Ultralow-power nanoscale optical data storage in a nanocomposite based on up-conversion nanoparticles and graphene oxide

A thesis submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy

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Dedicated to My Beloved Family.
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

The up-conversion nanoparticles used for the work included in this PhD thesis were synthesised by Dr. Y. Wu under the supervision of Professor X. Liu (Department of Chemistry, National University of Singapore, Singapore 117543, Singapore).

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<th>Description</th>
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<tr>
<td>1D:</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D:</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D:</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>B:</td>
<td>Byte</td>
</tr>
<tr>
<td>kB:</td>
<td>Kilobyte</td>
</tr>
<tr>
<td>MB:</td>
<td>Megabyte</td>
</tr>
<tr>
<td>GB:</td>
<td>Gigabyte</td>
</tr>
<tr>
<td>TB:</td>
<td>Terabyte</td>
</tr>
<tr>
<td>PB:</td>
<td>Petabyte</td>
</tr>
<tr>
<td>EB:</td>
<td>Exabyte</td>
</tr>
<tr>
<td>ZB:</td>
<td>Zettabyte</td>
</tr>
<tr>
<td>YB:</td>
<td>Yottabyte</td>
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<tr>
<td>CD:</td>
<td>Compact Disc</td>
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<tr>
<td>DVD:</td>
<td>Digital Versatile Disc</td>
</tr>
<tr>
<td>BD:</td>
<td>Blu-ray Disc</td>
</tr>
<tr>
<td>AD:</td>
<td>Archival Disc</td>
</tr>
<tr>
<td>QD:</td>
<td>Quantum dot</td>
</tr>
<tr>
<td>MNP:</td>
<td>Metallic nanoparticle</td>
</tr>
<tr>
<td>RNC:</td>
<td>Rare-earth doped nanocrystal</td>
</tr>
<tr>
<td>UCNP:</td>
<td>Up-conversion nanoparticle</td>
</tr>
<tr>
<td>Ln:</td>
<td>Lanthanide</td>
</tr>
<tr>
<td>G:</td>
<td>Graphene</td>
</tr>
<tr>
<td>GO:</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>rGO:</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>DTE:</td>
<td>Diarylethene</td>
</tr>
<tr>
<td>YAG:</td>
<td>Yttrium aluminium garnet</td>
</tr>
<tr>
<td>ITO:</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>FRET:</td>
<td>Fluorescence resonance energy transfer</td>
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<tr>
<td>RET:</td>
<td>Resonance energy transfer</td>
</tr>
<tr>
<td>STED:</td>
<td>Stimulated emission depletion</td>
</tr>
<tr>
<td>SPIN:</td>
<td>Super-resolution photo-induction inhibited nanolithography</td>
</tr>
<tr>
<td>$I_s$:</td>
<td>Saturation intensity</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PSF</td>
<td>Point spread function</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>RESOLFT</td>
<td>Reversible saturable optical fluorescence transitions</td>
</tr>
<tr>
<td>fs</td>
<td>Femtosecond</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>HWP</td>
<td>Half waveplate</td>
</tr>
<tr>
<td>QWP</td>
<td>Quarter waveplate</td>
</tr>
<tr>
<td>VPP</td>
<td>Vortex phase plate</td>
</tr>
<tr>
<td>DC</td>
<td>Dichroic mirror</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>2P</td>
<td>Two-photon</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical aperture</td>
</tr>
<tr>
<td>ESA</td>
<td>Excited-state absorption</td>
</tr>
<tr>
<td>ETU</td>
<td>Energy transfer up-conversion</td>
</tr>
<tr>
<td>CSU</td>
<td>Cooperative sensitization up-conversion</td>
</tr>
<tr>
<td>EMU</td>
<td>Energy migration-mediated up-conversion</td>
</tr>
<tr>
<td>S</td>
<td>Sensitizer</td>
</tr>
<tr>
<td>L</td>
<td>Ladder</td>
</tr>
<tr>
<td>M</td>
<td>Migrator</td>
</tr>
<tr>
<td>A</td>
<td>Activator</td>
</tr>
<tr>
<td>ET</td>
<td>Energy transfer</td>
</tr>
<tr>
<td>QY</td>
<td>Quantum yield</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>SPAD</td>
<td>Single-photon avalanche diode</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint committee on powder diffraction standards</td>
</tr>
<tr>
<td>ICDD</td>
<td>International centre for diffraction data</td>
</tr>
<tr>
<td>RGB</td>
<td>Red green blue</td>
</tr>
<tr>
<td>SKA</td>
<td>Square Kilometre Array</td>
</tr>
<tr>
<td>BRAIN</td>
<td>Brain Research through Advancing Innovative Nanotechnologies</td>
</tr>
</tbody>
</table>
Abstract

As an inevitable outcome of the ‘information revolution’, a huge amount of digital information needs to be stored and continuously accessed over long-term periods. Current data centres are insufficient to tackle this demand and researchers must deal with the formidable responsibility of developing data storage memories with greater capacity, extended lifetime and minimal energy consumption. Optical data storage is a particularly encouraging approach to supply the required storage needs because of its exceptional performance and durability. Nevertheless, it is crucial to increment the capacity of contemporary optical media. Further increments in capacity can be accomplished by overcoming the diffraction-limit barrier and thus shrinking the data bit size to the nanoscale.

The recent invention of stimulated emission depletion (STED) microscopy and super-resolution photoinduction-inhibited nanolithography (SPIN) have permitted nanoscale imaging and writing of features, respectively, thereby offering the potential for data storage towards Petabytes. However, a suitable medium for nanoscale optical data storage is still lacking. Among the potential candidates, up-conversion nanoparticles appear to be very promising because they exhibit a fluorescence lifetime which is hundreds to thousands of times longer than other fluorophores, and provide a pathway for super-resolution optical activation with extremely low power required. Further, graphene oxide enables data recording through its reduction.

The fundamental aim of this PhD thesis is to achieve ultralow-power nanoscale optical data storage in an up-conversion nanoparticle- and graphene oxide-based nanocomposite. The optical activation is enabled by the up-conversion nanoparticles, while the data recording is achieved in graphene oxide through its reduction via resonance energy transfer. Further, the metastability of the energy levels in the up-conversion nanoparticles with a lifetime of up to milliseconds enables SPIN and STED microscopy for data writing and read-out, respectively, with low laser intensities. Thus, optical data storage with ultralow energy consumption can be obtained, which also guarantees a long lifetime for the optical memory devices.
The photochemical reduction of thin-film graphene oxide integrated with up-conversion nanoparticles under high-energy laser irradiation for the modulation of up-conversion fluorescence is first demonstrated. This provides a stepping stone towards encoding and retrieval in an up-conversion nanoparticles–graphene oxide nanocomposite. Initially, a 375-nm CW laser is used to photochemically reduce graphene oxide. The absorption change in the nanocomposite is accompanied by the quenching of the fluorescence from the up-conversion nanoparticles. Subsequently, a CW laser at 980 nm is used to excite the up-conversion nanoparticles, and detection of the decreased up-conversion fluorescence up to ~90% associated with quenching by reduced graphene oxide is achieved. Further, the fast reduction speed of using high-energy laser allows a decrease in the time to modulate up-conversion fluorescence down to milliseconds for individual pixels. Optical patterns are successfully achieved and retrieved distinctly using the up-conversion fluorescence quenching by reduced graphene oxide.

High-energy up-conversion fluorescent nanoparticles are developed for application in dual-laser photoactivated super-resolution systems, including their combination with graphene oxide. Theoretical and experimental investigations are conducted to individuate the key features of the nanoparticles for efficient photoactivation in applications beyond the diffraction-limit barrier in energy transfer–driven systems. The nanoparticles are then tested under dual-beam super-resolution optical techniques, such as STED microscopy. First, optical depletion efficiency of 450-nm up-conversion fluorescence up to ~90% is achieved for 4% Tm-doped nanoparticles with a saturation intensity of ~375 kW cm$^{-2}$ (~1.5 mW). Second, super-resolution imaging of the up-conversion nanoparticles is undertaken via STED microscopy using a Gaussian-shaped 980-nm CW laser for excitation and a doughnut-shaped 808-nm CW laser for depletion, reaching a resolution of 64 nm with an intensity of 11.25 MW cm$^{-2}$. The values of intensity of the excitation and depletion beams are one hundredth to one thousandth of those required for typical STED imaging using other fluorophores, which is very attractive for applications with low power consumption in photoactivated systems.

The high-energy up-conversion fluorescent nanoparticles are then conjugated with single-layer graphene oxide nanosheets, obtaining an efficiency of ~83% of resonance energy transfer in the up-conversion nanoparticles–graphene oxide system. Demonstration of the photochemical reduction of graphene oxide in the nanocomposite is then reported under
Abstract

near-infrared laser excitation. Specifically, a CW laser at 980 nm is used to excite the up-conversion nanoparticles and produce up-conversion to levels with high energy, which triggers the dissociation of the oxygen groups in graphene oxide for reduction through resonance energy transfer. This mechanism demonstrates a suitable pathway for optical data writing. Two channels are then used to monitor the reduction process, which can thus be used for optical data reading: the quenching of 450-nm fluorescence from the up-conversion nanoparticles, which is quenched by ~40%, and the decrease of 650-nm two-photon excited fluorescence from graphene oxide, which is reduced by ~50%.

The up-conversion nanoparticles–graphene oxide nanocomposite is tested under dual-laser irradiation comprising a CW laser at 980 nm for excitation and CW laser at 808 nm for depletion. A value of ~95% optical depletion efficiency of the 450-nm up-conversion fluorescence is achieved. The saturation intensity is ~250 kW cm\(^{-2}\) (~1.0 mW), corresponding to several orders of magnitude reduction of energy consumption by using this novel nanocomposite to encode information bits in comparison with other nanomaterials used in super-resolution optical methods. In addition, the 808-nm CW laser can effectively inhibit up-conversion to high-energy levels in the up-conversion nanoparticles, resulting in prevented reduction of graphene oxide. Finally, ultralow-power nanoscale optical data storage is achieved in the nanocomposite. Nano-sized features with a size of 61 nm are produced by SPIN and subsequently retrieved by fluorescence quenching microscopy combined with STED microscopy, obtaining an estimated capacity of ~200 TB per disc.

The work included in this PhD thesis provides a comprehensive insight into the demonstration of ultralow-power nanoscale optical data storage in a novel nanocomposite based on up-conversion nanoparticles and graphene oxide. This achievement is a conceptual breakthrough compared with the current state-of-the-art optical data storage systems and will enable to encode optical data bits beyond the diffraction-limit barrier. Hence, increased capacity of individual optical data storage memories is expected for sustainable growth.
Chapter 1

Introduction

1.1 Big data and long data

Data are growing at an unprecedented rate. The International Data Corporation has predicted that digital information being produced worldwide will rise from 33 zettabytes (ZB) in 2018 to 175 ZB by 2025 (1 ZB equals 1 billion terabytes [TB]) [1]. Analysts have coined the term ‘big data’ to describe the huge volume of information that inundates businesses and companies daily (Figure 1a). In addition, research institutes and corporations need to readily access data over an extended time span, which is referred to as ‘long data’ [2] (Figure 1b). For instance, the Square Kilometre Array (SKA) telescope generates 160 TB s\(^{-1}\) [3], and the first detection of gravitational waves [4] has initiated century-long astronomic observations. Additionally, the BRAIN Initiative—a revolutionary programme for mapping the human brain—may have to deal with one yottabyte \(10^{12}\) TB of data [5]. Hence, data will not only have to be stored, but will also need to be repeatedly accessed over prolonged periods.
Current data centres enabled by magnetic hard disk drives and solid-state drives, with limited lifetime and large electricity consumption [6, 7], are insufficient to tackle the aforementioned demands. Thus, researchers must now deal with the formidable responsibility of developing data storage memories with greater capacity, extended lifetime and minimal energy consumption.
1.2 Optical data storage

Optical data storage is a particularly encouraging approach to supply the required storage needs because of its exceptional performance and durability. Nevertheless, it is crucial to increment the capacity of contemporary optical media. In optical data storage, photons are used to produce confined physical and/or chemical changes within the properties of a recording medium as an information storing process. When the optical device is scanned with a tightly-focused laser beam, the encoded data are retrieved through the change of intensity of the read-out beam (Figure 1.2).

![Working mechanism of optical data storage. a) Information bits are written through confined physical and/or chemical variations in the properties of an optically-readable medium. b) Information bits are then retrieved through change of intensity of the read-out beam.](image)

The ever-growing demand for capacity has compelled the constant improvement of optical media, which have evolved from 2D devices—such as the commercially-available compact disc (CD), digital versatile disc (DVD), Blu-ray disc (BD) and archival disc (AD)—to 3D multi-layer devices and multidimensional optical data storage devices, reaching a maximum recording capacity in the order of TBs per disc. The evolution of commercial and prototypical optical memory devices is reported in the following sections.
1.2.1 Two-dimensional optical data storage

Optical data storage began with 2D systems in which a single or few layers of data were recorded underneath the surface of the optical device. The working principle of 2D optical devices is to distinguish between pits (recorded areas) and lands (areas without recording) through variation in the reflected intensity of the reading beam. For the diffraction-limited case, the resolution $R$ is [8]:

$$ R = \frac{0.61\lambda}{NA} $$

where $\lambda$ is the laser wavelength and $NA$ is the numerical aperture of the objective lens. Given an optical disc of standard dimensions, the storage capacity is dependent on the size of the recorded bits. Resolution improvement has been achieved by shortening the recording laser wavelength from infrared to blue and violet, and by increasing the $NA$ from 0.45 to 0.85 to reduce the focal spot size. A dramatic increase in storage capacity has subsequently been obtained, while also maintaining the standard format of the optical discs. Commercially-available optical memory devices have developed from CDs to DVDs and BDs, and recently to ADs [9, 10], reaching a maximum recording capacity of 1 TB per disc and a lifespan of one century (Figure 1.3).
Figure 1.3: Development of optical discs. a) Working mechanism of the CD, DVD, BD and AD. b) Capacity and lifetime of the different formats.
As a result of being inexpensive, easy to produce and portable, optical discs gained rapid popularity and expansion, compared with other information memory devices. However, they are now becoming obsolete and are often substituted by hard disk drives and solid-state drives. In fact, many users are moving to the Cloud, enabled by data centres, and accessing data remotely [11]. Therefore, the market of storage devices is gradually targeting professional-level customers, rather than consumers. Nowadays, huge data volumes are retained for protracted periods and without erasure. ‘Cold data’ account for 50 to 80% of the total amount of data globally, and require storage with inexpensive long-term reliability and without detrimental effects on the environment. With their major advantage of durability, optical disc media are considered the best-suited candidate to accommodate this massive amount of information (Figure 1.4).

![Figure 1.4: Classification of digital data into ‘hot data’, ‘warm data’ and ‘cold data’, depending on the frequency of access and best-suited memory device for each data type. Optical disc media are predicted to be the best-suited candidate for ‘cold data’, which account for 50 to 80% of the total amount of data worldwide. Source: news.panasonic.com/](image)

Accordingly, next-generation optical memory devices will be required to possess a large capacity and quick time response to rapidly access information. In addition, they should consume little energy to minimise environmental degradation, while having a long lifespan to ensure protracted data storage and diminish expenditure on recurring information transfer. Finally, the format needs to be compatible with the present technologies. Table 1.1 summarises the benchmark parameters and performance goals for next-generation optical memory devices for use in the archival market. These features are greatly beneficial in individual devices and will ultimately provide sustainable allocation of data.
Table 1.1: Benchmark parameters and performance targets for next-generation optical memory devices for application in the archival market.

<table>
<thead>
<tr>
<th>Benchmark parameter</th>
<th>Performance target</th>
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<tbody>
<tr>
<td>Storage capacity</td>
<td>Petabytes per disc (PBs/disc)</td>
</tr>
<tr>
<td>Writing/reading speed</td>
<td>Gigabits per second (Gbits s⁻¹)</td>
</tr>
<tr>
<td>Lifetime</td>
<td>Century-long (&gt; 100 years)</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>Femtojoules per bit (fJs bit⁻¹)</td>
</tr>
<tr>
<td>Format</td>
<td>Compatible with current standard</td>
</tr>
<tr>
<td>Cost</td>
<td>US cents per gigabyte (~$0.01 GB⁻¹)</td>
</tr>
</tbody>
</table>

1.2.2 Three-dimensional optical data storage

Increasing the capacity of single optical discs to supply market needs has been the aim of a great number of researchers. In 2D optical data storage, the bits of information are recorded just one or a few layers underneath the surface of the device; thus, the volume of the optical device remains unused. The main challenge is that focusing the recording beam deep into the disc’s volume results in scattering loss. Specifically, scattering losses are higher for shorter wavelengths, thereby strongly limiting sub-surface penetration [12]. Consequently, the fabrication of 3D DVDs or BDs is very difficult. To solve this issue, two-photon (2P) excitation has been exploited for 3D optical data storage [13, 14]. 2P absorption occurs through the simultaneous absorption of two photons. Given that this process depends on the square of the incident laser intensity [15, 16], excitation is localised only in a small volume in the focal region, which results in reduced separation between recording layers, without crosstalk. For this purpose, a high-energy pulsed laser source can be employed to produce excitation only within a small region of the focal spot in the recording medium. Over the years, the axial spread of the point spread function (PSF) has been reduced, improving the resolution along the axial dimension. 2P excitation can also propagate deeply into the optical device by using an infrared wavelength, which encounters reduced scattering loss. High-density 3D optical data storage using 2P excitation has been achieved in photopolymerisable materials [14, 17], photochromic materials [13, 16, 18, 19], photorefractive materials [20, 21] and photobleaching materials [22, 23]. In addition, a prototypical 3D optical disc based on 2P excitation has been fabricated, obtaining 300 Gbits cm⁻³ of capacity and a recording and reading speed similar to that currently used for the DVDs [16].
1.2.3 Multidimensional optical data storage

3D optical memory devices based on 2P excitation still have limited capacity because the dimension of the written bits is restricted in resolution by diffraction. In fact, a maximum theoretical value of only 3.5 Tbits cm$^{-3}$ can be achieved [24]. The need for higher capacity compelled the invention of multidimensional multiplexed systems, in which more than one individual information bit can be stored in a single location within the optical medium. For instance, data have been multiplexed through other physical dimensions of the recording beam, such as polarisation or wavelength, which may greatly increase the data storage capacity. Over the years, multidimensional systems have been developed to employ different types of material, such as rare-earth ions in crystals, quantum dots (QDs), magnetic nanoparticles (MNPs), rare-earth doped nanocrystals (RNCs) and graphene (G)/graphene oxide (GO) (Figure 1.5).

![Timeline of the evolution of capacity of multidimensional optical memory devices using different types of materials, such as rare-earth ions in crystals, QDs, MNPs, RNCs and G/GO.](image)

**Figure 1.5:** Timeline of the evolution of capacity of multidimensional optical memory devices using different types of materials, such as rare-earth ions in crystals, QDs, MNPs, RNCs and G/GO.
Rare-earth ions in crystals were used for multidimensional optical data storage via spectral hole burning [25]. QDs were incorporated into photoswitchable molecules, such as photorefractive and photoisomerisation materials, to demonstrate polarisation-sensitive four-dimensional optical data storage [26]. In 2009, an innovative method for data multiplexing was proposed by introducing nanoplasmonics into the field of optical data storage. Given that the surface plasmon resonance of MNPs relies on the wavelength and polarisation, these two physical dimensions were combined with the three spatial domains for five-dimensional optical data storage [27]. Samples consisting of polyvinyl alcohol doped with gold nanorods were irradiated at the surface plasmon resonance frequency of the nanorods to induce a thermal rise beyond their melting point and induce reshaping into spheres, which possess higher thermal stability. This photoexcitation-induced phase change was used to permanently encode data bits. Via irradiation with suitable polarisation and wavelength, multiplexed data bits were retrieved distinctively and with no crosstalk via 2P excitation. An envisaged capacity of 1.6 TB was achieved for a standard DVD using this method. Further advances may be expected by encoding data also in the orbital angular momentum of the writing laser to potentially take advantage of six physical dimensions [28]. Data multiplexing was obtained using RNCs by controlling their fluorescence lifetime [29]. Finally, graphene and graphene oxide were employed in multimode information encoding through bit-by-bit 3D optical data storage combined with holography data storage [30, 31]. The fluorescence emission of graphene oxide and its huge refractive index change have been used for data writing and reading. However, the size of the encoded bits achieved using the described methods is still limited by diffraction, and a capacity of only a few TBs per disc can be obtained even through multidimensional multiplexing. Thus, there is an urgent demand for super-resolution techniques to achieve nanoscale optical data storage.

1.2.4 Nanoscale optical data storage

Conventional optical methods are restricted by diffraction, which renders them insufficient to sustainably accommodate the huge amount of data generated worldwide. Further increments in capacity for individual devices can be accomplished by overcoming the diffraction-limit barrier and thus shrinking the information bit size to the nanoscale. The recent breakthroughs in nanophotonics have provided novel avenues for interaction between light and matter, and enable manipulation of materials at the nanoscale through laser. An example is the
development of far-field super-resolution optical microscopy and nanolithography, which overcome the physical boundary imposed by diffraction by switching samples between an ‘ON’ and ‘OFF’ state in a controllable manner. In particular, stimulated emission depletion (STED) microscopy and super-resolution photoinduction-inhibited nanolithography (SPIN) have permitted nanoscale imaging and writing of features, respectively, thereby offering the potential for high-capacity optical data storage towards PBs [32]. However, a suitable medium for nanoscale optical recording and reading is still lacking. In this context, inorganic nanomaterials are exceptional choices for use in super-resolution optical data storage media. This emerging class of materials has large one- and two-photon absorption cross-sections, broad absorption bandwidth, high quantum yield and long fluorescence lifetime. Further, they are highly photo-stable and resistant to photobleaching. Among the potential candidates, up-conversion nanoparticles appear to be very promising because they exhibit a fluorescence lifetime which is hundreds to thousands of times longer than other fluorophores, and provide a pathway for super-resolution optical activation with extremely low power required. Further, graphene oxide enables data recording through its reduction to reduced graphene oxide. In addition, the solubility in water and organic solvents of these two nanomaterials facilitates their incorporation into suitable matrices for the massive production of low-priced optical memory devices. The combination of up-conversion nanoparticles and graphene oxide thus offers a feasible pathway to achieve nanoscale optical data writing and reading on the same materials platform.

1.2.4.1 Fundamental limitation in conventional optical data storage

Resolution is the ability to distinguish two point-like objects that are closely adjacent to each other. Although technological developments and improved manufacturing processes have led to great image quality and high fabrication resolution, there exists an intrinsic limit to the resolution that any conventional optical system can achieve because of the diffraction of light. The limiting resolution is described by Abbe’s law:

$$d = \frac{\lambda}{2n \sin \theta}$$  \hspace{1cm} (1.2)

where \(d\) is the shortest span between two detectable features, \(\lambda\) is the wavelength, \(n\) is the refractive index of the medium and \(\theta\) is half of the angle subtended by the objective. The
term $nsin\theta$ is often referred to as numerical aperture $NA$, and can be 1.4 to 1.6 in modern optics. For example, considering a typical green laser ($\lambda = 532$ nm) and an air objective lens ($NA = 0.95$), the resolution is:

$$d \sim \frac{\lambda}{2}$$

(1.3)

Thus, the resolution of conventional optical systems results in approximately half of the wavelength of the laser in use. Specifically, the minimum achievable spot size is roughly between 250 and 300 nm for the lateral directions ($x, y$) and roughly between 500 and 700 nm for the axial direction ($z$).

### 1.2.4.2 Concept of nanoscale optical data storage

The pioneering invention of super-resolution optical microscopy has enabled researchers to break through the diffraction-limit resolution barrier, thereby allowing the detection of features down to the nanoscale. Researchers realised that successfully overcoming the fundamental optical diffraction limit could potentially provide innovative technologies for optical memories with increased capacity. Near-field techniques [33-35] were initially considered to achieve nanoscale optical data storage. Their working principle exploits the properties of evanescent waves in proximity to the recording sample. However, near-field optical microscopy only works at a tiny distance from the surface of the medium, allowing 2D applications only. In contrast, far-field super-resolution techniques are promising for nanoscale 3D optical data storage. These techniques exploit the fluorescence properties of dye molecules or adjacent objects, and use interstate transitions to switch them between bright and dark states to generate sequential emission. In STED microscopy [36], two overlapped lasers selectively activate and deactivate fluorophores, allowing only molecules that are located at the centre of the excitation laser to fluoresce. STED microscopy is based on the physical principles of fluorescence and STED (Figure 1.6).
Figure 1.6: Principles of fluorescence and STED. Consequent to absorption of light, the sample is excited from $S_0$ (ground state) to $S_1$ (excited state). Then it can spontaneously return to $S_0$, accompanied by emission of fluorescence, unless forced down to the ground state by STED.

In STED microscopy, the laser for depletion is spatially engineered into the shape of a doughnut and features a point with zero intensity centrally located in the focal spot and strong nonzero intensity at the outer ring. Thus, fluorescence is quenched only at the periphery of the excitation focal spot, where the nonzero intensity of the depletion beam overlaps the excitation beam (Figure 1.7a). The key feature to achieve super-resolution using STED microscopy is that the depleted electrons nonlinearly depend on the intensity of the STED laser. For STED laser intensity that is greater than a threshold called ‘saturation intensity’, the spontaneous fluorescence is effectively suppressed. These concepts are outlined by the modified Abbe’s law:

$$d = \frac{\lambda}{2nsin\theta \sqrt{1 + \frac{I_{STED}}{I_s}}}$$

where $I_{STED}$ is the STED laser beam intensity and $I_s$ is the fluorophores’s saturation intensity, corresponding to the input intensity for a fluorescence drop to exactly half. Super-resolution in STED microscopy can be obtained when the ratio $I_{STED}/I_s$ is much larger then unity. By increasing the depletion laser beam intensity, the saturated depletion region progressively enlarges, shrinking the effective PSF to the nanoscale (Figure 1.7b).
Figure 1.7: Principles of STED microscopy. a) Schematic of laser beam configuration in STED microscopy: a Gaussian-shape excitation beam (green) switches the sample to an ‘ON’ state, and a doughnut-shape depletion beam (red) switches the sample back to an ‘OFF’ state, leaving an effective PSF at the nanoscale. b) Reduced full width at half maximum (FWHM) of effective focal spot by increasing the depletion intensity.

Images of features beyond the diffraction limit can be collected by raster scanning the sample with the effective PSF, and a theoretical unlimited spatial resolution can be obtained under ideal conditions. Yet the resolution is limited in practice by the high intensity of the depletion laser beam, which might cause photobleaching of the sample. The principles of STED microscopy have been applied to a newly-developed technique called REversible Saturable Optical Fluorescence Transitions (RESOLFT), which has been used for super-resolution optical data storage. The recording medium consists of a reversibly-switchable fluorescent protein, and has demonstrated a resolution below 40 nm [37] (Figure 1.8).
In this work, a doughnut-shaped laser beam at 491 nm was used to switch off the fluorescence of the protein; therefore, the ‘ON’ state was restricted to a region smaller than the diffraction limit in the centre of the doughnut. Consequently, laser irradiation at 532 nm made the ‘ON’ state molecules permanent through photobleaching. Laser irradiation at 405 nm switched the molecules from an ‘OFF’ state back to an ‘ON’ state, thereby enabling the writing of another feature in sub-diffraction limit distance. However, the drawback of this method is that laser intensities as high as ~1 GW cm$^{-2}$ were required to transfer ‘ON’ state fluorescent proteins to a permanent ‘OFF’ state by photobleaching, resulting in extremely high power consumption for real application in optical data storage.

Recently, STED-like nanolithography techniques have been developed for direct laser fabrication. Optical lithography based on a dual-beam system, termed SPIN [38], was used to fabricate sub-diffraction limit features. Photoinhibition has been achieved through photodeactivation [39], photochromism [40] and generation of photoradicals [38, 41]. SPIN has allowed fabrication of 9-nm sized features in a 2P absorption polymer [38, 42], providing a potential pathway towards a storage capacity in the order of 1 PB per disc [32]. Nanolithography for writing and super-resolution optical microscopy for reading using inorganic nanomaterials have the potential for bit-by-bit 3D nanoscale optical data storage. Hence, a dramatic expansion of capacity in individual optical memory devices is expected.
However, the optical materials presently used for SPIN methods comprise initiating and inhibiting molecules that require a high intensity of the inhibition beam and cannot be optically excited after SPIN technique for writing. Thus, a newly-developed optical medium platform is in high demand for nanoscale optical data storage.

1.2.4.3 Challenges of nanoscale optical data storage

Although super-resolution techniques, such as STED microscopy and SPIN, offer the potential for a single-disc capacity towards PBs, the requirements of optical activation/deactivation in the same material platform and the high intensity of the deactivation beam present several challenges for achieving nanoscale optical data storage. The first challenge is to find an appropriate optically-activatable medium that can be used in far-field super-resolution techniques for the writing and reading processes of data bits beyond the diffraction-limit barrier. Currently available optical materials for SPIN cannot be excited using optical methods after the SPIN process. Thus, the development of a novel optical medium that allows optical excitation both in data writing and reading at the nanoscale is essential. The second challenge is represented by the tremendous intensity of the inhibition beam for super-resolution optical writing using currently available media. The high intensity of the inhibition beam not only produces a temperature rise in the material, causing degradation in the neighbouring areas of the recorded data bits, but also has the major drawback of high energy consumption, which is not suitable for sustainable implementation of next-generation high-capacity optical data storage memories.

In this context, up-conversion nanoparticles and graphene oxide offer enormous potential for nanoscale optical data storage because of their intriguing optical properties and high thermal and chemical stability. Up-conversion nanoparticles provide a feasible pathway for super-resolution optical activation in both writing and reading processes by exploiting their electronic transitions. In addition, the long-lived energy levels in up-conversion nanoparticles guarantee low saturation intensity, which results in a reduction of the inhibition beam power. Further, the reduction of graphene oxide by removal of its oxygen groups can be used to permanently record optical data bits. Indeed, investigations of the electronic transitions of up-conversion nanoparticles in conjugation with graphene oxide are of great interest for achieving ultralow-power nanoscale optical data recording and reading with potential for high-capacity optical data storage devices.
1.3 Objectives of this thesis

The fundamental aim of this PhD thesis is to achieve ultralow-power nanoscale optical data storage in an up-conversion nanoparticle- and graphene oxide-based nanocomposite. The optical activation will be enabled by the up-conversion nanoparticles, while the data recording will be achieved in graphene oxide through its reduction via resonance energy transfer. Further, the metastability of the energy levels in the up-conversion nanoparticles with a lifetime of up to milliseconds will enable SPIN for data writing and STED microscopy for data reading with low intensity of the inhibition beam and depletion beam, respectively, thereby resulting in optical data storage with ultralow energy consumption, which also guarantees a long lifetime for the optical data storage device.

First, the up-conversion nanoparticles and graphene oxide will be synthesised and characterised. Second, the up-conversion nanoparticles will be conjugated to graphene oxide to form a novel nanocomposite material that will function as the encoding medium. Third, the process of data recording through the photochemical reduction of graphene oxide induced by the up-conversion nanoparticles will be investigated for writing bits at the nanoscale. The optical excitation of the up-conversion nanoparticles will be modulated to produce a permanent physical and chemical structural change in graphene oxide through resonance energy transfer when the nanoparticles are irradiated by the recording beam. Fourth, the read-out process will be accomplished using the up-conversion nanoparticles as an emission source, which is also switchable by two wavelengths, and by detecting the difference in up-conversion fluorescence quenching by graphene oxide and its reduced form. The study of the modulation of the electronic transition rates in the up-conversion nanoparticles–graphene oxide system is fundamental to reduce the intensity of the inhibition beam from \( \sim \)MW cm\(^{-2}\) down to tens of \( \sim \)kW cm\(^{-2}\), and drastically drop the energy per recorded bit from picojoule to femtojoule level. Nanoscale encoding and retrieving information based on the combination of up-conversion nanoparticles and graphene oxide will provide a fully optical pathway for sustainable data storage devices towards petabyte-level capacity in a single optical disc.

1.4 Preview of this thesis

The research conducted in this PhD project comprises selection, synthesis, characterisation and testing of innovative materials, which will result in the development of a new
nanocomposite based on up-conversion nanoparticles and graphene oxide for ultralow-power nanoscale optical data storage. For data writing, the up-conversion nanoparticles will be used for optically-activatable SPIN and to trigger the process of photochemical reduction of graphene oxide via resonance energy transfer. For data reading, the up-conversion nanoparticles will function as an emission source in fluorescence quenching microscopy combined with STED microscopy. The different properties of absorption between graphene oxide and its reduced form will allow the formation of high-contrast images because of their different degree of fluorescence quenching efficiency.

After this introduction, in Chapter 2, the principles and features of up-conversion nanoparticles and graphene oxide are surveyed and their adoption in optical data storage and super-resolution microscopy techniques is reported.

In Chapter 3, the photochemical reduction of thin-film graphene oxide integrated with up-conversion nanoparticles is studied under high-energy laser irradiation. The reduction is accompanied by a variation of absorption between graphene oxide and its reduced form. Consequent modulation of up-conversion fluorescence from the nanoparticles through quenching is achieved, providing the stepping stone for feasible optical data storage based on up-conversion nanoparticles and graphene oxide towards nanoscale recordings.

In Chapter 4, the preparation and testing of up-conversion nanoparticles suitable for ultralow-power nanoscale optical data storage in combination with graphene oxide are presented. The key features of the up-conversion nanoparticles include intense high-energy up-conversion fluorescence emission for effective photochemical reduction of graphene oxide, optimal concentration of the dopants for efficient optical depletion of up-conversion, and small size and narrow size distribution for efficacious resonance energy transfer. Further, super-resolution imaging of the up-conversion nanoparticles by STED microscopy is demonstrated, underlying the potential for super-resolution optical data read-out.

In Chapter 5, ultralow-power nanoscale optical data storage in the nanocomposite based on up-conversion nanoparticles and graphene oxide is achieved. The novel concept of using up-conversion nanoparticles to induce the photochemical reduction of graphene oxide via resonance energy transfer is proven. Optical data bits are recorded beyond the diffraction-limit barrier using SPIN technique and read-out by fluorescence quenching microscopy combined with STED microscopy through the quenching of fluorescence emission from the up-conversion nanoparticles by graphene oxide and its reduced form.

In Chapter 6, the conclusion of the research undertaken during this PhD project is presented, and future research perspectives are explored.
Chapter 2

Literature review

2.1 Introduction

Ingenious solutions will be needed to meet the growing demand for optical data storage systems with greater capacity, extended lifetime and minimal energy consumption. Inorganic nanomaterials, such as up-conversion nanoparticles and graphene oxide, hold great potential for innovative optical data storage devices because they are potentially suitable for use in far-field super-resolution optical techniques. Since their introduction in the 1960s [43], up-conversion nanoparticles have attracted great attention from researchers because they can convert low-frequency photons into photons with higher frequency more efficiently than other materials. This property has been exploited in various emerging applications, such as bio-imaging and labelling, biosensors and temperature sensors, assays and detection, drug release and delivery, photo-switching, displays, solar cells, security, barcoding, up-conversion lasers, RGB printing and recently in optical data storage [44]. Graphene oxide has initially been considered for potentially easier, more efficient, inexpensive, high-yield and scalable ways to synthesise graphene. Elimination of graphene oxide’s oxygen groups and recovery of the honeycomb hexagonal lattice of graphene can restore the electrical and thermal conductivity typical of the ‘miracle material’. Moreover, the reduction of graphene oxide has been exploited in many other applications in electronics for graphene-based field effect transistor and electrodes; for energy storage in lithium ion batteries, super-capacitors
and solar cells; for biomedical applications for drug delivery systems and energy transfer–based biosensors; and recently for optical data storage [45].

This chapter reviews the recent developments of up-conversion nanoparticle and graphene oxide, with a focus on their advantages for application in ultralow-power nanoscale optical data storage. An outline of the principles, properties and state-of-the-art applications of up-conversion nanoparticles and graphene oxide are presented in Sections 2.2 and 2.3, respectively. Specifically, these sections review the use of these two types of nanomaterials in optical data storage and super-resolution microscopy techniques. In Section 2.4, the concepts of resonance energy transfer are summarised, with specific attention devoted to energy transfer in up-conversion nanoparticles and graphene oxide-based systems. Section 2.5 illustrates the advantages of combining up-conversion nanoparticles with graphene oxide for energy transfer–driven ultralow-power nanoscale optical data storage, while Section 2.6 summarises Chapter 2.

2.2 Up-conversion nanoparticles

2.2.1 Principles of up-conversion nanoparticles

Up-conversion nanoparticles have been widely adopted in biology, electronics and photonics [46] because of their appealing optical properties, such as up-conversion fluorescence. Photon up-conversion occurs when two or multiple photons with low energy are absorbed and combined in a nonlinear medium, leading to emission of photons with higher energy and a frequency that is the sum of that of the absorbed photons. Thus, up-conversion nanoparticles can efficiently emit visible and ultraviolet fluorescence under near-infrared excitation with low pump intensities (1 to 10³ W cm⁻²) [47]. Up-conversion necessitates electronic excited states with long lifetimes and a ladder-like energy levels structure. Given that the above-mentioned features can be found in the rare-earth elements, up-conversion nanoparticles are usually made of an inorganic matrix with a crystalline structure that is doped with rare-earth ions in low concentration (Figure 2.1a). The doping ions are responsible for the fluorescence emission, while the matrix hosts them into optimal locations. The reciprocal separation, spatial distribution and coordination number of ions are fundamental elements for efficient up-conversion.
Figure 2.1: Principles of up-conversion nanoparticles. a) Physical structure of up-conversion nanoparticles comprising an inorganic host matrix (grey) doped with lanthanide ions (red). b) Energy scale of the electronic structure of lanthanides. c) Schematic of the energy level diagrams reported for up-conversion in the nanoparticles.

Up-conversion nanoparticles exhibit a longer fluorescence lifetime (ranging from microseconds to milliseconds) compared with other fluorophores because of the Laporte forbidden transitions in rare-earth ions [44, 48] (Figure 2.1b). The up-conversion mechanisms involving lanthanides-doped nanoparticles can be divided into four classes [44, 46]: excited-state absorption (ESA), energy transfer up-conversion (ETU), cooperative sensitisation up-conversion (CSU) and energy migration-mediated up-conversion (EMU) (Figure 2.1c). In ESA, two photons are successively absorbed in a single lanthanide. In ETU, two neighbouring lanthanide ions absorb a photon of identical energy, thereby promoting one of
the ions to a higher-energy emitting state via non-radiative energy transfer. In CSU, cooperative energy transfer occurs from two excited sensitisers and emission occurs from an activator. In EMU, four kinds of lanthanide ions are involved. Excitation energy is initially transferred from a sensitisier (S) to an accumulator working as a ladder (L). Subsequently, the energy is passed to a migrator (M). The energy travels via the sublattice of the migrator and is trapped by the activator (A), with consequent emission of up-converted fluorescence. Typically, photon up-conversion of lanthanide ions such as Ho$^{3+}$, Er$^{3+}$ and Tm$^{3+}$ occurs via either ETU or ESA, exploiting metastable intermediate states to store the energy. In contrast, photon up-conversion can be achieved by CSU or EMU when those physically-existent intermediate states are absent, such as in the case of Tb$^{3+}$. In EMU, Tm$^{3+}$ acts similarly to a ladder (L) to prompt energy transfer (ET) from a sensitisier (S) to a migrator (M) and later to an activator (A). The well-known process of photon avalanche that occurs in bulk materials rarely occurs in up-conversion nanoparticles because of the specific conditions that are necessary to establish an avalanche regime [49].

Typical synthesis procedures for up-conversion nanoparticles include co-precipitation, thermal decomposition, hydro- or solvothermal synthesis, sol–gel and microwave-assisted synthesis [50]. Usual inorganic crystalline hosts are yttrium aluminium garnet (YAG), NaYF$_4$, Y$_2$O$_3$, Gd$_2$O$_2$S and NaPrF$_4$. Specifically, the NaREF$_4$ series has been demonstrated to be the most efficient because it has relatively low phonon energy and is chemically stable [51]. In fact, hosts, including cations, such as Na$^+$ and Y$^{3+}$, with comparable ionic radii to rare-earth dopants avoid defects and stress in the crystals, while fluoride materials show metastability of the excited states because of the low phonon energy (ca. 350 cm$^{-1}$) of the lattice. The stability at high temperature of these nanomaterials guarantees a long lifespan to optical memory devices. Thin films of up-conversion nanoparticles can be promptly fabricated and the combination of up-conversion nanoparticles with other types of nanomaterials provides innovative avenues for manipulation of fluorescence or preparation of novel functional nanocomposites [52].
2.2.2 Up-conversion fluorescence emission

An energy levels diagram, the typical up-conversion fluorescence emissions and the corresponding transitions in lanthanide ions [53] are reported in Figure 2.2 and listed in Table 2.1, respectively.

Figure 2.2: Energy levels diagram of the lanthanide ions [53]. The main excited states from which up-conversion fluorescence emission occurs and ground level are indicated in red and blue, respectively.
Table 2.1: Typical up-conversion fluorescence emissions and corresponding transitions in lanthanide ions.

<table>
<thead>
<tr>
<th>Activator</th>
<th>Up-conversion fluorescence emission (nm)</th>
<th>Corresponding transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$^{3+}$</td>
<td>485, 520, 538, 605, 635, 645, 670, 690, 720</td>
<td>$^{3}P_0 \rightarrow ^{3}H_4$, $^{3}P_1 \rightarrow ^{3}H_5$, $^{3}P_0 \rightarrow ^{3}H_6$, $^{3}P_0 \rightarrow ^{3}F_2$, $^{3}P_0 \rightarrow ^{3}H_6$, $^{3}P_1 \rightarrow ^{3}F_3$, $^{3}P_0 \rightarrow ^{3}F_3$, $^{3}P_0 \rightarrow ^{3}F_4$</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>430, 482, 525, 535, 580, 600, 664, 766</td>
<td>$^{4}P_{1/2} \rightarrow ^{4}I_{9/2}$, $^{4}P_{1/2} \rightarrow ^{4}I_{11/2}$, $^{4}P_{1/2} \rightarrow ^{4}I_{13/2}$, $^{4}G_{7/2} \rightarrow ^{4}I_{9/2}$, $^{2}P_{1/2} \rightarrow ^{4}I_{15/2}$, $^{4}G_{7/2} \rightarrow ^{4}I_{11/2}$ and $^{4}G_{5/2} \rightarrow ^{2}G_{7/2} \rightarrow ^{4}I_{9/2}$, $^{4}G_{7/2} \rightarrow ^{4}I_{13/2}$, $^{4}G_{7/2} \rightarrow ^{4}I_{15/2}$</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>520, 541, 555, 590, 646, 657, 700, 799–873</td>
<td>$^{4}G_{7/2} \rightarrow ^{4}H_{5/2}$, $^{4}F_{3/2} \rightarrow ^{4}H_{6/2}$, $^{4}G_{5/2} \rightarrow ^{4}H_{5/2}$, $^{4}G_{5/2} \rightarrow ^{6}H_{7/2}$, $^{4}G_{7/2} \rightarrow ^{6}H_{9/2}$, $^{4}G_{5/2} \rightarrow ^{6}H_{11/2}$, $^{6}F_{11/2}$, $^{6}H_{13/2}$</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>416, 429, 490, 510, 535, 554, 590, 613</td>
<td>$^{5}D_{3} \rightarrow ^{7}F_{1}$, $^{5}D_{3} \rightarrow ^{7}F_{2}$, $^{5}D_{2} \rightarrow ^{7}F_{2}$, $^{5}D_{2} \rightarrow ^{7}F_{3}$, $^{5}D_{1} \rightarrow ^{7}F_{1}$, $^{5}D_{1} \rightarrow ^{7}F_{2}$, $^{5}D_{0} \rightarrow ^{7}F_{1}$, $^{5}D_{0} \rightarrow ^{7}F_{2}$</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>278, 305, 312</td>
<td>$^{6}I_{7/2} \rightarrow ^{6}S_{7/2}$, $^{6}P_{5/2} \rightarrow ^{6}S_{7/2}$, $^{6}P_{7/2} \rightarrow ^{6}S_{7/2}$</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>381, 415, 438, 489, 541, 584, 619</td>
<td>$^{5}D_{3} \rightarrow ^{7}F_{6}$, $^{5}D_{3} \rightarrow ^{7}F_{5}$, $^{5}D_{3} \rightarrow ^{7}F_{4}$, $^{5}D_{4} \rightarrow ^{7}F_{6}$, $^{5}D_{4} \rightarrow ^{7}F_{5}$, $^{5}D_{4} \rightarrow ^{7}F_{4}$, $^{5}D_{4} \rightarrow ^{7}F_{4}$, $^{5}D_{4} \rightarrow ^{7}F_{3}$</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>378, 408, 487, 543, 569, 570, 610, 655, 663</td>
<td>$^{4}G_{11/2} \rightarrow ^{6}H_{13/2}$, $^{4}G_{9/2} \rightarrow ^{6}H_{13/2}$, $^{4}G_{9/2} \rightarrow ^{6}H_{11/2}$, $^{4}I_{15/2} \rightarrow ^{6}H_{13/2}$, $^{4}G_{11/2} \rightarrow ^{6}H_{13/2}$, $^{4}G_{11/2} \rightarrow ^{6}H_{11/2}$, $^{4}F_{15/2} \rightarrow ^{6}H_{13/2}$, $^{4}G_{15/2} \rightarrow ^{6}H_{11/2}$, $^{4}G_{11/2} \rightarrow ^{6}H_{13/2}$, $^{4}F_{15/2} \rightarrow ^{6}H_{11/2}$</td>
</tr>
<tr>
<td>Ho$^{3+}$</td>
<td>542, 655</td>
<td>$^{5}F_{4}$, $^{5}S_{2} \rightarrow ^{5}I_{8}$, $^{5}F_{5} \rightarrow ^{5}I_{8}$</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>415, 525, 542, 655</td>
<td>$^{2}H_{9/2} \rightarrow ^{4}I_{15/2}$, $^{2}H_{11/2} \rightarrow ^{4}I_{15/2}$, $^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$, $^{4}F_{9/2} \rightarrow ^{4}I_{15/2}$</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>290, 345, 362, 450, 475, 644, 694, 800</td>
<td>$^{1}I_{6} \rightarrow ^{3}H_{6}$, $^{1}I_{6} \rightarrow ^{3}F_{4}$, $^{1}D_{2} \rightarrow ^{3}H_{6}$, $^{1}D_{2} \rightarrow ^{3}F_{4}$, $^{1}G_{4} \rightarrow ^{3}F_{4}$, $^{3}F_{3} \rightarrow ^{3}H_{6}$, $^{3}H_{4} \rightarrow ^{3}H_{6}$</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>450–500</td>
<td>$2 \times ^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$ (cooperative emission)</td>
</tr>
</tbody>
</table>
The fluorescence of up-conversion nanoparticles spans from the ultraviolet to near-infrared because of the abundant emission lines in the lanthanide ions. Fluorescence can thus be accurately tuned by optimising the dimension of the up-conversion nanoparticles and their doping concentration [54]. However, radiation-less deactivation may occur for high concentrations, while cross-relaxation represents a major drawback. The upper concentration limit for the activators is around 2%. However, light absorption is inadequate for up-conversion at this value of concentration, requiring the addition of ions with strong absorption called ‘sensitisers’, which are added in the nanoparticles to provide effective energy transfer to the activators. In the case of up-conversion based on Er$^{3+}$ and Tm$^{3+}$, Yb$^{3+}$ is generally used with the function of sensitiser and co-doped with high concentrations (generally 18 to 20%). The energy difference between excited and ground states in Yb$^{3+}$ matches well the gaps of those in Er$^{3+}$ and Tm$^{3+}$, providing efficient energy transfer to the latter. For instance, up-conversion nanoparticles with intense fluorescence emission comprise the co-doping of the sensitiser Yb$^{3+}$ and Er$^{3+}$ or Tm$^{3+}$ as emitters into the NaYF$_4$ host matrix. Yb$^{3+}$ possesses a relatively large absorption cross-section, which is $1.2 \times 10^{-20}$ cm$^2$ for 980 nm [55], and energy of the excited states with similar gaps to those of Er$^{3+}$ and Tm$^{3+}$. Yb$^{3+}$ absorbs the near-infrared photons and excites the neighbouring Er$^{3+}$ or Tm$^{3+}$ through energy transfer without radiation. Er$^{3+}$ or Tm$^{3+}$ ions can then produce fluorescence emission in the range between ultraviolet to near-infrared [54] (Figure 2.3).
Figure 2.3: Energy diagram and fluorescence of Er,Tm-doped up-conversion nanoparticles [54]. a) Energy level diagram. b) Corresponding fluorescence emission of Er,Tm-doped up-conversion nanoparticles. Yb$^{3+}$ is the sensitiser, while Er$^{3+}$ and Tm$^{3+}$ are the activators.

An important parameter to understand the mechanism of up-conversion fluorescence emission is the number of photons participating in the up-conversion [56]. The up-conversion fluorescence intensity $I_{UC}$ is nonlinearly dependent on the power $P$ of the excitation laser:

$$I_{UC} \propto P^n$$  \hspace{1cm} (2.1)

where $n$ is approximately equal to the number of photons participating in the excitation and corresponds to the slope of the $I-P$ curves. When using a laser at 980 nm to excite the
nanoparticles, up-conversion emissions from the \( \text{Er}^{3+} \) and \( \text{Tm}^{3+} \) ions span from the near-infrared to the ultraviolet. For \( \text{Tm}^{3+} \)-doped up-conversion nanoparticles, ultraviolet emissions, visible emissions and near-infrared emission can all occur at the same time under laser excitation at 980 nm. The \( I-P \) curves for \( \text{NaYF}_4: \text{Yb}^{3+}/\text{Tm}^{3+} \) up-conversion nanoparticles indicate that 290- and 345-nm emissions derive from processes involving five photons, while 362- and 450-nm emissions, 475- and 644-nm emissions, and 694- and 800-nm emissions originate from four-, three- and two-photon processes, respectively [57].

### 2.2.3 Modelling up-conversion

To investigate the underlying mechanism of up-conversion fluorescence emission, rate equations systems are generally considered to theoretically describe the population of electrons occupying the various energy levels in the up-conversion nanoparticles under suitable conditions of laser excitation. A simplified model for two-photon ETU in up-conversion nanoparticles is reported in Figure 2.4.

**Figure 2.4:** Simplified model for two-photon ETU in up-conversion nanoparticles.
Under the assumption that all the excited activators generate up-conversion fluorescence, and excluding non-radiative decay processes, a set of rate equations can be used to describe the populations of electrons in these states:

\[
\frac{dn_5}{dt} = \Phi_P n_4 - \tau_5^{-1}n_5 - W_{ET}n_5n_1 - W_{ETU}n_5n_2 \tag{2.2}
\]

\[
\frac{dn_2}{dt} = W_{ET}n_5n_1 - \tau_2^{-1}n_2 - W_{ETU}n_5n_2 \tag{2.3}
\]

\[
\frac{dn_3}{dt} = W_{ETU}n_5n_2 - \tau_3^{-1}n_3 \tag{2.4}
\]

where \( n_i \) (\( i = 1–5 \)) are the populations of electrons in the five different energy levels, \( \tau_j \) (\( j = 2, 3, 5 \)) are the lifetimes of the excited energy levels, \( \Phi_P \) is the pumping rate, and \( W_{ET} \) and \( W_{ETU} \) are the coefficients of energy transfer (designated as 1) and ETU (designated as 2), respectively. For the steady-state case, the quantum yield (\( QY \))—which is the ratio between the photons emitted and photons absorbed—is:

\[
QY = \frac{A_3n_3}{\Phi_P n_4} = \frac{1}{2} \left[ 1 - \frac{1}{\Phi_P} \left( \frac{1}{\tau_2 n_4} + \frac{1}{\tau_5 n_4} \right) \right] \tag{2.5}
\]

where \( A_3 \) is the rate of spontaneous transition from the emitting level to the ground level of the activator. Improvement of the quantum yield can be achieved by employing activators that have metastable intermediate states. According to Eq. 2.5, the theoretical value of quantum yield for the two-photon up-conversion is 50\%, while, for multi-photon up-conversion, it must be divided by the number of involved photons. However, values obtained by using an integrating sphere to determine the quantum yield [58] are usually low because surface quenching results dominate in the case of small nanoparticles. Different strategies can be adopted to improve the up-conversion emission efficiency, such as using different combinations of lanthanide dopants and controlling their concentrations, tuning the inorganic crystalline host, introducing extraneous energy levels, luminescence resonance energy transfer, tailoring the crystal field or the size and structure of the nanoparticles, and constructing core/shell structures.
2.2.4 Up-conversion nanoparticles for optical data storage

Optical data storage has been achieved using up-conversion materials by multiplexing information via spectral hole burning [25, 59]. The spectral hole burning is the selective bleaching of frequencies in the absorption spectrum of a material, obtaining an enhanced transmission at the chosen frequency. The absorption associated with rare-earth ions decreased when the electrons in the ground level were depopulated by photoexcitation. When cooled to a temperature below 20 K, the rare-earth ions in the crystal possess homogeneously broadened absorption lines that are narrower than the inhomogeneously broadened absorption lines. Therefore, spectral multiplexing has been obtained in a single spatial location through spectral hole burning (Figure 2.5a). An estimated 20 GB per disc capacity was achieved using a writing beam at 1.0 mW and reading beam at 1.4 mW [60].

Figure 2.5: Up-conversion-based optical data storage. a) The spectral hole burning in up-conversion materials [25]. Spectral holes occur in the inhomogeneous absorption of the sample under illumination with narrowband light. b) Lifetime multiplexing in up-conversion nanoparticles with different concentration of dopants [29]. Images were imprinted using up-conversion nanoparticles with different ratios of Yb³⁺ and Tm³⁺, and distinguished images were read out by time-resolved scanning.
Chapter 2

Optical data storage has also been realised through lifetime multiplexing by manipulating the fluorescence lifetime of NaYF₄:Yb³⁺,Tm³⁺ up-conversion nanoparticles [29]. The lifetime has been modulated from 48 to 668 μs by varying the doping concentration in the nanoparticles and thus changing the separation of Yb³⁺ sensitisers and Tm³⁺ emitters [29, 61]. Multiplexed information bits with distinctive lifetimes have then been retrieved through fluorescence lifetime imaging microscopy (Figure 2.5b).

In recent years, up-conversion nanoparticles have been combined with photochromic switches, such as diarylethene (DTE) molecules, to fabricate composite materials for optical data storage devices. Rewritable 2D optical data storage was obtained in a thin film composed by up-conversion nanoparticles combined with organic molecules through modulation of up-conversion fluorescence [62]. The organic layer consisted of strong DTE molecules, which could reversibly be switched between an open- and closed-ring configuration under visible and ultraviolet irradiation, respectively. Optical data bits were erased through ultraviolet irradiation, rewritten through visible irradiation to activate energy transfer from the up-conversion nanoparticles to DTE molecules, and finally read out through near-infrared irradiation (Figure 2.6a).

**Figure 2.6:** Optical data storage using up-conversion nanoparticles combined with DTE molecules. a) Rewritable optical data storage through the modulation of fluorescence emission from up-conversion nanoparticles by DTE molecules [62]. b) Working mechanism of a rewritable optical memory device comprising core-shell up-conversion nanoparticles with DTE molecules: under laser excitation at 980 nm, the up-conversion nanoparticles emit ultraviolet fluorescence, which activates the cyclisation reaction of the photochromic DTE molecules, while under 1,550-nm laser excitation, the up-conversion nanoparticles emit green fluorescence, which leads to reversal ring-closed reaction of the photochromic DTE molecules. 5 × 5 pattern demonstrating erasing and rewriting in the optical memory [63].
Core-shell up-conversion nanoparticles were mixed with photochromic DTE molecules for rewritable optical data storage [63]. The core-shell configuration enabled the nanoparticles to possess distinct emission bands under 980- and 1,532-nm laser excitation (Figure 2.6b). The ultraviolet fluorescence from the up-conversion nanoparticles excited by a laser at 980 nm activated the cyclisation of DTE molecules through the formation of C–C bonds, whereas the green fluorescence by the nanoparticles under excitation at 1,532 nm led to the cleavage of the formed C–C bonds. This mechanism was exploited to demonstrate erasing and rewriting in the optical memory through a $5 \times 5$ pattern.

2.2.5 Up-conversion nanoparticles in super-resolution optical techniques

Up-conversion nanoparticles have been employed in super-resolution optical microscopy through the detection of up-conversion fluorescence. The first work reporting super-resolution optical imaging of up-conversion nanoparticles was based on a STED-like technique for excitation and depletion of up-conversion in a YAG crystal doped with praseodymium ions (Pr$^{3+}$:YAG). A 50 nm resolution was achieved with a power of 29 mW [64] (Figure 2.7). Up-conversion fluorescence in Pr$^{3+}$ ions occurs through two-step excitation ($^3\text{H}_4 \rightarrow ^1\text{D}_2$ and $^1\text{D}_2 \rightarrow 4f5d$) by laser pulses at 609 and 532 nm, respectively. Super-resolution images were obtained by employing a 690-nm laser for excitation, a 532-nm laser for depletion and a 532-nm laser for probing. The laser at 609 nm initially populated the $^1\text{D}_2$ state, which is metastable. The 532-nm depletion laser shaped into a doughnut depopulated the $^1\text{D}_2$ state, excluding the up-conversion nanoparticles in the centre of the doughnut. The residual electrons in the $^1\text{D}_2$ state were excited by a 532-nm probe beam, producing fluorescence signal with sub-diffraction limit resolution.
Figure 2.7: STED-like super-resolution optical microscopy of Pr$^{3+}$:YAG up-conversion crystal [64]. a) Schematic diagram of the electronic states of Pr$^{3+}$ in YAG crystal: a pump laser at 609 nm populates the $^1D_2$ state; a depletion laser at 532 nm depletes the $^1D_2$ state, excluding the up-conversion nanoparticles in the centre of the doughnut; and a 532-nm probe laser excites the residual electrons in the $^1D_2$ state. b) Confocal image and super-resolution image of a cluster of Pr$^{3+}$:YAG nanoparticles, where the shape of the aggregated nanoparticle was successfully resolved.

Figure 2.8: STED microscopy using highly Tm-doped up-conversion nanoparticles [65, 66]. a) Schematic of the energy level diagram of highly Tm-doped up-conversion nanoparticles under 980-nm laser for excitation and under combined 980-nm laser for excitation and 808-nm laser for depletion [65]. b) Images of highly Tm-doped up-conversion nanoparticles by confocal and STED microscopy [65]. Scale bar: 500 nm. c) Images of cellular cytoskeleton labelled with antibody-conjugated highly Tm-doped up-conversion nanoparticles by confocal and STED microscopy [66]. Scale bar: 1 μm.
Recently, up-conversion nanoparticles doped with high Tm$^{3+}$ concentration have been used for super-resolution imaging by STED microscopy technique [65, 66] (Figure 2.8). Highly Tm-doped up-conversion nanoparticles established a population inversion in the long-lived $^3\text{H}_4$ intermediate level, compared with $^3\text{H}_6$ ground level, under laser irradiation at 980 nm [65] (Figure 2.8a). This is because the reduced separation between emitters with high Tm$^{3+}$ doping led to strong cross-relaxation between neighbouring ions. Subsequently, irradiation by an 808-nm laser, which matches the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ transition, triggered amplified stimulated emission to deplete the $^3\text{H}_4$ intermediate level; thus, the up-conversion pathways could be optically inhibited. STED microscopy was achieved with a resolution of 28 nm (Figure 2.8b) and reduced the saturation intensity by two orders of magnitude compared with other currently used fluorescent probes. STED microscopy of up-conversion nanoparticles has also been reported for life science studies. Two-colour STED microscopy images using up-conversion nanoparticles were achieved under dual-irradiation comprising a 980-nm excitation laser and 808-nm depletion laser, and a resolution of 66 nm was obtained. Further, super-resolution images of immune-stained cytoskeleton structures of fixed cells were obtained with a resolution of around 82 nm [66] (Figure 2.8c).

The unique structure of the energy levels in up-conversion nanoparticles enables their implementation in STED microscopy methods for super-resolution read-out of information bits in optical memory devices. In addition, the precise modulation of the optical properties of up-conversion nanoparticles permits the use of continuous wave (CW) lasers, which conveniently simplify the optical system setup compared with expensive and elaborated fs lasers. Also, the metastability of the excited states of up-conversion nanoparticles with a lifetime of up to milliseconds offers the potential for data reading using low power for activation and deactivation; thus, a drop of energy consumption is expected for the overall data storage process. Up-conversion nanoparticles combined with other recording media that exhibit high stability, such as graphene oxide, may represent the best-suited solution for application in optical memories with a long lifespan. Other merits of up-conversion nanoparticles include their facile synthesis procedure and the convenient deposition methods through spin-coating for the massive production of optical discs.
2.3 Graphene and graphene oxide

2.3.1 Principles of graphene and graphene oxide

Consequent to the isolation of single nanosheets [67], graphene has generated enormous attention among researchers because of its phenomenal properties [68]. Graphene is composed of carbon atoms that form a monolayer lattice with hexagonal configuration that has a thickness of only 3.35 Å [69, 70] (Figure 2.9).

Graphene shows extraordinary electron mobility [71] and absorption of light with values as high as 2.3% for single-layer configuration for radiations ranging between mid-infrared and ultraviolet [72]. The electrons in graphene are easily excited into the conduction band. Under strong intensity of irradiation, the concentration of photo-generated carriers increases and the states near the edge of the conduction and valence bands are filled, precluding additional absorption through the Pauli blocking [73]. Therefore, graphene can be promptly saturated under visible and near-infrared irradiation because of its broadband absorption and zero band gap. Graphene’s optical nonlinearity is increased in a resonance manner because of its strong linear absorption and results broadband and independent from the wavelength. For instance, second-harmonic generation has been observed for graphene under 800-nm fs laser irradiation [74]. The most commonly used methods for the preparation of graphene are mechanical cleavage, chemical synthesis, thermal chemical vapour deposition and reducing graphene oxide [75]. Specifically, the reduction of graphene oxide represents a facile and inexpensive pathway to retrieve the features of graphene, starting from cheap graphite.
Graphene oxide is typically obtained through the Hummers’ method [76] or its modifications. The chemical structure of graphene oxide has not yet been identified accurately because of its complexity and complicated characterisation [77] (Figure 2.9). Graphene oxide is generally defined as a non-stoichiometric layer of carbon bonded with a variety of oxygen groups [78]. The oxygen groups along with the partial sp\(^3\) hybridisation of its carbon atoms cause a deformation of graphene oxide’s structure. Graphene oxide exhibits broad fluorescence [79, 80], which originates from the defect states of the oxygen groups. Specifically, two-photon excitation fluorescence has been reported for graphene oxide under 800-nm laser [81], offering the potential for use in 3D optical data storage. In addition, graphene oxide exhibits high hydrophilicity and stability in water. Therefore, it can be used in conjugation with convenient water-soluble polymers, including polyvinyl alcohol, and allows facile and homogeneous deposition of thin films. Graphene oxide is thermally stable [82] and exhibits non-photobleaching properties, ensuring a long lifespan for the optical memories produced using this nanomaterial.

### 2.3.2 Photochemical reduction of graphene oxide

Graphene and graphene oxide are promising for use in optical memory devices primarily because the properties of the latter can be varied through reduction of its oxygen groups [83, 84]. Therefore, permanent bits of information can be written through the modification of graphene oxide’s structure. The outcome of the reduction is termed ‘reduced graphene oxide’ (rGO) and resembles graphene. The photoreduction of graphene oxide by photothermal [85] and photocatalytic [86] processes has been achieved, providing a pathway for direct laser fabrication of micro- and nano-devices and patterning [86]. Although very promising, the reduction of graphene oxide through these methods still relies on conventional techniques and is thus diffraction-limited, which prevents its implementation in super-resolution methods. A way to surpass the limit imposed by diffraction is by producing photochemical reduction of graphene oxide, in which the removal of the oxygen groups is controlled at the nanoscale.

The photochemical reduction of graphene oxide was reported under ultraviolet light irradiation at room temperature without heating [87, 88]. These studies suggested that the quantum efficiency of the photochemical reduction depends on the energy of the incident photons, whereby photons with higher energy are more effective. The energy boundary to trigger the photochemical reduction in graphene oxide was estimated to range between 3.06
and 3.4 eV [89], which coincides with the bond energy of most oxygen groups in graphene oxide. The energy threshold of excitation causing photolysis was 3.2 eV (390 nm) and the quantum efficiency to remove the oxygen groups increased along with the increase in the exciting light energy over the threshold value (Figure 2.10a).

**Figure 2.10:** The process of photochemical reduction of graphene oxide. a) Quantum efficiency for incident photons with different energy [89] and b) Depiction of the process of photochemical reduction of graphene oxide [92].

The mechanism of photochemical reduction in graphene oxide has been identified to substantially differ from that of photothermal reduction. While photothermal reduction occurs from the basic electron state and is caused only by the energy of the bonds of the oxygen groups with the graphene nanosheet, photochemical reduction occurs through the dissociation of bonds from electronically excited states whose mechanism can be explained through photochemical processes in polyatomic aromatic molecules [90, 91]. To corroborate the occurrence of photo-dissociation from electronically excited states, it has been reported that graphene oxide undergoes photolysis even at 77 K [92], at which point photothermal processes can be completely excluded. A sequential mechanism has been suggested for the photochemical reduction of graphene oxide [90-92] (Figure 2.10b). At the initial stage, the photo-dissociation of the oxygen groups located on the graphene nanosheet plane occurs. Specific photolytic processes of the functional groups include direct hydroxyl, epoxy, carboxyl and carbonyl dissociation. In addition, more complex, light-induced chemistries can also occur, in which several functional groups (primarily hydroxyls) interact to produce water
Upon bond photolysis, functional group migration to the boundary of graphene oxide’s basal plane or that of the structural defects occurs. Hydroxyl and epoxy groups hop between carbon atoms, accompanied by the transition of the carbon atoms from sp$^3$ into sp$^2$ hybridisation and the formation of π-conjugated domains. These groups eventually localise at the boundary of the basal plane and structural defects, and consequently detach following the aforementioned chemical processes. As a result, H$_2$O, O$_2$, CO and/or CO$_2$ molecules are generated. Notably, the production of water via direct dissociation of hydroxyl groups or hydroxyl–hydroxyl interactions determines the reduction of graphene oxide, avoiding losses of carbon atoms [94]. In contrast, other processes of dissociation that require greater energies—such as the dissociation of epoxy, hydroxyl and carboxyl groups—result in the elimination of carbon atoms through the emission of CO and CO$_2$ molecules. This process causes the breakdown of graphene oxide’s/reduced graphene oxide’s carbon network in the basal plane under prolonged irradiation [94].

Single-layer graphene oxide has been photochemically reduced under wide-field 405-nm CW laser excitation with relatively low irradiation intensity (I$_{exc}$ ~ 220–380 W cm$^{-2}$) [93, 94]. In this work, the reduction of graphene oxide was reported to occur through photolysis, as the used wavelength was resonant with the transitions of graphene oxide’s oxygen groups. In fact, highly-oxidised graphene oxide shows n–π* transitions ranging from 400 to 420 nm [95], while molecular-like transitions reaching 550 nm were reported in graphene oxide [96]. These processes were confirmed by density functional theory calculations, indicating that oxygen-functionalised sp$^2$ clusters show electronic transitions all through the visible [97]. Further, excitation wavelength-dependent investigations qualitatively supported a mechanism proceeded by photolytic reduction in single-layer graphene oxide. Graphene oxide specimens were tested under 405-, 520- and 640-nm laser irradiation (I$_{exc}$ ~ 700 W cm$^{-2}$) [94]. Longer wavelengths were not considered because photolytic reduction was excluded under prolonged red laser irradiation. Emission quenching and brightening occurred when single graphene oxide nanosheets were irradiated with 405 and 520-nm laser, confirming that both frequencies were resonant with graphene oxide’s oxygen groups [95-97], while 640-nm excitation lied off resonance with transitions associated with the oxygen moieties. Finally, upon 520 nm irradiation, the reduction process occurred with remarkably slower kinetics because of the smaller abundance of redder transitions.
2.3.3 Graphene and graphene oxide for optical data storage

The reduction of graphene oxide by laser induces permanent chemical and optical changes that can be exploited as a mechanism for recording bits of information. The reduction of graphene oxide by ultrafast laser has proven to be highly effective and inexpensive, and provides rigorous control [98]. The photoreduction of graphene oxide by fs laser [30, 31] is demonstrated in Figure 2.11.

Figure 2.11: The photoreduction of graphene oxide by fs laser for multimode optical data storage [31]. a) Illustration of the photothermal reduction under fs laser. b) Fluorescence images and holograms encoded and retrieved in the graphene oxide-based device.
The intrinsic fluorescence of graphene oxide decreased after irradiation under fs laser because of the elimination of the oxygen groups from which the signal originated. This variation in fluorescence was used for data read-out through imaging with high contrast. The reported capacity resulted in 290 GB per disc [31]. Along with the fluorescence drop, the refractive index was widely modulated by laser irradiation, with values up to $10^{-1}$ for holographic recording [31]. Additionally, the bit size produced by photoreduction was confined by precisely controlling the photothermal effect by single-laser pulse irradiation [30]. As a result of its special fluorescence and huge refractive index variation, graphene oxide has been used for multimode recordings through the combination of bit-by-bit 3D optical data storage and holographic data storage in the same optical medium.

### 2.3.4 Graphene and graphene oxide in super-resolution optical techniques

Detection of nano-sized features in graphene and graphene-like materials was achieved by transient absorption microscopy [99, 100] and fluorescence quenching microscopy combined with STED microscopy [101, 102]. These two techniques have proven the feasibility of super-resolution read-out for use in nanoscale optical data storage. In transient absorption microscopy, the density of free carriers in graphene is modulated with a pump laser, and the transient absorption response is subsequently detected with a probe laser [99, 100] (Figure 2.12). The pump laser is used for excitation of the electrons to the conduction band, reducing the transient absorption of the probe laser because of Pauli blocking. Subsequently, the modulation is transferred to the probe laser. Super-resolution was obtained by introducing a non-modulated laser for depletion in the system comprising pump and probe lasers [99]. The depletion laser was shaped into a doughnut to shrink the effective PSF. Moreover, it had an identical wavelength to the pump laser, but with stronger intensity to produce saturation of the transient absorption and depletion of the process of transferring modulation from the pump laser to the probe laser. A resolution of 249 nm was obtained using less than 15 mW.
Figure 2.12: Super-resolution imaging graphene through the transient absorption method [99]. a) Time-resolved transient absorption spectroscopy on graphene in the presence or absence of the saturation laser. b) Transient absorption image of graphene with the saturation laser switched ‘ON’ (left) and ‘OFF’ (right). Scale bars: 20 µm.

The other super-resolution method for imaging graphene beyond the diffraction-limit barrier is fluorescence quenching microscopy combined with STED microscopy [101, 102], which is particularly suitable for super-resolution read-out in nanoscale optical data storage. Graphene-based nanosheets show efficient quenching because of their broadband absorption; therefore, they are useful for super-resolution imaging of a broad range of luminescent materials. Graphene nanosheets deposited onto Pr\(^{3+}\):YAG crystal were imaged with a resolution of 30 nm and a power of 55 mW [102] (Figure 2.13a).
Figure 2.13: Imaging graphene and graphene-like materials by fluorescence quenching microscopy. a) Super-resolution imaging of graphene by fluorescence quenching microscopy combined with STED microscopy [102]: confocal (left) and super-resolution image (right), achieving a resolution of 30 nm. b) Imaging single-layer graphene and graphene-like nanomaterials by fluorescence quenching microscopy [103]: a cross-deposited sample showing GO, rGO + GO, rGO and empty domains (counter-clockwise) onto a coverslip.

Graphene, graphene oxide and reduced graphene oxide nanosheets onto fluorescent substrates were visualised with high contrast because of the different properties of absorption that are characteristic of these nanomaterials [103] (Figure 2.13b). The experimental results proved that graphene and graphene oxide can be adopted for super-resolution read-out with high contrast in nanoscale optical data storage.

The low power consumption for the photoreduction of graphene oxide and for fluorescence quenching microscopy renders graphene oxide an excellent candidate for sustainable optical data storage. However, the size of the optical recordings produced with the writing methods previously described is restricted by diffraction. Thus, the foreseen capacity for 3D multiplexing optical memory devices using graphene or graphene oxide is lower than a few TBs per disc. Nanolithography and super-resolution microscopy using up-conversion nanoparticles in conjunction with graphene oxide can thus be combined and applied as a unique technology for nanoscale writing and reading of information.

2.4 Fluorescence resonance energy transfer

Fluorescence resonance energy transfer (FRET) is a mechanism describing distance-dependent interactions through transfer of energy quanta from an excited donor to an acceptor through dipole–dipole coupling without radiation [104] (Figure 2.14).
Figure 2.14: Schematic of the concepts of FRET. Initially, the donor absorbs a photon and becomes excited (upwards solid blue arrow). Typically, the donor relaxes back and generates fluorescence (downwards dashed yellow arrow). However, if a suited acceptor is nearby, the donor energy can be transferred to the acceptor, producing excitation of the acceptor (upwards dashed yellow arrow) and fluorescence (downwards solid green arrow).

The conditions for efficient FRET are reported as follows [105]. First, the emission of the donor and absorption of the acceptor need to spectrally overlap. Second, the donor-to-acceptor separation has to be a few nanometres. Third, because FRET is based on dipole–dipole coupling, the emission and absorption dipoles need to be opportunely mutually oriented. Finally, high fluorescence quantum yield of the donor is essential. The FRET efficiency, $E$, depends on the donor-to-acceptor distance, $r$, with an inverse sixth-power law:

$$E = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6}$$  \hspace{1cm} (2.6)

where $R_0$ is the Förster distance—that is, the donor-to-acceptor distance for 50% energy transfer efficiency. $R_0$ depends on the spectral overlap integral of the donor’s emission and the acceptor’s absorption and their mutual molecular orientation [105]:

$$R_0^6 = \frac{9 \cdot (\ln 10) \cdot k^2 \cdot J(\lambda) \cdot Q}{128 \cdot \pi^5 \cdot n^4 \cdot N_A}$$  \hspace{1cm} (2.7)
where \( k^2 \) is dipole orientation factor, \( Q \) is the donor’s fluorescence quantum yield, \( n \) represents the index of refraction, \( N_A \) is Avogadro’s number, and \( J(\lambda) \) is the overlap integral of the donor’s emission and acceptor’s absorbance spectra, expressed as [105]:

\[
J(\lambda) = \int f_D(\lambda) \cdot \varepsilon_A(\lambda) \cdot \lambda^4 \, d\lambda
\]  

(2.8)

where \( f_D(\lambda) \) is the donor’s normalised emission spectrum and \( \varepsilon_A(\lambda) \) is the acceptor’s molecular extinction coefficient. \( k^2 = 2/3 \) is typically considered for systems in which molecules can rotate freely and with isotropic orientation. FRET-based systems have been broadly used for biomedical applications and recently to demonstrate reversible switching in a quantum rods-sensitised photoisomerisation polymer for four-dimensional optical data storage [26].

Graphene-based structures have shown super-quenching of fluorescence and have been employed as energy acceptors in FRET sensors. For instance, graphene oxide was used as quencher with ultrahigh efficiency for ssDNA-functionalised up-conversion nanoparticles for a FRET-based highly sensitive bio-sensing platform [106]. Given that ssDNA can steadily adsorb onto graphene oxide nanosheets, the strong quenching of the fluorescence from ssDNA–up-conversion nanoparticles is derived from FRET between up-conversion nanoparticles and graphene oxide (Figure 2.15a). The up-conversion fluorescence emission from the nanoparticles was completely quenched upon bonding with graphene oxide, thereby demonstrating highly effective energy transfer within these two nanomaterials (Figure 2.15b).

**Figure 2.15:** Efficient FRET between up-conversion nanoparticles and graphene oxide for a highly sensitive bio-sensing platform [106]. a) Mechanism for transfer of energy within the ssDNA–up-conversion nanoparticles and graphene oxide system. b) Up-conversion fluorescence emission quenching by graphene oxide in the ssDNA–up-conversion nanoparticles and graphene oxide bio-sensing platform.
2.5 Advantages of up-conversion nanoparticles and graphene oxide for ultralow-power nanoscale optical data storage

The combination of up-conversion nanoparticles and graphene oxide for energy transfer–driven high-density optical data storage can greatly improve the capacity of currently available optical devices and influence the field of photonics because of the special properties of these two nanomaterials. This largely derives from the characteristics of up-conversion nanoparticles and graphene oxide, which are inaccessible to other types of nanomaterials and render up-conversion nanoparticles and graphene oxide employable in far-field super-resolution optical techniques for information storage beyond the diffraction-limit barrier.

The advantages of using up-conversion nanoparticles can be specifically assigned to the following features:

- Long-lived excited states (ranging from microseconds to milliseconds) attributed to the Laporte forbidden 4f-4f transitions in lanthanide ions, which result in several orders of magnitude reduced transition rates compared with those in organic initiators and inhibitors currently applied in super-resolution optical methods;
- Control over the physical and chemical features of the nanoparticles, such as their size, shape and concentration of lanthanide dopants, for further reduction of the transition rates, which can lead to significantly reduced inhibition beam intensity.

The advantages of using graphene oxide can be attributed to the following characteristics:

- Giant change in its physical and chemical properties through reduction, offering the potential for a solid, chemically-stable platform for information encoding;
- Broadband absorption providing an efficient acceptor with a high degree of spectral overlapping in energy transfer–driven optical data storage devices.

These distinctive attributes render up-conversion nanoparticles and graphene oxide the most suitable candidates to achieve encoding of data at the nanoscale for applications in data storage devices with ultrahigh capacity. Further, they ensure the reduction of the inhibition beam intensity from the current values of ~MW cm\(^2\) to tens of ~KW cm\(^2\), corresponding to a drastic energy reduction from picojoules to femtojoules per bit for ultralow-power consumption. This merit also results in enhanced stability of the optical storage devices for ultralong lifetimes.
2.6 Chapter summary

This chapter has reviewed the recent developments of up-conversion nanoparticles and graphene oxide towards application in ultralow-power nanoscale optical data storage. The principles, features and uses of up-conversion nanoparticles and graphene oxide have been summarised with a focus on the adoption of these two unique nanomaterials in optical data storage and super-resolution microscopy techniques. Up-conversion nanoparticles, emitting from ultraviolet to near-infrared, possess a fluorescence lifetime that is 100 to 1,000 times longer than that of other fluorophores, and appear to be particularly suitable for super-resolution data read-out with little power consumption. In addition, the reduction of graphene oxide permanently varies its chemical and optical properties, providing a mechanism for data recording. Thus, the conjugation of up-conversion nanoparticles with graphene oxide for energy transfer-driven systems offers enormous potential towards data recording and reading at the nanoscale; hence, improvement in the storage capacity of individual optical devices is expected.

Chapter 3 investigates the feasibility of photochemical reduction of thin-film graphene oxide integrated with up-conversion nanoparticles under high-energy laser irradiation. Variation in absorption between graphene oxide and its reduced form, accompanied by the reduction process and the consequent modulation of up-conversion fluorescence from the nanoparticles through quenching, will be achieved, thereby providing the stepping stone for data encoding in an up-conversion nanoparticles–graphene oxide nanocomposite towards nanoscale optical data storage.

In Chapter 4, high-energy up-conversion fluorescent nanoparticles will be selected, synthesised and tested under dual-beam irradiation towards use in ultralow-power nanoscale optical data storage.

In Chapter 5, the novel concept of energy transfer-driven photochemical reduction of graphene oxide triggered by up-conversion nanoparticles will be demonstrated, and encoding of information beyond the diffraction-limit barrier will be achieved.

Finally, the conclusions of the research work undertaken during this PhD project will be drawn and the future perspectives in the field of optical data storage will be examined in Chapter 6.
Chapter 3

Ultraviolet laser-induced reduction of graphene oxide for modulation of up-conversion fluorescent nanoparticles

3.1 Introduction

Up-conversion nanoparticles can yield high-energy photons by sequential absorption of two or multiple photons with lower energy through the nonlinear optical process of up-conversion. This characteristic makes up-conversion nanoparticles appealing for use in several fields, including multimodal imaging, theranostics, volumetric displays and optical data storage [44, 46]. Particularly interesting is the use of up-conversion nanoparticles for non-destructive optical memory and photo-switching applications, based on the modulation of up-conversion fluorescence emission in combination with DTE molecules [62, 63]. Despite the attractive prospects, these demonstrations are constrained by several drawbacks, including complex synthesis procedures, slow rates of photo-induced transitions, the use of elaborate optical system setups, and the inherent deficiency of considerable intensity manipulation because of the lack of a suitable modulator. Ultimately, it appears to be difficult to effectively modulate the emission of the up-conversion nanoparticles to entirely quench their anti-Stokes fluorescence with high contrast, low power consumption and fast reaction speed. In this regard, the current study reasoned that a combination of up-conversion
nanoparticles with graphene oxide—which can be reduced by laser—would enable high-performance modulation of up-conversion fluorescence emission. Graphene oxide and its reduced form are effective quenchers because they have strong absorption across a large range of wavelengths. Further, the reduction of graphene oxide can be obtained photochemically under ultraviolet irradiation with low power [89]. Thus, the careful design of a novel nanocomposite material based on up-conversion nanoparticles combined with graphene oxide is much-needed for a plethora of purposes, including optical data storage. The goal of this chapter is to investigate the photochemical reduction of thin-film graphene oxide integrated with up-conversion nanoparticles under high-energy laser irradiation for the modulation of up-conversion fluorescence emission. The variation of absorption between graphene oxide and its reduced form accompanied by reduction is exploited to achieve modulation of the fluorescence emission from the up-conversion nanoparticles through quenching. This provides the stepping stone towards encoding and retrieval in a up-conversion nanoparticles–graphene oxide nanocomposite with the potential for nanoscale optical data storage.

Initially, the up-conversion nanoparticles were synthesised and characterised. Subsequently, the up-conversion nanoparticles and commercially-available graphene oxide were conjugated in water solution and deposited through vacuum filtration to form a thin film. Following this, the novel nanocomposite based on up-conversion nanoparticles and graphene oxide was tested under high-energy laser irradiation. A 375-nm CW laser was used to photochemically reduce graphene oxide to its reduced form. The process of reduction was accompanied by increased absorption intensity by reduced graphene oxide, which was the basis for modulation of the fluorescence emission from the up-conversion nanoparticles through quenching. A 980-nm CW laser was then adopted for excitation of the up-conversion nanoparticles and detection of the variation in up-conversion fluorescence emission that decreased because of quenching by reduced graphene oxide.

After the introduction, Section 3.2 reports the synthesis and characterisation of NaGdF$_4$-based up-conversion nanoparticles and graphene oxide. Section 3.3 presents the fabrication of a graphene oxide thin film integrated with up-conversion nanoparticles, while Section 3.4 demonstrates the photochemical reduction of graphene oxide by ultraviolet laser and the modulation of fluorescence emission from the up-conversion nanoparticles through quenching. Finally, Section 3.5 presents the conclusions to this chapter.
3.2 Synthesis and characterisation of up-conversion nanoparticles and graphene oxide

3.2.1 Synthesis of hydrophilic up-conversion nanoparticles

To synthesise the up-conversion nanoparticles, gadolinium (III) acetate hydrate (99.9%), ytterbium (III) acetate tetrahydrate (99.9%), thulium (III) acetate hydrate, sodium hydroxide (98%), ammonium fluoride (98%), 1-octadecene (90%) and oleic acid (90%) were purchased from Sigma-Aldrich. Initially, NaGdF$_4$:Yb/Tm (49%, 1%) core up-conversion nanoparticles were prepared. For this purpose, 2 mL of Ln(CH$_3$CO$_2$)$_3$ (0.2 M, Ln = Yb, Tm and Gd) water solution was poured into a 50 mL flask that contained 4 mL of oleic acid. The mixture was heated at 150°C for 30 minutes to allow elimination of water. A solution of 1-octadecene (6 mL) was then rapidly poured into the flask and the resulting mixture was heated at 150°C for an additional 30 minutes, and then cooled to 50°C. Subsequently, 5 mL of methanol solution that contained NH$_4$F (1.36 mmol) and NaOH (1 mmol) was poured, and the resultant solution was stirred for 30 minutes. After the evaporation of methanol, the solution was heated to 290°C under argon for 1.5 hours and then cooled to room temperature. The as-synthesised nanoparticles with a yield of 80 mg were precipitated by adding ethanol, collected through centrifugation at 6,000 rpm for five minutes, washed with ethanol and re-dispersed in 4 mL of cyclohexane.

Given that shell passivation of core up-conversion nanoparticles is a well-known pathway to avoid surface quenching and obtain brighter nanoparticles, the researchers proceeded by coating the as-prepared core structures with an inert shell. The NaGdF$_4$:Ln shell precursor was first prepared by mixing 2 mL of Ln(CH$_3$CO$_2$)$_3$ (0.2 M, Ln = Gd) water solution and 4 mL of oleic acid in a 50-mL flask and subsequently heating at 150°C for 30 minutes. Then 1-octadecene (6 mL) was added and the mixed solution was heated at 150°C for an additional 30 minutes before cooling to 50°C. Later, the NaGdF$_4$:Yb/Tm (49%, 1%) core nanoparticles (40 mg) dispersed in 2 mL of cyclohexane were added, along with 5 mL methanol solution of NH$_4$F (1.36 mmol) and NaOH (1 mmol). The resulting mixture was stirred at 50°C for 30 minutes and then heated to 290°C under argon for 1.5 hours. Finally, the solution was cooled to room temperature. The resulting NaGdF$_4$:Yb/Tm (49%, 1%) @NaGdF$_4$ core-shell up-conversion nanoparticles were precipitated by adding ethanol, collected by centrifugation at
6,000 rpm for five minutes, washed with ethanol several times and re-dispersed in 4 mL of cyclohexane.

To obtain hydrophilic up-conversion nanoparticles and thus possess the major advantage of water dispersibility for the preparation of a nanocomposite in combination with graphene oxide, the oleic acid ligand was removed from the surface of the up-conversion nanoparticles. For this purpose, the nanoparticles capped with oleic acid were dispersed in a 2mL of HCl solution (0.1 M) and ultrasonicated for 15 minutes to allow removal of the surface ligands. After that, the nanoparticles were collected via centrifugation at 16,500 rpm for 20 minutes and purified by addition of acidic ethanol solution (pH 4; prepared by mixing 0.1 M HCl aqueous solution with absolute ethanol). Ethanol and deionised water were used to wash the nanoparticles several times, which were then re-dispersed in deionised water. Figure 3.1 illustrates the steps undertaken for the preparation of oleic acid ligand free NaGdF₄-based core-shell up-conversion nanoparticles.

Figure 3.1: Schematic procedure of the synthesis of oleic acid ligand free NaGdF₄-based core-shell up-conversion nanoparticles.

### 3.2.2 Characterisation of the up-conversion nanoparticles and graphene oxide

The NaGdF₄-based up-conversion nanoparticles were characterised by transmission electron microscope (TEM) (JEOL 1010 TEM [2001]) at an acceleration voltage of 100 keV (Figure 3.2a) and X-ray diffraction (XRD) (Bruker Axs D4 Endeavor) (Figure 3.2b).
Figure 3.2: Characterisation of the physical features of the as-prepared NaGdF₄-based up-conversion nanoparticles. a) Transmission electron micrograph and corresponding size distribution of the up-conversion nanoparticles. The coefficient of variation is below 3%, displaying monodispersed samples. Scale bar: 20 nm. b) XRD spectra of the up-conversion nanoparticles and corresponding standard pattern for NaGdF₄ hexagonal phase (JCPDS #27-0699).
As shown in Figure 3.2, the synthesised monodispersed up-conversion nanoparticles had an average diameter of 33.4 and 35.5 nm for the core and core-shell structures, respectively. In addition, the coefficient of variation—which is the ratio of the standard deviation, $\sigma_d$, to the mean diameter, $d_{mean}$—was below 3%, calculated considering 200 nanoparticles. The XRD analysis showed the hexagonal phase of the nanoparticles with all peaks, which matched the JCPDS file number 27-0699.

The fluorescence emission spectra of the up-conversion nanoparticles were collected using a 980-nm CW laser for excitation at 1 mW (Andor Shamrock 500i Spectrograph equipped with iXon EMCCD camera) (Figure 3.3a). The nanoparticles exhibited characteristic emissions that can be ascribed to the $^6P_{7/2} \rightarrow ^8S_{7/2}$ (310 nm) transition of Gd$^{3+}$ and the $^1I_6 \rightarrow ^3F_4$ (345 nm), $^1D_6 \rightarrow ^3H_6$ (360 nm), $^1D_6 \rightarrow ^3F_4$ (450 nm), $^1G_4 \rightarrow ^3H_6$ (475 nm) and $^1G_4 \rightarrow ^3F_4$ (650 nm) transitions of Tm$^{3+}$. These observations well agreed with the literature [107] and confirmed efficient up-conversion through the gadolinium sublattice–mediated Yb$^{3+} \rightarrow$ Tm$^{3+} \rightarrow$ Gd$^{3+}$ energy transfer pathway, depicted in Figure 3.3b.

As can be seen from Figure 3.3, the core-shell up-conversion nanoparticles were one order of magnitude brighter than the core-only structures, thereby confirming surface quenching prevention by the inert shell. As a result of their stronger fluorescence emission, which

**Figure 3.3:** Up-conversion fluorescence emission in the as-prepared NaGdF$_4$-based up-conversion nanoparticles. a) Fluorescence emission spectra of the core and core-shell up-conversion nanoparticles under excitation using a CW laser at 980 nm. b) Energy level diagrams of Yb$^{3+}$, Tm$^{3+}$ and Gd$^{3+}$ and the involved mechanism for up-conversion fluorescence emission in Tm$^{3+}$ and Gd$^{3+}$.
results in an enhanced signal for high-contrast imaging, the up-conversion nanoparticles with a core-shell configuration were chosen for the further work presented in this chapter. The elemental composition of the NaGdF₄:Yb/Tm (49%, 1%) @NaGdF₄ core-shell up-conversion nanoparticles was characterised by energy dispersive X-ray (EDX) analysis (JEOL 2100F FEGTEM/STEM [2011], equipped with an Oxford X-MaxN 80T EDX Detector [2014]) (Figure 3.4a). The abundant Gd, Yb, Na and F elements were detected in the spectrum, while the Tm element was not detected because of its low doping concentration of only 1%. To validate the achievement of a heterogeneous core-shell structure, the local elemental mapping was undertaken by an EDX line scan to address the composition across the nanoparticles (Figure 3.4b). The researchers observed that the elemental distribution of the Gd element was higher in the outer layer of the nanoparticle, while the Yb element was confined predominantly to the centre, thereby confirming the formation of a core-shell system. Although scanning transmission electron microscope (STEM) enabled accurate imaging, the core and shell could not be differentiated directly from the image because of their similar crystalline structures and compositions.

Figure 3.4: Characterisation of the elemental composition of the NaGdF₄:Yb/Tm (49%, 1%) @NaGdF₄ core-shell up-conversion nanoparticles. a) EDX spectrum confirming the presence of the abundant Gd, Yb, Na and F elements. The peak associated with copper is attributed to the TEM grid. b) EDX line scan revealing the signal intensity for Gd and Yb elements across an individual nanoparticle. The Gd element content at the margin of the particle was higher than that in the interior, thereby validating the formation of a core-shell structure. Inset: STEM image of the investigated nanoparticle.
Graphene oxide (2 mg mL\(^{-1}\), water solution) was purchased from Sigma-Aldrich and tested to confirm the quality of the received material. Figure 3.5a reports the UV–Vis absorption spectrum (Agilent Cary 60 UV-Vis Spectrophotometer) of the graphene oxide in water. Graphene oxide possessed typical absorption spanning from 200 to 1,000 nm, with a maximum 230 nm related to the \(\pi-\pi^*\) transition of aromatic C=C bonds and a shoulder around 300 nm related to the n–\(\pi^*\) transition of C-O bonds [108].

![Graphene oxide UV-Vis absorption spectrum and XPS analysis](image)

**Figure 3.5:** Characterisation of graphene oxide. a) UV–Vis absorption spectrum of graphene oxide in water. Inset: Photograph of graphene oxide in water and graphene oxide flake deposited onto silicon/silicon dioxide substrate imaged by optical microscopy in reflection mode. Scale bar: 10 µm. b) X-ray photoelectron spectroscopy (XPS) analysis spectra of graphene oxide after deconvolution.

**Table 3.1:** Binding energy and relative atomic percentage of the functional groups determined by XPS analysis of graphene oxide.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Binding Energy (eV)</th>
<th>Relative Atomic Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp(^2)</td>
<td>284.4</td>
<td>8.3</td>
</tr>
<tr>
<td>C-OH</td>
<td>285.3</td>
<td>19.0</td>
</tr>
<tr>
<td>C-O</td>
<td>287.2</td>
<td>51.8</td>
</tr>
<tr>
<td>C=O</td>
<td>288.8</td>
<td>14.9</td>
</tr>
<tr>
<td>COOH</td>
<td>290.2</td>
<td>6.0</td>
</tr>
</tbody>
</table>
XPS spectroscopy was used to determine the oxygen groups present in graphene oxide and the carbon and oxygen bonds (Figure 3.5b and Table 3.1). The measurement was obtained by using high-resolution C1s spectra (Thermo Scientific K-Alpha XPS). Deconvolution of the C1s peak revealed the C atom bonded to the oxygen groups, which primarily consisted of sp² (284.4 eV), C–OH (285.3 eV), C–O (287.2 eV), C=O (288.8 eV) and COOH (290.2 eV). When graphene is converted to graphene oxide, the hybridization of carbon changes from sp² to sp³, and results in many negatively charged oxygen-containing groups on the monolayer carbon. Given that photoelectrons are susceptible to inelastic scattering during their transport from the excitation point to the surface of the sample, which results in inelastic background intensity, Shirley’s background subtraction was conducted before deconvolution to establish the area of single peaks. Asymmetric fitting was used for the sp² component, whereas symmetric fitting was used for the sp³ carbon and functionalised carbon components.

3.3 Fabrication of a graphene oxide thin film integrated with up-conversion nanoparticles

3.3.1 Conjugation of the up-conversion nanoparticles with graphene oxide

Controlled electrostatic self-assembly was selected to conjugate the core-shell up-conversion nanoparticles with graphene oxide. Table 3.2 reports the zeta potentials of water-dispersed core-shell up-conversion nanoparticles and graphene oxide. The zeta potential values indicate that up-conversion nanoparticles and graphene oxide are a pair of oppositely charged colloids in water solution, and thus tend to strongly adsorb onto each other when mixed.

Table 3.2: Zeta potential values of water-dispersed NaGdF₄:Yb/Tm (49%, 1%) @NaGdF₄ core-shell up-conversion nanoparticles and graphene oxide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaGdF₄:Yb/Tm @NaGdF₄</td>
<td>20.1 ± 2.0</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>-54.9 ± 2.1</td>
</tr>
</tbody>
</table>
The electrostatic attraction between the core-shell up-conversion nanoparticles with positive charge and the graphene oxide with negative charge offers the possibility to electrostatically self-assemble the two nanomaterials when mixed in water solution.

A homogeneous and dense loading of up-conversion nanoparticles onto graphene oxide nanosheets is an essential requirement for efficient energy transfer and quenching of up-conversion fluorescence. Thus, a concentration-dependent study of the loading of up-conversion nanoparticles onto graphene oxide mixed in water solution was conducted. The amount of up-conversion nanoparticles assembled onto the nanosheets of graphene oxide was controlled by tuning the initial concentrations of the nanoparticles in water solution to fully cover the graphene oxide nanosheets. The up-conversion nanoparticles were diluted to 0.8, 4, 20, 100 and 500 mM in 1 mL of deionised water, while graphene oxide was maintained at 0.4 mg mL$^{-1}$. Figure 3.6 displays the TEM images of graphene oxide nanosheets loaded with core-shell up-conversion nanoparticles at increasing concentrations from 0.8 to 500 mM.

![TEM images of graphene oxide nanosheets loaded with core-shell up-conversion nanoparticles at increasing concentrations from 0.8 to 500 mM.](image)

**Figure 3.6:** Loading up-conversion nanoparticles onto graphene oxide. a) TEM images of graphene oxide nanosheets loaded with core-shell up-conversion nanoparticles at a concentration of 0.8, 4, 20, 100 and 500 mM. The initial concentration of graphene oxide in water solution was 0.4 mg mL$^{-1}$. Scale bar: 500 nm.

The loading of up-conversion nanoparticles onto graphene oxide nanosheets increased by increasing the concentration of the core-shell up-conversion nanoparticles in solution from 0.8 to 500 mM. Optimal concentration has been individuated to be of 20 mM, which provides homogeneous coverage of nanoparticles onto individual graphene oxide nanosheets. Further increase of the concentration of the nanoparticles resulted in their aggregation and the generation of wrinkles in the nanosheets of graphene oxide around the nanoparticles.
3.3.2 Thin film deposition through vacuum filtration

The graphene oxide thin film integrated with core-shell up-conversion nanoparticles was fabricated through facile and reproducible vacuum filtration. Vacuum filtration comprises the filtration of the suspension of graphene oxide conjugated with nanoparticles through a commercial mixed cellulose ester membrane. When the suspension permeates the pores of the membrane, the liquid passes, yet the graphene oxide nanosheets conjugated with the nanoparticles are retained. The permeation rate of the water is modulated by the lodgement of the graphene conjugated with the nanoparticles onto the filter. By increasing the amount of deposition at a certain spot on the membrane, the filtration rate diminishes with a slower speed for thinner or uncovered locations. Therefore, the process self-regulates, enabling control of the film thickness at the nanoscale by merely changing the concentration of the graphene oxide or the filtered amount. The graphene oxide nanosheets conjugated with the nanoparticles on the filter membrane can then be transferred by dissolving the membrane using acetone, thereby obtaining a uniform graphene oxide thin film integrated with up-conversion nanoparticles. Hydrogen-bonding interactions between graphene oxide nanosheets conjugated with the nanoparticles enable the thin film to be highly stable once dried. The reported method is easy to scale up, and controllable thickness of the thin film from micrometre to nanoscale dimensions can be obtained.

In this study’s preparation, 200 μL of graphene oxide water solution was diluted to 10 ml with deionised water and then sonicated for 30 minutes. Then, 20 μL of up-conversion nanoparticles solution (20 mM, dispersion in water) was diluted up to 10 ml using deionised water and sonicated for 30 minutes. The solutions of graphene oxide and up-conversion nanoparticles were combined and stirred for 10 minutes. The mixture was filtrated through a mixed cellulose ester membrane filter with 0.22 μm pore size, forming a superimposed thin film with controllable thickness onto the membrane filter. The thin film was dried at room temperature and subsequently immersed in acetone to remove the membrane filter. Finally, the free-floating thin film was fished out using a coverslip glass, and let to dry at room temperature. Accompanied by the volatilisation of acetone, the free-standing thin film of graphene oxide integrated with up-conversion nanoparticles was easily separated from the membrane filter and deposited onto a suitable substrate for testing.
Figure 3.7: Graphene oxide thin film integrated with core-shell up-conversion nanoparticles deposited through vacuum filtration. a) Schematic preparation of a graphene oxide thin film integrated with core-shell up-conversion nanoparticles through vacuum filtration. b) Optical images and c) Step-height measurement of the graphene oxide thin film integrated with core-shell up-conversion nanoparticles onto coverslip glass.
Figure 3.7a illustrates the steps for fabricating free-floating thin-film graphene oxide integrated with core-shell up-conversion nanoparticles through vacuum filtration. The procedure consists of preparing graphene oxide conjugated with up-conversion nanoparticles thin film on a mixed cellulose ester membrane filter through vacuum filtration, followed by a distinctive separation and retrieval using a coverslip glass substrate. To separate the thin film from the filter, an efficient approach was to dissolve the supporting mixed cellulose ester membrane using acetone. After complete elimination of the membrane, a coverslip glass substrate was used to retrieve the free-standing thin film from the organic solvent. Figure 3.7b reports the optical images of the graphene oxide thin film integrated with up-conversion nanoparticles at different magnifications. The thin film appeared uniform under transmitted white light and its thickness could be controlled from micrometre to nanometre scale by dosing the colloidal dispersion of graphene oxide nanosheets mixed with the up-conversion nanoparticles. The thin film was 143.2 nm thick (Figure 3.7c) measured through step-height profiling (Tencor Profilometer).

3.4 Modulation of up-conversion fluorescent nanoparticles through reduction of graphene oxide by ultraviolet laser

Figure 3.8 displays the principle of modulating the fluorescence emission from the up-conversion nanoparticles via the reduction of graphene oxide induced under ultraviolet laser. A 375-nm CW laser beam was used to induce the photochemical reduction of the graphene oxide in the thin-film graphene oxide integrated with up-conversion nanoparticles (Figure 3.8a). The reduction was controlled by tuning the laser power; therefore, precise modulation of absorption intensity between graphene oxide and its reduced form could be accomplished. Through laterally moving the sample, reduced patterns could be produced. Subsequently, a 980-nm CW laser excited the fluorescence emission from the up-conversion nanoparticles, which was hugely quenched by the reduced graphene oxide and allowed retrieval of the reduced patterns with high contrast (Figure 3.8b).
Figure 3.8: The principle of modulating up-conversion fluorescent nanoparticles through the reduction of graphene oxide by ultraviolet laser. a) A 375-nm CW laser induces photochemical reduction of graphene oxide to its reduced form accompanied by a variation of absorption intensity. b) A 980-nm CW laser excites the fluorescence emission from the up-conversion nanoparticles, which are hugely quenched by the reduced graphene oxide.
3.4.1 Experimental setup

The experimental optical system setup for the photochemical reduction of the graphene oxide thin film integrated with up-conversion nanoparticles and detection of the quenching of fluorescence emission from the up-conversion nanoparticles was built on a typical confocal microscopy system (Figure 3.9).

![Diagram](image)

Figure 3.9: Scheme of the experimental setup. M = mirror, FM = flipping mirror, L = lens, DC = dichroic mirror, FDC = flipping dichroic mirror, HWP = half waveplate, P = polariser, SPAD = single-photon avalanche diode.

The graphene oxide thin film integrated with up-conversion nanoparticles was placed on a high-precision nanopositioning system based on three-axis piezo stage (P-562 PIMars Nanopositioning Stage, Physik Instrumente). A 375-nm CW laser (OBIS 375 nm LX 50 mW, Coherent) was employed to produce the reduction of graphene oxide. An objective (M Plan Apochromat MPLAPON-Oil, NA = 1.4, 100X, Olympus) focused the laser beam onto
the sample. The reduced pattern was achieved by lateral movement of the sample across the focal plane. A 980-nm CW laser (BL976-PAG900, Thorlabs) was adopted to excite the up-conversion nanoparticles. The up-conversion fluorescence was collected by the same objective, divided from the excitation by a dichroic mirror, and coupled into a multimode fibre (FG050LGA, Thorlabs), which was connected to an SPAD (SPCM-AQRH-14-FC, Excelitas Technologies). A band pass filter (FF01-442/46-25, Semrock) was inserted in the detection pathway to select the up-conversion fluorescence band. To measure up-conversion fluorescence emission spectra, the signal was directed to the spectrometer (Andor Shamrock 500i Spectrograph equipped with iXon EMCCD Camera) using a flipping mirror. A half waveplate and Glan-Thompson prisms were employed to control the power of the laser beams.

### 3.4.2 Photochemical reduction of graphene oxide by ultraviolet laser

The photochemical reduction of graphene oxide was obtained under 375-nm CW laser irradiation at different powers. The reduction was apparent by micro-Raman spectroscopy (LabRAM HR Evolution). The Raman spectra of the graphene oxide thin film integrated with up-conversion nanoparticles sample displayed two wide peaks at 1,354 and 1,599 cm$^{-1}$, which corresponded to the D and G bands, respectively (Figure 3.10). The D band suggests the existence of disorder in the sp$^2$-hybridised carbon structure, which is typical of graphene, while the G band results from the E2g mode at the Γ-point and is ascribed to the vibrations in the C–C bonded atoms in graphitic materials. Under increasing power of the 375-nm CW laser, the peaks that corresponded to the D and G bands of reduced graphene oxide became discernible and the bandwidths were narrower in comparison with those of the graphene oxide. The ratio between the intensities of the D and G bands ($I_D/I_G$)—which relates to the elimination of oxygen groups that produce defects within the carbon basal plane of graphene oxide and thus give insight into the reduction process—varied from 1.08 of graphene oxide before irradiation to 0.91 of its reduced form after irradiation with the 375-nm CW laser at 100 μW. This result can be interpreted as a diminished dimension of the graphene oxide domains [109], indicating that the 375-nm CW laser irradiation eliminated the oxygen groups and successfully restored the sp$^2$ C=C bonds.
Figure 3.10: Raman spectra of the graphene oxide thin film integrated with up-conversion nanoparticles before (purple solid line) and after irradiation with a 375-nm CW laser at 10, 25, 50, 75 and 100 μW (from light blue to black solid lines). The spectra consisted of D and G bands at 1,354 and 1,599 cm$^{-1}$, respectively (dashed lines). Under irradiation of the 375-nm CW laser, the $I_D/I_G$ varied from 1.08 of graphene oxide to 0.91 of its reduced form.

To confirm the occurrence of the photochemical reduction in the graphene oxide thin film integrated with up-conversion nanoparticles under 375-nm CW laser irradiation at different powers, the researchers also performed Fourier-transform infrared (FTIR) spectroscopy (Figure 3.11). A series of overlapping bands were detected between 3,000 and 3,700 cm$^{-1}$, which were ascribed to the stretching of the O–H bond. In addition to the 3,406 cm$^{-1}$ band, shoulders at 3,610 and 3,215 cm$^{-1}$ were noticed, which may be related to the OH groups. The band at 1,730 cm$^{-1}$ could be ascribed to the stretching of C=O in carbonyl groups or in ketones. Other bands located at 1,360 to 1,380 cm$^{-1}$, 1,220 to 1,230 cm$^{-1}$ and 1,060 to 1,080 cm$^{-1}$ are typically ascribed to the vibrations of the C–OH bond and C–O–C bonds phenyl/hydroxyl groups, respectively. The spectrum of the graphene oxide thin film integrated with up-conversion nanoparticles changed significantly after irradiation under 375-nm CW laser at different powers, compared with before irradiation. This was a result of the decreased intensity of the bands caused by the vibrations of the O–H (3,410 cm$^{-1}$) and C–OH (1,380 cm$^{-1}$). It may be noted that all other peaks showed decreased intensity compared with before irradiation.
Figure 3.11: FTIR spectra of the graphene oxide thin film integrated with up-conversion nanoparticles before (purple solid line) and after irradiation with a 375-nm CW laser at 10, 25, 50, 75 and 100 μW (from light blue to black solid lines).

The physical and chemical change of graphene oxide through reduction under ultraviolet laser creates the potential for modulation of up-conversion fluorescence emission through quenching in this study’s newly-developed thin-film nanocomposite. This achievement enables application in a variety of emerging fields, including optical data storage.

3.4.3 Up-conversion fluorescence modulation by quenching

The as-prepared graphene oxide thin film integrated with up-conversion nanoparticles was highly fluorescent under excitation using a CW laser at 980 nm. The fluorescence arose from the up-conversion nanoparticles. With the occurrence of reduction of graphene oxide under 375-nm CW laser irradiation, the variation of absorption intensity between graphene oxide and its reduced form produced quenching of up-conversion fluorescence and thus decreased emission intensity from the up-conversion nanoparticles. Figure 3.12 displays the 450-nm up-conversion fluorescence emission after the reduction of graphene oxide under 375-nm CW laser irradiation at different powers normalised to the intensity before reduction. It can be clearly seen that irradiation of the ultraviolet laser caused a significant decrease in 450-nm up-conversion fluorescence emission because of the quenching of the up-conversion nanoparticles by reduced graphene oxide. Further, 450-nm up-conversion
fluorescence quenching could be precisely modulated by controlling the photochemical reduction process through judicious tuning of the 375-nm CW laser power.

![Figure 3.12](image)

**Figure 3.12:** 450-nm up-conversion fluorescence emission quenching in the graphene oxide thin film integrated with up-conversion nanoparticles after irradiation with 375-nm CW laser at 10, 25, 50, 75 and 100 μW. Exposure time: 100 ms.

From Figure 3.12, it is evident that the response upon 375-nm CW laser irradiation of the thin-film nanocomposite was a significant drop in 450-nm fluorescence emission, associated with the quenching of the up-conversion nanoparticles by reduced graphene oxide. Values of 450-nm up-conversion fluorescence quenching up to ~90% were obtained for irradiation of the graphene oxide thin film integrated with up-conversion nanoparticles with the 375-nm CW laser at 100 μW. These results provide clear evidence of the superior capability of modulating the fluorescence intensity generated from the up-conversion nanoparticles by graphene oxide and its reduced form, compared with previously-used combinations of materials [62, 63]. Further, it proves the feasibility of patterning and retrieval in the thin-film graphene oxide integrated with up-conversion nanoparticles, which can find application in high-contrast optical data storage via photochemical reduction of graphene oxide and up-conversion fluorescence quenching.

The researchers calculated the total associated 375-nm CW laser photon dose, $\Phi$, for the photochemical reduction of graphene oxide, giving ~90% up-conversion fluorescence quenching, according to Eq. 3.1 [93, 94]:

$$\Phi = \text{constant} \times \text{exposure time} \times \text{power}$$
\[ \Phi = I \times \left( \frac{\lambda}{hc} \right) \times t \] (3.1)

where \( I \) is the 375-nm CW laser intensity, \( \lambda \) is the irradiation wavelength, \( h \) is Plank’s constant, \( c \) is the light speed and \( t \) is the exposure time. The values used for the calculation were: \( I = 25 \, kW \, cm^{-2}, \lambda = 375 \, nm, \, hc = 1.99 \times 10^{-25} \, J \cdot m \) and \( t = 100 \, ms \). The resulting 375-nm CW laser photon dose, \( \Phi \), was \( 4.7 \times 10^{21} \, photons \, cm^{-2} \). The researchers estimated the quantum efficiency of 375-nm photons to produce the photochemical reduction of graphene oxide according to the literature [89], and obtained good agreement between the calculated photon dose, \( \Phi \), for the process of photochemical reduction, considered in comparison with previously reported results about photochemical reduction of graphene oxide using different laser sources [93, 94].

To pin down the mechanism behind the decreased up-conversion fluorescence emission, up-conversion fluorescence lifetime measurements were performed in the graphene oxide thin film integrated with up-conversion nanoparticles. The 975-nm CW excitation laser was modulated using an acousto-optic modulator (MT110-A1-VIS/IR/1064, AA OPTO-ELECTRONIC) for 50-\( \mu \)s pulses with frequency of 100 Hz. The emitted photons, going through a 442-nm band pass filter (CFW-BP01-Clin-25, Semrock), were detected by a SPAD (SPCM-AQRH-13-FC, Excelitas Technologies) and the trigger signal from the acousto-optic modulator was synchronised with a SPAD using a data acquisition (DAQ) card (cDAQ-9171, National Instruments) (Figure 3.12).

**Figure 3.13:** Schematic of the experimental configuration for up-conversion fluorescence lifetime measurements.
Figure 3.14: Decay behaviour of the 450-nm up-conversion fluorescence emission from the graphene oxide thin film integrated with up-conversion nanoparticles. 450-nm up-conversion fluorescence lifetime before (black solid line) and after irradiation with a 375-nm CW laser at 10, 25, 50, 75 and 100 µW (from red to purple solid lines) decreasing from 403 to 175 µs.

The 450-nm up-conversion fluorescence lifetime decreased when the nanocomposite was irradiated under 375-nm CW laser, varying from 403 µs before irradiation to 175 µs after irradiation at a power of 100 µW. Based on the up-conversion fluorescence lifetime decrease, the quenching of fluorescence emission from the up-conversion nanoparticles in the nanocomposite was attributed to resonance energy transfer because of the variation of absorption between graphene oxide and its reduced form.

3.4.4 Optical patterning in the graphene oxide thin film integrated with up-conversion nanoparticles

Photochemically reducing graphene oxide by ultraviolet laser and consequent quenching of fluorescence emission from the up-conversion nanoparticles under near-infrared excitation enabled optical patterning and retrieval in the graphene oxide thin film integrated with up-conversion nanoparticles through direct laser writing. Representations of a leaf, a kangaroo and the Sydney Opera House were fabricated and recovered in the nanocomposite (Figure 3.15). The power of the 375-nm CW laser focused through a 1.4 NA objective lens was of 100 µW and the exposure time was 100 ms. During patterning,
the 375-nm CW laser induced the photochemical reduction in graphene oxide to its reduced form, accompanied by a variation in absorption intensity. Consequently, the fluorescence emission from up-conversion nanoparticles under excitation using a CW laser at 980 nm was quenched. The optical patterns were retrieved by raster scanning the sample and detecting the up-conversion fluorescence quenching using a 980-nm CW laser for excitation at 500 µW. The pixels exhibited decreased up-conversion fluorescence emission because of the quenching by reduced graphene oxide. The results indicated an average pixel size of 475 nm—close to the expected diffraction-limit value for the considered wavelength. The photochemical reduction of graphene oxide exhibited a high spatial confinement, which is greatly desirable in encoding applications.

![Figure 3.15: Optical patterning in the graphene oxide thin film integrated with up-conversion nanoparticles. Normalised up-conversion fluorescence emission scan of optical patterns in the nanocomposite displaying representations of a leaf, a kangaroo and the Sydney Opera House (left to right). The patterns were 50 × 50 pixels, with a pixel spacing of 0.97 µm. Scale bar: 20 µm. Inset: Detailed image of the individual pixels. Scale bar: 1 µm.](image)

### 3.5 Chapter conclusions

This chapter has demonstrated the photochemical reduction of thin-film graphene oxide integrated with up-conversion nanoparticles under high-energy laser irradiation for the modulation of up-conversion fluorescence emission. This provides a stepping stone towards encoding and retrieval in an up-conversion nanoparticles–graphene oxide nanocomposite. Initially, NaGdF$_4$-based up-conversion nanoparticles and graphene oxide were synthesised and characterised. Following this, a graphene oxide thin film integrated with NaGdF$_4$-based up-conversion nanoparticles was prepared through vacuum filtration. A
375-nm CW laser was used to irradiate the nanocomposite and photochemically reduce graphene oxide. Specifically, the photochemical reduction of graphene oxide under ultraviolet laser was characterised using Raman spectroscopy and FTIR spectroscopy. The absorption change in the nanocomposite was accompanied by the quenching of the fluorescence emission from the up-conversion nanoparticles. Thus, a CW laser at 980 nm excited the up-conversion nanoparticles, and detection of the decreased up-conversion fluorescence emission associated with quenching by reduced graphene oxide was achieved. Further, up-conversion fluorescence lifetime measurements were performed to pin down the mechanism of fluorescence quenching. The decreased up-conversion fluorescence lifetime was related to the occurrence of resonance energy transfer between the up-conversion nanoparticles and graphene oxide/reduced graphene oxide. Optical patterns were successfully achieved in the graphene oxide thin film integrated with up-conversion nanoparticles and retrieved distinctly using the up-conversion fluorescence emission quenching by reduced graphene oxide.

The presented demonstration offers a great improvement over currently available methods for modulation of the fluorescence emission from up-conversion nanoparticles. This advancement is mostly due to the super-quenching property of reduced graphene oxide, which can quench up-conversion fluorescence up to ~90%. In addition, the fast reduction speed of using high-energy laser allows a decrease in the time to modulate up-conversion fluorescence from minutes, such as in the case of up-conversion nanoparticles coupled with DTE molecule, down to the millisecond range for individual pixels in this study’s newly-developed nanocomposite. This improvement is due to the rapid process of ultraviolet laser-induced reduction of graphene oxide and fluorescence emission quenching of the up-conversion nanoparticles, which rely on the instantaneous physical and chemical change of graphene oxide through reduction, compared with the slow closed-/open-ring processes in the case of DTE molecule. Moreover, as a result of the low power required and the use of CW lasers, low energy consumption for the process of optical patterning has been achieved. Finally, understanding the physics behind ultraviolet laser-induced photochemical reduction in graphene oxide and the quenching of fluorescence emission from the up-conversion nanoparticles by reduced graphene oxide lays the scientific foundation for the development of a suitable optically-activatable nanocomposite towards ultralow-power nanoscale optical data storage.
Chapter 4

Development of high-energy up-conversion fluorescent nanoparticles for dual-laser photoactivated super-resolution systems

4.1 Introduction

In recent years, up-conversion nanoparticles have become a powerful tool for optical methods because they can convert near-infrared excitation photons into shorter-wavelength, near-infrared, visible and ultraviolet fluorescence emission. This property has enabled various applications, including optical imaging with improved penetration depth and without photobleaching, photo-blinking, tissue autofluorescence and light toxicity [110]. Moreover, efficient optical modulation of up-conversion nanoparticles has been achieved, resulting in super-resolution fluorescence imaging techniques, such as STED microscopy [65, 66]. However, the research efforts exploring optical depletion in up-conversion nanoparticles have resulted in the synthesis of nanoparticles that exhibit minimal or absent fluorescence emissions in ultraviolet. This drawback hinders the application of these up-conversion nanoparticles in energy transfer–driven systems, which require high-energy photons for activation—such as for the photochemical reduction of graphene oxide. Thus, the researchers devoted themselves to developing up-conversion nanoparticles that not only show efficient optical depletion under dual-laser irradiation, but also possess intense high-energy up-conversion fluorescence, which would enable nanoscale photoactivation in energy transfer–driven systems.
This chapter presents the development of high-energy up-conversion fluorescent nanoparticles suitable for use in dual-laser photoactivated super-resolution systems, including their combination with graphene oxide. The objective of the theoretical and experimental investigation in this chapter is to provide the key features of the nanoparticles for efficient energy transfer–driven photoactivation in applications beyond the diffraction-limit barrier. Section 4.2 outlines a theoretical framework for the process of up-conversion in the nanoparticles and energy transfer to graphene oxide. Further, simulation results indicate the potential for resolution improvement in the up-conversion nanoparticles–graphene oxide system, providing a feasible pathway for energy transfer–driven photoactivation at the nanoscale. The synthesis and testing of these up-conversion nanoparticles in super-resolution optical techniques are conducted in Sections 4.3 and 4.4, respectively. Finally, Section 4.5 presents the conclusions of this chapter.

4.2 Selection of the up-conversion nanoparticles

Selective activation of up-conversion nanoparticles beyond the diffraction-limit barrier using optical techniques, such as STED microscopy and SPIN, relies on the combination of a Gaussian-shaped laser beam and doughnut-shaped laser beam to shrink the effective PSF to the nanoscale. The theoretical investigation of dual-laser super-resolution systems based on up-conversion nanoparticles and up-conversion nanoparticles in combination with graphene oxide for energy transfer–driven applications can be conceptually summarised as follows. At every spot of the focal region, the photoactivation under dual-laser super-resolution irradiation is described by differential equations that define the processes of up-conversion in the nanoparticles and energy transfer to graphene oxide at the nanoscale. For this purpose, a steady-state model is used to describe the up-conversion and energy transfer involved during dual-laser super-resolution irradiation of the up-conversion nanoparticles and up-conversion nanoparticles–graphene oxide system. By simulating the profile of the photoactivated region, the resolution improvement of the formed features beyond the diffraction-limit barrier is evaluated.
4.2.1 Key features

Identifying the optimal features of the up-conversion nanoparticles in terms of composition and the doping concentration of the lanthanide ions, along with their structural characteristics, such as size and shape, represents the fundamental step for using these nanoparticles in dual-laser photoactivated super-resolution systems with the potential for energy transfer-driven applications. First, a combination of lanthanide ions that enables intense high-energy up-conversion fluorescence is essential for activation in energy transfer-driven systems, such as the photochemical reduction of graphene oxide. Second, efficient optical depletion of up-conversion fluorescence is required for implementation in super-resolution techniques. Thus, the composition of the lanthanide dopants must enable efficient optical depletion of up-conversion under dual-laser irradiation. Third, homogeneous nanoparticles with small size and narrow distribution are necessary to satisfy the requirements for energy transfer, which most effectively occurs for distances within a few nanometres. Therefore, the key features of the up-conversion nanoparticles can be summarised as follows:

- intense high-energy up-conversion fluorescence;
- efficient optical depletion of up-conversion fluorescence;
- small size and narrow size distribution.

As a result of their unique ladder-like electronic energy structure, Tm$^{3+}$ ions can produce up-conversion fluorescence emission from high energy levels. Therefore, a combination of thulium (Tm$^{3+}$) ions as activators and ytterbium (Yb$^{3+}$) ions as sensitisers was selected for up-conversion fluorescence in the ultraviolet and blue through ETU [111]. The expected up-conversion fluorescence emission wavelengths for Yb,Tm-doped nanoparticles are 345, 360 and 450 nm, which well suit the requirements for high-energy photon up-conversion fluorescence. Moreover, recent studies on the relationship between high-energy up-conversion fluorescence intensity and Yb$^{3+}$ ions doping have indicated that 30 mol% represents the optimal concentration [63]; thus, this value was chosen for the work presented in this chapter. In addition, high Tm$^{3+}$ doping concentration is considered for efficient optical depletion of up-conversion fluorescence under dual-laser irradiation. High doping concentration of Tm$^{3+}$ ions in up-conversion nanoparticles determines reduced inter-emitter distance and the occurrence of intense cross-relaxation between neighbouring Tm$^{3+}$ ions [65, 66]. Consequently, a population inversion can be established in the metastable $^3$H$_4$ excited level, compared with the $^3$H$_6$ ground level in Tm$^{3+}$. Thus, through overlapping a second laser
beam with suitable wavelength matching the $^3\text{H}_4 \rightarrow ^3\text{H}_6$ transition, which is 808 nm, efficient optical depletion can be achieved.

Typical wet-chemical synthesis procedures can be used for the preparation of the up-conversion nanoparticles. Generally, the reported size for up-conversion nanoparticles is around 20 to 25 nm in diameter, which falls within the requirements for efficient resonance energy transfer. Further, it results in an optimised trade-off between the minimum size of the nanoparticles, which would give the highest resolution improvement, and up-conversion fluorescence emission intensity, which is necessary for fast and effective activation through energy transfer.

### 4.2.2 Modelling dual-laser photoactivation in the up-conversion nanoparticles–graphene oxide system

The steady-state model presented here for dual-laser photoactivation in the up-conversion nanoparticles–graphene oxide system is based on the processes of up-conversion and energy transfer. The proposed mechanism for photoactivation is illustrated in Figure 4.1, whereby the photon up-conversion includes absorption of excitation photons at 980 nm by the Yb$^{3+}$ with the function of sensitisers, energy transfer to the Tm$^{3+}$ activators, up-conversion to the high-energy $^1\text{D}_2$ and $^1\text{I}_6$ levels in Tm$^{3+}$, and resonance energy transfer to graphene oxide, which enables reduction to its reduced form. Having established a population inversion in $^3\text{H}_4$ intermediate level relative to the $^3\text{H}_6$ ground state level, an 808-nm laser can produce STED of the $^3\text{H}_4$ level and consequently inhibit up-conversion to high-energy excited levels, such as the $^1\text{D}_2$ and $^1\text{I}_6$. In this case, the energy transfer to graphene oxide, and thus its reduction, are effectively inhibited.
Figure 4.1: Schematic of proposed mechanism for dual-laser photoactivation in up-conversion nanoparticles–graphene oxide system. a) Upon excitation at 980 nm, up-conversion to high-energy levels, such as \( ^1D_2 \) and \( ^1I_6 \), occurs in \( \text{Tm}^{3+} \) and resonance energy transfer (RET) induces photochemical reduction of graphene oxide to its reduced form (left). Upon combined irradiation at 980 and 808 nm, up-conversion to the high-energy levels in \( \text{Tm}^{3+} \) is inhibited, preventing photochemical reduction of graphene oxide (right). b) Diagram of energy levels in \( \text{Yb},\text{Tm} \)-doped up-conversion nanoparticles–graphene oxide system under irradiation of laser at 980 nm (left) and under combined irradiation of lasers at 980 and 808 nm (right).
The processes of up-conversion and energy transfer in the Yb,Tm-doped up-conversion nanoparticles–graphene oxide system have been described by rate equations of optical excitation and depletion and interionic energy transfer. The simplified energy level diagram of the Yb,Tm-doped up-conversion nanoparticles–graphene oxide system presented in Figure 4.1 is redrawn in Figure 4.2, illustrating the processes of activation under 980-nm laser irradiation, up-conversion energy transfer between excited Yb$^{3+}$ and Tm$^{3+}$, radiative and non-radiative decays, cross-relaxation, resonance energy transfer from the up-conversion nanoparticles to graphene oxide, and deactivation using 808-nm laser.

Under the assumption of fast non-radiative decay for the $^3H_5 \rightarrow ^3F_4$ and $^3F_{2,3} \rightarrow ^3H_4$ transitions, and thus combining each pair of energy levels into a single level, the following set of rate equations is established.

**For Yb$^{3+}$ ions:**
- Yb$^{3+}$ ($^2F_{7/2}$), ground state $n_{S1}$:
  \[
  \frac{dn_{S1}}{dt} = -\frac{dn_{S2}}{dt} \quad \text{(4.1)}
  \]
Yb$^{3+}$ ($^2F_{5/2}$), excited state $n_{s2}$:

$$\frac{dn_{s2}}{dt} = P_{980}n_{s1} - W_{n_{s2}} \tag{4.2}$$

$$- (c_1n_1 + c_2n_2 + c_3n_3 + (1 - ET_{n_5})c_4n_4 + (1 - ET_{n_6})c_5n_5)n_{s2}$$

For Tm$^{3+}$ ions:

- Tm$^{3+}$ ($^3H_6$), ground state $n_1$:

$$\frac{dn_1}{dt} = - \sum_{i=2}^{6} \frac{dn_i}{dt} \tag{4.3}$$

- Tm$^{3+}$ ($^3F_{4, 3H_5}$), excited state $n_2$:

$$\frac{dn_2}{dt} = c_1n_{s2}n_1 - c_2n_{s2}n_2 - W_2n_2 + b_32W_3n_3 + b_42W_4n_4 + b_52(1 - ET_{n_5})W_5n_5$$

$$+ b_62(1 - ET_{n_6})W_6n_6 + 2k_31n_1n_3 + k_41n_1n_4 \tag{4.4}$$

- Tm$^{3+}$ ($^3H_4, ^3F_{2, 3}$), excited state $n_3$:

$$\frac{dn_3}{dt} = P_{808}(n_1 - n_3) + c_2n_{s2}n_2 - c_3n_{s2}n_3 - W_3n_3 + b_43W_4n_4$$

$$+ b_53(1 - ET_{n_5})W_5n_5 + b_63(1 - ET_{n_6})W_6n_6 - k_31n_1n_3 + k_41n_1n_4$$

$$+ 2k_51n_1n_5 \tag{4.5}$$

- Tm$^{3+}$ ($^1G_4$), excited state $n_4$:

$$\frac{dn_4}{dt} = c_3n_{s2}n_3 - (1 - ET_{n_5})c_4n_{s2}n_4 - W_4n_4 + b_54(1 - ET_{n_5})W_5n_5$$

$$+ b_64(1 - ET_{n_6})W_6n_6 - k_41n_1n_4 \tag{4.6}$$

- Tm$^{3+}$ ($^1D_2$), excited state $n_5$:

$$\frac{dn_5}{dt} = (1 - ET_{n_5})c_4n_{s2}n_4 - (1 - ET_{n_6})c_5n_{s2}n_5 - (1 - ET_{n_5})W_5n_5$$

$$+ b_65(1 - ET_{n_6})W_6n_6 - k_51n_1n_5 \tag{4.7}$$

- Tm$^{3+}$ ($^1I_6$), excited state $n_6$:

$$\frac{dn_6}{dt} = (1 - ET_{n_6})c_5n_{s2}n_5 - (1 - ET_{n_6})W_6n_6 \tag{4.8}$$
For graphene oxide:

- Graphene oxide, ground state $n_{GO1}$:
  \[
  \frac{dn_{GO1}}{dt} = - \frac{dn_{GO2}}{dt} \tag{4.9}
  \]

- Graphene oxide, excited state $n_{GO2}$:
  \[
  \frac{dn_{GO2}}{dt} = ET_{n5} \frac{dn_5}{dt} + ET_{n6} \frac{dn_6}{dt} - W_{GO2} n_{GO2} \tag{4.10}
  \]

where $P_{980} = \left( \frac{\sigma_{Yb} \lambda_{980} I_{980}}{hc} \right)$ refers to the excitation rate of Yb$^{3+}$ under a 980-nm laser and $I_{980}$ refers to the 980-nm excitation laser intensity; $P_{808} = \left( \frac{\sigma_{STEM} \lambda_{808} I_{808}}{hc} \right)$ refers to the absorption/stimulated emission rate of Tm$^{3+}$ under an 808-nm laser, so that the term of $\left( \frac{\sigma_{STEM} \lambda_{808} I_{808}}{hc} \right) (n_1 - n_3)$ is the net effect of absorption/stimulated emission and $I_{808}$ refers to the 808-nm depletion laser intensity; $\sigma_{Yb}$ is the absorption cross-section of Yb$^{3+}$ for a laser at 980 nm; $\sigma_{STEM}$ is the absorption/stimulated emission cross-section of Tm$^{3+}$ for a laser at 808 nm; $\lambda_{980}$ is the wavelength of the laser for activation; $\lambda_{808}$ is the wavelength of the laser for deactivation; $h$ is the Planck’s constant; $c$ is the light speed; $W$ is the intrinsic decay rate of the excited Yb$^{3+}$; $c_i$ is the up-conversion coefficient between the excited Yb$^{3+}$ and Tm$^{3+}$ on level $i$; $W_i$ is the intrinsic decay rate of Tm$^{3+}$ on level $i$; $b_{ij}$ is the branching ratio for Tm$^{3+}$ decaying from level $i$ to level $j$, satisfying $\sum_{j=1}^{i-1} b_{ij} = 1$; $k_{ij}$ is the cross-relaxation coefficient between Tm$^{3+}$ on level $i$ and level $j$; $ET_{nm}$ is the energy transfer from the high-energy levels of Tm$^{3+}$ to graphene oxide; and $n$ is the electronic population in a specific energy level fulfilling the following conditions:

\[
\begin{align*}
  n_{S1} + n_{S2} &= 1 \tag{4.11} \\
  n_1 + n_2 + n_3 + n_4 + n_5 + n_6 &= 1 \tag{4.12} \\
  n_{GO1} + n_{GO2} &= 1 \tag{4.13}
\end{align*}
\]

In this model, the following assumption was considered: the transfer of energy quanta from the up-conversion nanoparticles to graphene oxide is only considered efficient from the high-energy $^1D_2$ and $^1I_6$ excited levels of Tm$^{3+}$, while it is considered negligible from lower energy excited states. In fact, the optical band gap of graphene oxide is in the range 2.7 to 3.5 eV [112, 113] and corresponds to a larger energy gap than the $^1G_4$ energy level and lower energy
levels in Tm$^{3+}$ to the $^3$H$_6$ ground state. Further, spectroscopy evidence shows much weaker absorption of graphene oxide at longer up-conversion fluorescence emission wavelengths compared with the ultraviolet and blue emission generated from the $^1$D$_2$ and $^1$I$_6$ excited levels.

The model presented herein involves parameters specific to the material properties of the up-conversion nanoparticles and graphene oxide. The reaction constants can be fixed, leaving only the laser intensities $I_{980}$ and $I_{808}$ of the activation and deactivation lasers as variables. To validate the model, a combination of highly-doped Yb,Tm-doped up-conversion nanoparticles and graphene oxide was simulated using the following parameters:

$$\sigma_{Yb} = 1.2 \times 10^{-20} \text{ cm}^2 \ [114]; \ \sigma_{STED} = 6 \times 10^{-21} \text{ cm}^2 \ [115]; \ \hbar c = 1.99 \times 10^{-25} m^3 \cdot kg \cdot s^{-2}; \ W_s = 8 \times 10^3, \ W_2 = 6 \times 10^3, \ W_3 = 2 \times 10^4, \ W_4 = 1 \times 10^4, \ W_5 = 3 \times 10^3, \ W_6 = 1 \times 10^5 \ [65, 116]; \ W_{GO2} \ is \ considered \ negligible \ because \ of \ the \ ultrafast \ relaxation \ dynamics \ in \ graphene \ oxide, \ with \ decay \ kinetics \ ranging \ from \ 1 \ ps \ to \ 2 \ ns \ [117, 118]; \ c_1 = 6 \times 10^4, \ c_2 = 6 \times 10^4, \ c_3 = 7 \times 10^4, \ c_4 = 5 \times 10^3, \ c_5 = 5 \times 10^4 \ [65]; \ b_{31} = 0.27, \ b_{32} = 0.73, \ b_{41} = 0.18, \ b_{42} = 0.24, \ b_{43} = 0.58, \ b_{51} = 0.24, \ b_{52} = 0.23, \ b_{53} = 0.20, \ b_{54} = 0.33, \ b_{61} = 0.09, \ b_{62} = 0.58, \ b_{63} = 0.18, \ b_{64} = 0.14, \ b_{65} = 0.01 \ [65, 116]; \ k_{31} = 1.5 \times 10^5, \ k_{41} = 1.8 \times 10^5 \ and \ k_{51} = 4.8 \times 10^5 \ [65]; \ ET_{n5} = 0.8 \ and \ ET_{n6} = 0.8, \ considering \ high-efficiency \ energy \ transfer \ from \ the \ \text{1}D_2 \ and \ \text{1}I_6 \ excited \ levels \ of \ Tm^{3+} \ ions \ to \ graphene \ oxide.

Figure 4.3 presents a plot of the simulated power-dependent optical depletion efficiency of 450-nm fluorescence emission from the up-conversion nanoparticles-only and up-conversion nanoparticles–graphene oxide system under dual-laser irradiation comprising 980-nm excitation and 808-nm depletion.
Figure 4.3: Simulated power-dependent optical depletion efficiency of 450-nm fluorescence emission from the up-conversion nanoparticles-only (black solid curve) and up-conversion nanoparticles–graphene oxide (red solid curve) system under laser at 980 nm for excitation and laser at 808 nm for depletion with increasing intensity. Depletion efficiency of ~90% and ~95% were predicted for the up-conversion nanoparticles-only and the up-conversion nanoparticles–graphene oxide system, respectively. Saturation intensities, $I_s$, were estimated to be ~0.38 MW cm$^{-2}$ (~1.5 mW) for the up-conversion nanoparticles-only and ~0.25 MW cm$^{-2}$ (~1.0 mW) for the up-conversion nanoparticles–graphene oxide system, respectively.

From the simulation results reported in Figure 4.3, the optical depletion of 450-nm fluorescence emission in the up-conversion nanoparticles-only and up-conversion nanoparticles–graphene oxide system under dual-laser irradiation comprising a laser at 980 nm for excitation and laser at 808 nm for depletion increased by progressively increasing the depletion beam intensity up to ~4 MW cm$^{-2}$, reaching the value of 10% and 5% residual fluorescence intensity, respectively. The value for the saturation intensity, $I_s$, was determined to be ~0.38 MW cm$^{-2}$ (~1.5 mW) for the up-conversion nanoparticles-only and ~0.25 MW cm$^{-2}$ (~1.0 mW) for the up-conversion nanoparticles–graphene oxide system. The higher optical depletion efficiency of the 450-nm fluorescence emission intensity and lower saturation intensity, $I_s$, for the up-conversion nanoparticles–graphene oxide system compared with the up-conversion nanoparticles-only system was produced by the occurrence of energy transfer between the up-conversion nanoparticles and graphene oxide. This process provides
a further relaxation pathway for the depopulation of electrons from the high-energy \(^1\text{D}_2\) and \(^1\text{I}_6\) levels of \(\text{Tm}^{3+}\) ions. In contrast, the conjugation with graphene oxide maintained the population of the lower energy levels in \(\text{Tm}^{3+}\) ions as unchanged. Thus, in the case of the up-conversion nanoparticles–graphene oxide system, the introduction of the 808-nm depletion laser, which could produce stimulated emission to deplete the \(^3\text{H}_4\) level, determined a faster rate of 450-nm up-conversion fluorescence emission depletion, which resulted in higher optical depletion efficiency and lower values of saturation intensity.

4.2.3 Simulated resolution improvement under dual-laser super-resolution irradiation

In dual-laser super-resolution optical techniques, such as STED microscopy and SPIN, a doughnut-shaped deactivation laser beam is spatially overlapped with a Gaussian-shaped activation laser beam, thereby confining the effective PSF to the centre of the doughnut at the nanoscale. For the photoactivatable up-conversion nanoparticles–graphene oxide system, the Gaussian-shaped beam excites up-conversion nanoparticles to produce up-conversion to high energy levels, and induces transfer of energy quanta to graphene oxide, while the doughnut-shaped beam is used to deactivate up-conversion and consequently energy transfer to graphene oxide at the doughnut ring. Therefore, the reduction of graphene oxide is limited to the centre of the focal spot, which can lead to smaller features and finer resolution, thereby overcoming the limit imposed by diffraction. The rate equations previously developed determined the population of electrons in the different energy levels of the up-conversion nanoparticles–graphene oxide system. Thus, by simulating the distribution of the intensities of the focused 980-nm activation and 808-nm deactivation laser beams in the focal region, it was possible to evaluate the resolution improvement of the formed features at the nanoscale. For the activation, this study considered a circularly polarised laser focused with a high numerical aperture objective lens. For the deactivation, this study considered a circularly polarised vortex laser generated with a circular polarised laser passing through a \(2\pi\) vortex phase plate with helical phase retardation from zero to \(2\pi\) and focused with a high \(NA\) objective lens. The electric field in the focal region was \([119-122]\):
where \( r, \phi \) and \( z \) are the cylindrical coordinates; \( \phi \) is the azimuthal angle of the incident laser; \( k = 2\pi/\lambda \) is the wave vector; \( f \) is the focal length of the high \( NA \) objective; \( \alpha \) is the maximal \( NA \) angle; and \( \theta \) is the \( NA \) angle that varies between 0 and \( \alpha \). Assuming that the optical system is in free space (i.e., the index of refraction \( n \) is 1), the maximal angle \( \alpha \) is \( \alpha = \arcsin (\frac{NA}{n}) \), where \( n \) is the index of refraction of the material in the focal region, \( A(\theta) \) is the pupil apodisation function at the surface of the objective’s aperture, and \( \exp(\imath m\phi) \) is the vortex phase factor of the incident laser. For the activation beam, \( m = 0 \), while, for the deactivation beam passing through the \( 2\pi \) phase plate, \( m = 1 \). The symbol \( \pm \) relates to the handedness of the circular polarised beams. Right circular polarised beams were considered in this calculation. For the focal spot calculation, the considered \( NA \) for the objective lens was 1.4. Figure 4.4 displays the theoretical focal spot profiles of the activation laser at 980 nm and the deactivation laser at 808 nm.

**Figure 4.4:** Profiles of the 980-nm activation laser beam and 808-nm deactivation laser beam in the x-y plane of the focal region. Scale bar: 500 nm.
Having established the 450-nm up-conversion fluorescence emission depletion efficiency in the up-conversion nanoparticles-only and up-conversion nanoparticles–graphene oxide system under combined CW laser at 980 nm for activation and CW laser at 808 nm for deactivation, the researchers determined the intensity distribution in the focal region applying the vectorial Debye theory [119-122]. The vectorial Debye diffraction theory of a high numerical aperture objective investigates high $NA$ focusing processes from the vectorial nature of light, considering the effects of amplitude, phase and polarisation distribution of the incident beams. Specifically, when an incident wave illuminates the back aperture and is focused using a high $NA$ objective, the wavefront of the incident wave is refracted by the objective lens and becomes a spherical surface converging at the focus. The Debye diffraction theory is used to describe the focusing process with the superposition of all the wavelets within the maximum convergence angle, $\alpha$, determined by the $NA$ of the lens. Figures 4.5 and 4.6 show the simulated size reduction and resolution improvement in the up-conversion nanoparticles-only and up-conversion nanoparticles–graphene oxide system via irradiation with a combined 980-nm circularly polarised beam and an 808-nm circularly polarised vortex beam for the generation of a super-resolution PSF.
Figure 4.5: Photodeactivation-induced resolution improvement and size reduction in the up-conversion nanoparticles under combined irradiation with a 980-nm circularly polarised beam and 808-nm circularly polarised vortex beam. a) Resolution improvement as a function of the intensity of the 808-nm deactivation laser beam. b) Simulated focal spot size in the up-conversion nanoparticles plotted under combined irradiation by 980-nm activation laser beam and 808-nm deactivation laser beam at different powers. Scale bar: 100 nm.
Figure 4.6: Photodeactivation-induced resolution improvement and size reduction in the up-conversion nanoparticles–graphene oxide system under combined irradiation with a 980-nm circularly polarised beam and 808-nm circularly polarised vortex beam. a) Resolution improvement as a function of the intensity of the 808-nm deactivation laser beam. b) Simulated focal spot size in the up-conversion nanoparticles–graphene oxide system plotted under combined irradiation by 980-nm activation laser beam and 808-nm deactivation laser beam at different powers. Scale bar: 100 nm.
Figures 4.5 and 4.6 indicate that improvement of resolution in the up-conversion nanoparticles-only and up-conversion nanoparticles–graphene oxide system could be achieved by increasing the intensity of the 808-nm deactivation beam. Features with size smaller than 100 nm could be obtained for the 808-nm laser beam intensity of ~4 MW cm$^{-2}$, using a combination of a 980-nm circularly polarised laser beam and an 808-nm circularly polarised vortex beam. This is because the deactivation beam was used to inhibit up-conversion at the outer region of the doughnut-shaped deactivation beam and thus prevent energy transfer–driven reduction of graphene oxide.

4.3 Synthesis and characterisation of Yb,Tm-doped up-conversion nanoparticles

4.3.1 Synthesis

The typical inorganic crystalline host NaYF$_4$ was chosen for the Yb$^{3+}$ and Tm$^{3+}$ ions in the synthesis of the Yb,Tm-doped up-conversion nanoparticles. The NaYF$_4$ matrix guarantees intense up-conversion fluorescence and chemical stability to the nanoparticles. The synthesis was undertaken through the widely-used method of co-precipitation. The chemicals were purchased from Sigma-Aldrich, and included yttrium (III) acetate hydrate (99.9%), ytterbium (III) acetate hydrate (99.9%), thulium (III) acetate hydrate (99.9%), sodium hydroxide (> 98%), ammonium fluoride (> 98%), oleic acid (90%) and 1-octadecene (90%).

For the preparation, 2 mL of RE(CH$_3$CO$_2$)$_3$ (0.4 mmol, RE = Y, Yb and Tm) in water were poured into a 50-mL flask containing 3 mL of oleic acid and 7 mL of 1-octadecene. The mixture was heated at 150°C for 1.5 hours to promote the formation of the RE-oleate complexes, and subsequently allowed to cool to 50°C. Then, 6 mL of methanol solution with NH$_4$F (1.6 mmol) and NaOH (1 mmol) was poured into the flask, and the resulting solution was stirred for 30 minutes. The temperature was then raised to 100°C to prompt the evaporation of methanol. After degassing for 20 minutes, the resulting mixture was heated to 290°C, maintained under a flow of nitrogen for two hours, and cooled to room temperature. The as-synthesised Yb,Tm-doped up-conversion nanoparticles were collected via centrifugation, washed with cyclohexane and ethanol, and finally re-dispersed in cyclohexane (4 mL). Finally, the nanoparticles were made hydrophilic by removing oleic acid ligand from
their surface, and were re-dispersed in deionised water. The compositions of the up-conversion nanoparticles were:

- NaYF₄:Yb/Tm (30%, 1%) (sample 1);
- NaYF₄:Yb/Tm (30%, 2%) (sample 2);
- NaYF₄:Yb/Tm (30%, 4%) (sample 3);
- NaYF₄:Yb/Tm (30%, 6%) (sample 4);
- NaYF₄:Yb/Tm (30%, 8%) (sample 5).

4.3.2 Characterisation

The morphological and structural characterisation of the as-prepared Yb,Tm-doped up-conversion nanoparticles was performed by TEM (JEOL 1010 TEM [2001]) at an acceleration voltage of 100 kV (Figure 4.7a) and X-ray diffraction (Bruker Axs D4 Endeavor) (Figure 4.7b). According to the TEM images in Figure 4.7a, the as-synthesised up-conversion nanoparticles were monodispersed with an average diameter of 21.5, 23.1, 24.2, 22.6 and 20.8 nm for the samples from 1 to 5, respectively, which was within the optimal range for efficient resonance energy transfer between the up-conversion nanoparticles and graphene oxide. The XRD crystal phase analyses of the up-conversion nanoparticles reported in Figure 4.7b showed their high crystallinity and well matched the corresponding standard pattern of hexagonal β-NaYF₄ phase (ICDD PDF 16-334).
Figure 4.7: Morphological and structural characterisation of the Yb,Tm-doped up-conversion nanoparticles. a) TEM images and size distribution of as-synthesised Yb,Tm-doped up-conversion nanoparticles (left to right, sample 1 to 5). Scale bar: 50 nm. b) XRD spectra of the Yb,Tm-doped up-conversion nanoparticles (from black to light blue solid lines, sample 1 to 5) and corresponding standard pattern of hexagonal phase of β-NaYF₄ (ICDD PDF 16-334).
The researchers measured the up-conversion fluorescence emission of the as-prepared up-conversion nanoparticle under laser excitation at different wavelengths ranging from 700 to 1,020 nm (Figure 4.8) at constant power of 1 mW. As expected, the researchers observed that the best wavelength for efficient excitation of the up-conversion nanoparticles corresponded to ~980 nm, which was then selected as the excitation wavelength for the following work in this chapter.

**Figure 4.8:** Up-conversion fluorescence emission intensity of the up-conversion nanoparticles under laser excitation at different wavelengths ranging from 700 to 1,020 nm at constant power.

Figure 4.9 reports the luminescence photographs and spectra of the fluorescence emission of the up-conversion nanoparticles recorded using an Andor Spectrograph equipped with an iXon EMCCD camera using a CW laser at 980 nm for excitation at 1 mW. The synthesised nanoparticles emitted intense ultraviolet and blue up-conversion fluorescence with 345, 360 and 450 nm peaks.
Figure 4.9: Up-conversion fluorescence emission from as-prepared Yb,Tm-doped nanoparticles. a) Luminescence photographs and b) Fluorescence emission spectra of up-conversion nanoparticles. NaYF₄:Yb/Tm (30%, 1%) (sample 1) (black solid line); NaYF₄:Yb/Tm (30%, 2%) (sample 2) (red solid line); NaYF₄:Yb/Tm (30%, 4%) (sample 3) (green solid line); NaYF₄:Yb/Tm (30%, 6%) (sample 4) (blue solid line) and NaYF₄:Yb/Tm (30%, 8%) (sample 5) (light blue solid line).

The researchers investigated the dependence of the 345-, 360- and 450-nm up-conversion fluorescence emissions from the nanoparticle on the power of excitation with the 980-nm CW laser to confirm the multi-photon nature of up-conversion emission. The slope values in the log-log plot in Figure 4.10a provide information about the number of photons absorbed to produce up-conversion fluorescence emission. Slope values of 4.5, 3.7 and 3.5 were determined for the 345-, 360- and 450-nm up-conversion fluorescence emissions, respectively, indicating that five, four and three photons were involved in the process of up-
conversion. These observations agree well with previously reported results for Yb,Tm-doped up-conversion nanoparticles [122]. Figure 4.10b displays a schematic of the energy levels of Yb$^{3+}$ and Tm$^{3+}$ ions and the proposed mechanism for the up-conversion fluorescence emissions. Initially, the Yb$^{3+}$ ions absorbed 980-nm photons and became excited. Subsequently, the Yb$^{3+}$ ions transferred the energy to the Tm$^{3+}$ ions and prompted excitation from the ground state up to the $^1I_6$ state. The 345-nm fluorescence originated from the $^1I_6 \rightarrow ^3F_4$ transition, while the 360- and 450-nm fluorescence arose from the $^1D_2 \rightarrow ^3H_6$ and $^1D_2 \rightarrow ^3F_4$ transitions in the energy levels of Tm$^{3+}$ ions, respectively.

**Figure 4.10:** Mechanism of up-conversion fluorescence emission in the Yb,Tm-doped nanoparticles. a) Log–log plot of the power dependence of the 345-, 360- and 450-nm up-conversion fluorescence from the nanoparticles under excitation using CW laser at 980 nm. b) Energy level diagram of Yb$^{3+}$ and Tm$^{3+}$ ions and the mechanism for up-conversion fluorescence from Tm$^{3+}$.

### 4.4 Dual-laser super-resolution imaging of Yb,Tm-doped up-conversion nanoparticles

Controlling the electronic transitions in the up-conversion nanoparticles to switch them between two optically distinguishable ‘ON/OFF’ states is an exciting pathway to circumvent the limit imposed by diffraction. This approach has enabled the implementation of up-
conversion nanoparticles in super-resolution fluorescence microscopy, such as in STED microscopy [65, 66], for imaging with nanoscale resolution. The following sections report the dual-laser super-resolution imaging of the synthesised high-energy up-conversion fluorescent Yb,Tm-doped up-conversion nanoparticles to demonstrate the precise control of up-conversion at the nanoscale towards implementation in photoactivated systems beyond the diffraction-limit barrier.

### 4.4.1 Experimental setup

The optical system for achieving super-resolution using a combination of two lasers was constructed based on a confocal microscopy setup using a three-axis piezo stage (P-562 PIMars Nanopositioning Stage, Physik Instrumente) for sample scanning (Figure 4.11).

**Figure 4.11:** Schematic of experimental super-resolution optical system setup. M = mirror, FM = flipping mirror, L = lens, DC1 and DC2 = dichroic mirrors, HWP = half waveplate, VPP = vortex phase plate, QWP = quarter waveplate, SPAD = single-photon avalanche diode.
A single-mode 980-nm CW laser (BL976-PAG900, Thorlabs) was used as the irradiation source to excite the up-conversion nanoparticles. After being collimated, the excitation beam passed through two long-pass dichroic mirrors and was then focused by an oil-immersion objective (M Plan Apochromat MPLAPON-Oil, NA = 1.4, 100X, Olympus). The first dichroic mirror DC1 (FF850-Di01-t1-25x36, Semrock) also allowed a collimated 808-nm CW laser (LU0808M250, Lumics) to combine with the 980-nm CW laser. The fluorescence signal was collected by the same objective, separated from the excitation and depletion laser by the second dichroic mirror, DC2 (FF705-Di01-25x36, Semrock), and coupled into a multimode fibre (FG050LGA, Thorlabs), which was connected to an SPAD (SPCM-AQRH-14-FC, Excelitas Technologies). Band pass filters (FF01-442/46-25, Semrock) were inserted in the detection path to select the fluorescence emission band for confocal imaging and lifetime measurements. A flipping mirror was also inserted to couple the fluorescence signal with a spectrometer (Andor Shamrock 500i Spectrograph equipped with an iXon EMCCD camera). For super-resolution imaging, a quarter waveplate (WPQ10M-808, Thorlabs) was employed to convert the laser at 808 nm into circular polarised. A half waveplate (WPH10M-808, Thorlabs) was also employed to optimise the quality of the circular polarisation. Finally, a vortex phase plate (VPP-1a, RPC Photonics) was placed in the path of the laser at 808 nm to generate a PSF with the shape of a doughnut in the focal plane.

4.4.2 Optical depletion of up-conversion fluorescence

The optical depletion efficiency of the 450-nm fluorescence emission from the up-conversion nanoparticles is defined as follows:

\[
\text{Depletion Efficiency} = 1 - \frac{I_{450}^{980}}{I_{450}^{980\&808}}
\]

where \(I_{450}^{980}\) is the intensity of the 450-nm up-conversion fluorescence under excitation using a laser at 980 nm only and \(I_{450}^{980\&808}\) is the intensity of the 450-nm up-conversion fluorescence emission under a combination of a laser at 980 nm for excitation and a laser at 808 nm for depletion. The researchers measured the optical depletion efficiency of the 450-nm fluorescence emission from the up-conversion nanoparticles with different concentrations of Tm\(^{3+}\) doping (Figure 4.12a). The depletion efficiency of the 450-nm up-conversion
fluorescence emission exhibited strong dependence on the Tm$^{3+}$ doping concentration, with the best value of depletion efficiency of ~90% achieved for the up-conversion nanoparticles with 4% Tm$^{3+}$ doping concentration. The degree of optical depletion efficiency was validated by spectroscopy measurements, which are reported in Figure 4.12b.

**Figure 4.12:** Optical depletion of 450-nm fluorescence in Yb,Tm-doped up-conversion nanoparticles co-irradiated using a CW laser at 980 nm for excitation and a CW laser at 808 nm for depletion. a) Depletion efficiency of 450-nm up-conversion fluorescence emission in the nanoparticles with different concentrations of Tm$^{3+}$ doping (1, 2, 4, 6 and 8%). The power of the CW laser at 980 nm for excitation and CW laser at 808 nm for depletion were 0.5 and 15 mW, respectively. b) Fluorescence emission spectroscopy of the up-conversion nanoparticle with 4% Tm$^{3+}$ doping, achieving ~90% depletion efficiency.
The results reported in Figure 4.12 show increasing optical depletion efficiency of the 450-nm up-conversion fluorescence emission by incrementing the doping of Tm$^{3+}$ in the up-conversion nanoparticles. The highest value of depletion efficiency was obtained when the Tm$^{3+}$ doping concentration reached 4%, and then decreased for higher concentration values. In particular, the results achieved ~90% depletion efficiency for NaYF$_4$:Yb/Tm (30%, 4%) by co-irradiation with the 980-nm CW laser for excitation at 0.5 mW and 808-nm CW laser for depletion at 15 mW. This result is consistent with previously reported studies in which optical depletion of the 450-nm fluorescence emission in the up-conversion nanoparticles required an adequately high Tm$^{3+}$ doping concentration [65, 66]. From Figure 4.12b, it can also be seen that the value of depletion efficiency was confirmed through spectroscopy measurements. Moreover, it should be noted that irradiation using an 808-nm CW laser only resulted ineffective for excitation of the up-conversion nanoparticles.

Figure 4.13 displays the ‘ON/OFF’ switching of the 450-nm fluorescence emission in the up-conversion nanoparticle drop-casted onto a coverslip under dual-laser irradiation. The intensity $I_{808}$ of the 808-nm CW laser for depletion at 3.75 MW cm$^{-2}$ was modulated by an optical shutter with an open/close cycle of 100 seconds, which resulted in periodical depletion of up-conversion fluorescence emission.

Figure 4.13: ‘ON/OFF’ switching of 450-nm fluorescence emission in the up-conversion nanoparticle under dual-laser irradiation. The 808-nm CW laser for depletion at 3.75 MW cm$^{-2}$ was modulated with open/close cycles of 100 seconds by an optical shutter.
The results shown in Figure 4.13 confirmed the high degree of optical control over the 450-nm up-conversion fluorescence depletion, as well as its reversible nature during ‘ON/OFF’ switching. Further, the characteristics of high stability over time and non-photobleaching of the as-prepared up-conversion nanoparticles were demonstrated.

Diluted up-conversion nanoparticles solution was drop-casted onto a coverslip glass for deposition of sparse or individual nanoparticles. Confocal images of the up-conversion nanoparticles were obtained under 980-nm CW laser and under dual-laser irradiation using the CW laser at 980 and 808 nm at 1.5 and 15 mW, which corresponded to the expected 50% and ~90% up-conversion fluorescence emission depletion, respectively (Figure 4.14).

**Figure 4.14:** Imaging sparse and individual up-conversion nanoparticles onto coverslip under dual-laser irradiation. a) (left to right) confocal images of the up-conversion nanoparticles under CW laser at 980 nm only and under dual-laser irradiation with 808-nm CW laser at 1.5 and 15 mW. Scale bar: 500 nm. b) Up-conversion fluorescence emission intensity profile along the white line for an individual nanoparticle under 980-nm CW laser only and under dual-laser irradiation with 808-nm CW laser at 1.5 and 15 mW, confirmed the expected 50% and ~90% up-conversion fluorescence emission depletion, respectively.
The researchers measured the power-dependent optical depletion efficiency of 450-nm fluorescence emission from the 4% Tm-doped up-conversion nanoparticles using a CW laser at 980 nm for excitation at 0.5 mW and 808-nm CW laser for depletion at increasing power (Figure 4.15). The results experimentally confirmed the theoretical prediction for optical depletion efficiency in the up-conversion nanoparticles with high concentration of dopants obtaining ~90% optical depletion efficiency and a value of saturation intensity $I_{sat}$ of ~375 kW cm$^{-2}$ (~1.5 mW).

![Figure 4.15](image)

**Figure 4.15**: Power-dependent depletion efficiency of 450-nm fluorescence emission from the 4% Tm-doped up-conversion nanoparticles using a CW laser at 980 nm with power of 0.5 mW for excitation and 808-nm CW laser for depletion at increasing power. The theoretical prediction for optical depletion efficiency was confirmed, obtaining ~90% depletion efficiency and a value of saturation intensity $I_{sat}$ of ~375 kW cm$^{-2}$ (~1.5 mW).

### 4.4.3 Super-resolution imaging by STED microscopy

The efficient optical depletion of 450-nm fluorescence emission from the 4% Tm-doped up-conversion nanoparticles enabled super-resolution imaging of the nanoparticles by STED microscopy. Figure 4.16a presents a schematic of the configuration of the laser beams comprising a Gaussian 980-nm CW laser for excitation and doughnut-shaped 808-nm CW laser for depletion.
Figure 4.16: Super-resolution imaging of the 4% Tm-doped up-conversion nanoparticles by STED microscopy. a) Schematic of the spatial overlap between a Gaussian-shaped excitation beam at 980 nm and a doughnut-shaped depletion beam at 808 nm for STED microscopy. b) Improvement of resolution obtained by increasing the depletion laser intensity. Insets: up-conversion nanoparticles imaged by STED microscopy using 808-nm CW laser at increasing intensity. c) Imaging individual up-conversion nanoparticle by confocal microscopy (left), STED microscopy (middle) and the corresponding line profiles of the images. The 980-nm CW excitation laser and 808-nm CW depletion laser intensities were 0.13 and 11.25 MW cm$^{-2}$, respectively. Scale bar: 500 nm.
A sequence of images of individual up-conversion nanoparticles on the coverslip substrate was collected by confocal microscopy and STED microscopy. Compared with confocal microscopy using a 980-nm CW excitation laser only, a significant increase in the spatial resolution was obtained by adding the doughnut-shaped 808-nm CW depletion laser. The measured FWHM for the individual nanoparticles was a convolution between the theoretically-achievable resolution and the nanoparticles’ dimension. Thus, the researchers proceeded with de-convoluting the obtained images, considering a theoretical PSF with the same size as the up-conversion nanoparticles. The line profile analysis for an individual nanoparticle indicated that the lateral imaging resolution reached ~64 nm after deconvolution. Moreover, the intensities for the two CW laser beams were one hundredth to one thousandth times lower in comparison with those required for typical STED imaging using other fluorophores [123-128], which is very attractive for applications in photoactivated systems with low power consumption.

4.5 Chapter conclusions

This chapter has developed high-energy up-conversion fluorescent nanoparticles for application in dual-laser photoactivated super-resolution systems, including their combination with graphene oxide. Theoretical and experimental investigations have been conducted to individuate the key features of the nanoparticles for efficient photoactivation in applications beyond the diffraction-limit barrier in energy transfer–driven systems. These characteristics are intense high-energy up-conversion fluorescence, efficient optical depletion of up-conversion fluorescence, and small size and narrow size distribution. Specifically, a theoretical framework for the process of up-conversion in the nanoparticles and energy transfer to graphene oxide has been outlined. Further, simulation results have indicated the potential for resolution improvement in the up-conversion nanoparticles–graphene oxide system, thereby providing a feasible pathway for energy transfer–driven photoactivation at the nanoscale.

The high-energy up-conversion fluorescent nanoparticles were then successfully prepared and tested under dual-beam super-resolution optical techniques, such as STED microscopy, thereby confirming the potential for applications beyond the diffraction-limit barrier. First, a study of the optical depletion efficiency of 450-nm up-conversion fluorescence emission was conducted, achieving ~90% depletion efficiency for 4% Tm-doped nanoparticles with a
saturation intensity of \(~375\ kW\ cm^{-2} \approx 1.5\ mW\). Second, super-resolution imaging of the up-conversion nanoparticles was undertaken via STED microscopy using a Gaussian-shaped 980-nm CW laser for excitation and a doughnut-shaped 808-nm CW laser for depletion, reaching a resolution of 64 nm with an intensity of 11.25 MW cm\(^{-2}\) of the depletion laser. The values of intensity of the excitation and depletion beams were one hundredth to one thousandth of those required for typical STED imaging using other fluorophores [123-128], which is very attractive for applications with low power consumption in photoactivated systems.
Chapter 5

Ultralow-power nanoscale optical data storage in a nanocomposite based on up-conversion nanoparticles and graphene oxide

5.1 Introduction

Up-conversion nanoparticles can efficiently convert excitation in the near-infrared into intense ultraviolet, visible and shorter-wavelength near-infrared fluorescence emissions, and are a pivotal material for next-generation optical data storage devices [62, 63, 129]. Further, they have been proven useful in super-resolution optical techniques that have resulted in low-power nanoscopy [65, 66]. Such localised control of this unique type of nanoparticle through manipulation of their electronic transitions by dual-laser super-resolution irradiation can allow photoactivation in energy transfer–driven systems beyond the diffraction-limit barrier. Thus, the researchers reasoned that high-energy up-conversion fluorescent nanoparticles could be used to induce nanoscale photochemical reduction of graphene oxide through resonance energy transfer, providing a suitable pathway for optical writing of nano-sized bits of information. Further, the varied absorption that is accompanied by reduction of graphene oxide can produce quenching of the fluorescence emission from the up-conversion
nanoparticles, offering a pathway for optical read-out beyond the diffraction-limit barrier. Thus, dual-laser super-resolution irradiation can confine the process of photoactivation in the up-conversion nanoparticles–graphene oxide system at the nanoscale, and subsequently achieve smaller voxels within the focal region compared with conventional optical data storage methods, thereby paving the way towards high-capacity optical data storage memory devices.

This chapter demonstrates ultralow-power nanoscale optical data storage in a nanocomposite based on up-conversion nanoparticles and graphene oxide. For this purpose, the up-conversion nanoparticles are first conjugated with graphene oxide to form a novel optically-activatable nanocomposite and to ensure efficient resonance energy transfer within the up-conversion nanoparticles–graphene oxide system. Subsequently, demonstration of the photochemical reduction of graphene oxide in the nanocomposite is reported under near-infrared laser excitation. The high-energy quanta transfer from the excited up-conversion nanoparticles to graphene oxide to trigger the dissociation of its oxygen groups. The reduction is accompanied by quenching of fluorescence emission from the up-conversion nanoparticles and decreased two-photon excited fluorescence from graphene oxide. Moreover, dual-laser super-resolution irradiation enables the tight confinement of photoactivation in the up-conversion nanoparticles–graphene oxide system at the nanoscale. First, optical depletion and inhibition are proven in the up-conversion nanoparticles–graphene oxide system, allowing for super-resolution imaging by STED microscopy and inhibition of the process of photochemical reduction of graphene oxide. Second, ultralow-power nanoscale optical data storage is achieved in the nanocomposite using SPIN for writing and fluorescence quenching microscopy combined with STED microscopy for reading bits of information beyond the diffraction-limit barrier.

This chapter includes seven sections, starting with this introduction. Section 5.2 reports about the characterisation of resonance energy transfer between the up-conversion nanoparticles and graphene oxide, which offers the fundamental knowledge for the energy transfer process within the up-conversion nanoparticles–graphene oxide system. Section 5.3 describes the development of an optically-activatable nanocomposite based on single-layer graphene oxide in conjugation with up-conversion nanoparticles. Section 5.4 presents the energy transfer–driven photochemical reduction of graphene oxide by the up-conversion nanoparticles under near-infrared excitation. Further, this section investigates quenching of the fluorescence emission from the up-conversion nanoparticles and decreased two-photon excited fluorescence from graphene oxide. These demonstrations lay the foundation for optical data
writing and read-out in the novel nanocomposite. Section 5.5 reports the use of the nanocomposite under dual-laser super-resolution irradiation, and studies the efficiency of up-conversion fluorescence emission depletion for super-resolution optical data reading and inhibition of reduction for super-resolution optical data writing. In Section 5.6, nano-sized features are produced by SPIN and retrieved by fluorescence quenching microscopy combined with STED microscopy, thereby demonstrating ultralow-power nanoscale optical data storage in this newly-prepared nanocomposite for the first time. Finally, Section 5.7 presents the conclusions of Chapter 5.

5.2 Resonance energy transfer between up-conversion nanoparticles and graphene oxide

Resonance energy transfer is a distance-sensitive interaction between an excited donor and a suitable acceptor without emission of photons. It has been documented that graphene oxide is an effective quencher of fluorophores, including organic dyes, QDs and up-conversion nanoparticles, through resonance energy transfer [130]. The fluorescence quenching usually occurs via non-covalent interactions, such as electrostatic interactions, hydrogen bonding, and hydrophobic and π–π interactions with graphene oxide.

Before demonstrating the novel concept of photochemically reduction of graphene oxide by up-conversion nanoparticles, the researchers confirmed that efficient resonance energy transfer could indeed occur from the up-conversion nanoparticles to graphene oxide when the two nanomaterials are conjugated with each other. The previously synthesised NaYF₄:Yb/Tm (30%, 4%) up-conversion nanoparticles were used in this chapter because of their reported features of intense high-energy up-conversion fluorescence, efficient optical depletion of up-conversion fluorescence, and small size and narrow size distribution, making them the best-suited candidate for energy transfer–driven photoactivation of the reduction of graphene oxide. The spectral overlap between the 4% Tm-doped up-conversion nanoparticles and graphene oxide is plotted in Figure 5.1.
Figure 5.1: Spectral overlap between the 4% Tm-doped up-conversion nanoparticles (UCNPs) and graphene oxide (GO), including absorption spectra of the up-conversion nanoparticles and graphene oxide, as well as fluorescence emission spectrum of the up-conversion nanoparticles.

For the resonance energy transfer pair composed of 4% Tm-doped up-conversion nanoparticles and graphene oxide, the spectral overlap integral $J$ was of $7 \times 10^{14} \text{ nm}^4 \text{ M}^{-1} \text{ cm}$ calculated using the software FluorTools and considering the wavelength ranging from 200 to 600 nm and maximum absorption coefficients of 180,000 L·mol$^{-1}$·cm$^{-1}$ for graphene oxide.

To demonstrate efficient resonance energy transfer within the up-conversion nanoparticles–graphene oxide system, the researchers measured up-conversion fluorescence quenching and performed time-resolved spectroscopy for mixed up-conversion nanoparticles and graphene oxide in water solution. The 4% Tm-doped up-conversion nanoparticles were diluted in deionised water with a final concentration of 10 µM in a quartz cuvette, and sonicated for 30 minutes. Then, the nanoparticles solution was mixed with graphene oxide in water at increasing concentration between 0 and 60 µg mL$^{-1}$. Spectroscopy measurements and fluorescence lifetime measurements were performed on the as-prepared up-conversion nanoparticles–graphene oxide water solutions. The up-conversion nanoparticles in water solution initially exhibited intense up-conversion fluorescence emission under excitation using a CW laser at 980 nm. However, the strong up-conversion fluorescence resulted progressively quenched upon the addition of increasing amount of graphene oxide in solution (Figure 5.2a).
Figure 5.2: Up-conversion fluorescence quenching and time-resolved spectroscopy in the up-conversion nanoparticles–graphene oxide system. a) Fluorescence emission spectra of 4% Tm-doped up-conversion nanoparticles mixed with graphene oxide at increasing concentration up to 60 µg mL$^{-1}$ in water solution, resulting in up-conversion fluorescence quenching. b) Decay profiles for 450-nm fluorescence emission from the 4% Tm-doped up-conversion nanoparticles mixed with graphene oxide at increasing concentration up to 60 µg mL$^{-1}$ in water solution.

When mixed in water solution, the positively charged up-conversion nanoparticles attached to the surface of the graphene oxide nanosheets with negative charge because of strong electrostatic interactions. Therefore, the up-conversion nanoparticles in proximity to graphene oxide nanosheets were quenched. As a result of the large value of spectral overlap between the up-conversion nanoparticles’ fluorescence emission and the graphene oxide’s
absorption, the strong up-conversion fluorescence quenching was ascribed to efficient resonance energy transfer.

Time-resolved studies of the fluorescence emission lifetime of the up-conversion nanoparticles were conducted to estimate the efficiency of resonance energy transfer in the up-conversion nanoparticles–graphene oxide system (Figure 5.2b). The experimental results revealed considerable shortening of the 450-nm fluorescence emission lifetime of the up-conversion nanoparticles when combined with graphene oxide, which provided efficient resonance energy transfer from the up-conversion nanoparticles to graphene oxide. Specifically, by incrementing the graphene oxide’s concentration in water, the 450-nm fluorescence emission lifetime of the up-conversion nanoparticles decreased from 1,108 to 184 μm. The efficiency $E$ of resonance energy transfer for the up-conversion nanoparticles–graphene oxide pair is expressed as:

$$E = 1 - \frac{\tau_{DA}}{\tau_D}$$  \hspace{1cm} (5.1)

where $\tau_{DA}$ and $\tau_D$ are the lifetimes of the up-conversion nanoparticles (donor) in the presence or absence of graphene oxide (acceptor). The efficiency $E$ resonance energy transfer reached the value of ~83%, yielding the fundament for energy transfer–driven reduction of graphene oxide induced by the up-conversion nanoparticles.

### 5.3 Development of nanocomposite based on up-conversion nanoparticles and graphene oxide

This section presents the development of a novel nanocomposite based on up-conversion nanoparticles and graphene oxide. It describes the theoretical foundation and experimental steps undertaken to obtain an optimal configuration of the up-conversion nanoparticles–graphene oxide system for application in dual-laser super-resolution techniques. The parameters considered are effective heat dissipation in the focal spot, which is essential to avoid unwanted thermal damage of the nanocomposite under laser irradiation; efficient resonance energy transfer from the up-conversion nanoparticles to graphene oxide, which best occurs when the up-conversion nanoparticles are brought in proximity to the graphene oxide; and the homogeneity, repeatability and scalability of the sample.
5.3.1 Temperature rise under laser irradiation

The temperature rise in graphene oxide caused by irradiation of the laser within the focal region leads to mass loss of oxygen groups, resulting in the process of photothermal reduction. Given that the photothermal reduction of graphene oxide causes photo-damage of the sample and cannot be controlled at the nanoscale, this process would prevent the achievement of high-capacity optical data storage beyond the diffraction-limit barrier. Thus, the researchers reasoned that a configuration based on single-layer graphene oxide would offer optimal heat dissipation to the surrounding environment and avoid the unwanted temperature increase in the nanocomposite based on up-conversion nanoparticles and graphene oxide.

Temperature rise in single-layer graphene oxide under laser irradiation has been determined through a theoretical model that relies on an energy balance argument [131]. The steady-state thermal increase, $\Delta T$, experienced by single-layer graphene oxide nanosheets upon absorbing laser irradiation is:

$$\Delta T = \frac{I \cdot (1 - 10^{-A_{\lambda}})}{(h_{\text{air}} + h_{\text{sub}})}$$  \hspace{1cm} (5.2)

where $I$ is the incident laser intensity, $A_{\lambda}$ is the absorbance at the irradiation wavelength and $h_{\text{air}}$ and $h_{\text{sub}}$ are the interfacial thermal conductance between graphene oxide and the surrounding air and substrate, respectively. In the case of this study’s dual-laser super-resolution laser system, the considered laser wavelengths are 980 and 808 nm. The absorbance of a single-layer graphene oxide sheet under laser irradiation at 980 and 808 nm was estimated to be $A_{980} = 3 \times 10^{-4}$ and $A_{808} = 5 \times 10^{-4}$, respectively [132]. Given that the values of $h_{\text{air}}$ and $h_{\text{sub}}$ for single-layer graphene oxide nanosheets are not available in the literature, estimations have been undertaken using the values for graphene [133]—in particular, $h_{\text{air}} \approx 1 \times 10^5 \text{Wm}^{-2} \text{K}^{-1}$ and $h_{\text{sub}} \approx 5 \times 10^7 \text{Wm}^{-2} \text{K}^{-1}$ for silica (SiO$_2$) and coverslip glass. Further, because $h_{\text{air}} \ll h_{\text{sub}}$, Eq. 5.2 can be simplified as follows:

$$\Delta T \approx \frac{I \cdot (1 - 10^{-A_{\lambda}})}{h_{\text{sub}}}$$  \hspace{1cm} (5.3)
Photothermal reduction of graphene oxide under laser irradiation has been reported at a temperature of ~230°C [134]; therefore, this study considered that $\Delta T = 200$ K can produce photothermal reduction of single-layer graphene oxide initially at room temperature. Estimations of the 980-nm CW laser and 808-nm CW laser intensities yielding $\Delta T = 200$ K from room temperature in single-layer graphene oxide deposited onto a coverslip glass substrate were several orders of magnitude higher than those used throughout this research. Even when considering more stringent conditions—such as the occurrence of photothermal reduction of graphene oxide at ~100°C [85] ($\Delta T = 70$ K from room temperature)—the thermal increase induced by the considered laser intensities was far below this threshold and thus negligible. The reason for this outcome was that thermal increase in the sample strongly depended on the properties of heat dissipation by the substrate onto which the single-layer graphene oxide was deposited. In this context, coverslip glass offered efficient heat dissipation away from graphene oxide, preventing thermal increase under the considered laser intensities. Thus, photothermal reduction of single-laser graphene oxide deposited onto a coverslip glass substrate could be excluded.

5.3.2 Preparation of the nanocomposite

The reactivity of nanomaterials, such as up-conversion nanoparticles and graphene oxide, closely relates to their size, shape and surface properties. For instance, after the removal of oleate ligands, up-conversion nanoparticles are positively charged because of surface protonation [135]. In the case of graphene oxide, its surface properties, including surface charge, relate to functional groups on its surface. For instance, negative charge can be developed by graphene oxide in solution because of deprotonation of its oxygen groups [136]. Zeta potential of the up-conversion nanoparticles and graphene oxide nanosheets in water solution revealed their positive and negative charge, respectively, indicating the possibility of electrostatic self-assembly when the two nanomaterials are mixed. Thus, the preparation of the nanocomposite based on single-layer graphene oxide in conjugation with up-conversion nanoparticles comprised two steps:

- **Step 1**: Deposition of single-layer graphene oxide onto coverslip;
- **Step 2**: Self-assembly of upconversion nanoparticles onto single-layer graphene oxide.
5.3.2.1 Deposition of single-layer graphene oxide onto coverslip

Single-layer graphene oxide nanosheets were deposited from water solution onto pre-cleaned and silanised ITO-coated coverslip glass substrates (ITO-Coated Cover Slips, SPI Supplies). The substrates were immersed in acetone for two minutes and then allowed to dry to ensure the absence of oil or water. The silane solution was prepared by mixing 200 μL of 3-triethoxysilylpropylamine solution ([3-aminopropyl]triethoxysilane 99%, Sigma-Aldrich) with 5 mL of acetone, obtaining a 2% solution. Then, the clean dry substrates were dipped into the silane solution for two minutes. The silane reacted with the -OH groups of glass, linking aminoalkyl groups to it through covalent bonds. Consequently, the resulting surface promoted the attachment of single-layer graphene oxide nanosheets to the glass. Finally, the substrates were individually washed with deionised water and allowed to dry.

Single-layer graphene oxide nanosheets were deposited onto silanised ITO-coated coverslip glass substrates by individually immersing each substrate into a water solution of graphene oxide at a concentration of $10 \mu\text{g} \text{mL}^{-1}$ for five seconds and then into a flask with deionised water for 30 seconds, and finally air dried. The deposited single-layer graphene oxide nanosheets onto ITO-coated coverslip glass substrates were examined by scanning electron microscope (SEM) (FEI Verios 460L FEGSEM) and atomic force microscope (AFM) (Dimension Icon) in tapping mode (Figure 5.3). The SEM images in Figure 5.3b revealed the deposition of single-layer graphene oxide nanosheets onto ITO-coated coverslip glass substrate. Figure 5.3c obtained by AFM in a tapping mode shows that the as-deposited single-layer graphene oxide nanosheets onto ITO-coated coverslip glass substrate were $\sim0.81$ nm thick, which is attributed to monolayer configuration [137].
Figure 5.3: Deposition of single-layer graphene oxide onto coverslip. a) Schematic of the deposition of single-layer graphene oxide onto ITO-coated coverslip glass substrates: ITO-coated coverslip glass substrates were silanised and dipped in graphene oxide water solution for the deposition of single-layer graphene oxide nanosheets. The samples were washed with deionised water and air dried. b) SEM images of the as-deposited single-layer graphene oxide nanosheets onto ITO-coated coverslip glass. Magnification: 6,500× (left) and 30,000× (right). Scale bars: 10 µm and 2 µm. c) AFM image of as-deposited single-layer graphene oxide sheet onto ITO-coated coverslip glass (left) and height profile derived from the marked line in the AFM image showing single-layer graphene oxide with a thickness of ~0.81 nm (right). Scale bar: 5 µm.
5.3.2.2 Self-assembly of up-conversion nanoparticles onto single-layer graphene oxide

Self-assembly was adopted in this preparation by exploiting the electrostatic attraction between up-conversion nanoparticles and graphene oxide nanosheets, which have positive and negative charge, respectively, in an aqueous environment. The up-conversion nanoparticles were self-assembled electrostatically onto single-layer graphene oxide nanosheets from colloidal solutions (Figure 5.4). Briefly, about 100 μL of 0.1 μM up-conversion nanoparticles solution was placed onto the ITO-coated coverslip substrates where single-layer graphene oxide was previously deposited, according to Step 1. The solution was kept for 30 minutes to enable self-assembly of the up-conversion nanoparticles to single-layer graphene oxide, and then the substrate was rinsed with deionised water to eliminate excess up-conversion nanoparticles solution. Typically, the density of the layer of nanoparticles increased with incrementing concentration and deposition time. By tuning the concentration of the nanoparticles in water and the deposition time, the density of the self-assembled nanoparticle layer could be controlled accurately. The nanoparticles deposited prevalently onto the graphene oxide nanosheets with a small residue onto the substrate because of the electrostatic repulsion between the nanoparticles and silane groups previously formed onto the ITO-coated coverslip glass.
Figure 5.4: Self-assembly of up-conversion nanoparticles onto single-layer graphene oxide. a) Schematic of the self-assembly of the up-conversion nanoparticles onto single-layer graphene oxide: a drop of up-conversion nanoparticles solution was placed for 30 minutes to allow self-assembly onto the single-layer graphene oxide nanosheets prepared according to Step 1. Then, the samples were rinsed with deionised water to eliminate excess up-conversion nanoparticles solution. b) SEM images of the self-assembled up-conversion nanoparticles onto single-layer graphene oxide. Magnification: 2,000× (left), 50,000× (middle) and 200,000× (right). Scale bars: 5 µm, 200 nm and 50 nm.

5.3.3 Confocal imaging of the nanocomposite

The nanocomposite based on up-conversion nanoparticles and single-layer graphene oxide was imaged using the home-built confocal optical microscopy system. Two-channel imaging was performed by exploiting the fluorescence emission from the up-conversion nanoparticles using a CW laser at 980 nm for excitation and two-photon excited fluorescence emission from graphene oxide under 880-nm fs laser excitation. Under fs laser excitation at 880 nm, a broad two-photon excited fluorescence peak centred at 650 nm was observed. The 650-nm fluorescence can be ascribed to graphene oxide, in agreement with previously reported studies [138]. This demonstration not only provides insight to the configuration of the newly-prepared nanocomposite, but also demonstrates that it can be optically activated using two different channels for excitation.
Figure 5.5: Confocal imaging of the nanocomposite based on up-conversion nanoparticles and graphene oxide. a) Schematic of the two-channel excitation confocal imaging: 980-nm CW laser was used for excitation of 450-nm fluorescence emission from the up-conversion nanoparticles; 880-nm fs laser was used for excitation of 650-nm two-photon excited fluorescence emission from graphene oxide. b) Confocal images of the 450-nm up-conversion fluorescence emission (left) and 650-nm two-photon excited fluorescence emission (right). Scale bar: 25 µm. Excitation powers: 1 mW.

5.4 Photochemical reduction of graphene oxide induced by up-conversion nanoparticles

The objective of this section is to demonstrate the innovative concept of using up-conversion nanoparticles to induce the photochemical reduction of graphene oxide through resonance energy transfer. In Section 5.2, occurrence of highly-efficient resonance energy transfer from the up-conversion nanoparticles to graphene oxide was demonstrated when the up-conversion nanoparticles were conjugated with graphene oxide. In addition, the unique fluorescence
properties of up-conversion nanoparticles emitting in the ultraviolet and blue are suitable to induce the photochemical reduction of graphene oxide, as reported in Section 2.2. To demonstrate the feasibility of energy transfer–driven photochemical reduction of graphene oxide induced by up-conversion nanoparticles by irradiation with a laser at 980 nm, the fluorescence from the up-conversion nanoparticles and two-photon excited fluorescence from graphene oxide were monitored under 980-nm CW excitation laser and 880-nm fs excitation laser, respectively.

The reduction of graphene oxide is accompanied by a variation of absorption [30, 31]. Specifically, because the absorption of reduced graphene oxide is higher than that of graphene oxide, the 450-nm fluorescence emission from the up-conversion nanoparticles will result quenched upon reduction. Further, because the reduction process occurs through the elimination of the oxygen groups that originate graphene oxide’s fluorescence [117], a decrease of the 650-nm two-photon excited fluorescence emission is also expected. By detecting the variation of fluorescence using these two emission channels, it is thus possible to monitor graphene oxide’s reduction in the newly-prepared nanocomposite. Figure 5.6 reports the proposed mechanism for the photochemical reduction of graphene oxide induced by the up-conversion nanoparticles under 980-nm CW laser.

Figure 5.6: Proposed mechanism for the photochemical reduction of graphene oxide induced by the up-conversion nanoparticles through resonance energy transfer.
When a 980-nm CW laser excites the up-conversion nanoparticles, the photochemical reduction of graphene oxide is triggered through resonance energy transfer from high-energy excited levels in the nanoparticles. The permanent physical and chemical change in graphene oxide can be used as a method for optical data writing. Further, the elimination of the oxygenated groups in graphene oxide determines a decrease in two-photon excited fluorescence emission, while the strong absorption of reduced graphene oxide can quench the fluorescence emission from the up-conversion nanoparticles, which can both be used as methods for optical data read-out.

Here, this study demonstrated the ability to optically encode and retrieve bits of information in the nanocomposite based on up-conversion nanoparticles and graphene oxide. Optical writing was performed by reducing graphene oxide using up-conversion nanoparticles under excitation by a CW laser at 980 nm, while optical reading was achieved by detecting either the 450-nm up-conversion fluorescence from the nanoparticles under excitation using a CW laser at 980 nm, or the 650-nm two-photon excited fluorescence from graphene oxide under 880-nm fs excitation laser.

Figure 5.7 indicates that the 450-nm fluorescence emission intensity from the up-conversion nanoparticles decreased over time under irradiation of the nanocomposite by a 980-nm CW laser at 500 μW. Specifically, the fluorescence emission intensity from the up-conversion nanoparticles decreased by ~40% after 30 seconds of irradiation under 980-nm CW laser, and then plateaued. The decreased fluorescence emission intensity from the up-conversion nanoparticles was attributed to the quenching by reduced graphene oxide as a consequence of its photochemical reduction.

Figure 5.8 indicates that the 650-nm two-photon excited fluorescence emission generated from graphene oxide under 880-nm fs laser excitation decreased over time under irradiation of the nanocomposite using a 980-nm CW laser at 500 μW. Specifically, the fluorescence emission intensity from the graphene oxide decreased by ~50% after 30 seconds of irradiation under 980-nm CW laser, and then plateaued. The drop of fluorescence intensity from the reduced graphene oxide was ascribed to the elimination of its oxygen groups during reduction, which are responsible for the fluorescence signal from graphene oxide.
Figure 5.7: Quenching up-conversion nanoparticles through reduction of graphene oxide under 980-nm CW laser irradiation. a) Schematic mechanism of quenching of 450-nm fluorescence emission from the up-conversion nanoparticles through reduction of graphene oxide under 980-nm CW laser irradiation. b) Time dependence of 450-nm fluorescence emission from the up-conversion nanoparticles in the nanocomposite under 980-nm CW laser irradiation. Inset: Confocal images of an individual up-conversion nanoparticle in the nanocomposite that is quenched by reduced graphene oxide under 980-nm CW laser irradiation. Scale bar: 200 nm.
Figure 5.8: Decrease of fluorescence emission from graphene oxide through up-conversion nanoparticles-induced reduction under 980-nm CW laser irradiation. a) Schematic mechanism of decreased 650-nm two-photon excited fluorescence emission from graphene oxide through up-conversion nanoparticles-induced reduction under 980-nm CW laser irradiation. b) Time dependence of 650-nm two-photon excited fluorescence emission from graphene oxide in the nanocomposite under 980-nm CW laser irradiation. Inset: Confocal images of graphene oxide in the nanocomposite exhibiting decreased two-photon excited fluorescence emission under 980-nm CW laser irradiation. Scale bar: 200 nm.
The quenching of the 450-nm fluorescence emission from the up-conversion nanoparticles, along with decreased 650-nm two-photon excited fluorescence emission from graphene oxide during irradiation of the nanocomposite under 980-nm CW laser, demonstrates the changed properties of graphene oxide. This variation can be explained with photochemical reduction produced by the transfer of high-energy quanta from the up-conversion nanoparticles excited by 980-nm CW laser and partly by photon reabsorption by graphene oxide of the ultraviolet and blue photons emitted by the up-conversion nanoparticles. Specifically, the achievement of the reduction of graphene oxide induced by the up-conversion nanoparticles in the newly-prepared optically-activatable nanocomposite has paved the way for applications of optical encoding.

Further improvement of the sample preparation—such as the synthesis of smaller nanoparticles—may result in enhanced quenching and thus reduced residual fluorescence emission for higher contrast. Moreover, brighter nanoparticles with increased high-energy up-conversion fluorescent emission intensity could be beneficial to speed up the process of reduction in graphene oxide and subsequently improve the performance of the nanocomposite towards practical optical data storage. However, it should be noted that there exists a trade-off between the size of the nanoparticles and their up-conversion fluorescence intensity. In fact, smaller nanoparticles have been reported to be less bright, which ultimately causes a reduction in the signal intensity in super-resolution applications. For these reasons, the as-synthesised up-conversion nanoparticles may currently be the optimal candidate to demonstrate optical data storage beyond the diffraction-limit barrier.

5.5 Dual-laser photoactivation in the nanocomposite based on up-conversion nanoparticles and graphene oxide

The nanocomposite based on 4% Tm-doped up-conversion nanoparticles and graphene oxide was tested under dual-laser irradiation comprising a 980-nm CW laser for activation and 808-nm CW laser for deactivation. The following results demonstrate the feasibility of optical depletion of up-conversion and photoinhibition of reduction in graphene oxide, which represent the key steps for achieving optical data storage at the nanoscale by employing super-resolution optical techniques. The optical depletion efficiency of the 450-nm up-conversion fluorescence emission in the nanocomposite based on up-conversion nanoparticles and graphene oxide was measured
under increasing 808-nm intensity, reaching a value of ~95% (Figure 5.9). Further, the saturation intensity \( I_{sat} \) was estimated to be ~250 kW cm\(^{-2}\) (~1.0 mW), which agrees with the theoretical prediction.

![Graph showing power-dependent depletion efficiency](image)

**Figure 5.9:** Power-dependent depletion efficiency of 450-nm fluorescence emission intensity in the nanocomposite based on 4% Tm-doped up-conversion nanoparticles and graphene oxide under excitation of a CW laser at 980 nm with a power of 0.5 mW and 808-nm CW laser for depletion at increasing power. The theoretical prediction for optical depletion efficiency was confirmed, obtaining ~95% depletion efficiency and a value of saturation intensity \( I_{sat} \) of ~250 kW cm\(^{-2}\) (~1.0 mW).

The efficient depletion of 450-nm fluorescence emission in the nanocomposite based on 4% Tm-doped up-conversion nanoparticles and graphene oxide under combined irradiation of CW laser at 980 nm for excitation and a CW laser at 808 nm for depletion enabled super-resolution imaging of individual up-conversion nanoparticles onto single-layer graphene oxide by STED microscopy (Figure 5.10). This experiment adopted a dual-laser configuration comprising a Gaussian-shaped 980-nm CW laser beam and doughnut-shaped 808-nm CW laser beam, as reported in Section 4.4.1 of this PhD thesis.
Figure 5.10: Super-resolution imaging of the 4% Tm-doped up-conversion nanoparticles onto single-layer graphene oxide by STED microscopy. a) Improvement of resolution obtained by increasing the depletion laser intensity. Insets: up-conversion nanoparticles onto single-layer graphene oxide imaged by STED microscopy using an 808 nm CW laser at increasing intensity. b) Imaging individual up-conversion nanoparticle onto single-layer graphene oxide by confocal microscopy (left) and STED microscopy (middle), and the corresponding line profiles of the images. The 980-nm CW excitation laser and 808-nm CW depletion laser intensities were 0.13 and 11.25 MW cm$^{-2}$, respectively. Scale bar: 100 nm.

Individual up-conversion nanoparticles onto single-layer graphene oxide were imaged by confocal microscopy and STED microscopy. A significant increase in the spatial resolution was achieved by adding the doughnut-shaped 808-nm CW depletion laser, compared with confocal microscopy using a 980-nm CW excitation laser only. The line profile analysis for an individual nanoparticle onto single-layer graphene oxide indicated that the achieved lateral imaging resolution was $\sim$56 nm after deconvolution with intensity of the doughnut-
shaped 808-nm CW laser depletion beam of 11.25 MW cm\(^{-2}\). This value represents a one to two order of magnitude reduction of laser intensity compared with typical STED imaging using other fluorophores [123-128]. Therefore, low power consumption is expected for use in optical data storage.

The researchers then proceeded by studying the effect of the 808-nm CW laser for photodeactivation of the processes of up-conversion and energy transfer to prevent the reduction of graphene oxide from occurring. The CW laser at 980 nm for excitation of the up-conversion nanoparticles was set at a power of 500 μW, which is suitable to activate the process of reduction of graphene oxide, and was combined with the 808-nm CW laser for inhibition at increasing powers. The 450-nm up-conversion fluorescence was measured as a function of time (Figure 5.11).

![Figure 5.11: Power-dependent photoinhibition efficiency of reduction in the nanocomposite based on 4% Tm-doped up-conversion nanoparticles and graphene oxide under CW laser at 980 nm for excitation and CW laser at 808 nm for inhibition. By increasing the power of the 808-nm inhibition laser, the process of reduction of graphene oxide was also inhibited.](image)

As can be seen from Figure 5.11, by increasing the power of the 808-nm CW laser for inhibition, the drop of 450-nm up-conversion fluorescence was progressively reduced. This result implied that the reduction of graphene oxide could be inhibited and the quenching of fluorescence emission from the up-conversion nanoparticles could be prevented. The efficiency of photoinhibition was higher by increasing the power of the 808-nm CW laser beam, and reduction could be effectively avoided when the inhibition power reached 10 mW.
This demonstration proved that the introduction of the 808-nm CW laser for inhibition could prevent up-conversion to high energy levels and thus stop the transfer of energy quanta to graphene oxide. Therefore, the process of reduction could be effectively inhibited, which paves the way towards implementation in optical data writing with resolution at the nanoscale.

5.6 Nanoscale optical encoding

Dual-laser photoactivation using the up-conversion nanoparticles to induce the photochemical reduction of graphene oxide enabled nanoscale optical recording and read-out in the nanocomposite based on up-conversion nanoparticles and graphene oxide for the first time. Figure 5.12a shows the principle of subdiffraction-limit selective quenching of an individual up-conversion nanoparticle through reduction of graphene oxide by SPIN using a Gaussian-shaped 980-nm CW laser for activation and doughnut-shaped 808-nm CW laser for inhibition. Initially, two neighbouring up-conversion nanoparticles in the nanocomposite could not be independently resolved by conventional confocal microscopy using single-beam excitation at 980 nm and detecting up-conversion fluorescence at 450 nm because of their subdiffraction-limit separation. However, the combined irradiation of a CW laser at 980 nm with a Gaussian shape used for excitation and a CW laser at 808 nm with a doughnut shape used for depletion allowed to independently discriminate each of the up-conversion nanoparticles by STED microscopy (Figure 5.12b). Further, an individual up-conversion nanoparticle in the nanocomposite could be selectively quenched through reduction of graphene oxide by SPIN, maintaining the neighbouring material unaffected. Conventional confocal microscopy using single-beam excitation at 980 nm was limited in detecting the subdiffraction-limit encoded feature, which was however discriminated by super-resolution methods using fluorescence quenching microscopy combined with STED microscopy (Figure 5.12c). This achievement is of great significance because it demonstrates the capability of selective quenching of individual nanoparticles in the nanocomposite based on up-conversion nanoparticles and graphene oxide by dual-laser irradiation, breaking the limit imposed by diffraction, and thus enabling to write and read-out information bits at the nanoscale.
Figure 5.12: Subdiffraction-limit selective quenching of an individual up-conversion nanoparticle through reduction of graphene oxide under dual-laser irradiation. a) Schematic of the subdiffraction-limit selective quenching of an individual up-conversion nanoparticle onto graphene oxide and imaging by confocal microscopy and STED microscopy. b) Confocal and STED microscopy of two neighbouring up-conversion nanoparticles onto graphene oxide: initially unresolvable by confocal microscopy, the two nanoparticles were distinguished by STED microscopy. c) Confocal and STED microscopy after selective quenching of one of the two nanoparticles through reduction of graphene oxide under dual-laser irradiation. The 980-nm CW excitation laser and 808-nm CW depletion laser intensities were 0.13 and 11.25 MW cm$^{-2}$, respectively. Scale bar: 100 nm.
A dual-laser configuration comprising a Gaussian CW laser at 980 nm and a doughnut-shaped CW laser at 808 nm was used for nanoscale optical data storage in the nanocomposite. Figure 5.13 shows encoding of nanoscale data bits with subdiffraction-limit separation in the nanocomposite based on up-conversion nanoparticles and graphene oxide by SPIN. Data could be retrieved back distinctively by fluorescence quenching microscopy combined with STED microscopy obtaining a super-resolution image. The size of the data bits was 61 nm with a spacing of 195 nm, which offers the potential for an estimated capacity of approximately 200 TB per disc [32]. The exposure time for each individual data bit was 30 s and the 980-nm CW activation laser and 808-nm CW deactivation laser intensities were 0.13 and 11.25 MW cm$^{-2}$, respectively. Therefore, the inhibition energy per each individual information bits was reduced towards femtojoule when up-conversion nanoparticles were employed.

**Figure 5.13:** Nanoscale optical recording and read-out of information bits in the nanocomposite based on up-conversion nanoparticles and graphene oxide. a) Normalised up-conversion fluorescence emission scan of nanoscale optical recordings displaying a representation of a leaf. The recordings were produced through the photochemical reduction of graphene oxide induced by the up-conversion nanoparticle through SPIN and retrieved by detecting the quenching of the fluorescence emission from the up-conversion nanoparticles by reduced graphene oxide through fluorescence quenching microscopy combined with STED microscopy. The 980-nm CW excitation laser and 808-nm CW depletion laser intensities were 0.13 and 11.25 MW cm$^{-2}$, respectively. The pattern was 50 × 50 bits, with a bit spacing of 195 nm. Scale bar: 2 μm. Insets: illustration of the shape of the leaf reproduced in the nanocomposite (top) and detailed image of two adjacent information bits (bottom). Scale bar: 50 nm. b) Line profiles analyses of the two adjacent information bits.
The combination of up-conversion nanoparticles and graphene oxide can thus not only provide a feasible pathway for achieving high-density optical memory devices but also enable information storage with ultralow-power consumption, which can significantly help to tackle the needs the ‘information revolution’ has brought about and offer a platform towards ‘green’ technologies.

5.7 Chapter conclusions

This chapter has demonstrated ultralow-power nanoscale optical data storage in a nanocomposite based on up-conversion nanoparticles and graphene oxide. For this purpose, the up-conversion nanoparticles were conjugated with graphene oxide to ensure efficient resonance energy transfer within the up-conversion nanoparticles–graphene oxide system. For the investigation of resonance energy transfer, measurements of up-conversion fluorescence quenching and fluorescence lifetime were conducted in the up-conversion nanoparticles–graphene oxide system, obtaining an efficiency of ~83%. Subsequently, a novel optically-activatable nanocomposite based on up-conversion nanoparticles in conjugation with graphene oxide was prepared through self-assembly of up-conversion nanoparticles onto graphene oxide nanosheets. A configuration of single-layer graphene oxide deposited onto coverslip glass was selected to guarantee efficient heat dissipation away from graphene oxide during laser irradiation, thereby preventing photothermal damage of the storage medium.

Demonstration of the photochemical reduction of graphene oxide in the nanocomposite was reported under near-infrared laser excitation. Specifically, a CW laser at 980 nm excited the up-conversion nanoparticles and produced up-conversion to levels with high energy, which triggered the dissociation of the oxygen groups in graphene oxide for reduction through resonance energy transfer. This mechanism demonstrated a suitable pathway for optical data writing. Two channels were used to monitor the reduction process, which can thus be used for optical data reading: the quenching of 450-nm fluorescence emission from the up-conversion nanoparticles under CW laser excitation at 980 nm, and the decrease of 650-nm two-photon excited fluorescence emission from graphene oxide under 880-nm fs laser excitation. Specifically, the fluorescence emission from the up-conversion nanoparticles was quenched by ~40% under CW laser at 980 nm, while the fluorescence emission intensity
from the graphene oxide decreased by ~50% under a 980-nm CW laser, thereby confirming the occurrence of reduction in graphene oxide through elimination of its oxygen groups. Moreover, the up-conversion nanoparticles–graphene oxide nanocomposite was tested under dual-laser irradiation comprising a CW laser at 980 nm for excitation and CW laser at 808 nm for depletion. A value of ~95% optical depletion efficiency of the 450-nm up-conversion fluorescence was achieved. The saturation intensity, $I_{sat}$, was ~250 kW cm$^{-2}$ (~1.0 mW), corresponding to several orders of magnitude reduction of energy consumption by using the nanocomposite based on up-conversion nanoparticles and graphene oxide to encode bits of information in comparison with other nanomaterials used in super-resolution optical methods. In addition, this chapter has demonstrated that the introduction of the 808-nm CW laser can effectively inhibit up-conversion to high-energy levels in the up-conversion nanoparticles, resulting in prevented reduction of graphene oxide. Finally, ultralow-power nanoscale optical data storage was achieved in the nanocomposite. Nano-sized features with a size of 61 nm and spacing 195 nm were produced by SPIN and subsequently retrieved by fluorescence quenching microscopy combined with STED microscopy, which offers the potential for an estimated capacity of approximately 200 TB per disc. Further, the inhibition energy per each individual information bits decreased towards femtojoule when up-conversion nanoparticles were employed and hence ultralow-power consumption is expected for optical data memory devices based on the combination of up-conversion nanoparticles with graphene oxide.
Chapter 6

Conclusions and future perspectives

6.1 Thesis conclusions

The research work included in this PhD thesis offers an exhaustive insight into the demonstration of ultralow-power nanoscale optical data storage in a novel nanocomposite material based on up-conversion nanoparticles in combination with graphene oxide for innovative optical data storage devices with ultrahigh capacity, ultralow power consumption and ultralong lifetime. This achievement is a conceptual breakthrough compared with the state-of-the-art optical data storage systems, and has enabled the researchers to optically encode and retrieve bits of information beyond the diffraction-limit barrier. Hence, a boost of capacity for individual optical data storage memories is prospected.

Three major areas of research have been investigated in this PhD project and can be summarised in the following key advancements.

1) Ultraviolet laser-induced reduction of graphene oxide for modulation of up-conversion fluorescent nanoparticles

This study has investigated the feasibility of photochemical reduction of graphene oxide under high-energy laser irradiation for the modulation of up-conversion fluorescent nanoparticles, providing the fundamental understanding towards data encoding and retrieval in an up-conversion nanoparticles–graphene oxide system. Up-conversion nanoparticles were
synthesised and conjugated with commercially-available graphene oxide to form a thin film through vacuum filtration. Subsequently, an ultraviolet laser was used to irradiate the nanocomposite and produce photochemical reduction of graphene oxide. The reduction process was accompanied by a variation of absorption in the nanocomposite and consequent quenching of the fluorescence emission from the up-conversion nanoparticles by reduced graphene oxide. Further, up-conversion fluorescence lifetime measurements were performed to pin down the mechanism of fluorescence quenching. The decreased up-conversion fluorescence lifetime was related to the occurrence of resonance energy transfer between the up-conversion nanoparticles and graphene oxide/reduced graphene oxide. Optical patterns were successfully fabricated in the graphene oxide thin film integrated with up-conversion nanoparticles and retrieved distinctly using the up-conversion fluorescence emission quenching by reduced graphene oxide.

The presented demonstration offers a great improvement over currently available methods for modulation of the fluorescence emission from up-conversion nanoparticles. This advancement is mostly due to the super-quenching property of reduced graphene oxide, which can quench up-conversion fluorescence up to ~90%. In addition, the fast speed of reduction of graphene oxide using high-energy laser irradiation allows reduction in the time for modulating up-conversion fluorescence from minutes (such as in the case of up-conversion nanoparticles coupled with DTE molecules) down to the millisecond range for individual pixels in this study’s newly-developed nanocomposite. This improvement is due to the rapid process of ultraviolet laser-induced reduction of graphene oxide and fluorescence emission quenching of the up-conversion nanoparticles, which rely on the instantaneous physical and chemical change in graphene oxide through reduction, compared with the slow closed-/open-ring processes in the case of DTE molecule [62, 63]. Moreover, owing to the little power required and the use of CW lasers, low energy consumption is achieved for the process of optical patterning. Finally, understanding the physics behind the ultraviolet laser-induced photochemical reduction of graphene oxide and the quenching of fluorescence emission from the up-conversion nanoparticles by reduced graphene oxide lays the scientific foundation for the development of a suitable optically-activatable nanocomposite towards ultralow-power nanoscale optical data storage.
2) Development of high-energy up-conversion fluorescent nanoparticles for dual-laser photoactivated super-resolution systems

This study has developed high-energy up-conversion fluorescent nanoparticles for application in dual-laser photoactivated super-resolution systems, including their combination with graphene oxide. Theoretical and experimental investigations have been conducted to individuate the key features of the nanoparticles for efficient photoactivation in applications beyond the diffraction-limit barrier in energy transfer–driven systems. Specifically, a theoretical framework for the process of up-conversion in the nanoparticles and energy transfer to graphene oxide has been outlined. The fundamental characteristics of the up-conversion nanoparticles are intense high-energy up-conversion fluorescence, efficient optical depletion of up-conversion fluorescence, and small size and narrow size distribution. A steady-state model based on rate equations has been used to describe the electronic transitions in the up-conversion nanoparticles–graphene oxide system, comprising the process of up-conversion in the nanoparticles and energy transfer to graphene oxide. Further, simulation results have indicated the potential for resolution improvement in the up-conversion nanoparticles–graphene oxide system, providing a feasible pathway for energy transfer–driven photoactivation at the nanoscale.

The up-conversion nanoparticles were then successfully prepared and tested under dual-beam super-resolution optical techniques, such as STED microscopy, thereby confirming the potential for applications beyond the diffraction-limit barrier. First, a study of the optical depletion efficiency of 450-nm up-conversion fluorescence emission was conducted, achieving \(~90\%\) depletion efficiency for a 4\% Tm-doped nanoparticle with a saturation intensity of \(\sim 375 \text{ kW cm}^{-2}\) (\(\sim 1.5 \text{ mW}\)). Second, super-resolution imaging of the up-conversion nanoparticles by STED microscopy was undertaken, using a Gaussian-shaped 980-nm CW laser for excitation and a doughnut-shaped 808-nm CW laser for depletion, reaching a resolution of 64 nm with an intensity of 11.25 MW cm\(^{-2}\). The values of intensity of the excitation and depletion beams were one hundredth to one thousandth lower than those required for typical STED imaging using other fluorophores [123-128], which is very attractive for applications with low power consumption in dual-laser photoactivated super-resolution systems.
3) Ultralow-power nanoscale optical data storage in a nanocomposite based on up-conversion nanoparticles and graphene oxide

This study has achieved the first demonstration of ultralow-power nanoscale optical data storage in a nanocomposite based on up-conversion nanoparticles and graphene oxide, leading to a conceptual breakthrough towards use in high-capacity optical data storage. For this purpose, SPIN and fluorescence quenching microscopy combined with STED microscopy were adopted for optical data writing and reading, respectively, beyond the diffraction-limit barrier in the same material platform.

Initially, the up-conversion nanoparticles were conjugated with graphene oxide to ensure efficient resonance energy transfer within the up-conversion nanoparticles–graphene oxide system. Specifically, measurements of up-conversion fluorescence quenching and fluorescence lifetime were conducted in the up-conversion nanoparticles–graphene oxide system, which demonstrated highly-efficient resonance energy transfer, reaching the value of ~83%. Subsequently, a novel optically-activatable nanocomposite based on up-conversion nanoparticles in conjugation with graphene oxide was prepared through self-assembly of up-conversion nanoparticles onto graphene oxide nanosheets. For this purpose, a configuration of single-layer graphene oxide deposited onto coverslip glass was selected to guarantee efficient heat dissipation away from graphene oxide during laser irradiation, thereby preventing photothermal damage of the storage medium.

Demonstration of the photochemical reduction of graphene oxide in the nanocomposite was reported under near-infrared laser excitation. Specifically, a 980-nm CW laser excited the up-conversion nanoparticles and produced up-conversion to high energy levels, which triggered the dissociation of the oxygen groups in graphene oxide for reduction through a resonance energy transfer. This mechanism demonstrated a suitable pathway for optical data writing. Two channels were used to monitor the reduction process, which can thus be used for optical data reading: the quenching of 450-nm fluorescence emission from the up-conversion nanoparticles by reduced graphene oxide under 980-nm CW laser excitation, and the decrease of 650-nm two-photon excited fluorescence emission from graphene oxide under 880-nm fs laser excitation. Specifically, the fluorescence emission from the up-conversion nanoparticles was quenched by ~40% under a 980-nm CW laser, while the fluorescence emission intensity from the graphene oxide decreased by ~50% under a 980-nm
CW laser, thereby confirming the occurrence of reduction in graphene oxide through elimination of its oxygen groups.

Moreover, the up-conversion nanoparticles–graphene oxide nanocomposite was tested under dual-laser irradiation comprising a CW laser at 980 nm for excitation and an 808-nm CW laser for depletion. A value of ~95% optical depletion efficiency of the 450-nm upconversion fluorescence was achieved. The saturation intensity, $I_{sat}$, was ~250 kW cm$^{-2}$ (~1.0 mW), corresponding to several orders of magnitude reduction of energy consumption by using the nanocomposite based on up-conversion nanoparticles and graphene oxide to encode bits of information, in comparison with other nanomaterials used in super-resolution optical methods. In addition, it has been demonstrated that the introduction of the 808-nm CW laser can effectively inhibit up-conversion to high-energy levels in the up-conversion nanoparticles, resulting in prevented reduction of graphene oxide.

Finally, ultralow-power nanoscale optical data storage was achieved in the nanocomposite. Nano-sized features were produced by SPIN and subsequently retrieved by fluorescence quenching microscopy combined with STED microscopy achieving a resolution of 61 nm and spacing 195 nm between neighbouring information bits, which offers the potential for an estimated capacity of approximately 200 TB per disc (Figure 6.1a). Further, the inhibition energy per information bit decreased towards femtojoule when up-conversion nanoparticles were employed (Figure 6.1b) and hence ultralow-power consumption is expected for optical data memory devices based on the combination of up-conversion nanoparticles with graphene oxide. The newly-developed nanocomposite based on up-conversion nanoparticles and graphene oxide has thus proven the best-suited candidate for sustainably accommodate the requirements of the ‘information revolution’.
Figure 6.1: Performance of the up-conversion nanoparticles–graphene oxide nanocomposite for ultralow-power nanoscale optical data storage. a) Projected maximal optical data storage capacity for a single disc as a function of the feature size of the recorded bits. For the calculation, the lateral and axial distances were 2.5× and 8× the feature size, respectively [32]. b) Estimated energy consumption using up-conversion nanoparticles or other nanomaterials (such as nitrogen vacancy [NV] centres in diamond, fluorescence dyes and QDs for optical data storage) through super-resolution techniques. Inhibition energy per optical data bit decreased from picojoule to femtojoule per bit when up-conversion nanoparticles were employed.
6.2 Future perspectives

Regarding the future work of this PhD thesis, two potential directions could be worth investigation. One is to further study the electronic transitions underlying up-conversion and energy transfer in the up-conversion nanoparticles–graphene oxide system for individualization of the optimal wavelength for the deactivation process. This may result in additional reduction of power consumption for optical data storage. The other is to proceed towards the fabrication of a high-capacity optical memory prototype by embedding the up-conversion nanoparticles in combination with graphene oxide into a suitable host matrix.

6.2.1 Photo-deactivation of up-conversion nanoparticles through multi-state process

Chapters 4 and 5 investigated the up-conversion nanoparticles–graphene oxide system under excitation using a CW laser at 980 nm and an 808-nm CW laser for deactivation. The irradiation at 808 nm matched the energy gap between the $^3\text{H}_4$ excited state and the $^3\text{H}_6$ ground state in Tm$^{3+}$ ions, thereby resulting in efficient STED. In fact, the fundamental requirement for the STED process is that the wavelength of the STED laser is in the range of fluorescence wavelength [36]. Table 6.1 and Figure 6.2a show that the energy differences for the $^1\text{D}_2 \rightarrow ^1\text{G}_4$, $^1\text{G}_4 \rightarrow ^3\text{F}_3$, $^3\text{F}_3 \rightarrow ^3\text{H}_5$ and $^3\text{H}_4 \rightarrow ^3\text{F}_4$ transitions in Yb,Tm-doped up-conversion nanoparticles meet the essential condition for the STED process under a 1,550-nm laser for depletion. Recently, it has been reported that NaYF$_4$:Yb$^{3+}$,Tm$^{3+}$ up-conversion nanoparticles were used to demonstrate the STED process under simultaneous irradiation with a CW laser at 980 nm for excitation and a 1,550-nm CW laser for depletion [139]. In this study, the intensity of the 1,550-nm depletion laser beam was < 0.1 KW cm$^{-2}$ because of the multiple states involved in the depletion process, with potential for achieving super-resolution with only one thousandth of the usual laser intensity for STED nanoscopy. Therefore, the researchers speculate that the use of a 1,550-nm laser beam for deactivation in the up-conversion nanoparticles–graphene oxide system considered in this PhD thesis could further diminish the power consumption for applications in optical data storage beyond the diffraction-limit barrier (Figure 6.2b).
Table 6.1: Energy difference between transitions in Yb,Tm-doped up-conversion nanoparticles and energy of 1,550-nm photon matching these transitions for possible STED processes.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy Difference (cm⁻¹)</th>
<th>Energy of 1550-nm photon (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹D₂ → ¹G₄</td>
<td>5455-7836</td>
<td></td>
</tr>
<tr>
<td>¹G₄ → ²F₃</td>
<td>5894-7481</td>
<td></td>
</tr>
<tr>
<td>³F₃ → ²H₅</td>
<td>5872-6786</td>
<td></td>
</tr>
<tr>
<td>²H₄ → ²F₄</td>
<td>6439-7220</td>
<td>6452</td>
</tr>
</tbody>
</table>

Figure 6.2: Deactivation through multi-state process in the up-conversion nanoparticles–graphene oxide system. a) Energy level diagrams of Tm³⁺ ions, including the potential STED processes under 1,550-nm depletion laser. b) Inhibition energy per optical data bit using up-conversion nanoparticles deactivated through single-state process (980 nm + 808 nm) and multi-state process (980 nm + 1,550 nm), and compared with other nanomaterials for super-resolution techniques.
6.2.2 Fabrication of high-capacity optical memory device

To fabricate optical memory devices with high capacity using a combination of the up-conversion nanoparticles and graphene oxide, a suitable host matrix needs to be individuated. Given that laser irradiation may induce unwanted temperature rise in the nanocomposite and produce photothermal reduction of graphene oxide and consequent photo-damage, an appropriate support material with high thermal conductivity needs to be selected. This material that embeds or surrounds the up-conversion nanoparticles conjugated with graphene oxide comprises a thermal conductor in thermal contact with the graphene oxide to mitigate photothermal reduction of the graphene oxide in the focal region. Thus, the temperature rise can be alleviated, thereby reducing photothermal reduction that may cause reduction of a larger area compared with the photochemical reduction alone.

Any thermal conductor may be suitable for use in the optical data storage material described herein, provided it effectively mitigates photothermal reduction of the graphene oxide, is compatible with the up-conversion nanoparticles and graphene oxide, and is suitable for use in optical data storage systems, including allowing optical transmission at writing and reading wavelengths. Examples of suitable materials include inorganic thermal conductors, including silica, alumina, quartz, zirconia, YAG, hafnia and their combinations. Embedding the up-conversion nanoparticles combined with graphene oxide into a thermal conductor may be performed by methods such as hydrolysis and condensation of functional metal alkoxides, which may be a highly flexible, inexpensive and/or low-energy synthesis route [140]. The choice of an inorganic material can be particularly advantageous because it can also provide chemical stability to the device. This ensures a significantly longer lifetime relative to the optical memory, in terms of both shelf-life and ability to preserve optically written data over long periods of time.
References


silicon by fluorescence quenching. *Journal of the American Chemical Society*, 131(43), 15576-15577.


Publications of the author

Journal Publications

• Ultraviolet laser-induced reduction of graphene oxide for modulation of up-conversion fluorescent nanoparticles (in preparation).
• Ultralow-power nanoscale optical data storage in a nanocomposite based on up-conversion nanoparticles and graphene oxide (in preparation).

Conference Publications