability in organic systems is strongly influenced by how optical feedback is engineered in the cavity and by how responsive media such as liquid crystals are used to provide spectral control. Two distinct perspectives can be drawn from recent reports, one emphasizing cavity design in solid organic systems and the other highlighting the role of photonic regulation in cholesteric liquid crystal resonators. In solid-state organic lasers the wavelength of emission is primarily governed by the structure of the resonator. Organic semiconductors incorporated into Fabry-Pérot cavities rely on the distance between reflective facets to select lasing modes. When crystalline organic microstructures serve as both gain medium and resonator, the crystal length and orientation define the

feedback conditions. Periodic feedback structures such as distributed Bragg reflectors and distributed feedback gratings provide another approach, where the periodicity of the lattice determines the spectral region of amplification. Micro-resonators that support whispering-gallery modes, including disks, rings, and rods, allow light to circulate along curved interfaces and select specific modes according to the diameter and refractive index. In each of these cases, control of geometry provides a direct way to tailor the lasing wavelength, and in practice researchers have demonstrated wide spectral coverage by fabricating microcavities of different sizes or by incorporating gratings with varied periods.^[31-33] Organic chemistry also plays a role, as changes in molecular design alter the gain bandwidth and therefore the spectral window available to the cavity.

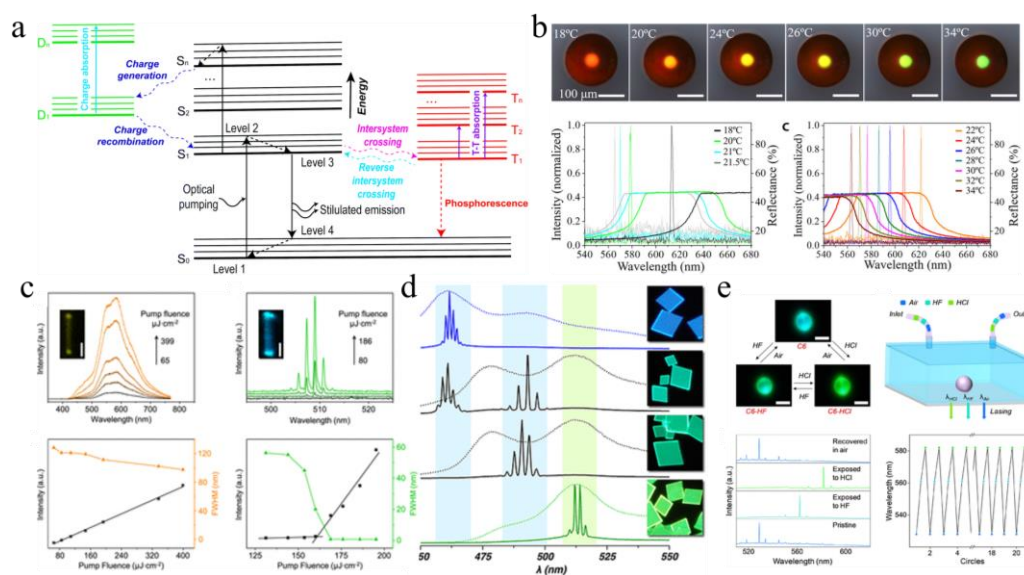


Figure 2.4 **a)** Energy level diagram of an organic semiconductor, showing dynamic energy transfer. **b)** Temperature-dependent lasing spectra based on liquid-crystal. **c)** Molecular self-assembly driven tunable lasing. **d)** FRET-based tunable organic lasing. **e)** Proton-controlled organic microlaser switch.^[34, 27-30]

In cholesteric liquid crystal systems, the approach to wavelength control relies on the intrinsic periodic order of the helical phase.^[29<, >34-35] Cholesteric structures possess a photonic stop band that reflects light within a certain spectral window. When the material is doped with a gain dye, lasing occurs at the edge of this stop band. The position of the bandgap is directly tied to the pitch of the helical structure, and the pitch can be altered by external parameters such as temperature or the incorporation of chiral dopants. By modestly changing these conditions, researchers have achieved smooth spectral shifts of the lasing wavelength. Encapsulation of cholesteric liquid crystals into core-shell capsules has further expanded this strategy. The inner aqueous shell promotes molecular alignment and enhances stability, while the outer elastic shell preserves the capsule in air and allows mechanical or chemical manipulation. These capsules act as reconfigurable micro-lasers that not only maintain omnidirectional emission but also provide continuous and stable tunability across a useful spectral range. The structural flexibility of the liquid crystal phase combined with the microfluidic fabrication of capsules creates a pathway toward robust devices that can be tuned in situ.

2.2.2 Metal Halide Perovskites (MHPs)

Perovskite lasers reach wavelength control through two linked levers: gain-spectrum engineering and resonator engineering by composition regulation and dimensional engineering.^[36-42] The gain spectrum shifts when halide composition, dimensionality, or excitonic coupling changes. The resonator selects one or a few optical modes from that spectrum. Broad tuning begins at the material level. Mixed-halide alloys in single-crystal nanowires (CsPbX_3 , $\text{X} = \text{Cl/Br/I}$) move the bandgap across green to red by exchanging or fractionally mixing halides; nanowire geometry supplies natural Fabry-Pérot (FP) feedback along the axis, so the emission wavelength follows the alloyed band edge while the longitudinal mode index determines the exact line, which enables continuous sweeps by incremental composition and length control.^[41] Quasi-2D Ruddlesden-Popper perovskites introduce quantum and dielectric confinement that tighten excitons; adjusting the inorganic layer thickness and organic spacer modifies the exciton resonance, so the lasing line tracks layer count with modest cavity redesign. Perovskite quantum dots embedded in host matrices or liquid-crystal hosts extend this idea; by choosing dot size and halide composition, the gain window can be positioned, then a soft cavity chooses the lasing edge. In all these material routes, minimizing nonradiative loss and Auger gain clamping remains essential for stable tuning; improved crystal quality, stoichiometry control, and passivated surfaces raise photoluminescence quantum yield and keep thresholds low enough for dense wavelength sampling.

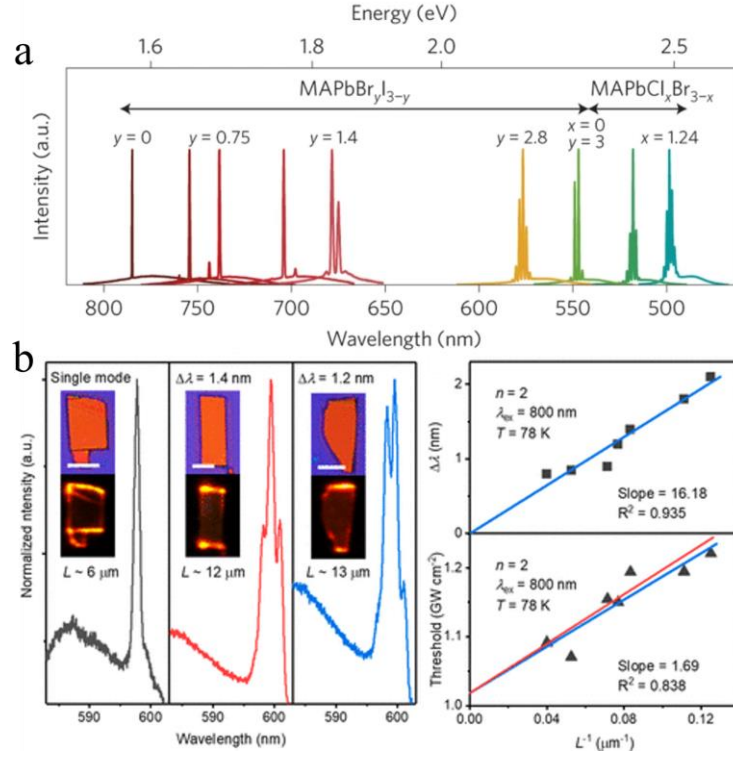


Figure 2.5 **a)** Composition-based perovskite lasing.^[42] **b)** Dimensional engineering for tunable lasers.^[36]

Resonator design then fixes spectral selectivity and fine tunability.^[38<, >43] FP cavities in micro- and nanostructures form the basic template. Straight nanowires behave as axial FP cavities with mirrorless end facets; changing length or refractive index adjusts longitudinal spacing and lets the lasing line ride on the moving gain edge during halide mixing. More complex FP geometries such as cube-corner pyramid cavities create longer effective paths and multi-pass trajectories, which narrow mode spacing and enable line selection near the gain maximum with small geometric tweaks; polished or high-index facets reduce scattering and stabilize single-mode output at room temperature. Whispering-gallery resonators (spheres, capillaries, disks) confine light azimuthally; diameter sets the free spectral range, so diameter arrays deliver discrete

color sets, while gentle radius changes or local index shifts move lines continuously around the band edge. Planar photonic crystals and distributed-feedback gratings add Bragg selectivity; lattice period or fill factor sets the Bragg wavelength, and small period variations or infiltration with index-tunable overlayers provide continuous pulls of several to tens of nanometers. Perovskite thin films patterned by nanoimprint or top-down lithography can host high-Q vertical cavities and photonic crystals; controlling stopband position, etch depth, and mirror phase makes the lasing wavelength follow a designed map across a chip, which supports dense wavelength grids and on-silicon integration. ^[44-45]Hybrid photonic environments provide another tunability handle. Dye-doped cholesteric or nematic liquid-crystal cavities already offer band-edge selection through helical pitch; replacing the dye with perovskite quantum dots or co-doping with perovskite nanocrystals couple perovskite gain to a thermally or electrically adjustable photonic stopband, so pitch variation moves the lasing line while the perovskite maintains high gain. In capsule or microfluidic geometries, shell elasticity and interfacial alignment stabilize planar ordering and allow reversible shape changes, which shift mode conditions without damaging the gain medium. Random or multiple-scattering resonators represent a complementary path; controlled disorder generates coherent loops with an effective path length that depends on scattering strength and boundary reflections. When random feedback is combined with FP enhancement or with energy-transfer networks, the dominant loop selects a narrow line within a broad perovskite gain window; tuning follows changes in scatterer density, correlation length, or interfacial reflectivity. Energy-transfer engineering adds spectral

steering without rebuilding the cavity; Förster or cavity-mediated transfer funnels excitation from a broadband donor network into a target perovskite domain whose emission peak is pre-set by composition, so modifying donor–acceptor ratio or spacing moves the lasing wavelength while preserving threshold. Continuous-wave operation and room-temperature single-mode behavior then rely on reducing modal loss and mode competition. High-Q designs, smooth sidewalls, low-loss mirrors, and defect control suppress parasitic modes while improved thermal paths limit index drift. With these measures, composition and cavity knobs act independently enough to map color across wide spans, from halide-driven bandgap shifts at the tens-of-nanometers scale down to cavity-driven steps at the sub-nanometer scale, enabling practical wavelength-agile perovskite laser platforms for integrated photonics and spectroscopy.

2.2.3 Lanthanide-doped Materials

Rare-earth-doped materials represent one of the most mature and reliable classes of optical gain media, with a long history in solid-state laser technology.^[46-55] Ions such as Nd^{3+} , Er^{3+} , and Yb^{3+} incorporated into crystalline or glass hosts provide sharp emission lines arising from well-defined 4f–4f electronic transitions. These transitions are shielded from the surrounding lattice by outer 5s and 5p electrons, granting remarkable spectral stability and minimal inhomogeneous broadening. As a result, rare-earth-doped systems can sustain highly coherent emission with narrow linewidths and excellent long-term reliability. The strengths of these materials also define their limitations. Because these optical transitions are fixed by atomic energy levels, their

emission wavelengths cannot be tuned over a broad range as in semiconductors or organic systems. Furthermore, the relatively low emission cross-sections of rare-earth ions necessitate longer gain lengths or high doping concentrations to achieve efficient lasing. At the same time, concentration quenching and upconversion processes can reduce efficiency at high dopant levels. These intrinsic restrictions mean that rare-earth-doped systems are less adaptable for applications requiring broad spectral tunability or ultrafast dynamic modulation.

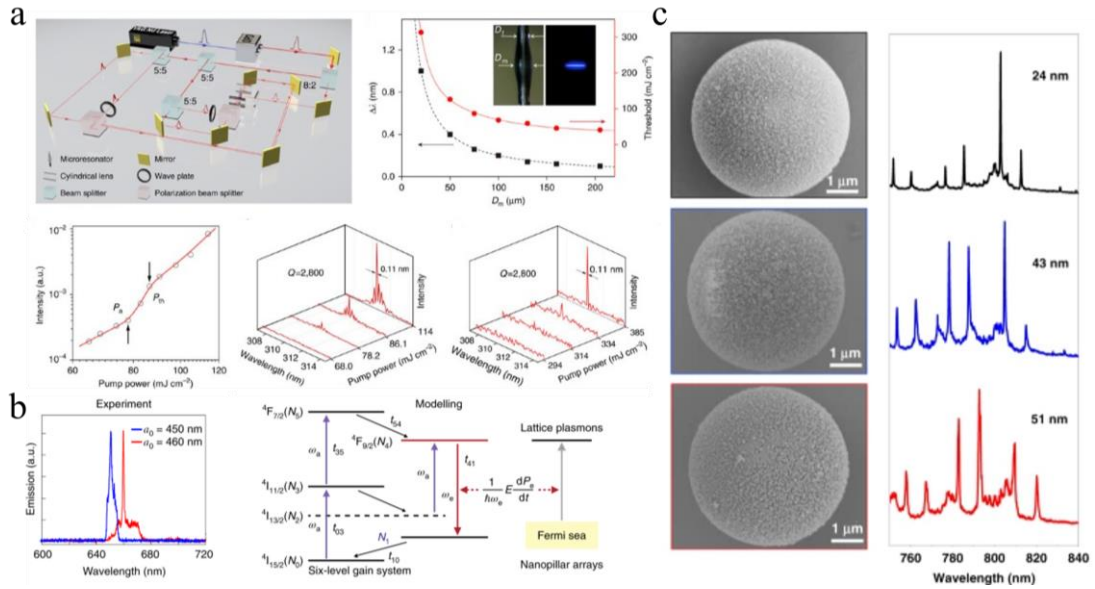


Figure 2.6 a) Optical set-up for the five-pulse excitation scheme and corresponding single-mode lasing spectra based on external cavity. b) Lasing spectra from different mode and six-level model systems describing upconverting nanolasing and the associated population inversion. c) Continuous-wave microsphere lasing with different radius.^[46-47, >50]

Despite these constraints, rare-earth-doped materials remain indispensable in contexts where stability, efficiency, and robustness are paramount. Their long excited-state lifetimes enable high-energy Q-switched and mode-locked lasers, making them

central to industrial machining, medical surgery, and telecommunications. When combined with external modulation techniques—such as acousto-optic tuning or cavity engineering—they can provide limited but valuable degrees of tunability without sacrificing reliability. This balance between inherent spectral rigidity and operational stability ensures that rare-earth-doped lasers continue to play a foundational role in the development of dynamically controlled laser systems.

2.2.4 Quantum Dots-based Materials

Quantum dots represent a highly versatile class of nanocrystalline semiconductors whose optical properties are dominated by quantum confinement effects.^[56-60] By tailoring the size and composition of QDs, researchers can achieve precise control of emission wavelengths across the visible and near-infrared spectrum. Their strong excitonic features, high photoluminescence quantum yields, and solution-based synthesis routes make them attractive for integration into diverse photonic architectures, from thin films to microcavities. These advantages have positioned QDs as one of the most flexible optical gain platforms for next-generation lasers. Despite these appealing characteristics, QD-based lasers face important challenges. Auger recombination, a non-radiative process that scales strongly with carrier density, limits the ability to achieve continuous-wave lasing at room temperature. In addition, surface states and incomplete passivation can lead to trap-assisted losses and spectral instability. Environmental sensitivity and thermal quenching further complicate device performance. Advances such as core-shell engineering, ligand modification, and

encapsulation techniques are actively addressing these limitations, extending the operational stability and efficiency of QD-based systems.^[61-67]

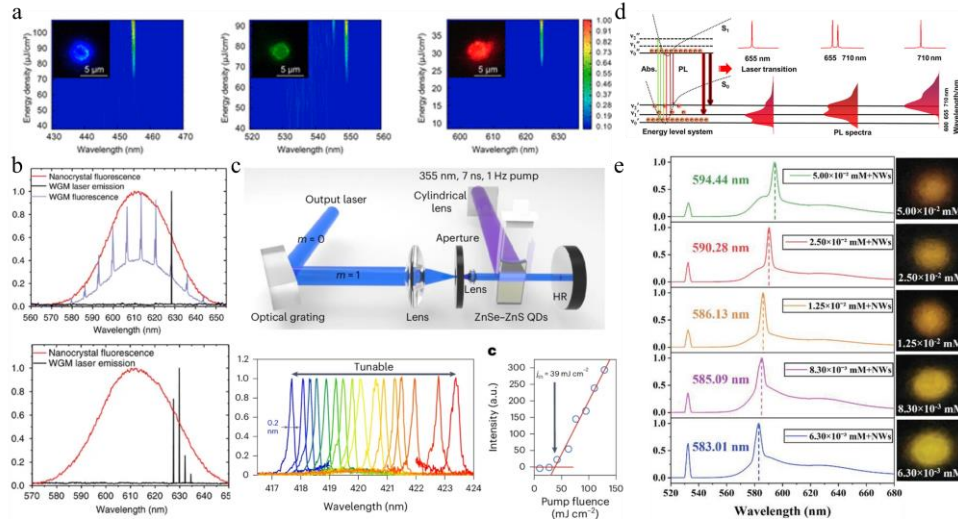


Figure 2.7 a) 2D pseudocolor plot of lasing emission spectra of blue to red CQDs. b) Single-mode lasing based on WGM microsphere. c) Tunable liquid lasing from a Littrow cavity. d-e) Concentration-dependent tunable CQDs lasing.^[22<, >57<, >60-62<, >66-69]

In terms of dynamic modulation, QDs offer unique opportunities. Their emission energy can be shifted by external electric fields, strain, or optical pumping intensity, while their nanoscale dimensions allow facile integration with photonic crystals, plasmonic resonators, and metasurfaces. This combination enables real-time tuning of wavelength, emission directionality, and coherence properties. By bridging intrinsic quantum-level control with extrinsic photonic engineering, quantum dots not only expand the functional versatility of laser devices but also provide a pathway toward compact and highly adaptive light sources suitable for applications in quantum information, sensing, and integrated photonics.

2.3 Summary and Outlook

The exploration of novel optical gain materials has revealed the richness and diversity of strategies for achieving dynamic lasing modulation. From organic semiconductors with their molecular flexibility, to perovskites with compositional tunability, to rare-earth ions offering spectral purity, and quantum dots enabling size-dependent emission, each class of material provides distinct advantages while facing inherent limitations. Two-dimensional materials further expand this landscape, adding atomically thin architectures and gate-tunable optical properties to the set of tools available for constructing reconfigurable lasers. Collectively, these studies confirm that the advancement of laser technology is inseparable from material innovation.

A unifying theme is the trade-off between adaptability and stability. Materials such as organics and perovskites excel at tunability but face durability concerns, whereas rare-earth-doped systems are exceptionally robust yet spectrally rigid. Quantum dots and 2D materials occupy an intermediate position, offering both tunability and compact integration potential but requiring solutions to overcome non-radiative losses and environmental degradation. These comparative insights suggest that future development will rely heavily on hybrid systems, where complementary properties of different materials can be combined to achieve balanced performance. Looking forward, two directions stand out for their strategic importance. First, rare-earth-doped gain media will continue to serve as foundational platforms due to their unmatched stability, efficiency, and suitability for high-power applications. Their role as “anchor materials”

ensures that dynamic modulation can be introduced without compromising robustness. Second, carbon quantum dots (CQDs) emerge as a promising frontier, combining solution-processability, low toxicity, and excitation-dependent emission. Their environmental stability and compatibility with large-scale fabrication give them advantages over traditional QDs, making them suitable candidates for sustainable and tunable photonic devices. Together, the established reliability of rare-earth systems and the emerging versatility of carbon-based nanomaterials point toward a future where laser platforms achieve both endurance and adaptability, aligning with the evolving demands of integrated photonics, sensing, and quantum technologies.

Chapter 3 Spatial Ln³⁺-enrichment in nanophases and kinetic pulse-compression on multiphoton upconversion pumping towards ultraviolet lasing glass-ceramics

3.1 Introduction

Ultraviolet (UV) light sources are in high demand for applications in photocatalysis, sterilization and biomedicine.[68-71] Multiphoton upconversion converting low-energy photons into high-energy photons in lanthanide (Ln) ions offers an attractive approach for achieving bright UV emission.[72-74] Compared to non-linear conversion[75] or wide-bandgap semiconductor[76] technologies, upconversion offers a pathway to cost-effective, compact and miniaturized UV devices. However, practical implementation has been hindered by a limited proportion of photons emitted in the UV range and resultant low emission intensity. This inefficiency arises because UV emissions from high-lying excited states of Ln³⁺ ions are significantly weakened by energy losses in intermediate excited states. These losses occur through multiple pathways, including radiative transitions, cross-relaxation (CR), multiphonon-assisted nonradiative decay, and energy migration to quenching centers.[77]

Fluoride glass-ceramics (GCs) containing Ln³⁺ doped nanocrystals exhibit significant potential as efficient NIR-to-UV upconversion luminescent materials due to their distinct advantages: i) low intrinsic absorption (or high transmittance) in the UV spectral range for reducing UV photon loss;[78] ii) high optical damage threshold for supporting high power excitation;[79] iii) low phonon energy and crystal field

environment for reducing non-radiative relaxation;[80] iv) easy large-scale preparation and processing into various laser resonators (e.g. fiber[81], microsphere[82], waveguide[83]). To achieve intense multiphoton upconversion emission in fluoride GCs, the key lies in constructing an efficient energy transfer (ET) mechanism to the high-lying excited states of Ln^{3+} ions. This requires precise control over the spatial distribution of Ln^{3+} ions to optimize energy migration pathways.

Besides optimizing the composition and structure of Ln^{3+} doped GC materials, another approach to manipulate upconversion behavior involves the external control of excitation dynamics. Specifically, population dynamics across excited states and targeted luminescence enhancement at desired wavelengths can be achieved through precise control of excitation laser parameters, including power density, frequency, pulse-width, pump scheme, two- or multi-wavelength pumping techniques.[84-86] For instance, recent experimental studies[87-90] have shown that pulse-width modulation enables effective color tuning of visible upconversion emissions in nanocrystals. However, extending this approach to high-order multiphoton upconversion for enhancing UV emissions remains underexplored. The underlying non-steady multiphoton upconversion mechanisms, which govern these processes, present both fundamental interest and technical challenges.

Herein, we combine MD simulations and experimental approaches to design transparent GCs containing solid-solution nanocrystals with tailored stoichiometric ratios. This enables precise control over the spatial distribution of Ln^{3+} ions.

Furthermore, by modulating the excitation pulse-width, we regulate the dynamics of upconversion processes, significantly enhancing UV emission intensity in Yb-Tm-Gd multiphoton upconversion systems. The non-steady upconversion mechanism is explained by using rate equation model combined with experiments. Finally, we demonstrate room-temperature, multiwavelength random lasing in the UV range, originating from Gd^{3+} ions.

3.2 Experimental Section

3.2.1 Fabrication of fluoroaluminate glasses and GCs.

Fluoroaluminate glasses and GCs were prepared by a conventional melting-quenching route and subsequent crystallization of heat-treatment method. In a typical experiment, raw materials of AlF_3 , CaF_2 , SrF_2 , BaF_2 , YbF_3 , TmF_3 , GdF_3 with analytical purity grade that were purchased from Aladdin were well mixed homogeneously and ground into powders with an automated agate mortar. Subsequently, the well-ground compounds were put into an alumina/platinum crucible and melted in 930 °C for 15 min and fell to 730 °C for 15 min. Then the melt was poured onto a 370 °C preheated brass mold and pressed with a preheated brass plate quickly. After that, the precursor glass was annealed in air at 400 °C for 2 h to release internal stress. Finally, the precursor glass was heat-treated at 450°C for 10 h and 490°C for 2 h to form abundant nanocrystals. Note that the above mentioned two-temperature melting and hot-pressing procure are important for controlling the viscosity of melt to form highly transparent precursor glass.

3.2.2 General Characterization

Differential scanning calorimetry (DSC) curves were carried out on a SDT Q600, from 50 to 800 °C. Raman spectra were recorded on a Raman Laser confocal Raman spectrometer (LabRAM HR Evolution made by Horiba Jobin Yvon) with the excitation of 532 nm laser. XRD measurement was performed on Shimadzu XRD-7000 with Cu-K α radiation. TEM, HRTEM and SAED analysis were performed on a FEI Tencai G2 F20 S-TWIN field emission transmission electron microscopy operating at an acceleration voltage of 200 KV. The transmittance spectra were recorded in UV-Vis spectrophotometer (Hitachi U-4100). Photoluminescence and decay curves were recorded on an FLSP920 spectrometer (Edinburgh Instrument Ltd., Livingston, UK) with excitation by a 980 nm laser diode and a was used to modulate the pump light.

3.2.3 Molecular dynamic simulation

The MD simulations of fluoroaluminate glass structures were carried out using the DL_POLY 2.20 software package[112] and the partially charged Teter potential modified by Cormack and Du.[113, 114] In the simulation, based on the high-temperature melt-rapid cooling method in the experiment, the substance is first heated to the highly disordered state at the time of melting, then maintained for a certain period of time, and finally gradually cooled (rapidly cooled) to room temperature to obtain the simulated structure of the glass.

The specific simulation process is: 1. Initial structure relaxation, that is, for the

initially created CONFIG file (with random atomic positions and a speed of 0), perform 60 ps (60,000 steps) calculations respectively under the regular ensemble (fixed number of particles N, volume V, temperature T, abbreviated as NVT) and the micro-regular ensemble (fixed number of particles N, volume V, energy E, abbreviated as NVE) at 0K and 0Pa to obtain a reasonable random initial structure. 2. Gradual heating process: The simulation system is gradually raised to 6000K in the ‘heating – holding’ process of 0K → 2000 K → 4000 K → 6000 K. Each round of heating and holding lasts for 60 ps. The holding process is to enable the system to reach thermal equilibrium at this temperature. 3. Gradual cooling process: The simulation system is gradually cooled to 300K in the "cooling - holding" process of 6000 K → 4000 K → 3000 K → 2500 K → 2000 K → 1500 K → 1000 K → 750 K → 500 K → 300 K. The duration of each round of cooling and holding is also set at 60 ps. 4. Final structural relaxation: At a temperature of 300K, the isothermal and isobaric ensemble (with a fixed number of particles N, pressure P, and temperature T, abbreviated as NPT) and the NVE ensemble were respectively operated for 60ps to achieve structural relaxation to the equilibrium state, thereby obtaining a more reasonable glass structure.

The bond angle distribution (BAD) function refers to the angle distribution formed by the central atom j and its two adjacent atoms i and k. Its calculation formula is:

$$a_{ijk}(\theta) = \frac{1}{N_a} \sum_{l=1}^{N_a} \delta(\theta - (\theta_{ijk})_l)$$

where N_a is the number of bond angles formed by all i-j-k atoms, and θ_{ijk} is the bond angle formed by i-j-k atoms.

3.3 Results and Discussions

3.3.1 Theoretical Analysis of the Spatial and Temporal Control of Multiphoton Upconversion Strategy

According to Forster-Dexter theory^[70], the dipole-dipole energy transfer rate W_{ET} decreases with the donor-acceptor distance (r), falling at a rate of $1/r^n$ ($n=6$ for resonant ET and $n=4$ for phonon-assisted ET). In fluoroaluminate glass, the distribution of doped Ln^{3+} ions is relatively random and homogenous. Owing to the necessary existence of many glass network former ions (Al^{3+}) and modifier ions (Ca^{2+} , Sr^{2+} , Ba^{2+}), the spatial distance among Ln^{3+} ions is relatively large, resulting in low W_{ET} . In addition, in the long-distance energy migration of Ln^{3+} ions, energy is readily transferred to the defects in glass which quench the luminescence. Thanks to the driving force provided by the glass heat-treatment, Ca^{2+} , Sr^{2+} , Ba^{2+} and Ln^{3+} can form solid solution nanocrystals with different stoichiometric ratio through a distance-limited ion migration, which can shorten the distance between Ln^{3+} ions and increase the W_{ET} . When the formed nanocrystal contains a higher content of Yb^{3+} ions, the spatial distance between Yb^{3+} - Yb^{3+} and Yb^{3+} - Ln^{3+} will decrease, thereby increasing the ET rate of Yb^{3+} - Ln^{3+} , which is conducive to the enhancement of multiphoton upconversion emission at UV range[92, 93] (**Figure 3.1a**). For example, to obtain UV emissions in Yb-Tm-Gd upconversion system, it is very important to increase the population of the $Tm^{3+}: ^1D_2$ state, which are achieved by cross-relaxation (CR) process ($^3F_{2,3} + ^3H_4 \rightarrow ^3H_6 + ^1D_2$) between two neighboring Tm^{3+} ions. The average Tm^{3+} - Tm^{3+} spatial distance in 0.07 mol% Tm^{3+}

ions doped fluoroaluminate glass, $\text{Sr}_{0.8}\text{Yb}_{0.2}\text{F}_{2.2}$ nanocrystal GC and $\text{Sr}_{0.2}\text{Yb}_{0.8}\text{F}_{2.8}$ nanocrystal GC are 42.70, 27.49 and 19.03 Å respectively (**Note S1**). Thus, the WET of CR process in nanocrystals can be enhanced (**Figure 3.1b**). Similarly, the WET of Yb^{3+} - Tm^{3+} and Tm^{3+} - Gd^{3+} ET processes can also be enhanced by their reduced spatial distance. Those enhanced ET would be beneficial for multiphoton upconversion emission at UV wavelength.

Shortening the spatial distance among Ln^{3+} ions increases the forward W_{ET} that plays important role in enhancing ETU process. However, it also enhances the back ET between activators and un-excited sensitizer ($\text{A1} \rightarrow \text{S2} \rightarrow \text{S1}$), the cross-relaxation between high-lying and low-lying states of activator A1 which can promote large population density in mid-lying states and slowly reach a steady-state plateau. In this process, the depopulation rate is mainly dependent on the population of A1 excited state and is gradually increased until it is equal to the population rate. When using conventional continuous-wave or long-pulse excitation with lower peak power, the multiphoton upconversion DUV emission is weak due to the low population in high-lying state. Through a short-pulse with high peak-power excitation, the population rate is always higher than the depopulation rate, and the fast rise process in high-lying state is stronger than the slow accumulation process in mid-lying state. Accordingly, the population in the high-lying state of A1 is largely increased. However, the population in the high-lying state of A1 are easily consumed through processes such as radiatively transitioning to mid-lying states or undergoing cross-relaxation with the population in the ground state. Therefore, an activator A2 with large energy gap can be introduced to

receive energy transfer from the high-lying state of A1. Due to the absence of mid-lying states in A2, the above consumption processes can be avoided, and thus the population in the high-lying state can be largely reserved which are responsible for emitting high-energy photons at UV wavelength (**Figure 3.1c**). We developed a rate equation model[94] for $\text{Yb}^{3+}\text{-Tm}^{3+}\text{-Gd}^{3+}$ upconversion kinetics using Python-assisted numerical simulations and parameter optimization (**Note S2**). Figure 1d presents the statistics of the integrated intensity of the population of the NT2, NT3, NT4, NT5 (Tm^{3+} : $^3\text{H}_4$, $^1\text{G}_4$, $^1\text{D}_2$ and $^1\text{I}_6$) and NG1 (Gd^{3+} : $^6\text{P}_j$) energy levels varying with pulse-width after the rate equation simulation. It can be observed that as the pulse width shortens and the peak power increases, the growth rate of the population in the high energy levels is much greater than that in the low energy levels.

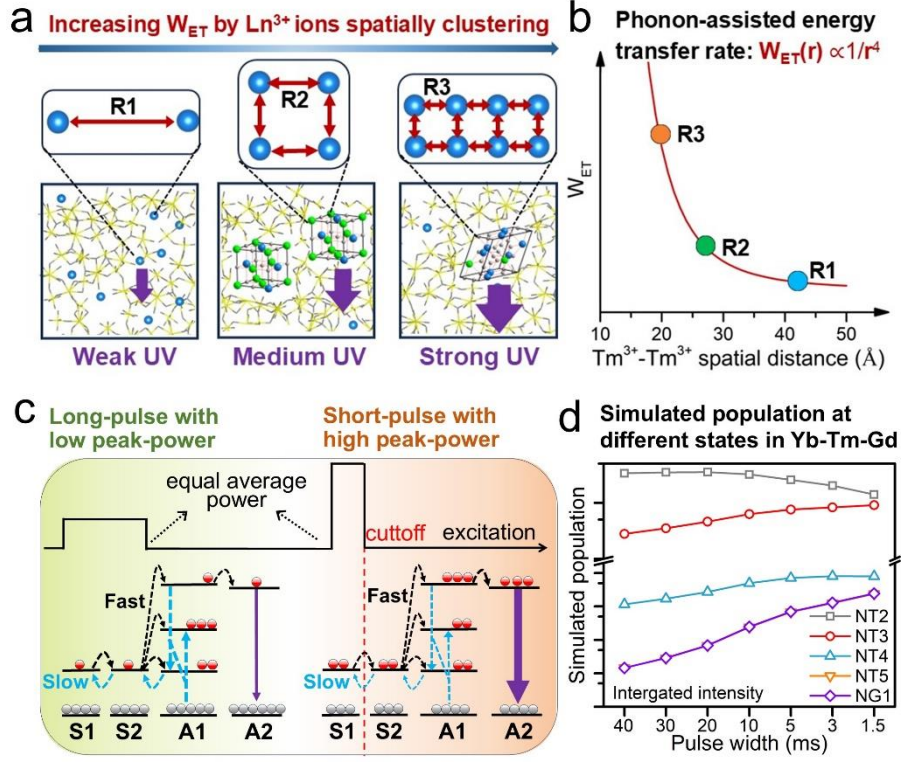


Figure 3.1 Schematic representation showing the spatial and temporal control of energy transfer in solid for multiphoton upconversion. **a** Spatially tuning Ln^{3+} ions distribution and ET in bulk solid by controllable precipitation of alloyed nanocrystals with varying (Ca, Sr, Ba)/Ln ratio. The enhancement of multiphoton upconversion can be achieved by increasing Ln^{3+} - Ln^{3+} average distance and ET rates. **b** The dependence of phonon-assisted energy transfer (cross-relaxation) rate W_{ET} on the average spatial distance r of Tm^{3+} - Tm^{3+} ions in glass, $Sr_{0.8}Yb_{0.2}F_{2.2}$ nanocrystal GC and $Sr_{0.2}Yb_{0.8}F_{2.8}$ nanocrystal GC. **c** Temporally tuning pulsed-width of excitation laser for increasing population in high-lying state of A1 and A2 ions. Note that the long-pulse has a lower peak power and the short-pulse has a higher peak power, but they have the same average power. S1 and S2 denote sensitizer Yb^{3+} that are far from and close to the activator, respectively. A1 and A2 denote activator Tm^{3+} with fast decay at high-lying state and activator Gd^{3+} with slow decay at high-lying state, respectively. **d** Simulated population of NT2, NT3, NT4, NT5 and NG1 with varied pulse durations.

3.3.2 Transparent Glass-Ceramic with Tunable Ln^{3+} ions Spatial Distance designed by Molecular Dynamic Simulation

To achieve DUV upconversion emission, desired crystalline phase with short Ln^{3+} - Ln^{3+} ions distance should be homogenously precipitated in DUV-transparent fluoroaluminate glass (**Figure 3.2**). For such purposes, the materials design approach through molecular dynamic (MD) simulation is utilized to ascertain the glass networks with cluster structural similar to target lattices.[95] Considering that high concentration of Yb^{3+} is required as sensitizer in high-order upconversion, Yb^{3+} is used to represent Ln^{3+} for the design of nanocrystal host. The simulated glasses have the following composition: $(30+x)\text{AlF}_3-(54-x)(\text{Ca}, \text{Sr}, \text{Ba})\text{F}_2-16\text{YbF}_3$ ($x = 0, 3, 6, 9$ and 12 , in mol %, named as G-30Al, G-33Al, G-36Al, G-39Al and G-42Al, respectively).

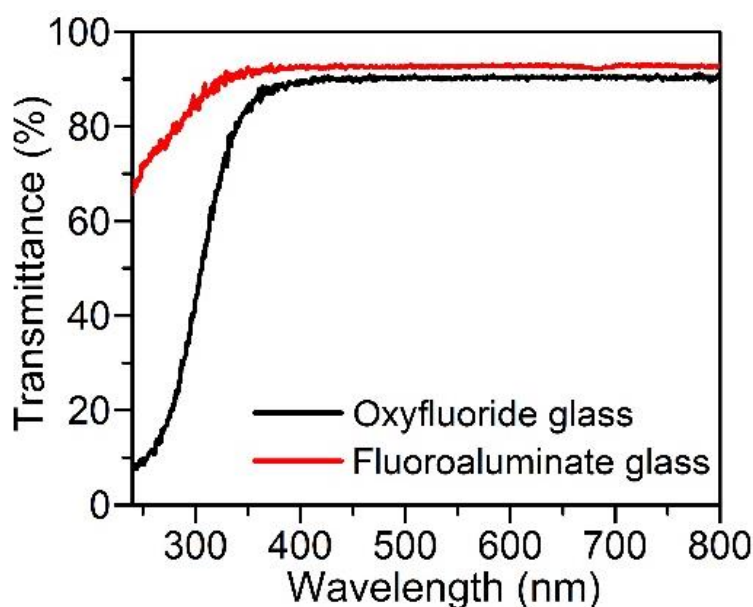


Figure 3.2 Transmittance curve of fluoroaluminate and oxyfluoride glasses.

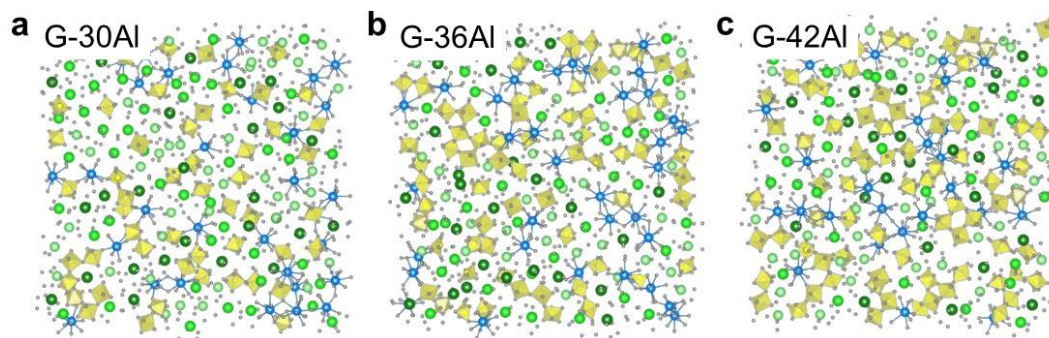


Figure 3.3 Snapshots of molecular dynamic simulation of (a) 30Al, (b) 36Al and (c) 42Al glasses.

From the molecular dynamic simulations (**Figure 3.3**), it showed the fluoroaluminate glass comprises a network of non-periodically linked $[AlF_6]$ and $[YbF_x]$ polyhedral with Ca^{2+} , Sr^{2+} and Ba^{2+} ions occupying irregular positions in space between the polyhedral, as described by Poulain's ionic glass model.[18] Bond angle distribution functions, pair distribution functions and coordination number for cation-cation pairs and cation-anion pairs were calculated (**Figure 3.4-8**) to reveal ion clustering behavior. The coordination number of Al is fixed to 6 originating from $[AlF_6]$ polyhedral, while other cations have mixed coordination number mainly ranging from 7 to 10. As the content of AlF_3 increases, Yb ions are distributed homogenously and surrounded by fewer alkali-earth (Ca^{2+} , Sr^{2+} , Ba^{2+}) ions (**Figure 3.5d; Figure 3.6**). That is, $xYbF_3-y(Ca, Sr, Ba)F_2$ cluster structure with increased x/y ratio were formed in glass. For G-33Al (**Figure 3.9a**), the glass network is relatively loosened, and the $[YbF_x]$ polyhedral are surrounded by nanoscale $(Ca, Sr, Ba)^{2+}$ cluster and interstitial fluoride ions. One can predict that such a cluster region (**Figure 3.9b**) can readily convert into $(Ca, Sr, Ba)_1-xYb_xF_{2+x}$ crystalline phase (**Figure 3.9c**) through atomic rearrangement during

experimental heat-treatment driven nucleation and crystal growth. Simultaneously, (Ca, Sr, Ba)F₂-AlF₃ solid solution nanocrystals with higher crystallization activation energy can be subsequently formed by the [AlF₆] polyhedral and [(Ca, Sr, Ba)Fm] polyhedral (**Figure 3.5**). For G-39Al (**Figure 3.9e**), the glass network is relatively compact, and the [YbF_x] polyhedral are surrounded by fewer (Ca, Sr, Ba)²⁺ ions (**Figure 3.9f**). The bond angle distribution statistic also indicates that the linkages of Yb-F-(Ca, Sr, Ba) and Yb-F-Yb are less in G-39Al (**Figure 3.9i** and **Figure 4**). Thus, it is reasonably predicted that the first crystallization phase of G-39Al glass would be Yb_{1-y}(Ca, Sr, Ba)_yF_{3-y}. Meanwhile, there are more [AlF₆] polyhedral in G-39Al glass, which can compete with [YbF_x] polyhedral as neighbors of [(Ca, Sr, Ba)Fm] polyhedral to form (Ca, Sr, Ba)F₂-AlF₃ nanocrystals as the second crystalline phase of the glass. Through the experiments of preparing corresponding glasses and GCs (**Figure 3.10**), the above inference is well approved on diverse crystallization procedures of the glasses. There are identified with high crystallinity of cubic fluorite-type (Ca, Sr, Ba)_{1-x}Yb_xF_{2+x} (~ 52.21%) and low crystallinity of (Ca, Sr, Ba)F₂-AlF₃ (~ 21.19%) precipitated in G-33Al glass via heat-treatment at 530°C for 2h (**Figure 3.9d** and **Figure 3.11**), while the crystallinity of tysonite-type Yb_{1-y}(Ca, Sr, Ba)_yF_{3-y} precipitation (~ 41.11%) and (Ca, Sr, Ba)F₂-AlF₃ precipitation (~ 34.97%) are comparable in G-39Al via heat-treatment at 550°C for 2h. As a mixed case, both (Ca, Sr, Ba)_{1-x}Yb_xF_{2+x} and Yb_{1-y}(Ca, Sr, Ba)_yF_{3-y} nanocrystals would be precipitated in the G-36Al sample. Therefore, (Ca, Sr, Ba)F₂-YbF₃ solid solution nanocrystals with different stoichiometric ratio, including cubic fluorite-type (Ca, Sr, Ba)F₂-YbF₃ and/or hexagonal tysonite-type Yb_{1-y}(Ca, Sr, Ba)_yF_{3-y}.

y nanocrystals in the glasses could be correlated and regulated with the chemical composition (**Figure 3.12**).

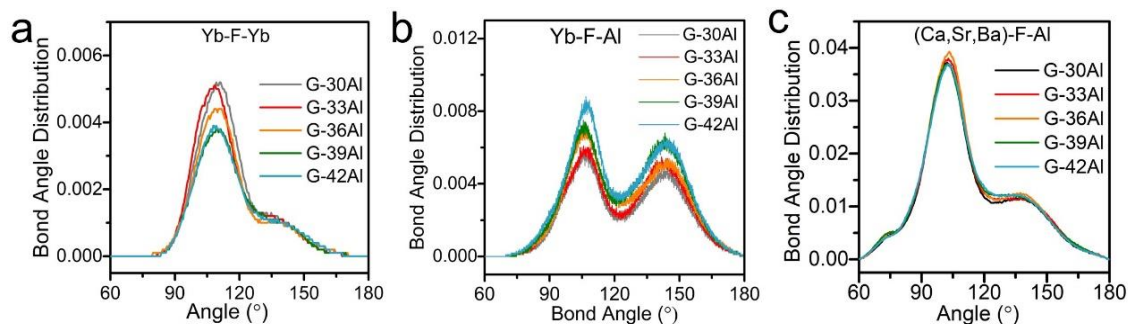


Figure 3.4 Bond angle distribution functions of (a) Yb-F-Yb, (b) Yb-F-Al and (c) (Ca, Sr, Ba)-F-Al in glasses with varied AlF₃ determined from the traditional MD simulation structure.

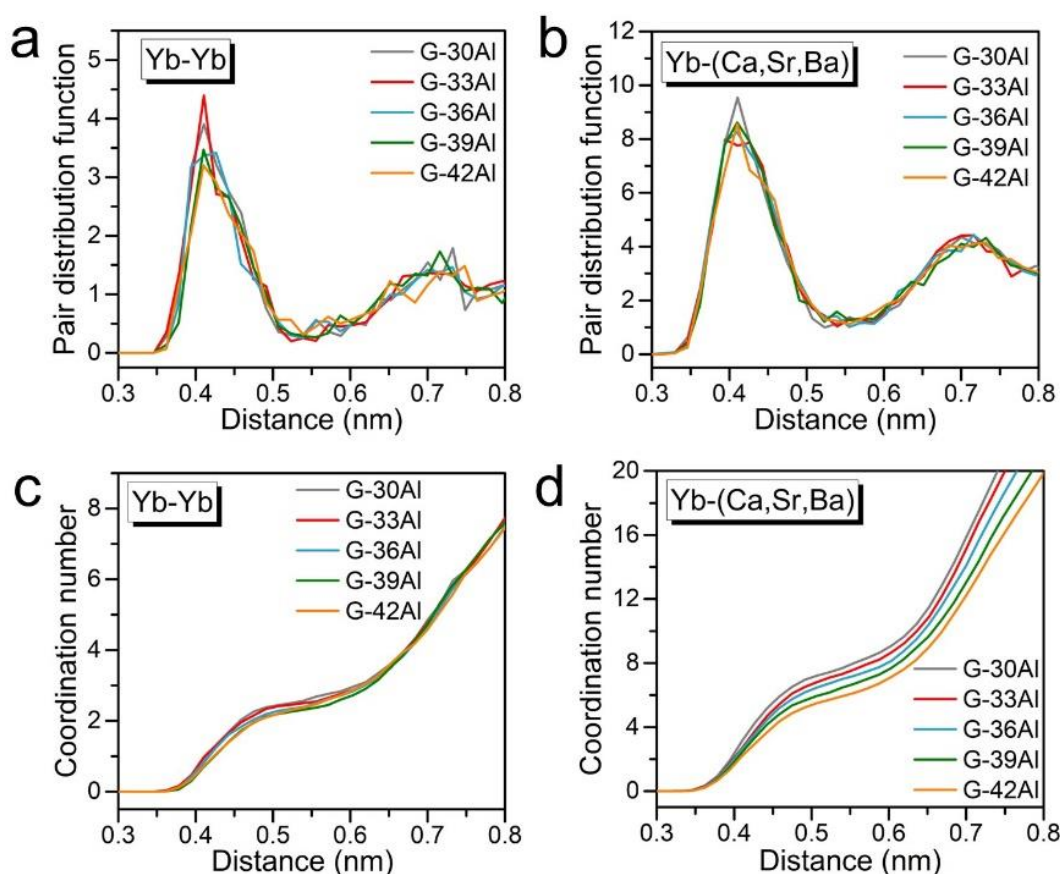


Figure 3.5 (a-b) Pair distribution functions and (c-d) coordination number curve of Yb-Yb and Yb-(Ca, Sr, Ba) in glasses with varied AlF₃ determined from the traditional MD simulation structure.

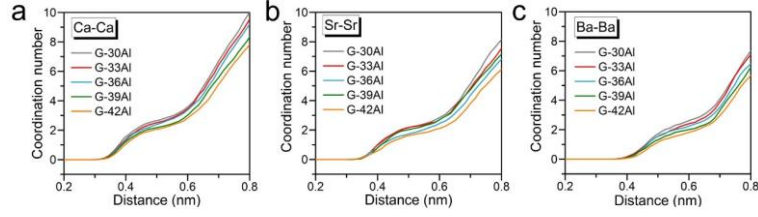


Figure 3.6 Coordination number curve of (a) Ca-Ca, (a) Sr-Sr and (c) Ba-Ba in glasses with varied AlF₃ determined from the traditional MD simulation structure.

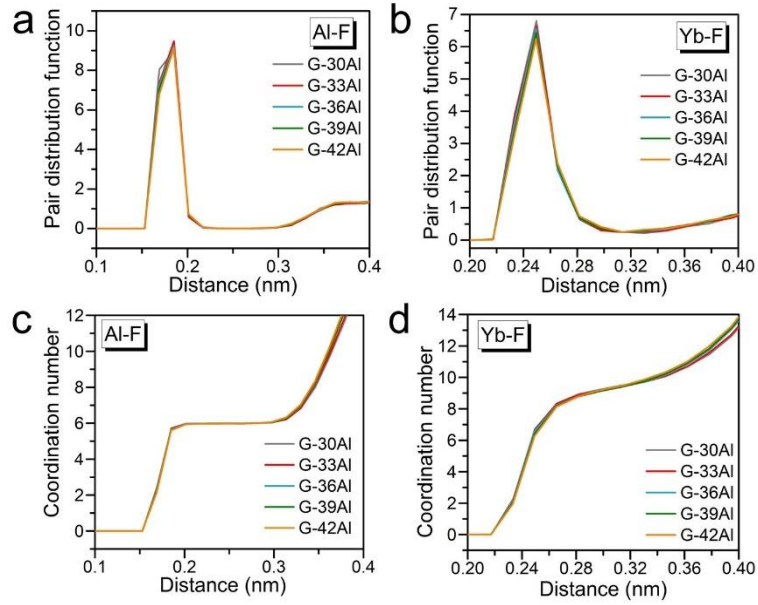


Figure 3.7 (a-b) Pair distribution functions and (c-d) coordination number curve of Al-F and Yb-F in glasses with varied AlF₃ determined from the traditional MD simulation structure.

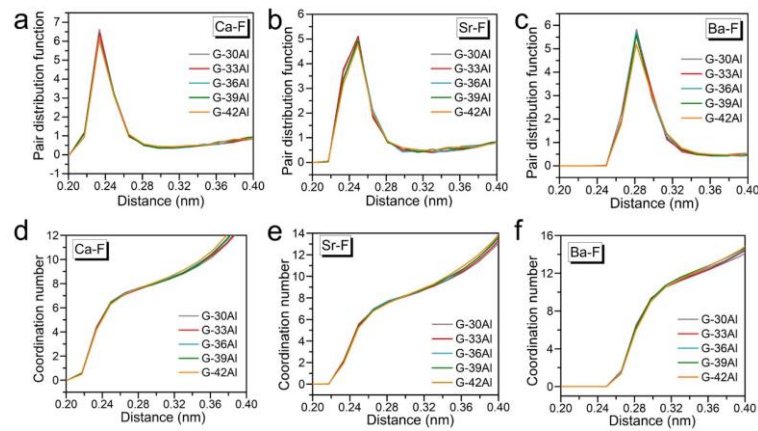


Figure 3.8 (a-c) Pair distribution functions and (d-f) coordination number curve of Ca-F, Sr-F and Ba-F in glasses with varied AlF₃ determined from the traditional MD simulation structure.

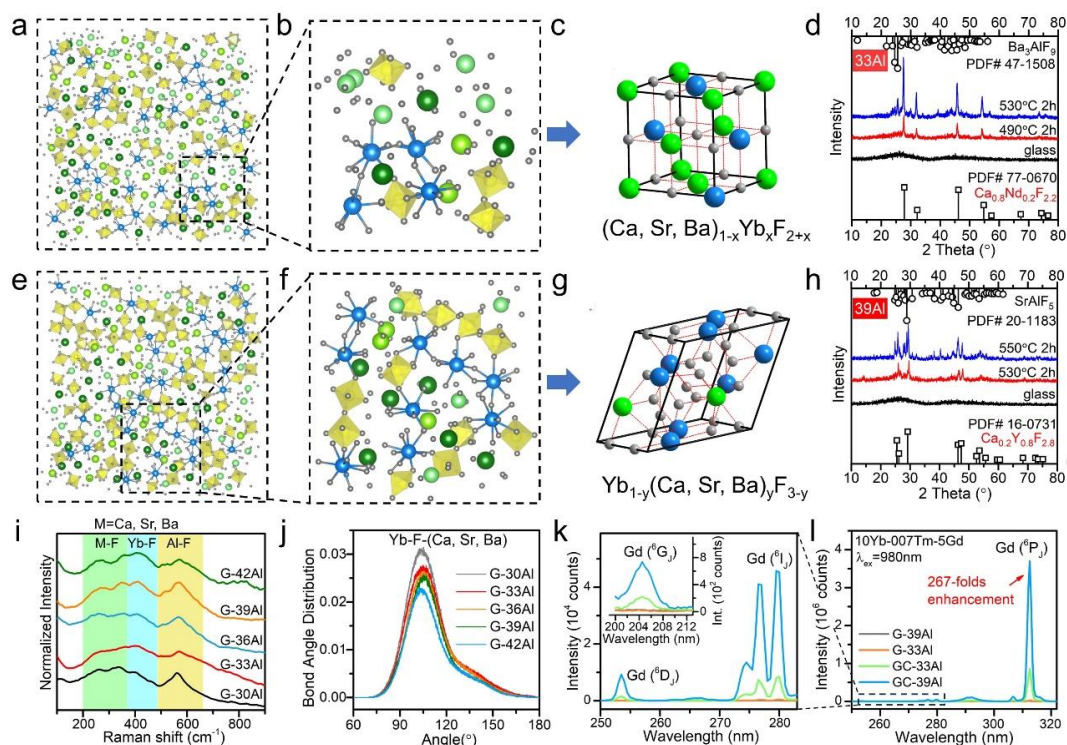


Figure 3.9 Structural design of the amorphous structure for precipitating alloyed nanocrystals with varying (Ca, Sr, Ba)/Yb ratio and enhancing multiphoton upconversion. a-e Snapshots of molecular dynamic simulation of a G-33Al and e G-39Al glasses, and the magnification of local structure of b G-33Al and f G-39Al glasses; the local structures possibly convert into crystalline phases of c $(\text{Ca, Sr, Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}$ and g $\text{Yb}_{1-y}(\text{Ca, Sr, Ba})_y\text{F}_{3-y}$; Ball: yellow, Al; green, Ca/Sr/Ba; blue: Yb; grey, F. XRD patterns of precursor glass and corresponding glass ceramics with different heat treatment condition for d G-33Al and h G-39Al. i Raman spectra of glasses with different Al. j Bond angle distribution of Yb-F-(Ca, Sr, Ba) in glasses with different Al determined from the simulation structure. k, l DUV upconversion emission spectra of G-33Al, GC-33Al, G-39Al and GC-39Al.

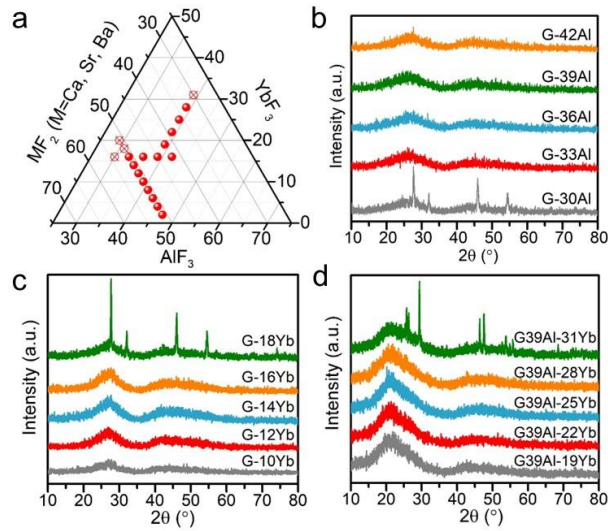


Figure 3.10 (a) Phase diagram of AlF_3 -(Ca, Sr, Ba) F_2 - YbF_3 glass; XRD curves of (b) G-(30+3x)Al, (c) G-zYb and (d) G39-(16+3y)Yb fluoroaluminate glasses.

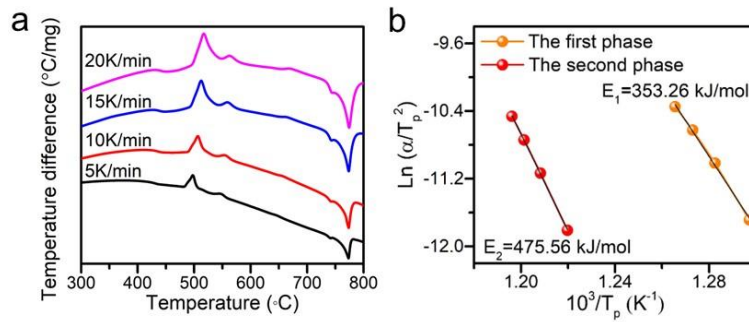


Figure 3.11 (a) Non-isothermal DSC curves of G-33Al glass run at different heating rates; (b) Determination of activation energy for two crystallization phases by using Ozawa's method.

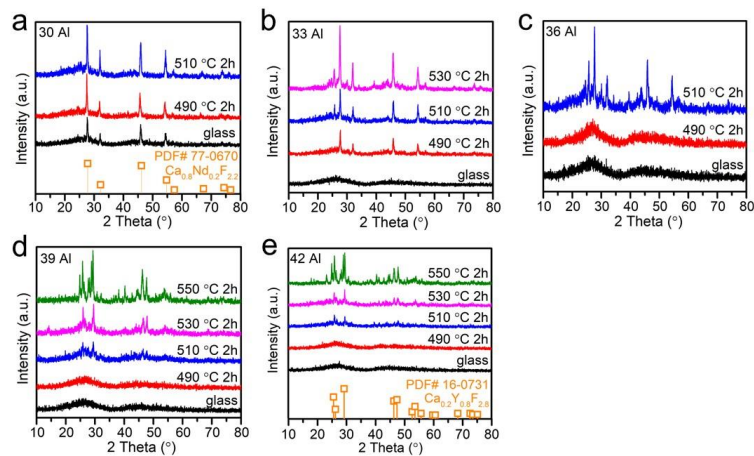


Figure 3.12 XRD patterns of fluoroaluminate glasses and glass ceramics containing with AlF_3 concentration of (a) 30, (b) 33, (c) 36, (d) 39 and (e) 42 mol%.

Hexagonal $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}$ nanocrystals, rather than cubic $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}$ nanocrystals, was then revealed as better host lattice for tri-doped $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Gd}^{3+}$ to get DUV upconversion emission. DUV upconversion emission spectra ranging from 200 to 320 nm of $10\text{Yb}^{3+}\text{-}0.07\text{Tm}^{3+}\text{-}5\text{Gd}^{3+}$ co-doped G-39Al, G-33Al, GC-33Al and GC-39Al excitation with a 980 nm laser diode were measured (**Figure 3.9k and l**). The spectra comprise characteristic emission peaks that can be assigned to ${}^6\text{G}_J$, ${}^6\text{D}_J$, ${}^6\text{I}_J$ and ${}^6\text{P}_J \rightarrow {}^8\text{S}_{7/2}$ (205, 253, 277 and 312 nm) transitions of Gd^{3+} , and ${}^1\text{I}_6 \rightarrow {}^3\text{H}_6$ (290 nm) transition of Tm^{3+} , respectively. (**Figure 3.13**) It was found that the overall upconverted DUV emission intensity has the following relationship: GC-39Al > GC33Al > G33Al > G39Al. The 312 nm emissions intensity of GC-39Al is around 267 folds higher than the precursor G-39Al (**Figure 3.9l**). The 205 nm emission originating from Gd^{3+} : ${}^6\text{G}_J \rightarrow {}^8\text{S}_{7/2}$ transition was reported to be a seven-photon upconversion emission.^[71] This emission rarely emerged in GC-39Al and GC-33Al (inset of **Figure 3.9k**), and it was observed in bulk material for the first time.

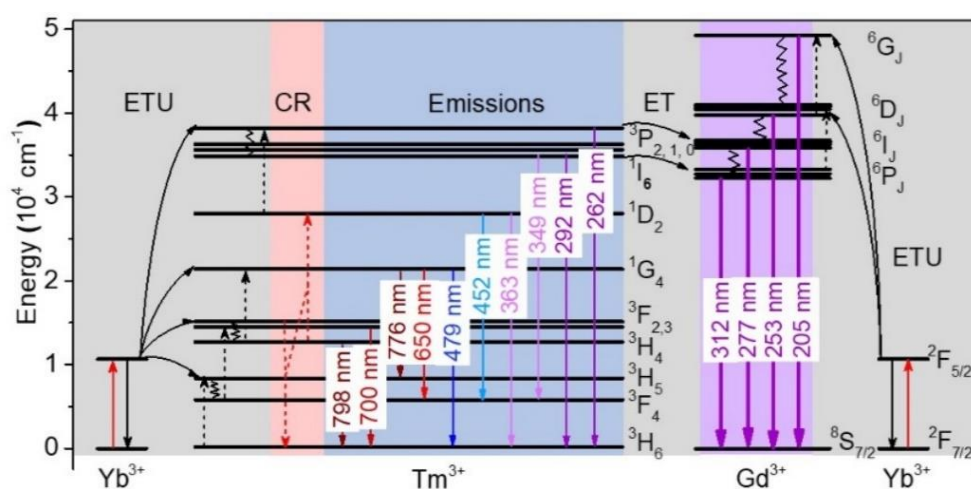


Figure 3.13 Energy level diagram of Yb-Tm-Gd system and possible seven-photon upconversion mechanism under 980 nm excitation.

3.4 Spatial Control of Multiphoton Upconversion for DUV enhancement

The doping system of $\text{Yb}^{3+}\text{-Ln}^{3+}\text{-Gd}^{3+}$ ($\text{Ln}^{3+}=\text{Tm}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$) and the doping concentration of Tm^{3+} and Gd^{3+} ions were optimized for matching energy level structure and reducing the concentration quenching effect, respectively. Firstly, $\text{Yb}^{3+}\text{-Tm}^{3+}$ ions has proven to be better sensitized couple for emitting DUV upconversion emission than $\text{Yb}^{3+}\text{-Ho}^{3+}$ or $\text{Yb}^{3+}\text{-Er}^{3+}$ sensitized couple in $\text{Yb}^{3+}\text{-Ln}^{3+}\text{-Gd}^{3+}$ doping systems (**Figure 3.14**). Secondly, Tm^{3+} concentration was optimized to be 0.07 mol% in 10Yb-xTm ($x=0.02, 0.05, 0.07, 0.10$ and 0.15 mol%) doped GCs (**Figure 3.15a** and **Figure 3.16**, **Note S3**). Such a high $\text{Yb}^{3+}/\text{Tm}^{3+}$ doping concentration ratio (~ 143) is conducive to the rapid energy migration among Yb-Yb and effectively improves the ETU rate of Yb-Tm. Thirdly, Gd^{3+} concentration was optimized to be 5 mol% in 10Yb-0.07Tm-yGd ($y=0, 3, 4, 5$ and 6 mol%) doped GCs (**Figure 3.15b** and **Figure 3.17**, **Note S4**). The excited states of Gd^{3+} have the advantage of long millisecond-level fluorescence lifetime (**Figure 3.18**) and can be used for the reservoir and emitter of DUV photons. Benefiting from the supersaturation effect^[72-74] of our designed GC material, the six-photon high-order upconversion of Gd^{3+} : 253 nm can be easily transformed into two-photon upconversion at high power, thereby significantly enhancing DUV emission.

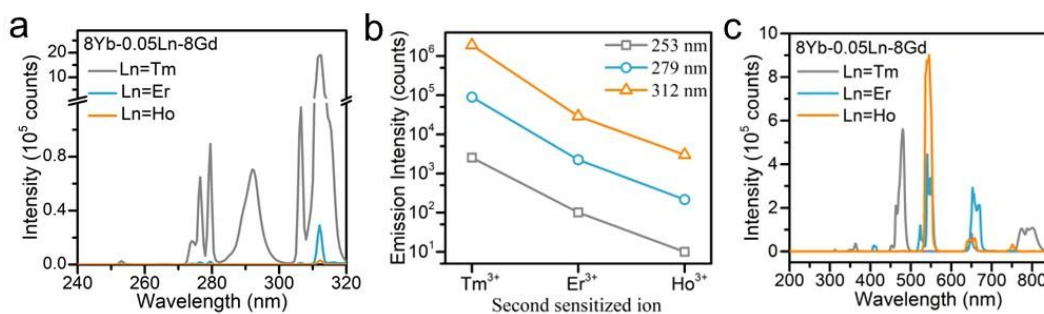


Figure 3.14(a) DUV upconversion emission spectra, (b) emission intensity at 312, 277 and 253 nm, (c) UV-VIS-NIR upconversion emission spectra of 8Yb - 0.05Ln - 8Gd ($\text{Ln}^{3+}=\text{Tm}^{3+}$, Er^{3+} , Ho^{3+}) codoped fluoroaluminate GCs containing $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Ln}^{3+}$, Gd^{3+} nanocrystals pumped by 980 nm.

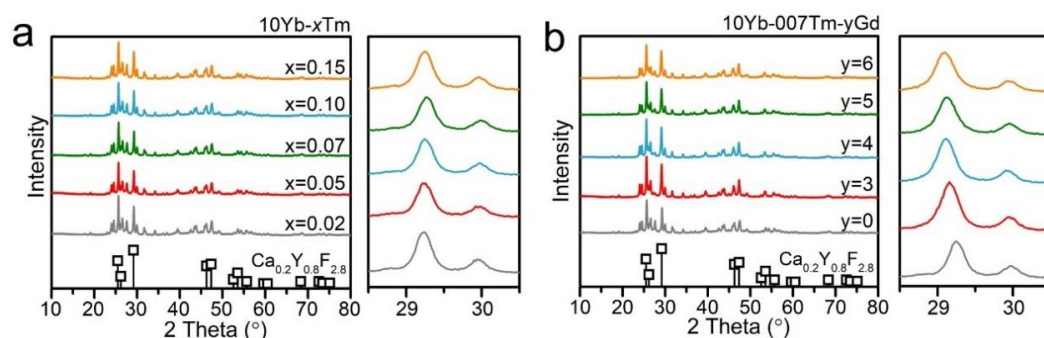


Figure 3.15 XRD patterns of (a) 10Yb - xTm ($x=0.02, 0.05, 0.07, 0.10, 0.15$ mol%) codoped GCs and (b) 10Yb-0.07Tm-yGd ($y=0, 3, 4, 5, 6$ mol%) co-doped GCs.

Note S3 Concentration optimization in Yb-Tm doped GC

To enhance the UV emission of Gd^{3+} ions, it is necessary to firstly pump more photons to the high-lying excited states of Tm^{3+} (above $^1\text{I}_6$ state). Due to the abundant excited states of Tm^{3+} , the concentration of Tm^{3+} plays an important role in the upconversion process of $\text{Yb}^{3+}\text{-Tm}^{3+}$. Therefore, 10Yb-xTm ($x=0, 0.02, 0.05, 0.07, 0.10, 0.15$ mol%) doped $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}$ GCs were prepared to study the UV upconversion luminescence performance. The $\text{Yb}^{3+}: ^2\text{F}_{5/2}$ can strongly absorb the light from near-infrared semiconductor lasers (**Figure 3.16**) and emit a relatively wide near-infrared emission peak (**Figure 3. 16b**). This energy can also be transferred to Tm^{3+}

through phonon assistance. With the increase of Tm^{3+} concentration, the energy transfer rates between Yb^{3+} and Tm^{3+} in both glasses and GCs keep increasing (**Figure 3. 16c**). Moreover, due to nano-crystallization, the spatial distance of Yb^{3+} - Tm^{3+} ions shortens in GCs, and the energy transfer rates in GCs are significantly higher than those in glasses. At the same Tm^{3+} concentration (0.1 mol%), the Yb-Tm energy transfer rate ($\sim 2000 \text{ s}^{-1}$) in $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}$ GCs is also higher than that in common fluorosilicate GC ($\sim 800 \text{ s}^{-1}$).

It can be seen that the emission intensity at 292 nm first increases and then decreases with the concentration of Tm^{3+} (**Figure 3. 16e**), which is a typical concentration quenching phenomenon. On the one hand, the average distance between Yb^{3+} and Tm^{3+} decreases with Tm^{3+} concentration increases, and their energy transfer rate increases, which will be conducive to the energy transfer upconversion to the high-lying excited state of Tm^{3+} . This is confirmed by that the rising edge of the time-dependent curve of 292 nm luminescence becomes steeper with the increase of Tm^{3+} concentration (inset in **Figure 3. 16e**). On the other hand, the increase in Tm^{3+} concentration can also cause cross-relaxation between the high-lying state and the ground state of Tm^{3+} or back energy transfer between Tm^{3+} and Yb^{3+} , which is manifested as faster decay at 292 nm.

It is worth noting that the critical concentration of Tm^{3+} in GC is only 0.07 mol%, which is much lower than that of other glasses and GCs. The corresponding concentration ratio of $\text{Yb}^{3+}/\text{Tm}^{3+}$ is approximately 143, which is much higher than that of other glasses and GCs. This is because the fluoroaluminate GC containing $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}$ nanocrystals we designed has a high Ln^{3+} doping concentration, crystallinity and Ln^{3+} ion enrichment degree. Therefore, the distance among Ln^{3+} ions is very short and the interaction is strong, which is conducive to the rapid energy migration of Yb^{3+} - Yb^{3+} and the ETU of Yb^{3+} - Tm^{3+} system. This low critical concentration of Tm^{3+} will be conducive to the rapid saturation of the intermediate state energy level of Tm^{3+} and the latter-mentioned supersaturation effect of Yb^{3+} - Tm^{3+} - Gd^{3+} upconversion emission under high-power excitation.

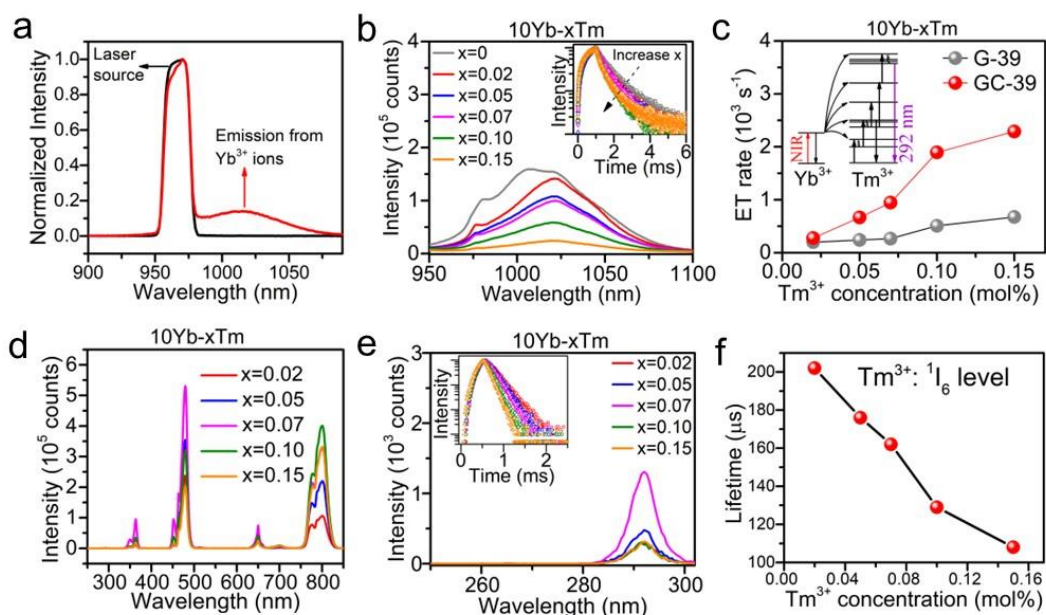


Figure 3.16 Effect of Tm^{3+} concentration on luminescent properties in 10Yb-xTm ($x=0.02$, 0.05 , 0.07 , 0.10 , 0.15 mol. %) co-doped GCs. (a) near-infrared emission spectra of blank and sample under 980 nm excitation; (b) NIR emission spectra of samples pumped by 940 nm, inset shows dynamic emission profiles of Yb^{3+} at around 1020 nm of samples pumped by 980 nm; (c) Calculated ET rate between Yb^{3+} and Tm^{3+} ions based on the measured Yb^{3+} lifetimes, inset shows the Yb-Tm energy level diagram and ET processes; (d) UC emission spectra; (e) Steady state and dynamic emission profiles of Tm^{3+} at 292 nm of Yb-Tm co-doped samples with different Tm^{3+} ions concentration pumped by 980 nm; (f) Dependence of lifetime of $\text{Tm}^{3+}: ^1\text{I}_6$ level with Tm^{3+} concentration.

Note S4 Concentration optimization in Yb-Tm-Gd doped GC

To determine the optimal doping concentration of Gd^{3+} , $10\text{Yb-}0.07\text{Tm-yGd}$ ($y=0$, 3 , 4 , 5 , 6 mol%) doped $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ GCs were prepared to study the UV upconversion emission performance (**Figure 3.17a**). It can be seen that the emission intensities of Gd^{3+} at 253 , 277 and 311 nm all increase firstly and then decrease with the concentration of Gd^{3+} , and the UV emission intensity is the highest at 5 mol%. The decrease in the upconversion emission intensity when the concentration of Gd^{3+} is

6 mol% may be caused by the back energy transfer between Gd^{3+} and Tm^{3+} . Under the excitation of 253 nm light that can only be absorbed by Gd^{3+} , the characteristic emission of Tm^{3+} at 345 and 363 nm was observed (**Figure 3.17b**), confirming the existence of energy transfer behavior between Gd^{3+} and Tm^{3+} .

The UV upconversion emission intensity in the 10Yb-0.07Tm-5Gd GC sample shows an interesting ‘supersaturation effect’ phenomenon. The double logarithmic function of the emission intensity of Gd^{3+} at 253, 277 and 311 nm and Tm^{3+} at 292 nm with the excitation power was measured (**Figure 3.17c**), where the slope n represents the number of photons required to generate emission at the corresponding wavelengths. Take the 253 nm luminescence of Gd^{3+} as an example. The n value is 5.54 at low power, while it drops to 1.65 at high power. This means that the 253 nm emission of Gd^{3+} is transformed from the inefficient six-photon upconversion mechanism to an efficient "similar to two-photon" upconversion mechanism. This supersaturation effect can be described as the following process: Fast energy migration occurs among high-concentration Yb^{3+} , and Yb^{3+} can continuously transfer energy to Tm^{3+} ; Low-concentration Tm^{3+} is easily excited to the excited states and saturates successively from bottom to top; Gd^{3+} also undergoes a similar supersaturation effect when receiving the energy transferred from the high-lying state of Tm^{3+} .

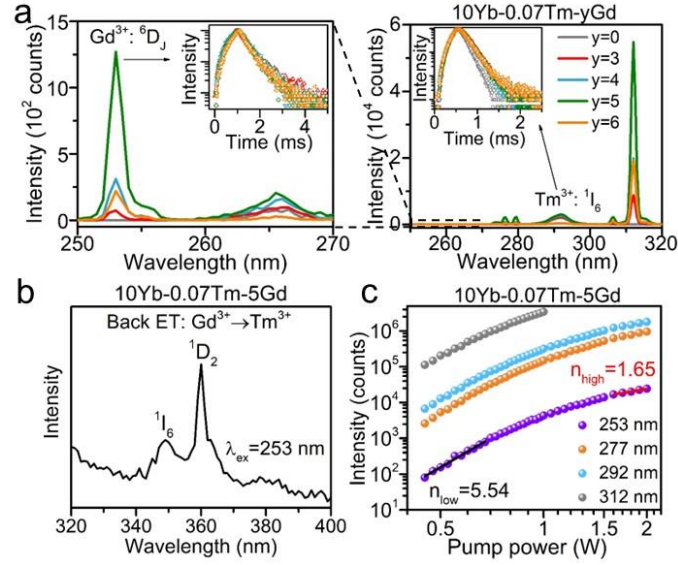


Figure 3.17 (a) Deep-UV emission spectra of Yb-Tm-Gd co-doped GCs with different Gd^{3+} ions concentration, inset show dynamic emission profiles of Tm^{3+} at 292 nm and Gd^{3+} at 253 nm respectively; (b) Emission spectrum of 10Yb-0.07Tm-5Gd co-doped GCs excited by 253 nm; (c) Pump power dependence of the upconverted Gd^{3+} emission at 253, 277, 292 and 312 nm in 10Yb-0.07Tm-5Gd co-doped GC sample.

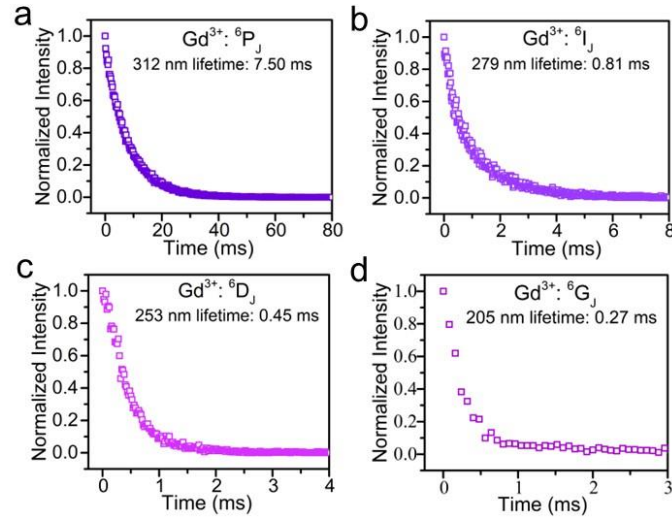


Figure 3.18 Decay curves of Gd^{3+} emissions at 312, 279, 253 and 205 nm of 10Yb-0.07Tm-5Gd co-doped samples. Note that the counts of 205 nm are less because the peak counts are set to a lower value for weak 205 nm emission intensity.

Note S5: The structures of 10Yb-0.07Tm-5Gd doped G-39Al, G-33Al samples and GC-33Al, GC-39Al samples were comparatively studied. The G-39Al and G-33Al samples present a typical "broad peak" of amorphous structure (**Figure 3.20**). The GC-33Al samples precipitated $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}:\text{Tm}, \text{Gd}$ crystal phases (**Figure 3.21**), whose peaks are matched well with the standard $\text{Ca}_{0.8}\text{Nd}_{0.2}\text{F}_{2.2}$ (PDF # 77-0670). It can be seen from the TEM image of GC-33Al (**Figure 3.21b**) that spherical or ellipsoidal $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}:\text{Tm}, \text{Gd}$ nanocrystals with diameters of 30-60 nm are distributed in the glass matrix. **Fig. S14c** shows the SAED image of the GC-33Al, with clear Laue diffraction spots appearing. The electron diffraction rings of obtained $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}:\text{Tm}, \text{Gd}$ nanocrystals show very good consistency with the (111), (220) and (311) crystal planes of $\text{Ca}_{0.65}\text{La}_{0.35}\text{F}_{2.35}$ nanocrystals. The high-resolution TEM (HR-TEM) image of a single $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}:\text{Tm}, \text{Gd}$ nanocrystal shows its lattice spacing is 0.327 nm (Fig. S14d). According to the standard PDF card (#87-0975), it corresponds to the (111) crystal plane of the $\text{Ca}_{0.65}\text{La}_{0.35}\text{F}_{2.35}$ cubic phase ($d_{111}=0.326$ nm).

The GC-39Al samples precipitated $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ crystal phases (Fig. S13a), whose peaks are matched well with the standard $\text{Ca}_{0.2}\text{Y}_{0.8}\text{F}_{2.8}$ (PDF # 16-0731). It can be seen from the TEM image of GC-39Al (**Figure 3.22b**) that rod-shaped $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ nanocrystals with diameters of 30-80 nm are distributed in the glass matrix. Fig. S15c shows the SAED image of the GC-39Al, with clear Laue diffraction spots appearing. The electron diffraction rings of obtained $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ nanocrystals show very good consistency with the (002), (110), (113)

and (302) crystal planes of $\text{Ca}_{0.2}\text{Y}_{0.8}\text{F}_{2.8}$ nanocrystals. The HR-TEM image of a single $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ nanocrystal shows its lattice spacing is 0.339 nm (**Figure 3.22d**). According to the standard PDF card (#16-0731), it corresponds to the (110) crystal plane of the $\text{Ca}_{0.2}\text{Y}_{0.8}\text{F}_{2.8}$ hexagonal phase ($d_{110}=0.340$ nm).

Spatial distance was then revealed as the main reason for enhancing the multiphoton upconversion emission by increasing the rates of energy transfer upconversion, cross-relaxation and energy transfer processes. $10\text{Yb}-0.07\text{Tm}-5\text{Gd}$ doped G-39Al, GC-39Al, GC-33Al and G-33Al were prepared for studying the effect of spatial distance on DUV upconversion emission. The amorphous structure of G-39Al and G-33Al are confirmed by XRD, TEM and SAED results (**Figure 3.19a**, **Figure 3.20**, **Figure 3.21a** and **Figure 3.22a**), indicating a homogenous distribution of the $\text{Yb}^{3+}\text{-Tm}^{3+}\text{-Gd}^{3+}$ ions with large spatial distance. Through heat-treatment, GC-33Al containing $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}:\text{Tm}, \text{Gd}$ nanocrystals (**Figure 3.19b**, **Figure 3.20** and **Figure 3.21b-d**) and GC-39Al containing $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}^{3+}, \text{Gd}^{3+}$ nanocrystals (**Figure 3.19**, **Figure 3.20** and **Figure 3.22b-d**) can be also obtained (**Note S5**), respectively, in which the $\text{Yb}^{3+}\text{-Tm}^{3+}\text{-Gd}^{3+}$ ions were enriched in corresponding nanocrystals. Due to the light scattering of formed nanocrystals in glass, the GC-33Al and GC-39Al are translucent (**Figure 3.23**). These results indicate that the spatial distance of $\text{Yb}^{3+}\text{-Tm}^{3+}\text{-Gd}^{3+}$ ions in glass can be well regulated by nano-crystallization and phase type transformation. According to Dexter theory, the resonant ET rate W_{DD} and the phonon-assisted ET rate W_{DA} are both inversely proportional to the exponent of $\text{Ln}^{3+}\text{-Ln}^{3+}$ distance r . After heat-treatment, the $\text{Yb}^{3+}\text{-Tm}^{3+}\text{-Gd}^{3+}$ ions are solutions to

form nanocrystals, which can shorten their spatial distance, helping to obtain higher WDD and WDA (**Figure 3.15d**). Moreover, compared with $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}$: Tm, Gd nanocrystals, there are less optical silent $(\text{Ca}, \text{Sr}, \text{Ba})^{2+}$ ions in $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}$: Tm, Gd nanocrystals that can increase ET rates among the Yb^{3+} - Tm^{3+} - Gd^{3+} ions. Therefore, superior DUV upconversion properties are obtained in GC-39Al containing $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}$: Tm, Gd nanocrystals. These results indicate that the spatial distance of Yb^{3+} - Tm^{3+} - Gd^{3+} ions in glass can be well regulated by nano-crystallization and phase type transformation. After heat-treatment, the Yb^{3+} - Tm^{3+} - Gd^{3+} ions are solution to form nanocrystals, which can shorten their spatial distance, helping to obtain higher W_{ET} . To confirm the enhanced ET through Ln^{3+} ions spatially clustering strategy, Yb doped sample and Yb-Tm co-doped samples were prepared to evaluate the W_{ET} of donor-accepter. The W_{ET} of Yb^{3+} -to- Tm^{3+} can be quantitatively calculated from the following equation:

$$W_{\text{ET}} = 1/\tau_{\text{Yb}} - 1/\tau_{\text{Yb-Tm}}$$

where τ_{Yb} and $\tau_{\text{Yb-Tm}}$ are measured decay lifetime of Yb^{3+} ions in Yb doped sample and Yb-Tm co-doped sample, as shown in **Figure 3.24**. The calculated W_{ET} of Yb^{3+} -to- Tm^{3+} for G-39Al, GC-33Al and GC-39Al are 352, 678 and 950 s^{-1} respectively, which are inversely correlated with their spatial distance.

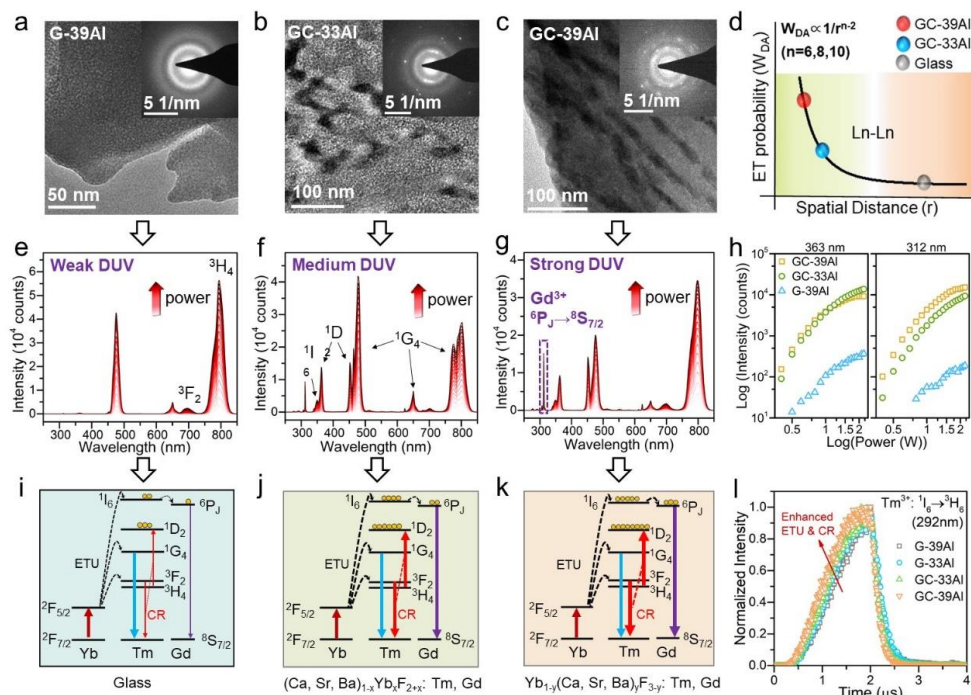


Figure 3.19 Probing the multiphoton upconversion process in Yb^{3+} - Tm^{3+} - Gd^{3+} co-doped transparent glass and translucent GCs with different spatial distribution. TEM and SAED images of a G-39Al, b GC-33Al and c GC-39Al. d The dependence of the measured energy transfer rate WET on the average spatial distance r of Yb^{3+} - Tm^{3+} ions based on measured decay lifetime of Yb^{3+} ions at 1020 nm in Yb doped samples and Yb-Tm co-doped samples. Upconversion emission spectra of e G-39Al, f GC-33Al and g GC-39Al under NIR excitation. h Pump power dependence of the upconverted Tm^{3+} emission at 363 nm and Gd^{3+} emission at 311 nm in G-39Al, GC-33Al and GC-39Al. Schematic representation of the partial energy level diagram for Yb^{3+} - Tm^{3+} - Gd^{3+} and upconversion scheme of in i glass, j $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}$: Tm, Gd and k $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}$: Tm, Gd nanocrystals. l Time-dependent evolution curves of Tm^{3+} emissions at 292 nm in G-39Al, GC-33Al and GC-39Al under pulsed excitation at 980 nm with a duration of 2 μs .

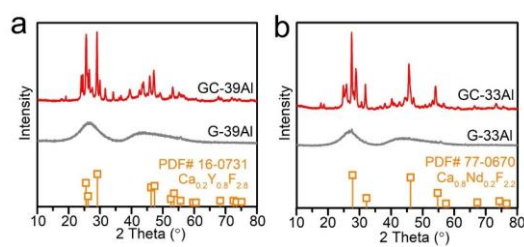


Figure 3.20 XRD patterns of (a) G-39Al, GC-39Al and (b) G-33Al, GC-33Al.

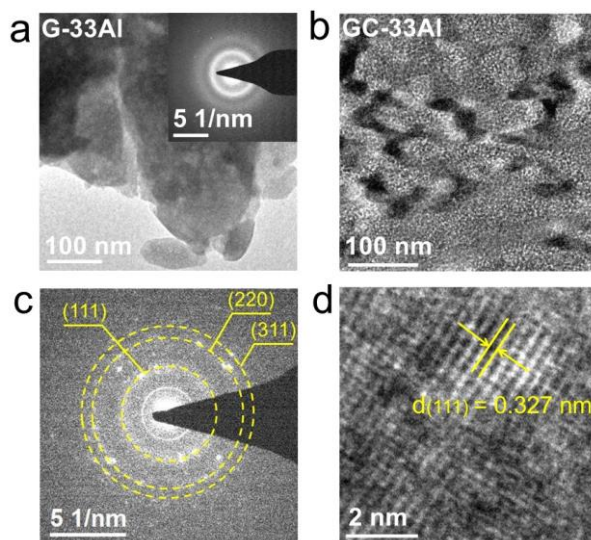


Figure 3.21 (a) TEM and SAED images of G-33Al, (b) TEM and (c) SAED images of G-33Al, (d) HR-TEM image of $(\text{Ca, Sr, Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}:\text{Tm, Gd}$ nanocrystals in GC-33Al.

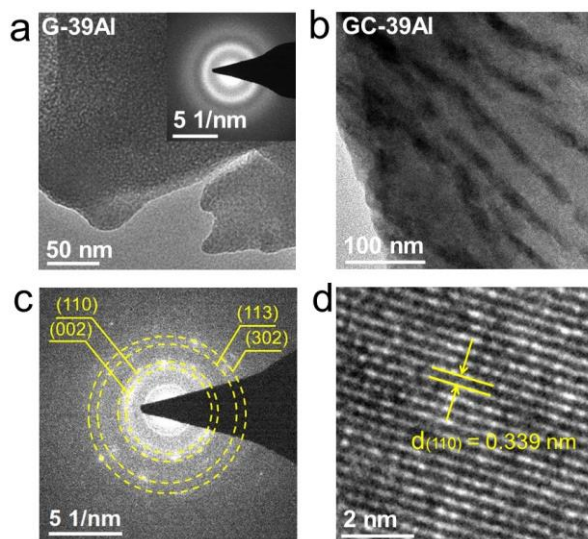


Figure 3.22 (a) TEM and SAED images of G-39Al, (b) TEM and (c) SAED images of GC-39Al, (d) HR-TEM image of $\text{Yb}_{1-y}(\text{Ca, Sr, Ba})_y\text{F}_{3-y}:\text{Tm, Gd}$ nanocrystals in GC-39Al.

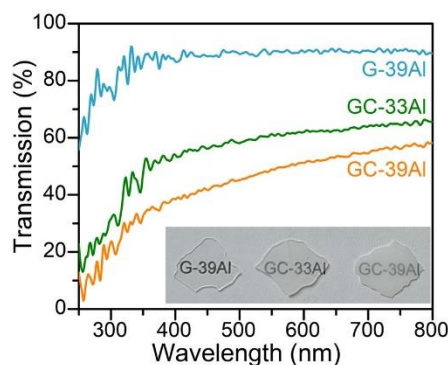


Figure 3.23 Transmission spectra of G-39Al, GC-33Al and GC-39Al samples, inset show the corresponding photos.

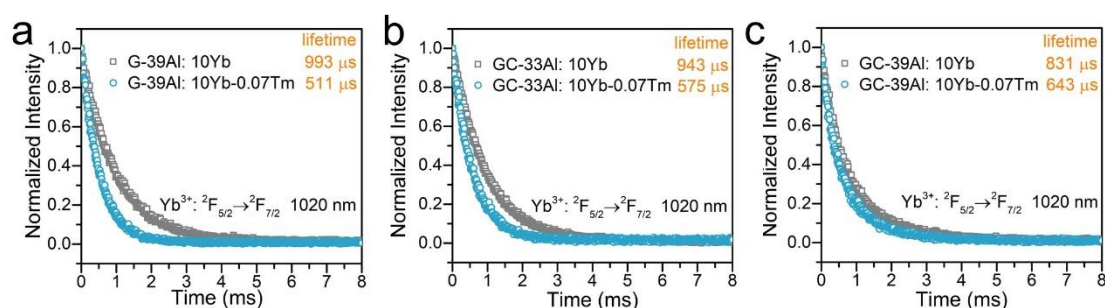


Figure 3.24 Decay curves at 1020 nm and lifetime for **a)** G-39Al: 10Yb and G-39Al: 10Yb-0.07Tm samples, **b)** GC-33Al: 10Yb and GC-33Al: 10Yb-0.07Tm samples, **c)** GC-39Al: 10Yb and GC-39Al: 10Yb-0.07Tm samples under 980 nm pulsed laser (100Hz, 1ms) excitation.

More specific ET processes can be deduced from the power-dependent (0.40 W to 2.20 W) UC emission spectra of G-39Al, GC-33Al and GC-39Al. In G-39Al sample (**Figure 3.19e**), the main emission peaks are emitted from Tm^{3+} : $^3\text{H}_4$ and $^1\text{G}_4$ levels by two-photon and three-photon UC respectively. However, higher order multiphoton UC emissions are notably weak even under high power NIR laser excitation. In GC-33Al sample (**Figure 3.19f**), more emission peaks at UV range can be obviously observed, which are emitted from Tm^{3+} : $^1\text{D}_2$ and $^1\text{I}_6$ levels by four-photon and five-photon UC respectively. Besides, the DUV emission at 312 nm from Gd^{3+} : $^6\text{P}_J \rightarrow ^8\text{S}_{7/2}$ transition is

significantly enhanced, but its intensity is lower than the emission intensity at 363 or 450 nm. In GC-39Al sample (**Figure 3.19g**), the strongest DUV emission intensity at 312 nm is found, and its intensity is higher than the emission intensity at 363 or 450 nm. The double-exponential plots of the upconversion emission intensity as a function of excitation power are shown in **Figure 3.19h**. Note that the $\text{Tm}^{3+}: {}^1\text{D}_2$ state cannot be populated directly by the energy transfer from excited Yb^{3+} ions, due to a large energy mismatch between $\text{Yb}^{3+}: {}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ and $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^1\text{D}_2$. Instead, the cross-relaxation process (${}^3\text{F}_{2,3} + {}^3\text{H}_4 \rightarrow {}^3\text{H}_6 + {}^1\text{D}_2$) between two neighboring Tm^{3+} ions may play significant role in populating the $\text{Tm}^{3+}: {}^1\text{D}_2$ state.^[75-77] Accordingly, the population of $\text{Tm}^{3+}: {}^1\text{D}_2$ state is highly dependent on the average distance between Tm^{3+} ions. In G-39Al, the large $\text{Tm}^{3+}\text{-Tm}^{3+}$ spatial distance (42.69 Å) and inefficient CR process would make it difficult to populate the $\text{Tm}^{3+}: {}^1\text{D}_2$ and higher states, leading to weak DUV emissions even in high-power excitation (**Figure 3.19i**). The nano-crystallization shortens the spatial distance between Tm^{3+} ions in GC-33Al and (27.49 Å) and GC-39Al (19.03 Å), which enable an efficient CR process and much stronger DUV emissions (**Figure 3.19j and k**). The rise slope of time-dependent curves (**Figure 3.19l**) for $\text{Tm}^{3+}: {}^1\text{I}_6$ state have the following order: GC-39Al > GC-33Al > G-33Al > G-39Al, which further confirms that the shortened $\text{Yb}^{3+}\text{-Tm}^{3+}$ ions spatial distance is conducive to higher population rate of high-lying state. Moreover, the distance between Tm^{3+} and Gd^{3+} ions in GC-39Al (4.59 Å) is lower than that in GC-33Al (6.63 Å), resulting in an enhanced ET between Tm^{3+} and Gd^{3+} ions and higher intensity ratio of 312 and 345 nm emissions.

Crystal structure and the maximum phonon energy of material may also contribute to the enhancement of DUV multiphoton upconversion emission in GC-39Al. The $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ nanocrystals possess hexagonal structure (space group 165, P-3c1), whereas the $(\text{Ca}, \text{Sr}, \text{Ba})_{1-x}\text{Yb}_x\text{F}_{2+x}:\text{Tm}, \text{Gd}$ nanocrystals have face-center cubic structure (space group 225, Fm-3m) with high-symmetry. The lower symmetry in hexagonal phase could facilitate the electronic 4f-4f transitions with parity selection rules and increase the radiative probability, which has been demonstrated in well-studied cubic and hexagonal NaYF_4 upconversion nanocrystals. The multi-phonon assisted non-radiative transition rate W_{MP} was given by

$$W_{\text{MP}}(T) = W_0 \left[\frac{\exp(\hbar\omega_i/kT)}{\exp(\frac{\hbar\omega_i}{kT}) - 1} \right]^{\Delta E/\hbar\omega}$$

where $\hbar\omega_i$ is the maximum phonon energy and ΔE is the energy gap. As shown in Raman spectra (**Figure 3.1h**), the maximum phonon energy of $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ nanocrystals ($\sim 400 \text{ cm}^{-1}$ of Yb-F bond) is lower than that of glass ($\sim 580 \text{ cm}^{-1}$ of Al-F bond). It enables a much lower multi-phonon assisted non-radiative transition rate especially for small energy gaps between excited states, which is beneficial for the population of high-lying states.

3.5 Temporal Control of Multiphoton Upconversion for DUV enhancement

DUV emission can be further enhanced through temporal control of multiphoton upconversion. **Figure 3.25a** displays the upconversion emission spectra of the $10\text{Yb}-0.07\text{Tm}-5\text{Gd}$ co-doped sample under 980 nm laser excitation. The excitation laser was modulated using a pulse generator (**Figure 3.26**) with a 20 Hz period and pulse-widths ranging from 40 ms to 0.5 ms, ensuring synchronized modulation of the 980 nm laser output. The average energy density was maintained at $2.55 \times 10^5 \text{ mJ} \cdot \text{cm}^{-2}$ across all

pulse-width conditions. With the transition from continuous waves to pulse width-adjustable incident light, the thermal effect weakens, leading to a gradual increase in multiphoton emission. **Figure 3.25b** shows the ratio of emission intensities corresponding to specific energy levels of Tm^{3+} and Gd^{3+} ions relative to the total emission intensity.

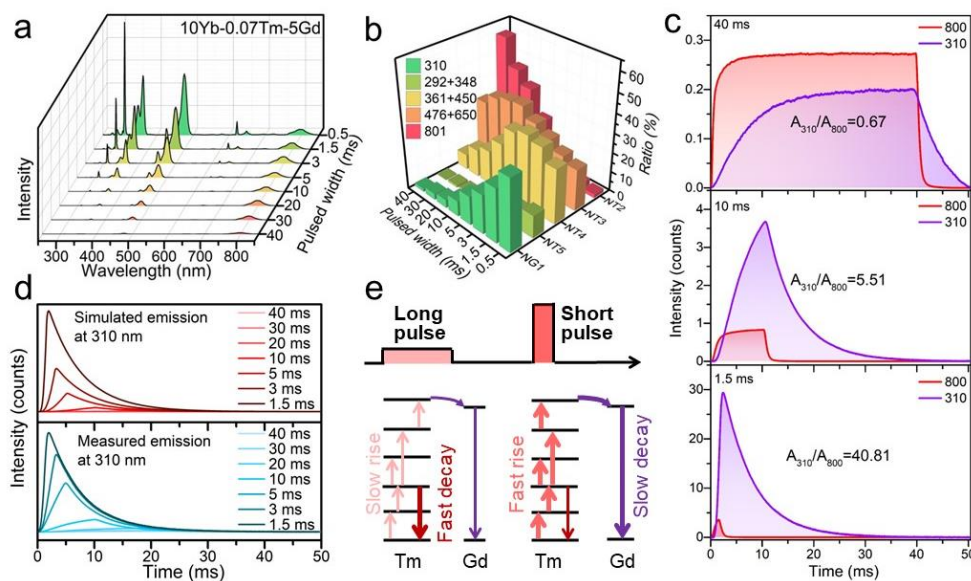


Figure 3.25 Temporally tuning energy transfer for enhancing multiphoton upconversion. **a** Pulse-width dependent PL spectra under excitation of 980 nm diode laser. **b**. Intensity ratio of different fluorescent peak (800 nm, 476 nm, 361 nm, 347 nm, 310 nm) under different excitation pulse-width with frequency of 20 Hz and incident power density of $2.55 \times 10^5 \text{ mJ} \cdot \text{cm}^{-2}$. **c** Time-dependent spectra of 800 nm and 312 nm at pulse-width of 40, 10 and 1.5 ms. **d** Simulated and measured time-dependent spectra of 312 nm at pulse-width of 40, 30, 20, 10, 5, 3 and 1.5 ms. **e** Schematic diagram of fast or slow rise and decay processes of Tm-Gd receiving energy from Yb under long pulse and short pulse excitation.

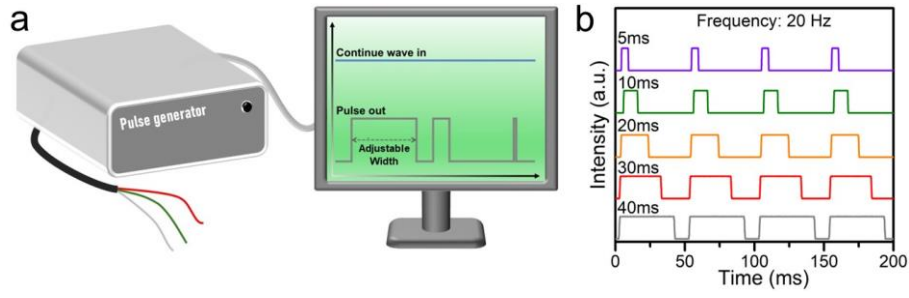


Figure 3.26 (a) Schematic diagram of pulsed lasers generating different pulse widths; (b) Spectra of pulsed laser with different pulse widths at a fixed frequency of 20 Hz.

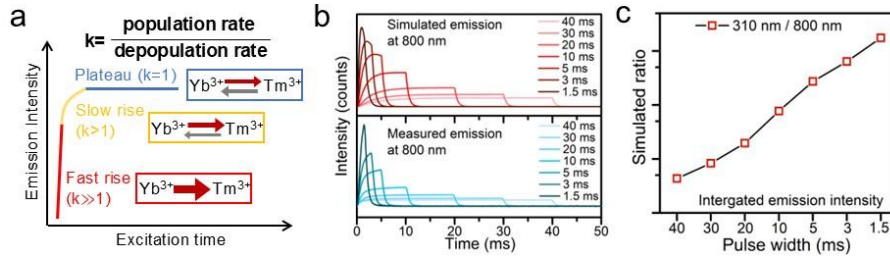


Figure 3.27 (a) The relationship between emission intensity and excitation time, indicating the rise rate is dependent on the ratio between population rate and depopulation rate; (b) Simulated and measured temporal 800 nm emission under 980 nm excitation with varied pulse durations; (c) Simulated ratio between 311 nm and 800 nm emissions with varied pulse durations.

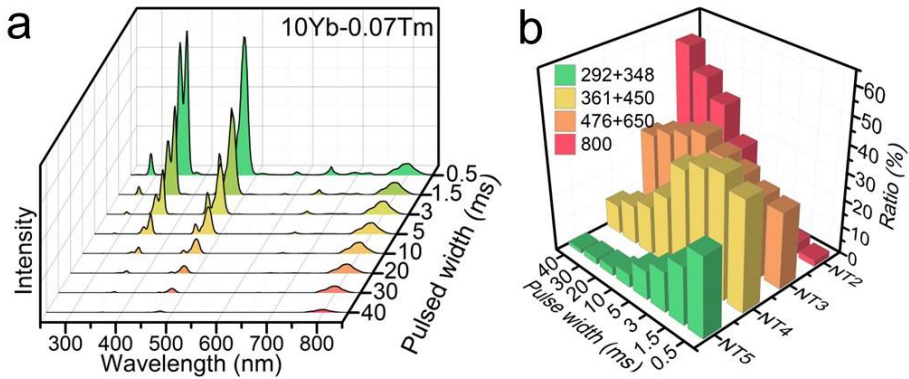


Figure 3.28 (a) Upconversion emission spectra in 270-850 nm range of 10Yb-0.07Tm codoped sample under 980 nm excitation with varied pulse durations; (b) the corresponding ratio of spectral intensity of excited energy levels to integrated emission intensity over 270-850 nm range.

As the pulse-width decreases from 40 to 0.5 ms, the emission ratio from the low energy level NT2 (800 nm) gradually decreases, while the proportion of emission from the high energy level NT5 (292 and 348 nm) and NG1 (310 nm) increases. Importantly, the combined ratio of DUV emission (Tm^{3+} :292 nm and Gd^{3+} : 310 nm) rises from 1.61% to 38.81%. This pulse width dependence of multiphoton upconversion emission intensity can be explained by upconversion luminescence kinetic studies. **Figure 3.25c** shows the experimentally measured time-dependent emission curves for the 800 nm and 310 nm wavelength, where the integrated area under each curve corresponds to the average emission intensity. Under excitation with pulse-width of 40 ms, 10 ms and 1.5 ms pulse widths, the ratio of integral area of 310 nm and 800 nm emission increases sequentially from 0.67% to 5.51% and ultimately to 40.81%, further validating the efficacy of pulses modulation in the enhancement of average DUV output emission.

To understand the mechanisms underlying the enhanced multiphoton upconversion emission under pulse-width modulation excitation, numerical simulation of Yb-Tm-Gd non-steady upconversion was studied. Numerical simulations and experimental time-resolved spectra (**Figure 3.25d**, **Figure 3.27**) reveal a significant increase in both the rise and decay areas (integrated intensities) of the Gd^{3+} : 311 nm emission. The increased rise area is because the nonlinear increase caused by the increase in excitation peak power is much greater than the linear decrease caused by the decrease in excitation pulse-width. The large energy gap and slow decay dynamics of Gd^{3+} ions critically enable the retention of UV photons, suppressing back ET to Yb^{3+} ions and parasitic visible transitions in Tm^{3+} ions. In the absence of Gd^{3+} doping, short pulse-width excitation increases the UV emission ratio in $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped systems only marginally from 0.11% to 4.16% (**Figure 3.28**). Therefore, the remarkable enhancement of multiphoton UV under short pulse-width excitation can be attributed to the faster rise of ETU and CR process and the reserve capacity of Gd^{3+} ions with slow decay for UV photons (**Figure 3.25e**).

The large energy gap and slow decay dynamics of Gd^{3+} ions critically enable the retention of DUV photons, suppressing back ET to Yb^{3+} ions and parasitic visible transitions in Tm^{3+} ions. In the absence of Gd^{3+} doping, short pulse-width excitation increases the DUV emission ratio in $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped systems only marginally from 0.11% to 4.16% (**Figure 3.29**). Therefore, the remarkable enhancement of multiphoton DUV under short pulse-width excitation can be attributed to the faster rise of ETU and CR process and the reserve capacity of Gd^{3+} ions with slow decay for DUV photons (**Figure 3.19e**).

3.6 DUV Random Lasing through Multiphoton Upconversion

Room temperature DUV random lasing action in the GC-39Al containing with $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ nanocrystals was demonstrated by characterizing optical emissions under 980 nm ns laser pulse excitation at varying powers. The lasing mechanism arises from stochastic optical feedback within the randomly distributed $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ nanocrystals in the glass matrix (**Figure 3.29a**). The laser spectra at 310 nm and the corresponding light emission intensity versus pump power density are shown in **Figure 3.29b–c**. As the pump power density exceeds the lasing threshold ($\sim 15 \text{ mJ}\cdot\text{cm}^{-2}$), discrete narrow peaks emerge, with their number increasing with pump intensity.[26] In addition, when the energy density just exceeds the threshold, only a few spikes appear (**Figure 3.29b-d**). As energy density gradually increases, the number of spikes with extremely narrow half-widths (0.25 nm, 0.14 nm, 0.18 nm) increases, appearing in very random positions, which are typical characteristics of random lasers. The lasing threshold of 310 nm lasing in GC-39Al is around $15 \text{ mJ}\cdot\text{cm}^{-2}$, which is lower than that of NaLnF_4 upconversion nanocrystals with optimized core-shell-shell structure ($85 \text{ mJ}\cdot\text{cm}^{-2}$). Unlike colloidal nanocrystals, GC-39Al eliminates the need for silica resin microcavities, which introduce inherent absorption losses,

thereby achieving higher optical gain and lower thresholds. Furthermore, GC-39Al enables 253 nm and 275 nm lasing from Gd^{3+} ions with exceptionally large anti-Stokes shifts—a feat rarely achieved in bulk materials.

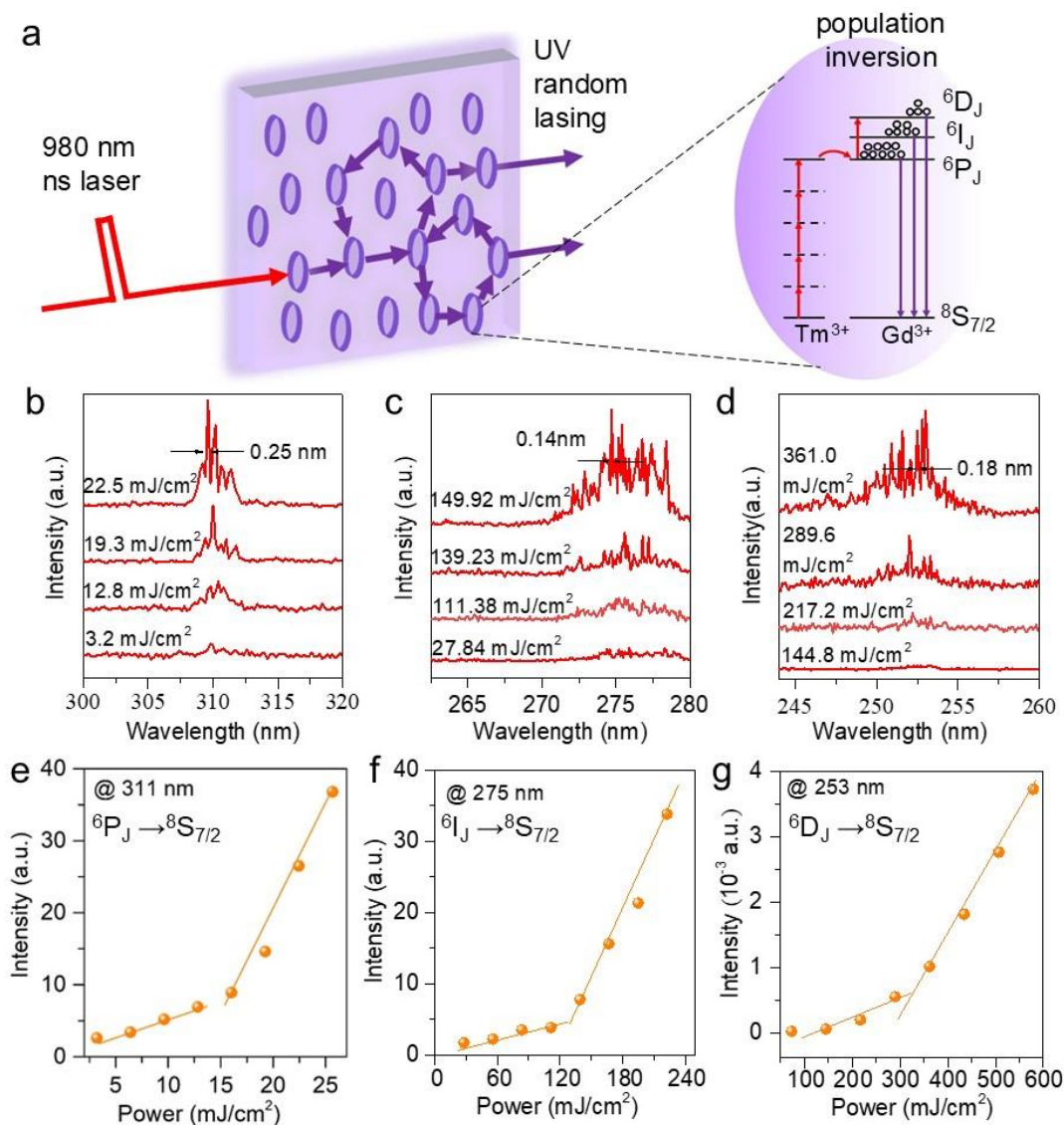


Figure 3.29 Demonstration of multiphoton upconversion UV random lasing. a Schematic diagram for multiphoton upconversion UV random lasing realized by the coherent feedback among Yb_{1-y}(Ca, Sr, Ba)_yF_{3-y}: Tm, Gd nanocrystals distributed in UV-transparent bulk solid; b-d Lasing spectra and e-g light-light curves for Gd³⁺ emission at 311 nm, 275 nm and 253 nm under 980 nm ns pulsed excitation operating at room-temperature.

3.7 Simulation processes

Note S1 The calculation of $\text{Ln}^{3+}\text{-Ln}^{3+}$ distance in glass and nanocrystals

The average distance for $\text{Ln}^{3+}\text{-Ln}^{3+}$ ($\text{Ln}=\text{Yb, Tm, Gd}$) in glass is calculated using the following equation:

$$R = \left(\frac{M}{N_A \rho x} \right)^{1/3}$$

where M is the mean molecular weight of fluoroaluminate glass, N_A is the Avogadro number ($6.0210^{23} \text{ mol}^{-1}$), ρ is the bulk density, and x is the total concentration of the studied Ln^{3+} ion pairs.

The average distance for $\text{Ln}^{3+}\text{-Ln}^{3+}$ ($\text{Ln}=\text{Yb, Tm, Gd}$) in nanocrystals (making the approximation that the volume takes the shape of a sphere) are calculated using the following equation:

$$R = 2 \left(\frac{3V}{4\pi x_c Z} \right)^{1/3}$$

where V is the volume of the unit cell, x_c refers to the doping concentration and Z is the number of formula units per unit cell.

Table S1 Glass and crystal structure data and the calculated average Ln^{3+} - Ln^{3+} spatial distance R for 10Yb-0.07Tm-5Gd co-doped glass and GCs.

Glass	M	$\rho(\text{g/cm}^3)$	$R_{\text{Yb-Tm}} (\text{\AA})$	$R_{\text{Tm-Tm}} (\text{\AA})$	$R_{\text{Tm-Gd}} (\text{\AA})$
G-39Al	123.64	3.77	8.15	42.69	10.29
Crystal	$V(\text{\AA}^3)$	Z	$R_{\text{Yb-Tm}} (\text{\AA})$	$R_{\text{Tm-Tm}} (\text{\AA})$	$R_{\text{Tm-Gd}} (\text{\AA})$
$\text{Sr}_{0.8}\text{Yb}_{0.2}\text{F}_{2.2}$	189.51	4	5.25	27.49	6.63
$\text{Yb}_{0.8}\text{Sr}_{0.2}\text{F}_{2.8}$	103.8	6	3.63	19.03	4.59

Note S2 Simulation of rate equations for Yb-Tm-Gd upconversion

The rate equation set is an expression that summarizes and simplifies the physical process of the population at different energy levels of lanthanide ions in luminescent materials. In order to deeply study the UV upconversion kinetic process of $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}$: Tm, Gd GCs, a rate equation model describing the kinetic equation of the system was established under weak excitation. **Figure 3.30** shows the schematic diagram of the $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Gd}^{3+}$ energy levels and upconversion process, including energy transfer upconversion, cross relaxation, radiative transition, multi-phonon nonradiative relaxation, energy transfer and back energy transfer. For convenience, the $^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$ energy levels of Yb^{3+} are represented by Y0 and Y1 respectively. The $^3\text{H}_6$, $^3\text{F}_4$, $^3\text{H}_5$, $^3\text{H}_4$, $^3\text{F}_{2,3}$, $^1\text{G}_4$, $^1\text{D}_2$ and $^1\text{I}_6$ energy levels of Tm^{3+} are represented by T0, T1, T1', T2, T2', T3, T4 and T5 respectively. The $^8\text{S}_{7/2}$ and $^6\text{G}_J$ energy levels of Gd^{3+} are represented by G0 and G1 respectively. The rate equations are derived as follows:

$$\begin{aligned}
\frac{dN_{Y1}}{dt} &= \sigma_{Yb}\rho N_{Y0} - W_{Y1}N_{Y1} - (k_0N_{T0} + k_1N_{T1} + k_2N_{T2} + k_4N_{T4})N_{Y1} + \\
&\quad k_{b2}N_{T2}N_{Y0} + k_{b3}N_{T3}N_{Y0} + k_{b4}N_{T4}N_{Y0} + k_{b5}N_{T5}N_{Y0} \\
\frac{dN_{T0}}{dt} &= -k_0N_{Y1}N_{T0} + W_{T1}N_{T1} + W_{T1'}N_{T1'} + W_{T20}N_{T2} + W_{T2'}N_{T2'} + W_{T30}N_{T3} + \\
&\quad W_{T40}N_{T4} + W_{T50}N_{T5} + k_{b2}N_{T2}N_{Y0} + c_{T22}N_{T2}N_{T2} \\
\frac{dN_{T1'}}{dt} &= k_0N_{Y1}N_{T0} - W_{T1'}N_{T1'} - m_1N_{T1'} + W_{T21'}N_{T2} + W_{T31'}N_{T3} + W_{T41'}N_{T4} + \\
&\quad W_{T51'}N_{T5} + k_{b3}N_{T3}N_{Y0}
\end{aligned}$$

$$\begin{aligned}
\frac{dN_{T1}}{dt} &= m_1 N_{T1'} - k_1 N_{Y1} N_{T1} - W_{T1} N_{T1} + W_{T21} N_{T2} + W_{T31} N_{T3} + W_{T41} N_{T4} + \\
&W_{T1} N_{T5} + k_{m2} N_{T2} N_{T3} \\
\frac{dN_{T2'}}{dt} &= k_1 N_{Y1} N_{T1} - W_{T2'} N_{T2'} - m_2 N_{T2'} + W_{T32'} N_{T3} + W_{T42'} N_{T4} + W_{T52'} N_{T5} + \\
&k_{b4} N_{T4} N_{Y0} - c_{T22'} N_{T2} N_{T2'} \\
\frac{dN_{T2}}{dt} &= m_2 N_{T2'} - k_2 N_{Y1} N_{T2} - (W_{T20} + W_{T21} + W_{T21'}) N_{T2} + W_{T32} N_{T3} + \\
&W_{T42} N_{T4} + W_{T52} N_{T5} - k_{b2} N_{T2} N_{Y0} - c_{T22'} N_{T2} N_{T2'} \\
\frac{dN_{T3}}{dt} &= k_2 N_{Y1} N_{T2} - (W_{T30} + W_{T31} + W_{T31'} + W_{T32} + W_{T32'}) N_{T3} + W_{T43} N_{T4} + \\
&W_{T53} N_{T5} - k_{b3} N_{T3} N_{Y0} + k_{b5} N_{T5} N_{Y0} \\
\frac{dN_{T4}}{dt} &= c_{T22'} N_{T2} N_{T2'} - k_4 N_{Y1} N_{T4} + W_{T54} N_{T5} - k_{b4} N_{T4} N_{Y0} - (W_{T40} + W_{T41} + \\
&W_{T41'} + W_{T42} + W_{T42'} + W_{T43}) N_{T4} \\
\frac{dN_{T5}}{dt} &= k_4 N_{Y1} N_{T4} - k_{TG} (N_G - N_{G1}) N_{T5} - (W_{T50} + W_{T51} + W_{T51'} + W_{T52} + W_{T52'} + \\
&W_{T53} + W_{T54}) N_{T5} - k_{b5} N_{T5} N_{Y0} \\
\frac{dN_{G1}}{dt} &= k_{TG} (N_G - N_{G1}) N_{T5} - W_{G10} N_{G1}
\end{aligned}$$

where N_{Yi} , N_{Ti} and N_{Gi} are the population on level i of Yb^{3+} , Tm^{3+} and Gd^{3+} , respectively; W_{Yij} , W_{Tij} and W_{Gij} are the radiative rate from level i to j of Yb^{3+} , Tm^{3+} and Gd^{3+} , respectively; m_1 and m_2 are the multi-phonon nonradiative relaxation rates from energy level T1 'to T1 and from energy level T2' to T2 of Tm^{3+} , respectively; k_i is the energy transfer coefficient between Y1 of Yb^{3+} and Ti of Tm^{3+} ; k_{bi} is the back energy transfer coefficient between Tm^{3+} on level Ti and Y0 of Yb^{3+} ; k_{TG} is the energy transfer coefficient between T5 of Tm^{3+} and G0 of Gd^{3+} ; C_{Tij} is the cross-relaxation coefficient between Tm^{3+} on level i and level j ; σ_{Yb} is the absorption cross-section of Yb^{3+} at 980 nm; ρ is the pumping rate of the 980 nm pumped laser, which can be obtained by the formula $\rho=P/h\nu$, where P is the time-dependent power density of the pumped laser, h is

the Planck constant, and ν is the frequency of the pumped light. The concentration of Ln^{3+} is calculated by the formula $N=(\rho/M)N_A x\%/v\%$, where ρ is the density, M is the average molecular weight of the glass, N_A is Avogadro's constant, $x\%$ is the percentage of the molar concentration, and $v\%$ is the crystallinity. The radiation rate W_{Ti} is obtained by the formula $W_{\text{Ti}}=\beta_{ij}/\tau_{\text{Ti}}$, where β_{ij} is the fluorescence branching ratio and τ_{Ti} is the radiation lifetime of the Ti energy level. At an extremely low Tm^{3+} concentration, τ_{Ti} is approximately equal to the measured fluorescence lifetime of the Ti energy level (**Figure 3.31**).

The process of rate equation numerical simulation and parameter optimization based on Python is schematically shown in **Figure 3.32**. First of all, set the target curve (experimental curve), the search space of parameters and the parameters of the differential evolution algorithm. The Odeint function of the Scipy library was used to numerically simulate the randomly generated initial population to produce discretized results, and the Matplotlib was used to visualize them as curves. The multiple target curves (experimental curves) and simulation curves containing 2500 evenly divided feature points were standardized by using Procrustes analysis. Their Frechet distances were calculated to describe the path similarity of the two curves, and the parameters were judged by the differential evolution algorithm to improve the similarity. That is, continuously iterate the free parameters until they gradually converge, thereby finding the free parameters with the best fitting effect in the search space.

There are many unknown parameters in the rate equations of high-order

multi-upconversion, which are prone to overfitting and falling into the local optimum trap. Therefore, we designed a concentration gradient experiment to obtain parameters in a progressive manner (**Figure 3.33**). Firstly, in the cases of weak excitation and ultra-low Tm^{3+} concentration, the BET between the excited state Tm^{3+} and the ground state Yb^{3+} can be ignored. Therefore, the parameters k_0 , k_1 , k_2 and k_4 of the ETU and the parameter c_{T22} of the CR can be obtained by fitting the experimental and simulation curves of the 10Yb-0.02Tm sample (**Figure 3.34**). Secondly, in the case of a higher Tm^{3+} concentration, the BET between the excited state Tm^{3+} and the ground state Yb^{3+} is obvious. Therefore, the parameters k_{b2} , k_{b3} , k_{b4} and k_{b5} of BET can be obtained by fitting the experimental and simulation curves of the 10Yb-0.15Tm sample (**Figure 3.35**). Then, the reliability of the obtained parameters was verified by comparing the experimental and simulation curves of the 10Yb-0.07Tm sample with the Tm^{3+} concentration in the middle (**Figure 3.36**). Finally, the Gd^{3+} ion was introduced to fit the experimental and simulation curves of the 10Yb-0.07Tm-5Gd sample and obtain the ET parameters k_{TG} of Tm^{3+} and Gd^{3+} (**Figure 3.37**). Based on the progressive optimization of the parameters of the high-order upconversion rate equation in the above experimental design, the simulation curves and experimental curves of luminescence at multiple energy levels can be well matched. Therefore, the dynamics of upconversion luminescence of 10Yb-0.07Tm-5Gd doped GC can be described well.

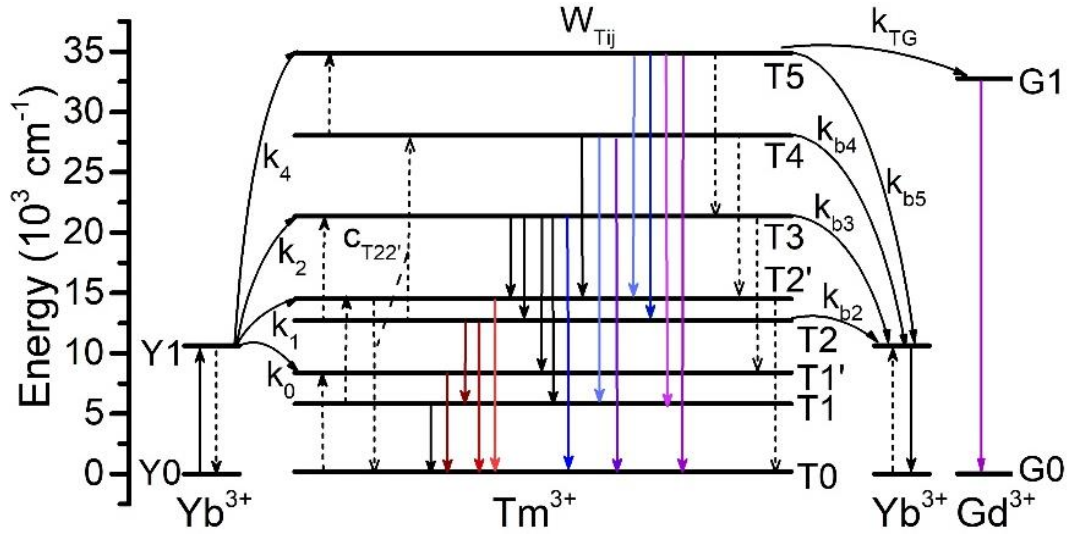


Figure 3.30 Energy level and transition diagram of Yb-Tm-Gd codoped system under 980 nm excitation.

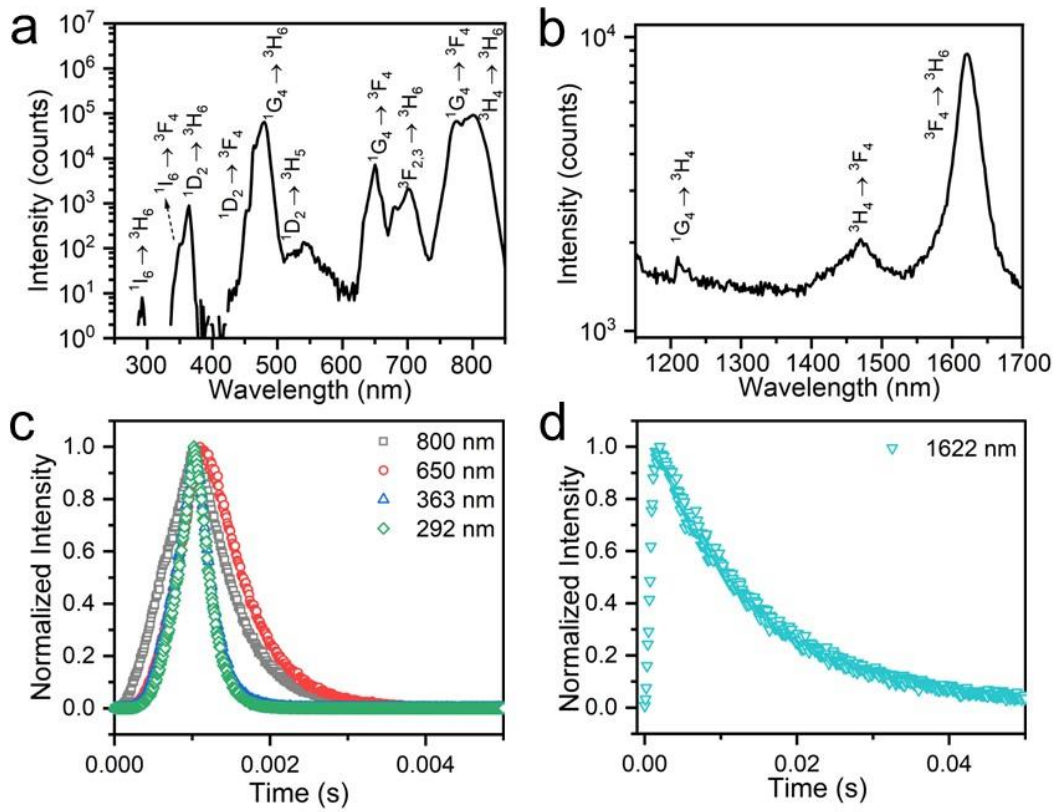


Figure 3.31 Steady-state and non-steady-state down-conversion and upconversion emission spectra of 10Yb-0.02Tm co-doped GC sample under 980 nm excitation.

Table S2 Parameters in the numerical simulation of rate equations describing the upconversion emission of Yb-Tm-Gd co-doped system^[78-79]

Parameter	Value	Parameter	Value	Parameter	Value
$N_{Yb} (cm^{-3})$	1.1810^{22}	$W_{T21'} (s^{-1})$	5	$W_{T42'} (s^{-1})$	20
$N_{Tm} (cm^{-3})$	9.410^{19}	$W_{T2'0} (s^{-1})$	1351	$W_{T43'} (s^{-1})$	20
$N_{Gd} (cm^{-3})$	5.5910^{21}	$W_{T30} (s^{-1})$	801	$W_{T50} (s^{-1})$	464
$P (W/cm^2)$	9.69	$W_{T31} (s^{-1})$	133	$W_{T51} (s^{-1})$	2824
$\rho (cm^{-2}s^{-1})$	4.7810^{19}	$W_{T31'} (s^{-1})$	576	$W_{T52} (s^{-1})$	795
$\sigma_{Yb} (cm^2)$	1.0810^{-20}	$W_{T32} (s^{-1})$	200	$W_{T52'} (s^{-1})$	254
$W_{Y1} (s^{-1})$	435	$W_{T32'} (s^{-1})$	200	$W_{T53} (s^{-1})$	1278
$W_{T1} (s^{-1})$	74	$W_{T40} (s^{-1})$	2100	$W_{G1} (s^{-1})$	170
$W_{T1'} (s^{-1})$	171	$W_{T41} (s^{-1})$	2100	$m_1 (s^{-1})$	210^4
$W_{T20} (s^{-1})$	1785	$W_{T41'} (s^{-1})$	20	$m_2 (s^{-1})$	6.810^5
$W_{T21} (s^{-1})$	144	$W_{T42} (s^{-1})$	20		

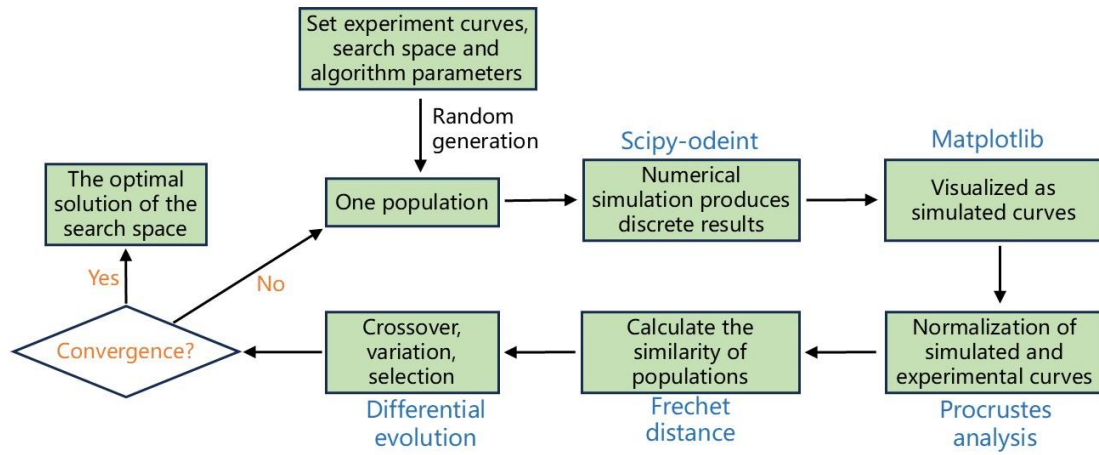


Figure 3.32 Flow chart of rate equations numerical simulation and parameter optimization based on Python.

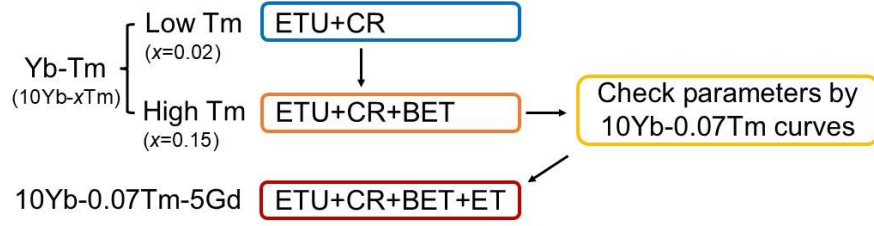


Figure 3.33 Proposed optimization route for the multi-parameter rate equation of Yb-Tm-Gd co-doped system designed by combining numerical simulation and experimental concentration gradient.

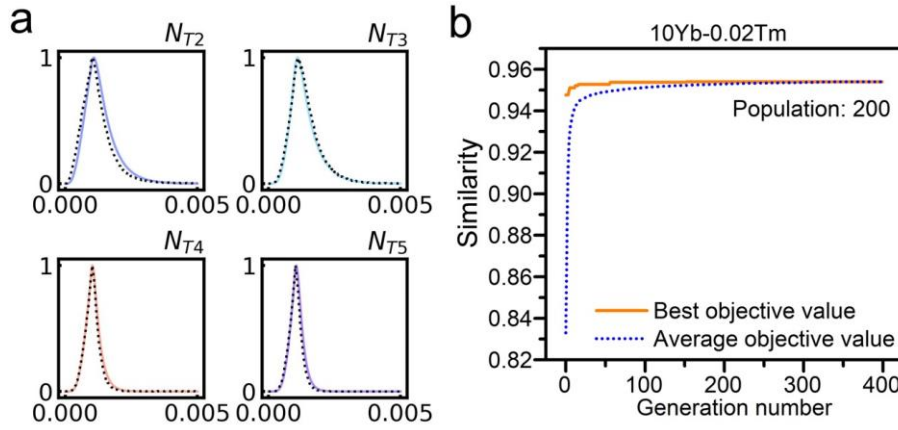


Figure 3.34 (a) Experimental and simulated temporal dependence of upconversion emission intensity at each energy level in 10Yb-0.02Tm codoped sample under pulse 980 nm laser excitation. (b) The variation curves of the best value and average value of a single population fitting the multi-objective curves of 10Yb-0.02Tm codoped sample with the generation number in the differential evolution.

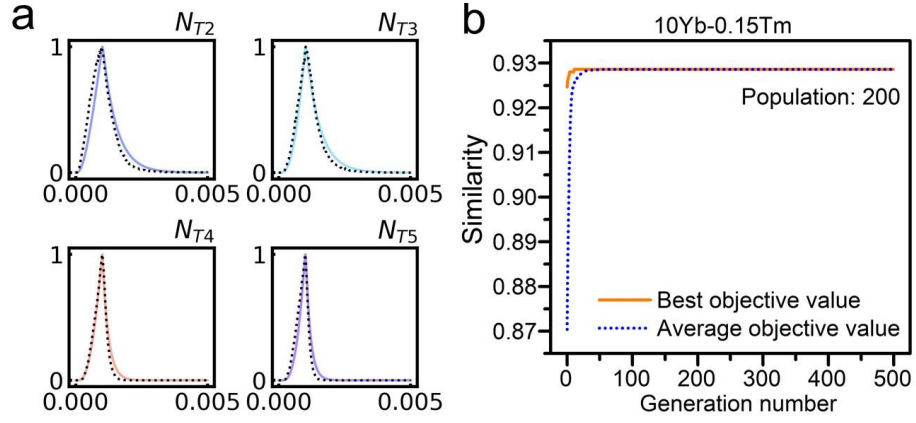


Figure 3.35 (a) Experimental and simulated temporal dependence of upconversion emission intensity at each energy level in 10Yb-0.15Tm co-doped sample under pulse 980 nm laser excitation. (b) The variation curves of the best value and average value of a single population fitting the multi-objective curves of 10Yb-0.15Tm co-doped sample with the generation number in the differential evolution.

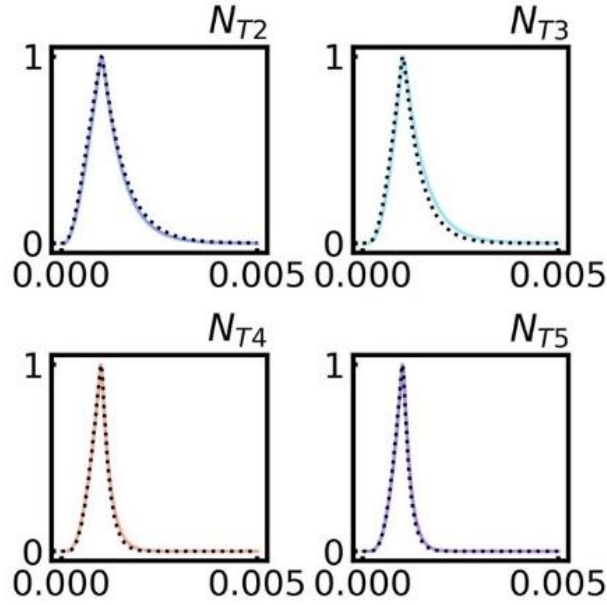


Figure 3.36 Experimental and simulated temporal dependence of upconversion emission intensity at each energy level in 10Yb-0.07Tm co-doped sample under pulse 980 nm laser excitation.

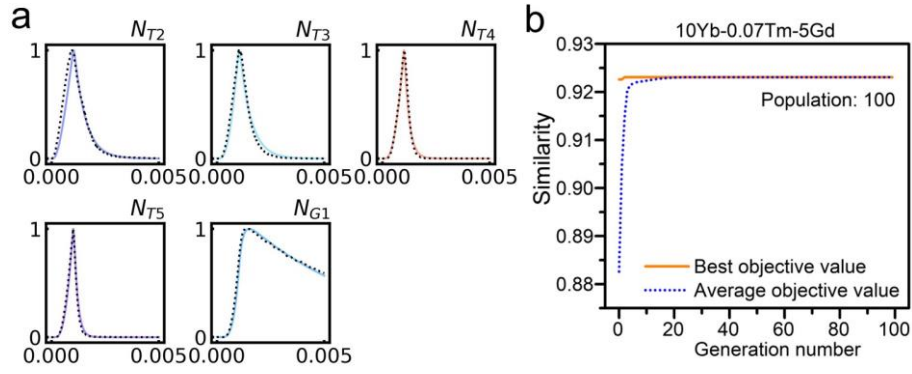


Figure 3.37 (a) Experimental and simulated temporal dependence of upconversion emission intensity at each energy level in 10Yb-0.07Tm-5Gd co-doped sample under pulse 980 nm laser excitation. (b) The variation curves of the best value and average value of a single population fitting the multi-objective curves of 10Yb-0.07Tm-5Gd co-doped sample with the generation number in the differential evolution.

3.8 Conclusion

In summary, our experimental study demonstrates a remarkable enhancement of NIR-to-DUV multiphoton upconversion emission intensity in GCs containing $\text{Yb}_{1-y}(\text{Ca}, \text{Sr}, \text{Ba})_y\text{F}_{3-y}:\text{Tm}, \text{Gd}$ nanocrystals under short pulse-width excitation. In the GC-39Al system, the minimized spatial distance between Yb^{3+} , Tm^{3+} , and Gd^{3+} ions enables accelerated ET rates, faster supersaturation dynamics, and significantly amplified UV upconversion emission. Besides, a non-steady multiphoton up-conversion process can further suppress the energy depletion in the intermediate energy levels of Tm^{3+} ions and back ET and thus enhance the intensity of multiphoton upconversion UV emission. This study advances the feasibility of developing compact, integrated, all-solid-state UV laser devices with broad applicability in medical and industrial fields.

Chapter 4 Tunable-Wavelength Broadband Liquid-State Carbon-Quantum-Dot Lasers

4.1 Introduction

Owing to their low cost and ease of synthesis, carbon quantum dots (CQDs) have garnered significant attention as promising solution-processable candidates for next-generation light sources, including light-emitting devices and lasers.[1–4] A defining feature of CQDs is their tunable energy levels, which stem from surface reactivity and diverse functional groups (e.g., carboxyl, amine, and epoxy groups).[5–8] This tunability enables CQDs to emit light across a broad spectrum, spanning ultraviolet to near-infrared regions—a capability that surpasses many conventional nanomaterials.[9,10] Consequently, CQDs are considered a potential candidate for realizing wide-bandwidth tunable lasing devices.[11–13] Compact CQD-based lasers can commonly be realized using quartz cuvettes filled with CQDs uniformly dispersed in a solvent as a liquid gain medium.[14,15] However, achieving multi-wavelength lasing requires precise integration of mirrors directly onto quartz surfaces alongside controlled beam collimation, often necessitating external mounts that introduce alignment instability.[16,17] These complexities complicate the fabrication of tunable CQD lasers. A further challenge arises from weak light scattering caused by Rayleigh scattering in the solvent dispersed with CQDs, which reduces the optical gain of CQDs.[18–20] Achieving compact, low-cost, and wavelength-tunable CQDs lasers requires a thorough understanding and precise control of lasing physics in liquid gain

media—a significant challenge in current research.[21] Key obstacles include overcoming limitations in optical confinement, ensuring precision in component alignment, and seamlessly integrating external components with the liquid-filled cuvette.

In this study, we introduce an innovative gain-guided waveguide framework for cuvette-based color-tunable carbon quantum dots (TCQDs) as a laser cavity.[22–24] By leveraging the aggregation-induced Förster resonance energy transfer (FRET) effect, we achieve spontaneous emission across a broad wavelength range (587–710 nm). This approach simultaneously enables light confinement within the cavity and external collimation of propagating light, facilitated by a solvent whose refractive index matches that of the cuvette. This refractive index matching enhances coupling efficiency between the output laser and the external cavity. By integrating the cuvette with an external flat aluminum mirror, we demonstrate that strong optical feedback coupling drives a critical transition from random lasing to controlled Fabry–Pérot multimode and single-mode lasing regimes. This advancement in lasing device design enables the fabrication of low-cost, compact CQDs lasers with programmable modal control, enhancing precision and adaptability for photonic systems applications. Hence, we delineate a pathway to achieving precise control over lasing properties, thereby paving the way for future developments in wavelength-tunable photonic systems. This study not only contributes to the growing body of knowledge on CQDs but also sets the stage for the next generation of adaptable, high-performance photonic devices.

4.2 Experimental Section

4.2.1 Materials

O-phenylenediamine (99.9%), Sulfuric acid (95.0-98.0%), Sodium hydroxide (98%), Anhydrous ethanol (99.9%), Acetone (99.5%), N,N-Dimethylformamide ($\geq$ 99.8%), Dimethyl sulfoxide ($\geq$ 99.8%) were all purchased from Sigma-Aldrich without further purification.

4.2.2 Preparation of Color-Tunable Carbon Quantum dots (TCQDs)

TCQDs were synthesized via a solvothermal approach. Initially, *O*-phenylenediamine (0.6 g) was ultrasonically dissolved in cooled concentrated sulfuric acid (4.6 M, 20 mL) to obtain a transparent solution. This solution was transferred into a 50 mL PTFE autoclave and heated at 200 °C for 12 hours. After cooling to room temperature, the crude products were centrifuged at 10,000 rpm for 10 minutes to eliminate insoluble materials, followed by filtration through 0.22 μ m PTFE microporous membranes. The filtrate was subsequently mixed with a rotating solution of sodium hydroxide (1.25 M, 50 mL) and stirred for an additional 60 minutes, with a sealing membrane used to retain the heat generated by acid-base neutralization. Finally, the products were collected by centrifugation at 10,000 rpm for 10 minutes, washed 3 to 4 times with a mixture of anhydrous ethanol and water, and dried in an oven at 60 °C to yield TCQDs powder.

4.2.3 Preparation of Oxidized Carbon Dots (OCDs)

20 mg of TCQDs were ultrasonically dispersed in ethanol (20 ml) and subsequently subjected to an additional solvothermal reaction at 200 °C for 12 hours. After cooling to room temperature (RT), the crude product was centrifuged to obtain the OCDs powder, followed by washing with a mixed solvent of distilled water and ethanol.

4.2.4 Computer Simulations

The electric field experienced by QDs was simulated using finite element method (FEM) from COMSOL Multiphysics software. A wave optics module was selected to build the model, with two ports along the extension direction of the waveguide set to simulate the guided light wave. The frequency of the light wave at our target was input to solve the corresponding electric field distribution. All materials were considered homogeneous and were defined by input refractive indices.

4.2.5 General Material Characterizations

Low- and high-resolution transmission electron microscopy (TEM) measurements were conducted using a JEM-2100F transmission electron microscope (JEOL) operating at an acceleration voltage of 200 kV. UV-Vis spectra were acquired using a Shimadzu UV-2550 spectrophotometer. Steady-state fluorescence spectra were measured with an Edinburgh Instruments FLS920 spectrometer equipped with a xenon arc lamp excitation source. Time-resolved photoluminescence (TRPL) measurements

were conducted via a time-correlated single-photon counting (TCSPC) system, utilizing a 375 nm picosecond-pulsed laser for excitation. Transient absorption spectroscopy was conducted using 400 nm, 50 fs pulses as the pump source and continuum white-light, 50 fs pulses as the probe source. FT-IR data were acquired using a Bruker Vertex-70 FTIR spectrometer in ATR mode. X-ray photoelectron spectroscopy (XPS) data were obtained using a Nexsa G2 surface analysis system (Thermo Scientific™).

4.2.6 Lasing Characterizations

The lasing characteristics of the samples in the cuvette were examined under optical excitation with and without optical feedback using a frequency-doubled Q-switched Nd:YAG laser operating in pulsed mode (532 nm, ~ 6 ns pulse width, 10 Hz repetition rate). The experimental setup is illustrated in **Figure 5.1**. A 5 mm-long pump stripe with a thickness of ≤ 100 μm was projected onto the shorter edge of the cuvette, which was filled with a liquid gain medium, by focusing the 532 nm laser beam through a cylindrical lens. Upon excitation, the generated light was confined in the y - and z -directions and propagated along the x -direction, forming a gain-guided waveguide. This configuration facilitated light emission through the two surfaces of the cuvette's longer edges in the direction perpendicular to the x -axis. To introduce optical feedback along the x -direction, an optically flat aluminum mirror was positioned parallel to one of the cuvette's longer edges, while lasing emission was collected from the opposite side. The separation between the mirror and the cuvette was precisely adjusted using a three-axis translation stage.

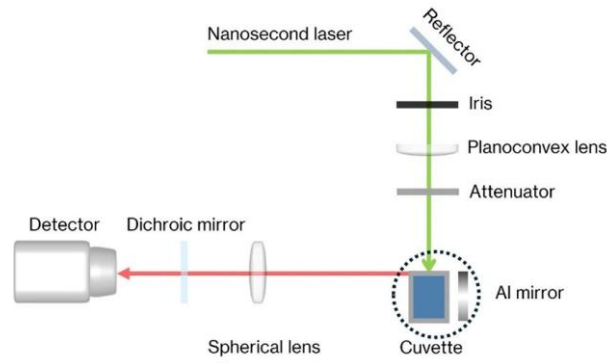


Figure 4.1 Schematic diagram of the experimental setup for programmable mode-spacing lasers. The incident strip-shaped light hits the front of the cuvette, while the signal is captured on the other side of the container that is perpendicular to the incident light. Dichroic mirror was used for eliminated incident light. For taking a far-field photo, replace the detector with a CCD.

4.2.7 Optical Gain and Loss Measurement

The optical gain of the carbon dots was measured using the variable stripe length (VSL) method. The photoluminescence intensity, $I(\lambda)$, emitted from the edge of the cuvette was coupled to a spectrum analyzer (SPEC-CMS960). The net optical gain, $G(\lambda)$, was calculated by fitting the equation $I(\lambda) = I_{sp}(\lambda) (\exp[G(\lambda)L] - 1)/G(\lambda)$ to measure $I(\lambda)$ values across a range of stripe lengths, L , where λ represents the emission wavelength and $I_{sp}(\lambda)$ is the spontaneous emission intensity. Cavity loss in the carbon dots solution was measured using the variable cavity length (VCL) method. Incident laser light at the emission wavelength of the carbon dots was focused onto the cuvette surface, and the transmitted power was measured using a power meter positioned behind the cuvette. The cavity loss, α_{cav} , was calculated by fitting the equation $\ln(T(\lambda)) = -2\alpha_{cav}L$, where T is the transmittance ratio, λ is the emitting wavelength and L corresponds to the optical path length.

4.3 Results and Discussion

4.3.1 FRET-induced fluorescent color shift and multiband lasing

A class of size-homogeneous, monodisperse, *O*-phenylenediamine-based TCQDs was synthesized by a solvothermal method to serve as the liquid-state gain medium (see Experimental Section for details). Steady-state photoluminescence (PL) and absorption spectra at concentrations ranging from $2^{-5} \text{ g}\cdot\text{L}^{-1}$ to $1 \text{ g}\cdot\text{L}^{-1}$ were analyzed to elucidate the energy transfer process, see **Figure 4.2 a-b**. The modification of energy transfer pathway was confirmed by the emergence of new absorption peaks at 630 nm at $2^{-3} \text{ g}\cdot\text{L}^{-1}$, compared to the peaks at 480 nm, 515 nm, and 545 nm dominated at lower concentrations. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images (see **Figure 4.3**) confirmed the uniform spherical morphology of the TCQDs, with an average lateral size of 4 nm and a well-defined lattice spacing of 0.21 nm, corresponding to the (100) plane of graphene. The TCQDs demonstrated aggregation-induced redshifted radiative channels, with emission spanning from 585 nm at concentrations of $2^{-5} \text{ g}\cdot\text{L}^{-1}$ to 700 nm at $1 \text{ g}\cdot\text{L}^{-1}$. These emissions were deconvoluted into 3 stable luminescent centers at $\sim 600 \text{ nm}$, $\sim 630 \text{ nm}$, and $\sim 700 \text{ nm}$) under varying excitation wavelengths (see **Figure 4.4**), verified by a visible color transition from bright orange to deep red under UV illumination, see **Figure 4.2c**. Concentration-dependent shifts in PL excitation peaks (see **Figure 4.5**) further revealed excited-state transitions. A progressive blue shift in the short-wavelength excitation peak ($2^{-5} \text{ g}\cdot\text{L}^{-1}$, 520 nm) and a concomitant red shift in the long-wavelength excitation

peak ($2^{-5} \text{ g}\cdot\text{L}^{-1}$, 612 nm) competitively emerged, aligning with the evolution of absorption spectra. The increasing overlap between PL and absorption spectra confirmed FRET.[25]

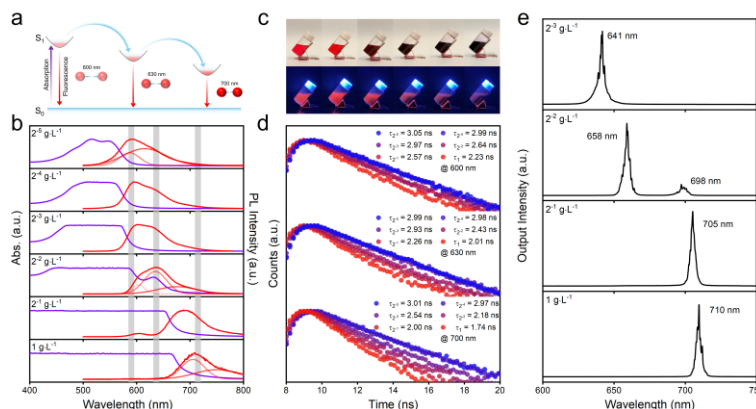


Figure 4.2 a) Schematic of the concentration-dependent FRET process within multi-level systems. b) Concentration-dependent optimal PL spectra and absorption spectra from $2^{-5} \text{ g}\cdot\text{L}^{-1}$ to $1 \text{ g}\cdot\text{L}^{-1}$ in DMF. c) Photos of different concentration TCQDs under sunlight (top) and UV lamp (bottom). d) Concentration-dependent TRPL spectra at 600 nm, 630 nm, and 700 nm. e) Tunable multiband lasing due to FRET. From bottom to top, the corresponding concentration is $2^{-3} \text{ g}\cdot\text{L}^{-1}$, $2^{-2} \text{ g}\cdot\text{L}^{-1}$, $2^{-1} \text{ g}\cdot\text{L}^{-1}$, $1 \text{ g}\cdot\text{L}^{-1}$.

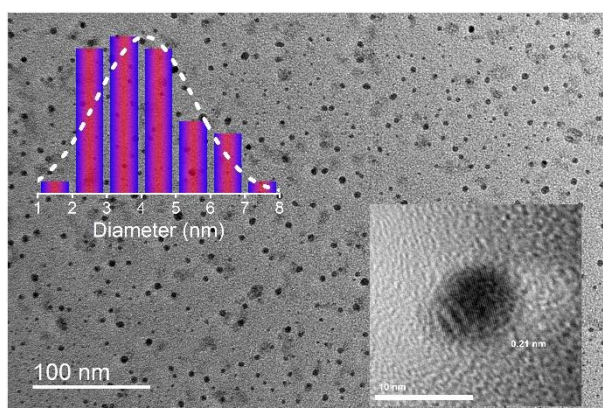


Figure 4.3 TEM images of TCQDs. Size distribution of TCQDs (counted 100, insert in the upper left corner) and High-resolution TEM images (insert in the lower right corner).

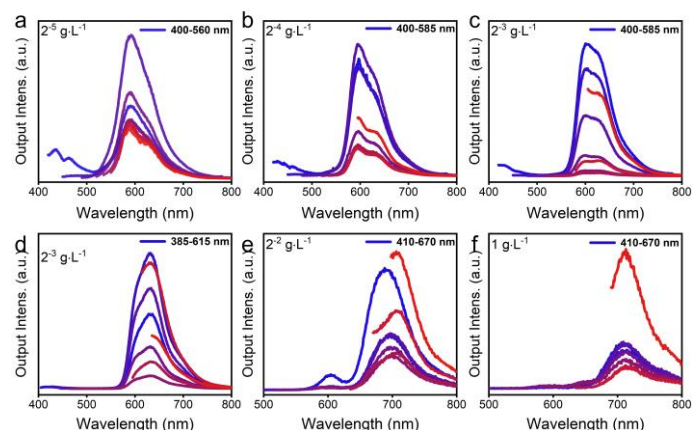


Figure 4.4 Excitation-dependent PL spectra of TCQDs at different concentration from (a-f) 2^{-5} $\text{g}\cdot\text{L}^{-1}$ to $1 \text{ g}\cdot\text{L}^{-1}$.

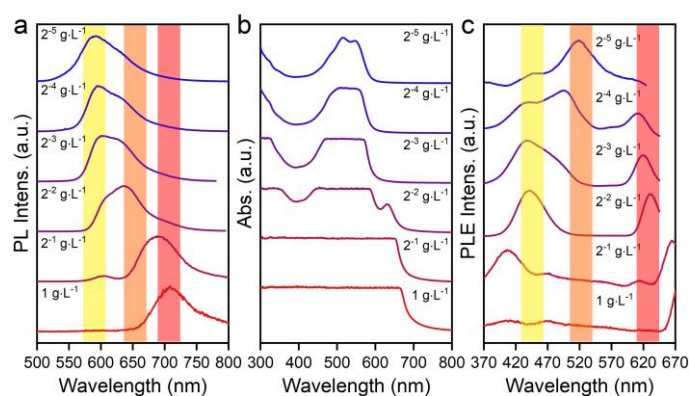


Figure 4.5 a) Normalized optimal PL spectra. b) Normalized absorption spectra. c) Normalized optimal PLE spectra at different concentration.

Time-resolved photoluminescence (TRPL) decay trends, see Figure 1d, provided robust evidence of FRET effect. The observed decrease in fluorescence lifetime (3.05 ns to 2.23 ns at 600 nm, 2.99 to 2.01 ns at 630 nm, 3.01 ns to 1.74 ns at 700 nm) followed with gradual increase of the concentration of TCQDs indicated that the FRET phenomenon effectively enhanced the probability of photon population at lower energy levels.[26] The coefficient of FRET, calculated as $\eta_{\text{FRET}} = 1 - (\tau_{\text{DA}}/\tau_{\text{D}})$ (where τ_{DA} and τ_{D} are lifetimes with and without the acceptor, respectively), increased significantly

(see **Figure 4.6**) as the 630 nm absorption peak intensified at $2^{-3} \text{ g}\cdot\text{L}^{-1}$, confirming efficient photon redistribution to lower energy states. This analysis highlights the critical role of concentration-dependent carrier dynamics in optimizing luminescent properties, providing key insights for designing advanced photonic materials.

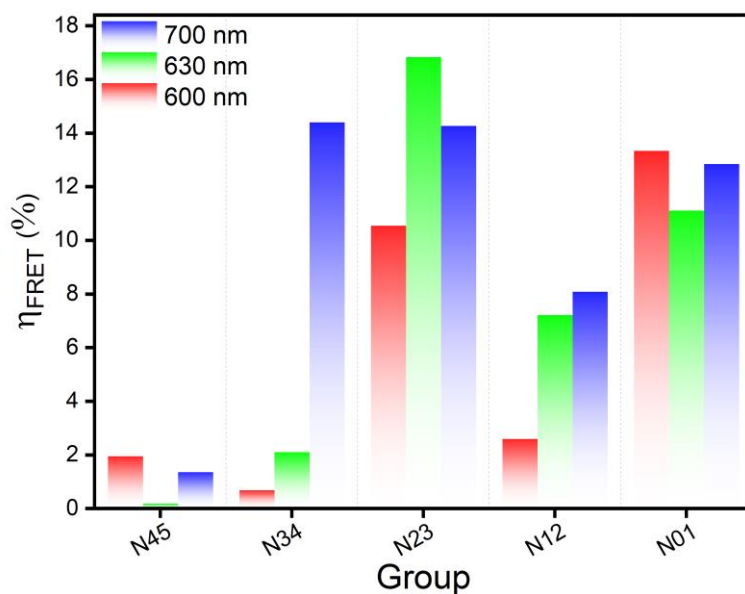


Figure 4.6 FRET efficiency of different concentration groups.

An intriguing phenomenon was observed when the concentration of TCQDs was halved progressively, resulting in a blue shift of the laser peak from 710 nm to 641 nm (**Figure 4.7**). Significantly, the emission spectra exhibited random lasing characteristics, with the lasing threshold increasing from $1.91 \text{ mJ}\cdot\text{cm}^{-2}$ to $27.85 \text{ mJ}\cdot\text{cm}^{-2}$ as the TCQD concentration was reduced from $2^{-3} \text{ g}\cdot\text{L}^{-1}$ to $1 \text{ g}\cdot\text{L}^{-1}$. At low concentrations near the lasing threshold, the emission spectrum exhibits a single lasing spike. As excitation power increases, additional spikes emerge, suggesting that the liquid medium functions as a weakly scattering random system with coherent optical feedback, indicative of closed-loop cavity formation within the medium. At higher concentrations and

excitation powers exceeding the threshold, multiple spikes emerge and merge due to spectral overlap, a phenomenon attributed to the increased density of overlapping closed-loop cavities in high-concentration solutions. Fourier transform analysis of the laser emission spectra further reveals that the cavity lengths associated with these random modes are below 100 μm and decrease with increasing concentration, aligning with the principle that higher scattering medium concentrations reduce lasing thresholds. On the other hand, when the gain medium concentration was further reduced to $2^{-4} \text{ g}\cdot\text{L}^{-1}$, population inversion could not be sustained at wavelengths near 600 nm and 630 nm (**Figure 4.8**).

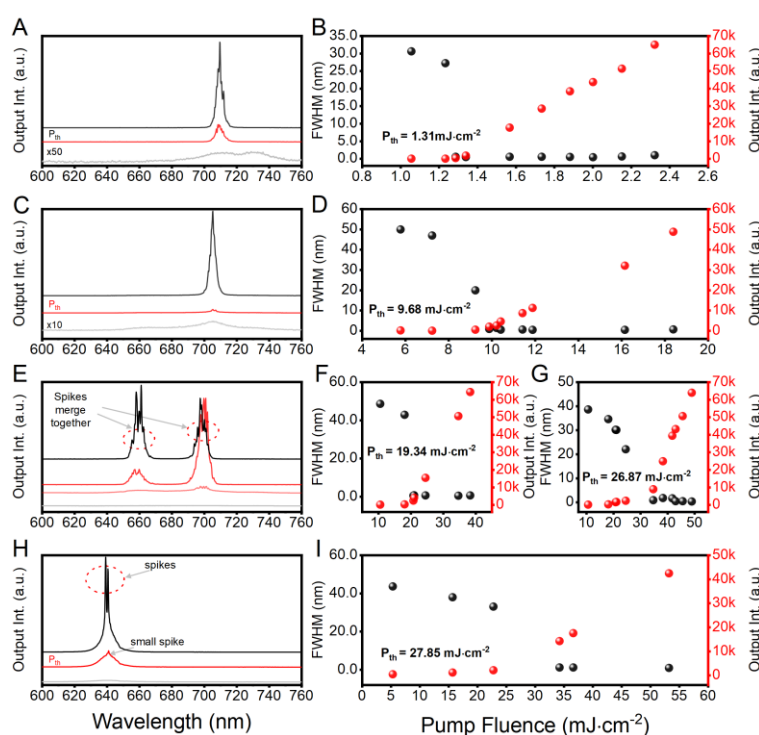


Figure 4.7 Characterization of concentration-dependent random lasing of TCQDs in DMF.

Emission spectra versus pump fluence of a) $1 \text{ g}\cdot\text{L}^{-1}$. c) $2^{-1} \text{ g}\cdot\text{L}^{-1}$. e) $2^{-2} \text{ g}\cdot\text{L}^{-1}$. h) $2^{-1} \text{ g}\cdot\text{L}^{-1}$.

Integrated PL intensity (red line) and FWHM (black line) versus the power density of b) $1 \text{ g}\cdot\text{L}^{-1}$

¹ at 710 nm. d) $2^{-1} \text{ g}\cdot\text{L}^{-1}$ at 705 nm. $2^{-2} \text{ g}\cdot\text{L}^{-1}$ at f) 705 nm and g) 660 nm. i) $2^{-3} \text{ g}\cdot\text{L}^{-1}$ at 641 nm.

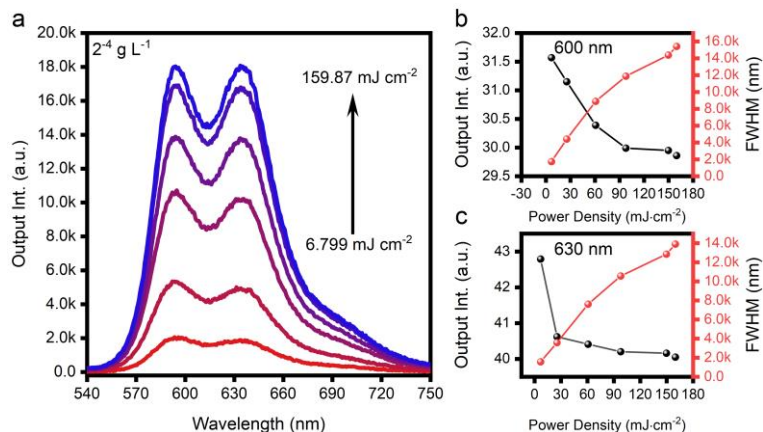


Figure 4.8 PL characterizations of TCQDs in DMF with concentration of 2^{-4} g L^{-1} . a) Steady state emission spectra versus pump fluence. b-c) Integrated PL emission intensity (Black line) and FWHM (Red line) versus the power density of 600 nm and 630 nm.

4.3.2 Explanation on the Formation of Gain-guided Waveguide

Figure 4.9a illustrates the design of the CQD laser with external optical feedback. The quartz cuvette is filled with a solvent containing uniformly dispersed CQDs. The solvent's refractive index is selected to closely match that of the quartz cuvette, thereby preventing the formation of an index-guided structure. To create a gain-guided waveguide within the cuvette, a cylindrical lens focuses the 532 nm excitation beam into a line along the cuvette's length (x-axis). The resulting emission (600–700 nm) is confined along the z-direction due to a gain difference between excited and unexcited regions. Simultaneously, the excitation light penetrates the solvent, providing gain confinement along the y-axis with a penetration depth $< 500 \mu\text{m}$. This configuration achieves two-dimensional light confinement (z- and y-directions), forming a gain-guided waveguide (red channel in **Figure 4.9a**). The waveguide dimensions are $\sim 200 \mu\text{m}$ in height (z-axis) and $< 500 \mu\text{m}$ in width (y-axis), while light propagates freely

along the x-axis. Optical feedback is established through an external mirror, forming a coupled cavity with the cuvette. The coupled cavity and the air-cuvette interfaces on the opposing sides of the quartz cuvette define the resonant cavity for the gain-guided laser system. The optical gain coefficient and cavity loss of TCQD solutions ($1 \text{ g}\cdot\text{L}^{-1}$ in DMF) were quantified using the VSL and VCL methods. The measured optical gain of 4.85 cm^{-1} exceeds the cavity loss of 4.773 cm^{-1} under an incident pump fluence of $1.217 \text{ mJ}\cdot\text{cm}^{-2}$. At higher excitation power, the gain coefficient increases linearly to 50.17 cm^{-1} , representing the highest value recorded for carbon dots (**Figure 4.10**). This confirms that the design of TCQDs cavity is capable of supporting lasing emission.

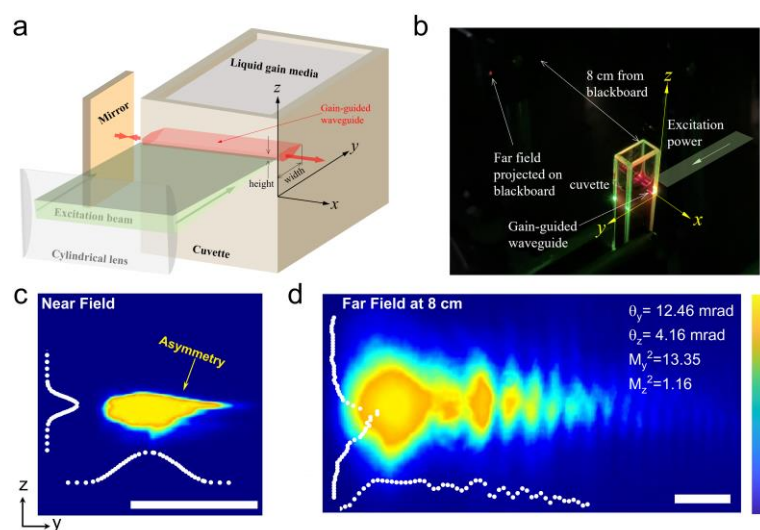


Figure 4.9 a) Schematic diagram of gain-guided waveguide based on cuvette filled with TCQDs solutions. b) Photo – experimental setup for the measurement of far-field laser beam emitted from the TCQDs filled cuvette without external mirror. c) Near-field beam profile. d) Far-field beam profile captured at a distance of 8 cm from the cuvette. Inset curves are measured profile in the y and z direction. 500-micrometer scale bar is inserted in the lower right corner of the image.

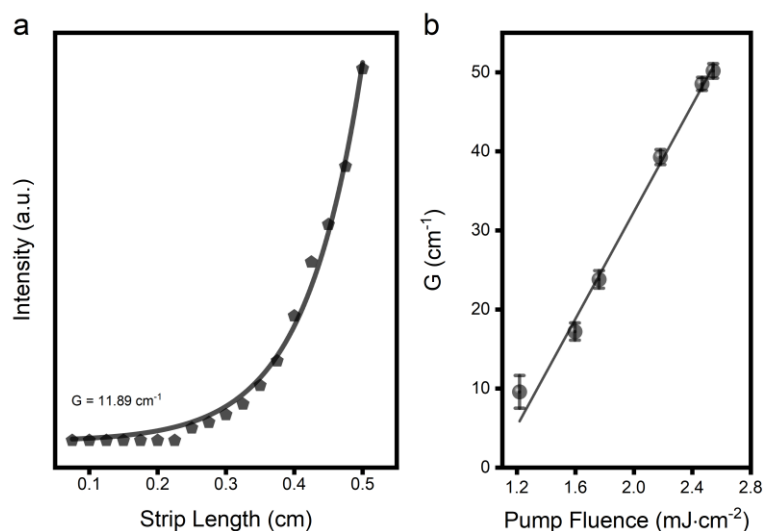


Figure 4.10 Gain spectra of TCQDs. a). Optical gain at $1.217 \text{ mJ}\cdot\text{cm}^{-2}$. b). Optical gain versus incident power density.

Figure 4.9c and d show the near- and far-field profiles, respectively, measured using a spot analyzer from the cuvette, as captured by the setup illustrated in **Figure 4.1**. The near-field emission beam exhibits a “water droplet” spatial profile with an extended tail along the y-axis, measuring $\sim 488 \mu\text{m}$ in width and $\sim 254 \mu\text{m}$ in height along the z-axis. This droplet-shaped emission arises from the spatially non-uniform excitation profile of the 532 nm pump light along the y-axis. Due to absorption in the liquid gain medium, the pump intensity decays exponentially with penetration distance, resulting in stronger light generation near the cuvette edge (smaller y) and diminished emission at larger y, thereby forming the observed droplet profile. The current excitation geometry—using a cylindrical lens to focus the pump beam into a line on the liquid gain medium—inherently produces this asymmetric near-field emission. To mitigate the elongated tail of the droplet profile, a viable strategy involves reducing the excitation beam’s thickness by narrowing its transverse width along the z-axis. This

adjustment would spatially confine the excitation region, flatten the intensity gradient along the y-direction, and yield a more uniform emission profile. The near-field's droplet-shaped profile adversely impacts far-field beam quality, producing a meteor-shaped far-field beam with $1/e^2$ intensity half-widths of 847.5 μm and 342.5 μm . The calculated divergence angles of $\theta_y = 12.46$ mrad and $\theta_z = 4.16$ mrad confirm low-beam divergence over a long-distance propagation. Therefore, the far-field profile projected onto a blackboard 8 cm from the cuvette (**Figure 4.9b**) demonstrates a collimated beam, verifying that the gain-guided waveguide provides strong light confinement within the cuvette and maintains collimation outside, making it suitable for use as a laser cavity.

4.3.3 Programmable mode-spacing liquid laser based on external mirror.

Figure 4.11a illustrates how external optical feedback tailors the laser mode from random lasing to Fabry–Pérot lasing by adjusting the spacing, L , between an aluminum mirror and one side of the quartz cuvette filled with TCQD solution ($1 \text{ g}\cdot\text{L}^{-1}$ in DMF). **Figure 4.11c** demonstrates the emission spectral changes of the cuvette without and with optical feedback via the external Al mirror (see also **Figure 4.12**). While the cuvette inherently supports random lasing, the introduction of the external Al mirror modifies the modal characteristics to Fabry–Pérot modes, arising from the coupled external cavity. Furthermore, the mode spacing $\Delta\lambda$ increases as L decreases. The linear relationship between L^{-1} (the reciprocal of L) and $\Delta\lambda$ is shown in **Figure 4.11b**. As L decreases from 485.23 μm to 53.28 μm , $\Delta\lambda$ increases from ~ 0.71 nm to ~ 4.66 nm,

with single-mode lasing achieved at $L \sim 38.04 \mu\text{m}$. The measured $\Delta\lambda$ and L are fitted to the Fabry–Pérot cavity model: $\Delta\lambda = \lambda^2/(2n_{\text{eff}}L)$ where λ is the lasing wavelength and n_{eff} (effective refractive index of the coupled external cavity) is found to be 1.00029. The proximity of n_{eff} to the refractive index of air confirms that the air gap between the Al mirror and cuvette (i.e., external cavity) defines the Fabry–Pérot modes, independent of the cuvette’s physical cavity length (0.5 cm). The measured cavity loss of the liquid gain medium (4.773 cm^{-1}) corresponds to a penetration length of 0.2 cm, which value is compatible with the cuvette’s cavity length. Consequently, the strong optical feedback with Fabry–Pérot modal characteristics suppresses closed-loop cavities (cavity length $< 100 \mu\text{m}$). Furthermore, the refractive index match between the solvent and quartz cuvette prevents constructive or destructive interference of the feedback light, enabling the Fabry–Pérot modes from the coupled external cavity to propagate and emit from the cuvette. A further advantage of strong optical feedback is the enhancement of the Q-factor in CQD lasers. As shown in Figure 4.11b, the introduction of an aluminum mirror reduces the lasing linewidth from $\sim 6 \text{ nm}$ (random lasing) to $\sim 2 \text{ nm}$ (single-mode lasing), resulting in a threefold improvement in the Q-factor.

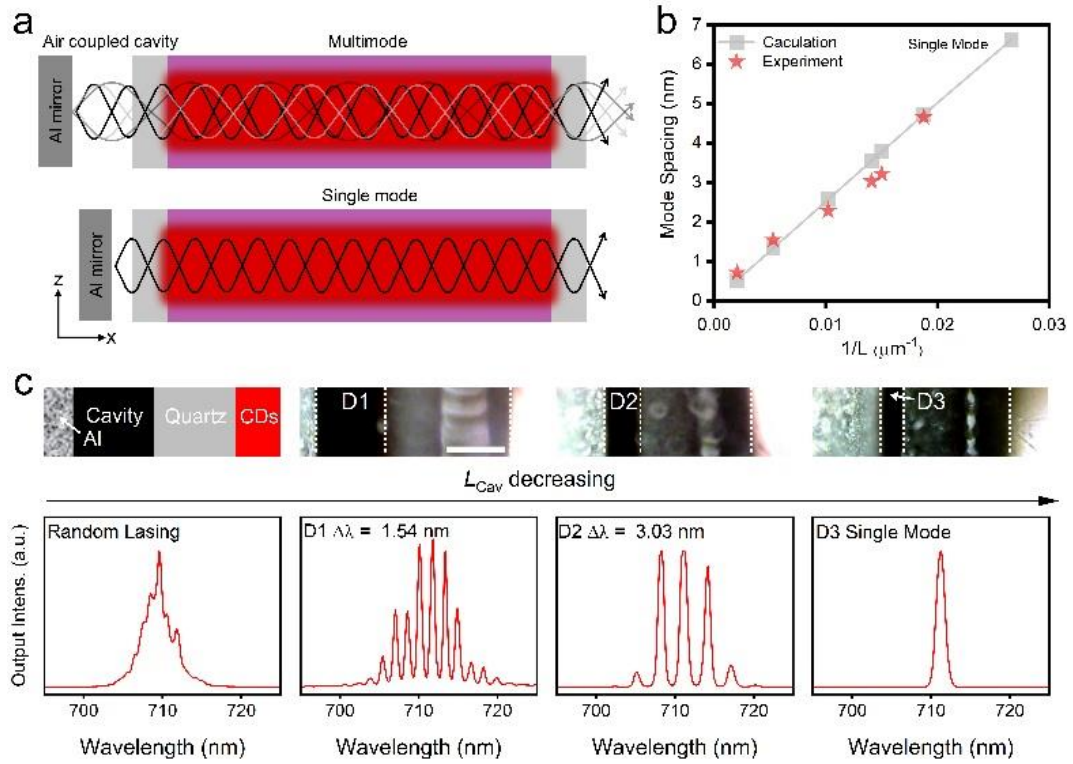


Figure 4.11 a) Schematic diagram of a TCQD solution filled quartz cuvette with an external Al mirror (left-hand side). b) The linear relationship between mode spacing $\Delta\lambda$ and L^{-1} (reciprocal of L) of TCQDs solution. c) Lasing spectra versus different of spacings, L . As the air gap spacing, L , between the mirror and cuvette decreases, the lasing mode transitions sequentially from random lasing regime to Fabry–Pérot multi-mode lasing and ultimately to single-mode lasing.

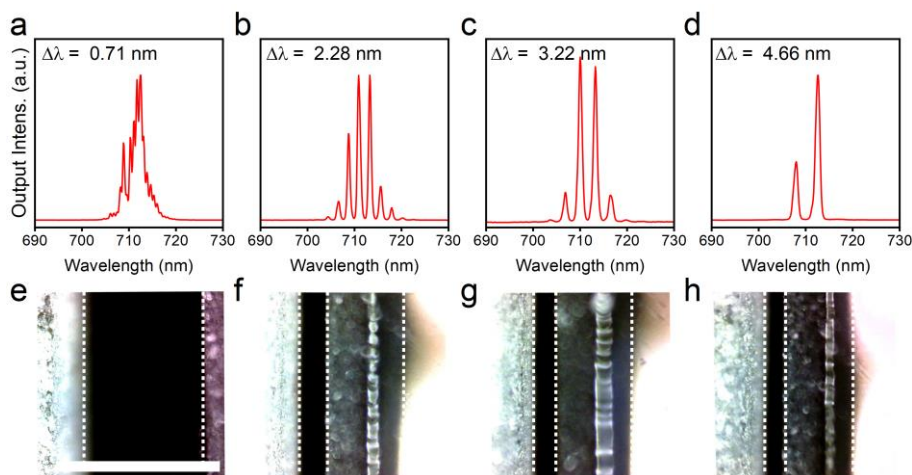


Figure 4.12 Lasing spectra and photos of air-cavity versus different cavity length. In each photo e to h), the left part is Al mirror, the middle part is air, the right part is cuvette contained with sample. A 500-micronmeters scale bar is inserted in the lower right corner of the image.

We examined the impact of refractive index on phase coherence using four types of solvents, with effective refractive indices of 1.499 for DMSO, 1.450 for DMF, 1.38 for ethanol, and 1.37 for acetone. Surprisingly, lasing was observed only in DMSO and DMF, where refractive indices matched or slightly exceeded than that of the quartz cuvette wall. Similar to DMF, TCQDs in DMSO also exhibited mode spacing modulation (**Figure 4.13**). The refractive index critically influenced the laser performance, as indicated by the larger number of spikes observed in DMF compared to DMSO (Figure S10a). In contrast, only spontaneous emission was detected in ethanol and acetone, which have lower refractive indices. To gain deeper insights into these observations, we conducted simulations of the electric field distribution using two different refractive indices to investigate why higher refractive indices enhance laser performance (**Figure 4.14b**). In environments with low refractive indices, standing waves struggle to localize and accumulate in the desired direction. Conversely, in

solutions with higher refractive indices, emitted light was effectively confined within the spacer formed by the cuvette walls. These simulations revealed that coherence diminishes when light interacts with materials that have refractive indices significantly lower than that of quartz. In experiments with higher refractive indices, intense interference was observed, facilitating light propagation in the desired direction along the active region. This understanding underscores the critical role of refractive index in optimizing laser performance.

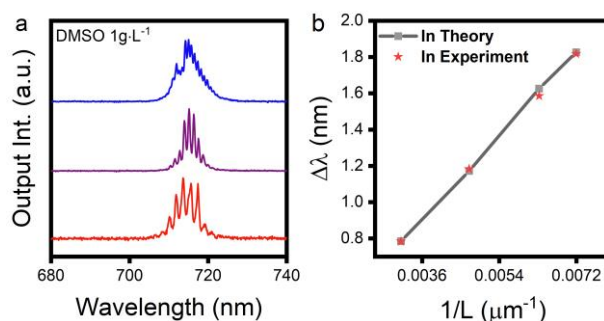


Figure 4.13 Characterization of programmable lasing in DMSO ($1 \text{ g} \cdot \text{L}^{-1}$). a) Lasing spectra with tunable length of air-cavity. b) Linear relationship between mode spacing and L^{-1} .

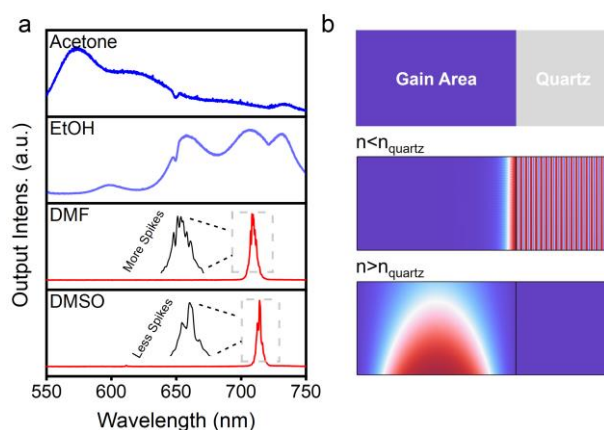


Figure 4.14 Effect of refractive index on optical feedback. a) Emission spectra of TCQDs in solvents with different refractive index. Lasing happened when the refractive index close or greater than n_{quartz} (1.45). b) Low refractive index solvent preserved light in the quartz spacer. High refractive index solvents favor propagation out of quartz interfaces.

4.3.4 Transient state absorption of TCQDs solution

Due to the low transmittance of high-concentration solutions, transient absorption (TA) spectra of $2^{-2} \text{ g} \cdot \text{L}^{-1}$ were selected to study carrier dynamics under varying incident power densities (1.19 to $3.58 \text{ J} \cdot \text{cm}^{-2}$, **Figure 4.15**). Two distinct opposing signals are observed in the TA spectra (**Figure 4.16a**). The negative region before 570 nm is attributed to ground state bleaching (GSB), consistent with the steady-state UV-Vis absorption spectra. TA spectra at different delay times within a timescale of 5 ns explored the carrier dynamics in depth. The first process, occurring within 1.09 ps , illustrated the dynamics, where absorption peaks at 515 nm and 550 nm appeared and gradually increased as the delay time progressed. Meanwhile, the peak attributed to excited state absorption (ESA) at 600 nm continued rising, corresponding to significant absorption loss in the excited state, which is detrimental to population inversion. The second process occurred within a delay time range of 1.61 - 6.14 ps . The initial two peaks at 515 nm and 550 nm gradually decreased with a slight blue shift, while the peak at 470 nm continued to grow, consistent with the photoluminescence excitation (PLE) spectra. As the delay time increased further, the absolute values of all peaks significantly decreased, except for GSB at 450 nm .

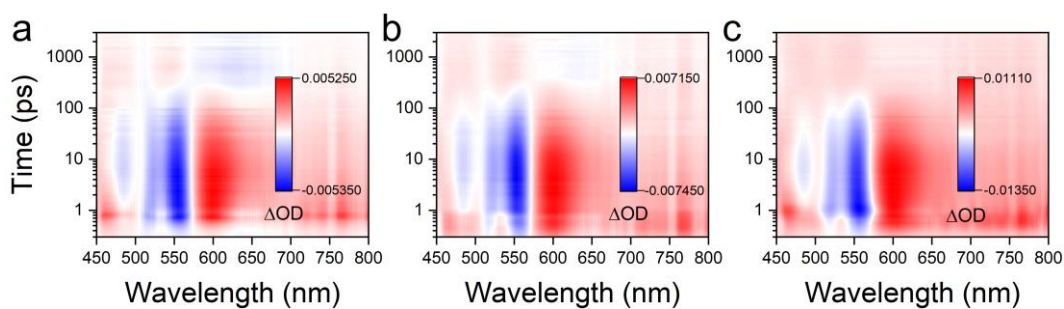


Figure 4.15 TA spectra of TCQDs in DMF with 2^{-2} g·L $^{-1}$. Pseudocolour images of TA spectra for the TCQDs under different incident power a) 1.19 J·cm $^{-2}$. b) 1.29 J·cm $^{-2}$. c) 2.79 J·cm $^{-2}$.

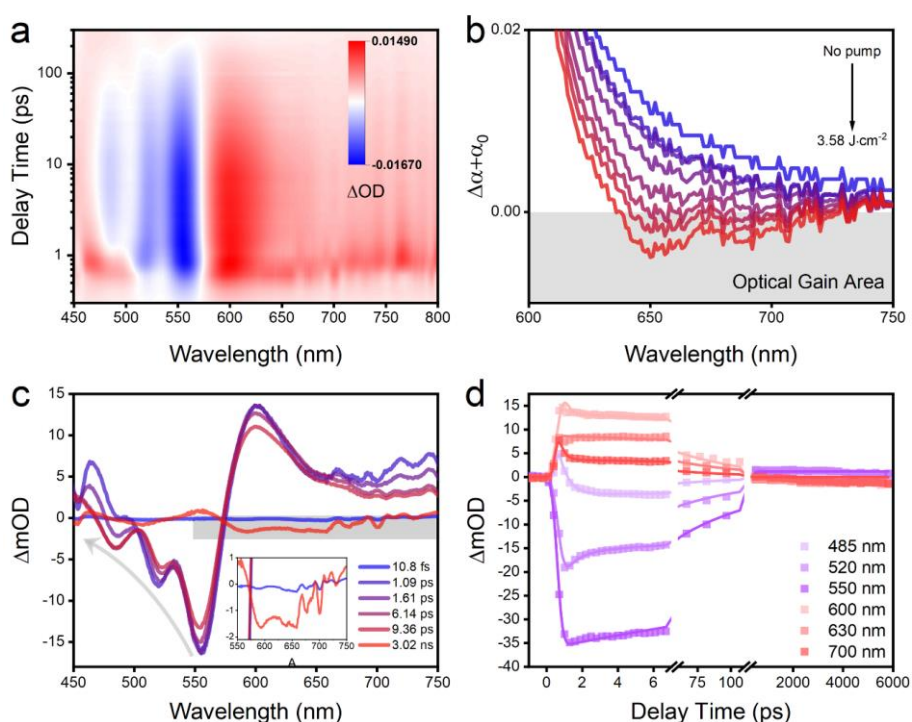


Figure 4.16 a) Pseudocolour images of TA spectra for the TCQDs (2^{-2} g·L $^{-1}$) under incident excitation power of 3.58 J·cm $^{-2}$. b) Optical gain obtained by the TA and steady-state absolute absorption of the TCQDs solutions recorded at a delay time of $\approx$ 500 ps. c) TA spectra of TCQDs solution (2^{-2} g·L $^{-1}$) probed at different time scales. d) TA kinetics of TCQDs solution (2^{-2} g·L $^{-1}$) probed at different wavelengths.

The observations suggest that pump light excitation rapidly induces two distinct transition pathways, generating photogenerated carriers that populate absorption bands at 515 nm and 550 nm, with dominant photon emission at 600 nm. Ground state bleaching (GSB) at 515 nm emerged as the dominant signal immediately following initial excitation. Subsequently, after 6.14 ps, the higher energy level at 470 nm began to play a more prominent role, leading to the emission of longer-wavelength photons. This photo-excitation process indicates that energy levels corresponding to wavelengths above 630 nm achieved population inversion (**Figure 4.17**). Analysis of the excitation dynamics reveals that the 520 nm peak attains its maximum intensity within a few femtoseconds, followed by energy dissipation to other energy bands (**Figure 4.17c**). A similar trend was observed for the emission energy levels (**Figure 4.17d**). This analysis underscores the rapid transitions and energy redistribution occurring in the system, which are critical for understanding lasing dynamics.

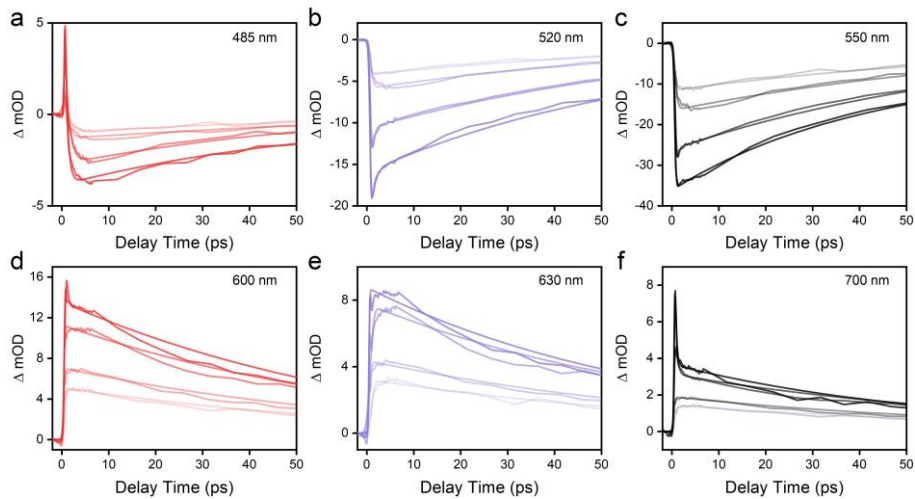


Figure 4.17 TA dynamics spectra at different energy levels. f) 485 nm. g) 520 nm. h) 550 nm. i) 600 nm. j) 630 nm. k) 700 nm.

4.3.5 Chemical structure analysis

The chemical structure of CQDs was also analyzed to elucidate the principles underlying lasing performance. TCQDs underwent post-treatment via secondary solvothermal processing using a mixture of ethanol and ammonia, resulting in a product referred to as oxidized carbon dots (OCDs, Experimental Section). After treatment, the optical properties of OCDs were characterized by steady-state PL and absorption spectra (**Figure 4.18 and 4.19**). Similar concentration-dependent performances were observed, with the PL spectra covering a range from 585 nm to 680 nm (**Figure 4.20**). However, no new absorption or PLE peaks emerged in the spectra, indicating that the FRET effect led to an increase in non-radiative channels, thereby disrupting the process of population inversion (**Figure 4.21**). OCDs could not emit lasing even under ultrahigh energy excitation (**Figure 4.22**).

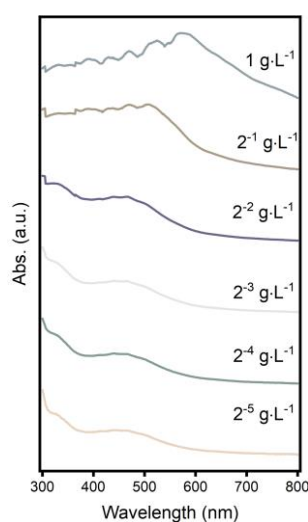


Figure 4.18 Normalized absorption spectra of OCDs at different concentrations.

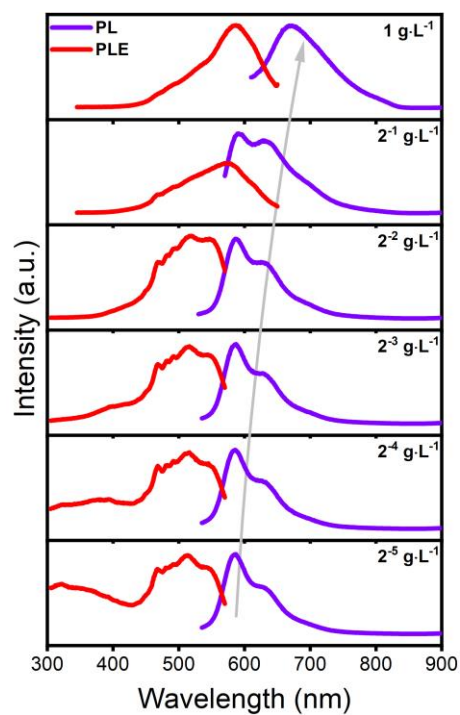


Figure 4.19 Optimal PL and PLE spectra of OCDs at different concentrations.

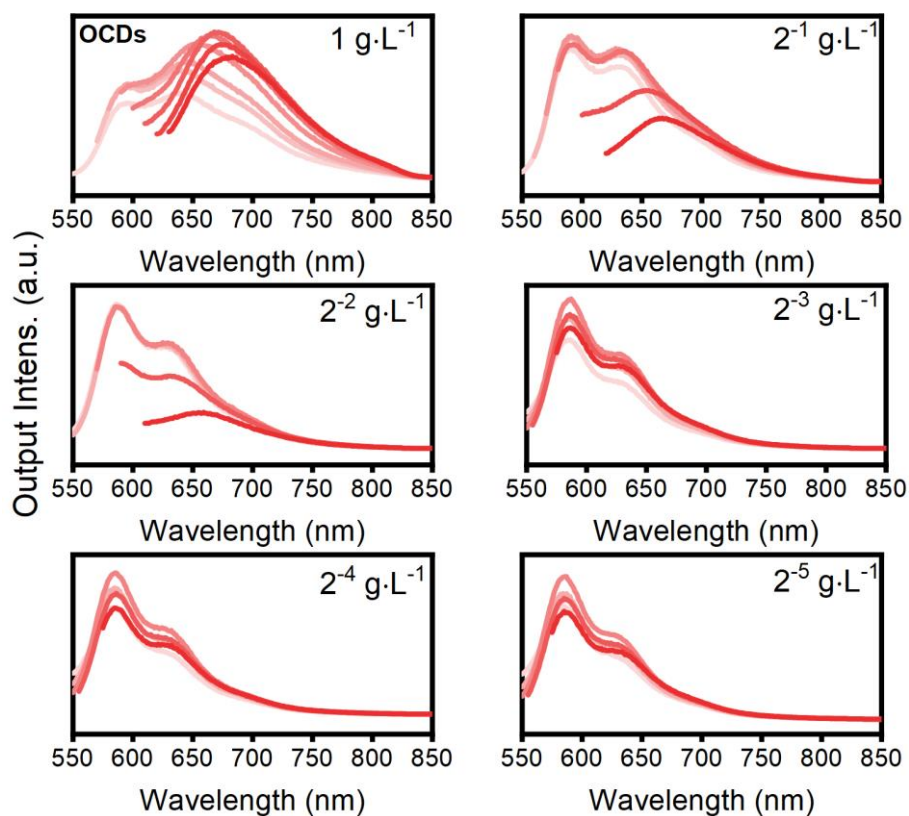


Figure 4.20 Excitation-dependent PL spectra of OCDs at different concentrations from $2^{-5} \text{ g}\cdot\text{L}^{-1}$

^{1} to $1 \text{ g}\cdot\text{L}^{-1}$.

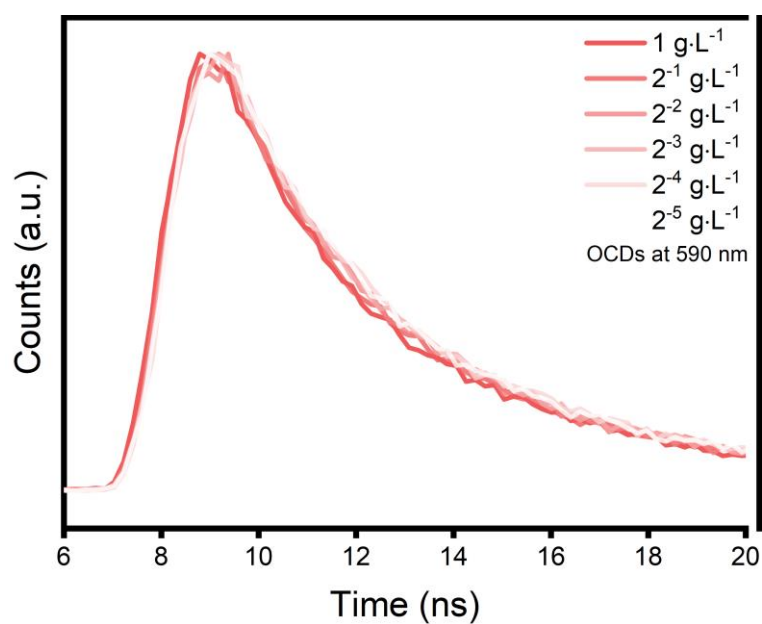


Figure 4.21. TRPL of OCDs at different concentrations at 590 nm.

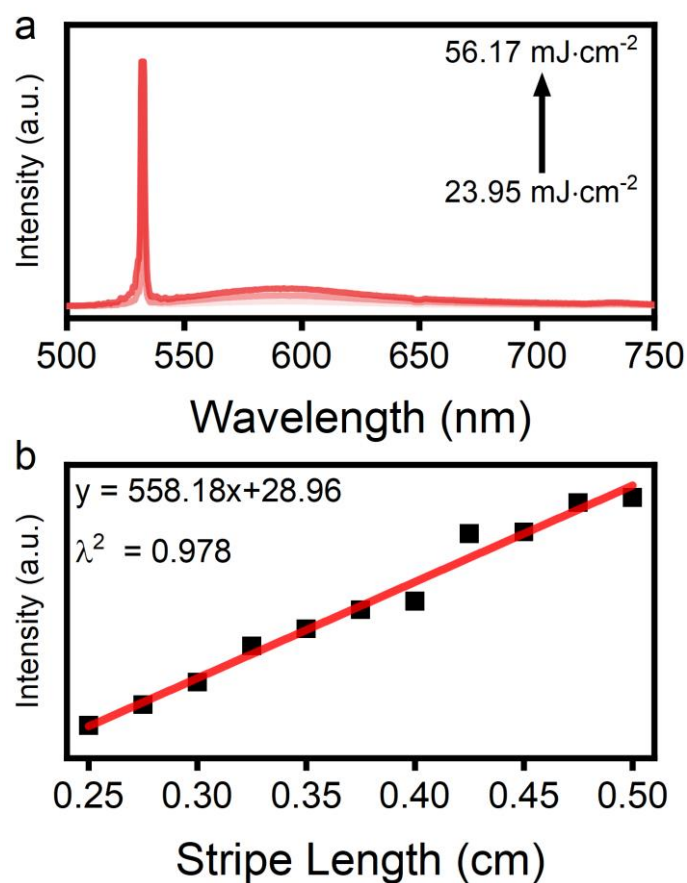


Figure 4.22 Characterization of OCDs. a) PL spectra versus incident power density of OCDs

(2-1 g·L⁻¹). b) PL Intensity at 590 nm versus variable stripe length with 56.17 mJ·cm⁻².

X-ray photoelectron spectroscopy (XPS) was employed to investigate the elemental composition and chemical structures of both carbon dot variants (**Figure 4.23a-h, Table 1**). The detailed composition of each element is presented in **Table 1**. The percentages of the four elements showed minimal change after secondary solvothermal treatment, except for an increase in the content of C=C and C-C bonds, indicating a higher degree of graphitization, which is a normal phenomenon following high-temperature and high-pressure reactions. Notable changes in elemental analysis were observed in the oxygen- and nitrogen-related compositions.[27-28] After the reaction, N-H functional groups in OCDs disappeared compared to TCQDs, along with the C=O group. These significant differences suggest that functional groups, such as amides and carboxylic acids, attached to the surface of TCQDs were substituted by other active groups. Interestingly, the amino group did not increase despite the introduction of ammonia during the reaction, indicating that ammonia acted solely as a solvent to create an extreme environment rather than as a precursor. Similar results were obtained from Fourier-transform infrared spectroscopy (FT-IR) (**Figure 4.23i, j**), where the stretching vibration of N-H at around 3250 cm⁻¹ was not detected after the reaction.

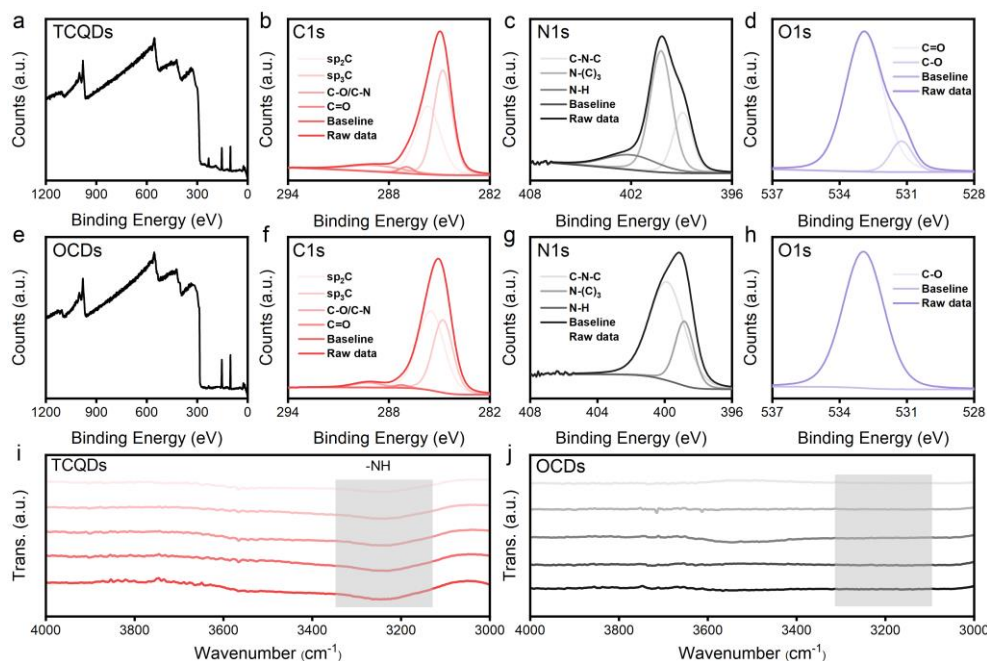


Figure 4.23 Elemental Analysis of TCQDs and OCDs. XPS survey spectra of a) TCQDs and e) OCDs. High-resolution spectra of C1s, N1s, O1s of b-d) TCQDs and f-h) OCDs. i) and j) FT-IR spectra of TCQDs and OCDs with different concentration, from bottom to top: $1 \text{ g} \cdot \text{L}^{-1}$, $2^{-1} \text{ g} \cdot \text{L}^{-1}$, $2^{-2} \text{ g} \cdot \text{L}^{-1}$, $2^{-3} \text{ g} \cdot \text{L}^{-1}$, $2^{-4} \text{ g} \cdot \text{L}^{-1}$.

4.3.6 Concentration-dependent programmable mode spacing laser

Similar tunable mode-spacing trends were observed in the lasing spectra for the three additional concentrations as shown in **Figure 4.24**. For solutions with $2^{-1} \text{ g} \cdot \text{L}^{-1}$ in DMF, the mode spacing could be adjusted from 0.89 nm to 2.57 nm as the cavity length was reduced. Interestingly, at $2^{-2} \text{ g} \cdot \text{L}^{-1}$, two lasing peaks with controllable mode spacing emerged simultaneously in a single PL spectrum. Calculation using the equation $\Delta\lambda = \lambda^2/(2n_{\text{eff}}L)$ showed that the variation range for 655 nm (1.28 nm to 3.33 nm) was narrower than that for 703 nm (1.50 nm to 3.98 nm) as the cavity length changed. At a lower concentration of $2^{-3} \text{ g} \cdot \text{L}^{-1}$, a shorter modulable lasing band appeared at 641 nm,

with mode spacing ranging from 2.02 nm to 3.03 nm. All experimental results align with theoretical predictions (**Figure 4.25**). Reducing CQDs concentration decreases scattering losses but elevates the lasing threshold, complicating the suppression of competing modes. Future efforts will focus on designing more precise cavity geometries to achieve single-mode lasing across a wider spectral range.

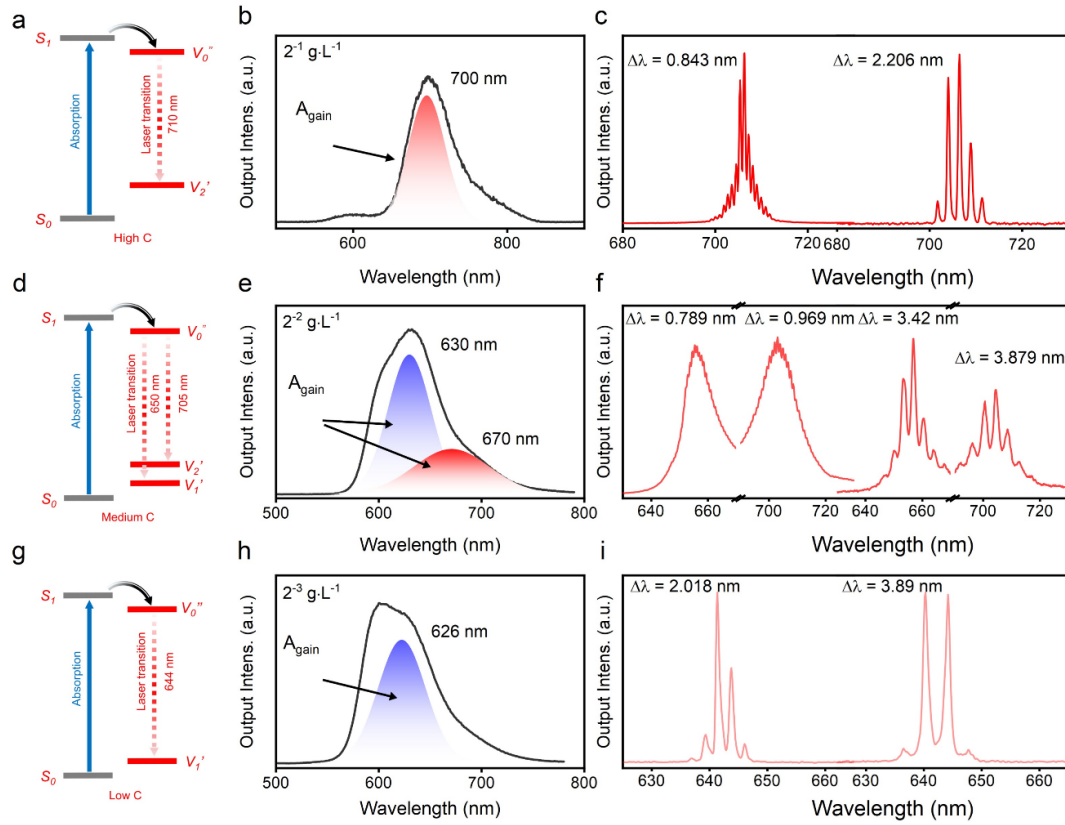


Figure 4.24 Schematic diagrams of various concentration-dependent lasing transitions at a) 2^{-1} g·L $^{-1}$. d) 2^{-2} g·L $^{-1}$. g) 2^{-3} g·L $^{-1}$. Fitted emission spectra at gradient concentration. b) 2^{-1} g·L $^{-1}$. e) 2^{-2} g·L $^{-1}$. h) 2^{-3} g·L $^{-1}$. All the spectra can be deconvoluted to 3 peaks around 600 nm, 630 nm, and 700 nm. Lasing spectra of TCQDs solution in DMF with a concentration of c) 2^{-1} g·L $^{-1}$. f) 2^{-2} g·L $^{-1}$. i) 2^{-3} g·L $^{-1}$ under the influence of external mirror.

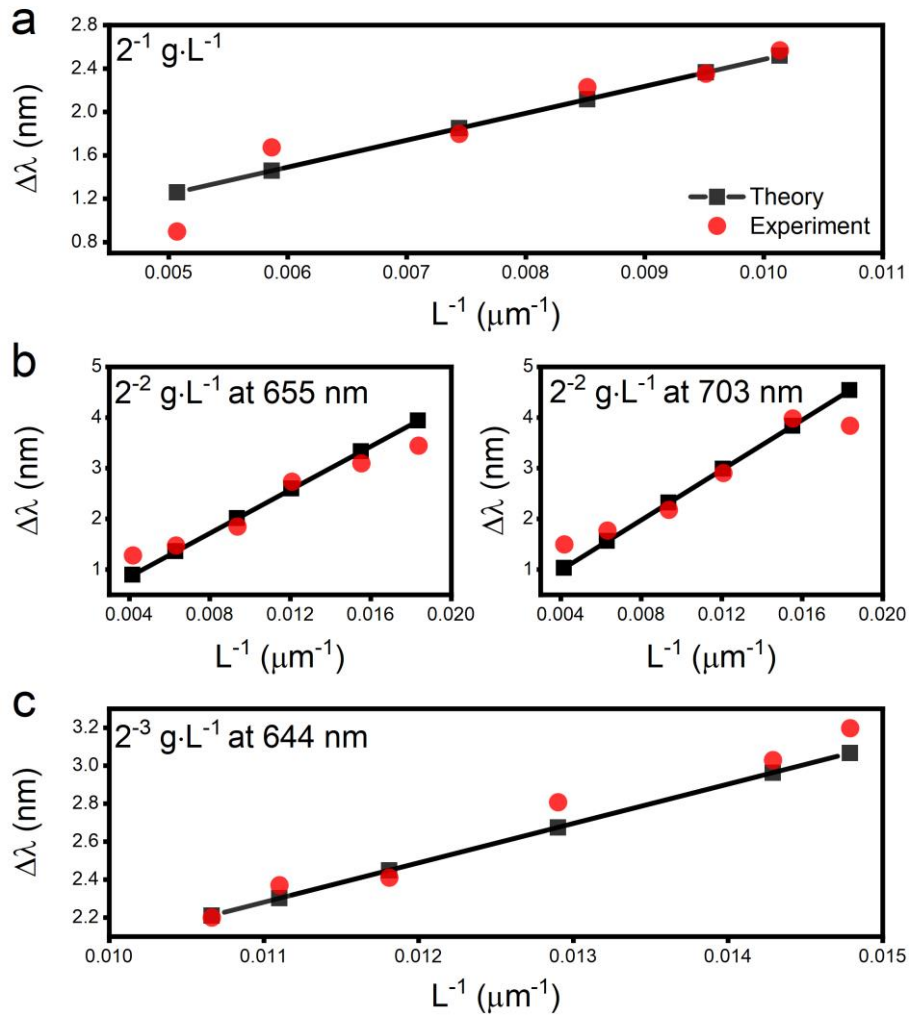


Figure 4.25 Linear relationship between mode spacing and L^{-1} of TCDs solution at concentration of a) $2^{-1} \text{ g}\cdot\text{L}^{-1}$. b) $2^{-2} \text{ g}\cdot\text{L}^{-1}$. c) $2^{-3} \text{ g}\cdot\text{L}^{-1}$.

To validate the broader applicability of the adjustable mode-spacing technique for liquid gain media, we tested two organic dye solutions: Rhodamine B (RhB) and Nile Blue (**Figure 4.26**). At a concentration of $1 \text{ g}\cdot\text{L}^{-1}$, the RhB laser exhibited tunable mode spacing from 0.85 nm to 2.35 nm with decreasing cavity length, while Nile Blue demonstrated mode spacing ranging from 1.063 nm to 1.625 nm. All experimental results align closely with theoretical predictions derived from the Fabry-Pérot cavity model (**Figure 4.26d, h**).

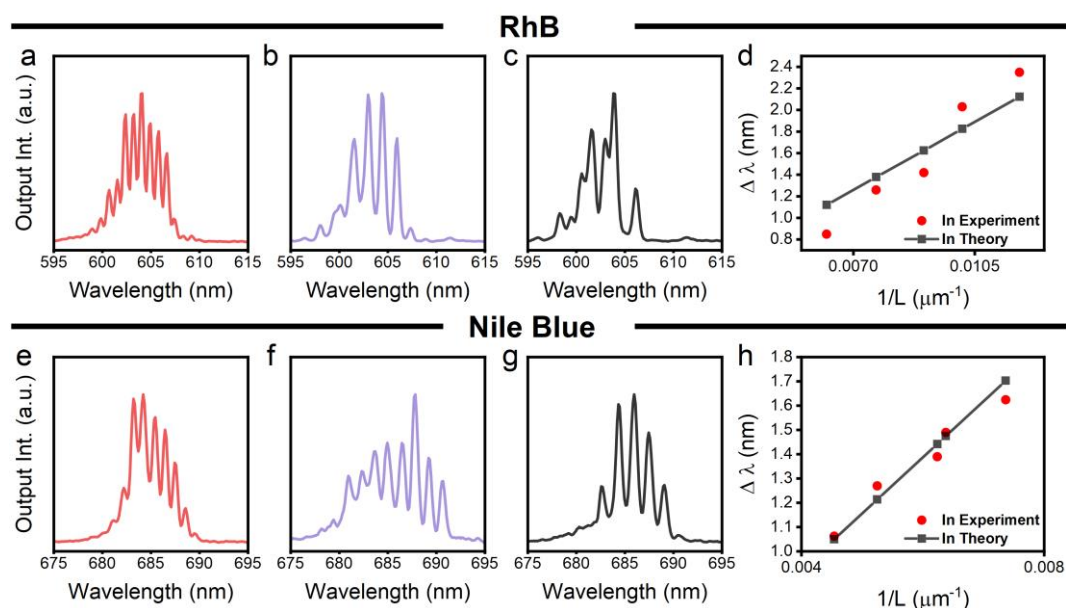


Figure 4.26 Universality of mode tuning methods in organic dyes. Lasing spectra of organic dyes with tunable air-cavity length. a-c) Rhodamine B. e-g) Nile blue. Linear relationship between mode spacing and L^{-1} (reciprocal of the cavity length) of d) Rhodamine B. h) Nile blue.

4.4 Conclusion

In summary, we employed a quartz cuvette filled with CQDs dispersed in DMF as the liquid gain medium. The FRET-based multi-level system in CQDs enables population inversion at low energy thresholds and delivers a broad gain bandwidth between 641 nm and 710 nm. The refractive index matching between the liquid gain medium and the quartz cuvette enables the formation of a gain-guided optical waveguide, producing low-divergence-angle beam emission. This emission facilitates efficient coupling of external optical feedback, as the collimated beam propagation ensures that reflected light from the external mirror retains minimal divergence, thereby enhancing the feedback mechanism's efficiency. By precisely adjusting the external mirror separation, we achieved modal control of the liquid-based CQD laser, enabling

transitions from random lasing to multimode Fabry–Pérot lasing and finally single-mode lasing. The strong optical feedback, characterized by its long penetration length, suppresses random modes associated with short closed-loop cavities, stabilizing Fabry–Pérot mode operation. Stable single-mode lasing at 715 nm was achieved through meticulous mirror positioning. This methodology is broadly applicable to colloidal quantum dots as liquid-state gain media, establishing a universal platform for spectrally tunable lasers.

Chapter 5 Conclusions and Outlook

The advancements presented in this thesis on non-steady-state regulation of laser emission through spatial and temporal control of energy transfer dynamics open promising avenues for future research and technological applications in photonics. By demonstrating significant enhancements in NIR-to-UV upconversion in lanthanide-doped fluoroaluminate glass-ceramics and tunable broadband lasing in carbon quantum dots (CQDs) systems, this work establishes a foundational framework that can be extended to address ongoing challenges and explore new frontiers.

One key direction for future work involves the integration of these materials into practical devices. For the lanthanide-doped glass-ceramics explored in Chapter 3, the achieved spatial Ln^{3+} -enrichment in nanophases and kinetic pulse-compression have enabled low-threshold UV random lasing at wavelengths as short as 205 nm, holding immense potential for compact, solid-state UV sources in applications such as photocatalysis, water sterilization, high-resolution lithography, and biomedical diagnostics. Further optimization could focus on hybridizing these glass-ceramics with waveguide structures or photonic crystals to enable directional output and single-mode operation, potentially reducing thresholds even further and improving beam quality. Additionally, exploring co-doping with other lanthanides (e.g., Pr^{3+} or Ce^{3+}) or incorporating plasmonic nanostructures could enhance energy transfer efficiencies and extend emission into the vacuum UV regime, addressing the current limitations in photon energy and quantum yield. Building on the MD-guided design and rate-equation

modeling from Chapter 3, future studies might investigate scaling up the precipitation of tunable nanocrystals with varying (Ca, Sr, Ba)/Ln ratios to achieve even shorter inter-ion distances, thereby boosting multiphoton upconversion rates and realizing efficient NIR-to-DUV conversion in larger-scale devices.

In the realm of CQDs, the development of tunable-wavelength broadband liquid-state lasers spanning 641–710 nm paves the way for flexible, solution-processable photonic devices in integrated optics, sensing, and display technologies. Future efforts could emphasize improving photostability and gain coefficients by advanced surface passivation techniques or embedding CQDs in solid matrices like aerogels or polymers to mitigate scattering losses and enable long-term operation. Moreover, extending the FRET-based tuning mechanism to other quantum dot families, such as perovskite or colloidal QDs, could broaden the spectral range into the blue and green regions, facilitating full-color lasing platforms. The gain-guided waveguide approach demonstrated here could also be adapted for microfluidic lasers, where dynamic refractive index modulation via external fields enables real-time tunability.

A broader challenge lies in scaling these non-steady-state strategies to higher powers and efficiencies while maintaining cost-effectiveness. Molecular dynamics simulations and rate-equation modeling, as refined in this thesis, could be augmented with machine learning algorithms to predict optimal compositions and pulse parameters for new host materials, accelerating material discovery. Investigating the interplay between spatial enrichment and temporal pulse compression in hybrid systems—

combining lanthanide-doped hosts with CQDs—might yield multifunctional lasers capable of simultaneous upconversion and downconversion, ideal for quantum information processing or multi-modal sensing.

Finally, this framework underscores the need for interdisciplinary collaboration between materials science, photonics, and computational modeling to overcome barriers like defect quenching and thermal management. As global demands for sustainable and efficient light sources grow, the principles of spatiotemporal energy transfer control outlined here could inspire next-generation lasers that are not only performant but also environmentally benign, contributing to advancements in renewable energy, healthcare, and information technologies. Continued exploration in these areas promises to transform non-steady-state laser regulation from a niche concept into a cornerstone of modern optics.

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