

Rare-Earth Doping in Nanostructured Inorganic Materials

Bingzhu Zheng, Jingyue Fan, Bing Chen, Xian Qin, Juan Wang,* Feng Wang,* Renren Deng,*
and Xiaogang Liu*



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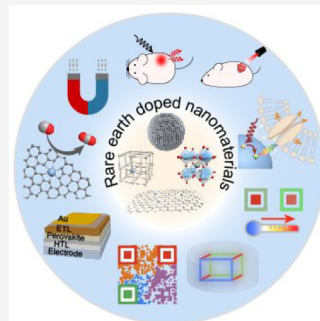


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ABSTRACT: Impurity doping is a promising method to impart new properties to various materials. Due to their unique optical, magnetic, and electrical properties, rare-earth ions have been extensively explored as active dopants in inorganic crystal lattices since the 18th century. Rare-earth doping can alter the crystallographic phase, morphology, and size, leading to tunable optical responses of doped nanomaterials. Moreover, rare-earth doping can control the ultimate electronic and catalytic performance of doped nanomaterials in a tunable and scalable manner, enabling significant improvements in energy harvesting and conversion. A better understanding of the critical role of rare-earth doping is a prerequisite for the development of an extensive repertoire of functional nanomaterials for practical applications. In this review, we highlight recent advances in rare-earth doping in inorganic nanomaterials and the associated applications in many fields. This review covers the key criteria for rare-earth doping, including basic electronic structures, lattice environments, and doping strategies, as well as fundamental design principles that enhance the electrical, optical, catalytic, and magnetic properties of the material. We also discuss future research directions and challenges in controlling rare-earth doping for new applications.



CONTENTS

1. Introduction	5520
2. Characteristics of Rare-Earth Elements	5521
2.1. Electronic Structures and Basic Properties	5521
2.2. Characteristic Properties	5521
2.2.1. Sc^{3+} , Y^{3+} , La^{3+} , and Lu^{3+}	5521
2.2.2. Ce^{3+} and Ce^{4+}	5521
2.2.3. Pr^{3+}	5522
2.2.4. Nd^{3+}	5524
2.2.5. Pm^{3+} and Sm^{3+}	5524
2.2.6. Eu^{3+} and Eu^{2+}	5524
2.2.7. Gd^{3+}	5524
2.2.8. Tb^{3+}	5525
2.2.9. Dy^{3+}	5525
2.2.10. Ho^{3+} , Er^{3+} , and Tm^{3+}	5525
2.2.11. Yb^{3+}	5526
3. Doping Strategies	5526
3.1. Principal Factors in Doping	5526
3.1.1. Ionic Size	5526
3.1.2. Valency	5527
3.1.3. Reactivity	5527
3.1.4. Doping in Nanostructures	5527
3.2. Doping in Various Substrates	5528
3.2.1. Rare-Earth Compounds	5528
3.2.2. Alkaline-Earth Compounds	5534
3.2.3. Semiconductor Quantum Dots	5536
3.2.4. Metal–Organic Frameworks	5539
3.2.5. 2D Layered Nanomaterials	5541
4. Technological Applications	5543

4.1. Bioapplications	5543
4.1.1. Bioimaging	5543
4.1.2. Photothermal Therapy	5547
4.1.3. Photodynamic Therapy and Phototherapy	5548
4.1.4. Drug Delivery	5550
4.1.5. Optogenetics	5550
4.2. Optical Sensing	5551
4.2.1. Temperature Sensing	5552
4.2.2. Pressure Sensing	5554
4.2.3. pH Sensing	5557
4.2.4. Molecular Detection	5557
4.3. Catalysis	5558
4.3.1. Ceria-Based Catalysis	5558
4.3.2. Photocatalysis	5559
4.3.3. Single-Atom Catalyst	5561
4.4. Lighting and Displays	5561
4.4.1. Nanoparticle Lasing	5561
4.4.2. Displays	5561
4.4.3. Information Storage	5562
4.4.4. Anticounterfeiting	5563
4.5. Photodetectors	5564

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4.5.1. Microwaves	5564
4.5.2. Infrared	5565
4.5.3. Ultraviolet–Visible	5565
4.5.4. X-rays and γ -rays	5565
4.6. Photovoltaics	5566
4.7. Nanomagnets and Magneto-optic Devices	5568
5. Summary and Outlook	5569
Author Information	5569
Corresponding Authors	5569
Authors	5570
Notes	5570
Biographies	5570
Acknowledgments	5570
Abbreviations and List of Acronyms	5570
References	5571

1. INTRODUCTION

Impurity doping is a technique that can be used to modify material properties. Doping rare-earth ions into nanomaterials can modulate the crystallographic phases, morphologies, sizes, and electronic configurations of inorganic nanomaterials. In addition, doping with rare-earth ions can impart rich optical, electrical, magnetic, and catalytic properties, making doped nanomaterials attractive for many technological applications. The rare-earths are a group of 17 elements composed of scandium, yttrium, and 15 lanthanides (ranging from lanthanum to lutetium) that have many similar physical/chemical properties and often coincide in geological deposits. The history of rare-earth elements can be traced back to 1751, when the first rare-earth mineral was discovered in Sweden.¹ However, this mineral was initially mistaken for a calcium iron silicate. In 1787, another similar mineral was found by Carl Arrhenius at Ytterby in Sweden. In 1794, a Finnish chemist Johan Gadolin first isolated a new oxide from the Ytterby ore and named it ytterbia. Later in 1842, Mosander further separated the ytterbia oxide into yttria, erbia, and terbia, although later studies revealed that these three oxides were also rare-earth mixtures. Because rare-earth elements have similar chemical properties, isolation of all 17 rare-earths was not accomplished until 1908–1909, when a repetitive fractional crystallization technique was implemented. In 1914, Henry Moseley used X-ray spectroscopy to confirm all rare-earth elements, except for radioactive element promethium (Pm). Promethium was not characterized until 1945 at Clinton Laboratories, now Oak Ridge National Laboratory.

Although all rare-earth elements have been identified, the isolation and large-scale production of individual rare-earth compounds remained a challenge. Prior to World War II, only europium could be extracted on an industrial scale as EuSO_4 because europium ions are more easily reduced from trivalent to divalent than other rare-earths.² As a result of rapid scientific and technological development during the war, the first effective rare-earth isolation technique was developed based on ion exchange chromatography. This technique exploited the differences in stability between different rare-earth citrate chelates. In about 1954, another effective method, liquid–liquid extraction, was developed and successfully used in commercial production.³

The mass production of rare-earth compounds provides a solid foundation for their practical application in modern society. For instance, Eu^{3+} -doped yttrium vanadate became the first red phosphor, enabling the development of color

television screens. Since the 1950s, rare-earths have facilitated the advancement in the materials industry in many categories, including phosphors, magnets, metallurgy, catalysts, and glass. In many cases, rare-earths are used as additives or dopants in materials. The beauty of using rare-earths is that even in small quantities, they can significantly alter material properties. As a result, rare-earths have been recognized as “vitamins” of modern industry, and the development of rare-earth-doped materials has become one of the most essential components of technological progress.

Since the 1990s, when the study of nanoscience and nanotechnology entered the fast lane, the potential of rare-earth-doped nanomaterials for diverse applications has been gradually recognized. Initial work was mainly devoted to rare-earth-doped luminescent nanoparticles, inspired by the invention of colloidal quantum dots and other inorganic nanophosphors.^{4–7} The initial motivation was to reduce the size of conventional rare-earth-doped luminophores to make them dispersible in colloidal suspension for new applications, such as biolabeling and biosensing. One of the first attempts was reported in 1990 by Beverloo et al., who used $0.1\text{--}0.3\ \mu\text{m}$ $\text{Y}_2\text{O}_3\text{:S:Eu}$ microparticles as luminescent biolabels for immunoassays.⁸ The advantages of using rare-earth-doped luminescent materials include high photochemical stability, narrow emission bandwidth, and long luminescence lifetime, as well as the ability to achieve UV/visible emission upon near-infrared (NIR) excitation through a unique process known as upconversion.^{9–11} However, at the outset, these nanophosphors could only be prepared by crushing bulk phosphors through ball milling. This limited the minimum size of the phosphors to a few hundred nanometers, which prevented wider use of these materials.

It was not until the beginning of the 21st century that new synthetic approaches to producing high-quality crystals less than 100 nm in size spurred growth in this area. Thanks to recent advances in new synthetic strategies such as thermal decomposition, coprecipitation, and hydro(solvo)thermal processing, monodisperse rare-earth-doped nanomaterials with easily controllable size, morphology, and crystallinity can now be prepared reliably with rationally designed structures.^{12–15} Rare-earth-based nanomaterials have become a highly interdisciplinary field of research that straddles the boundary between materials science and solid-state chemistry (Figure 1). Because of their intriguing material properties, a wide range of applications have been developed, from healthcare (bioimaging and therapy) to environmental protection (catalytic treatment of pollutants and clean energy development) to breakthrough science and technology (optical communications and three-dimensional displays).

Despite an enormous number of publications on the subject, previous reviews focused mainly on the optical properties of these nanomaterials. In particular, much attention has been paid to the applications of rare-earth-doped nanocrystals. There is a lack of a comprehensive review that summarizes the developments of rare-earth-doped nanomaterials in a broader context. To this end, we hope that this review can be a useful guide to the recent development of rare-earth-doped inorganic nanomaterials. This review highlights the unique properties of rare-earth-doped materials at the nanoscale and their applications. The review is organized as follows. In section 2, we provide an overview of the basic properties of all rare-earths and briefly summarize the utility of each rare-earth for various applications. In section 3, we discuss strategies for doping

various nanosized substrates with rare-earth ions. We highlight recent advances in the strategic design of these nanomaterials (core–shell structures, spatially confined doping strategies, and organic–inorganic hybrid nanocomposites) to generate multifunctional materials with remarkable properties. In section 4, we review a wide range of applications that arise from material properties. We conclude with a brief overview of the prospects for the future development of rare-earth-doped inorganic nanomaterials.

2. CHARACTERISTICS OF RARE-EARTH ELEMENTS

The properties of doped materials depend largely on the doping elements. Because of their chemical similarity, different rare-earth ions can be incorporated simultaneously into a substrate with controlled concentrations and compositions. In material design, it is essential to choose the right doping formula to achieve the desired property. This section summarizes the general properties and most common applications of individual rare-earth dopants in nanomaterial hosts.

2.1. Electronic Structures and Basic Properties

By definition, rare-earths are the 15 lanthanides (La–Lu) and 2 group IIIB elements (Sc and Y), all of which have a similar ground state electronic configuration. For Sc and Y, the ground state configurations are $[\text{Ar}]3d^14s^2$ and $[\text{Kr}]4d^15s^2$, respectively. For the 15 lanthanides, La, Ce, Gd, and Lu share the $[\text{Xe}]4f^{0-1}5d^16s^2$ configurations, while other lanthanides share $[\text{Xe}]4f^06s^2$ configurations (Figure 2). Although electrons in the 5s and 5p orbitals of lanthanides have lower energy than those in the 4f orbitals, the 5s and 5p orbitals are more dispersive than the 4f orbitals. Consequently, fully filled $5s^2$ and $5p^6$ closed subshells are still outside the 4f orbitals, resulting in weak shielding of the 4f electrons.⁴⁷

In similar $4f^{0-1}5d^16s^2$ or $4f^06s^2$ outer electron configurations, the two electrons on the 6s orbital and one electron on the 5d or 4f orbital of rare-earths are relatively easy to lose. As a result, rare-earths exhibit stable trivalent ionic states. Trivalent lanthanide ions from La^{3+} to Lu^{3+} have the same configuration $[\text{Xe}]4f^{0-1}$. This causes the ionic radius to decrease systematically across the lanthanide series, which is known as lanthanide contraction.⁴⁸ Therefore, the ionic radii fall into a small range across the lanthanide series, with the radius of Ho^{3+} being close to that of Y^{3+} (Table 1). This makes it possible to incorporate different rare-earth ions into a single-phase material, which is essential for the development of crystalline multicomponent materials with exciting and diverse properties.

Although the trivalent rare-earths are the most stable oxidation states, Ce^{4+} ($[\text{Xe}]4f^0$), Eu^{2+} ($[\text{Xe}]4f^7$), Tb^{4+} ($[\text{Xe}]4f^7$), and Yb^{2+} ($[\text{Xe}]4f^{14}$) can also be found in certain compounds. This is because the electronic states involving empty ($4f^0$), half-filled ($4f^7$), and fully filled ($4f^{14}$) 4f orbitals are more stable than other configurations. In addition, the thermochemical properties of lanthanide elements also contribute significantly to the stability of their oxidation states.

Another attractive property of rare-earths in doped nanomaterials is their narrow-band optical absorption and emission originating from intra-atomic 4f–4f electron transitions. Due to the shielding effect of the 5s and 5p electrons, the 4f electrons are not directly involved in bonding with surrounding molecules. Therefore, emission energies from 4f–4f transitions are rather stable to environmental changes and exhibit quasi-atomic behavior. When a lanthanide ion is doped into a crystal

lattice, its 4f–4f transition energies retain almost the same as those of the corresponding free ion.

Moreover, most trivalent lanthanides are paramagnetic in the ground state, with the exception of La^{3+} and Lu^{3+} , which are diamagnetic. This discrepancy is attributed to unpaired 4f electrons. The shielding effect also makes the magnetic moments of lanthanides independent of the coordination environment. Rare-earths generally exhibit strong spin–orbital coupling and weak ligand-field splitting, leading to zero-field splitting and magnetic anisotropy in given crystals. This characteristic property has driven the development of rare-earth permanent magnetic materials. In nanomaterials research, rare-earth-doped paramagnetic nanomaterials have been widely used as contrast agents in magnetic resonance imaging (MRI).

2.2. Characteristic Properties

In this section, we summarize the characteristic properties (optical, magnetic, and catalytic) of each rare-earth ion and their main applications in doped nanomaterials.

2.2.1. Sc^{3+} , Y^{3+} , La^{3+} , and Lu^{3+} . Sc^{3+} and Y^{3+} have no 4f electrons, while the 4f orbitals of La^{3+} and Lu^{3+} are either empty or completely filled. These ions have no unpaired 4f electrons and are all diamagnetic and free of 4f–4f transition-based photoluminescence. Therefore, these four ions are ideal host cations for lanthanide doping to achieve luminescence and magnetic modulation. Indeed, many nanomaterials are based on these cations, such as rare-earth fluorides, alkaline rare-earth oxyhalides, rare-earth oxysulfides, rare-earth oxides, and alkaline rare-earth fluorides.

Rare-earth ions can also act as Lewis acids and catalyze organic synthesis. For instance, La^{3+} ions have been doped into nanostructured catalysts to enhance their photocatalytic activity toward organic pollutants by reducing bandgaps, trapping photoinduced electrons, and suppressing electron–hole recombination.⁵¹ In addition, nanometric La–Na–Cu–O perovskite-like complex oxides have been shown to be effective in removing soot and simultaneously accelerating NO_x reactions.⁵² Lu^{3+} ions have been doped into CeO_2 to oxidize soot and incorporated into Ni to produce carbon nanotubes.^{53,54}

2.2.2. Ce^{3+} and Ce^{4+} . Owing to its allowed 4f–5d transition, Ce^{3+} can be efficiently excited by UV photons.⁵⁵ The luminescence of Ce^{3+} ions usually shows a tunable emission band in the UV-blue region, depending on the crystal structures of host materials.⁵⁶ Compared to the parity forbidden 4f–4f transitions of other rare-earth ions, the 4f–5d transition of Ce^{3+} is markedly efficient with a much larger absorption coefficient. Therefore, Ce^{3+} ions in many doped luminophores serve as sensitizers to absorb UV excitation and transfer energy to other lanthanide ions (Pr^{3+} , Sm^{3+} , Dy^{3+} , Eu^{3+} , and Tb^{3+}) for luminescence.^{57–59} Ce^{4+} ions have no emission or absorption in the visible spectral region.

The experimental magnetic moment of Ce^{3+} is $2.4 \mu_B$, whereas Ce^{4+} has no magnetic moment. However, Ce^{3+} and Ce^{4+} can coexist in some hosts. Unlike bulk paramagnetic CeO_2 materials, nanostructured CeO_2 materials are ferromagnetic.^{60,61} Ferromagnetism is thought to arise from exchange interactions between unpaired 4f electrons of Ce^{3+} and oxygen vacancies on nanostructured surfaces.^{62,63} Ce^{3+} -doped BiFeO_3 nanoparticles exhibit weak ferromagnetism at room temperature, while undoped BiFeO_3 counterparts display antiferromagnetic behavior.⁶⁴ In Ce^{3+} -doped BiFeO_3 nanoparticles, the

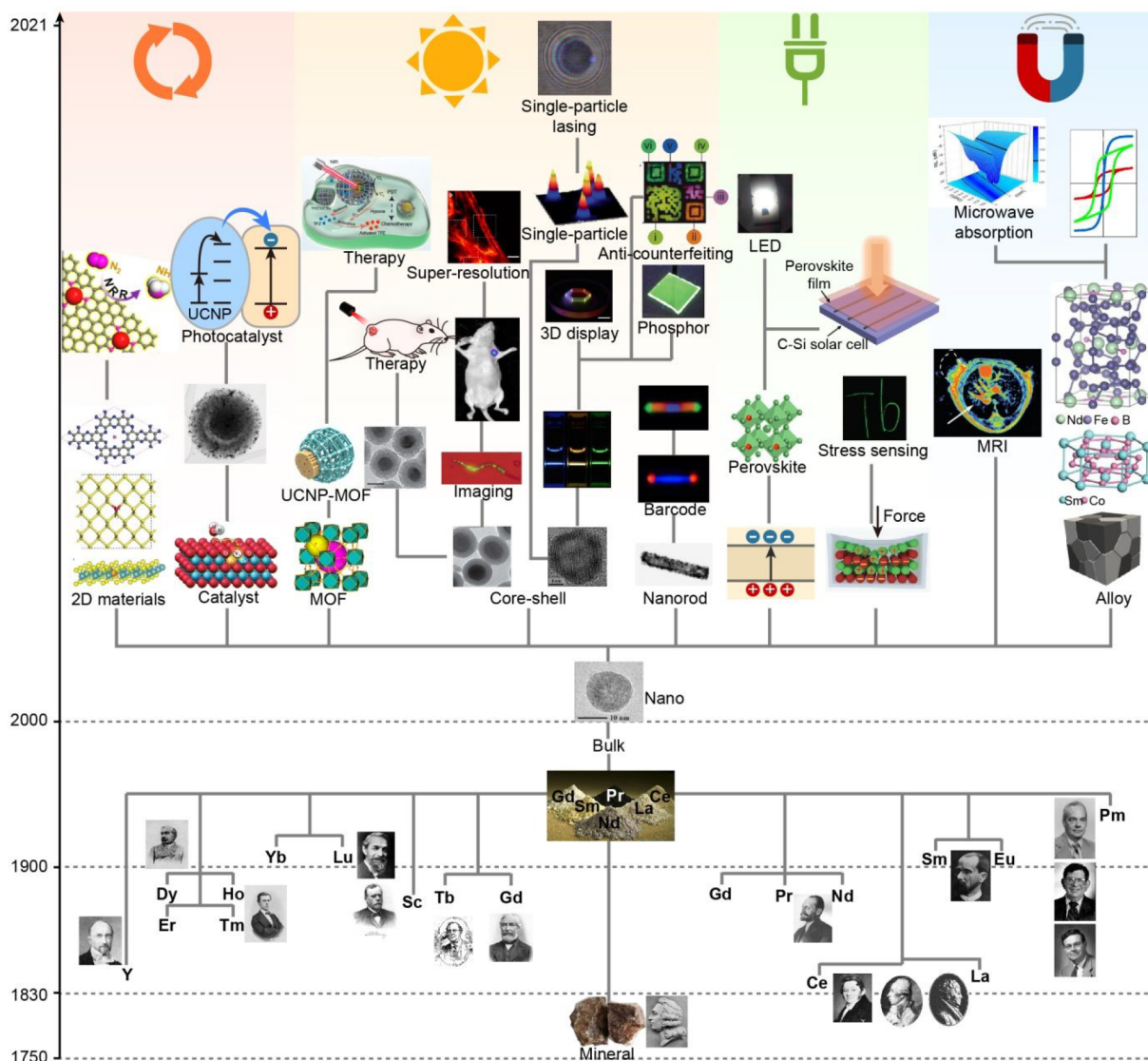


Figure 1. Development and application of rare-earth-based nanomaterials. The history of rare-earths begins with the discovery of rare-earth minerals and their separation and purification by scientists. Since the advent of nanotechnology, doping of rare-earths in nanomaterials of different morphology and composition has enabled many technological applications (Adapted with permission from refs 16–46. Copyright 2006, 2012, 2013, 2017, 2018, 2019, 2020 American Chemical Society; Copyright 2016 The Owner Societies; Copyright 2006, 2016 The Royal Society of Chemistry; Copyright 2019 AIP Publishing; Copyright 2015, 2016, 2017, 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2020 American Association for the Advancement of Science; Copyright 2012, 2015, 2017, 2018, 2020 Nature Publishing Group; Copyright 2012 The Royal Society of Chemistry; Copyright 2005 Elsevier Ltd.; Copyright 2021 the Partner Organisations; Copyright 2018 IOP Publishing Ltd.).

collapse of the cycloidal spin structure of BiFeO_3 caused by doping and the size effect leading to increased uncompensated surface spins contribute to the ferromagnetism. In Ce^{3+} -doped SnO_2 nanofibers, the room-temperature ferromagnetism is believed to arise from strong coupling between the f electrons of Ce^{3+} and the s electrons of the SnO_2 host.⁶⁵

Among rare-earth-doped materials, Ce-based compounds, especially CeO_2 , are widely used for catalysis. Nanostructured CeO_2 has been used as a primary or auxiliary catalyst in various catalytic oxidations, such as soot combustion,^{53,66,67} three-way catalysis,⁶⁸ conversion of CO ,^{69,70} steam reforming of methane,⁷¹ selective oxidation of organic molecules,^{72,73} and water–gas shift reaction.⁷⁴ Ce undergoes rapid redox/oxidation cycling between Ce^{3+} and Ce^{4+} states. This enables the local storage/release of oxygen in Ce-based compounds and influences catalytic reactions through synergistic effects.⁷⁴ In bioapplications, CeO_2 nanoparticles have also been used as

nanoenzymes that mimic the function of biological enzymes, such as superoxide dismutase and catalase.⁷⁵

2.2.3. Pr^{3+} . Pr^{3+} has the ground state $^3\text{H}_4$ and the main excited states $^3\text{P}_0$, $^1\text{D}_2$, and $^1\text{G}_4$. Pr^{3+} typically shows blue emission at ~ 483 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition),⁷⁶ orange emission at ~ 610 nm ($^3\text{P}_0 \rightarrow ^3\text{H}_6$ and $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transitions),^{77,78} and red emission at ~ 643 nm ($^3\text{P}_0 \rightarrow ^3\text{F}_2$ transition).⁷⁹ Although the $^3\text{P}_0 \rightarrow ^3\text{H}_5$ and $^3\text{P}_0 \rightarrow ^3\text{F}_{3,4}$ transitions can also be detected with emission at ~ 540 and ~ 725 nm, respectively, their emission intensities are usually relatively weak.^{80,81}

In addition to the radiative relaxation paths, Pr^{3+} in combination with Yb^{3+} can be used for downconversion emission, also called quantum cutting, because the $^1\text{G}_4$ intermediate state of Pr^{3+} and the $^2\text{F}_{5/2}$ state of Yb^{3+} are almost at the same level. During the process, a high-energy photon from the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} splits into two

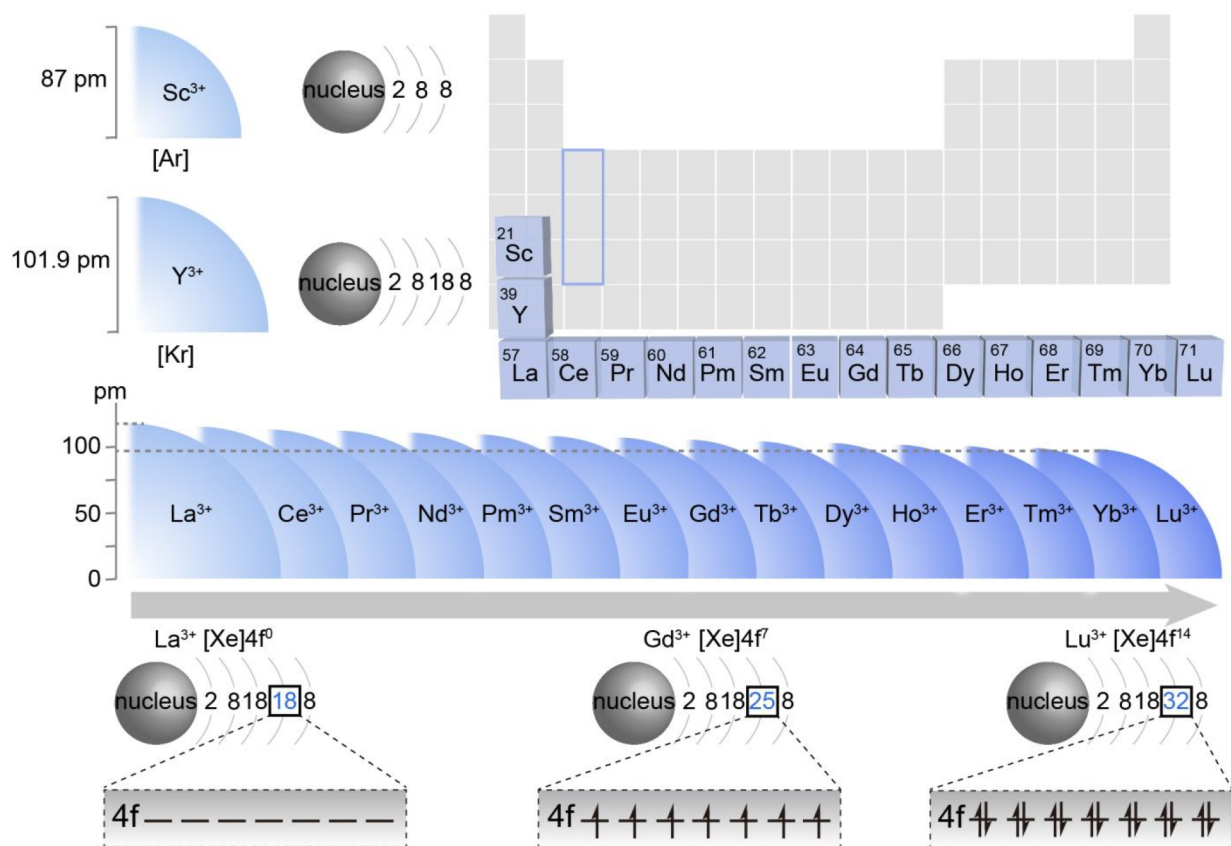


Figure 2. Ionic radius and valence configuration of rare-earths. From La^{3+} to Lu^{3+} , the number of electrons on the 4f orbitals increases with increasing atomic number. The electron configurations of La^{3+} , Gd^{3+} , and Lu^{3+} show empty, half-filled, and completely filled 4f orbitals, respectively.

Table 1. Basic Properties of Rare-Earth Elements

atomic number (Z)	name	symbol	ground state configuration	metal radius (pm) ^a	electron configuration of RE^{3+}	ionic radius (pm) ^b +2	+3	+4	application
21	scandium	Sc	$[\text{Ar}]3d^14s^2$	164.06	$[\text{Ar}]$	/	87	/	host material; catalysis; magnet; ferroelectricity; piezoelectricity
39	yttrium	Y	$[\text{Kr}]4d^15s^2$	180.12	$[\text{Kr}]$	/	101.9	/	host material; catalysis; ferrimagnetism; superconductivity; ferroelectricity
57	lanthanum	La	$[\text{Xe}]5d^16s^2$	187.91	$[\text{Xe}]4f^0$	/	116	/	host material; catalysis; superconductivity
58	cerium	Ce	$[\text{Xe}]4f^15d^16s^2$	182.47	$[\text{Xe}]4f^1$	/	114.3	97	sensitizer; catalysis; ferromagnetism
59	praseodymium	Pr	$[\text{Xe}]4f^36s^2$	182.79	$[\text{Xe}]4f^2$	/	112.6	96	quantum cutting; ferromagnetism; catalysis
60	neodymium	Nd	$[\text{Xe}]4f^46s^2$	182.14	$[\text{Xe}]4f^3$	129	110.9	/	sensitizer; down conversion
61	promethium	Pm	$[\text{Xe}]4f^56s^2$	181.10	$[\text{Xe}]4f^4$	/	109.3	/	radioactive
62	samarium	Sm	$[\text{Xe}]4f^66s^2$	180.41	$[\text{Xe}]4f^5$	127	107.9	/	magnetism; catalysis
63	europium	Eu	$[\text{Xe}]4f^76s^2$	204.18	$[\text{Xe}]4f^6$	125	106.6	/	downconversion; catalysis; phosphor
64	gadolinium	Gd	$[\text{Xe}]4f^75d^16s^2$	180.13	$[\text{Xe}]4f^7$	/	105.3	/	host material; MR imaging; magnetism; catalysis
65	terbium	Tb	$[\text{Xe}]4f^96s^2$	178.33	$[\text{Xe}]4f^8$	/	104	88	upconversion; phosphor; ferromagnetism
66	dysprosium	Dy	$[\text{Xe}]4f^{10}6s^2$	177.40	$[\text{Xe}]4f^9$	119	102.7	/	MR imaging; ferromagnetism; catalysis
67	holmium	Ho	$[\text{Xe}]4f^{11}6s^2$	176.61	$[\text{Xe}]4f^{10}$	/	101.6	/	upconversion; MR imaging
68	erbium	Er	$[\text{Xe}]4f^{12}6s^2$	175.66	$[\text{Xe}]4f^{11}$	/	100.4	/	upconversion; photocatalysis; MR imaging; NIR II imaging
69	thulium	Tm	$[\text{Xe}]4f^{13}6s^2$	174.62	$[\text{Xe}]4f^{12}$	/	99.4	/	upconversion; photocatalysis
70	ytterbium	Yb	$[\text{Xe}]4f^{14}6s^2$	193.92	$[\text{Xe}]4f^{13}$	114	98.5	/	sensitizer; MR imaging; NIR imaging
71	lutetium	Lu	$[\text{Xe}]4f^{14}5d^16s^2$	173.49	$[\text{Xe}]4f^{14}$	/	97.7	/	host material

^aWith a coordination number of 12. ^bWith a coordination number of 8.^{49,50}

low-energy photons from the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb^{3+} by energy transfer, resulting in a photoluminescence quantum yield of 200%.^{82,83}

Pr^{3+} ion with a magnetic moment of $3.5 \mu_B$ has been used to tune antiferromagnetic hosts, such as BiFeO_3 , from magnetic

to ferromagnetic.^{84,85} Pr(OH)₃ nanowire bundles exhibit ferromagnetic behavior at room temperature.⁸⁶

Pr₆O₁₁ can enhance the catalyst performance for ethanol electrooxidation.⁸⁷ Pr³⁺ ions can be incorporated as aliovalent dopants in a CeO₂ host to introduce oxygen vacancies and thus improve the oxygen storage capacity and catalytic properties of the hosts.⁸⁸ Doping semiconductor hosts, such as TiO₂ and CdSe, with Pr³⁺ ions in can also enhance the photocatalytic activity of these semiconductors.^{89,90}

2.2.4. Nd³⁺. Upon energy absorption, Nd³⁺ ions in the ground state (⁴I_{9/2}) can be excited to the ²P_{1/2} and ⁴G_{7/2} states. Nd³⁺ typically emits at approximately 413 nm (²D_{5/2}, ²P_{1/2} → ⁴I_{9/2} transitions), 523 nm (⁴G_{7/2}, ²K_{13/2}, ⁴G_{9/2} → ⁴I_{9/2} transitions), 588 nm (²G_{7/2}, ²G_{5/2} → ⁴I_{9/2} transitions), 640 nm (²H_{11/2} → ⁴I_{9/2} transition), 661 nm (⁴F_{9/2} → ⁴I_{9/2} transition), 869–900 nm (⁴F_{3/2} → ⁴I_{9/2} transition), 1060 nm (⁴F_{3/2} → ⁴I_{11/2} transition), and 1330 nm (⁴F_{3/2} → ⁴I_{13/2} transition).^{91–93} Nd³⁺ is usually used for its efficient NIR emission at ~1060 nm when excited at 740 or 800 nm.⁹¹ Since both the excitation and emission are within the optical window (700–1100 nm), Nd³⁺-doped nanoparticles are ideal NIR nanophosphors for biological imaging.⁹⁴

In addition to downshifting emission, Nd³⁺ can be employed to upconvert luminescence. Given its relatively large absorption coefficient of the ⁴I_{9/2} → ⁴F_{5/2} transition, Nd³⁺ can serve as sensitizers in Yb³⁺/Er³⁺, Yb³⁺/Tm³⁺, or Yb³⁺/Ho³⁺-codoped upconversion systems under 800 nm excitation.^{31,93,95,96} With rationally designed core–shell structures, upconversion emission of Nd³⁺ can be achieved at ~382 nm (⁴D_{3/2} → ⁴I_{11/2} transition) and at ~413 nm (⁴D_{3/2} → ⁴I_{13/2} transition).⁹⁷

Nd–Fe–B-based compounds are among the most prominent rare-earth permanent magnets and have captured a large portion of the global market share.⁹⁸ Nanosized Nd–Fe–B compounds, such as Nd₂Fe₁₄B nanoparticles, have been prepared using a sol–gel method.⁹⁹ These magnetic nanoparticles have potential applications in ferrofluids, coolants, high-density information storage, and biomedicine.¹⁰⁰

Nd³⁺ ions have been doped into wide bandgap semiconductors, such as TiO₂,¹⁰¹ and ZnO,¹⁰² to make them available for visible-light photocatalysis.¹⁰³ In some cases, Nd³⁺ can be directly excited and acts as an electron sink to improve the catalytic performance by suppressing electron–hole recombination in photocatalysts.¹⁰⁴ Beyond photocatalysts, Nd³⁺ has been doped into nanostructured hosts to impart novel catalytic activities for various applications, including selective hydrogenation,¹⁰⁵ CO conversion,¹⁰⁶ and asymmetric nitroaldol reactions.^{107,108}

2.2.5. Pm³⁺ and Sm³⁺. Promethium is radioactive and can be used for applications such as radiotherapy, but current studies on Pm³⁺-related nanomaterials are rather limited. For this reason, we will focus only on Sm³⁺ in this subsection.

Sm³⁺ has the ground state ⁶H_{5/2} and a well-utilized excited state ⁴G_{5/2}. Typical emissions from excited Sm³⁺ are ⁴G_{5/2} → ⁶H_{5/2} at ~566 nm, ⁴G_{5/2} → ⁶H_{7/2} at ~602 nm, ⁴G_{5/2} → ⁶H_{9/2} at ~649 nm, and ⁴G_{5/2} → ⁶H_{11/2} at ~728 nm.^{109–111} Sm³⁺ is mainly used as a downshifting emitter for red/orange emission.

Due to the exchange interaction between the conduction electrons of transition metals and the local spin-polarized electrons of Sm,¹¹² a transition metal–Sm alloy, such as Co–Sm, is one of the best known permanent magnets at room temperature and is widely used for high-density magnetic recording and energy storage. In nanomaterials, Sm–Co

nanoparticles (e.g., Sm₂Co₁₇ and SmCo₅) exhibit size-dependent magnetic properties.¹¹³ Sm³⁺ ions have been used to enhance the magnetization of BiFeO₃ nanosubstrates.⁶¹

Sm³⁺ has been doped into nanostructured catalysts, such as manganese ferrite,¹¹⁴ zinc spinel ferrite,¹¹⁵ perovskite bismuth ferrite,¹¹⁶ and TiO₂,¹¹⁷ to enhance the photocatalytic activity toward organic pollutants by narrowing the bandgap, trapping photoinduced electrons, and suppressing the recombination of electrons and holes. Considering the UV-absorbing ability of Sm³⁺, several Sm compounds, such as Sm(OH)₃,¹¹⁸ can also serve as photocatalysts for photodegradation reactions.

2.2.6. Eu³⁺ and Eu²⁺. Eu³⁺ has a ground state of ⁷F₀ and excited states of ⁵D_J (J = 0–3). It is the most common dopant used to achieve red emission. Typical emission bands of Eu³⁺ are ⁵D₂ → ⁷F₃ at ~510 nm, ⁵D₁ → ⁷F₁ at ~536 nm, ⁵D₁ → ⁷F₂ at ~555 nm, ⁵D₁ → ⁷F₃ (⁵D₀ → ⁷F₀) at ~584 nm, ⁵D₀ → ⁷F₁ at ~591 nm, ⁵D₀ → ⁷F₂ at ~615 nm (most intense), ⁵D₀ → ⁷F₃ at ~645 nm, and ⁵D₀ → ⁷F₄ at ~696 nm.^{110,119,120}

Eu³⁺ is paramagnetic at room temperature. Although its ⁷F₀ ground state is diamagnetic, the experimental magnetic moment of Eu³⁺ at room temperature is around 3.4 μ_B, which is due to the close proximity of the ⁷F₁ and ⁷F₂ states. Doping of Eu³⁺ in nanosized barium hexaferrite enhances superexchange interactions and magnetocrystalline anisotropy, which increases the saturation magnetization and coercivity of the doped sample.¹²¹ Eu³⁺ ions have been doped in Bi₂WO₆, ZnO, MoO₃, YVO₄, Bi₂S₃, and TiO₂ to promote catalytic activity toward organic molecules.^{122–127}

Eu²⁺ ions are commonly used as inorganic luminophores for blue–green emission arising from the 4f⁶5d¹ → 4f⁷ transition.¹²⁸ The ionic radius of Eu²⁺ is around 17% larger than that of Eu³⁺, which makes difficult to incorporate a large amount of Eu²⁺ into many host materials that can accommodate trivalent RE³⁺ at high doping concentrations. Typical nanomaterials for Eu²⁺ include SrAl₂O₄, CaS, and Sc₂O₃.^{129–132} Another interesting property of Eu²⁺ is its persistent luminescence when codoped with other lanthanides, such as Dy³⁺, Ce³⁺, and Tm³⁺.^{133,134}

2.2.7. Gd³⁺. The energy levels of Gd³⁺ ions have been studied in great detail. By virtue of the large energy gap between the ⁸S_{7/2} ground state and the ⁶P_{7/2} first excited state (~32 000 cm^{−1}), direct excitation of Gd³⁺ ions to the ⁶P_{7/2} state can be achieved by UV irradiation at ~310 nm. Due to the relatively high energy of the ⁶P_{7/2} state, excited Gd³⁺ ions can serve as an energy reservoir to realize energy migration-mediated emission of other activators.¹³⁵ Typical emissions of excited Gd³⁺ ions include ⁶D_J → ⁸S_{7/2} (J = 1/2, 3/2, 5/2, 7/2) at 246 nm, ⁶D_{9/2} → ⁸S_{7/2} at 253 nm, ⁶I_J → ⁸S_{7/2} (J = 7/2–15/2) at ~270–281 nm, ⁶P_{5/2} → ⁸S_{7/2} at ~305 nm, ⁶P_{7/2} → ⁸S_{7/2} at ~311 nm (particularly intense).^{136,137} NaGdF₄ nanocrystals are excellent host materials for doping lanthanide emitters with emissions in the visible or NIR region. In some cases, Gd³⁺ can be used as a sensitizer to facilitate the emission of Eu³⁺, Tb³⁺, Dy³⁺, and Sm³⁺ ions through energy migration.¹³⁵

Gd³⁺ has a highly symmetric ground state with seven unpaired 4f electrons and the largest magnetic moment of any lanthanide. Accordingly, this ion is strongly paramagnetic. Gd³⁺-containing nanomaterials, such as NaGdF₄, Gd₂O₃, GdF₃ and GdPO₄, are the most efficient positive contrast agents (T₁), widely used in magnetic resonance imaging.^{138–142} Gd₂O₃ and Gd₂BaNiO₅ nanoparticles have also found potential applications in cryomagnetic refrigeration due to their magnetocaloric effect.^{62,143} KGdF₄ nanoparticles have

been reported to exhibit temperature-dependent magnetic properties: paramagnetic at 300 K and superparamagnetic at 2 K.¹⁴⁴

Gd₂O₃ nanorods show high catalytic activity for the conversion of CO even at a low temperature of 100 °C.¹⁴⁵ Gd³⁺ has also been doped into semiconducting nanomaterials, such as TiO₂ and CdSe, to enhance the photocatalytic capacity.^{146–148} Gd(OH)₃ nanorods can support Pd nanoparticles for hydrogenation or serve as main catalysts for Cr(VI) photoreduction in water.^{149,150} When Gd³⁺ or Gd₂O₃ are doped into ZSM-5 zeolite catalysts, the coking effect, which blocks active sites and deactivates the catalysts, is effectively suppressed, making the composite catalysts coke-compatible and having a long service life.^{151–153} Gd₂O₃ and Gd(OH)₃ nanorods exhibit peroxidase-like enzyme activity.¹⁵⁴ Gd₂O₃ nanoparticles have also been used as catalysts for the electrochemical reduction of CO₂ to CO.¹⁵⁵

2.2.8. Tb³⁺. Tb³⁺ is a highly efficient green emitter in rare-earth-doped luminophores. Energy transitions from the excited states ⁵D₃/⁵D₄ to the ground state ⁷F₆ are mainly investigated in Tb³⁺-doped phosphors. Typical emissions from excited Tb³⁺ are ⁵D₃ → ⁷F₆ at ~380 nm, ⁵D₃ → ⁷F₅ at ~414 nm, ⁵D₃ → ⁷F₄ at ~435 nm, ⁵D₄ → ⁷F₆ at ~486 nm, ⁵D₄ → ⁷F₅ at ~541 nm (most intense), ⁵D₄ → ⁷F₄ at ~587 nm, and ⁵D₄ → ⁷F₃ at ~622 nm.¹⁵⁶ Nanoparticles codoped with Ce³⁺/Tb³⁺ show a strong downward shift in the luminescence of Tb³⁺ under UV excitation.¹⁵⁷ Tb³⁺ can also be coupled with Yb³⁺ to generate upconversion emission through a Yb-assisted cooperative process under 980 nm excitation.^{156,158} Moreover, Tb³⁺/Yb³⁺-encoded systems are known to exhibit downconversion photoluminescence. When Tb³⁺ is excited with a high energy visible photon, two NIR photons from Yb³⁺ can be emitted by energy transfer from one Tb³⁺ ion to two Yb³⁺ ions.¹⁵⁹

Tb³⁺ is paramagnetic at room temperature and has a magnetic moment of 9.5 μ_B. Tb³⁺ has been frequently used to tune the magnetic behavior of nanomaterials. For example, Tb³⁺ can impart paramagnetic properties to nanostructured diamagnetic hosts, such as ZnS.¹⁶⁰ ZnO:Tb³⁺ nanorod bundles have been reported to exhibit superparamagnetism at room temperature and ferromagnetism at 5 K.¹⁶¹ ZnO:Tb³⁺ nanoparticles with an average size of less than 20 nm also possess ferromagnetism at room temperature.¹⁶² Compared to undoped nanoparticles, multiferroic BiFeO₃ nanoparticles doped with Tb³⁺ exhibit increased magnetic saturation.¹⁶³ Doping Nd₂Fe₁₄B with Tb³⁺ ions increases the coercivity due to the higher anisotropy field when Nd³⁺ is partially replaced by Tb³⁺.¹⁶⁴ It has been reported that Tb₂O₃ nanoparticles exhibit ferromagnetism at 5 K.¹⁶⁵

When Tb³⁺ is doped into a Pd-containing catalyst, it tends to lose electrons and reduce Pd ions to Pd metals, which improves the performance of Pd-based catalysts.¹⁶⁶ In ethanol electrooxidation, doping with Tb³⁺ can increase the adsorption of OH[−], which enhances the catalytic activity of the Pb–Tb composite.¹⁶⁷ Furthermore, when doping Ca₂Ta₃O₁₀ nanocrystals, Tb³⁺ can stabilize the charge separation state, which benefits the catalytic activity of the main catalyst for hydrogen production from water.¹⁶⁸ Tb³⁺ ions have also been doped into semiconductors such as ZrO₂ to promote photocatalytic degradation of organic molecules.¹⁶⁹

2.2.9. Dy³⁺. Dy³⁺ with ground state ⁶H_{15/2} shows efficient emission due to transitions between I and F levels. There are two intense emissions of Dy³⁺: ⁴F_{9/2} → ⁶H_{15/2} at ~480 nm and ⁴F_{9/2} → ⁶H_{13/2} at ~570 nm.¹⁷⁰ There are also two less intense

emissions: ⁴F_{9/2} → ⁶H_{11/2} at ~673 nm and ⁴F_{9/2} → ⁶H_{9/2} at ~756 nm.^{171,172} Dy³⁺ has a high magnetic moment due to its unpaired 4f electrons. Dy³⁺-doped ZnO nanoparticles exhibit tunable ferromagnetism at room temperature, which depends on the concentration of Dy³⁺ dopants.¹⁷³ Many Dy³⁺-based nanoparticles, including DyF₃, NaDyF₄, and Dy₂O₃, have been employed as T₂ contrast agents for MRI.^{174–176}

Dy₂O₃ nanorods are efficient catalysts for the conversion of CO.¹⁴⁵ Dy³⁺ dopants facilitate the separation of electron and hole pairs in Bi₂MoO₆ or ZnO host materials and improve their photocatalytic performance.^{177–179} Dy₂O₃ nanoparticles can be used as catalysts for the electrocatalytic reduction of CO₂.¹⁵⁶ Dy³⁺ has also been doped in chitosan as a nanocatalyst for the synthesis of hexahydropyrimidine derivatives.¹⁸⁰

2.2.10. Ho³⁺, Er³⁺, and Tm³⁺. Ho³⁺, Er³⁺, and Tm³⁺ are best known in the lanthanide series for their upconversion properties. These three ions all have ladder-like, well-ordered energy levels with almost uniformly distributed energy gaps between adjacent levels. Since their energy gaps resemble the ²F_{5/2} → ²F_{7/2} transition of Yb³⁺, ion pairs of Er³⁺–Yb³⁺, Tm³⁺–Yb³⁺, and Ho³⁺–Yb³⁺ can achieve efficient energy transfer upconversion with the Yb³⁺ ion as the sensitizer.¹¹

Ho³⁺ has a ground state of ⁵I₈ and exhibits excited states of ⁵F₄, ⁵F₅, and ⁵I₆. Typical emissions include ⁵F₄ → ⁵I₈ at ~525 nm, ⁵F₅ → ⁵I₈ at ~650 nm, and ⁵I₆ → ⁵I₈ at ~1150 nm.¹⁸¹ Ho³⁺-doped nanoparticles such as HoF₃ and NaHoF₄ exhibit much larger r₂ than r₁, making them promising candidates as T₂ MRI contrast agents.^{174,182} Ho³⁺ ions have also been doped into TiO₂ and ZnO to enhance their catalytic activity.^{183,184}

Besides the direct doping strategy, YF₃:Ho@TiO₂ core–shell nanoparticles have been prepared to facilitate visible absorption by upconversion of Ho³⁺.¹⁸⁵ Moreover, Ho³⁺ ions have been used to prepare bimetallic Ni/Ho catalysts for the synthesis of carbon nanotubes.¹⁸⁶

Er³⁺ has a ground state of ⁴I_{15/2} and features excited states of ²H_{9/2}, ²H_{11/2}, ⁴S_{3/2}, and ⁴F_{9/2} as the most useful excited states. Typical emissions are ²H_{11/2} → ⁴I_{15/2} at ~525 nm, ⁴S_{3/2} → ⁴I_{15/2} at ~546 nm, ⁴F_{9/2} → ⁴I_{15/2} at ~660 nm, ²H_{9/2} → ⁴I_{15/2} at ~410 nm, and ⁴I_{13/2} → ⁴I_{15/2} at ~1550 nm.^{181,187} The emission of ⁴I_{13/2} → ⁴I_{15/2} at ~1550 nm is interesting due to its transparency in biological tissue.¹⁸⁸ Moreover, Er³⁺ can be used as a sensitizer for excitation at 1550 nm to achieve upconversion emission from Er³⁺ alone¹⁸⁹ or from other lanthanides (e.g., Yb³⁺, Ho³⁺, Tm³⁺).^{190,191}

Due to its large intrinsic magnetic moment, NaErF₄ nanomaterials have been used as T₂ contrast agents for magnetic resonance imaging.¹⁹² Doping of ZnO nanostructures with Er³⁺ ions leads to magnetic transition from diamagnetism to ferromagnetism at room temperature.¹⁹³ Pure NaErF₄ nanocrystals have been shown to be effective contrast agents for T₂-weighted magnetic resonance imaging.¹⁹⁴ BiFeO₃ nanoparticles doped with Er³⁺ exhibit enhanced ferromagnetism compared to undoped BiFeO₃.¹⁹⁵

Er³⁺ ions have been doped into semiconductors, such as TiO₂, In₂O₃, Bi₂WO₆, ZnO, PbSe, ZnS, and ZnSe, to improve their catalytic performance.^{196–202} When Er³⁺ was codoped with Yb³⁺, the enhanced upconversion process and energy transfer to the primary catalyst improved catalytic efficiency through NIR harvesting.²⁰³ NaYF₄:Er nanoparticles served as a cataluminescent sensor for ketones.²⁰⁴ Er(OH)₃ nanoparticles served as a catalyst for the photocatalytic reduction of Cr(VI) ions.²⁰⁵ When Er³⁺ was codoped with Yb³⁺ into fluorine-doped

tin oxides to fabricate counter electrodes in dye-sensitized solar cells, the overall cell efficiency was improved due to photocatalytic I^-/I_3^- circulation and accelerated I^- regeneration.²⁰⁶ Er_2O_3 nanorods showed high catalytic activity in the dehydration of 1,4-butanediol.²⁰⁷ Er^{3+} served as both catalyst and dopant in the preparation of optically active silica nanowires.²⁰⁸

Typical emissions of Tm^{3+} ions include $^1D_2 \rightarrow ^3H_4$ at ~ 359 nm, $^1D_2 \rightarrow ^3F_4$ at ~ 450 nm, $^1G_4 \rightarrow ^3H_6$ at ~ 477 nm, $^1G_4 \rightarrow ^3F_4$ at ~ 650 nm, $^3F_2 \rightarrow ^3H_6$ at ~ 695 nm, and $^3H_4 \rightarrow ^3H_6$ at ~ 800 nm.^{209,210} The transition from the 3H_4 to the 3H_6 manifold dominates the 800 nm emission at low pump powers, while the 800 nm emission at high-power excitation is likely due to the $^1G_4 \rightarrow ^3H_6$ transition. Research on the magnetic properties of Tm^{3+} -doped nanomaterials is still limited. As with other lanthanide ions, doping with Tm^{3+} causes nanoscale $BiFeO_3$ to exhibit ferromagnetic behavior.²¹¹

For catalytic applications, Tm^{3+} ions are usually codoped with Yb^{3+} into various inorganic host materials ($NaYF_4$, YF_3 , $NaLuF_4$, and $BiPO_4/BiVO_4$),^{212–217} which are then combined with TiO_2 or graphitic C_3N_4 to form nanocomposite catalysts.^{218,219} Through an upconversion process, composite catalysts can convert NIR light to ultraviolet or visible light and subsequently increase catalytic efficiency.^{220,221}

2.2.11. Yb^{3+} . Yb^{3+} has an electronic configuration of $[Xe]4f^{13}$ with only one unpaired electron, leading to a characteristic $4f-4f$ transition at ~ 980 nm. Owing to its efficient absorption and energy level matching Er^{3+} , Tm^{3+} , and Ho^{3+} emitters, Yb^{3+} effectively absorbs the excitation energy and transfers that energy to the intermediate energy levels of those emitters. Therefore, Yb^{3+} ions have been widely used as sensitizers and codoped with other lanthanides.²²² In addition, Yb^{3+} has been used as an emitter in conjugation with sensitizers such as Ce^{3+} , Pr^{3+} , Tb^{3+} , Tm^{3+} and Er^{3+} , for the downconversion of visible/UV to infrared light.^{40,223,224} On a separate note, Yb^{3+} can be used as a paramagnetic ion to develop $NaYbF_4$ -based T_2 -MRI contrast agents.²²⁵

The unique properties of individual rare-earth ions are determined by their electronic structures. Sc^{3+} , Y^{3+} , La^{3+} , and Lu^{3+} ions are optically and magnetically inert and are mainly employed as host cations for doping with metal ions. Although each rare-earth ion behaves differently, different rare-earth ions can be combined to form nanocrystals with controlled optical, electrical, and magnetic properties. This combination makes rare-earth-doped nanocrystals special and is the reason for their enormous potential, which has been tapped in recent decades. Furthermore, rare-earth dopants can undergo reversible valence changes (e.g., Ce^{3+}/Ce^{4+}) and improve the performance of nanocatalysts by modulating the electrical properties of the host lattice.

3. DOPING STRATEGIES

Doping, which enables one or more types of atoms or ions to be incorporated into a host material, has a long and distinguished history of imparting diverse properties to solids. In the past, metallic dopants such as iron (Fe^{2+} and Fe^{3+}), chromium (Cr^{3+}), cobalt (Co^{2+} and Co^{3+}), manganese (Mn^{2+} and Mn^{4+}), and copper (Cu^+ and Cu^{2+}) ions were employed to endow glass with vivid colors in the visible spectrum. Impurity doping also makes possible to control the transport of electrons and holes in semiconductors, which is the most critical concept of modern electronic and information technology. Rare-earths have become an important class of

dopants for glasses or crystalline materials to control optical, electrical, catalytic, and magnetic properties. In recent years, the advent of nanostructured materials, together with advances in chemical synthesis, has greatly expanded the scope of rare-earth doping. The precise incorporation of rare-earths can now be achieved in a broad spectrum of nanomaterials ranging from crystalline insulators and semiconductors to inorganic–organic hybrid materials, leading to many remarkable properties and functionalities.

3.1. Principal Factors in Doping

Rare-earth doping is often carried out simultaneously with the synthesis of host materials. Alternatively, doping can be performed by cation exchange on preformed substrates. In both cases, the effectiveness of doping is determined by the degree of chemical similarity between the host cations and the rare-earth dopants.

3.1.1. Ionic Size. Ionic size is determined by the distance between ions in different compounds.²²⁶ The crystal structure of an ionic compound is primarily dictated by the ratio of ionic radii of the cation and anion, as stable crystal structures are formed when a central cation is surrounded by a maximum number of anions in contact with each other. Therefore, the size of ions is one of the most critical parameters to be considered in the substitution of host cations by rare-earth dopants.

In general, ions of similar size can substitute for each other in a crystalline compound without any noticeable change in crystal structure. Because of the similar size of rare-earth ions (Table 1), most of their compounds can form complete solid solutions, allowing convenient doping with other rare-earth ions at arbitrary concentrations. For example, in an early study, Haase and co-workers doped $LaPO_4$ nanocrystals with 60 mol % Ce^{3+} and Tb^{3+} .²²⁷ The efficient luminescence process observed in these nanocrystals (QY > 60%) suggests that heavy doping has negligible deleterious effects. In recent years, heavy doping with rare-earths has been demonstrated in a variety of nanocrystals and hierarchical nanostructures, such as $NaYF_4$ and $NaGdF_4@NaYF_4$, which have become indispensable for achieving unprecedented luminescence phenomena.^{228–231}

Although rare-earth ions of similar size can replace one another over a considerable compositional range, extensive substitution of host cations can lead to significant changes in the thermodynamic properties of the crystal. For example, van Veggel and co-workers found that doping GdF_3 with 30 mol % La^{3+} can trigger a phase transformation from an orthorhombic to a trigonal structure that is thermodynamically more stable.²³² In another representative demonstration, Liu and co-workers observed simultaneous changes in the phase (cubic to hexagonal) and size (~ 30 to 10 nm) of $NaYF_4:Yb/Er$ nanocrystals after gadolinium doping, due to changes in the dipole polarizability and surface charge.²³³ According to density functional theory calculations, the substitution of Y^{3+} ions with Gd^{3+} increased the formation energy per atom by about 0.7 eV, indicating that $NaGdF_4$ is more energetically stable than $NaYF_4$ in the hexagonal phase. Moreover, the electron charge density of the crystal surface also increased after Gd^{3+} doping, which effectively enhanced charge repulsion and delayed the deposition of F^- on the crystal surface. These findings have inspired a versatile approach to controlling the nanocrystal formation of various nanomaterials, such as CaF_2 , $NaLuF_4$, $NaYbF_4$, In_2O_3 , and $ScOOH/Sc_2O_3$.^{234–240} For example, Yan and co-workers reported that doping a $NaYbF_4$

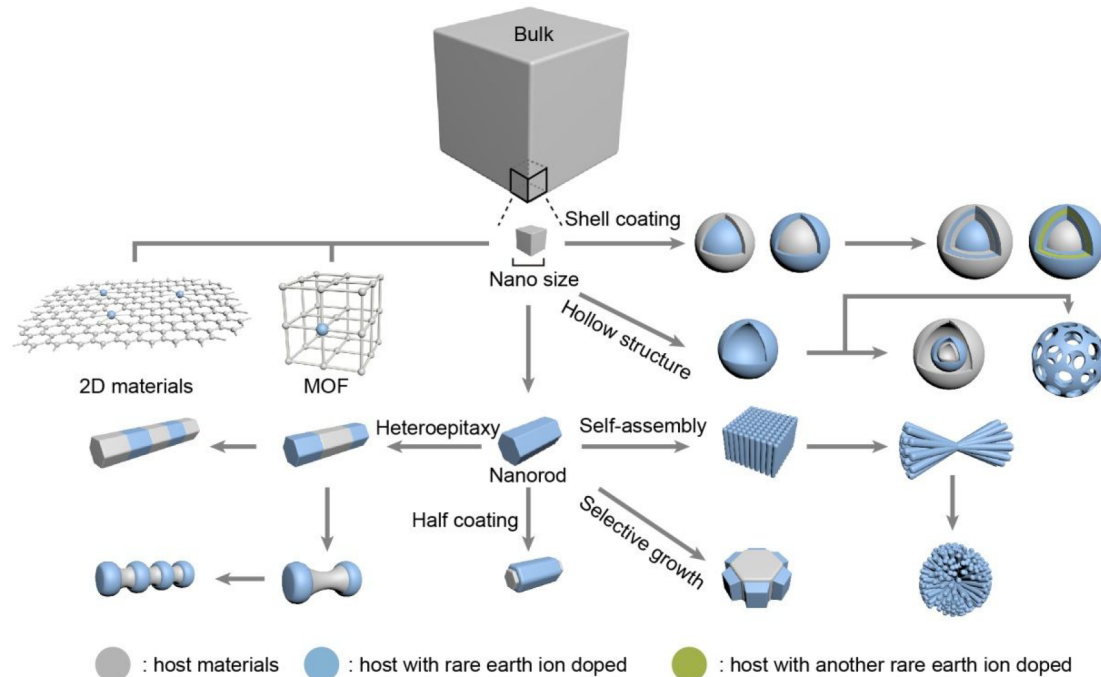


Figure 3. Selective doping of rare-earth ions in various nanomaterials via diverse strategies.

lattice with Gd^{3+} ions facilitates the phase transformation from cubic to hexagonal.²⁴¹ Furthermore, increasing the Gd^{3+} content decreases the average size of hexagonal $\text{NaYb}_{1-x}\text{Gd}_x\text{F}_4$ nanocrystals. Rare-earth dopants such as Dy^{3+} , Tb^{3+} , Eu^{3+} , Sm^{3+} , Nd^{3+} , Pr^{3+} , Ce^{3+} , and La^{3+} with larger radii than Yb^{3+} usually show similar effects to Gd^{3+} .²³³

Nevertheless, doped ions may not penetrate the host lattice if the size differences between the rare-earth dopant and the host cation are significant. In addition, rare-earth dopants are preferentially stabilized at cationic sites with high coordination numbers ($\text{CN} \geq 6$), such as octahedral sites ($\text{CN} = 6$) and cubic sites ($\text{CN} = 8$). However, for semiconductors with sphalerite, chalcopyrite, and wurtzite structures such as InP , CuInS_2 , ZnS , and CdSe , tetragonal coordination ($\text{CN} = 4$) is unfavorable for rare-earth doping because their cationic sites are too small to accommodate large dopants. Only a small percentage (typically less than 1 mol %) of rare-earth ions can be doped in these crystals, and most of the dopants are located on crystal surfaces.²⁴²

3.1.2. Valency. In general, it is easy to dope a rare-earth ion into an isovalent cation site, because the local structure of the host is least disturbed. However, the valences of the dopant and the substituted host cation are not necessarily identical. For instance, rare-earth ions, although unfavorable, can be doped into CdS and CdSe at divalent cationic sites.^{243,244} Aliovalent substitution often introduces point defects to maintain charge neutrality. Typical charge balancing defects include interstitial ions and vacancies.²⁴⁵

Compounds such as CaF_2 and SrF_2 with large cationic sites and a high coordination environment ($\text{CN} = 8$) are excellent candidates for rare-earth dopant incorporation.^{246–248} However, due to charge balancing and the associated local lattice distortion, the upper limit of the dopant concentration can be reduced. For example, the ion sizes of Ca^{2+} and Eu^{3+} are relatively close (1.12 vs 1.07 Å). Due to the intercalation of interstitial F^- ions, the CaF_2 host typically takes up less than 20

mol % Eu^{3+} dopants.²⁴⁹ Further increasing the dopant concentration requires careful control of experimental variables.²⁵⁰

3.1.3. Reactivity. In order to penetrate the host lattice and form stable substitutes, rare-earth dopants must have similar reactivity to the host cations. A large difference in chemical reactivity leads to the exclusion of ions that are not in equilibrium from the crystal lattice. For example, halides are less reactive with rare-earths than with lead. Accordingly, the substitution of Pb^{2+} by rare-earth ions in perovskite crystals such as CsPbBr_3 is characterized by low doping efficiency despite the small differences in ion size. In the wet chemical synthesis of $\text{CsPbBr}_3:\text{Ce}$ nanocrystals, the actual doping ratio of Ce^{3+} was 2.88%, as opposed to a 30% reaction ratio, corresponding to a relatively low doping efficiency of about 10%.²⁵¹ A similar mechanism could apply to the ineffective incorporation of rare-earth ions into Bi-based hosts such as Bi_2S_3 .²⁵²

3.1.4. Doping in Nanostructures. Unlike doped bulk materials, rare-earth doping in nanoscale crystals is not limited to single-phase materials. The development of nanostructures with various dimensions and shapes (e.g., nanoparticles, nanoplates, nanosheets, nanorods, nanowires, and irregular nanostructures) has allowed researchers to spatially limited doping sites to a few nanometers, enabling diverse strategies for multicomponent dopant incorporation (Figure 3).

For example, doped nanoparticles can be fabricated with core–shell architectures in which different dopants are incorporated into the inner core and the outer shell. One example is the synthesis of $\text{NaYF}_4:\text{Yb}/\text{Er}@\text{NaYF}_4$ and $\text{NaGdF}_4:\text{Yb}/\text{Tm}@\text{NaGdF}_4$ upconversion nanoparticles (UCNPs), in which the active Yb^{3+} , Er^{3+} , and Tm^{3+} dopants in the core are covered with an inert NaYF_4 shell to separate them from surface quenching sites, such as nonradiative surface defects, ligands, and solvent molecules.^{253,254} Another prominent example is core–shell nanocomposites that

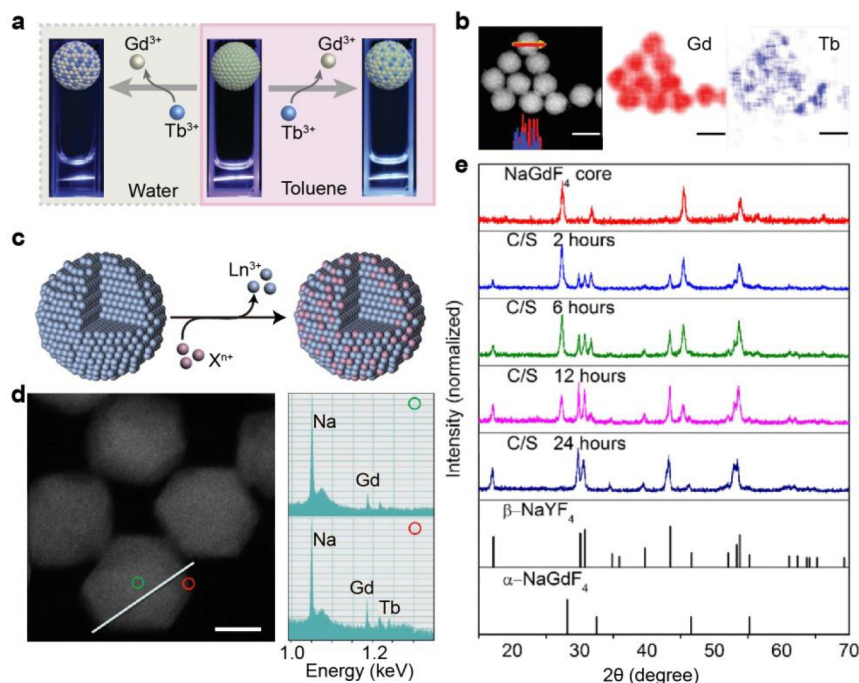


Figure 4. (a) Luminescence photos of UCNPs during cation exchange in water. (b) HRTEM and EELS images of $NaGdF_4:Yb/Tm$ UCNPs after cation exchange. Scale bars are 25 nm. (c) Schematic of a typical cation exchange process occurring at the particle surface. (d) Typical STEM imaging of UCNPs after cation exchange and EELS point analysis taken at the green and red circles in the left image. The scale bar is 10 nm. (e) XRD patterns of $NaGdF_4$ core nanocrystals and $NaGdF_4@NaYF_4:Yb/Er$ nanocrystals with different reaction times (Reprinted with permission from refs 286–288. Copyright 2018 The Royal Society of Chemistry; Copyright 2016 Nature Publishing Group; Copyright 2017 Springer).

combine hard and soft magnetic materials such as $SmCo_5@Sm_2O_3$ nanoparticles.²⁵⁵ The coupling of hard- and soft-magnetic components enables the formation of high-performance magnets based on exchange coupling for many applications.

In addition, spherical nanoparticles can be further transformed into hollow or mesoporous structures, such as Gd_2O_3 , $GdPO_4$, and CeO_2 nanoparticles.^{256–258} With a larger surface-to-volume ratio, these nanostructures can have more dopants on the surface, which is crucial for applications such as catalysis and drug loading.

On the other hand, doped nanomaterials with anisotropic structures such as segmented nanorods, nanohourglasses, nanoblossoms, nanodumbbells, and nanocylinders can be developed.²⁵⁹ Controlled epitaxial growth can selectively introduce multiple dopants into different segments of these heterogeneous structures. Moreover, rare-earth ions can be dispersed as single atoms onto two-dimensional (2D) supports such as graphitic carbon nitrides,²⁶⁰ or incorporated as metal centers in metal–organic frameworks.²⁶¹

3.2. Doping in Various Substrates

A large collection of materials is available for rare-earth doping, such as metal oxides, metal fluorides, metal oxyhalides, metal oxysulfides, metal oxysalts, and inorganic minerals. Moreover, various heterogeneously structured host materials have been developed to control the spatial distribution of rare-earths. Depending on the composition and structure of the host materials, different synthesis protocols and doping strategies are required.

3.2.1. Rare-Earth Compounds. Rare-earth compounds are ideal hosts for doping all types of rare-earth ions, because the physicochemical properties of the rare-earth series are

similar. Common rare-earth-based nanomaterials include fluorides, oxyhalides, oxysulfides, and oxysalts.

3.2.1.1. Rare-Earth Fluorides and Tetrafluorides. Fluorides are the most commonly used hosts for rare-earth dopants due to their mild synthesis conditions, high photochemical stability, and low phonon energy. Early studies on fluoride hosts mainly employed simple rare-earth fluorides such as LaF_3 and GdF_3 because they are easy to synthesize. For example, well-crystallized LaF_3 nanoparticles can be readily synthesized in an aqueous solution above room temperature.^{262,263} Subsequently, efforts have been made to incorporate rare-earth ions into various rare-earth fluorides, such as Na_xScF_{3+x} , $KScF_7$, $BaYF_5$, $BaGdF_5$, KYb_2F_7 , K_2GdF_5 , and $NaLaF_4$.^{264–270} Nevertheless, current studies primarily focus on tetrafluoride hosts (e.g., $LiLnF_4$, $NaLnF_4$, $KLnF_4$; $Ln = Y, Gd, Lu$) because of their well-established synthetic approaches and efficient luminescence processes, such as photon upconversion.^{12,271–280}

Although rare-earth fluoride nanocrystals can be synthesized according to various protocols, high-quality synthesis is typically performed in organic solvents at elevated temperatures (~ 250 – 300 °C). A commonly used solvent is 1-octadecene (ODE) in combination with oleic acid (OA) and oleylamine (OM) as capping ligands.^{12,281} Reactions involved include coprecipitation of metal oleate precursors with fluoride and thermal decomposition of metal trifluoroacetate. Rare-earth doping can be achieved quite simply by partially replacing the host precursor with doping ions during synthesis. Elemental analysis can help determine the dopant concentrations in the resulting nanocrystals, and a satisfactory match with the feed ratio in the precursor largely reflects the chemical similarity between dopants and host ions.²⁸²

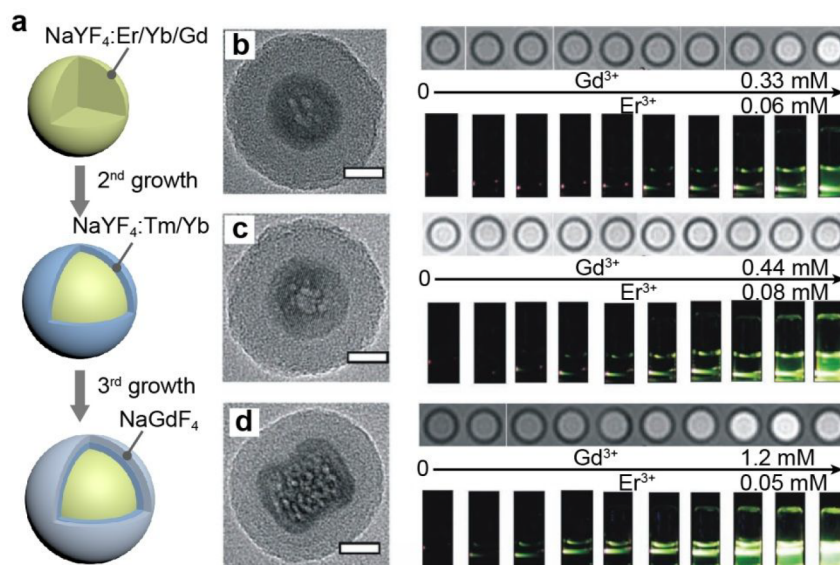


Figure 5. (a) Schematic representation of the synthesis of core–multishell UCNP. (b–d) TEM images, T_1 -weighted MRI contrast images, and digital photographs, respectively, of core, core–shell, and core–shell–shell samples with different Gd/Er concentrations. The scale bar is 10 nm (Adapted with permission from ref 300. Copyright 2011 Wiley VCH Verlag GmbH & Co. KGaA, Weinheim).

Hexagonal-phase NaYF₄ (β -NaYF₄) is considered one of the most efficient host materials for achieving efficient lanthanide luminescence, especially for upconversion emission. Accordingly, many efforts have been made to dope β -NaYF₄ nanoparticles with rare-earth ions of different composition and concentration. For example, Wang and Liu synthesized NaYF₄ nanocrystals doped with ten different concentration ratios of Yb³⁺, Er³⁺, and Tm³⁺.²⁸³ Hirsch and Resch-Genger and co-workers prepared Yb³⁺/Er³⁺-encoded NaYF₄ nanoparticles by thermal decomposition.²⁸⁴ Gd³⁺ ions at various concentrations (0–60%) were also introduced into the NaYF₄ host to tune the resulting particle sizes.²³³

Doping of rare-earth fluoride nanoparticles can alternatively be achieved by cation exchange. Dong and van Veggel found that La³⁺ ions could replace Gd³⁺ ions in GdF₃ by dispersing citrate-stabilized GdF₃ nanocrystals in a solution containing an excess of La³⁺ and citrate.²⁸⁵ This cation-exchange reaction was relatively fast, and about 92% of the Gd³⁺ ions were replaced by La³⁺ in 1 min. Similarly, La³⁺ ions in LaF₃ nanocrystals could also be replaced by Gd³⁺ ions, but the degree of exchange was relatively small. The authors found that cationic exchange can occur between many pairs of LnF₃ and Ln³⁺, such as EuF₃ with Gd³⁺ and NdF₃ with La³⁺. Based on these cation exchange features, it can be argued that controlling the reaction time and diffusion rate of dopant ions can regulate the doping depth of lanthanide ions in fluoride hosts.

Doping via cation exchange has also been realized in tetrafluoride UCNP. van Veggel et al. used cation exchange to replace the surfaces of β -NaYF₄:Yb/Tm nanoparticle with thin NaGdF₄ shells.²⁸⁶ Recently, cation exchange has been demonstrated as a general approach to rapidly introduce various luminescent dopants (e.g., Tb³⁺, Eu³⁺, Mn²⁺, Dy³⁺, and Ce³⁺) into β -NaGdF₄:Yb/Tm@NaGdF₄ nanoparticles and modulate the luminescence (Figure 4a–d).^{287,288} It has also been reported that heterogeneous α -NaGdF₄@ β -NaYF₄:Yb/Er structures can be fabricated by cation exchange at the interface (Figure 4e).²⁸⁹

Occasionally, nanoparticle units can be assembled into a hierarchical structure by controlling experimental variables

such as extending the reaction time, increasing reaction temperature, or adjusting the pH of the reaction. In one exciting example, olive-shaped GdF₃ nanoparticles doped with Eu³⁺, Tb³⁺, and Dy³⁺ ions were assembled into a series of hierarchical structures by simply changing the pH of the reaction.²⁹⁰

In addition to the aggregates of homogeneous nanoparticles, hierarchical core–shell nanostructures were also used for rare-earth doping. A prominent feature of the core–shell technique is that different rare-earth ions can be spatially confined in separate layers, leading to controllable interactions between the dopants and their environment. The manufacture of rare-earth-doped, core–shell nanoparticles typically requires a layer-by-layer growth process in which the doping ions are added during layer growth. It is unlikely that precise doping in core–shell nanostructures can be achieved by cation exchange, especially if multiple shell layers are required, as the exchange reaction occurs predominately at nanoparticle surfaces.

Core–shell nanostructures were initially developed to enhance luminescence intensity by eliminating surface quenching, i.e., nonradiative decay of dopant ions caused by high-energy surface oscillators.²⁹¹ Organic groups of surface capping ligands (e.g., –OH and –NH₂) can serve as vibrational deactivation centers to quench excited lanthanide dopants via multiphonon relaxation. By coating the luminescent core with an inert protective shell, the lanthanide-doped core can be shielded from environmental influences.²⁹² For example, Skripka et al. reported that the absolute PLQY of NaGdF₄:Nd nanoparticles increased from 8.2% to 17.4% after coating with NaGdF₄ in hexane.²⁹³

An important mechanism responsible for concentration quenching is energy migration through a dopant network that brings excitation energy to the surface quenchers.²⁹⁴ The core–shell engineering thus provides a simple solution to concentration quenching by isolating the luminescent core from the surface quenchers. Several groups have observed strong attenuation of quenching in core–shell UCNP doped with high concentrations of Yb³⁺ or Er³⁺ in the core.^{30,192,295,296} Control experiments by Almutairi and co-

workers verified that strong concentration quenching can be induced by incorporating Yb^{3+} or Nd^{3+} dopants into the inert shell, which bridges energy transfer from the core to the surface quenchers.²⁹⁷

For core–shell nanoparticles, the surface passivation efficiency is positively correlated with the shell thickness. Emission intensity typically saturates at a critical shell thickness at which surface quenching is sufficiently suppressed. Chen et al. prepared highly uniform $\text{LiLuF}_4:\text{Yb}/\text{Ln}@\text{LiLuF}_4$ ($\text{Ln} = \text{Tm}, \text{Er}$) UCNP. They showed that thicker LiLuF_4 shells lead to high quantum yields of 5.0 and 7.6% for Er^{3+} and Tm^{3+} emission, respectively. Li et al. investigated the optimal shell thickness in two sets of $\text{NaYF}_4:\text{Yb}/\text{Tm}@\text{NaYF}_4$ nanocrystals prepared by coprecipitation.²⁹⁸ The surfaces of the nanocrystals were coated with hydrophobic OA molecules or hydrophilic OH groups. They found that the OH groups have a stronger quenching effect due to their high vibrational energy. Hence, a thicker shell is required to suppress the quenching by OH groups. The optimal shell thickness is 3.5 nm. In contrast, the optimal thickness of OA-coated nanocrystals is 1.6 nm. Notably, thicker shells (>10 nm) are usually required to protect heavily doped cores, likely due to intense interactions between the surface quenchers and heavily doped ions.²⁹⁹

Among the various core–shell nanostructures, partially inert Gd-based shells are widely used by the upconversion community. The paramagnetic Gd^{3+} ion has seven unpaired $4f^7$ electrons, which alter the longitudinal relaxation of the surrounding water protons. Therefore, shell layers containing Gd^{3+} ions can be used as T_1 -weighted MRI contrast agents in clinical diagnosis. Note that the position of Gd^{3+} ions in the core–shell structure greatly affects the MRI capabilities of the nanoparticles. Shi, Bu, and co-workers designed a $\text{NaYF}_4:\text{Yb}/\text{Er}/\text{Gd}$ core continuously coated with an epitaxial $\text{NaYF}_4:\text{Yb}/\text{Tm}$ inner shell and a NaGdF_4 outer shell (Figure 5).³⁰⁰ The growth of the epitaxial shells increased the total emission intensity (7.4- and 37.3-fold, respectively) compared to the bare $\text{NaYF}_4:\text{Yb}/\text{Er}/\text{Gd}$ core. The authors attributed this emission increase to the lattice shielding of the shell. However, the $\text{NaYF}_4:\text{Yb}/\text{Tm}$ shell (~4 nm thick) almost completely shielded the longitudinal relaxivity of the Gd^{3+} dopants in the core. The authors concluded that the rigid crystal of the core–shell nanostructure almost completely isolated the Gd^{3+} ions in the core from the surrounding water protons. This isolation was interpreted as a negative lattice shielding effect for Gd^{3+} dopants. The longitudinal relaxivity of the Gd-doped UCNP was restored by coating the second epitaxial shell with NaGdF_4 . Moreover, the authors also prepared Gd^{3+} -free $\text{NaYF}_4:\text{Yb}/\text{Er}$ cores with NaGdF_4 shells of different thicknesses (0.2–3.7 nm). They found that a thicker NaGdF_4 shell has a more negative shielding effect on Gd^{3+} ions. There are also many other reports of Gd^{3+} -based core–shell structures for MRI, and the Gd^{3+} ions are generally distributed in the outermost layer of the shell to provide high water accessibility, such as $\text{NaGdF}_4:\text{Yb}/\text{Er}@\text{NaGdF}_4:\text{Nd}/\text{Yb}$, $\text{NaYF}_4@\text{NaNdF}_4@\text{NaYF}_4@\text{NaGdF}_4$, and $\text{NaYbF}_4:\text{Er}@\text{NaGdF}_4$.^{301–303}

Outer layers of core–shell nanoparticles can be doped with optically active lanthanide ions to harvest excitation energy and sensitize the emitter in the core. Vetrone et al. demonstrated this effect by coating $\text{NaGdF}_4:\text{Yb}/\text{Er}$ core nanoparticles with an undoped NaGdF_4 shell and an active $\text{NaGdF}_4:\text{Yb}$ shell.³⁰⁴ They found that the emission from $\text{NaGdF}_4:\text{Yb}/\text{Er}@\text{NaGdF}_4:\text{Yb}$ nanoparticles was more intense than that from a $\text{NaGdF}_4:\text{Yb}/\text{Er}@\text{NaGdF}_4$ counterpart. In addition, a control

sample of $\text{NaGdF}_4:\text{Yb}/\text{Er}$ nanoparticles was prepared with the same total Yb^{3+} dopant concentration as $\text{NaGdF}_4:\text{Yb}/\text{Er}@\text{NaGdF}_4:\text{Yb}$ nanoparticles. The emission intensity of the control sample was much lower than that of the nanoparticles with active cores and active shells. It was concluded that the active $\text{NaGdF}_4:\text{Yb}$ shell not only protects the luminescent core from nonradiative decay but also transfers the absorbed NIR energy to the upconversion core. Moreover, Zhu et al. reported that the active-core/active-shell structure can also promote downconversion luminescence in $\text{NaGdF}_4:\text{Yb}/\text{Pr}@\text{NaYF}_4:\text{Yb}$ nanoparticles. They found that intense NIR luminescence can be achieved by downconversion of Yb^{3+} when additional Yb^{3+} ions are doped into the shell layer.³⁰⁵

Inspired by the active-core/active-shell structure, the effect of the doping site on the luminescence properties of core–shell nanoparticles has been studied. Bhuckory et al. recently prepared three types of $\text{NaGdF}_4:\text{Yb}/\text{Er}$ -based UCNP, including a $\text{NaGdF}_4:\text{Yb}/\text{Er}$ nanoparticle without a shell, an active $\text{NaGdF}_4:\text{Yb}/\text{Er}$ core with a passivating NaGdF_4 shell, and an undoped NaGdF_4 core with an active $\text{NaGdF}_4:\text{Yb}/\text{Er}$ shell.³⁰⁶ The strongest luminescence was emitted by $\text{NaGdF}_4:\text{Yb}/\text{Er}@\text{NaGdF}_4$ nanoparticles, followed by $\text{NaGdF}_4:\text{Yb}/\text{Er}$ and $\text{NaGdF}_4@\text{NaGdF}_4:\text{Yb}/\text{Er}$ nanoparticles. The passivating NaGdF_4 shell of $\text{NaGdF}_4:\text{Yb}/\text{Er}@\text{NaGdF}_4$ nanoparticles protected the emitters in the core from surface quenching. In contrast, the other two types of nanoparticles had no such structural advantage. Abnormally, the photoluminescence decay time of $\text{NaGdF}_4@\text{NaGdF}_4:\text{Yb}/\text{Er}$ nanoparticles was the largest, followed by $\text{NaGdF}_4:\text{Yb}/\text{Er}@\text{NaGdF}_4$ and $\text{NaGdF}_4:\text{Yb}/\text{Er}$ nanoparticles. The authors offered two explanations for this order of decays. One was that some Yb^{3+} and Er^{3+} dopants migrated into the boundary layer of the shell and even into the inner core during the coating of the active shell. Therefore, Er^{3+} ions were effectively sensitized and protected at the interface of $\text{NaGdF}_4@\text{NaGdF}_4:\text{Yb}/\text{Er}$ nanoparticles. The other reason was that the confinement of Yb^{3+} ions in the thin NaGdF_4 shell can suppress luminescence quenching by nonradiative defects. As a result, the sensitization of Er^{3+} ions with excited Yb^{3+} ions was enhanced, leading to long decay times.

Core–shell nanostructures are also frequently used to regulate energy exchange interactions between dopants. In an early study, Ballato and co-workers investigated the energy transfer between Eu^{3+} and Tb^{3+} dopants in a series of LaF_3 core–shell architectures, including $\text{LaF}_3:\text{Eu}/\text{Tb}@\text{LaF}_3$, $\text{LaF}_3:\text{Eu}@\text{LaF}_3:\text{Tb}@\text{LaF}_3$, and $\text{LaF}_3:\text{Eu}@\text{LaF}_3@\text{LaF}_3:\text{Tb}@\text{LaF}_3$.³⁰⁷ In these particles, the outermost LaF_3 shell acted as a passivation layer to prevent surface quenching. The intercalated LaF_3 layer in $\text{LaF}_3:\text{Eu}@\text{LaF}_3@\text{LaF}_3:\text{Tb}@\text{LaF}_3$ nanoparticles served as an energy barrier to tune the energy transfer between Eu^{3+} - and Tb^{3+} -ions confined in different layers. They demonstrated that the energy exchange between Eu^{3+} and Tb^{3+} can be completely blocked when a $\text{LaF}_3:\text{Eu}@\text{LaF}_3@\text{LaF}_3:\text{Tb}@\text{LaF}_3$ nanostructure with a thick inner LaF_3 layer (>2 nm) is used. A similar multilayer design allowed diverse luminescence processes to be integrated into a single class of nanoparticles without noticeable crosstalk, resulting in orthogonal or multimodal emissions.^{34,308–314}

An exciting achievement using a core–shell nanostructure to regulate complex energy transfer between lanthanide dopants was demonstrated by Liu and co-workers.¹³⁸ In their study, Yb^{3+} , Tm^{3+} , and Tb^{3+} (or Eu^{3+} , Dy^{3+} , Sm^{3+}) were incorporated into core and shell layers, respectively, of $\text{NaGdF}_4@\text{NaGdF}_4$

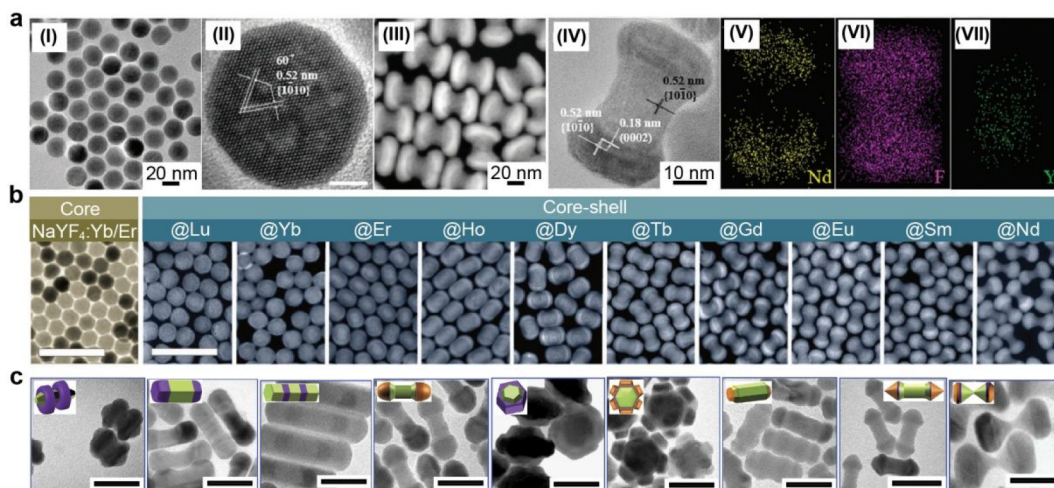


Figure 6. (a) (I) TEM and (II) HRTEM images of core nanoparticles (the scale bar in II is 5 nm). (III) STEM and (IV) HRTEM images of dumbbell-shaped core-shell nanoparticles. (V–VII) Elemental mapping of the distribution of Nd^{3+} , Y^{3+} , and F^{-} ions within a single dumbbell-shaped nanocrystal. (b) TEM imaging of the $\text{NaYF}_4:\text{Yb}/\text{Er}$ core and HAADF-STEM imaging of the corresponding $\text{NaYF}_4:\text{Yb}/\text{Er}@\text{NaREF}_4$ core-shell nanoparticles. Scale bars are 100 nm. (c) Complex NaLnF_4 nanostructures synthesized under different reaction conditions. Scale bars are 50 nm (Adapted with permission from refs 259, 320, and 322. Copyright 2016 The Royal Society of Chemistry; Copyright 2019 Wiley VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2016 Nature Publishing Group).

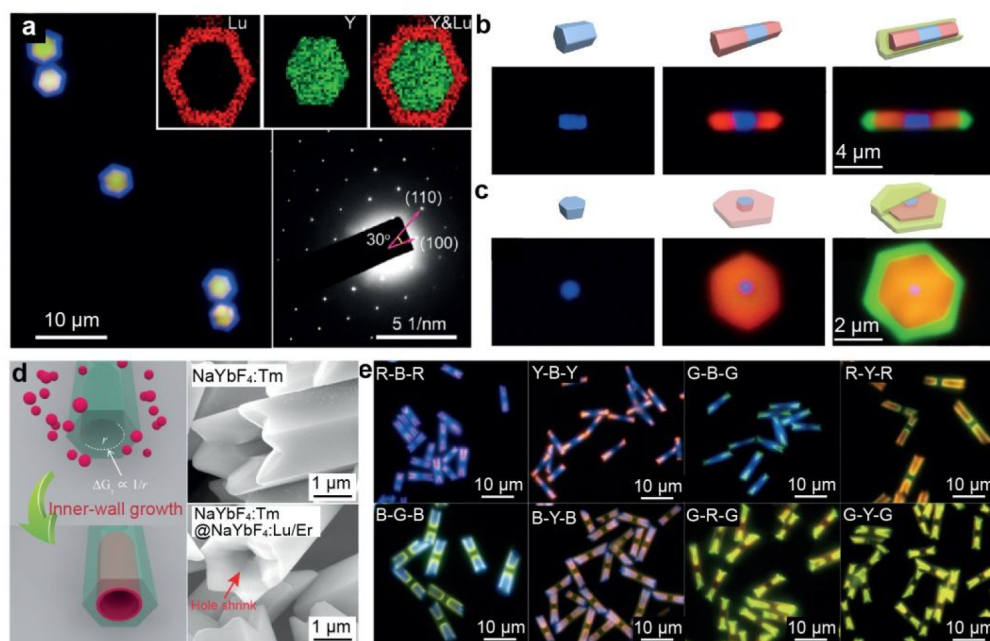


Figure 7. (a) Upconversion luminescent micrographs of core-shell crystals under 980 nm excitation. (top inset) Elemental mapping performed on a single core-shell crystal. (bottom inset) Electron diffraction pattern of a selected region recorded at the edge of a core-shell crystal. (b) Diagrams and optical micrographs showing the evolution from microrod seed to tricolor microrod. (c) Diagrams and optical micrographs showing evolution from microrod seed to three-color microplate. (d) Growth of the inner wall on tubular microrods because of the relatively low surface energy of the concave wall. (e) Optical micrographs of microrods fabricated with different combinations of substrate microrods and coating layers (Adapted with permission from refs 36 and 324. Copyright 2016 and 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

nanoparticles. The spatial separation of the two doped groups eliminated the nonradiative quenching caused by deleterious cross-relaxation. Meanwhile, energy migration through the Gd^{3+} sublattice at the core-shell interface bridged the selective energy transfer from the core to the shell, resulting in unprecedented upconversion emission of Tb^{3+} , Eu^{3+} , Dy^{3+} , and Sm^{3+} ions without intermediate energy levels.³¹⁵ The strategy of core-shell engineering combined with energy migration is

now routinely used to generate novel luminescence processes.^{34,316–319}

Besides conformal core-shell nanoparticles, anisotropic epitaxial nanostructures have been synthesized by controlling the epitaxial growth process. The epitaxial shape is governed by both intrinsic mismatches between the core and shell lattices and synthetic variables.^{320,321} Xu et al. prepared dumbbell-shaped $\text{NaYF}_4:\text{Yb}/\text{Er}@\text{NaNdF}_4:\text{Yb}$ heterostructures.³²² The $\text{Yb}^{3+}/\text{Er}^{3+}$ and Yb^{3+} dopants were individually distributed in

different regions of the nanocrystal, and the doping concentration of Yb^{3+} in the NaYF_4 domain was higher than that in the NaNdF_4 domain (Figure 6a). The authors concluded that the dumbbell morphology is more advantageous for photodynamic therapy than the conformal core-shell structure.

Zhao et al. have shown that epitaxial growth on hexagonal phase NaREF_4 nanocrystals is subject to anisotropic interfacial strain.³²⁰ In general, epitaxial deposition on the [001] facet is subject to less mismatch strain than that on the [100] facet. As a result, preferential epitaxial growth is often observed along the *c*-axis. Due to anisotropic interfacial tension, the prism shell may eventually decompose to minimize the global free energy, resulting in dumbbell-shaped morphologies (Figure 6b). The biaxial strain in the dumbbell-shaped $\text{NaYF}_4\text{:Yb/Er@NaGdF}_4$ UCNPs affected the relative intensity of red and green emissions from the Er^{3+} dopants.

In addition to interfacial strain, surface capping ligands also have an important function in forming core-shell nanocrystals with the desired morphology. Liu et al. found that the oleate anion (OA^-) tends to bind to the (100) facet of NaREF_4 crystals in hexagonal phase, while the oleic acid (OA) molecule has a particular affinity for the (001) facet.²⁵⁹ They choose a hexagonal NaYF_4 nanocrystal as a model and designed epitaxial growth of the NaLnF_4 ($\text{Ln} = \text{Y, Gd, Nd, Lu}$) shell on the NaYF_4 core by controlling the ratio of OA^-/OA . The high concentration of NaOH resulted a large ratio of OA^-/OA , which promoted epitaxial growth along the longitudinal direction of the NaYF_4 nanocrystal. Epitaxial growth along the transverse direction of the hexagonal NaYF_4 nanocrystal can be achieved by decreasing the NaOH concentration, which increases the OA concentration (Figure 6c).

Anisotropic core-shell morphology offers a new dimension for controlling the optical properties of nanoparticles as well as their interactions with the surroundings. Carefully selection of core nanoparticles and precise control of synthesis methods can achieve highly directional epitaxial growth, leading to segmented nanostructures.^{36,311,323,324} For example, Zhang et al. prepared multicolored rod- and plate-shaped upconversion barcodes based on precise control of the shell thickness and growth direction of epitaxial layers on $\beta\text{-NaYbF}_4$ seeds.³⁶ The authors synthesized small $\beta\text{-NaYbF}_4$ nanorods and epitaxially grew different lanthanide dopants in horizontal or vertical orientation. The epitaxial growth of RE^{3+} was carried out by mixing cubic-phase NaLuF_4 or NaYF_4 nanoparticles with $\beta\text{-NaYbF}_4$ microrods under hydrothermal conditions. Multicolored $\beta\text{-NaYF}_4$ microrods and microplates with localized Ln^{3+} dopants were obtained, and the growth direction was tuned by controlling favorable growth along different facets of the nanocrystals (Figure 7a–c). Wang and co-workers prepared NaYbF_4 microrods in hexagonal phase with isolated holes along the longitudinal axis.³²⁴ They succeeded in controlling epitaxial growth in the inner walls of holes to obtain multicolor emission from different sections of the microrods (Figure 7d and e). In another interesting example, Li, Zhang, and co-workers synthesized a series of $\text{NaYF}_4\text{:Yb/Er@NaGdF}_4\text{:Yb@NaNdF}_4\text{:Yb}$ core-shell-shell nanoplates with controllable surface roughness.³²⁵ The authors employed a successive layer-by-layer strategy to grow NaLnF_4 shells on nanoplates and then control the kinetics of shell coating during the process. In this way, hexagonal disk and multipetal core-shell nanoplates with different degrees of surface roughness were obtained. Interestingly, the authors demonstrated that

nanoplates with the highest surface roughness were able to pass blood–brain barriers in living mice, which was impossible with conventional core-shell nanostructures.

3.2.1.2. Rare-Earth Oxyhalides. The excited-state energy and transition probability of rare-earth dopants are largely influenced by the host materials. In recent years, rare-earth oxyhalides have been recognized as a significant class of host materials for rare-earth dopants. Several methods have been reported for fabrication of rare-earth-doped oxyfluorides nanocrystals, including hydrothermal synthesis followed by heat treatment,^{326,327} coprecipitation,³²⁸ thermolysis of rare trifluoroacetate,³²⁹ and the sol–gel Pechini methods.³³⁰

In 2009, Yan's group reported the synthesis of sub-2 nm EuOF nanowires by decomposition of the corresponding trifluoroacetates at elevated temperatures.³²⁹ The authors used $\text{Eu}(\text{CF}_3\text{COO})_3$ as a precursor to obtain Eu^{3+} and F^- by thermolysis in a mixed solvent containing OA and OM. During the synthesis, a $\text{Eu}(\text{CF}_3\text{COO})_{3-x}(\text{OA})_x$ intermediate was generated to control the nucleation and further growth of EuOF nanowires in subsequent steps. In a later study, Chen, Tu, and co-workers doped Ce^{3+} , Eu^{3+} , $\text{Ce}^{3+}/\text{Tb}^{3+}$, $\text{Yb}^{3+}/\text{Er}^{3+}$, and $\text{Yb}^{3+}/\text{Ho}^{3+}$ into LaOBr nanocrystals by a modified thermal decomposition approach.³³¹ By analyzing the downshifting emission of LaOBr:Eu^{3+} , the authors identified several doping site symmetries in nanocrystals, including C_{4v} , C_1 , C_s , C_2 , and C_{2v} . In a recent demonstration, Du et al. synthesized $\text{Pr}^{3+}/\text{Gd}^{3+}$ -encoded $\text{Lu}_6\text{O}_5\text{F}_8$ nanocrystals by thermal decomposition.³³² The host lattice was chosen so that the $4f^25d^1$ energy level can be tuned to achieve upconversion emission from Pr^{3+} in the deep ultraviolet region via sequential absorption of two blue excitation photons through $^3\text{H}_4(4f^2) \rightarrow ^3\text{P}_0(4f^2)$ and $4f^2 \rightarrow 4f^15d^1$ transitions.

Lin and co-workers reported the synthesis of LaOF nanocrystals by a hydrothermal method followed by heat treatment.³²⁶ Doping nanocrystals with a series of lanthanide dopants, including Eu^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} , Tm^{3+} , and Ho^{3+} , yielded characteristic f–f emissions with red, blue–green, orange, yellow, blue, and green colors under ultraviolet and low-voltage electron beam excitation. Two-step hydrothermal methods have also been utilized to prepare rare-earth oxyfluorides in the Vernier phase, such as V-YOF ($\text{Y}_6\text{O}_5\text{F}_8$), V-YbOF ($\text{Yb}_6\text{O}_5\text{F}_8$), and V-LuOF ($\text{Lu}_6\text{O}_5\text{F}_8$) nanoparticles.^{327,333–335} With multiple low-symmetry doping sites (C_1 , C_2 , and C_s), V-rare-earth oxyfluorides are essential for the development of highly efficient multicolor nanophosphors.

In 2016, You's group developed a topotactic transformation route to prepare GdOF:Ln^{3+} ($\text{Ln} = \text{Eu, Tb, Eu/Tb, Ce/Tb, Yb/Er, and Yb/Tm}$) nanocrystals.³³⁶ Brucite-like $\text{Gd}_2(\text{OH})_5\text{NO}_3 \cdot 0.9\text{H}_2\text{O}$ was first converted into layered $\text{Gd}(\text{OH})_2\text{F}$ with large {0001} facets by ion exchange. Topotactic *in situ* growth of GdOF from $\text{Gd}(\text{OH})_2\text{F}$ was then achieved by thermal decomposition due to the structural correspondence between [0001] $\text{Gd}(\text{OH})_2\text{F}$ and [110] GdOF facets. In a parallel development, You, Liu, and colleagues used $\text{RE}(\text{OH})\text{CO}_3$ as both precursor and template.³³⁷ By calcining $\text{RE}(\text{OH})\text{CO}_3$ together with KHF_2 , they obtained porous REOF:Ln^{3+} spheres ($\text{RE} = \text{Y, Gd, Lu; Ln} = \text{Ce, Eu, Tb, Ce/Tb, Yb/Er, Yb/Ho, or Yb/Tm}$). These structures exhibit a large surface-to-volume ratio and have the potential for applications in photocatalysis and drug delivery.

Rare-earth-doped oxyfluoride nanoparticles can be prepared with heterogeneous nanoscale architectures. Gao and co-workers synthesized YOF:Yb/Er@YOF nanoparticles by

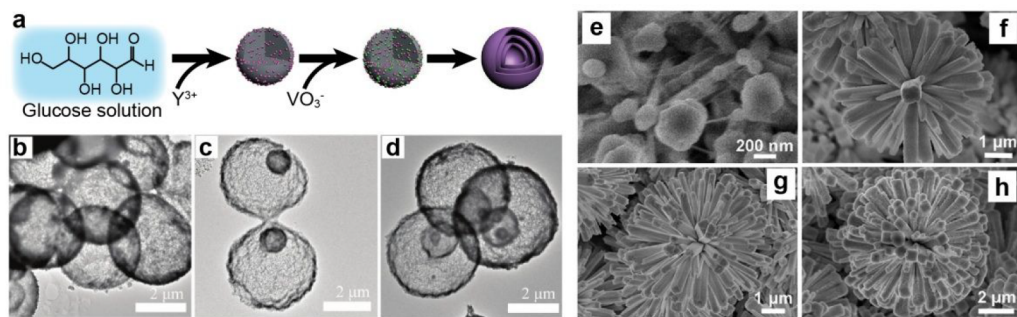


Figure 8. (a) Schematic synthesis of multilayered YVO₄ hollow spheres. (b–d) TEM images of single-, double-, and triple-shell YVO₄ hollow spheres, respectively. (e–h) SEM images of the samples, prepared at 260 °C for 5 h with different molar ratios of Na₂H₂L/Gd³⁺: (e) 2, (f) 2.60, (g) 2.76, and (h) 2.80 (Adapted with permission from refs 341 and 342. Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2016 Elsevier B.V.).

thermolysis of rare-earth trifluoroacetates.³³⁸ These as-prepared core–shell nanoparticles exhibited stronger red upconversion emission than their core-only counterparts. These nanoparticles can be further rendered hydrophilic and conjugated with antibodies to label and image cancer cells. Yan et al. produced ultrasmall (~5 nm) GdOF nanoparticles that can be readily functionalized with peptides to specifically image the cytoplasm and nucleus.³³⁹ Lin's group established a protocol to prepare yolklake, mesoporous GdOF:Ln@SiO₂ (Ln = Yb, Er, Mn) nanoparticles with various functional groups and demonstrated their utility as a multifunctional platform for multimodal image-guided therapies.³⁴⁰

3.2.1.3. Oxsulfides. Oxsulfides such as Gd₂O₂S, Y₂O₂S, Tb₂O₂S, La₂O₂S, Eu₂O₂S, and Lu₂O₂S are popular host materials for rare-earth doping.^{343–353} Traditional doping methods with oxsulfides include solid–gas reaction, solid thermal evaporation, liquid thermal decomposition, sol–gel processing, laser ablation, and solvothermal treatment. In the last two decades, special synthetic methods have been reported. For example, in 2000, Qian and co-workers reported a solvothermal gel method for the preparation of nanocrystalline La₂O₂S in polar solvents.³⁵⁴ In 2006, Gao's group developed the facile colloidal synthesis of monodisperse Eu₂O₂S and Gd₂O₂S:Eu nanocrystals with tunable size and shape.³⁵¹ The entire preparation process was conducted under ambient atmosphere. The size and shape of the doped RE₂O₂S nanocrystals were precisely controlled by surfactants of OA and OM. With the help of a mild, self-templating approach, Huang and co-workers used supramolecular lanthanide–cholate hydrogels to prepare Eu³⁺-doped Gd₂O₂S and Y₂O₂S nanotubes, which exhibited efficient luminescence.³⁵⁵ Ding et al. demonstrated that doping with Na⁺ can facilitate the formation of high-quality monodisperse, ultrathin La₂O₂S nanoplates.³⁵⁶ The authors found that Na⁺ can be doped into La₂O₂S nanocrystals at a high concentration, determined by the trapped-dopant model. Theoretical calculations revealed that introduction of Na⁺ significantly reduced the repulsion in the sublattice, resulting in doped La₂O₂S nanocrystals.

3.2.1.4. Rare-Earth Oxyalts. Rare-earth oxyalts represent a broad class of host materials, characterized by high thermal stability. However, many RE oxyalts must crystallize at temperatures above 500 °C and are unlikely to form uniform nanocrystals by wet chemical synthesis. Commonly studied rare-earth oxyalt nanoparticles include orthophosphates, vanadates, borates, tungstates, and molybdates.

Orthophosphates, a series of inorganic hosts that exist in the form of three free ions, H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻, have found widespread applications as phosphors, laser materials, humidity sensors, biomarkers, and catalysts.^{357–363} For example, Haase and co-workers used the core–shell nanostructure in the preparation of colloidal CePO₄:Tb@LaPO₄ nanoparticles by a wet chemical method.³⁶⁴ Growth of a LaPO₄ shell around the core nanoparticles significantly increased the luminescence quantum yield of Tb³⁺ from 43 to 70%. Recently, You's group developed a topotactic transformation method to prepare YPO₄:Ln³⁺ (Ln = Ce, Eu, Tb) micro/nanocrystals.³⁶⁵ In this strategy, the topotactic structure of the precursor determines the resulting phase of YPO₄:Ln nanoparticles. Indeed, layered Y₂(OH)₅NO₃ induced the formation of hexagonal-phase YPO₄:Ln, while amorphous Y(OH)CO₃ favored the formation of tetragonal YPO₄:Ln. They also found that additives such as Na₂CO₃ and NH₄HCO₃ determined precursor structures. The ratio of additives to Na₃PO₄ can be varied to tune the crystal size of the resulting products.

Precursor engineering is suitable for imparting a specific structure to the rare-earth-doped oxyalt nanoparticles. For example, Jia et al. prepared a rare-earth hydroxycarbonate precursor by homogeneous precipitation of RE(NO₃)₃ with urea.³⁶⁶ Hydroxycarbonates can be converted in the liquid phase into more thermodynamically stable structures containing precursor counteranions, such as fluorides, phosphates, or vanadates. Therefore, hydroxycarbonates can serve as templates for the formation of dispersible inorganic nanostructures by wet chemical methods. Jia et al. treated rare-earth hydroxycarbonates with PO₄³⁻ and VO₄³⁻ anions to obtain rare-earth-doped YPO₄ and YVO₄ nanospheres with hollow structures.

Many strategies have accelerated the development of rare-earth orthovanadates for applications in optical devices.^{367–373} In principle, rare-earth orthovanadates have two polymorphs, the monoclinic monazite and the tetragonal zircon structures. Large rare-earth ions prefer the monazite type because of its higher oxygen coordination number (CN = 9) than the zircon type (CN = 8). However, the monazite host is neither suitable for luminescence activators nor promising for catalysis compared to zircon-type orthovanadates. Hence, the design of an effective strategy for preparing metastable orthovanadates, such as zircon-type LaVO₄, is of great interest. In that regard, Zhao's group prepared Ln³⁺-doped zircon-type LaVO₄ by a simple hydrothermal method without the need for

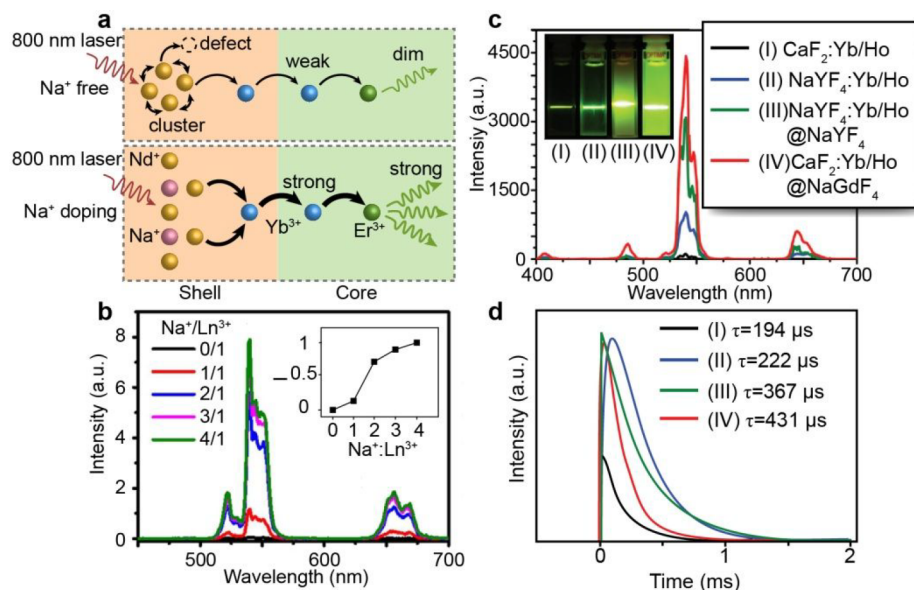


Figure 9. (a) Schematic of energy transfer in CaF₂:Yb/Er@CaF₂:Nd/Yb nanoparticles with and without Na⁺ ions in the shell. (b) UCL emission spectra of CaF₂:Yb/Er@CaF₂:Nd/Yb nanoparticles synthesized at different molar ratios of Na⁺/Ln³⁺ upon excitation at 800 nm. (c) UC PL spectra and corresponding photographic digital images of colloidal (I) cubic CaF₂:20%Yb/2%Ho, (II) hexagonal NaYF₄:20%Yb/2%Ho, (III) hexagonal (NaYF₄:20%Yb/2%Ho)@NaYF₄, (IV) cubic (CaF₂:20%Yb/2%Ho)@NaGdF₄. (d) Decay behavior of photoluminescence at 540 nm in colloidal (I), (II), (III), and (IV), respectively (Adapted with permission from refs 391 and 398. Copyright 2017 American Chemical Society; Copyright 2015 The Royal Society of Chemistry).

catalysts or templates.³⁷⁴ They found that the variation of pH can control the phase and shape of LaVO₄. When the pH was less than 3.5, only irregular nanoparticles of LaVO₄:Ln with the monazite phase were obtained. When the pH was between 4.5 to 6.0, uniform LaVO₄:Ln nanorods with the tetragonal zirconium phase were obtained. When the pH was further increased to above 6.0, the obtained LaVO₄:Ln nanocrystals exhibited particlelike morphology. To control the dimension of orthovanadates, Lin's group utilized an electrospinning technique after a sol-gel process to prepare one-dimensional YVO₄:Ln³⁺ (Ln = Eu, Sm, Dy) nanofibers.¹⁰⁹ Antić et al. employed a pulsed laser deposition technique to fabricate zirconia thin films of GdVO₄:Dy on thermally grown SiO₂ substrates.³⁷⁵ These physical techniques can effectively construct Ln³⁺-doped nanocrystals with various shapes.

Rare-earth orthovanadate nanocrystals may self-assemble into ordered structures that provide great opportunities for device applications as well as mechanistic investigations of optical and electronic properties. Weng et al. reported a hydrothermal synthesis of LnVO₄ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) nanorods that can self-assemble into different aggregates, depending on pH, reaction time, and EDTA concentration.³⁷⁶

In another interesting study, Zong et al. used yttrium-carbon spheres as templates to build YVO₄:Yb/Er hollow structures with single shells, double shells, and triple shells (Figure 8a–d).³⁴¹ The number of shell layers could depend on the calcination temperature and time, heating rate, and concentration of VO³⁺. By adjusting the ratio of surfactants (Na₂H₂L) and rare-earths, Amurisana et al. developed a one-pot hydrothermal route that enabled the synthesis of GdVO₄ superstructures with well-controlled flowerlike morphology (Figure 8e–h).³⁴²

Apart from orthophosphates and orthovanadates, attempts have also been made to prepare other types of nanocrystals

based on rare-earth oxysalts such as borates, tungstates, and molybdates. Yan, Sun, and co-workers employed a sol-gel pyrolysis method to prepare hexagonal-phase YBO₃:Eu (0–30 mol %) nanocrystals with different sizes and size-dependent coloration.³⁷⁷ Li and co-workers developed a solvothermal liquid–solid solution method and prepared YBO₃ nanocrystals with better monodispersity.³⁷⁸ In 2013, a triclinic form of GdBO₃:Eu nanocrystals was synthesized by Szczeszak et al. via a hydrothermal method.³⁷⁹

Rare-earth tungstates and molybdates form in several variants, such as NaRE(MO₄)₄, RE₂M₃O₁₂, and RE₂MO₆, where M stands for W⁶⁺ or Mo⁶⁺. The compositional variability provides great flexibility in tailoring the material properties. For example, orthorhombic RE₂M₃O₁₂ crystals such as Yb₂W₃O₁₂ and Sc₂Mo₃O₁₂ exhibit negative thermal expansion, which is critical for attenuating luminescence quenching at elevated temperatures.^{380,381} However, as with many other rare-earth oxysalts, only a small number of nanocrystalline rare-earth tungstates and molybdates have been reported. In 2016, Zhong, Meijerink, and co-workers synthesized sub-50 nm NaRE(WO₄)₂ nanocrystals with a uniform diamond shape using a solvothermal method.³⁸² The researchers used hexacarbonyl tungsten as a W⁶⁺ source and mixed it with rare-earth acetate and sodium hydroxide in a mixed solution of OA, OM, and ODE. The new synthetic route for nanosized tungstates may promote new applications for these hosts in the future.

3.2.2. Alkaline-Earth Compounds. Host materials containing alkaline-earth metal ions can provide different chemical environments to control the valence of rare-earth dopants. Owing to the considerable size similarity between rare-earths and alkaline-earths (e.g., Ca²⁺, Sr²⁺, Ba²⁺), alkaline-earth compounds can readily accommodate high doping concentrations (>10%) of rare-earth ions.

3.2.2.1. Alkaline-Earth Halides. Alkaline-earth fluorides (MF_2 , $\text{M}^{2+} = \text{Ca}^{2+}$, Sr^{2+} , Ba^{2+}) have received considerable attention for rare-earth doping due to their high optical transparency and high chemical and thermal stability.^{283,383–388} Rare-earth-doped MF_2 nanoparticles can be prepared using protocols similar to those developed for preparing rare-earth fluorides and tetrafluorides.

In a representative example from Wang's group, ~ 3 nm $\text{BaF}_2\text{:Yb/Tm}$ nanoparticles were prepared by a solvothermal method and subsequently used as core nanoparticles for the epitaxial growth of $\text{SrF}_2\text{:Nd}$ shells by thermal decomposition.⁹⁴ In this architecture, the SrF_2 shell not only contributed to the enhancement of the NIR-to-NIR upconversion luminescence of the $\text{BaF}_2\text{:Yb/Tm}$ core but also acted as a host for the realization of the NIR-to-NIR downshifting of the Nd^{3+} emission. Wang's group also reported that aliovalent rare-earth dopants can control the size and shape of alkaline-earth fluoride nanocrystals (MF_2 , $\text{M} = \text{Ca}$, Sr , Ba).^{389,390} Substitution of M^{2+} by Ln^{3+} in MF_2 required an additional F^- for charge compensation. Introduction of such F^- ions into the grain surface can induce transient electric dipoles with their negative poles directed outward. These transient electric dipoles hinder the diffusion of F^- ions, which are required for crystal growth, from the solution to the grain surface, thus retarding the growth of MF_2 .

For charge compensation, it is possible to introduce Na^+ together with rare-earth ions into CaF_2 host lattices. Xu et al. reported an enhancement of upconversion emission in $\text{CaF}_2\text{:Yb/Er@CaF}_2\text{:Nd/Yb}$ nanoparticles by Na^+ doping (Figure 9a,b).³⁹¹ The researchers argued that doping a CaF_2 lattice with rare-earth and Na^+ ions can maintain charge neutrality and reduce defect formation in the host, leading to high upconversion efficiency.

MF_2 materials are widely used as hosts for isovalent rare-earth dopants such as Eu^{2+} . Hong and Kawano treated $\text{CaF}_2\text{:Eu}^{3+}$ nanoparticles in a thermal carbonaceous atmosphere at 500–900 °C, which reduced Eu^{3+} into Eu^{2+} .³⁹² They found that the particle size and $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio increased with increasing temperature from 600 to 900 °C. Eu^{2+} ions enter the cubic CaF_2 lattice by Ca^{2+} substitution, and each Eu^{2+} ion coordinates with eight fluorine anions. The octahedral crystal field splits the 5d level of Eu^{2+} into two orbital groups with different energies. Consequently, the $4f^7\text{--}4f^65d$ transition of Eu^{2+} is highly sensitive to chemical bonding between Eu^{2+} and F^- ions.

Obtaining Eu^{2+} -doped nanoparticles usually requires post-synthetic annealing to reduce the oxidation state of europium from trivalent to divalent. The heating process often leads to undesirable coalescence of the particles, resulting in increased particle size and the formation of hard agglomerates. To overcome this problem, Wickleder and co-workers have recently developed a simple strategy using ionic liquid that harnesses the power of ultrasonic waves to synthesize BaFCl:Eu^{2+} nanocrystals under mild conditions.³⁹³ This sonochemical technique produces Eu^{2+} -doped BaFCl nanocrystals with a relatively narrow size distribution.

Interestingly, it is easy to grow epitaxially heterogeneous $\text{NaREF}_4\text{@CaF}_2$ core-shell nanostructures using conventional wet chemical methods because the CaF_2 crystal is isostructural to NaREF_4 tetrafluorides in cubic phase. A variety of $\text{NaREF}_4\text{@CaF}_2$ nanocomposites, such as $\text{NaYbF}_4\text{:Tm@CaF}_2$, $\text{NaYbF}_4\text{:Tm/Nd@CaF}_2$, $\text{Nd@CaF}_2\text{:Yb/Er}$ nanoparticles, $\text{NaYbF}_4\text{:Tm@CaF}_2\text{:alpha-NaDyF}_4$, $\text{NaYbF}_4\text{@CaF}_2$, and

$\text{CaF}_2\text{@NaGdF}_4$ nanoparticles, have been developed (Figure 9c,d).^{394–398} Despite dissimilar crystal structures, the group of Yan and Sun synthesized $\beta\text{-NaLnF}_4\text{@CaF}_2$ core-shell nanoparticles.³⁹⁹ The authors demonstrated that the evolution of nanoparticle surfaces from hexagonal to cubic was triggered by the preferential exchange between Ca^{2+} and Na^+ cations. This removed the large barrier and allowed heteroepitaxial growth of cubic CaF_2 shell on the hexagonal NaLnF_4 . Compared to homogeneous $\text{NaREF}_4\text{@NaREF}_4$, the heterogeneous $\text{NaREF}_4\text{@CaF}_2$ core-shell structures can suppress the ion leakage between core and shell layers.⁴⁰⁰ In addition, the CaF_2 shell is considered to be more biocompatible than rare-earth fluorides for *in vivo* biological applications.

3.2.2.2. Alkaline-Earth Sulfides. Alkaline-earth sulfides are useful for the uptake of divalent rare-earth dopants. The most representative examples are Eu^{2+} -doped CaS and SrS synthesized by alkoxide and coprecipitation.^{131,401,402} Due to the high sensitivity of the f–d transition of Eu^{2+} to the local lattice environment, the emission wavelength of Eu^{2+} can be used to verify the incorporation of Eu^{2+} into the octahedral site of the CaS lattice. Meijerink and co-workers reported an approach to doping CaS and SrS materials with Eu^{2+} using one precursor.⁴⁰¹ They found that the reactivity of the dopant and the host precursor determines the doping efficiency. Precursors with low reactivity require a relatively high decomposition temperature to promote the diffusion of Eu^{2+} through the SrS lattice.

Moreover, Eu^{2+} -doped CaS nanomaterials exhibited persistent luminescence when codoped with other trivalent lanthanides. For example, Capobianco's group prepared $\text{CaS:Eu}^{2+}/\text{Dy}^{3+}$ nanophosphors that showed persistent red emission.⁴⁰³ They demonstrated that Eu^{2+} dopants can produce shallow traps below the conduction band of CaS , while the addition of Dy^{3+} as a codopant can produce shallow and deeper traps, resulting in prolonged afterglow of 5 h. Chen's group has codoped Eu^{2+} and Sm^{3+} into CaS nanocrystals.⁴⁰⁴ They found that the resulting nanocrystals exhibit intense luminescence of Eu^{2+} at 650 nm, which responds quickly to NIR stimulation, lasts longer than 2 h, and has a low power density threshold of 10 mW cm^{-2} .

Owing to their low phonon energies, alkaline-earth sulfides are also suitable hosts to achieve NIR luminescence by rare-earth doping. For example, Chen and co-workers reported the synthesis of $\text{Ce}^{3+}/\text{Er}^{3+}$ - and $\text{Ce}^{3+}/\text{Nd}^{3+}$ -codoped CaS nanoparticles that exhibited blue-LED-excitable NIR luminescence.⁴⁰⁵ Ce^{3+} ions in CaS can be efficiently excited by blue-light through the 4f–5d transition and can subsequently sensitize the 4f–4f emissions of Er^{3+} and Nd^{3+} in the NIR region.

3.2.2.3. Alkaline-Earth Oxides/Nitrides. Alkaline-earth oxides and nitrides are commonly used to accommodate rare-earth ions and can also accommodate unusual valences such as Ce^{4+} and Eu^{2+} . The resulting materials are mainly for catalysis and photoluminescence.

For example, the lattices of alkaline-earth aluminates are suitable for isovalent doping with Eu^{2+} ions.⁴⁰⁶ Co-combustion of $\text{Al}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, $\text{Eu}(\text{NO}_3)_3$, and $\text{CO}(\text{NH}_2)_2$ incorporated Eu^{2+} ions into the SrAl_2O_4 host.⁴⁰⁷ This combustion reaction was an exothermic process that avoided extensive thermal treatment. Meanwhile, $\text{CO}(\text{NH}_2)_2$ produced a reducing atmosphere to convert Eu^{3+} to Eu^{2+} . Coprecipitation of metal nitrates with $(\text{NH}_4)_2\text{CO}_3$ followed by annealing led to the production of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ nanoparticles encoded with Eu^{2+}

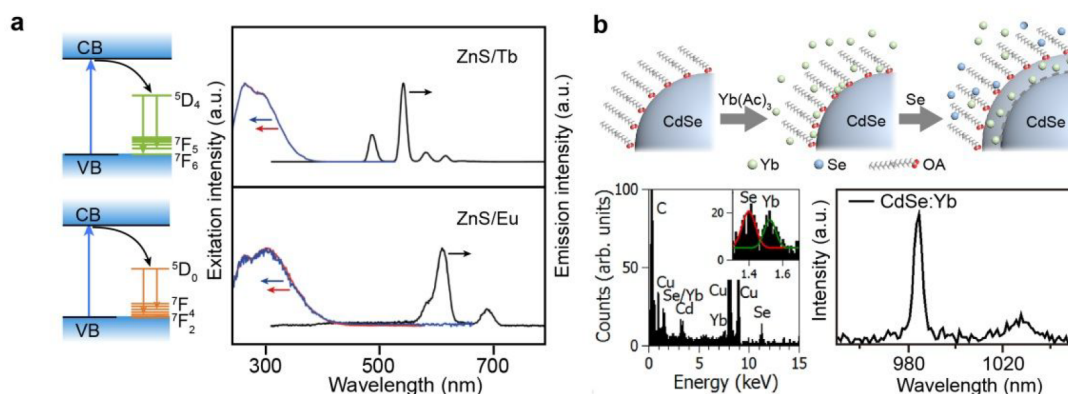


Figure 10. (a) Illustration of the energy transfer process from ZnS to rare-earth ions and normalized time-gated excitation and emission spectra of ZnS/Tb [$\lambda_{\text{ex}} = 300$ nm (black), $\lambda_{\text{em}} = 490$ nm (red), $\lambda_{\text{em}} = 545$ nm (blue)] (top panel) and ZnS/Eu [$\lambda_{\text{ex}} = 300$ nm (black), $\lambda_{\text{em}} = 616$ nm (red), $\lambda_{\text{em}} = 696$ nm (blue)] (bottom panel) nanoparticles. (b) Illustration of the three-step synthesis process, EDS analysis, and emission spectrum of CdSe:Yb (Adapted with permission from refs 242 and 244. Copyright 2010 and 2013 American Chemical Society).

and Dy^{3+} .⁴⁰⁸ Other examples of isovalent Eu^{2+} doping include $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ by solution combustion methods^{409,410} and $\text{Sr}_8\text{CaSc}(\text{PO}_4)_7:\text{Eu}^{2+}$ by thermal treatment in a reducing atmosphere CO at high temperatures.⁴¹¹ Another notable example is $\text{Sr}_2\text{Si}_3\text{N}_8$ phosphors doped with Eu^{2+} used in solid-state lighting.⁴¹²

Ce^{4+} can be incorporated into cation sites (IV) in oxometallates. For example, Zhang et al. investigated the preparation of Ce^{4+} -doped BaZrO_3 phosphors by a hydrothermal method,⁴¹³ in which Ce^{4+} doping was achieved by replacing Zr^{4+} sites in the crystal lattice. Incorporation of Ce^{4+} into the BaZrO_3 lattice enhanced the dual-frequency sonocatalytic generation of reactive oxygen species in aqueous solvents. Extensive studies have explored the isovalent doping of Ce^{4+} in TiO_2 and ZrO_2 nanostructures.^{414–418} Because the ionic size of Ce^{4+} is much larger than that of Ti^{4+} (1.02 versus 0.68 Å), the doping process can cause lattice defects, such as dislocations, in TiO_2 , leading to changes in the binding energies of Ti and O.⁴¹⁹

3.2.3. Semiconductor Quantum Dots. Semiconductor quantum dots (QDs) are characterized by large absorption coefficients ($\epsilon > 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and tunable emission energies. It has been shown that efficient energy transfer between QDs and rare-earth ions can be readily achieved in hybrid systems.⁴²⁰ Doping QDs with rare-earth ions can greatly enhance the luminescence of rare-earth dopants due to the antenna effect of the QD host. On the other hand, doping with rare-earth ions can affect the crystalline and electronic structures of QDs and alter their excitonic properties, resulting in enhanced band-edge emission or improved photocatalysis.⁴²¹ Based on various element combinations, QDs of group II–VI and halide perovskites are commonly explored for rare-earth doping.

3.2.3.1. Group II–VI Quantum Dots. Group II–VI QDs, such as CdSe, CdTe, and ZnS, have attracted the most attention and can now be routinely prepared by several synthetic protocols with precise control over particle size and morphology. However, it remains challenging to incorporate rare-earth ions into these QDs due to the wide large variation in ionic radii and charge imbalance between the Ln^{3+} ions and the host cations.

In most doping processes, rare-earth ions are mainly located at the surface of the host QDs. For example, Døssing et al. have attempted to dope CdSe QDs with Ln^{3+} ($\text{Ln} = \text{Tb}, \text{Eu}, \text{Gd}$) by

a thermal decomposition reaction.⁴²² In their method, the temperature and the addition of amine were two crucial factors in the preparation of Ln^{3+} -modified CdSe QDs. The surface-doped Ln^{3+} ions decreased the quantum yield and shortened the lifetime of the excited states of CdSe QDs. In addition, sensitization of surface dopants required high-energy excitation larger than the lowest absorption band of the CdSe QDs. The researchers treated the surface dopants as energy traps with decay kinetics independent of the dopants in the core. They also proposed that Ln^{3+} -related traps are associated with the surface of CdSe hosts. Therefore, surface dopants quench the photoluminescence, but hot excitons produced at the dopant sites can trigger the sensitization and emission of Ln^{3+} dopants.

Petoud, Waldeck, and colleagues successfully doped Ln^{3+} ($\text{Ln} = \text{Tb}, \text{Eu}$) ions onto the surface of ZnS QDs by a postsynthetic modification, based on the addition of excess $\text{Ln}(\text{NO}_3)_3$ salts into the reaction during thermal decomposition (Figure 10a).⁴²³ To locate Ln^{3+} dopants, they measured the luminescence decay rate of excited Eu^{3+} ions and the intensity ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ as a standard of comparison. Since these two factors depend on the symmetry of the Eu^{3+} coordination environment, the $^5D_0 \rightarrow ^7F_2$ transition (~ 616 nm) of Eu^{3+} , which has an electric dipole character, is usually forbidden in a perfectly octahedral environment, while it is allowed in a less symmetric environment and has a higher oscillator strength. In contrast, the $^5D_0 \rightarrow ^7F_1$ transition (~ 590 nm) of Eu^{3+} is a magnetic dipole transition that is insensitive to its environment. Surface sites are more asymmetric than inner core sites. According to emission data, Eu^{3+} dopants are mainly located at particle surfaces. In addition, ZnS QDs can act as antennae to sensitize Ln^{3+} emission that is stable for several weeks.

Organic molecules have been used to control rare-earth doping on the surfaces of QDs. To investigate the effect of spatial confinement on the energy transfer between ZnS QDs and Tb^{3+} ions, a reverse micelle method (water/sulfosuccinate/isooctane) was used to synthesize different types of ZnS QDs in the presence of Tb^{3+} ions.⁴²⁴ Tb^{3+} ions and ZnS nanoparticles were separated by an organic sulfosuccinate layer, and ZnS sensitized the Tb^{3+} emission through an intramolecular energy transfer mechanism.

To improve rare-earth doping of QDs, Martín-Rodríguez et al. adopted a three-step method to incorporate Yb^{3+} ions into CdSe QDs.²⁴⁴ First, CdSe nanocrystals were prepared by

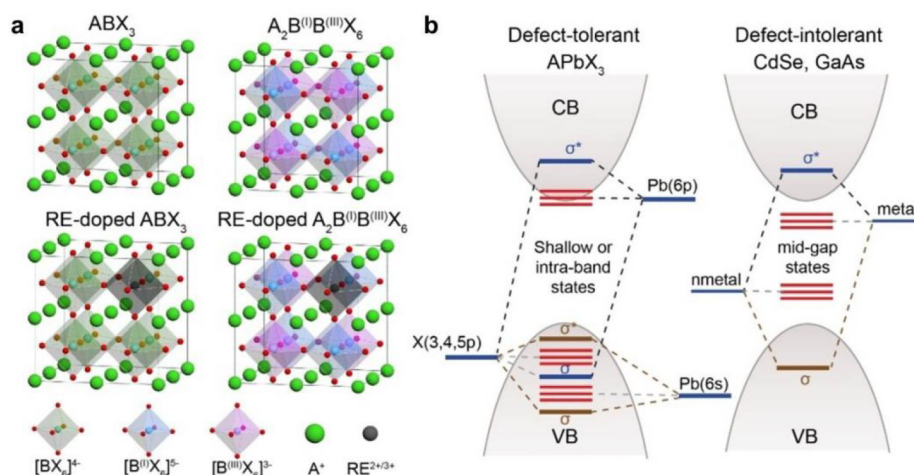


Figure 11. (a) Structural diagrams of the untreated perovskites ABX_3 and $A_2B^{(I)}B^{(III)}X_6$ and their rare-earth-doped counterparts. (b) Schematic diagrams of the electronic band structures of defect-tolerant ABX_3 perovskites and defect-intolerant semiconductors (CdSe and GaAs). σ and σ^* refer to bonding and antibonding orbitals, respectively (Adapted with permission from ref 426. Copyright 2017 American Chemical Society).

heating Cd-oleate and Se powder in trioctylphosphine. Yb^{3+} ions were then adsorbed onto nanocrystal surfaces, followed by the growth of a CdSe shell (Figure 10b). In a similar process, a model with trapped doping was used to fabricate Eu-encoded ZnS QDs.⁴²⁵ In this model, a new strategy was also used to adsorb Eu^{3+} ions onto the surface of ZnS QDs. Incorporation of Eu^{3+} ions into ZnS nanocrystals was achieved by further growth of an additional ZnS shell.

For Cd-based QDs, the significant toxicity usually hinders the practical application of these phosphors in the biological field. To improve the cytocompatibility of CdTe QDs, Schiff base ligands were employed to coordinate them with Ln^{3+} ($Ln = Yb, Tb, \text{ and } Gd$) ions by a microwave-assisted method.^{426,427} These doped QDs possess greater cytocompatibility than their unmodified counterparts and show potential for biolabeling in various environments.

In addition, divalent rare-earth ions such as Eu^{2+} , which allow 4f–5d transitions with stronger oscillator strengths, can be doped into QDs of Groups II–VI. For example, doping of ZnS nanoparticles with Eu^{2+} has been achieved by coprecipitation at elevated temperatures.^{428,429} Despite numerous efforts to dope II–VI QDs with rare-earth ions, the emission performance of the resulting nanoparticles is relatively modest. A more comprehensive summary of this field can be found in a recent review by Marin and Jaque.⁴³⁰

3.2.3.2. Halide Perovskite Quantum Dots. ABX_3 -type perovskites have become popular in recent years, owing to their excellent photoluminescence and photoelectronic properties, such as high quantum yield (>90%), narrow emission bandwidth (<100 meV), large absorption coefficient ($\sim 10^4 \text{ cm}^{-1}$), and tunable bandgaps (1.5–3 eV).⁴³¹ In cubic ABX_3 perovskite lattices, the A site is occupied by either cesium (Cs^+), methylammonium (MA ; $CH_3NH_3^+$), or formamidinium (FA ; $CH(NH_2)_2^+$). The B site is usually occupied by Pb^{2+} , and the X site by halide anions such as Cl^- , Br^- , and I^- . The $[BX_6]^{4-}$ octahedra are connected in a three-dimensional network, while the A-site cations reside in the large voids between them (Figure 11a). The structural stability of halide perovskites can be evaluated by the Goldschmidt tolerance factor. The maximum tolerance factor, as mentioned above, limits the choice of A-site cations, considering the suitability of

12-coordinate geometry for the tightest possible packing configuration.⁴³²

An attractive feature of these perovskites is their unique “defect tolerance.” Lead halide perovskite nanocrystals retain good photoluminescent or photoelectric properties even when they contain a high density of defects (e.g., vacancies and interstitials, up to 1–2 at %).^{432,433} Such defect-tolerance has been attributed to the antibonding nature in the valence band (VB) maximum and the strong spin–orbit coupling in the conduction band (CB) minimum.⁴³⁴ Theoretical calculations suggest that lattice defect-induced impurity states reside either in the VB or CB bands or slightly below these bands, forming shallow or intraband states with no states in the middle of the bandgap (Figure 11b).⁴²⁶ This is thus quite different from the cases in conventional semiconductors such as CdSe and InP, whose defect states are mainly located within the bandgap.

Because of the high defect tolerance, it is expected that rare-earth ions can be doped into perovskite hosts without significant lattice distortion.^{435–437} First, the six-coordinate environment of the Pb^{2+} site is suitable for rare-earth substitution, and the slightly smaller size of rare-earth ions compared to Pb^{2+} (ionic radius 1.19 Å) makes them viable as dopants (Table 1). On the other hand, introduction of emitting lanthanide dopants is expected to broaden the luminescence spectrum of perovskites. In addition, defect tolerance has enabled analogs of $AB^{(I)}B^{(III)}X_6$ halide double perovskites such as $Cs_2AgInCl_6$ and $Cs_2AgBiBr_6$.^{438–442} Bi^{3+} and In^{3+} sites are also suitable for occupation by trivalent rare-earth ions.

Rare-earth-doped halide perovskites can be prepared using conventional synthetic approaches derived directly from the preparation of pristine halide perovskites. For instance, colloidal rare-earth-doped halide perovskite nanocrystals have been prepared by ultrasonic treatment,⁴⁴³ hot injection method,^{40,251,444,445} room-temperature supersaturated recrystallization,⁴⁴⁶ and *in situ* generation.^{39,447,448} Among these techniques, the hot injection method has the advantage of providing nanocrystals with good colloidal dispersibility and size tuning.

In 2017, Song and co-workers reported the synthesis of rare-earth-doped $CsPbX_3$ ($X = Cl, Br$) nanocrystals by hot injection.⁴⁰ In their work, $CsPbCl_xBr_{3-x}$ nanocrystals doped

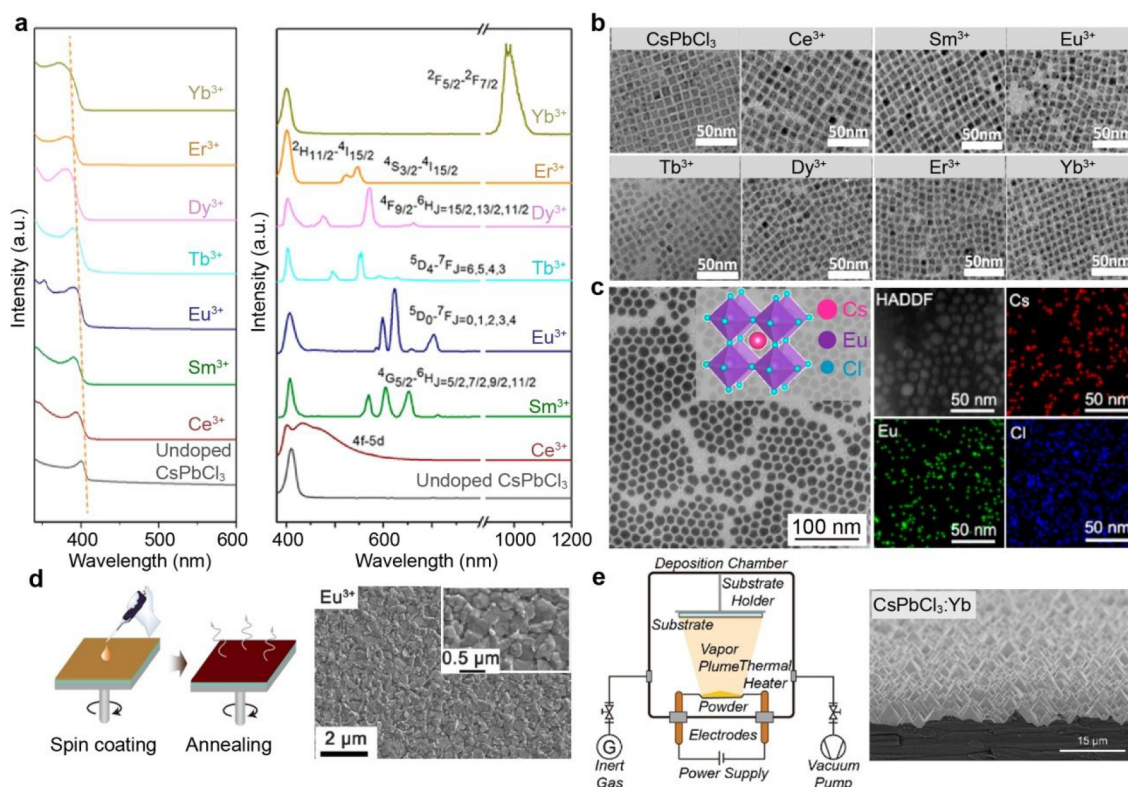


Figure 12. (a) Absorption and emission spectra of CsPbCl₃ nanocrystals doped with different rare-earth ions. (b) TEM images of CsPbCl₃ nanocrystals doped with various rare-earth ions. (c) TEM image and EDS mapping of CsEuCl₃ nanocrystals. (inset) Extended unit cell of CsEuCl₃. (d) Schematic of spin-coating method and SEM images of a typical CsPbI₃:Eu²⁺ formation by chemical vapor deposition. (e) Schematic of the chemical vapor deposition method and SEM images of typical CsPbCl₃:Yb³⁺ films formed by chemical vapor deposition (Adapted with permission from refs 444 and 449–451. Copyright 2017, 2019, 2020 American Chemical Society; Copyright 2019 American Association for the Advancement of Science).

with Yb³⁺/Er³⁺/Ce³⁺ were fabricated by injecting a hot Cs-oleate precursor into a mixed solvent of ODE, OM, and OA in the presence of lanthanide chlorides and PbBr₂ at 200 °C. The existence of lanthanide elements in CsPbCl₃Br_{3-x} hosts was confirmed by XRD, ICP-OES, XPS, and photoluminescence characterizations. In another study, Song and co-workers extended rare-earth doping in the CsPbCl₃ host system to almost the entire lanthanide family, including Ce³⁺, Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Er³⁺, and Yb³⁺, using a similar protocol (Figure 12a,b).⁴⁴⁴ CsPbCl₃ quantum dots doped with rare-earths exhibited cubic shapes with an average size of 7.8 to 6.3 nm. The particle size decreased with increasing atomic number of the rare-earth dopant. XRD characterization showed that diffraction peaks of rare-earth-doped nanocrystals gradually shifted toward large angles in contrast to untreated samples, which was attributed to lattice contraction caused by the smaller ionic radii of lanthanide dopants (1.03 Å for Ce³⁺ and 0.86 Å for Yb³⁺) compared to Pb²⁺ (1.19 Å).⁴⁵²

In addition to CsPbCl₃ hosts, rare-earth-doped CsPbBr₃ nanocrystals can also be synthesized using metal bromides as precursors. This was well exemplified by Yao et al., who reported the synthesis of CsPbBr₃:Ce³⁺ nanocrystals by injecting the Cs-oleate precursor into a hot mixture of ODE, OM, and OA in the presence of metal bromides at 185 °C.²⁵¹ The successful doping with Ce³⁺ was confirmed by EDS mapping. Notably, the actual doping concentration of Ce³⁺ in the host was an order of magnitude lower than the feed ratio in the reaction precursor, which can be attributed to the

unbalanced reaction activities between Pb²⁺ and RE³⁺ with halide anions.

Intriguingly, divalent rare-earths are more easily incorporated into CsPbX₃ hosts, as manifested by extremely high doping concentrations. In 2019, Lee and co-workers discovered that injection of a Cs-oleate precursor at 180 °C into organic solvents in the presence of YbI₂ and PbI₂ leads to cubic CsYbI₃ nanocrystals in which Pb²⁺ sites are completely replaced by Yb²⁺ ions.⁴⁵³ The Goldschmidt tolerance factor (*t*) and octahedral factor (*μ*) were calculated to be 0.86 and 0.46, indicating that cubic CsYbI₃ is highly stable at room temperature. High-resolution TEM images of the synthesized nanocrystals revealed a monodisperse cubic morphology with an average diameter of 9.5 nm, consistent with the calculated and experimental XRD patterns. Similar results were also shown in a recent study of Eu²⁺-doped CsPbCl₃ nanocrystals, in which 100% substitution of Pb²⁺ by Eu²⁺ was achieved (Figure 12c).⁴⁴⁹

During hot injection, metal bromide and iodide species decompose at high temperatures, limiting reaction temperatures to below 200 °C and disfavoring the formation of high-crystallinity products. To address this problem, a reverse injection route at relatively high temperatures for rare-earth doping has been developed by several groups using metal acetates in organic solvents. For example, the Gamelin,^{454,455} Wu,⁴⁵⁶ and Artizzu⁴⁵⁷ groups independently reported doping CsPbCl₃Br_{3-x} nanocrystals with La³⁺, Yb³⁺, or Er³⁺ by injecting a trimethylchlorosilane (TMS-Cl) or trimethylbromosilane (TMS-Br) precursor into a mixture of ODE, OM, and OA with

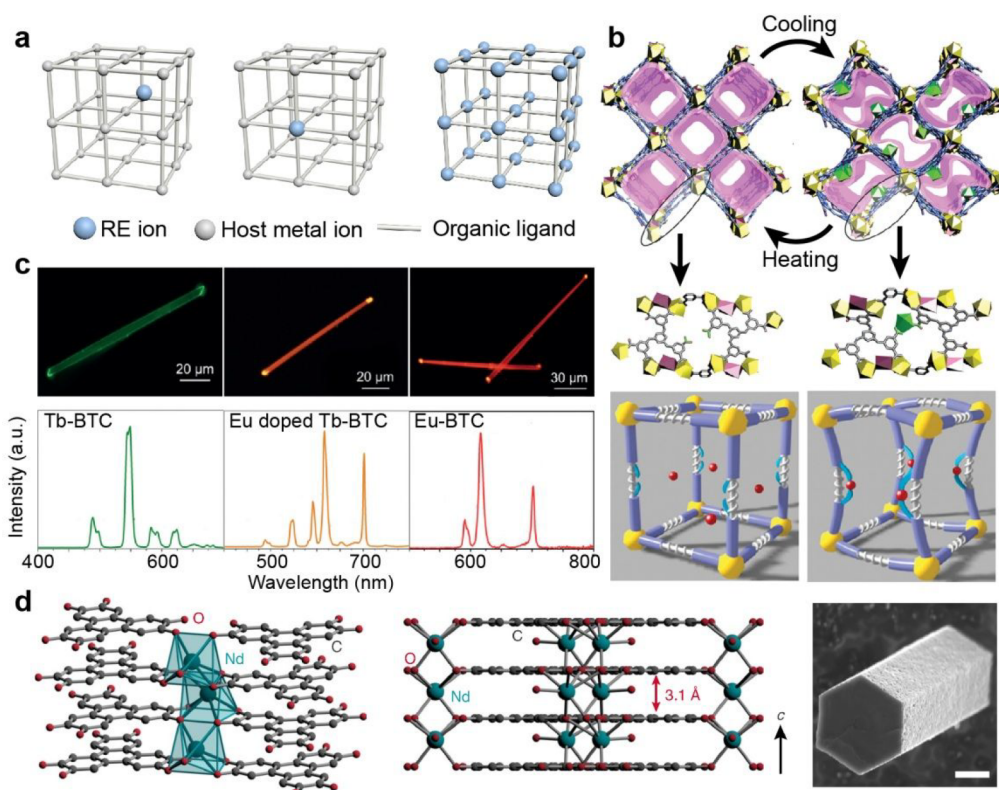


Figure 13. (a) Schematics of MOFs with absorbed, doped, or lattice-occupied rare-earth ions. (b) Schematic of the temperature-induced single-crystal to single-crystal transformations of rare-earth-doped MOFs. (c) Photoluminescence microscopy images and emission spectra of crystalline RE-BTC microrods. (d) Structural representation and SEM image of a NdHHTP crystal. The scale bar is 1 μm (Adapted with permission from refs 476–478. Copyright 2015, 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2020 Nature Publishing Group).

lanthanide and lead acetates at $\sim 240^\circ\text{C}$. This approach yielded larger nanocrystals with a typical size over 10 nm. Importantly, this protocol can be easily extended to the synthesis of rare-earth-doped halide double perovskites, such as $\text{Cs}_2\text{AgInCl}_6$, $\text{Cs}_2\text{AgBiCl}_6/\text{Cs}_2\text{AgBiBr}_6$, and $\text{Cs}_2\text{AgIn}_{1-x}\text{Bi}_x\text{Cl}_6$ nanocrystals.^{458–460} It is worth noting that the reaction temperature for the preparation of halide double perovskites is generally lower than that for lead halide perovskites due to the low decomposition temperature of the silver precursors.

Apart from colloidal nanocrystals, rare-earth-doped halide perovskite thin films have also been prepared by spin coating or chemical vapor deposition (CVD). In typical spin coating, precursors of metal halides (lead, rare-earth, and cesium halides) or MA and FA halides were first dissolved in a polar solvent (e.g., DMF and DMSO). The solutions were then spin-coated on a substrate, after which the remaining solvent was removed by annealing to obtain dense perovskite films with uniform grain size (Figure 12d).⁴¹⁹ Using this protocol, Tang and co-workers doped Sm^{3+} , Tb^{3+} , Ho^{3+} , Er^{3+} , and Yb^{3+} ions into CsPbBr_3 thin films on fluorine-doped TiO_2 substrates.⁴⁶¹ These rare-earth dopants were incorporated into the CsPbBr_3 lattice, as confirmed by combined characterizations including XRD, ICP-AES, and XPS. Additionally, $\text{MAPbI}_3\text{:Eu}^{2+}$, $\text{MAPbI}_3\text{:Eu}^{2+}/\text{Eu}^{3+}$, $\text{MAPbI}_3\text{:Nd}^{3+}$, $\text{CsPbI}_3\text{:Eu}^{3+}$, and $\text{CsPbBr}_3\text{:Eu}^{2+}$ were also successfully prepared by spin coating.^{450,462–465}

Despite its usefulness, spin coating is a solution-based process that may impose certain limitations on film manufacture. For example, although the precursors PbBr_2 , PbI_2 , and MAI are readily soluble in common solvents, Cs-

based halide salts generally disperse poorly in liquids, limiting the range of compositions available for synthesis. Moreover, spin coating cannot be performed on substrates with irregular topology. This limitation can be resolved by the solvent-free CVD method, which allows thin film deposition on arbitrary substrates. Gamelin and co-workers have recently demonstrated a single-source CVD method for preparing $\text{CsPbCl}_3\text{:Yb}^{3+}$ and $\text{CsPbCl}_{1.5}\text{Br}_{1.5}\text{:Yb}^{3+}$ films on substrates suspended 5–20 cm above the source at rates ranging from ~ 0.05 to $\sim 1000 \text{ \AA s}^{-1}$ (Figure 12e).⁴⁵¹ A crucial point is that the feedstocks were mechanochemically prepared prior to deposition using a planetary ball mill, circumventing the nonstoichiometry caused by unbalanced decomposition temperatures in conventional multisource coevaporation routes. The perovskite film preserved the features of the patterned submicron structures in the silicon substrates, which is useful for photon absorption.^{466,467}

3.2.4. Metal–Organic Frameworks. Metal–organic frameworks (MOFs) are organic–inorganic hybrid crystalline porous materials consisting of a three-dimensional network of metal ions or clusters connected by multidentate organic molecules.^{468–470} These organic molecules typically contain carboxylate, phosphonate, and pyridyl functional groups. The bonding energy between the metal ion and the organic molecule is moderate, which allows reversible bond formation and dissolution during MOF synthesis.²⁶¹ MOFs have large pore sizes (3–100 $\text{\AA}$), high porosity (up to 90%), large surface areas (up to $7000 \text{ m}^2 \text{ g}^{-1}$), and low densities ($\sim 0.13 \text{ g cm}^{-3}$).^{471,472} In addition, many organic ligands with large light absorption coefficients can act as antennas to sensitize

luminescent metal centers in the systems. In principle, rare-earth ions can be directly incorporated into MOF hosts, either as guests (rare-earth-absorbing MOFs), as dopants (rare-earth-doped MOFs), or as metal nodes (rare-earth-based MOFs) (Figure 13a). Incorporated rare-earth ions can work as luminescent centers, while connecting ligands can serve as luminescent antennas that participate in energy transfer processes.^{473,474}

3.2.4.1. Rare-Earth-Absorbed MOFs. The large pore structure in MOFs can accommodate RE ions. In a representative example, Rosi and co-workers developed a series of “bio-MOFs-1” ($\text{Zn}_8(\text{ad})_4(\text{BPDC})_6\text{O} \cdot 2\text{Me}_2\text{NH}_2$, 8DMF, 11 H_2O) with columnar zinc-adeninate assemblies and biphenyl dicarboxylate linkers.⁴⁷² The bio-MOF-1 was anionic with mobile DMA cations located in 1-D channels.⁴⁷⁵ Therefore, labile DMA cations can be easily replaced with lanthanide ions by soaking them in DMF solutions of lanthanide nitrate salts. Successful incorporation of lanthanide ions in bio-MOFs-1 was made evident by fluorescence measurements. The emission spectra of the chromophoric structure in the bio-MOF-1 clearly showed characteristic $f-f$ transitions of Sm^{3+} , Tb^{3+} , Eu^{3+} , and Yb^{3+} under 340 nm excitation. It is noteworthy that rare-earth emissions can be detected even under aqueous conditions, although they are strongly attenuated by water molecules. This suggests that the bio-MOF-1 scaffold can sensitize rare-earth dopants and protect guest ions from extraction by solvents.

In another study, Yan and co-workers reported the preparation of Eu^{3+} -encapsulated MIL-53-COOH(Al)MOFs by immersing pristine MOFs in corresponding lanthanide salt solutions.⁴⁷⁹ Trivalent rare-earths were encapsulated in the one-dimensional pore channels of MOFs due to interactions with the carboxyl groups of the ligands. These Eu^{3+} -encapsulated MOFs can be used to detect Fe^{3+} ions because the luminescence of Eu^{3+} emission is quenched by energy transfer. Similarly, Cui, Qian, and co-workers reported Tb^{3+} -encapsulated MIL-100(In)MOFs with strong oxygen-sensitive emission of Tb^{3+} , which makes them attractive for the development of highly sensitive oxygen sensors.⁴⁸⁰

Incorporation of rare-earth ions into MOFs can alter local structures. This was illustrated by Zhang and co-workers, who prepared Eu^{3+} -encapsulated MOFs in the form of $(\text{H}_3\text{O}^+)-\text{Eu}_{0.5}[\text{EuNa}_{0.5}\text{L}(\text{DMF})(\text{H}_2\text{O})] \cdot (\text{solvent})_x$ (**EuL**).⁴⁷⁶ Due to structural transformation by cleavage and formation of dynamic $\text{Eu}-\text{O}$ bonds, **EuL** MOFs can transform between $C2/c$ and $P2_1/n$ space groups, which is accompanied by rapid release or deposition of free Eu^{3+} ions in the channels. This reversible structural transformation can be triggered by varying the temperature. At a low temperature (193 K), free Eu^{3+} ions can be trapped by free carboxylate groups, leading to immediate conformational changes in the **EuL** MOFs. When the temperature is gradually increased to room temperature, trapped Eu^{3+} ions gradually escape from the encapsulation, and the MOFs return to their original structures (Figure 13b).

3.2.4.2. Rare-Earth-Doped MOFs. Apart from occupying the pores of MOFs, rare-earth ions often occupy nodal points as dopants. The main methods for preparing rare-earth-doped MOFs are cation exchange and hydrothermal synthesis.

An early example is the preparation of Dy^{3+} -doped $\text{Cd}_{1.5}(\text{H}_3\text{O})_3[(\text{Cd}_4\text{O})_3(\text{hett})_8] \cdot 6\text{H}_2\text{O}$ MOFs through cation exchange by soaking pristine MOFs in lanthanide nitrate solution for 3 weeks.⁴⁸¹ Crystallographic studies showed that the original topology was preserved after Dy^{3+} doping, except

that hydroxybridged square planar $\{\text{Dy}_4(\mu_2\text{-OH})\}^{11+}$ units replaced the $\{\text{Cd}_4(\mu_4\text{-O})\}^{6+}$ units at vertices of the octahedron in the parent MOFs. Because of aliovalent substitution, positively charged MOFs were assumed to be compensated by negatively charged NO_3^- anions confined in MOF channels.

Cation exchange at room temperature is usually time-consuming but can be accelerated by heating. For example, Lejaeghere and co-workers demonstrated a fast and simple microwave method for doping UiO-66 MOFs with rare-earth ions (Ce^{4+} , Nd^{3+} , Eu^{3+} , and Yb^{3+}).⁴⁸² Incorporation of rare-earth ions into the Zr sites of MOFs was confirmed by XRD characterization, which showed a shift of the diffraction peaks to low angles. Dopant distributions were further verified by EDX elemental mapping, which showed homogeneous distribution of Ce^{4+} ions with some aggregations at the edges, probably due to limited diffusion of rare-earth precursors in the materials. Doping of rare-earth ions in inorganic nodes can change the electronic structure of UiO-66 MOFs, improving the photocatalytic activity of the hosts. Doping induces a new energy band within the bandgap and promotes ligand-to-metal charge transfer (LMCT) between the metal node and the ligand.

Hydrothermal synthesis is a straightforward synthetic method for rare-earth-doped MOFs, by which the solubility of organic linkers in the solvent can be greatly promoted at high temperatures to facilitate material synthesis.^{483–485} For example, Nenoff and co-workers prepared Eu^{3+} -doped SMOF-1 ($(\text{In}(\text{BTB})_{2/3}(\text{OA})(\text{DEF})_{3/2})$) by reacting $\text{In}(\text{NO}_3)_3$ and EuCl_3 directly with 1,3,5-tris(4-carboxyphenyl)benzene (BTB) and oxalic acid in a mixture of N,N' -diethylformamide and ethanol at 115 °C for 4 days.⁴⁸⁶ The eight-coordinated indium sites in SMOF-1 can accommodate large Eu^{3+} ions. The pristine SMOF-1 showed broad emission centered at ~500 nm under excitation at 380 nm, which was attributed to the ligand-based $\pi-\pi^*$ transition and subsequent LMCT transition. Introduction of Eu^{3+} dopants resulted in a particularly narrow red emission band, offering new opportunities for the development of MOF-based solid-state illumination.

3.2.4.3. Rare-Earth-Based MOFs. Rare-earth-based MOFs refer to a special type of MOFs with nodes or lattice sites completely occupied by rare-earth ions or secondary building units.^{24,487} These MOFs have several advantages over conventional transition-metal-based MOFs.⁴⁸⁸ First, rare-earth ions have a high coordination number and flexible coordination geometry.⁴⁸⁹ Second, lanthanide ions are hard Lewis acids, with their coordination chemistry dominated by multidentate ligands featuring hard donor atoms such as oxygen and nitrogen.^{490,491} Last, rare-earth doping enables incorporation of multiple types of rare-earth ions into individual MOF hosts without causing noticeable crystal imperfections.⁴⁹² By doing so, tunable luminescence with controllable energy transfer processes can be achieved.⁴⁹³

Rare-earth-based MOFs are commonly synthesized by mixing organic ligands and rare-earths at mild temperatures (below 150 °C). For example, Eddaoudi and co-workers have prepared a series of RE-1,4-NDC-MOFs (RE = Eu, Tb) by heating 1,4- H_2NDC , $\text{Y}(\text{NO}_3)_3$, and 2-fluorobenzoic acid in a mixed solution of DMF, H_2O , and HNO_3 at 115 °C for 60 h.^{494,495} The size and morphology of the resulting MOFs can be regulated by reaction time, temperature, and solvent ratio.

Energy transfer processes and multicolor emissions have been extensively studied in MOFs containing $\text{Eu}^{3+}/\text{Tb}^{3+}$ ion pairs. An excellent example is Ln-BTC (Ln = Tb^{3+} , Eu^{3+} ; BTC

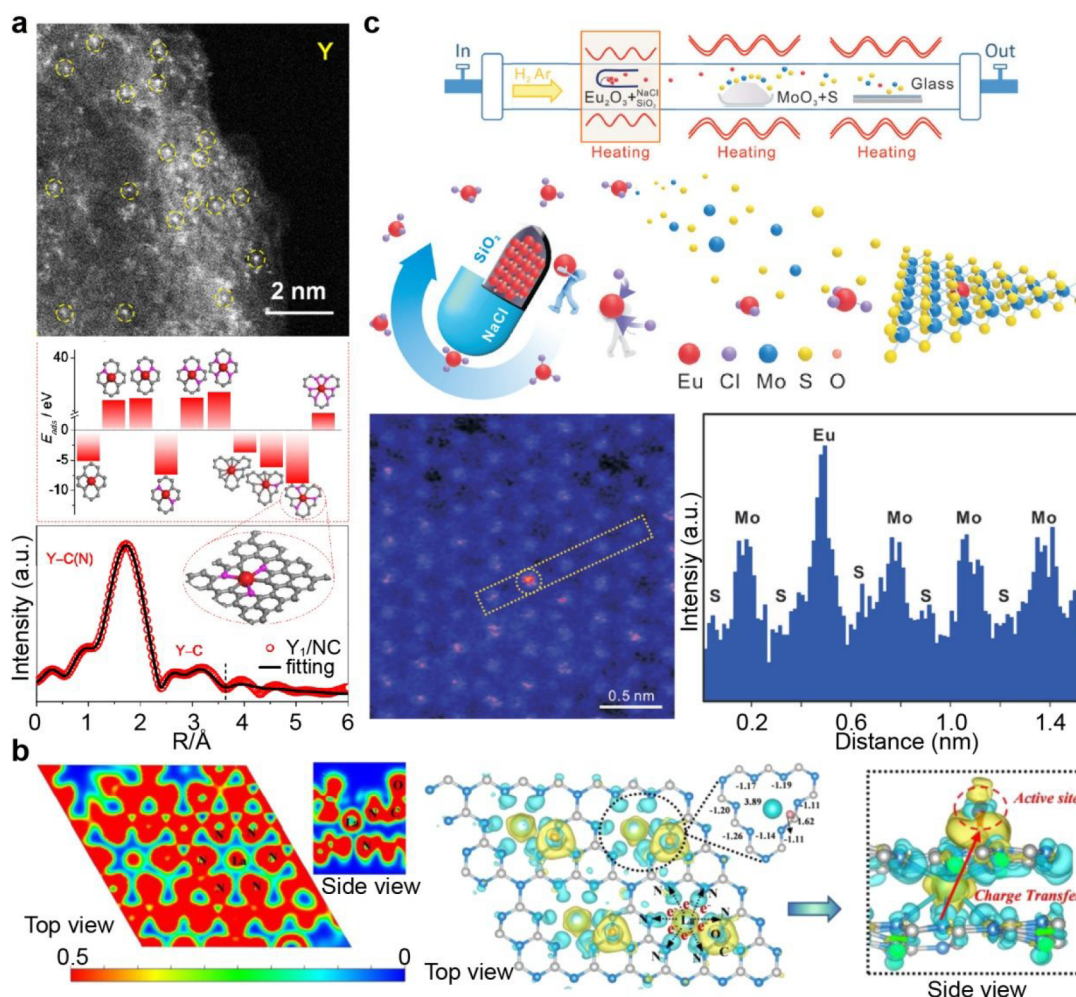


Figure 14. (a) HAADF-STEM images of Y₁/NC, calculated active site structures of a single yttrium atom and corresponding adsorption energies, as well as FT-EXAFS fit in R-space of Y₁/NC. (b) Electronic site function and differential charge density analysis of O/La-CN (the blue region indicates charge accumulation and the yellow region indicates charge loss), C, N, O, and La atoms are gray, blue, red, and green spheres, respectively. (c) Schematic of the MASR-CVD synthesis process for Eu-embedding MoS₂ single crystals, HAADF-STEM atomic image of Eu-embedding MoS₂, and intensity profile of the region marked with a dotted box (Adapted with permission from refs 16, 260, and 519. Copyright 2020 American Chemical Society; Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

= 1,3,5-benzenetricarboxylic acid) MOFs, in which luminescence spectra can be fine-tuned by adjusting the Eu³⁺/Tb³⁺ ratio (Figure 13c). Other examples include Eu_xTb_{1-x}-DMBDC (DMBDC = 2,5-dimethoxy-1,4-benzenedicarboxylate), Eu_xTb_{1-x}-BDC (BDC = 1,4-benzenedicarboxylate), Eu_xTb_{1-x}-DSB (DSB = 3,5-disulfobenzate), Eu_xTb_{1-x}-L (L = 1,3-bis(4-carboxyphenyl) imidazolium), Eu_xTb_{1-x}-hfa (hfa = hexafluoroacetylacetonate), and Eu_xTb_{1-x}-BTC (BTC = 1,3,5-benzenetricarboxylate).^{496–502}

Rare-earth-based MOFs are generally considered to have low conductivity because linking organic groups are mostly insulators with small π -orbital conjugation. Recently, it has been found that these special MOFs exhibit proton conductivity.^{503–505} For example, Dincă and co-workers reported that Ln-HHTP MOFs (Ln = La, Nd, Ho, Yb; HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene) exhibited efficient and tunable one-dimensional charge transport properties (Figure 13d).⁴⁷⁸ Among Ln-HHTP MOFs, Ho-HHTP MOFs exhibited the highest electrical conductivity of 0.05 S cm⁻¹ at 29 °C, which is within the range of the most conductive MOFs to date. In another representative work, Zaworotko and co-workers found that coordinate-saturated Gd

zeolite-like MOFs (Gd-ZMOFs) exhibit high longitudinal relaxivity.⁵⁰⁶ Compared with conventional Gd(III) complex-based contrast agents, these Gd-ZMOFs show higher stability and better contrast performance for MRI, which makes them attractive as potential contrast agents for clinical use.

3.2.5. 2D Layered Nanomaterials. Since the first isolation of graphene in 2004,⁵⁰⁷ two-dimensional (2D) layered nanomaterials have attracted great attention owing to their excellent chemical and physical properties. Recently, there has been growing research interest in doping 2D layered nanomaterials with rare-earth elements. They include graphene/graphene oxides,⁵⁰⁸ graphitic carbon nitrides,^{16,260,509–511} transition metal dichalcogenides (MoS₂, WS₂, WSe₂, or In₂Se₃),^{512–515} and layered metal oxides (layered RE hydroxides and 2D rare-earth oxides).^{516,517} Rare-earth dopants have been mainly introduced in these hosts as luminescent guests. They can also be employed to modify the electric and magnetic properties of 2D substrates. Owing to their high surface-to-volume ratios, rare-earth-doped 2D nanomaterials have great potential for miniaturization and intelligentization of functional devices in heterogeneous catalysis and optoelectronic applications.

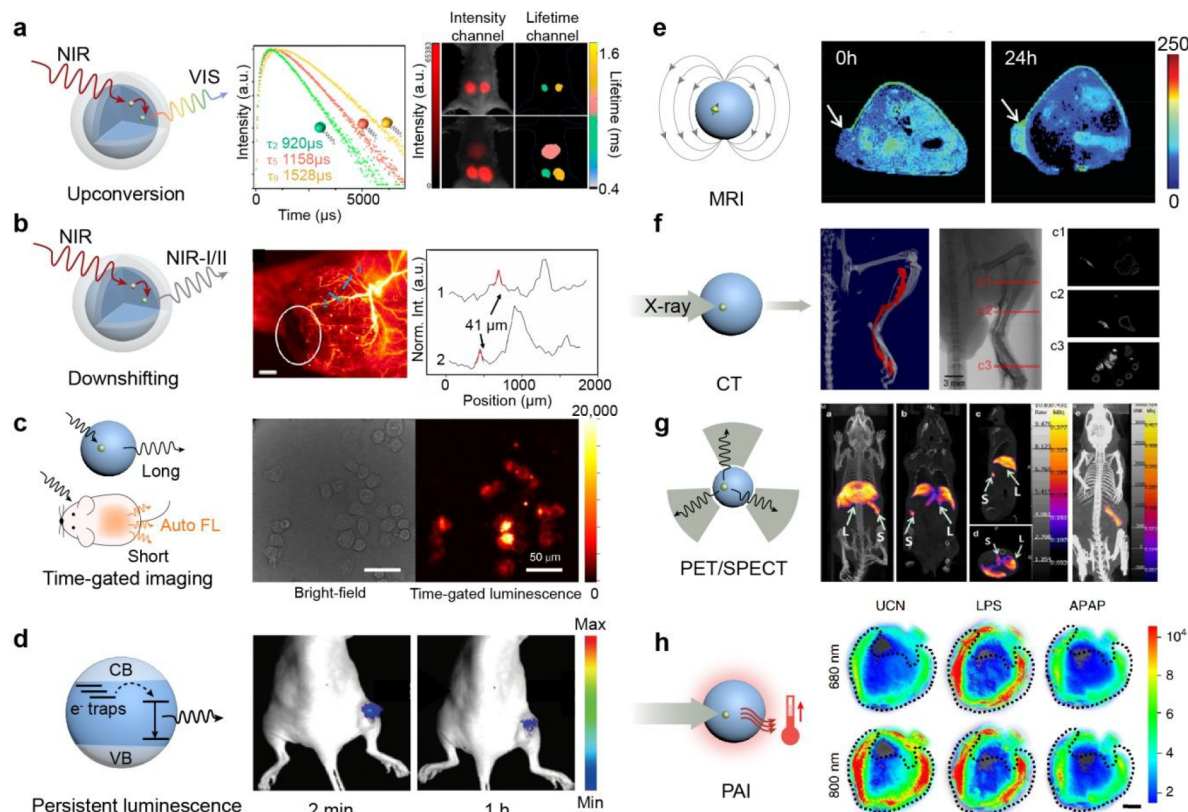


Figure 15. Schematic illustration of the principles of imaging modes and corresponding (a) visible fluorescence imaging, (b) near-infrared fluorescence imaging (scale bar, 2 mm), (c) time-gated imaging (scale bars, 50 μm), (d) persistent luminescence imaging, (e) magnetic resonance imaging (MRI), (f) computed tomography (CT scale bar, 3 mm), (g) positron emission computed tomography/single-photon emission computed tomography (PET/SPECT), and (h) photoacoustic imaging (PAI) of rare-earth-doped nanomaterials (Adapted with permission from refs 533–540. Copyright 2011, 2019, 2020 American Chemical Society; Copyright 2019 Nature Publishing Group; Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2013 Ivyspring International Publisher; Copyright 2012 Elsevier).

Graphene oxide nanosheets and rare-earth ions can form strong complexes through oxygen–metal coordination at the surface.⁵¹⁸ Shinde et al. synthesized graphene oxide nanosheets doped with La^{3+} , Eu^{3+} , or Yb^{3+} using a two-step method.⁵⁰⁸ Rare-earth ions were absorbed onto graphene in an acidic aqueous solution and then thermally exfoliated at high temperature. Successful doping the graphene substrate with rare-earths was mapped by EDS. Eu^{3+} -doped graphene improved the electrocatalytic performance, which can be attributed to additional doping sites and tuning the physical properties of the graphene substrate.

Moreover, rare-earth dopants can be atomically incorporated into layered carbon nitride structures via metal–nitrogen bonds. Shui and co-workers doped dispersed Y and Sc atoms into amorphous carbon supports.¹⁶ They showed that Y and Sc atoms were stabilized in large carbon voids by the coordination of six nitrogen and carbon atoms. This is in contrast to the conventional $\text{M}-\text{N}_4$ coordination structures ($\text{M} = \text{Fe}, \text{Co}, \text{Mn}$, etc.) in transition metal–carbon nitrides (Figure 14a). Y- and Sc-doped carbon nitrides were excellent single-atom catalysts, with high nitrogen and carbon dioxide reduction activity. In a parallel study, Dong and co-workers fabricated La single atoms on graphitic carbon nitrides using a one-step calcination method.²⁶⁰ XAS measurements and DFT calculations showed that La was complexed by both N and O groups in the substrates. In the structure, La–N facilitated energy transfer, which improved the selectivity in photocatalytic CO_2 reduction (Figure 14b).

Rare-earths can be introduced into 2D transition metal dichalcogenides. In 2016, Hao's group applied a two-step CVD method to fabricate large $\text{MoS}_2\text{:Er}$ thin films.⁵¹⁵ They first deposited Er^{3+} -doped Mo thin films on SiO_2/Si substrates and then sulfurized the samples by CVD. In a later study, Xu et al. designed a one-step matrix-assisted CVD method to synthesize Eu^{3+} -doped MoS_2 single crystals.⁵¹⁹ NaCl was added as a salt-assisted medium with Eu_2O_3 . The addition of salt supported the sustained release of Eu precursor and ensured the growth of high-quality Eu-doped MoS_2 single crystals on glass substrates (Figure 14c). The properties of doped 2D transition metal dichalcogenides are highly dependent on the nature of rare-earth dopants. While luminescent dopants such as Yb^{3+} , Er^{3+} , Eu^{3+} , and Ho^{3+} confer photoluminescence properties,^{513,520,521} doping MoS_2 with Dy^{3+} confers room-temperature ferromagnetism to the substrates.⁵²²

Layered rare-earth hydroxides (LRHs) are another type of promising 2D layered metal oxide for rare-earth doping. They typically contain layered $\text{RE}_x(\text{OH})_y \cdot n\text{H}_2\text{O}$ polyhydroxide structures with intercalated anions between the hydroxide layers.⁵²³ Suspended colloidal LRHs have been prepared mainly by top-down methods through exfoliation of bulk layered hydroxide crystals. Lee et al. first isolated thin nanosheets of LRHs from bulk $[\text{Gd}_2(\text{OH})_5(\text{H}_2\text{O})_x]\text{Cl}$ crystals by ultrasonic treatment in deionized water.⁵²⁴ Subsequent studies led to various colloidal LRHs, including Eu-hydroxide nanosheets,⁵²⁵ LGdH:RE ($\text{RE} = \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}$) nanosheets,⁵²⁶ LYH:Tb nanosheets,^{527,528} and LTbH/LEuH nano-

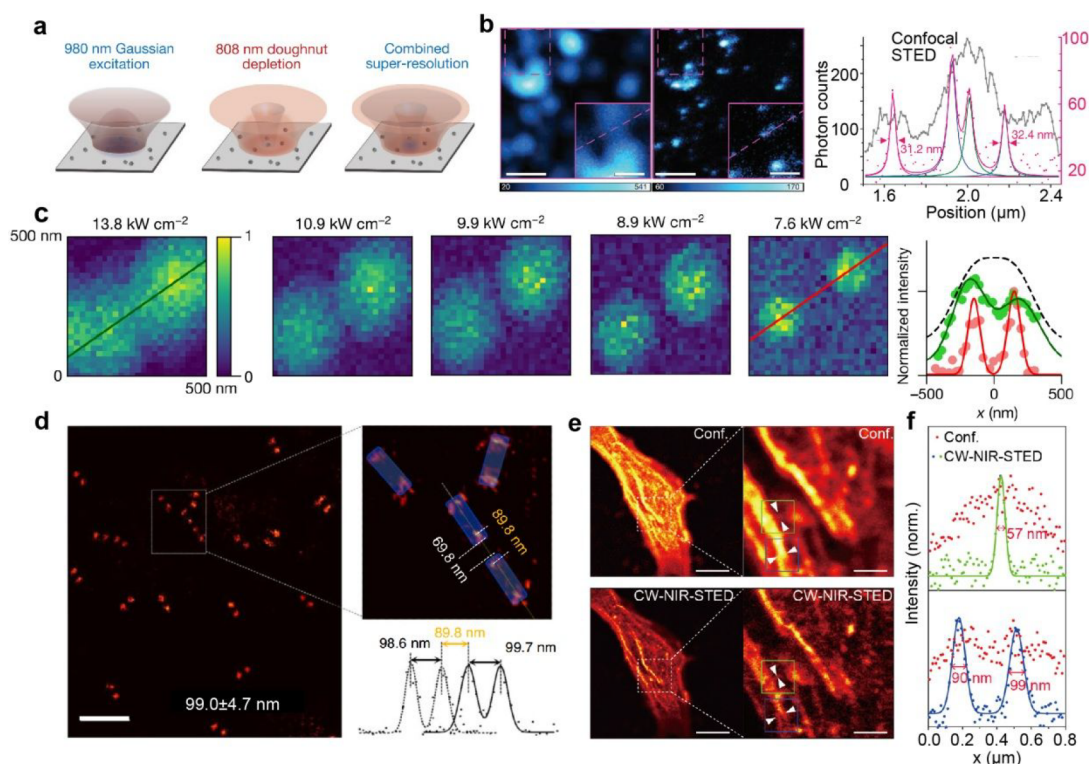


Figure 16. (a) Diagrams of upconversion-STED super-resolution imaging. (b) Comparison of confocal and super-resolution images and corresponding intensity profiles of 40 nm 8% Tm-doped UCNPs. Scale bars are 500 nm (main images) and 200 nm (insets). (c) Photon-avalanche single-beam super-resolution images and corresponding intensity profiles of Tm³⁺ avalanching nanoparticles. (d) Super-resolution image of heterogeneous nanorods. The scale bar is 400 nm. (e) Standard (top) and super-resolution (bottom) images of HeLa cells stained with Nd-doped nanoprobes. Scale bars are 10 μ m (original images) and 2 μ m (enlarged images). (f) Intensity profiles of selected areas from e (Adapted with permission from refs 543–546. Copyright 2017, 2020, 2021 Nature Publishing Group).

sheets.^{529,530} As an added benefit, LRHs can serve as templates for the synthesis of other ultrathin rare-earth substrates, such as Tm₂O₃ nanosheets and YPO₄:Eu nanophosphors.^{531,532}

4. TECHNOLOGICAL APPLICATIONS

To realize practical applications of rare-earth-doped nanomaterials, it is generally necessary to further functionalize these materials by assembling them with other types of nanostructured building blocks or integrating them into micro/nanosized devices. In the following, we provide an overview of a wide range of applications for rare-earth nanomaterials enabled by the complex interplay between the dynamics of doping and the underlying composite structures.

4.1. Bioapplications

There is particular interest in using rare-earth-doped nanomaterials for bioapplications, including bioimaging, single-particle biomarking, and therapeutics. Most current work focuses on rare-earth fluorides and oxysalt-based nanomaterials for bioapplications because they are chemical stable and biocompatible.

4.1.1. Bioimaging. Bioimaging is a subfield of biology that aims to image and understand the spatiotemporal mechanisms of biological processes, whether *in vivo*, *in vitro*, systematic, or cellular, for research and clinical purposes. Bioimaging is often combined with bioanalytical techniques to quantify these phenomena for meaningful interpretation. It is also combined with therapeutics to achieve image-guided treatment and intervention.⁵⁴¹ To date, a wide range of luminescent bioimaging techniques have been developed, including

upconversion luminescence, downshifting emission, time-gated luminescence imaging, and persistent luminescence imaging (Figure 15a–d).⁵⁴² Moreover, rare-earth-doped nanomaterials have been used as contrast agents to enhance the observability of specific targets for clinical imaging such as MRI, computed tomography (CT), positron-emission computed tomography/single-photon emission computed tomography (PET/SPECT), and photoacoustic imaging (PAI) (Figure 15e–h). Advances in the chemical and physical properties of rare-earth-doped nanomaterials can help address current bioimaging challenges. Developments in rare-earth-doped nanomaterials can improve chemical functionality for targeting, increase luminescence stability for long-term imaging, and push the boundaries of imaging biological events with unprecedented spatial and temporal resolution.

4.1.1.1. Upconversion Luminescence Imaging. Since the early 2000s, nanomaterials doped with rare-earth ions have served as luminescent probes for tissue and cell imaging. Upconversion luminescence imaging benefits from the NIR excitation of rare-earth-doped nanophosphors, which provides enhanced tissue penetration and suppression of the autofluorescence background.⁵⁴⁷ This technique has been widely applied to visualize biological activity for many applications. Many specific reports on upconversion nanophosphors for bioimaging have been written in the last decades.^{548–552} In the last five years, the application of upconversion luminescence imaging has been extended to include new features, such as spectral and temporal multiplexing⁵³³ and super-resolution imaging.^{29,553}

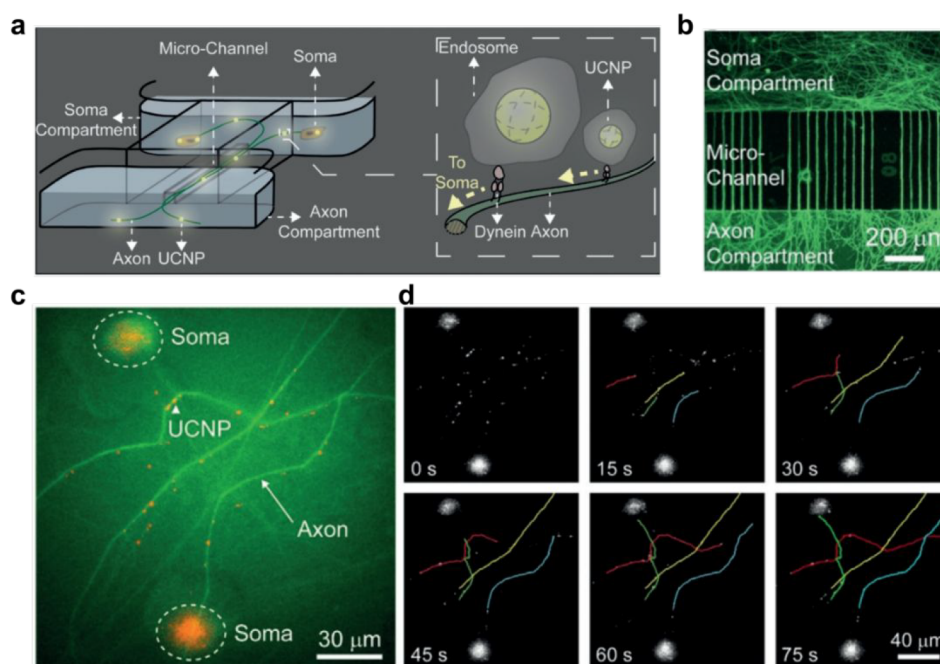


Figure 17. (a) Schematic illustration of a dual-chamber microchamber and tracking process. (b) Fluorescence microscopic image of calcein-labeled neurons. (c) Luminescence microscopic image showing typical dynein tracking. (d) Tracking of four individual upconversion luminescence spots (Adapted with permission from ref 560. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

In 2017, Liu et al. reported the use of $\text{Yb}^{3+}/\text{Tm}^{3+}$ -codoped NaGdF_4 nanoparticles for super-resolution imaging with stimulated emission depletion (STED).⁵⁴³ High Tm^{3+} doping (8 mol %) was used to induce strong cross-relaxation between activators and population inversion relative to the $^3\text{H}_6$ ground state of Tm^{3+} . The optimized spatial resolution is 28 nm, and the power of the depletion beam is much lower than conventional organic STED probes (Figure 16a and b). This method requires dual laser excitation at 980 and 808 nm to realize emission depletion for STED imaging. Single-beam super-resolution imaging has also been developed based on photon-avalanche upconversion.^{544,554} In 2019, Bednarkiewicz and co-workers theoretically predicted that photon-avalanching can constrain the point spread function in imaging.⁵⁵⁴ They investigated photon avalanche in Nd^{3+} -doped nanoparticles under nonresonant 1064 nm photoexcitation. The simulations resolved to 20 nm features when the avalanching-induced nonlinearity exceeded 80. In 2021, Lee et al. went a step further and experimentally demonstrated such an effect in Tm^{3+} -doped nanocrystals.⁵⁴⁴ In their experimental study, the avalanching emission from nanoparticles could scale nonlinearly with the 26th power of the pump intensity. Spatial resolution below 70 nm was achieved with single-beam excitation without the need for computational analysis (Figure 16c). In 2021, Liang et al. reported NIR-STED imaging based on downshifting lanthanide nanoparticles.⁵⁴⁶ This technique exploits population inversion through slow parity-forbidden transitions of quasi-four-level Nd^{3+} emitters and enables super-resolution imaging with lateral resolution below 20 nm and without photobleaching. The rapid development of super-resolution imaging techniques has found many applications, such as single-element analysis,⁵⁵⁵ structural decoding of heterogeneous nanoparticles,⁵⁴⁵ and super-resolution cell imaging (Figure 16d–f).⁵⁴⁶

Because of the high photostability of hosts, rare-earth-doped nanophosphors allow detailed molecular activities to be

visualized at the single-particle level.^{556–559} Rare-earth-doped NaREF_4 nanophosphors have recently been used for real-time tracking of motor proteins for axonal transport.⁵⁶⁰ Figure 17a,b shows a microchamber with a soma compartment, interconnected microchannels, and an axonal compartment. When UCNPs are introduced into the axonal compartment, they can be transported by motor proteins along axonal tracts, allowing in situ tracking of motor protein movement. Snapshots of emission were recorded in real-time at 7 Hz (Figure 17c,d). Continuous imaging of moving nanoparticles under wide-field illumination could be achieved because of the zero-autofluorescence and nonblinking properties of UCNPs. $\text{Yb}^{3+}/\text{Tm}^{3+}$ -codoped NaYF_4 nanophosphors have also been used to track and assess the biodistribution of natural killer cells *in vivo*.⁵⁶¹ Moreover, upconversion nanophosphors have been used as injectable retinal photoreceptors to enable NIR vision in mammals.⁵⁶² Nevertheless, most of the nanoparticles studied are much larger than organic probes, with the smallest sizes ranging from 5 to 10 nm. Any smaller size will affect the brightness of the luminescence due to surface quenching. Therefore, the development of smaller but brighter rare-earth-doped inorganic phosphors for targeting single molecules will be a significant step forward.^{52,563,564}

4.1.1.2. Downshifting Luminescence Imaging. Luminescence imaging in the NIR-II range (1000–1700 nm) has become another hot topic in bioimaging in last five years. NIR-II light offers deeper tissue penetration and lower scattering than UV/vis excitation.⁵⁶⁵ Rare-earth-doped nanomaterials are important candidates for NIR-II imaging because many dopants (e.g., Nd^{3+} , Pr^{3+} , Ho^{3+} , Tm^{3+} , Er^{3+} , and Yb^{3+}) exhibit downward emission due to deeper 4f–4f transitions.^{566–569} For example, Song et al. fabricated single-layered graphene-oxide-modified $\text{NaYF}_4\text{:Yb/Er@NaYF}_4$ nanocrystals and realized efficient cell uptake, excellent biocompatibility, flexible surface modifiability, and NIR-II imaging at 1532 nm.⁵⁷⁰ Zhao et al. combined NIR imaging at 1060 nm with ROS-activated

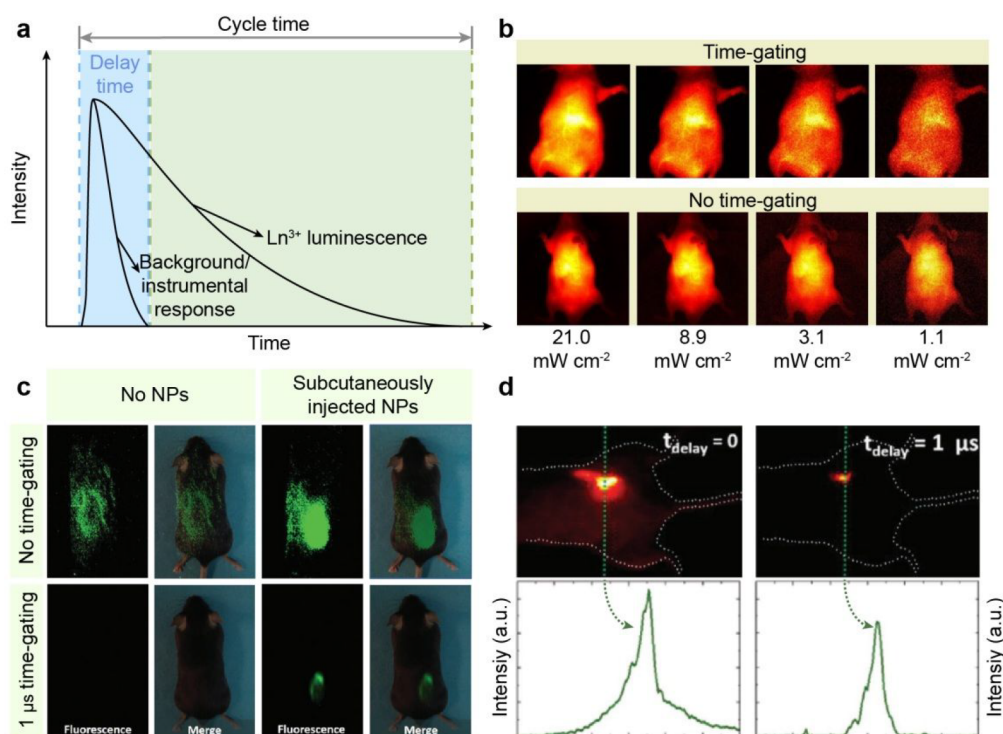


Figure 18. (a) Schematic of time-gated imaging. (b) Comparison of time-gated imaging (top) and normal imaging (bottom) of α -NaYbF₄@CaF₂ nanoparticles (NIR τ -dots). (c) Optical and NIR images of mice with and without Yb/Nd-doped nanoparticles, recorded at 0 and 1 μ s delay times. (d) NIR images and corresponding intensity profiles collected for a mouse subcutaneously injected with NaGdF₄:Nd nanoparticles with 0 and 1 μ s delay (Adapted with permission from refs 535, 567, and 580. Copyright 2019 Nature Publishing Group; Copyright 2018 The Royal Society of Chemistry; Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

cross-linking of luminescent probes to image inflammatory sites with greatly improved signal-to-noise ratios.⁵⁷¹

Many downshift NIR-II emitters such as Yb³⁺, Er³⁺, Ho³⁺, and Tm³⁺ suffer from luminescence quenching due to high-energy vibrations of solvent molecules. To improve NIR-II emission, Prasad, Chen, and co-workers developed dye-sensitized nanocrystals with enhanced emission in the NIR-II window.⁵⁷² They modified downshifting NaYF₄ core-shell nanocrystals with NIR dyes (indocyanine green) to gain more excitation energy through dye absorption, and the excitation energy was then transferred to nanocrystals. This approach enables enhanced NIR-II emission from a collection of rare-earth activators, such as Yb³⁺, Er³⁺, Ho³⁺, Tm³⁺, and Pr³⁺. In 2017, Dai and colleagues enhanced the downshifting emission of Er³⁺ by codoping with Ce³⁺ in NaYbF₄@NaYF₄ nanoparticles. Ce³⁺-doping modulated the intermediate 4f–4f transitions of Er³⁺, which increased luminescence at 1550 nm by 9-fold.⁵⁷³ Through efficient Yb–Er–Ce energy transfer, Chen's group achieved a maximum downshifting quantum yield of 32.8% of 1530 nm emission in NaCeF₄:Er/Yb nanocrystals upon excitation at 980 nm.⁵⁷⁴ Such a high NIR-II emission yield allows detection at a tissue depth of 10 mm, which offers the possibility of imaging organs and hindlimbs of mice at high resolution.

The development of efficient downshifting nanoprobe with rare-earth dopants has expanded the applicability of NIR-II imaging in many ways. For instance, these NIR-II phosphors have been used to visualize tiny metastatic tumors and brain vessels in living mice (Figure 15b).⁵³⁴ They have also been used to decipher complex biological processes such as

immunotherapeutic responses and *in situ* ATP metastases.^{575,576}

4.1.1.3. Time-Gated Imaging. Time-gated imaging techniques can be implemented with rare-earth-activated nanophosphors due to their long-lived luminescence. The 4f–4f luminescence lifetime of rare-earth activators is generally 2–3 orders of magnitude longer than that of organic dyes (typically several nanoseconds), ranging between microseconds and milliseconds. To improve image contrast due to long-lived phosphorescence, it is possible to eliminate interference from short-lived emissions, such as autofluorescence or light scattering, by collecting the luminescent signal from the phosphors after the background signal has completely decayed (Figure 18a).^{577–579}

Interestingly, the luminescence lifetime of rare-earth ions depends on many factors, including dopant concentration, susceptibility to surface quenching, phonon density, and specific crystal-field environment. Altogether, these factors provide a unique opportunity to multiplex the luminescence lifetime.^{581–584} As a typical example, Hao et al. have demonstrated the use of a multicompartiment core/shell structure to generate upconversion nanophosphors with tunable luminescence lifetimes.³¹⁰ Liu et al. have combined rare-earth emission with energy migration to achieve multiplexed lifetime tuning.³⁴ Recently, Gu et al. combined time-gated imaging with NIR excitation/emission to achieve multiplexed lifetime imaging in deep tissue (Figure 18b–d).^{535,567,580,585} They developed α -NaYbF₄@CaF₂ NIR τ -dots for time-gated imaging in the NIR-II window and demonstrated the utility of such imaging probes for visualization of internal organs at a power density of 1 mW cm^{−2} (Figure 18b).

A strong autofluorescence background was observed in the absence of time delay between the laser pulse and image acquisition (Figure 18c). At a delay of 1 μ s, the autofluorescence disappeared completely, allowing high-contrast imaging in deep tissue. Rosal et al. also performed time-gated imaging using NaGdF₄:Nd nanoparticles with an emission band centered at approximately 1060 nm upon 808 nm excitation. Accurate location of the subcutaneously injected nanoparticles was possible with a delay of 1 μ s. The intensity profiles also confirmed the elimination of the autofluorescence background (Figure 18d).

4.1.1.4. Persistent Luminescence Imaging. Persistent luminescence imaging with rare-earth-doped nanoparticles has recently drawn much interest. Persistent luminescent materials are characterized by ultralong decay times, which can be as long as several months. These materials are attractive for bioimaging because persistent luminescence does not require excitation during imaging, completely eliminating background interference.^{536,586} In 2007, le Masne de Chermont et al. demonstrated persistent luminescence imaging *in vivo* using Ca_{0.2}Zn_{0.9}Mg_{0.9}Si₂O₆:Eu²⁺/Dy³⁺/Mn²⁺ nanoparticles.⁵⁸⁷ In 2013, Abdulkayum et al. demonstrated ultralong NIR persistence luminescence of Zn_{2.94}Ga_{1.96}Ge₂O₁₀:Cr/Pr nanoparticles for 15 days after 5 min of UV irradiation.⁵⁸⁸ After further PEGylation and subcutaneous injection, these nanoparticles showed good biocompatibility and NIR imaging practicality in rodents.

To maximize applicability *in vivo*, persistent luminescent nanoprobes should be re-excitabile after injection into tissues. In this regard, several distinct NIR-excitabile upconversion persistent luminescent nanophosphors, such as Zn₃Ga₂GeO₈:Cr/Yb/Er and (Zn₂SiO₄:Mn):Y/Yb/Tm nanoparticles have been developed.^{589,590} Because of the deeper tissue penetration with NIR excitation, these nanophosphors can be recharged by an upconversion process to generate persistent bioimaging signals *in vivo*. However, the upconversion process still suffers from low conversion efficiency.

Recently, there has been a growing trend to use X-rays as an excitation source for *in vivo* persistent luminescence imaging. In 2017, Song et al. presented the use of soft X-ray excitation for repeatable activation of SrAl₂O₄:Eu²⁺ nanophosphors in *in vivo* imaging.⁵⁹¹ They demonstrated a maximum tissue penetration of 2.5 cm by X-ray excitation. Since then, X-rays have been utilized to activate various persistent luminescent nanophosphors *in vivo*, such as MgGeO₃:Mn²⁺/Yb³⁺/Li⁺, Zn₂GeO₄:Mn, and ZnGa₂O₄:Cr³⁺.^{592–594}

A major challenge in the development of persistent luminescent nanophosphors is that their brightness decreases significantly as the particle size decreases into the nanometer range. Surface passivation can improve the efficiency of persistent luminescence by preventing the energy loss due to surface quenching. However, most persistent luminescent nanomaterials currently in use were prepared under harsh conditions (>800 °C) that prevent core–shell modification. In 2021, Ou et al. reported persistent luminescence of NaLuF₄:Tb@NaYF₄ nanoparticles with a size of 27 nm upon X-ray irradiation.⁵⁹⁵ Compared with NaLuF₄:Tb core nanoparticles, these core–shell nanoparticles increased the radio-luminescence intensity by 1.5-fold. Shortly thereafter, Zhang, Yang, Fan and their collaborators developed NaY₂GdF₄:Ln@NaY₂GdF₄ (Ln = Er, Nd, Ho, Tm) nanoparticles that exhibit strong X-ray-activated persistent luminescence in the NIR-II region.⁵⁹⁶ The core–shell design enables tunable NIR-II

persistent luminescence from 1064 to 1525 nm and bioimaging at deep tissue depth (2–4 mm) with a 4-fold higher signal-to-noise ratio and 3-fold higher contrast. These findings shed light into the development of highly efficient persistent luminescent nanophosphors for bioimaging and therapeutics.

4.1.1.5. Contrast Agents. In addition to luminescence imaging, rare-earth-doped nanomaterials can serve as contrast agents for imaging modalities such as MRI, CT, PAI and cathodoluminescence microscopy. For instance, paramagnetic Gd³⁺ has the highest number of unpaired electrons (7), making it suitable as a positive (T_1) contrast agent for MRI.^{597,598} It shortens the spin–lattice relaxation time (or longitudinal relaxation time) of water protons. The other main class of MRI contrast agents works by changing the spin–spin (or transverse) relaxation time. They are negative (T_2) contrast agents because the image is obscured by the accumulation of contrast agents. Superparamagnetic iron oxide nanoparticles are the best known negative T_2 contrast agents.

For nanosized T_1 MRI contrast agents, it has been shown that only paramagnetic ions located near nanocrystal surfaces can contact water protons, thereby enhancing T_1 -weighted MRI contrast. Consequently, paramagnetic dopants need to be concentrated in the outermost layer to further improve the contrast performance. Two approaches have been used to increase surface dopants. One is the synthesis of small nanocrystals with a very high surface-to-volume ratio. The other is to dope metal ions locally on the surface using a surface doping strategy. For example, the r_1 relaxivity of Gd³⁺ nanoparticles can be increased by either using ultrasmall NaGdF₄ nanocrystals (sub-5 nm)⁵⁹⁹ or coating NaYF₄ nanocrystals with an ultrathin layer of NaGdF₄ (<1 nm).²⁸⁹ Furthermore, loading a nanocrystalline matrix with multiple Gd³⁺ ions allows a dramatic increase in the local surface concentration, which improves the imaging contrast.^{600,601} Cheung et al. made PAA-stabilized Gd³⁺ nanoparticle aggregates to increase the surface-to-volume ratio while maintaining a large size that promotes vascular retention at tumor sites.⁶⁰² Multifunctional MRI nanoparticles have also been reported. Wu et al. designed Eu³⁺-doped Gd₂O₃ nanoscrolls with encapsulated doxorubicin (DOX) drug molecules, which enabled dual MRI imaging and targeted tumor chemotherapy.⁶⁰³

Other paramagnetic rare-earth ions, such as Dy³⁺ and Ho³⁺, are suitable as negative (T_2) contrast agents because of their high magnetic moments ($\sim 10.6 \mu_B$) and short electronic relaxation times (~ 0.5 ps).⁶⁰⁴ Unlike Gd³⁺, the relaxation enhancement for Dy³⁺ is a bulk effect. Larger nanoparticles generally have a higher contrast effect. For instance, van Veggel and co-workers found that the T_2 contrast of NaDyF₄ and NaHoF₄ nanoparticles increased with increasing particle size and magnetic field strength.^{178,605} Size-dependent evaluation of T_2 relaxivity showed that imaging contrast increased with larger NaDyF₄ nanoparticles and higher field strength. Specifically, the largest nanoparticles (~ 20 nm) showed ~ 64 -fold higher contrast per nanoparticle and ~ 6 -fold higher contrast per Dy³⁺ ion at 9.4 T, compared to 3 T. Compared to clinically used T_2 contrast agents such as iron oxides, Dy³⁺/Ho³⁺-based nanoparticles provide higher signal-to-noise ratio and better spatial resolution for high-field MRI (>7 T) of vasculitis in the central nervous system.

Additionally, nanomaterials doped with rare-earths have long been utilized as contrast agents for X-ray CT imaging. Because of their high atomic number and lanthanide contraction,

lanthanide elements exhibit high electron density and thus high X-ray attenuation. Among lanthanides, lutetium (Lu) has the largest atomic number and is expected to have a large X-ray absorption coefficient. Lu³⁺-based nanoparticles, such as NaLuF₄ and LiLuF₄, have proven as efficacious CT contrast agents.^{277,539,606} In practical applications, rare-earth-doped nanoprobe have been used mostly in CT alongside other imaging modalities, such as MRI, luminescence imaging, PET, and SPECT.^{537,607–609}

In separate developments, research groups have demonstrated the use of rare-earth-doped nanoparticles as contrast agents for PAI.^{610,611} PAI is a relatively less explored modality compared to MRI and luminescence imaging. Based on current understanding, the observed photoacoustic property is attributed to nonradiative relaxation by surface quenching of excited lanthanide dopants, such as Yb³⁺ and Er³⁺ in NaYF₄. Apparently, the signal strength of the reported nanoparticle composition is rather weak compared with organic photoacoustic probes. Improvement by changing the host lattice or dopant composition might be possible. To improve the spatial and temporal resolution of imaging *in vivo*, Xing, Gao, and co-workers combined multispectral optoacoustic tomography with upconversion nanoprobe.⁵⁴⁰ They coupled UCNPs with radical-sensitive cyanine dyes to produce hybrid nanoprobe. These nanoprobe can respond orthogonally to disparate forms of oxidative and nitrosative stimulation, allowing *in vivo* visualization of endogenous redox biomarkers with high spatiotemporal resolution (Figure 15h).

Cathodoluminescence refers to optical emission under electronic beam excitation. It can be realized in scanning electron microscopy with a photomultiplier detector. Previous research has used rare-earth complexes to visualize multiple biological molecules in electron microscopy.⁶¹² However, the previous research requires a specific sensitizer for each type of rare-earth complex. In 2019, Prigozhin et al. examined the cathodoluminescence of rare-earth-doped nanoparticles with an average size of less than 20 nm.⁶¹³ They showed bright optical emissions under direct electron beam excitation. Although the emission spectra of individual particles show significant variations even among samples of the same batch and under the same illumination conditions, this study was an excellent demonstration of the cathodoluminescence of rare-earth-doped inorganic nanomaterials. Future mechanistic studies on factors affecting the cathodoluminescence intensity and line shape are needed.

4.1.1.6. Multifunctional Imaging Probes. Multimodal imaging provides different types of information about the same objects with a single dose of probes. There is a considerable interest in integrating multiple imaging modalities through rare-earth-doped nanoprobe.^{542,614} For instance, Sun et al. have developed multifunctional NaLuF₄:Yb/Tm@NaGdF₄(¹⁵³Sm) nanoprobe that integrate four modalities for tumor angiogenesis assays.⁶⁰⁷ The core structure is codoped with Yb³⁺, Tm³⁺ to achieve upconverted NIR emission at 800 nm. The Lu³⁺, Yb³⁺, and Gd³⁺ ions in the core and cladding layer provide X-ray attenuation and CT contrast. In addition, Gd³⁺ ions in the cladding layer provide T₁ contrast for MRI. Lastly, radioactive ¹⁵³Sm³⁺ dopants in the shell release γ rays to provide the fourth imaging contrast for SPECT.

It is interesting to selectively detect biological targets to obtain better imaging contrast and more detailed structural information. An effective strategy to impart molecular

specificity to imaging contrast agents is to develop imaging probes that can respond to changes in the environment.⁶¹⁵ For example, it is useful to design multifunctional rare-earth-doped nanoprobe whose luminescent signal responds to local pH or signal molecules. Combined with an external optical control for photoactivation, these multifunctional nanoprobe have been widely used in diagnostics and nanomedicine.^{616–618}

A potential limitation of rare-earth-doped nanoparticles for *in vivo* imaging is short circulation due to nanoparticle accumulation in the liver and spleen. To overcome this problem, Peng et al. reported an increase in blood circulation of rare-earth-doped nanoparticles to over half an hour using polyphosphoric acid ligands.⁶¹⁹ They administered nanoparticles functionalized with polyphosphoric acid to mice by injection into the tail vein. Upconversion luminescence and SPECT imaging allowed visualization of the main arteries and heart within the first half-hour after injection, whereas nanoparticle accumulation in the liver and spleen occurred later. For targeted bioimaging, Rao et al. recently reported precise tumor imaging by coating UCNPs with cancer cell membranes.⁶²⁰ This surface modification reduced nanoparticle uptake by the phagocyte-enriched reticuloendothelial system, leading to much improved specific nanoparticle accumulation at tumor targets.

Another limitation of rare-earth-doped nanoprobe for luminescence bioimaging is their low absorption coefficient. Several methods exist to improve light absorption, such as dye sensitization and plasmonic enhancement.^{621–625} Although luminescence intensity could be increased by more than 3–4 orders of magnitude in organic solvents, dye-sensitized nanoparticles become only a few dozen times brighter in the aqueous phase. In 2020, a team led by Liu and Li discovered that aggregation-induced quenching is the major limitation of dye-sensitized upconversion luminescence.⁶²⁶ By using hydrophobic interactions instead of direct coordination between the dye molecules on the surface and the lanthanide nanoparticles, aggregation-induced quenching can be reduced. The researchers modified the dye structure to minimize the retransfer of energy from the rare-earth ions to the dye. Overall, a more than 600-fold increase in luminescence was achieved.

4.1.2. Photothermal Therapy. Photothermal therapy (PTT) is a noninvasive treatment for diseases based on photothermal agents. Photothermal agents can convert absorbed light into heat to cause thermal ablation of damaged tissue, such as tumors and infected tissue (Figure 19a). PTT can be accomplished by combining rare-earth-doped nanoprobe with photothermal conversion materials.^{627,628}

Au and Ag nanostructures with strong heating effects due to surface plasmon resonance have been widely utilized as photothermal agents for PTT. Therefore, combining rare-earth-doped nanomaterials with Au or Ag nanoparticles could be an efficacious approach for improved PTT.^{629–633} In 2011, Liu, Shao, and co-workers constructed multifunctional UCNP-Fe₃O₄-Au nanomaterials for *in vivo* dual-mode upconversion luminescence/MR imaging and magnetically targeted PTT.⁶³⁴ Chan et al. coupled Au nanorods with Nd³⁺-sensitized UCNPs.⁶³⁵ This design enables upconversion emission and photothermal energy conversion at a single wavelength of 808 nm.

Furthermore, materials with strong light absorption, such as graphene oxide (GO), Cu_xS, and organic light absorbers, have been combined with rare-earth-doped nanomaterials as photothermal agents for PTT in refs 636–642. For instance,

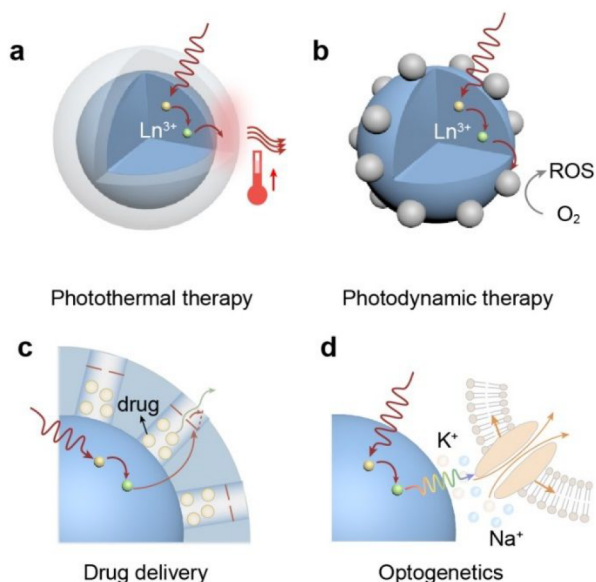


Figure 19. Schematics of rare-earth-doped nanomaterials for (a) photothermal therapy, (b) photodynamic therapy, (c) drug delivery, and (d) optogenetics.

Wang et al. reported the use of GO-covalently grafted UCNPs as a thermal platform for bioimaging and PTT.⁶⁴³ Lin and co-workers presented the synthesis of hollow $\text{Y}_2\text{O}_3\text{:Yb/Er-Cu}_x\text{S}$

nanospheres for image-guided PTT.⁶⁴⁴ Xu et al. recently combined CuS , $\text{g-C}_3\text{N}_4$ and UCNPs to achieve efficient PTT under NIR excitation.⁶⁴⁵ The researchers functionalized composite nanoparticles with polyethylene glycol and folic acid to target cancer cells and improve biocompatibility. In 2020, He and co-workers assembled poly(selenoviologen) on NaYF_4 UCNPs for PTT-based antibacterial therapy.⁶⁴⁶ These polymer-modified nanoparticles show good efficacy in killing methicillin-resistant *Staphylococcus aureus* both *in vitro* and *in vivo* (Figure 20a).

To minimize overheating during PTT, Zhu et al. demonstrated temperature-controllable PTT using $\text{NaLuF}_4\text{:Yb/Er@NaLuF}_4\text{:Yb/Er@carbon}$ nanoparticles.⁶⁴⁷ They used UCNPs with temperature feedback to monitor the local temperature in PTT. They found that the local temperature around nanoscale photothermal converters was sufficient to kill cancer cells if the temperature of the lesions was kept low enough to prevent damage to normal tissue. This allowed PTT-mediated tumor ablation with high spatial resolution and minimal damage to normal tissue. This PTT strategy has been combined with chemotherapy and immunotherapy to improve therapeutic performance.^{648,649}

4.1.3. Photodynamic Therapy and Photochemotherapy. Similar to PTT, photodynamic therapy (PDT) and photochemotherapy offer potential options for cancer treatment with minimal off-target effects.⁶⁵⁰ Both approaches typically use photosensitizers that can be activated by irradiation at specific wavelengths. These activated photo-

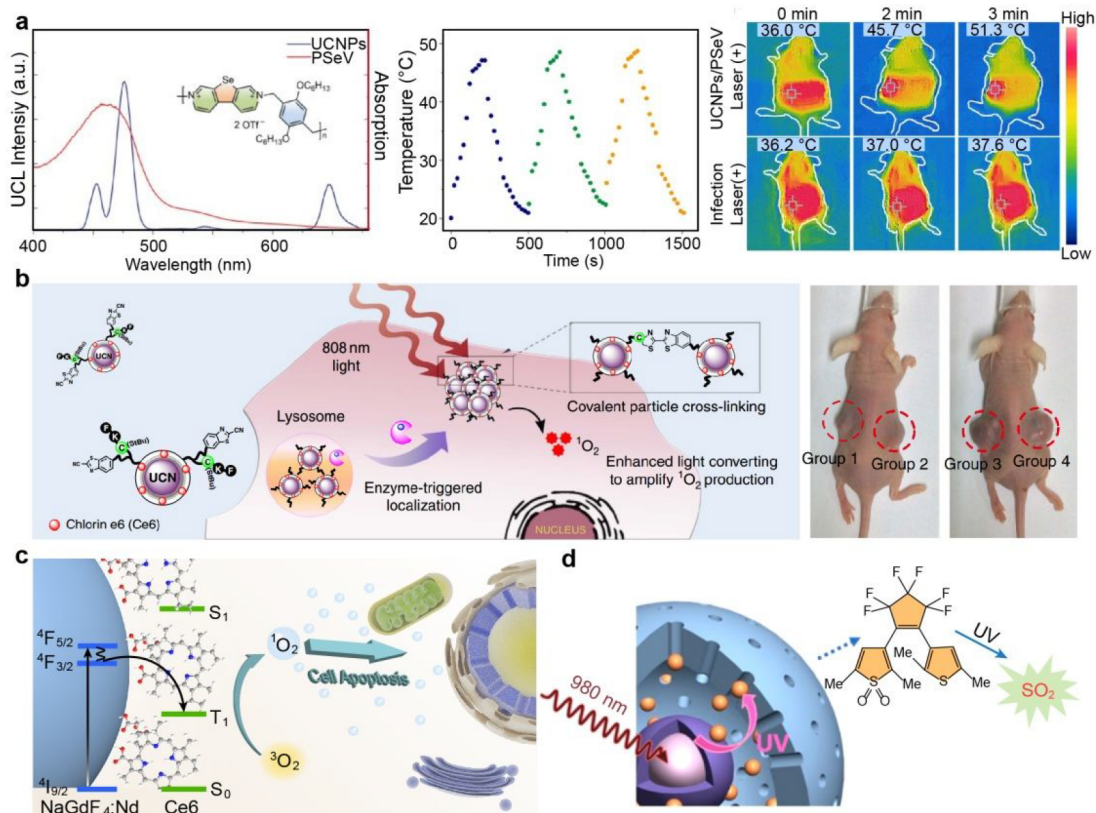


Figure 20. (a) Photothermal therapy with UCNPs/PSeV nanoconjugates under 980 nm irradiation. (b) Illustration of photodynamic therapy with covalent cross-linking of peptide-premodified UCNPs and photographs of tumor-bearing mice after treatment with UCNPs (group 1) and other control groups. (c) Proposed mechanism of nanoparticle-based photodynamic therapy with direct energy transfer from the excited triplet states of rare-earths. (d) Schematic of NIR-triggered SO_2 generation for gas therapy (Adapted with permission from refs 646 and 663–665. Copyright 2020 American Chemical Society; Copyright 2016 Nature Publishing Group; Copyright 2021 Elsevier Inc.).

sensitizers mediate *in situ* chemical reactions to generate cytotoxic species, such as reactive oxygen species (ROS). One of the main challenges for conventional photosensitizers is that they can only absorb light in the UV–visible range and therefore have limited penetration into biological samples. To overcome this problem, rare-earth-doped nanoparticles have been used as light transducers to enable PDT and photochemotherapy deep within tissues (Figure 19b).^{651–654}

For example, Xie and co-workers demonstrated X-ray-induced *in vivo* PDT for cancer treatment using Eu²⁺-doped SrAl₂O₄ nanoparticles.⁶⁵⁵ They coupled SrAl₂O₄:Eu²⁺ nanoscintillators with merocyanine 540, a photosensitizing dye. Under X-ray irradiation, SrAl₂O₄:Eu²⁺ nanoscintillators emitted visible photons, which subsequently photoactivated merocyanine 540 to generate cytotoxic singlet oxygen (¹O₂). This X-ray induction method overcame the shallow penetration limitation associated with conventional light sources for PDT.^{656,657} Scintillating nanoparticles with various compositions, such as SrAl₂O₄:Eu²⁺, LaF₃:Tb/Ce, Tb₂O₃, NaGdF₄:Tb, NaCeF₄:Gd/Tb, and Gd₂(WO₄)₃:Tb, have proven effective as X-ray transducers when combined with organic photosensitizers for PDT.^{658–664}

In addition to organic photosensitizers, rare-earth-doped nanoscintillators can also activate inorganic semiconductor photocatalysts. Zhang et al. prepared multilayer LiYF₄:Ce@SiO₂@ZnO nanoparticles that exhibited efficient energy transfer from Ce³⁺ (emission at 305 and 325 nm) to ZnO under X-ray irradiation.⁶⁶⁸ Such energy transfer facilitated the production of hydroxyl radicals in the presence of water, leading to deep-tissue PDT of tumor cancers. The core–shell design can make nanoscintillators multifunctional. For example, Chang and co-workers prepared NaLuF₄:Eu@NaLuF₄:Gd@NaLuF₄:Tb nanoparticles in conjugation with Rose Bengal and PEG-folic acids.⁶⁶⁹ These nanoparticles exhibited dual emission, one from Tb³⁺ at 543 nm for Rose Bengal activation and the other from Eu³⁺ at 614 and 695 nm for image-guided PDT. Rare-earth-doped nanoscintillators could also enable photochemotherapy by X-ray-controlled generation of peroxynitrite in tumors.⁶⁷⁰

For clinical use, the safe radiation dose of X-rays needs to be carefully evaluated, taking into account the potential photo-disturbances due to high ionization energy. Alternatively, NIR irradiation can be used as a safer light source than visible light to accomplish therapeutic treatment in deep tissue. An example of this in nanoscience is the use of UCNPs to convert NIR excitation to short-wavelength UV/visible emission.⁶⁵³ Since the early 2010s, upconversion-based PDT has been extensively explored, with significant advances in precision therapy, image-guided therapy, and multimodal synergistic therapy.^{25,671–676} In the last five years, research in this field has mainly focused on expanding the applicability of upconversion-based PDT through various approaches. For instance, to minimize the heating effect, Chan et al. demonstrated the use of Nd³⁺-sensitized UCNPs for PDT under 808 nm irradiation.⁶⁷⁷ Compared with the 980 nm irradiation employed for conventional Yb³⁺-sensitized upconversion, 808 nm NIR light achieved a high excitation amount for upconversion with minimal tissue overheating, which is more efficacious for cancer treatment. Nd³⁺-sensitized nanoparticles can be further modified with IR-808 and ICG dyes to increase absorbance and improve PDT performance at 808 nm irradiation.^{301,569}

To achieve targeted PDT, Sun et al. developed DNA-modified hierarchical nanocomposites comprising Au nanorods, UCNPs, and Ce6.⁵³⁷ These nanocomposites can be visualized and tracked *in vivo* by upconversion luminescence imaging, CT scanning, PAI, and T₁-MRI, enabling image-guided combination phototherapy. In 2020, Lin, Yang, and co-workers fabricated NaGdF₄:Lu/Yb/Er/Ce nanoparticles coated with copper and manganese silicate nanospheres. These exhibited combined chemodynamic/photodynamic effects and bright downshifting NIR-II luminescence suitable for image-guided phototherapy.⁶⁷⁸ To enhance site-specific, on-demand, antitumor activity, Xing and co-workers incorporated a peptide sequence that recognizes cathepsin B into Nd³⁺-sensitized UCNPs.⁶⁶⁵ This peptide modification confers sensitivity to the tumor microenvironment, triggering specific nanoparticle accumulation in cancer cells and subsequently enhancing ROS generation at targeted tumor sites (Figure 20b). In addition, upconversion PDT can be enhanced by improving the specificity of UCNPs to mitochondria, which promotes mitochondrial damage by ROS to induce apoptosis.^{679,680}

Upconversion-based PDT can respond to the tumor microenvironment. The microenvironment of a solid tumor has specific characteristics, such as low pH, high H₂O₂ and glutathione concentrations, and hypoxic conditions. These factors strongly influence *in situ* ROS generation and phototherapeutic performance. For instance, the anoxic environment of a solid tumor suppresses the efficacy of PDT due to the lack of oxygen for ¹O₂ production. To overcome this challenge, UCNPs have been modified with MnO₂, CeO₂, platinum(IV)–diazido complexes, Fe(OH)₃, etc.^{258,601,681–683} These materials are able to catalyze the degradation of endogenous H₂O₂ to O₂ and thus promote ¹O₂ production in tumor cells. It is also possible to combine UCNP-based PDT with hypoxia-activated prodrugs, such as tirapazamine or immune-responsive species, to enhance anticancer therapy.^{22,684–686}

Despite its usefulness, upconversion-based PDT generally requires a relatively high irradiance (typically >100 mW cm^{−2}). Moreover, the conversion efficiency is low due to the significant energy loss during multiphoton upconversion. Therefore, it is essential to develop highly efficient NIR-responsive PDT platforms that operate at relatively low excitation intensities. In 2021, Zheng et al. reported a novel concept to achieve PDT at ultraweak NIR irradiation that directly activates excited triplet states of organic photosensitizers without the need for intersystem crossing of higher singlets of the organics (Figure 20c).⁶⁶⁷ The researchers demonstrated an unusual energy transfer pathway via short-range Dexter-type interactions to realize photosensitization for ¹O₂ production via energy transfer from lanthanides to triplets. This approach enables the activation of a series of porphyrin and phthalocyanine sensitizers under low NIR irradiance (~10–80 mW cm^{−2}) of Nd³⁺- or Yb³⁺-doped NaGdF₄ nanoparticles. This work could expand the repertoire of rare-earth-doped materials for PDT and other biomedical applications.⁶⁸⁷

In addition to ROS, UCNPs can trigger the release of specific gas molecules for NIR-sensitive therapy. For example, upconverted visible emission can activate the production of nitric oxide (NO) from Roussin's black salt [Fe₄S₃(NO)₇][−] (RBS).^{688–691} In 2017, Zhang et al. combined Nd³⁺-sensitized UCNPs with RBS to trigger NO release.⁶⁹² Under 808 nm

excitation, this nanoplatfrom releases large amounts of NO that effectively destroy cancer stem cells *in vivo*. Apart from NO therapy, Li et al. recently demonstrated sulfur dioxide (SO₂) cancer therapy enabled by NIR-responsive UCNPs.⁶⁶⁶ The researchers constructed porous silica-coated upconversion nanoparticles and then loaded them with an SO₂ prodrug. These assembled nanostructures not only enable intracellular and *in vivo* delivery of the SO₂ prodrug but also on-demand release of SO₂ into deep tissue (Figure 20d).

4.1.4. Drug Delivery. Targeted drug delivery can be accomplished by conjugating nanomaterials with acceptor molecules that specifically recognize receptors on target organs and cells via ligand–acceptor or antigen–antibody interactions (Figure 21). Additionally, surface modification of nanomaterials

Strategy	Modification moiety	Function
SiO ₂ coating	SiO ₂ , mesoporous SiO ₂	Hydrophilicity, molecule loading and release
Yolk-shell SiO ₂ capsulation	Mesoporous SiO ₂	Hydrophilicity, molecule loading and release, gas release
Polymer coating	PAA, PEI, PEG, PVP...	Hydrophilicity, molecule encapsulation
Liposome	Membrane, lipid	Hydrophilicity, molecule encapsulation
Amphiphilic polymer coating	DSPE-PEG, pluronic F127...	Hydrophilicity, molecule loading and release
Protein modification	Bovine serum albumin, linker-protein G, enzyme, antibody...	Biocompatibility, connection with other materials, targeting
Nucleic acid modification	DNA	Hydrophilicity, connection with other materials, molecule loading, biosensing, DNA delivery
	RNA	Hydrophilicity, gene silencing, RNA delivery
Targeted molecule	Folic acid, hyaluronic acid...	Targeting

Figure 21. Strategies for surface modification of rare-earth-doped nanomaterials for bioapplications: PAA poly(acrylic acid); PEI poly(ether imide); PEG poly(ethylene glycol); PVP polyvinylpyrrolidone; DSPE distearoylphosphoethanolamine.

als through postsynthesis or *in situ* functionalization greatly enhances the efficacy of pharmaceutical payloads and alter drug solubility, stability, and metabolic pathways in living systems.^{695–698}

A unique feature of rare-earth-doped nanomaterials for drug delivery is that they provide additional external stimuli to manipulate pharmacokinetics and drug release (Figure 19c).^{697,699,700} This enables site-specific, spatiotemporally controlled drug release and localized functional regulation in nanomaterial-based delivery systems. As a representative example, UCNPs have been combined with photocleavable prodrugs for NIR-activated drug release.^{701–706} Recently, Chen et al. demonstrated NIR-controlled delivery of an enzyme inhibitor in living cells using hollow mesoporous silica nanocomposites containing NaYF₄:Tm/Yb@NaYF₄ UCNPs and photoactivatable Ru complexes.⁷⁰⁷ The photocaged Ru complex is designed to be photochemically cleaved to release the enzyme inhibitor upon stimulation with blue-emitting UCNPs. The released enzyme inhibitor inhibits the enzyme cathepsin K in living cells and controls local cell functionality

in deep tissue. In a separate study, Li and co-workers developed a gene delivery system that enabled NIR-initiated hybridization chain reaction (HCR) for spatiotemporally resolved imaging of mRNA in living cells.⁷⁰⁸ The researchers loaded HCR-functional DNA hairpins onto rare-earth-doped nanoparticles and introduced them into living cells. One of the DNA hairpins was modified by adding a short photocleavable linker to block the HCR reaction. After the cells endocytosed the DNA hairpins, HCR was restored by light-induced photolysis of the photocleavable linker. To date, NIR-activated delivery systems have found many applications, such as *in vivo* release of CRISPR-Cas9 for gene editing, localized DNA delivery to eliminate senescent cells, controlled release of small molecules to drive multidirectional differentiation of mesenchymal stem cells, and targeted delivery of drugs that trigger local antitumor immunity.^{709–714}

Another prominent approach for photoactivated drug-release can be realized by conformational changes, such as *cis–trans* isomerism in azobenzene derivatives (Figure 22).^{693,694,718} For instance, Zhang et al. encapsulated the anticancer drug DOX on the surface of NaYF₄:Tm/Yb@NaYF₄ nanoparticles using azo-functionalized DNA strands (Figure 22a).⁶⁹³ Under NIR excitation, these nanoparticles emitted UV and visible photons to initiate isomerization of the azo-compound, which triggered the continuous release of DOX from the nanocomposites. The researchers demonstrated a release of 86.7% of the compound after 30 min of irradiation. Yao et al. inlaid amphiphilic azobenzene derivatives into liposomes with encapsulated DOX and Yb/Tm-encoded UCNPs (Figure 22b,c).⁶⁹⁴ Upon irradiation at 980 nm, the blue/visible upconverted emission immediately excited the photosensitive azobenzene molecules. The reversible isomerization of the azobenzene disrupted the liposome scaffold and allowed the controlled release of DOX (Figure 22d). In addition to photochemical reactions, the photothermal effect of rare-earth-doped nanoparticles can also trigger targeted drug release.^{719,720} Han et al. reported a photothermal drug release system based on UCNPs prefucionalized with gold nanoparticles and hairpin DNA. The DOX drug, intentionally entrapped in the DNA hairpins, can be released from nanoparticle surfaces upon laser irradiation at 980 nm.⁷¹⁹

4.1.5. Optogenetics. Optogenetics is a revolutionary technique that uses light as a modality of biological control to manipulate cellular activities, neuronal functions, and even the behavior of living animals. This technique typically uses visible light to regulate the influx of ions such as Ca²⁺, Na⁺, and K⁺ through light-gated ion channels on cell membranes. This process is of particular interest in neuromodulation.^{721,722} By selective expressing light-sensitive channelrhodopsins (ChR) in neurons, light stimulation can precisely control the activation or inhibition of target neurons within milliseconds. Optogenetics can enable clinical exploration of numerous neuronal states and remediation of neuronal dysfunction. One of the challenges in optogenetics is the short working distance of light stimulation. This is because conventional ChR receptors can only absorb light in the visible range, typically between 430 and 650 nm, which penetrates tissue poorly.^{723,724} This challenge can be overcome by coupling optogenetics and rare-earth-doped nanoparticles that can convert NIR excitation into visible emission (Figure 19d).

Upconversion-mediated optogenetics was first demonstrated in 2015. Hososhima et al. reported using NaYF₄:Sc/Yb/Er UCNPs as NIR optical donors to stimulate C1 V1-expressing

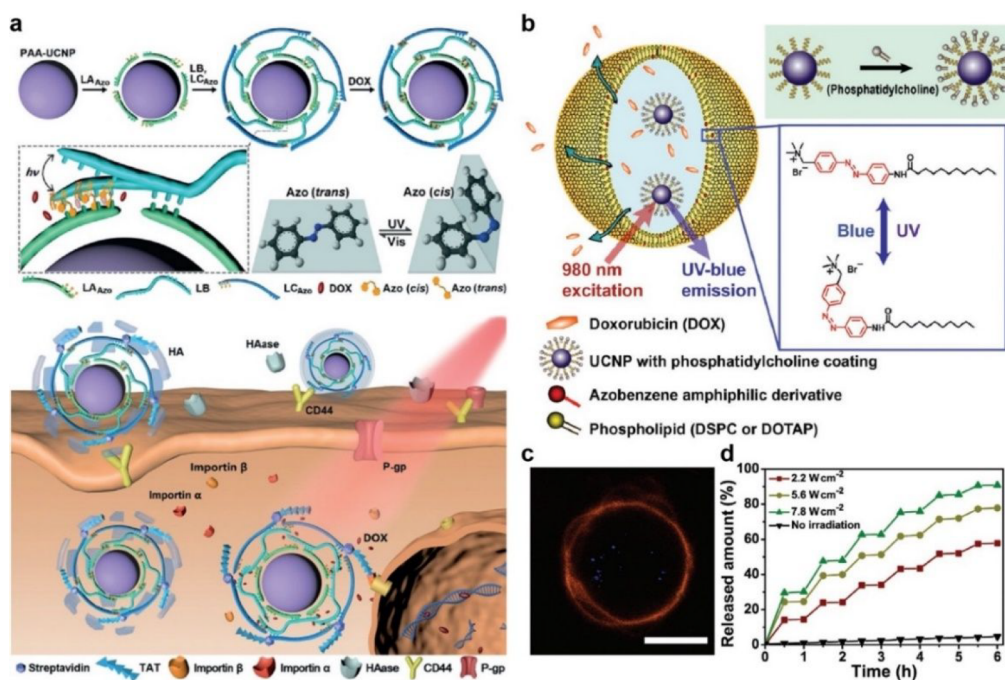


Figure 22. (a) Schematic of UCNP- $\text{LA}_{\text{Azo}}\text{BC}_{\text{Azo}}/\text{DOX}$ assembly and NIR-triggered drug release in living cells. (b) Schematic of NIR-triggered drug delivery using azobenzene-liposome/UCNP hybrid vesicles. (c) Confocal cross sections of azobenzene-liposome/UCNP/CdSe hybrid vesicles. The scale bar is 5 μm . (d) Power-dependent drug release curves in buffer under intermittent irradiation with 980 nm light (Adapted with permission from refs 693 and 694. Copyright 2016 and 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

ND7/23 cells at 975 nm irradiation.⁷²⁵ At the same time, Pang, Lee, and their co-workers used blue-emitting $\text{NaYF}_4:\text{Yb}/\text{Tm}@ \text{NaYF}_4$ UCNP to facilitate optogenetic activation of ChR2-expressing neuronal cells.⁷²⁶ Han and co-workers designed IR-806-sensitized $\text{NaYF}_4:\text{Yb}/\text{Er}@ \text{NaYF}_4:\text{Yb}$ UCNP as optical transducers for enhanced optogenetics under 800 nm excitation.⁷²⁷ They demonstrated efficient NIR activation of ReaChR in cultured hippocampal neurons.

Although UCNP have proven useful for *in vitro* NIR-activated optogenetics in cultured neurons, the overheating caused by NIR light still hinders the application of this technique *in vivo*. To address this problem, Zhang's group proposed quasi-CW NIR irradiation to improve the efficiency of multiphoton upconversion, while reducing the overheating caused by high-energy excitation.⁷²⁸ $\text{NaYF}_4:\text{Yb}/\text{Tm}@ \text{SiO}_2$ nanoparticles can be used to activate ChR2 in Hek293t cells at a low pump intensity under quasi-CW 980 nm excitation.

Under 980 nm laser irradiation, *in vivo* optogenetic manipulation has been demonstrated in ChR2-expressing *C. elegans* using UCNP. However, activation of ChR2 in this study requires a relatively high irradiance to trigger the reversal behavior of *C. elegans*. It is difficult to determine whether the observed reversal behavior is caused by activation of ChR2-expressing neurons or by an innate avoidance response to thermal or blue light irradiation. To avoid the photophobic response of *C. elegans*, Ao et al. employed a more sensitive optogenetic sensor Chrimson to manipulate the behavior of the *C. elegans* motor circuit with Nd^{3+} -sensitized green-emitting UCNP.⁷¹⁵ In that study, Chrimson protein was expressed in GABAergic class D motor neurons (D-MNs) and glutamatergic DVC interneurons. Upon NIR irradiation at 800 nm, D-MNs released GABA in muscle arms, inhibiting action potentials in body wall muscles and preventing locomotion. These nanoparticles exhibit negligible toxicity to neuron

development, growth, and reproduction. The 800 nm NIR energy required to elicit physiological responses does not activate the temperature response of *C. elegans* (Figure 23a). In another work, Ai et al. demonstrated NIR-activated optogenetic manipulation in zebrafish.⁷¹⁶ They activated ChR2 cell membrane channels under 808 nm irradiation with Nd^{3+} -sensitized UCNP (Figure 23b).

Upconversion-mediated optogenetics can be employed *in vivo* in mammals. For example, Wang, Shi, and co-workers embedded UCNP in a glass micropipette to form an ultrasmall, fully implantable device for optogenetic inhibition of target neurons in the mouse brain.⁷²⁹ The opto-gated inhibitory sensor was an enhanced Natronomonas halorhodopsin (eNpHR) protein expressed in the subthalamic nucleus of the rat brain. When the upconversion device was placed near the target sites in the brain, the electrical activities of eNpHR-expressing neurons were remotely inhibited by NIR illumination. The neurons' signals could be immediately restored after the NIR stimulation was turned off. In 2018, Chen, McHugh, Liu, and co-workers injected blue-emitting $\text{NaYF}_4:\text{Yb}/\text{Tm}@ \text{NaYF}_4@ \text{SiO}_2$ nanoparticles directly into dopaminergic neurons in the ventral tegmental area of ChR2-expressing rats.⁷¹⁷ Transcranial NIR irradiation was able to trigger blue upconverted emissions that elicited dopamine release from genetically labeled neurons in the ventral tegmental area. Activation of inhibitory neurons in the hippocampus of the medial septum induced brain oscillation, which a suitable means for seizure suppression (Figure 23c).

4.2. Optical Sensing

In recent decades, nanomaterial-based sensors have evolved into a suite of technologies for precise and sensitive detection of changes in the microenvironment (temperature, pressure, and pH). Due to their unique chemical and optical properties, rare-earth-based nanoparticles enable exquisite detection of

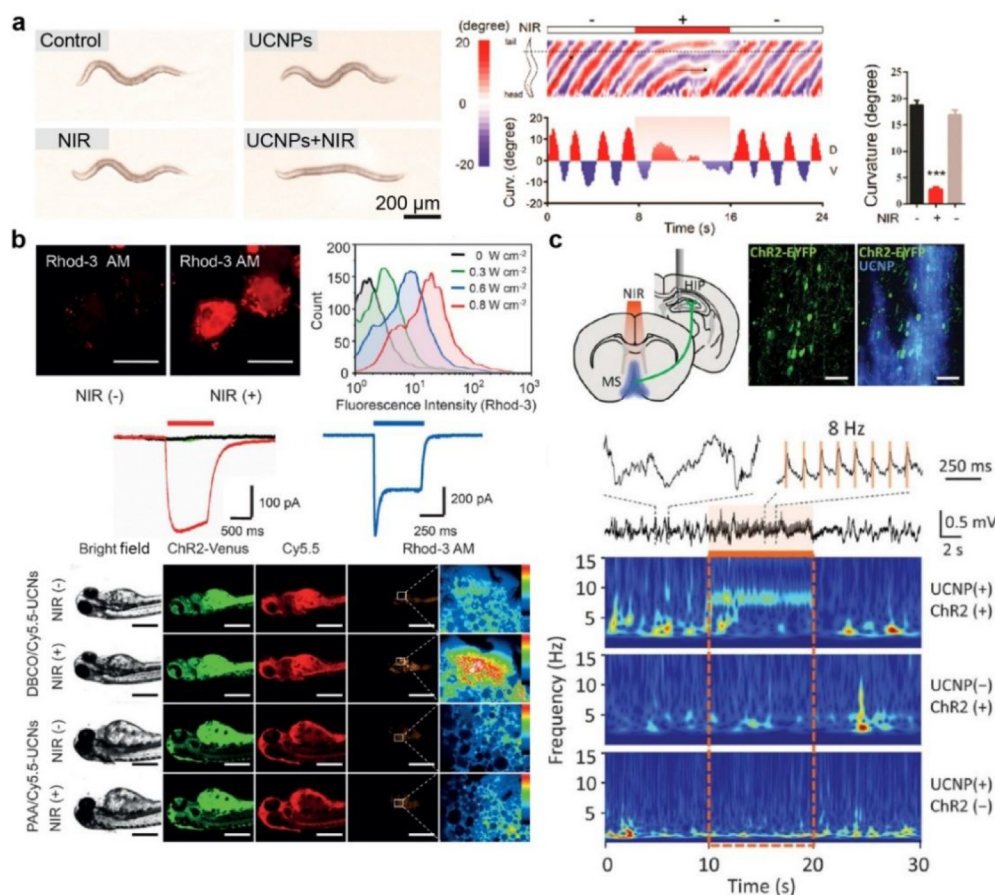


Figure 23. (a) NIR-triggered postural changes in *C. elegans* exposed to UCNPs. (b) *In vitro* and *in vivo* regulation of cell activities of zebrafish incubated with Cy5.5-UCNPs at 808 nm illumination. Scale bars are 20 μm (top) and 400 μm (bottom). (c) UCNP-mediated upconversion optogenetics for deep brain stimulation. The scale bar is 50 μm (Adapted with permission from refs 713–715. Copyright 2019 American Chemical Society; Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2018 American Association for the Advancement of Science).

changes in the microenvironment with unprecedented sensitivity. Moreover, they enable noncontact molecular detection of biomolecules, metal ions, anions, gases, and small molecules in deep tissue.

4.2.1. Temperature Sensing. In order to achieve highly accurate temperature measurements over wide ranges, non-contact luminescence nanothermometry has been explored.^{730,731} Given characteristic temperature-dependent luminescence properties, a plethora of rare-earth ions, including Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Tb³⁺, Ho³⁺, Er³⁺, and Tm³⁺, have been doped into different host materials for temperature sensing.^{732,733} Many variable optical parameters such as peak intensity ratio, emission wavelength, and luminescence lifetime have been used to probe temperature changes.^{381,734,735} The commonly studied mechanisms of temperature-dependent luminescence changes can be divided into two categories: (i) thermally coupled redistribution of excitation energy within a rare-earth emitter controlled by Boltzmann statistics and (ii) energy transfer between multiple dopants mediated by thermally induced phonon oscillations.

Among rare-earth emitters, Er³⁺ is the most studied element for temperature sensing and has been frequently coupled with Yb³⁺ and Nd³⁺ in nanocrystal hosts to improve the efficiency of upconversion from NIR to visible light. Temperature sensing with Er³⁺ is generally achieved by energy redistribution between the excited states ²H_{11/2} and ⁴S_{3/2}. When the

temperature changes, the fluorescence intensity ratio (FIR) of the two transitions (²H_{11/2} → ⁴I_{15/2} at 525 nm and ⁴S_{3/2} → ⁴I_{15/2} at 545 nm) changes according to the Boltzmann distribution law, which can be expressed as follows⁷³⁶

$$\text{FIR} = \frac{I_1}{I_2} = B \exp\left(-\frac{\Delta E}{kT}\right) \quad (1)$$

where B is a constant, ΔE is the energy difference between the two emission bands, and k is the Boltzmann constant. To evaluate the thermometric capacity, the absolute sensitivity (S_a) and the relative sensitivity (S_r) can be calculated as⁷⁴²

$$S_a = \frac{d\text{FIR}}{dT} = \text{FIR} \times \frac{\Delta E}{kT^2} \quad (2)$$

$$S_r = \frac{1}{\text{FIR}} \frac{d\text{FIR}}{dT} \times 100\% = \frac{\Delta E}{kT^2} \times 100\% \quad (3)$$

Since S_r is used on a larger scale, it allows comparison of the thermometric sensitivities of thermometers of different types and principles. The emission intensity of Er³⁺-doped luminophores at 525 nm increases with increasing temperature, accompanied by a decrease in emission intensity at 545 nm. For instance, Brites et al. reported a nanothermometer based on NaYF₄:Yb/Er@NaYF₄ with a relative thermal sensitivity of 1.15% K⁻¹ at 296 K.⁷³⁷ Thanks to its remarkable thermometric capacity and high spatial resolution (<1 μm), the

Table 2. Summary of Rare-Earth-Doped Nanomaterials for Temperature Sensing

host	dopant	exc (nm)	ratio of ems (nm)	maximum Sr^a (% K^{-1})	T (K)	range (K)	ref
NaYF ₄	Yb, Er	980	525/545	1.15	296	300–330	737
NaYF ₄	Yb, Er	980	525/545	1.8	/	298–343	738
NaYF ₄	Yb, Er	980	525/545	1.24	300	300–773	739
NaYbF ₄	Er	980	525/545	3.46	175	175–475	740
NaYF ₄ @SiO ₂	Yb, Er	975	525/545, 1010/810, 1010/660	1.10, 1.44, 0.79	313	299–337	741
YF ₃	Yb, Er	975	525/545	1.2	295	295–478	732
Bi ₅ IO ₇	Er	980	525/545	1.36	303	303–543	742
Bi ₂ SiO ₅ @SiO ₂	Yb, Er	977	525/545	1.1	300	80–800	743
SrF ₂	Yb, Er	980	525/545	1.2	298	298–383	744
α -NaGdF ₄	Yb, Er	980	525/550	/	/	293–363	745
β -NaGdF ₄							
β -NaGdF ₄ @SiO ₂							
LaPO ₄ /YPO ₄	Yb, Tm	975	700/800	/	/	293–773	352
α -NaYbF ₄ :Tm@CaF ₂ @NaYF ₄ :Yb/Er@CaF ₂	Yb, Tm, Er	980	801/820, 521/538	3.06	150	10–295	746
Bi ₂ O ₃	Yb, Tm	980	799/808	/	/	98–373	747
LaF ₃	Yb, Er	378	988/1540	6.6092	15	15–105	748
	Yb, Pr	/	/	1.08	25		
GdOF/SiO ₂	Yb, Nd, Er	808	534/543	1.6	260	260–490	749
Yb ₂ W ₃ O ₁₂ , Yb ₂ WO ₆	Er	980	523/660	/	573	303–573	381
SrF ₂	Yb, Tm	975	795/769	0.24	/	/	750
	Nd	808	869/905	0.17	/	/	
NaGdF ₄ :Yb/Er/Ho@NaGdF ₄ :Yb@ NaGdF ₄ :Yb/ Nd@NaGdF ₄	Yb, Er, Ho, Nd	806	1180/1340, 1550/1340	1.17, 1.1	/	293–323	751
KLu(WO ₄) ₂	Yb, Ho	980	545/650	0.54	300	297–673	752
NaGdF ₄	Yb, Ho, Ce	980	650/543	/	500	300–500	753
CsPbBr ₃ /EuPO ₄	Eu	393	611/516	1.8	420	303–480	754
Sc ₂ O ₃	Eu ²⁺ , Eu ³⁺	254	403/612	3.06	267	77–267	132
Mn:Zn ₂ SiO ₄ –Eu:Gd ₂ O ₃	Eu	260	612/520	3.05	303	303–623	755
SrZrO ₃	Eu	237	616/470	2.22	460	300–550	756
LaF ₃	Nd	808	865/885	0.25	/	303–343	757
Y ₃ Al ₅ O ₁₂	Nd	808	938/945	0.15	/	283–343	758
LiLuF ₄	Nd	808	862/866	0.62	77	77–275	759
LiLa _{0.4} Nd _{0.1} Yb _{0.5} P ₄ O ₁₂	Nd, Yb	808	870/980	0.4	330	93–663	760
TiO ₂	Eu	360	613/438	2.43	/	307–533	761
ZnSe	Er	980	656/547	8.61	77	77–298	762
TiO ₂	Sm	360	612/438	10.54	330.5	297–383	763
MoS ₂	Eu	282	612/437	1.4904	180	30–360	513
Eu _{0.2} Tb _{0.8} L	Eu, Tb	322	543/615	0.15	300	40–300	499
[Eu ₂ (QPTCA)(NO ₃) ₂ (DMF) ₄] (CH ₃ CH ₂ OH) ₃ ⊃perylene	Eu	388	615/473	1.28	293	293–323	764
Eu _{0.0066} Tb _{0.9934} L	Eu, Tb	335	542/612	3.76	450	77–450	765
Eu _{0.0089} Tb _{0.9911} L	Eu, Tb, Gd			2.71		430	
Eu _{0.013} Tb _{0.060} Gd _{0.927} L				6.11		400	
Eu _{0.033} Tb _{0.085} Gd _{0.882} L				3.62			
UiO-bpydc	Eu	395	530/614	2.99	293	293–353	766
(Me ₂ NH ₂) ₃ [Ln ₃ (FDC) ₄ (NO ₃) ₄] $\cdot$ 4H ₂ O	Eu	365	475, 575, 605, 640	2.7	170	12–320	767
Nd _{0.577} Yb _{0.423} BDC-F ₄	Nd, Yb	808	1060/980	0.816	313	293–313	768

^aRelative sensitivity.

researchers demonstrated that this nanothermometer can measure the instantaneous ballistic velocities of Brownian nanocrystals in colloidal suspensions.

There is growing interest in exploiting the anomalous effect of thermally enhanced luminescence in rare-earth-based nanothermometry.^{769–772} Normally, elevated temperatures are detrimental to nanophosphor luminescence because they enhance nonradiative pathways (phonon relaxation). Nevertheless, several groups have recently observed anomalous thermally enhanced upconversion luminescence in rare-earth-

doped crystals, such as NaGdF₄:Yb/Eu, NaYF₄:Yb/Tm, NaY(WO₄)₂:Yb/Er, and Yb₂W₃O₁₂:Er.^{381,773–775} Thermal enhancement has been linked to material properties such as particle size, dopant composition and concentration, crystal structure, and surface modification. Zhou et al. argued that the oxygen component on Yb³⁺/Tm³⁺-doped nanoparticle surfaces can form a stable [Yb...O] complex with Yb³⁺.⁷⁴⁴ The coupling of phonon vibrations with the excited intermediate state of Tm³⁺ could further facilitate the upconversion process at elevated temperatures. Lei et al. attributed this thermal

Table 3. Summary of Rare-Earth-Doped Nanomaterials for pH Sensing

host	dopant	exc (nm)	em (nm)	pH indicator	pH range	ref
NaYF ₄	Yb, Er	980	656/542	ETH 5418	6–11	793
NaYF ₄	Yb, Er	980	540	graphene oxide	5–8	794
NaYF ₄	Yb, Er	980	590/550	pHrodo Red	3–7	795
NaYF ₄	Yb, Er	980	540	pHAb	4–6	796
NaGdF ₄	Yb, Er	980	795/540	Ag ₂ S	4–9	797
NaGdF ₄	Yb, Er	980	650	bromothymol blue	6–8	798
NaYF ₄	Yb, Tm	980	528/648	BODIPY dye	5–9	799
NaGdF ₄	Yb, Tm	980	670	DNA	5.5–7.2	800
NaYF ₄	Yb, Tm	980	450/646	xylene orange	5–8	801
NaGdF ₄ @NaYF ₄ :Yb/Tm@NaYF ₄	Yb, Tm	980	650/513	hemicyanine dye	4–9	802
NaGdF ₄ :Yb/Tm@NaGdF ₄ :Nd/Yb@NaYF ₄	Nd, Yb, Tm	808	515/645	fluorescein	5–8	803
NaYF ₄ :Yb/Tm@NaYF ₄ :Yb@NaYF ₄ :Yb/Nd	Nd, Yb, Tm	808	474/643	FITC	3–8	804
NaGdF ₄	Ce, Tb	254	550	citric acid	3–10	805
NaGd(WO ₄) ₂	Eu	250, 490	512/611	fluorescein	4–10	806
NaGd(WO ₄) ₂ IOPC	Tb, Eu	280	620	phenol red	5–10	807
carbon quantum dots	Eu, Tb	365	438	/	1–14	808
JXNU-3 (MOF)	Tb	327	~550	/	3–7	809
[Eu ₅ (OH) ₆ (TZI) ₃ (DMA) _{1.5}](H ₂ O) _{10.5} ·DMA·0.5H ₂ O	Eu	/	616	/	3–10	810
MOF-253-Eu-TTA	Eu	375	614	/	5–7.2	811
[Ln ₂ (D-cam)(Himdc) ₂ (H ₂ O) ₂]	Eu	277	616	/	6.8–8.0	812
[Tb ₄ (μ ₃ -OH) ₄ L ₃ (H ₂ O) ₇]Cl _{0.63} ·(NO ₃) _{4.37} ·3H ₂ O	Tb	336	542	/	2–7	813

enhancement effect to the release of trapped electrons, while Hu et al. argued that the desorption of H₂O molecules was the key factor.^{776,777} Although the mechanism is still under debate,⁷⁷² this temperature effect has facilitated the design of rare-earth-based thermometers with ultrahigh thermal sensitivity. For example, Mi et al. reported combining thermal enhancement and thermal quenching within a nanoparticle to achieve high relative sensitivity.⁷⁷⁸ In their design, NaYF₄:Yb/Nd@NaYF₄@NaYF₄:Yb/Er nanoparticles with a core–shell–shell structure were prepared, in which Nd³⁺ luminescence was enhanced by phonon-assisted Yb³⁺–to–Nd³⁺ energy transfer and Er³⁺ luminescence was thermally quenched at elevated temperatures. A ratiometric thermometer with a maximum relative sensitivity of 9.6% K^{−1} at room temperature was obtained. New analytical methods in combination with ratiometric approaches will further improve the relative sensitivity of multiparametric luminescence thermometers.⁷⁷⁹ Other examples of recently developed rare-earth-based thermometers are summarized in Table 2.

Rare-earth-based optical thermometry has been combined with clinical therapeutic protocols to synchronously monitor lesion temperature.^{647,648} There is also a growing demand for the development of NIR-I/II luminescence nanothermometers capable of detecting localized microenvironments in biological systems. In this context, Yb³⁺, Nd³⁺, Ho³⁺, Er³⁺, and Tm³⁺ emitters have been used for NIR-based thermometry, which enables temperature sensing and luminescence lifetime measurements in deep tissues.^{757,780–783} For example, Nd³⁺–Yb³⁺ is a typical NIR-to-NIR emission system that has shown great potential for subcutaneous thermal biosensing based on phonon-assisted energy transfer from Nd³⁺ to Yb³⁺. Ximendes et al. found that thermal sensitivity was increased 4-fold when Nd³⁺ and Yb³⁺ were separated in the core and shell layers, respectively.⁷⁸⁰ These core–shell nanoparticles were used to measure subcutaneous temperatures in the NIR optical window with high accuracy.

4.2.2. Pressure Sensing. In addition to temperature sensing, rare-earth-doped nanomaterials have also been used to

measure pressure changes. Optical stress nanosensors have recently emerged for applications in robotics and materials research. It has long been known that the emission properties of certain rare-earth ions respond to pressure stimuli.^{784,785} To date, the pressure-stimulated responses of rare-earth-doped inorganic materials are thought to be mainly due to piezoelectric and crystal field effects. The application of pressure creates a piezoelectric field due to strong electron–lattice coupling, which triggers the separation of charge carriers trapped by defects in a transient state.⁷⁸⁶ Due to the slope of the energy bands below the internal piezoelectric potential, electrons in lattice defects can be easily detrapped after moving to a lower energy. Recombination of the released electron and hole pairs enables nonradiative energy transfer to doped rare-earth emitters, leading to spontaneous photon emission. This process, also known as mechanoluminescence, does not require additional photoexcitation to emit photons. Moreover, under high pressure, the interatomic distances and bond lengths shorten, the local symmetry around the rare-earth ions changes, and a phase transition can even occur, leading to altered luminescence characteristics upon photoexcitation.

CaZnOS, mCaO·Nb₂O₅, SrZn₂S₂O, and SrZnSO host crystals have been combined with rare-earth emitters to achieve efficient mechanoluminescence.^{787–789} In mechanoluminescence, external pressure stimuli can shift the emission wavelength by tuning crystal field effects. By applying stress stimuli, shifts in emission peaks and changes in emission ratios or lifetimes can be observed in different host materials.^{385,790,791} In 2020, Zhuang et al. reported stress sensing by force-induced charge carrier storage, using SrSi₂O₂N₂, BaSi₂O₂N₂, and (Sr_{0.5}Ba_{0.5})Si₂O₂N₂ materials doped with Eu²⁺, Yb²⁺, and Dy³⁺.⁷⁹² These stress-responsive materials are well suited for electronic signature documentation, fall monitoring, and traffic accident recording. It is also hoped that the stress-dependent color modulation of mechanoluminescent materials could be capitalized for biosensing applications, especially for detecting acute stress in cell membranes and living organisms. This would require the development of new synthetic

Table 4. Summary of Rare-Earth-Doped Nanomaterials for Biodetection

target	host	dopant	exc (nm)	em (nm)	sensitive indicator/acceptor	range	LOD ^a	ref
Amino Acid								
cysteine	NaYF ₄ @mSiO ₂	Yb, Tm	980	518,475	fluorescein-O,O'-diacrylate	20–200 μM	20 μM	815
cysteine	NaYF ₄	Yb, Er	980	540	rhodamine-oxaldehyde	10–100 μM	1.1 μM	816
tyrosine	NaYF ₄	Yb, Tm	980	490	tyrosine	0.8–100 μM	1.1 μM	817
cysteine/homocysteine	NaLuF ₄ @yolk shell	Yb, Er, Tm	980	540,800	ANP	0–18 equiv	28.5 μM	818
tryptophane	Zn-Hbct-BPY	Tb	300	546,370	/	3.92–100 ppm	3.1 ppm	819
L-lysine	[Dy(L)(H ₂ O)(DMF)] _n	Dy	290	372,584	rhodamine B	0–0.4 μM	0.024 μM	820
D-lysine							0.007 μM	
Nucleic Acid								
complementary ssDNA2	NaYF ₄	Yb, Tm	980	530, 480	SYBR green I	/	3.2 nM	821
ssDNA2-M3							7.6 nM	
microRNA-21	NaYF ₄ @NaYF ₄ :Yb/Er @NaYF ₄	Yb, Er	980	543	BHQ1	0.1 fM–0.1 nM	0.036 fM	822
miR-195	NaYF ₄	Yb, Tm	980	470	5-carboxyvinyl-2'-deoxyuridine	20 fM–500 pM	20 fM	823
ss-DNA	NaYF ₄	Yb, Tm	975	450–500	[(ppy) ₂ Ir(dcbpy)]PF ₆ -AuNP	1 pM–100 μM	1 pM	824
ss-DNA	NaYF ₄	Yb, Er	980	549, 654	graphene oxide	/	5 pM	825
Ebola virus oligonucleotide	BaGdF ₅	Yb, Er	980	540	Au nanoparticle	50–700 fM	300 fM	826
BACE-1, PCA3	NaYF ₄	Yb, Er	980	545	graphene oxide	200 fM–5 nM	500 fM	827
Peptide and Protein								
bovine hemoglobin	NaYF ₄	Yb, Er	980	543.5	bovine hemoglobin	0.1–0.6 mg/mL	0.062 mg/mL	828
glutathione	NaYF ₄	Yb, Er	980	550	dopamine–quinone	1–75 μM	0.29 μM	829
glutathione	NaYF ₄ :Yb/Er@NaYF ₄	Yb, Er	980	654	Au NP	0.05–2 μM	0.016 μM	830
glutathione	NaYF ₄	Yb, Er, Tm	980	540, 800	TCG	0–10 mM	0.83 mM	831
avidin	NaYF ₄	Yb, Tm	980	520, 480	FITC	0–4.5 nmol	48 pmol	832
alpha-fetoprotein	NaYF ₄	Yb, Tm	980	480	ZnO/Ag	0.05–100 ng/mL	40 pg/mL	833
cytochrome c	NaYF ₄	Yb, Er	980	543.5	cytochrome c	1–24 μM	0.73 μM	834
carcinoembryonic antigen	NaYF ₄	Yb, Tm	980	520, 480	FITC	0.1–100 ng/mL	0.89 ng/mL	835
prostate-specific antigen	NaYF ₄	Yb, Er	980	550	Au nanoparticle	0–500 pM	1 pM	836
CA-125 antibody	NaYF ₄	Yb, Tm	980	480	Ag nanoparticle	5–100 ng/mL	120 pg/mL	837
Caspase-9	NaYF ₄ : Yb/Er@NaGdF ₄	Yb, Er	980	655,541	Cy5	0.5–100 U/mL	0.068 U/mL	838
tyramine	NaGdF ₄ :Yb/Er@NaYF ₄	Yb, Er	980	541,655	/	0.167–33.3 μM	0.026 μM	839
tyrosinase						0.0033–1 U/mL	0.003 U/mL	
matrix metalloproteinase MMP-2	NaYF ₄ :Gd/Yb@NaYF ₄ : Yb/Tm/Er	Yb, Er, Tm	980	450,655	TAMRA	0.001–0.2 μg/mL	2.2 ng/mL	840
MMP-7				541,655	FITC	0.01–1 μg/mL	13.9 ng/mL	
insulin	Gd(L)(H ₂ O)(DMF)	Gd	490	525	FAM-P	0–1.72 μM	0.0012 μM	820
creatine kinase	Eu-QPTCA	Eu	373	615	/	1.2–156.2 U/L	1 U/L	841
tyrosinase	NaYF ₄	Yb, Tm	980	475	dopamine–quinone	0.001–0.1 U/mL	/	842
alkaline phosphatase					o-phospho-L-tyrosine	0.5–50 U/mL	/	
lysozyme	NaLu/GdF ₄ :Tb@NaYF ₄	Gd, Tb	X-ray	546	BHQ1-DNA	3–200 nM	0.94 nM	843
Small Molecule								
vitamin B12	NaYF ₄	Yb, Tm	980	345	vitamin B12	3–634 nM	3 nM	844
melamine	NaYF ₄	Yb, Er	980	550,650	melamine	5–100 nM	9.1 nM	845
ascorbic acid	NaYF ₄	Yb, Tm	980	360	cobalt oxyhydroxide	2–60 μM	0.2 μM	846
ascorbic acid	Eu _{0.07} Gd _{0.03} -MOF	Eu, Gd	UV	614,415	/	0–60 μM	0.184 μM	847
catecholamine	NaLuGdF ₄ –Fe ³⁺	Yb, Er	980	542	catecholamine	5–320 nM	2.8 nM	848
uric acid	NaYF ₄	Yb, Er, Mn	980	665	/	4 nM–10 μM	1.9 nM	849
uric acid	NaCeF ₄	Yb, Er	980	1530	/	0–900 μM	25.6 nM	574
glucose	NaYF ₄	Yb, Tm	980	450	MnO ₂	0–400 μM	3.7 μM	850
glucose	BaWO ₄ :Yb/Er@Au	Yb, Er	980	529	Au	0–0.1336 μM	3.1 nM	851
ATP	NaGdF ₄	Yb, Tm	980	360	DNA aptamer	1–10 nM	/	852

Table 4. continued

target	host	dopant	exc (nm)	em (nm)	sensitive indicator/acceptor	range	LOD ^a	ref
Small Molecule								
dopamine	NaYF ₄ :Yb@NaYF ₄ :Er@NaYF ₄ :Yb	Yb, Er	980	542	graphene oxide	1–10 pM	/	853
ppGpp	MoS ₂	Eu	254	616,410	/	50 nM–25 μM	44.4 nM	854
dipicolinic acid	Tb(BTC)(H ₂ O) ₆	Tb	290	545	/	1 nM–5 μM	0.04 nM	855
Free Radical								
ONOO [−]	NaYF ₄ @NaYF ₄ :Nd	Nd	808	1060	MY-1057	0–40 μM	/	856
ONOO [−]	NaYF ₄	Yb, Tm	980	800	Cy7	3.5–17.5 μM	0.08 μM	857
·OH	NaYF ₄ @NaYF ₄ :Yb/Tm@NaYF ₄	Yb, Tm	980	480	mOG	1.2–194.6 fM	/	858
H ₂ O ₂	NaErF ₄ :Ho@NaYF ₄	Er, Ho	1530	980, 1180	IR1061	0–100 μM	/	189
H ₂ O ₂	NaYF ₄	Yb, Tm	980	450	MnO ₂	0–350 μM	0.9 μM	850
H ₂ O ₂	NaYF ₄ @ZIF-NiS _x	Yb, Er	980	660, 540	ZIF-NiS _x	0.05–20 μM	0.037 μM	859
ClO [−]	NaGdF ₄	Yb, Tm	980	476	MoS ₂	0.5–15 μM	0.384 μM	860
ClO [−]	NaYF ₄ :Yb,Nd,Er@NaYF ₄ :Nd	Nd, Yb, Er	808	540, 654	hCy3	0–80 μM	27 ppb	861
Gas								
H ₂ S	NaLuF ₄ :Yb, Er,Tm@NaLuF ₄	Yb, Er, Tm	980	800/550, 654/550	Prussian Blue	0–150 μM	50 nM	862
H ₂ S	NaYF ₄	Yb, Er, Tm	980	540/800	merocyanines	0–115 μM	0.58 μM	863
H ₂ S	UiO-66-(COOH) ₂	Eu	305	615/393	/	0–625 μM	/	864
O ₂	NaYF ₄	Yb, Tm	980	613/477	[Ru(dpp) ₃] ²⁺ Cl ₂	0–39.16 mg/mL	/	865
O ₂	NaYF ₄	Yb, Er	980	645	PtOEP	0–100%	/	866
Cation								
Cu ²⁺	NaGdF ₄ @NaYF ₄ :Ce/Tb	Ce, Tb	254	548	/	0–0.08 μM	0.35 nM	867
Cu ²⁺	NaYF ₄ @NaYF ₄ :Er/Yb@NaYF ₄	Yb, Er	980	543/658	rhodamine B hydrazide	0–360 μM	5.4 nM	868
Cu ²⁺	SrF ₂	Ce, Tb	290	544	/	1–10 μM	2 nM	869
Cu ²⁺	[Tb ₃ (L) ₂ (HCOO)(H ₂ O) ₅].DMF·4H ₂ O	Tb	327	550	/	1 μM–10 mM	/	870
Pb ²⁺	NaY(MoO ₄) ₂ :Tm/Ho/Yb	Yb, Tm, Ho	975	657	/	62.5–500 μM	/	871
Pb ²⁺	NaYF ₄ :Yb/Tm	Yb, Tm	980	545	CdTe	20–3600 nM	80 nM	872
Fe ³⁺	graphene quantum dots	Er	360	440	/	0.01–120 μM	2.8 nM	873
Fe ³⁺			730	442	/	0.1–200 μM	28 nM	
Fe ³⁺	NaYF ₄ :Gd/Yb/Ho	Gd, Yb, Ho	980	546/758	EPA	0.25–50 μM	0.65 nM	874
Fe ³⁺	NaYF ₄ :Yb/Er/Tm@NaGdF ₄	Yb, Er, Tm	980	540	Nile Red derivative	0–30 μM	89.6 nM	875
K ⁺ , Fe ³⁺	[LnK(BPDSDC)(DMF)(H ₂ O)] _x (solvent)	Eu	316	618	/	0.01–1 mM	/	876
Fe ³⁺	[Tb ₄ (OH) ₄ (DSOA) ₂ (H ₂ O) ₈].8H ₂ O	Tb	350	542	/	10 ^{−6} –10 ^{−1} M	/	877
Cr ⁴⁺	carbon quantum dot	Eu, Tb	360	438	/	1–20 μM	0.175 μM	808
Hg ²⁺	ZnS	Ce	230	459/689	/	10–100 μM	0.82 μM	878
Hg ²⁺	NaYF ₄	Yb, Er, Tm	980	540/803	thiazole-derivative	0.8–5 mM	63 nM	879
Hg ²⁺	BA-Eu-MOF	Eu	275	620	/	0–240 μM	220 nM	880
CH ₃ Hg ⁺						0–200 μM	440 nM	
Ag ⁺	NaYF ₄	Yb, Er	980	543	graphene quantum dots	1–200 μM	60 pM	881
Ag ⁺	MIL-121	Sm	320	603	/	/	/	882
Zn ²⁺	NaYF ₄	Yb, Tm	980	475/654	compound 1	0–0.09 mM	/	883
Pb ²⁺	Tb(L)(H ₂ O) ₅	Tb	334	545	/	0.34–800 μM	0.34 μM	884
Anion								
F [−]	NaYF ₄	Yb, Er, Tm	980	546/758	curcumin	5–200 μM	5 μM	885
CN [−]	NaYF ₄ :Yb/Er@NaYF ₄ :Yb	Yb, Er	980	655	Au nanoparticle	0–200 μM	1.53 μM	886
CN [−]	NaYF ₄	Gd, Yb, Er	980	650/550	polydiacetylenes	10–25 mM	/	887

^aLimit of detection.

approaches for nanosized mechanoluminescent materials with well-controlled particle size, morphology, and surface modification.

4.2.3. pH Sensing. Since most rare-earth-doped nanophosphors are inert to pH changes, pH sensing based on these nanomaterials has been mainly accomplished by coupling pH-sensitive species such as molecular indicators (ETH 5418, pH-rodo red, bromothymol blue, etc.) and functional nanomaterials (graphene oxide, Ag₂S, etc.).^{793–795,797,798} The absorption of the pH indicators must overlap with the emission of the nanophosphors. Typically, pH changes can be identified by measuring variations in absorption wavelength, or absorption and emission intensities.⁸¹⁴

The 4f–4f transitions of rare-earth ions are relatively insensitive to environmental changes because the 4f electrons are shielded by filled 5s and 5p shells. Therefore, rare-earth emission can be employed as an internal reference for ratiometric pH measurement. For instance, Lei et al. proposed a new concept for rare-earth-based pH sensing by modulating an energy cascade from Ce³⁺ to the emitters.⁸⁰⁵ Ce³⁺ is a widely used sensitizer that absorbs ultraviolet light due to its 4f–5d transition facilitated by the electric dipole. In this sensor, citric acid was used as a pH-reactive ligand that combines with the nanoparticles. The electronegativity of citric acid decreases with increasing pH, which enhances the covalency between the ligand and Ce³⁺. This process disrupts the d–f transition and decreases the sensitization efficiency of Ce³⁺ toward the activators Tb³⁺, Eu³⁺, and Mn³⁺, leading to a decrease in emission intensity. Table 3 summarizes the recently reported pH sensors based on rare-earth-doped nanomaterials.

4.2.4. Molecular Detection. Rare-earth-doped nanomaterials have enabled the development of miniaturized, wearable molecular sensors with rapid signal responses. As these nanoparticles are largely inert to environmental changes, detection of molecules is mainly based on switching luminescence on and off by energy transfer, either by Förster resonance energy transfer (FRET) or by radiative reabsorption, between the nanoparticles and specific environmentally sensitive species (molecular biosensors and organic fluorophores).^{888,889} A number of species that provide detailed information about physiological state, including amino acids, nucleic acids, proteins, small molecules, free radicals, gases, and ions, have been detected with rare-earth-doped nanomaterials (Table 4).

To minimize background autofluorescence, NIR-to-visible UCNP are usually utilized. For instance, Tsang et al. combined BaGdF₅:Yb/Er UCNP and Au nanoparticles to construct a biodetection system for Ebola virus oligonucleotides.⁸²⁶ This detection was based on hybridization of Ebola virus oligonucleotides and complementary single-stranded oligonucleotides that brought UCNP and Au nanoparticles into close proximity to induce luminescence quenching. FRET-based molecular sensing normally requires high energy transfer efficiency to improve detection sensitivity. In this regard, Deng et al. utilized fluorescein NaGdF₄:Yb/Tm@NaGdF₄ nanoparticles to enhance FRET efficiency through Gd–Gd energy migration within the particles.⁷⁰⁵ Compared to conventional UCNP without energy migration within the particles, a >600-fold increase in acceptor emission was achieved in core–shell UCNP with an average size of 30 nm. By harnessing the effect of Tb–Tb energy migration within the NaYbF₄:Tb@NaTbF₄ nanoprobe, researchers have demonstrated quantitative anal-

ysis of photoreaction kinetics with single-molecule precision.⁸⁹⁰

In addition to upconversion from the NIR to the visible, Liu et al. recently designed H₂O₂ detection using NIR-to-NIR upconversion nanoprobe with both excitation and emission in the NIR-II window.¹⁸⁹ In that design, NaErF₄:Ho@NaYF₄ UCNP were employed as energy donors that generated upconverted NIR-II emission at 980 nm (⁴I_{11/2} → ⁴I_{15/2} transition of Er³⁺) and 1180 nm (⁵I₆ → ⁵I₈ transition of Ho³⁺) under 1530 nm excitation. Upconverted NIR-II emissions were quenched after conjugation with the organic chromophore IR1061. IR1061 decomposed in the presence of H₂O₂, leading to recovery in upconverted emission. Because of the low scattering and attenuation of NIR-II light in biological tissue, these nanoprobe enabled the detection of H₂O₂ with high spatial resolution (200 μm × 200 μm) in deep tissue.

The long lifetime of rare-earth emitters has enabled temporal imaging that avoids interference from short-lived autofluorescence. Zhang's group implemented luminescence lifetime-based *in situ* imaging of hepatocellular carcinoma using Nd³⁺-doped downshifting nanoparticles as energy donors.⁸⁵⁶ An ONOO[−]-sensitive dye (MY-1057) was coupled to these nanoparticles as an energy acceptor. The dye molecule absorbed the NIR-II emission and shortened the lifetime of Nd³⁺ emission. These dye-coupled nanoprobe distinguished lesions from normal liver tissue by imaging lifetime changes in response to ONOO[−] in the tumor microenvironment. Compared to conventional imaging intensity-based biosensing, luminescence lifetime measurement provides much higher spatial resolution with clear pattern discrimination between tumor lesions (275 ± 49 μs) and normal tissue (205 ± 7 μs).

Another intriguing detection method is the use of rare-earth-doped nanoparticles as single-particle counters for the quantification of target molecules. As a typical example, Mendez-Gonzalez et al. constructed an ingenious DNA detection scaffold based on UCNP. The researchers employed two oligonucleotide probes, "UC-probe" and "c-probe" for detection.⁸²³ In the presence of target DNA, these oligonucleotide probes hybridized and captured UCNP in microwells. The number of target DNA sequences can be determined by counting the number of UCNP bound in the microwells. Indeed, single-particle/single-molecule imaging is an emerging technique with the advantage of high sensitivity and low detection limits, and its application in molecular sensing has gained increasing attention.^{32,564} Liu's group has developed a hedgehog-like core–shell nanostructure for upconversion, which can be used to detect dithiothreitol.⁸⁹¹ This nanostructure was first modified with an MnO₂ layer to attenuate upconversion luminescence. After addition of dithiothreitol, a "turn-on" process of luminescence was observed at the single-particle level.

Rare-earth-doped nanomaterials can be applied to gas sensing by monitoring changes in electrical conductivity. Rare-earth oxides (Sm₂O₃, CeO₂, Dy₂O₃), rare-earth perovskite oxides (REFeO₃ and REMnO₃), and rare-earth-doped semiconductor nanocrystals (ZnO, NiO, SnO₂) have attracted considerable attention for gas sensing.^{892–899} When rare-earth-doped nanoprobe are exposed to air, adsorbed oxygen on the surface withdraws electrons from the conduction band of the host material, resulting in negatively charged chemisorbed species such as O[−], O₂[−], and O₂^{2−}. This leads to a layer with increased electron depletion. Binding gas molecules to nanoprobe surfaces leads to electron release into the

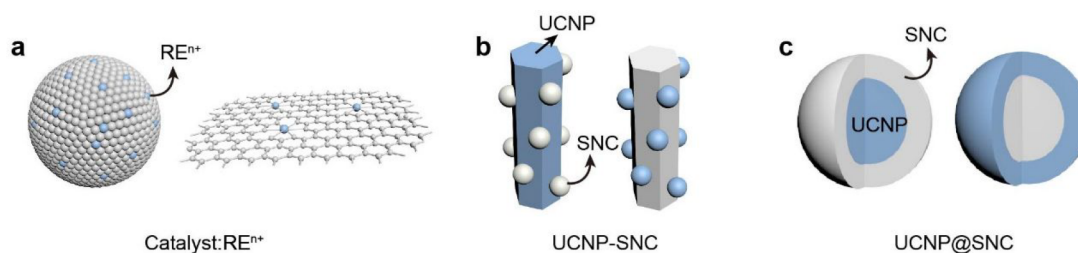


Figure 24. Schematic design of rare-earth-doped nanomaterials for catalysis. (a) Rare-earth-doped nanocatalysts. (b) Heterogeneous catalysts based on UCNP-semiconductor nanocrystal (SNC) hybrids. (c) UCNP@SNC core-shell catalysts.

conduction band, eliminating the electron depletion layer. For n-type semiconductors, the increased electrons enhance the electrical conductivity and decrease the resistance, while for p-type semiconductors, the increased electrons deplete hole density and increase the resistance. Gas molecules, including NO_x ,^{900,901} CO ,⁹⁰² CO_2 ,⁹⁰³ H_2 ,⁸⁹⁹ H_2S ,⁹⁰⁴ SO_2 ,⁹⁰⁵ NH_3 ,⁹⁰⁶ and volatile organic compounds such as acetone,⁹⁰⁷ ethanol,⁹⁰⁸ methanol,⁹⁰⁹ and formaldehyde,⁸⁹⁶ induce resistivity changes in rare-earth-based semiconductor nanopores.

Reactions with gas molecules can form an excited intermediate on material surfaces. This intermediate can emit photons when it returns to the ground state, a process known as cataluminescence.⁹¹⁰ Tang et al. developed a novel cataluminescent gas sensor based on $\text{NaYF}_4\text{:Er}$ nanocrystals.²⁰⁴ This gas sensor shows excellent selectivity for ketones, with detection limits of 1.7 and 0.7 $\mu\text{g mL}^{-1}$ for acetone and butanone, respectively. The sensor exhibits negligible cataluminescence for alcohols, aldehydes, acetonitrile, dipropylmethane, and ethyl acetate. Moreover, $\text{NaYF}_4\text{:Er}$ nanocrystals have a short response time of 3 s at 250 °C. Nevertheless, gas sensors based on resistance changes or cataluminescence generally require high working temperatures (>100 °C), which is unsuitable for daily use. There is still a huge need for the development of gas sensors based on nanomaterials that can operate at ambient temperature.

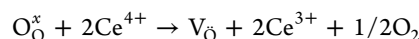
It is worth noting that optical materials are of great use in the development of wireless sensors for the internet of things (IoT).^{911,912} With the ability to measure multiple components simultaneously, IoT optical sensors can generate a wealth of data in various contexts, which can then be processed and leveraged remotely by users. Rare-earth-doped nanomaterials could impact the IoT sensor industry in the not-too-distant future.

4.3. Catalysis

Catalysis is essential for pollution control and all aspects of industry. Rare-earth elements are used as catalysts in various forms, such as alloys, rare-earth complexes, and photocatalysts.^{21,913,914} They are often combined with precious metals and semiconductor nanocrystals (Figure 24). The use of rare-earth nanomaterials could promote reactivity and facilitate solar energy harvesting.

4.3.1. Ceria-Based Catalysis. Catalysts based on ceria (CeO_2) have been widely used for water–gas reaction,^{915,916} steam reforming of methanol,⁹¹⁷ water splitting,^{918,919} and automobile exhaust treatment (e.g., CO oxidation^{920–922} and NO reduction^{923,924}). The catalytic property of CeO_2 is mainly due to the reversible valence change of $\text{Ce}^{4+}/\text{Ce}^{3+}$, which allows the simultaneous release/storage of oxygen to form CeO_x . Oxygen vacancies form in CeO_2 after the reduction of Ce^{4+} to Ce^{3+} . Oxygen vacancies can serve as active sites for

many reactions. Using Kröger–Vink notation, the reaction can be expressed as follows:



Since an oxygen vacancy can be generated and vanish in a short time, this reaction leads to a high oxygen storage capacity of CeO_2 .

Impurity doping can modify the catalytic performance of CeO_2 . A typical example is the doping of Zr^{4+} with CeO_2 , which strongly promotes the redox property of the catalyst.¹⁰ Esch and co-workers reported high-resolution scanning tunneling microscopy (STM) to study the (111) facet of CeO_2 with atomic resolution. They observed that oxygen vacancies tend to form linear clusters at high temperatures (300–400 °C).⁹²⁵ Zr^{4+} dopants can increase surface thermal stability and porosity, thus improving the catalytic performance of CeO_2 . Besides Zr^{4+} , other metals such as Au, Pt, Rh, Ti, Fe, and Cu have been incorporated into CeO_2 to form $(\text{Ce}_x\text{M}_{1-x})\text{O}_2$ solid solutions, which can be used to fine-tune the formation energy of oxygen vacancies in the oxides.^{922,926–930}

Apart from impurity doping, metal nanoparticles on nanocrystalline CeO_2 supports have attracted much attention for catalysis. Carrettin et al. deposited Au nanoparticles on nanocrystalline CeO_2 .⁹²⁰ This hybrid structure increased the catalytic activity of Au/ CeO_2 nanocomposites by 2 orders of magnitude in low-temperature CO oxidation in the presence of H_2 . Cargnello et al. investigated the size effect of nanoparticles deposited on a CeO_2 support.⁹³¹ Ni, Pd, and Pt nanoparticles of various sizes were deposited on a CeO_2 support to catalyze CO oxidation. The metal atoms at the interface between the metal nanoparticles, the CeO_2 support, and the atmosphere were determined to be the catalytic sites. Due to a larger contact area with the CeO_2 support, smaller metal nanoparticles showed higher catalytic activity for CO oxidation.

The enhanced catalytic properties of metal nanoparticles on CeO_2 supports are mainly due to the charge transfer resulting from metal–support interactions. Besides the particle size, the structure of the nanoparticles and the chemical properties of the support can also influence the dynamics of the charge transfer.⁹³² Additionally, nanocrystalline CeO_2 can serve as a support for single-atom catalysis. Nie et al. treated atomically dispersed Pt atoms on CeO_2 with high-temperature steam (750 °C) to promote the formation of active surface oxygen lattices in the vicinity of Pt sites.²¹ In this way, the oxidation of CO was dramatically accelerated at a much lower reaction temperature (lowered from 320 to 148 °C).

Nanoceria has shown great promise for biological catalysis. CeO_2 exhibits activities that mimic various enzymes such as photolases,⁹³³ phosphatases,⁹³⁴ oxidases,⁹³⁵ peroxidases,⁹³⁶

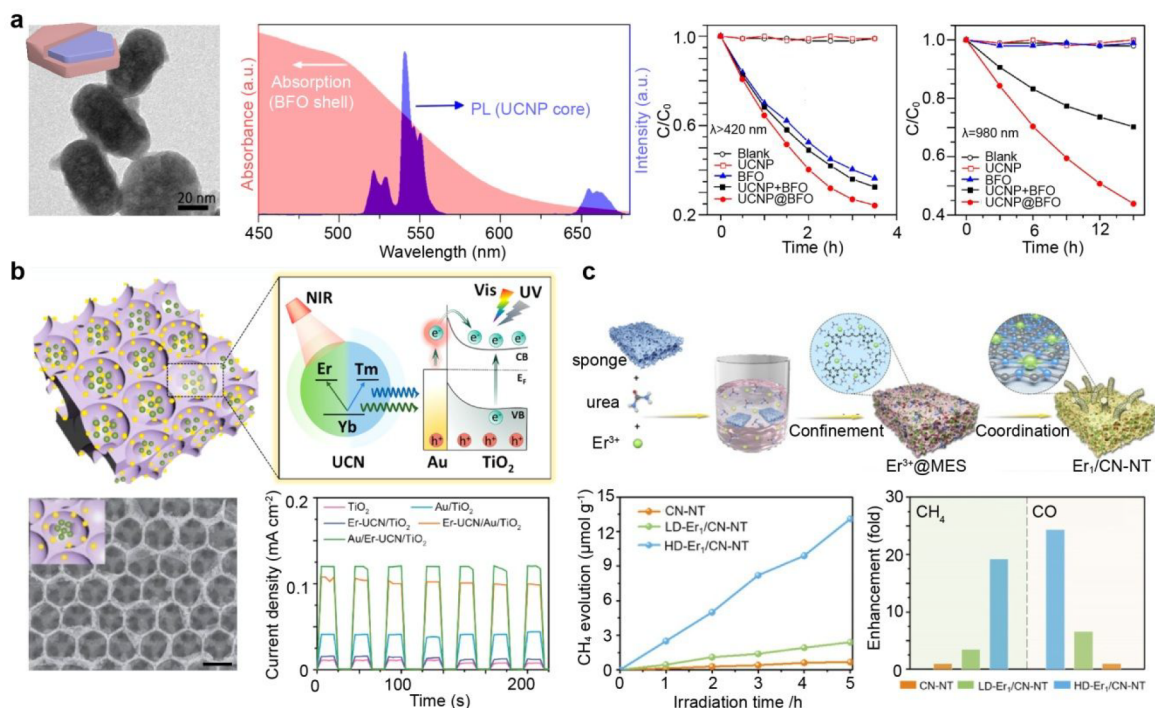


Figure 25. (a) Structure and catalytic properties of UCN@BiFeO₃ (BFO) core-shell nanoparticles. (b) Schematic of the photoinduced catalysis process and photoelectrochemical properties of UCN/Au/TiO₂ nanohybrids with inverse opal structures. The scale bar is 500 nm. (c) Schematic of the synthetic process and photocatalytic performance of single-atom Er₁/CN-NT catalysts (Adapted with permission from refs 510, 942, and 943. Copyright 2017, 2019 American Chemical Society; Copyright 2020 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

catalases,⁹³⁷ and superoxide dismutases.⁹³⁸ Recently, Zhao et al. constructed enzyme surrogates for inflammatory bowel disease therapy based on enzyme-mimicking CeO₂@montmorillonite (MMT) materials.⁹³⁹ In that design, a negatively charged MMT layer facilitated transportation of positively charged CeO₂ to the inflamed colon. CeO₂ efficiently scavenged ROS to alleviate tissue inflammation. Moreover, CeO₂ catalyzed the degradation of H₂O₂, mimicking superoxide dismutase and catalase. After oral administration, CeO₂@MMT inhibited colonic inflammation, diarrhea, and rectal bleeding and improved the histological appearance in dextran sulfate sodium-induced rodents.

Phosphatase is an enzyme capable of hydrolyzing organic deleterious phosphorus compounds.⁹⁴⁰ Mugesh's group reported that vacancy-engineered nanoceria (VE CeO₂) efficiently promoted the hydrolysis of organophosphate triester such as paraoxon *in vivo*.⁹⁴¹ Enrichment of oxygen vacancies endowed the nanoceria with phosphotriesterase-mimetic hotspots. VE CeO₂ nanoparticles exhibited much higher catalytic activity than pristine CeO₂ nanoparticles, indicating the versatility of vacancy engineering in tuning catalytic properties.

Nanosized ceria powder has also proven useful as a photocatalyst for medical treatment, gas conversion, and pollutant removal.^{944–946} Unlike bulk cerium oxide, the bandgap of nanoceria can be tuned by controlling its size and morphology. Yao et al. synthesized mesoporous Yb³⁺/Tm³⁺-codoped CeO₂ UCNPs with a 2.89 eV bandgap.²⁵⁸ Under 980 nm excitation, UV emission from Tm³⁺ sensitized CeO₂ and converted O₂ and H₂O into cytotoxic ROS. Due to the catalase-like activity of CeO₂, the abundant H₂O₂ molecules in tumor cells were decomposed while synergistically providing O₂. In 2019, Wang et al. improved the

photocatalytic activity of CeO_{2-x} for CO₂ reduction by introducing Cu to stabilize oxygen vacancies.⁹⁴⁷ The combination of Cu and CeO_{2-x} improved CO production 26-fold compared to pure CeO_{2-x} catalysts.

4.3.2. Photocatalysis. To harvest NIR light for photocatalysis, rare-earth-doped UCNPs can be combined with semiconductor photocatalysts. For instance, Qin et al. demonstrated the combination of TiO₂ and UCNP transducers for photocatalysis. They coated a TiO₂ shell on YF₃:Yb/Tm nanoparticles and then investigated the photocatalytic performance by monitoring the degradation of methylene blue (MB).⁹⁴⁸ About 60% of MB was degraded after 30 h of laser irradiation at 980 nm. In a follow-up study, the researchers also confirmed that the degradation of MB was mainly due to the photocatalytic generation of ROS, rather than a thermal effect caused by NIR irradiation.²¹⁹ Yu et al. combined NaYF₄:Yb/Tm nanoparticles with CdS nanoparticles, which resulted in ~23% degradation of rhodamine B after 3 h of NIR irradiation.⁹⁴⁹

Zhang et al. designed NaGdF₄:Yb/Er@BiFeO₃ nanoparticles for photodegradation of methylene orange (Figure 25a).⁹⁵⁰ BiFeO₃ is a multiferroic material with a bandgap of ~2.0–2.6 eV. The corresponding absorption of BiFeO₃ well matches the upconverted emission of Er³⁺. Under monochromatic NIR irradiation for 15 h, 55% degradation of methylene orange was achieved. In addition to NaYF₄, CaF₂ is also a suitable host with low phonon energy for efficient photon upconversion. Huang et al. deposited CaF₂:Yb/Er/Tm nanoparticles on the surface of BiVO₄ with dendritic morphology. Bi³⁺ can tailor the local crystal field of lanthanide dopants at the UCNP–BiVO₄ interface and enhance upconversion luminescence, which improves the photocatalytic performance.⁹⁵¹

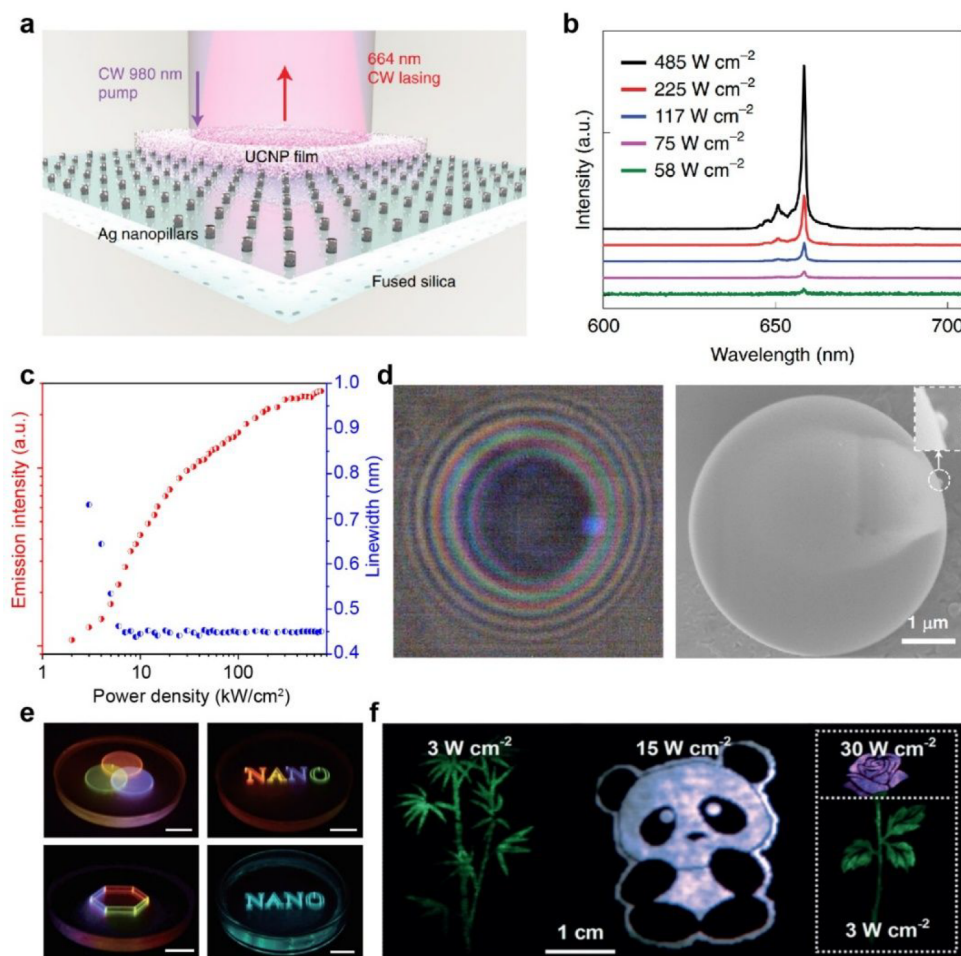


Figure 26. (a) Schematic of upconversion lasing based on UCNP-Ag arrays. (b) Power-dependent lasing spectra of UCNP-Ag arrays. (c) Excitation power-dependent emission intensities and spectral line width (peak@808 nm). (d) Wide-field image (left) and SEM image (right) of a single UCNP in a microcavity. (e) Luminescence color images generated in different nanocrystal/PDMS composite monoliths. Scale bars are 1 cm. (f) Images of bamboo, panda, and rose printed on a piece of A4 paper using the colloidal nanostructure as colorless ink (Adapted with permission from refs 33, 312, 965, and 973. Copyright 2015, 2019, 2020 Nature Publishing Group; Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

Besides binary nanocomposites, Zhang et al. fabricated TiO₂ nanofibers in combination with a large amount of NaYF₄:Yb/Tm nanoparticles and CdS nanospheres to achieve full-spectrum absorption.⁹⁵² In 2019, Boppella et al. deposited UCNPs and Au nanoparticles on an inverse 3D TiO₂ opal (Figure 25b).⁹⁴³ Incorporation of Au nanoparticles not only enhanced light collection but also promoted energy transfer from UCNPs to TiO₂ via surface plasmon resonance.⁹⁵³ They prepared NaYF₄:Yb/Er and NaYF₄:Yb/Tm UCNPs whose emission overlapped the absorption of Au nanoparticles. This composite device achieved a 10-fold increase in photocurrent upon exposure to vis–NIR irradiation, compared to control devices using pristine TiO₂. In addition to Au nanoparticles, graphene and graphene oxides can act as energy acceptors for UCNPs. Wang et al. employed reduced graphene oxide (RGO) as the support to fabricate NaYF₄:Yb/Tm@TiO₂/RGO nanocomposites.⁹⁵⁴ This nanocomposite showed improved photocatalytic performance under NIR irradiation because it can scavenge photoinduced electrons from TiO₂ and prevent e[−]–h⁺ recombination by RGO.

Rare-earth-doped nanomaterials are viable catalysts for water splitting. They are amenable to photoelectrochemical hydrogen production. Chen et al. constructed a photoelectrochem-

ical cell using CdTe QD-decorated ZnO nanorods as the photoanode, a Pt plate as the counter electrode, and Au-modified UCNPs attached to ZnO nanorods for NIR harvesting.⁹⁵⁵ When this photoelectrochemical cell was exposed to sunlight, electrons generated in ZnO transferred to Pt via an external circuit and subsequently reduced hydrogen ions to hydrogen. Meanwhile, photogenerated holes reacted with water to generate oxygen molecules.

Beyond broadening the absorption spectrum, the introduction of Nd³⁺, Sm³⁺, and Eu³⁺ ions can reduce semiconductor bandgaps (e.g., Ag₃VO₄). Trivalent dopants can also inhibit the recombination of photogenerated electron–hole pairs, improving the photocatalytic performance.^{956,957} Moreover, Xie et al. found that surface Nd³⁺ dopants can serve as Lewis acid to form complexes with dyes. The dyes can capture visible light and inject electrons into the conduction band of TiO₂. Subsequently, Nd³⁺ ions scavenge electrons transferred from TiO₂ to generate superoxide radical anions.⁹⁵⁸ Nd³⁺ can harness visible light while facilitating electron–hole separation. A similar phenomenon was recently reported by Wang et al.,⁹⁵⁹ who demonstrated that Gd³⁺-rich nanoparticles can enhance adhesion of organic molecules on UCNP–TiO₂ hybrid

catalysts, enhancing cycloreversion of organic chromophores during photocatalytic degradation.

4.3.3. Single-Atom Catalyst. Recently, rare-earths have drawn increasing attention to single-atom catalysis. In 2020, Liu et al. first demonstrated atomically dispersed Sc and Y as active sites for catalysis.¹⁶ Atomic Sc- and Y-doped C_3N_4 (Y_1/NC and Sc_1/NC) samples were synthesized by a simple solid-state reaction. Based on calculations and EXAFS analysis, rare-earth atoms preferred carbon defect sites where they were coordinated by six nitrogen and carbon atoms. The researchers also performed nitrogen and carbon dioxide reduction reactions to investigate the electrocatalytic performance of Y_1/NC and Sc_1/NC at room temperature. Both catalysts exhibited good stability and excellent catalytic properties.

Shortly afterward, Li's group employed Er atoms to fabricate single-atom photocatalysts supported by carbon nitride nanotubes ($Er_1/CN-NT$) using a strategy of atom confinement and coordination (ACC) (Figure 25c).⁵¹⁰ They demonstrated that the presence of Er atoms promoted absorption in the visible region. The production of CH_4 and CO was much faster with $Er_1/CN-NT$ than with pristine CN-NT. The researchers also used the ACC strategy to prepare single-atom catalysts other than Er. On a separate note, Dong's group reported La-doped carbon nitride single-atom catalysts with a La–N charge-transfer bridge as the active site, which exhibited high efficiency and selectivity in CO_2 reduction.²⁶⁰

4.4. Lighting and Displays

4.4.1. Nanoparticle Lasing. As a product of rapidly developing nanotechnology, nanolasers have recently received considerable attention for utilization in integrated circuits because they can be confined in cavities on the wavelength or subwavelength scale.⁹⁶⁰ Nanolasers consist of a gain medium and an optical cavity. Rare-earth-doped nanomaterials can act as the gain medium, while the optical cavities have different compositions and structures. Lowering the laser threshold has become the “holy grail” of the field, especially for upconversion lasers, since multiphoton upconversion emission usually requires a high energy input. Various methods have been explored to enhance light emission and lower the threshold. The most widely adopted technologies are plasmon amplification and whispering gallery mode (WGM).

Since surface plasmon resonance influences rare-earth luminescence in various settings,⁹⁶¹ this technique has been explored to develop rare-earth-doped nanolasers. By combining rare-earth-doped materials and noble metals, hybrid nanoparticle films and arrays have been prepared.^{962–964} Fernandez-Bravo et al. prepared Ag nanopillar arrays in a square lattice and subsequently coated $NaYF_4:Yb(20\%)/Er(20\%)@NaYF_4$ UCNP on the Ag nanopillar array (Figure 26a and b).⁹⁶⁵ The Ag nanopillar array has a lattice plasmon resonance that overlaps the red emission, arising from the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} . As a result, the red emission was greatly enhanced, and the pump threshold could decrease to 29 W cm^{-2} . Moreover, the change in the lattice constant, a_0 , of the nanopillars modulated upconversion emission due to a change in the plasmon resonance, revealing the feasibility of determining the laser power directly using single-lattice plasmon cavities. Intriguingly, plasmonic array upconverting lasers provide directional beamlike emission with a small divergence angle of $\sim 0.5^\circ$, which is different from nanolasers with spherical and cylindrical cavity geometries based on WGM. Meanwhile, Wu et al. reported superburst upconversion

by coupling gap plasmon modes with nanoparticle emitters.⁶²² A three-layer structure, consisting of a silver nanocube, a $NaYF_4:Yb/Er$ UCN layer, and a thin gold film was fabricated. This gap-mode nanocavity enabled an increase in upconversion emission by 4–5 orders of magnitude and a 166-fold increase in spontaneous emission with a lifetime of less than 2 μs .

Beyond the enhancement of surface plasmon resonance, WGM resonance has also received much attention. Under certain conditions, photons can be confined in a microscale or nanoscale cavity by total internal reflection. By preventing photons from losing energy, interactions between light and matter are efficiently enhanced. WGM is typically supported in spherical and cylindrical cavities, and many studies have focused on the coupling of WGM and rare-earth-doped nanoparticles.^{966–969} For example, Fernandez-Bravo et al. coated a layer ($\sim 100\text{ nm}$ thick) of Tm^{3+} -doped UCNP on $5\text{-}\mu m$ polystyrene microspheres.⁹⁷⁰ These microlasers exhibited upconverted lasing under excitation at 1064 nm with a low threshold of 14 kW cm^{-2} . Recently, Jin's group succeeded in generating an ultralow threshold laser from single UCNP by modulating cross-relaxation.³³ They argued that appropriate cross-relaxation can accumulate energy in excited intermediate states, facilitating population inversion and lowering the pump threshold by precisely controlling the doping concentration of the emitter. Single-layer $NaYF_4:Yb/Tm$ UCNP were deposited on polystyrene microspheres to form WGM cavities. By measuring emission intensity, the full width at half-maximum ($\sim 0.45\text{ nm}$) and laser threshold, optimal Tm^{3+} doping concentration and particle size were determined as 2% and 24 nm , respectively, at a pump power of $\sim 150\text{ W cm}^{-2}$. Furthermore, a single-particle laser with a peak at 808 nm was realized by depositing a single UCN on the polystyrene microsphere (Figure 26c,d).

Hyperbolic metamaterials are electromagnetic materials developed to enhance emission and create other fascinating applications.⁹⁷¹ The most commonly used hyperbolic metamaterials include alternating metal–dielectric layer structures and hyperbolic dispersed nanowire arrays embedded in a dielectric medium. Haider et al. reported a white-emitting random nanolaser by coupling UCNP with multilayer hyperbolic Au/MoO_3 metamaterials.⁹⁷² According to their design, Au/MoO_3 hyperbolic metamaterials were deposited beneath a thick layer of $NaYF_4:Yb/Er/Tm@NaYF_4:Eu$ nanoparticles, and SiO_2/Si was employed as the substrate. At 980 nm excitation, UCNP emitted red (Eu^{3+}), green (Er^{3+}), and blue (Tm^{3+}) light, rendering integrated white light output. Notably, variations in the filling ratio of the Au/MoO_3 multilayers change the wavelength for hyperbolic dispersion. Consequently, the intensities and lifetimes of red, green, and blue emissions, as well as the emitting color are tunable. In the optimal case, emission intensity was increased 50-fold when the pump threshold was lowered from 0.5 to 0.1 kW cm^{-2} .

4.4.2. Displays. White, full-color emission is essential for displays and lighting. However, conventional rare-earth-doped nanomaterials emit light with limited wavelength ranges. In 2015, Deng et al. reported the use of multilayer core–shell UCNP for full-color volumetric displays by modulating the pulse width of laser excitation (Figure 26e).⁹⁷³ They found that the pulse width of laser beams significantly influences luminescence, which is governed by a transient upconversion process. When the pulse width of the 980 nm excitation varied from $200\text{ }\mu s$ to 6 ms , the emission color of Ho^{3+} changed from

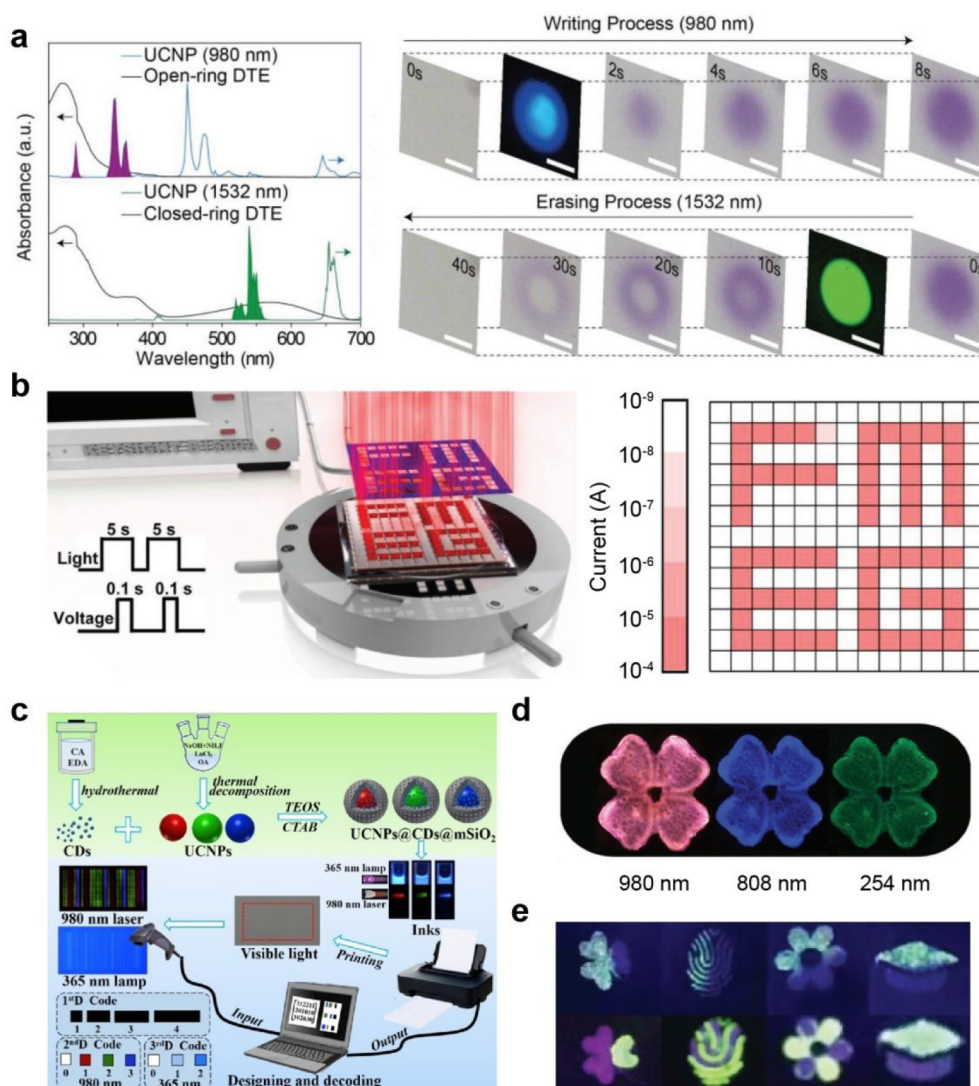


Figure 27. (a) Write and erase processes based on a PMMA film containing a UCNP-DTE hybrid under excitation at 980 and 1532 nm, respectively. Scale bars are 50 μm . (b) Schematic of information storage using an RRAM device based on MoS_2 -UCNPs under light illumination. (c) Schematic of inkjet-printing of UCNPs for anticounterfeiting applications. (d) Optical microphotographs of the patterns under 980, 808, and 254 nm excitation, respectively. (e) Patterns of Ce/Eu-doped nanoparticles under irradiation with a 254 nm UV lamp and a 980 nm defocusing laser (top) and patterns of Ce/Tb- and Ce/Eu-doped nanoparticles under irradiation at 245 nm (bottom) (Adapted with permission from refs 976–980. Copyright 2019 American Chemical Society; Copyright 2018,2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2017 The Royal Society of Chemistry).

green to red. Addition of a blue luminescence component under 808 nm laser excitation enabled a full-color display. In another work, Zhang et al. designed multilayer UCNP with an emission spectrum spanning the entire visible range.³¹² These nanoparticles consist of $\text{NaGdF}_4\cdot\text{Yb/Tm/Er}$ as the core for blue and green emission, $\text{NaGdF}_4\cdot\text{Eu}$ as the first shell, and NaYF_4 as the inert outer shell to minimize surface quenching. With the help of energy migration through Gd^{3+} ions, the excitation energy can be transferred from Tm^{3+} to Eu^{3+} for red emission. These nanoparticles can emit adjustable light from green to white when irradiated at 980 nm with $3\text{--}30\text{ W cm}^{-2}$ (Figure 26f).

In addition to efforts to manipulate emission colors, factors that contribute to practical displays, such as display flexibility and speed, are also considered. Park et al. reported a flexible transparent display integrating UCNP into a polymer waveguide that exhibited bright emission under 980 nm irradiation, irrespective of bending.⁹⁷⁴ In 2020, Gao et al.

reported a UCNP-based video-rate display by temporally synchronizing the excitation sampling time with the emission rise time of individual nanoparticles.⁹⁷⁵

4.4.3. Information Storage. Information recording began in ancient times with the notation of nodes. However, the arrangement was sophisticated and the storage density was low. In the digital era, ultrafast reading or erasing of large amounts of data has become possible. The optical format seems promising in transferring information over distances and achieving higher data density among various storage formats.⁹⁸¹ Rare-earth-doped phosphors with various colors have been widely used in information storage through defect engineering.^{982,983} In this section, we focus on the examples involving rare-earth nanomaterials.

A typical strategy for using rare-earth-doped nanoparticles for optically rewritable memories is to combine nanoparticles with photoswitchable organic compounds.^{981,984,985} In those systems, nanoparticle emission is utilized to trigger the write

process, while the erase process can be performed with heat or light. For example, Zheng et al. combined $\text{NaYF}_4:\text{Er}@\text{NaYF}_4:\text{Yb}/\text{Tm}@\text{NaYF}_4$ nanoparticles with the photochromic molecule diarylethene (DTE). Under 980 nm laser excitation, the blue emission of nanoparticles well matches the absorption of DTE in the open-ring form. In contrast, under 1532 nm irradiation, their green emission matches the absorption of DTE in the closed-ring form, resulting in structural transformation and color change (Figure 27a).⁹⁷⁶ To ensure high spectral purity, they developed multilayer $\text{NaYF}_4:\text{Er}@\text{NaYF}_4:\text{Yb}/\text{Tm}@\text{NaYF}_4$ UCNPs. The energy transfer from Yb^{3+} to Er^{3+} and cross-relaxation are efficiently hindered to avoid interference with DTE isomerization. The luminescence dynamics suggest that the energy transfer between UCNPs and DTE is due to an internal filtering effect instead of FRET. To verify and simulate writing and erasing, they prepared a thin film from a UCNP-DTE array and PMMA. Each dot of the array could be “painted” or erased with NIR light, forming distinctive patterns to record different types of information. Similar photochromism was accomplished by Wang et al., who fabricated a two-dimensional hybrid system of $\text{Yb}^{3+}/\text{Er}^{3+}$ -codoped UCNPs and $\{[\text{Fe}(\text{1,3-bpp})_2(\text{SCN})_2]_n\}$ nanosheets.⁹⁸⁶ These nanoparticles were hybridized with thiocyanate (SCN^-) ligands on both sides of the nanosheets. At 980 nm irradiation, upconversion luminescence weakened metal-to-ligand charge transfer (MLCT) and triggered the high-spin to low-spin transition. However, heating at 40 °C enhanced the MLCT, and the low-to-high spin transition occurred. This demonstrates that reversible molecular switching is possible by altering NIR irradiation and thermal stimulation.

The conversion of optical signals into electrical signals is important for photonic information storage. Zhai et al. integrated rare-earth-doped UCNPs with 2D semiconducting MoS_2 to fabricate a NIR-sensitive memory device based on a MoS_2 -UCNP heterostructure.⁹⁷⁷ The memory device consisted of a three-layer Al/MoS_2 -UCNP/ITO structure supported on a substrate. MoS_2 -UCNP serves as the active material for the memory device. When irradiated at 980 nm, the light emitted from UCNPs is absorbed by MoS_2 . The charge carriers generated are separated at the interface of MoS_2 and UCNPs under an applied electric field. Trapping/detrapping processes result in a switch between high-impedance and low-impedance states, allowing data to be written and erased (Figure 27b).

4.4.4. Anticounterfeiting. Colloidal nanocrystals doped with rare-earths have been utilized as luminescent inks to print various patterns for encryption and protection against counterfeiting (Figure 27c). In particular, these nanomaterials have multiple encryption modes to meet the complex requirements of anticounterfeiting in business and document and copyright protection. Patterns printed with colloidal solutions containing rare-earths are colorless under ambient light. When irradiated under a specific condition, these patterns emit visible light in different colors. Rational design in rare-earth doping renders nanocrystals with increased sensitivity to excitations or external stimuli, allowing fine-tuning of luminescence.^{34,987,988} Variation in dopant composition is often combined with other strategies to construct materials with multimodal encryption. Rare-earth-doped nanoparticles with different emission colors can be printed to create polychromatic patterns by single wavelength excitation, as the emission color can be easily varied by tuning the dopant composition and concentration.^{283,989}

Multicolor encryption can be realized in microscopic views by spatially controlling the doping with different rare-earth ions. Zhang et al. reported two-color, spatially encoded RE-doped microrods that can produce red emission at the end of the rods and green emission in the middle.³²³ These spatially distributed colors can only be distinguished at high microscopic magnification, providing additional confidence for multicolor labeling. In 2016, Zhang et al. reported three-color microbarcodes using upconversion microrods and microdisks.³⁶ These barcodes can be resolved to the single-particle level and have the potential for multiplexed labeling.

Time-domain optical anticounterfeiting can provide different colors or pattern information on different time scales after laser irradiation is turned off.⁹⁹⁰ The lifetime of rare-earth-doped nanomaterials can be tuned by varying the doping composition and concentration.^{300,581,991} Liu et al. designed a multilayered structure, $\text{NaYF}_4:\text{NaYF}_4:x\%\text{Yb}/1\%\text{Tm}@\text{NaYF}_4:y\%\text{Yb}@\text{NaYF}_4$, to modulate the emission intensity and lifetime independently by varying the doping concentration.⁹⁹² They also prepared two other types of UCNPs with different lifetimes to produce green and red colors. The three types of upconversion nanoparticles were encapsulated in polydimethylsiloxane (PDMS) beads with a specific mixing ratio, producing a colorful array. This array exhibits random patterns under continuous laser irradiation. However, in time-delay mode, irradiation with different lasers revealed hidden letters. This orthogonal manipulation enables multimode encryption, which extends the realm of multiplex luminescence imaging.

Han et al. reported that in addition to pulse width, repetition frequency can also contribute to color manipulation.⁹⁹³ They demonstrated that by varying the pulse width at a fixed frequency from 100 μs to 6 ms, the emission color of $\text{NaYF}_4:\text{Er}/\text{Tm}(2/0.5\%)@\text{NaYF}_4$ UCNPs can be tuned from green to red. When the pulse duration was set to 100 μs , increasing the frequency also resulted in a color change from green to red. By manipulating the pulse width, labeled patterns of UCNPs exhibited green, yellow, or red colors, allowing higher falsification reliability than single-mode emission. Intriguingly, Liu et al. reported multiplex coding by manipulating the luminescence kinetics of UCNPs.⁹⁹⁴ They showed that UCNPs exhibit a delayed luminescence maximum in the time trace in response to harmonic wave excitation (e.g., phase angle). By varying the phase angle of the materials, a kinetics-based optical encoding technique could be developed. UCNPs with different luminescence colors and phase angles were encapsulated into polymer beads. The array arranged by these polymer beads showed only encrypted letters with harmonic 980 nm laser excitation after phase angle analysis.

Liu et al. utilized plasmonic nanostructures in combination with UCNPs to provide a high degree of optical security.⁹⁹⁵ They constructed a sandwich metal-UCNP-metal nanostructure, in which a monolayer of UCNPs was sandwiched between an array of aluminum nanodisks and an aluminum thin film. Due to the surface plasmon diffraction of aluminum, these nanocomposites displayed a nonluminescent plasmonic color under ambient light. The embedded UCNPs emitted visible light only when excited by NIR irradiation. Both the nonluminescent and luminescent colors can be tuned by varying the diameter and spacing of the nanodisks. They designed a nonluminescent butterfly pattern with NaGdF_4 -containing plasmonic nanomaterials. The sandwich metal-UCNP-metal nanomaterials were filled into a reserved empty region of the butterfly pattern, forming hidden luminescent

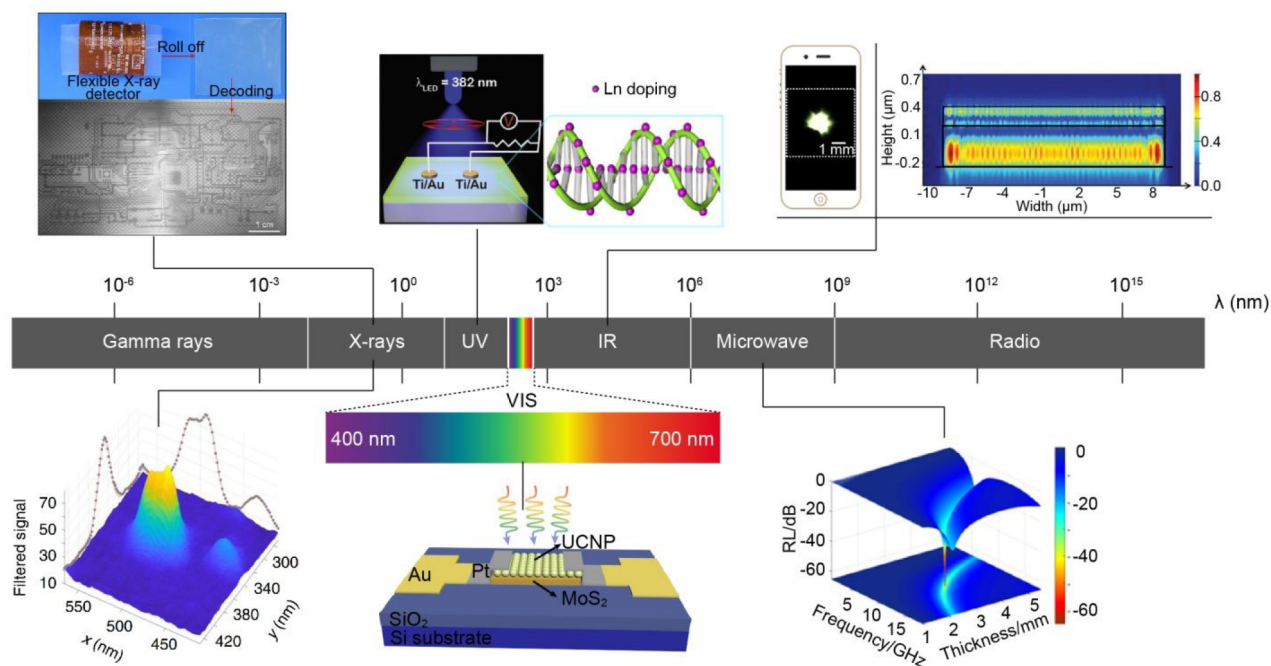


Figure 28. Schematic of the electromagnetic spectrum and examples of rare-earth-doped nanomaterials as photodetectors in various applications (Adapted from refs 595, 613, 1011, and 1014–1017. Copyright 2019, 2020 Nature Publishing Group; Copyright 2018 Elsevier B.V.; Copyright 2019 Elsevier Ltd.; Copyright 2016, 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2019 American Chemical Society).

patterns. This study provides a new way of optical security printing with different color patterns under white light and NIR irradiation.

By permutation and combination with different emitters, color groups of upconversion and downshift luminescence can be obtained under different excitation sources.^{996–1000} Sun et al. designed three types of rare-earth-doped nanoparticles ($\text{NaYF}_4\text{:Yb/Er@NaYF}_4$, $\text{NaYF}_4\text{:Yb/Tm@NaYF}_4$, and $\text{NaGdF}_4\text{:Ce/Tb}$) that emitted red, blue, and green under 980, 808, and 254 nm excitation, respectively.⁹⁷⁹ Mixtures of these nanoparticles can be used as security inks to print tamper-resistant patterns (Figure 27d). In addition to mixing multicomponent nanoparticles, Huang et al. combined upconversion and downshift luminescence in multilayer rare-earth-doped nanoparticles ($\text{NaYF}_4\text{:Nd/Yb@NaYF}_4\text{:Yb/Er@NaGdF}_4\text{:Yb/Tm@NaGdF}_4\text{:A@NaYF}_4$; A = Ce, Tb, Eu).⁹⁸⁰ Complex luminescence patterns can be obtained by modulating the excitation wavelength and power density (Figure 27e).

In 2013, Zhao et al. reported that bright upconversion luminescence of highly doped nanoparticles with suppressed concentration quenching can be achieved at ultrahigh excitation power density ($>10^6 \text{ W cm}^{-2}$).¹⁰⁰¹ When the nanocrystal solution was applied as a security ink to print a hidden pattern, the printed pattern remained dark at low excitation power (10^4 W cm^{-2}) but became visible at high excitation power (10^6 W cm^{-2}). Chen et al. demonstrated that color tuning from green to yellow and red in $\text{NaYF}_4\text{:Ho(1%)@NaYF}_4$ nanoparticles can be accomplished by varying the excitation power ($1.25\text{--}46.25 \text{ W cm}^{-2}$).¹⁰⁰² Compared to UCNPs with lower Yb^{3+} content, $\text{NaYF}_4\text{:Ho(1%)@NaYF}_4$ nanoparticles exhibited 5.6-fold enhanced power sensitivity, which is mainly due to the maximum utilization of incident energy. The improved power sensitivity is suitable for data decoding.

The temperature-dependent luminescence of rare-earth-doped nanomaterials has also been exploited for optical anticounterfeiting.¹⁰⁰³ For instance, Lei et al. demonstrated this concept using $\text{Na}_3\text{ZrF}_7\text{:Yb/Er@Na}_3\text{ZrF}_7$ nanocrystals with temperature-dependent emission profiles.⁷⁷⁷ After coating with poly(acrylic acid) (PAA) molecules, these nanocrystals were used as inks for pattern printing. The brightness of the pattern at 980 nm excitation increased as the temperature increased from room temperature to 413 K. Zou et al. reported a 29-fold increase in the green emission of $\text{Yb}_2\text{W}_3\text{O}_{12}\text{:Er}$ UCNPs by raising the temperature from 303 to 573 K.³⁸¹ At higher temperatures, there is contraction and distortion of the host lattice, resulting in altered crystal symmetry and enhanced energy extraction by the activator. They printed a two-color pattern using $\text{Yb}_2\text{W}_3\text{O}_{12}\text{:Er}$ as the green phosphor and $\text{Yb}_2\text{WO}_6\text{:Er}$ as the red phosphor. Of note, unlike $\text{Yb}_2\text{W}_3\text{O}_{12}$, the Yb_2WO_6 lattice expands at high temperatures. Hence, the sample showed enhanced green luminescence and decreased red luminescence at 573 K.

Quick response (QR) codes made of rare-earth inks can be smart labels for the IoT. Ramalho et al. designed multiplexed QR codes based on several lanthanide complexes and printed them on banknotes.¹⁰⁰⁴ They developed a mobile application to sort out multiplexed luminescent QR codes and provide an additional layer of security.

4.5. Photodetectors

Photodetectors have developed rapidly in recent decades because of their potential applications in research, military practice, medicine, and industry. Rare-earths have been incorporated into various nanomaterials to detect all types of electromagnetic radiation from microwaves to γ rays (Figure 28).

4.5.1. Microwaves. Microwave-absorbing materials are functional materials that can convert electromagnetic radiation into other forms of energy such as thermal energy or dissipate

electromagnetic radiation and reduce microwave reflection to a large extent. This unique property can be capitalized for applications in radar cloaking, communication security, and electromagnetic shielding. Microwave absorbing materials are mainly dielectric materials, which have two distinct loss mechanisms, namely dielectric loss and magnetic loss. To meet the critical requirements of microwave absorption, a combination of dielectric and magnetic materials is usually employed to achieve maximum absorption of electromagnetic energy.

In the last two decades, lanthanide doping techniques have also been applied to ferrite absorbers. The magnetic loss mechanisms of ferrites mainly include hysteresis loss and residual loss. Rare-earth ions possess relaxation characteristics that are likely to affect the electromagnetic properties of ferrites. Yang et al. synthesized cobalt ferrite (CoFe_2O_4) nanomaterials doped with La^{3+} , Ce^{3+} , or Y^{3+} ions and combined them with a conducting polymer, polyaniline, using a hydrothermal coordination oxidation method.¹⁰⁰⁵ Electromagnetic measurements showed that the microwave absorption capacity of La^{3+} -doped polyaniline- $\text{CoFe}_{2-x}\text{O}_4$ composites was better than that of Ce^{3+} - and Y^{3+} -substituted counterparts. By varying the doping concentration of La^{3+} , an optimal microwave absorption performance was achieved at $x = 0.15$, and the conductivity of the nanocomposite was $\sim 0.833 \text{ S cm}^{-1}$. Under these conditions, the nanocomposites showed excellent performance with a maximum reflection loss of -42.65 dB at 15.91 GHz . In addition to the above-mentioned elements, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm have been widely incorporated into ferrites and alloys for microwave absorption.^{1006–1012} Moreover, CeO_2 and $\text{Gd}(\text{OH})_3$ nanoparticles also exhibit efficient microwave absorption.^{1011,1013}

4.5.2. Infrared. All objects on Earth emit infrared radiation as heat.¹⁰¹⁸ Infrared waves have longer wavelengths than visible light and can penetrate dense tissue with less scattering and absorption. Nd^{3+} , Yb^{3+} , and Er^{3+} ions absorb infrared radiation at around 808, 908, and 1540 nm, respectively. The appropriately doped upconversion nanoparticles can convert infrared light into UV or visible emission, which can be observed directly with the naked eye or recorded by a camera or cell phone.^{1016,1017,1019} Au and Ag nanoparticles are often combined with rare-earth-doped nanoparticles to improve infrared detection.^{1016,1020} The detection result can be an optical or electrical signal, as photoelectric conversion materials such as perovskite nanocrystals, graphene, and semiconducting polymers are often combined with UCNPs.^{1021–1023} Excitation energy can be transferred to the photoelectric device nonradiatively, whereupon a photocurrent is generated. Since most photoelectric moieties absorb light in the UV or visible range, the hybrid material can also serve as a broadband photodetector.

4.5.3. Ultraviolet–Visible. For UV–vis detection, semiconductors such as CdS, ZnO, and TiO_2 are commonly doped with rare-earth ions to enhance the photodetection performance.^{1024–1027} Shkir et al. prepared Eu-doped CdS thin films by the spray pyrolysis method and investigated their optical and photoelectric properties.¹⁰²⁸ By varying the Eu doping concentration from 1 to 5 wt %, the direct bandgap could be tuned from 2.43 to 2.48 eV, which is attributed to electronic interactions between the 4f electrons of Eu and the s and p electrons of CdS. More importantly, at 5 wt % CdS:Eu, the photosensitivity increased almost 10-fold compared to undoped CdS. The external quantum efficiency was ~ 8 -fold

greater. Double-crossed DNA lattices formed by rare-earth doping can also increase the photocurrent and photovoltage under UV irradiation, due to enhanced charge carrier generation by both DNA and rare-earths.¹⁰¹⁴ Ghosh et al. designed a broadband (325–1064 nm) photodetector using $\text{NaGdF}_4\text{:Yb/Er}$ nanocrystals and MoS_2 flakes that were chemically exfoliated.¹⁰¹⁵ These nanocomposites were fabricated on a gold-patterned SiO_2/Si substrate and exhibited high sensitivity with a maximum value of 1254 A W^{-1} with $V_{\text{ds}} = 1 \text{ V}$ at 980 nm. They also showed excellent performance in normalized gain and detectivity with values of $7.12 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1}$ and $1.05 \times 10^{15} \text{ Jones}$ (at 980 nm, 1 V), respectively.

4.5.4. X-rays and γ -rays. X-rays and γ -rays are high-energy waves that can travel great distances at the speed of light and completely penetrate the human body. Since the discovery of X-rays and γ -rays in the late 19th century, they have become indispensable in defense science, industry, and medical treatment and have created a great demand for the detection of high-energy waves. A scintillator is a material that can absorb high-energy waves and emit UV–vis light, which enables the detection of high-energy radiation. Rare-earth-based phosphors have been extensively researched for detection of X-rays and γ -rays because rare-earths are heavy atoms that favor high energy absorption.¹⁰²⁹ Rare-earth halides, oxides, oxyhalides, oxysulfides, oxyorthosilicates, and perovskites possess excellent scintillation performance.¹⁰³⁰ In particular, Y, La, Gd, and Lu have been extensively studied as host lattices for controlling radioluminescence.¹⁰³¹ Rare-earth-doped nanoscintillators with fast decay or persistent luminescence are being developed for specific applications. Recent studies show a research trend for high-energy beam imaging, and nanoscintillators are typically embedded in organic and inorganic substrates such as poly(methyl methacrylate) (PMMA),¹⁰³² diamond,¹⁰³³ and glass^{1034,1035} to form a transparent mass for radiography.

Ou et al. developed a flat-panel-free X-ray luminescence extension imaging (Xr-LEI) technology using persistent luminescent nanoscintillators.⁵⁹⁵ They synthesized $\text{NaLuF}_4\text{:Tb}(15 \text{ mol } \%)\text{@NaYF}_4$ nanocrystals using a coprecipitation method. After X-ray irradiation was terminated, an afterglow was observed that lasted for more than 30 days. When Lu was replaced by Y, the afterglow intensity weakened, mainly due to the lower absorption coefficient of Y. The mechanisms of the ultralong afterglow can be described as follows. First, the incident X-ray energy is absorbed by Lu atoms, and electrons are generated by the photoelectric effect. Then, fluoride ions are displaced by elastic collisions with X-ray photons with large momentum, forming anion-Frenkel defects. The photogenerated electrons are captured by fluoride vacancy traps, while holes are trapped in interstitial sites. Finally, the trapped charge carriers migrate to Tb ions and electron–hole recombination takes place, which simultaneously causes the Tb emitters to light up. To realize Xr-LEI, nanoscintillators were embedded in a PDMS substrate to form a flexible detector for 3D imaging. This imaging capability was not available for conventional flat-panel X-ray detectors. Prigozhin et al. reported single-particle imaging of rare-earth-doped NaGdF_4 under a specific electron excitation flux (cathodoluminescence) with a sub-20 nm resolution.⁶¹³ Various rare-earth ions (Eu^{3+} , Er^{3+} , Ho^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} , Nd^{3+} , Tm^{3+} , and Yb^{3+}) were incorporated into NaGdF_4 , resulting in multicolor imaging with ultrahigh resolution.

Table 5. Summary of Rare-Earth-Doped Nanomaterials for Solar Cells

mode ^a (DS/ DC/UC)	sensitizer	emitter	host lattice	exc (nm)	em (nm)	solar cell	PLQY (%)	PCE (%)	ref
DS	VO ₄ ^{3−}	Eu ³⁺	YVO ₄	295	614	DSSC	/	8.11	1039
	TiO ₂	Eu ³⁺	TiO ₂	325	489, 586, 614, 622	DSSC	/	8.8	1040
	TiO ₂ , Eu	Eu ³⁺	TiO ₂	260–280, 384, 396, 415	578, 591, 614, 652, 700	PSC	/	15.79	1041
	VO ₄ ^{3−} , Bi ³⁺	Eu ³⁺	YVO ₄	220–350	621	PSC	/	17.9	1042
	VO ₄ ^{3−}	Eu ³⁺	YVO ₄	300–350	619	DSSC	/	/	1043
DC	Ce	Nd, Yb	NaGdF ₄	254	600–750, 850–900, 1064	c-Si	/	0.8 (254 nm)	1044
	AIEE dye(Tb)	Yb	NaYF ₄	405	980	c-Si	/	8% increase	1045
	Tm	Yb	Lu ₂ O ₃	463	~1000	/	148.2	/	1046
	CsPbCl ₃	Yb	CsPbCl ₃	365	990	c-Si	/	/	456
	CsPb(Cl _{1−x} Br _x) ₃	Yb	CsPb(Cl _{1−x} Br _x) ₃	375, 405	980	/	120 (AM1.5)	/	1047
	CsPbCl ₃	Yb	CsPbCl ₃	380	990	/	170	/	454
	CsPb(Cl _{1−x} Br _x) ₃	Yb	CsPb(Cl _{1−x} Br _x) ₃	375	979	/	200	/	455
	Pr ³⁺ , Ce ³⁺ , CsPbClBr ₂	Yb	CsPbClBr ₂	365	988	CIGS	173	19.1	38
	Ce, CsPbCl _{1.5} Br _{1.5}	Yb	CsPbCl _{1.5} Br _{1.5}	365	988	c-Si	146	21.5	40
	Pr	Pr	NaLaF ₄	180	~410, 480, 605	/	/	/	1048
	mCu _{2x} S	Er	Er ₂ O ₃	980	~550, 660	PSC	/	17.8	1049
	Er	Er	Y ₂ O ₃	980	525, 560, 660	DSSC	/	8.62	1050
	Yb	Er	NaYF ₄	980	522, 542, 655	PSC	/	19.7	1051
					525, 541, 654	PSC	/	20.19	1052
					408, 523, 543, 655	PSC	/	16	1053
					408, 523, 542, 655	PSC	/	17.8	1054
					522, 542, 655	DSSC	/	7.79 (980 nm)	1055
					543, 655	DSSC	/	6.34	1056
	Yb	Er	LiYF ₄	980	547, 556, 674	PSC	/	11.87	1057
	Yb	Er	CeO ₂	980	525, 550, 562	DSSC	/	6.66	1058
	Yb	Er	CeO ₂	980	517–532, 532–551, 659–679	DSSC	/	7.3	1059
UC	Ni ²⁺	Er	CaZrO ₃	1490, 1300	980	c-Si	/	/	1060
	IR-783, Nd	Er	NaYF ₄	808	414, 526, 546, 660	PSC	1.2 (UC)	20.5	1061
	IR783	Er	NaYF ₄	800	525, 540	DSSC	/	8.568	1062
	Nd	Er	NaYF ₄	808	525, 540, 654	DSSC	/	5.87	1037
	Yb	Ho	YbF ₃	980	545, 650, 750	DSSC	/	8	1063
	Yb	Ho	NaYbF ₄	980	540, 644, 750	PSC	/	14.32	1064
	UC/DS	Yb/Er	Er/Er	NaYF ₄	968, 400	c-Si	/	12.8	1065
	UC/DC	Tb/Er	Yb/Er	NaYF ₄	488, 1523	/	173 (DC)	/	1066

^aDS downshifting; DC downconversion; UC upconversion.

4.6. Photovoltaics

Rare-earth-doped nanomaterials have shown promise in improving the performance of photovoltaics by fully utilizing the solar spectrum for energy conversion. When integrated into photovoltaic devices, these nanomaterials have been employed as spectral converters to minimize energy losses.^{1018,1038} This has been achieved mainly by using downconversion (also known as quantum-cutting), upconversion, and downshifting nanophosphors (Table 5).

For instance, rare-earth-doped downconversion phosphors can convert one high-energy photon into two low-energy photons and thus increase the photocurrent of solar cells.^{1067,1068} Efficient downconversion from UV to NIR has been realized in various hosts using Pr³⁺, Gd³⁺, Tm³⁺, Er³⁺, Ho³⁺, Nd³⁺, and Yb³⁺ as dopants.^{1069–1074} A major challenge for the use of downconversion in photovoltaic applications is the low absorption cross-section of rare-earths. In this regard, Wang and co-workers demonstrated the use of broadband Ce³⁺-sensitized quantum cutting to enhance the power

conversion efficiency of hybrid crystalline silicon (c-Si) solar cells.¹⁰⁷⁵ The researchers synthesized NaGdF₄:Ce@NaGdF₄:Nd@NaYF₄ nanoparticles that exhibited parity-allowed 4f → 5d Ce³⁺ absorption and Ce³⁺-sensitized quantum cutting in Nd³⁺ ions. These nanoparticles enhanced the power conversion of c-Si in the UV range, resulting in a 1.2-fold increase in short-circuit current and a 1.4-fold increase (from 0.57 to 0.80%) in power conversion efficiency.

Recent investigations have shown that Yb³⁺-doped CsPbCl₃ and CsPbCl_xBr_{3−x} perovskite nanocrystals are promising spectral converters for downconversion.^{38,40,454,456} These nanocrystals display high luminescence quantum yields (>100%) and large absorption coefficients, which are ideal for practical photovoltaic applications. For instance, Song and co-workers have demonstrated a total emission quantum yield of 173% in Yb³⁺–Pr³⁺–Ce³⁺-tridoped CsPbClBr₂ perovskite nanocrystals.³⁸ Given this high quantum yield, these nanocrystals have been developed as efficient downconversion layers that have enhanced power conversion efficiency by a

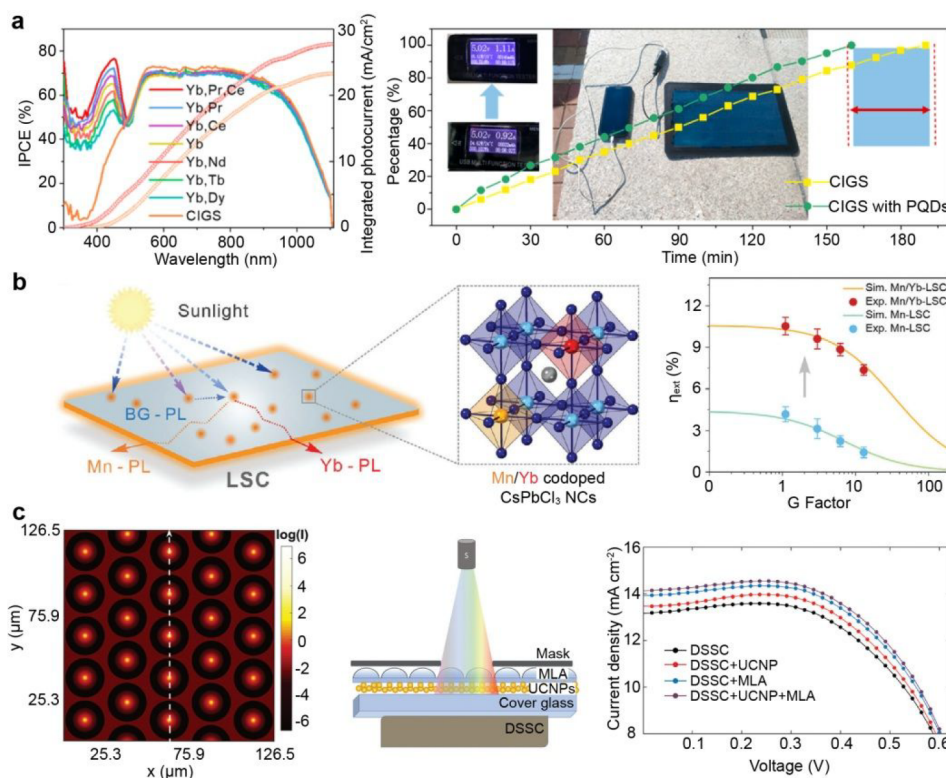


Figure 29. (a) Properties of CIGS solar cells coated with a rare-earth-doped perovskite film. (b) Mn²⁺/Yb³⁺-encoded CsPbCl₃ perovskite nanocrystals as luminescent solar concentrators. (c) MLA- and UCNP-coated DSSCs with enhanced photovoltaic performance (Adapted with permission from refs 38, 1036, and 1037. Copyright 2019 American Chemical Society; Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2019 The Royal Society of Chemistry).

factor of ~20% in c-Si and CuIn_{1-x}Ga_xSe₂ solar cells (Figure 29a). It would be even more attractive if rare-earth-doped perovskite nanocrystals could help break the Shockley–Quieser barrier of single-junction c-Si solar cells. Perhaps this will be achieved through a combination of multiple doping and device engineering.

As with downconversion nanophosphors, downshifting nanomaterials have also been used to increase the efficiency of photovoltaic devices that have a poor spectral response to short-wavelength radiation.^{1039,1042,1043,1076–1078} For example, Jin et al. incorporated YVO₄:Eu/Bi nanophosphors into a mesoporous TiO₂ layer of CH₃NH₃PbI₃ perovskite solar cells (PSCs).¹⁰⁴² Compared with the control device, these downshifting nanophosphors enhanced the power conversion efficiency from 16.3 to 17.9%. Meanwhile, these nanophosphors significantly prevented device degradation caused by UV light. In 2019, Alexandre et al. performed theoretical calculations and their study suggested that optimized downshifting materials can increase the photocurrent of PSCs by ~2% while reducing harmful UV photocarrier generation in TiO₂ and perovskite layers.¹⁰⁷⁹ In addition to absorbing harmful UV light, rare-earth dopants can be incorporated into perovskite structures to increase the durability of photovoltaic devices. A typical example is the incorporation of Eu³⁺ into MAPbI₃ and CsPbI₂Br to stabilize the perovskite phase at room temperature and thus significantly improve the operating lifetime of the corresponding PSCs.^{450,465} On the other hand, downshifting nanophosphors have been widely implemented as solar converters in luminescent solar concentrators.¹⁰⁸⁰ For example, Cai et al. demonstrated the use of Mn²⁺/Yb³⁺-encoded CsPbCl₃ perovskite nanocrystals as spectral con-

verters to achieve both downconversion and downshifting luminescence.¹⁰³⁶ These perovskite nanocrystals proved as efficient luminescent solar concentrators for photovoltaic applications due to their strong light-concentrating effect when embedded in a polydimethylsiloxane matrix (Figure 29b).

In addition, UCNPs are widely used to reduce the nonabsorption energy losses of photovoltaics by converting sub-bandgap radiation into visible emission.¹⁰⁶⁸ In an early experiment, Shalav et al. investigated the enhancement of the sub-bandgap NIR response of silicon solar cells by coupling NaYF₄:Er nanophosphors.¹⁰⁸¹ Under NIR excitation at 1532 nm, an external power conversion efficiency of ~2.5% was recorded, corresponding to an internal upconversion efficiency of 3.8% for the upconverted silicon solar cell. The power conversion efficiency can be further improved by increasing the luminescence quantum yield of upconversion phosphors. The highest quantum yield to date for Gd₂O₂S:10%Er phosphors is ~12%, reported by Martín-Rodríguez et al.¹⁰⁸² While Er³⁺-doped upconversion phosphors can be used for narrow bandgap c-Si solar cells ($E_g = 1.1$ eV), UCNPs codoped with Yb³⁺/Ln³⁺ (Ln = Er, Tm, Ho) are more suitable for wide bandgap photovoltaics, such as dye-sensitized solar cells (DSSCs) and PSCs.^{1054,1083} For instance, Demopoulos and co-workers reported the use of a backside layer of β-NaYF₄:Er/Yb nanoplates to improve the performance of DSSCs with a transparent TiO₂ layer.¹⁰⁸⁴ In their device, the nanoplate functioned as an external light-reflecting and NIR harvesting bifunctional layer, which enhanced the overall power conversion efficiency of DSSCs by approximately 10%. In 2016, He et al. demonstrated incorporation of NaYF₄:Yb/Er

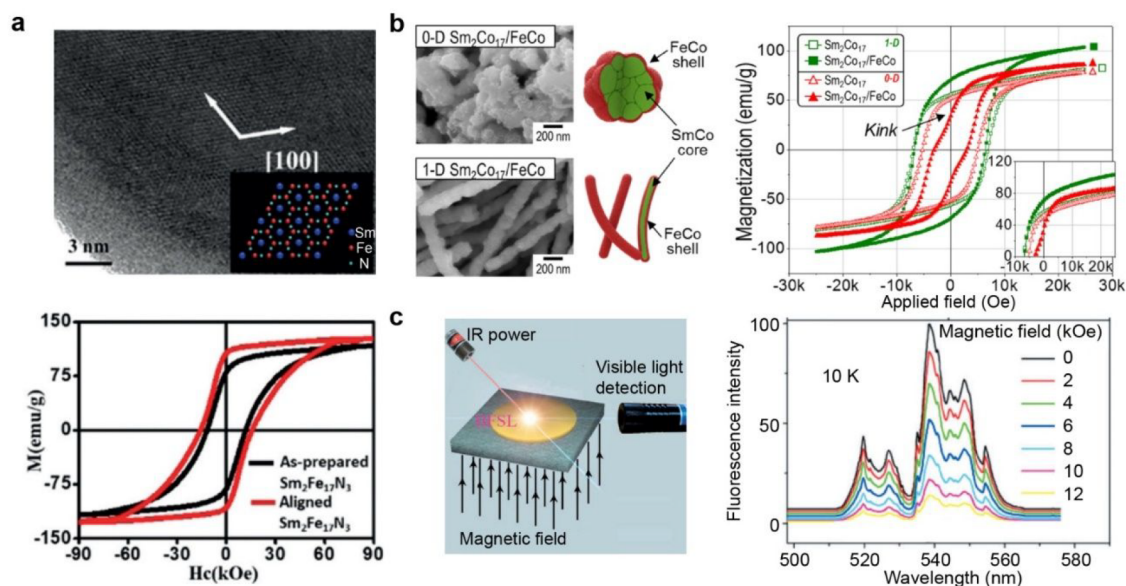


Figure 30. (a) HRTEM image of a $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ nanoparticle. (inset) Atomic model of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ structure projected along the *c*-axis and hysteresis loops of synthesized and aligned $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ nanoparticles at 300 K. (b) Structures of 0 and 1D $\text{Sm}_2\text{Co}_{17}/\text{FeCo}$ core-shell nanomaterials and magnetic properties of core and core-shell samples. (c) Effect of external magnetic field on fluorescence intensity of UCNPs (Adapted with permission from refs 1086–1088. Copyright 2013, 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim; Copyright 2019 American Chemical Society).

UCNPs as a mesoporous electrode in $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based PSCs, achieving a power conversion efficiency of 0.35%.¹⁰⁵⁴

A significant limitation of upconversion photovoltaics is that efficient upconversion luminescence generally requires concentrated irradiation, such as high-power laser excitation. To overcome this drawback, attempts have been made to improve the conversion efficiency of upconversion and to enable upconversion photovoltaics even at low irradiation power. For example, Zhou et al. reported the enhancement of broadband upconversion in $\text{mCu}_{2-x}\text{S}/\text{SiO}_2/\text{Er}_2\text{O}_3$ nanocomposites by using the broadband (800–1600 nm) plasmonic semiconductor mCu_{2-x}S .¹⁰⁴⁹ An internal quantum yield of 14.3% was achieved for Er_2O_3 using mCu_{2-x}S as an antenna to sensitize upconversion. These nanocomposites were used to enhance the power conversion efficiency of PSCs under irradiation of 15 suns. Besides plasmonic enhancement, dye-sensitized photon upconversion may be an effective way to improve upconversion photovoltaics.^{621,624,1085} In 2017, Hao et al. demonstrated the use of $\text{NaYF}_4:\text{Yb}/\text{Er}/\text{NaYF}_4:\text{Nd}$ nanocrystals functionalized with the dye IR783 to enhance broadband NIR harvesting in DSSC devices.¹⁰⁶² The dye modification increased upconversion luminescence by 9-fold. An increase of 13.1% was obtained in DSSCs coupled with dye-sensitized UCNPs. In 2019, Liu et al. developed a strategy to enhance upconversion luminescence by placing a polymer microlens array on UCNPs.¹⁰³⁷ They fabricated a photovoltaic device with a layered structure containing DSSCs, upconversion nanoparticles, and microlens arrays. This structure improved the performance of the DSSCs by a factor of 3.17% under one-sun irradiation (Figure 29c).

4.7. Nanomagnets and Magneto-optic Devices

Magnetism at the nanoscale has important implications for biomedicine, data storage, catalysis, and the development of permanent nanomagnets.^{100,1089,1090} Beyond controlling size, magnetocrystalline phases, and surface state, doping magnetic nanoparticles with impurities provides an alternative means of

controlling magnetic properties. Doping with magnetically susceptible elements can greatly affect the magnetism of nanoparticles.

Rare-earth doping of magnetic nanoparticles has been intensively investigated for magnetite (Fe_3O_4 or FeFe_2O_4) nanocrystals with a spinel structure, in which Fe^{3+} sites can be occupied by trivalent rare-earths (La, Ce, Sm, Eu, and Gd).^{1091,1092} In this crystal structure, O^{2-} forms a tight fcc packing, and Fe^{2+} or Fe^{3+} occupy either tetrahedral (T_d) or octahedral (O_h) interstitial sites. When these nanocrystals are exposed to an external magnetic field, the magnetic spins at the O_h sites align parallel to the external magnetic field, while the spins at the T_d sites align antiparallel. The antiferromagnetic interactions between T_d and O_h cannot fully compensate for this because the number of O_h sites is twice that of the T_d sites. The resulting uncompensated magnetic moments from dominant T_d – O_h interactions can then be modulated as a function of the doping ions occupying either T_d or O_h sites. Rare-earth-doped magnetite nanoparticles can be used as T_2 contrast agents for MRI. These nanoparticles are known to be effective adsorbents for the removal of antimony from aqueous solutions.^{1093,1094}

Rare-earth-based hard nanomagnets, such as NdFeB , SmCo , and SmFeN , have attracted much attention due to their potential utility in energy and sensing applications. However, the fabrication of monodisperse colloidal nanomagnets remains challenging due to the low chemical stability of rare-earths to oxidation. Currently, SmCo_5 nanomagnets with controllable size and morphology are mainly fabricated by a two-step approach involving high-temperature annealing in a CaO matrix.^{1095–1097} This method can produce uniform SmCo_5 nanoparticles with a high coercivity of up to 49.2 kOe. The two-step approach can also be used to synthesize hard magnetic $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ nanoparticles with controllable size and morphology (Figure 30a).¹⁰⁸⁶ It is possible to integrate rare-earth-based hard nanomagnets into soft magnetic nano-

composites to construct exchange-coupled SmCo@FeCo nanocomposites (Figure 30b).¹⁰⁸⁷ After dispersion as colloidal suspensions in a solution, these nanomagnets can serve as magnetic ink to build flexible and printable magnets, or they can be assembled with other components to construct powerful permanent magnets.

Paramagnetic hosts containing rare-earth luminescent dopants can exhibit a dual optical-magnetic function. This was first demonstrated by Li, Peng, and co-workers using NaGdF₄:Nd/Yb/Er nanoplatelets.¹⁰⁸⁸ In that study, the upconversion luminescence of the paramagnetic nanoplatelets decreased monotonically when the external magnetic field increased from 0 to 12 kOe (Figure 30c). The researchers attributed the magnetic tuning to the magnetic splitting of the ⁴S_{3/2} level of Er³⁺, which decreased the excitation population of that level. Recently, Dai et al. investigated the magnetic tuning of upconversion luminescence in Au-NaGdF₄:Yb/Er nanocomposites.¹⁰⁹⁸ They found that the luminescence of Au-coupled UCNP was independent of a magnetic field below 6 T due to the surface plasmon resonance of Au, whereas the luminescence intensity of pristine NaGdF₄:Yb/Er nanoparticles decreased monotonically with increasing external magnetic field from 0 to 37.1 T.

5. SUMMARY AND OUTLOOK

In the past decade, research in rare-earth-doped inorganic nanomaterials has grown faster than ever. Nanomaterial design provides an added dimension to control both physical and chemical interactions of rare-earths at the nanoscopic scale, enabling the development of diverse functional nanomaterials. These newly developed nanomaterials have created a kaleidoscopic toolbox that can be used to realize multidisciplinary applications, including bioimaging, therapy, drug delivery, neuroscience, sensing and detection, catalysis, light emission, information storage and encryption, nanolasing, and optical communication. In this review, we have summarized recent advances in rare-earth-doped inorganic nanomaterials in the context of material designs and new applications.

Further progress in this field will hinge upon the precise control of nanostructured architectures over an extended range of compositions. Although current methods have enabled structural engineering in rare-earth fluorides and semiconductors, it remains a formidable challenge to modulate the crystal size, morphology, and surface functionality of nanomaterials such as yttrium aluminum garnet, silicate glass, and magnetic rare-earth alloys, particularly in the fabrication of well-defined heterostructures. Successful implementation of sophisticated structural designs for these materials can lead to exotic optical and magnetic phenomena.

Nanostructured substrates can critically affect the physicochemical behavior of rare-earth ions. It is therefore crucial to continue the exploration of novel host materials, unconventional architectures, and associated properties. Along this line of effort, nanoscale engineering and hybridization may be a viable way to control rare-earth emission by various means such as light, electricity, mechanical force, and biological stimuli in unprecedented formats. In this context, quantum mechanical simulations and artificial intelligence based on machine learning can be adopted as complementary tools for screening new material substrates. For example, first-principles calculations based on density functional theory (DFT) have proven powerful in identifying and characterizing defects and corresponding defect levels in given materials.^{1099–1101} More-

over, the variation of DFT-calculated orbital energies can be considered as a descriptor for the change in optical transition energies of rare-earth ions.^{1102–1104} In addition, quantum mechanical calculations can be used to correlate substrate materials with the chemical/physical properties of rare-earth ions, enabling high-throughput computational structure design.¹¹⁰⁵ Apart from quantum simulations, machine learning has been applied in a variety of disciplines in recent years, including molecular design and photonics.^{1106–1110} Expanding the library of nanostructured hosts is likely to significantly advance basic research in rare-earth luminescence and facilitate many technological applications.

Another trend for future investigations is to open up new areas for rare-earth-doped inorganic nanomaterials. For instance, current applied research on how the luminescence properties of these nanomaterials affect the design of photodetectors with improved sensitivity needs to be refined. With recent advances in spectroscopy and imaging techniques, it is also useful to reconsider rare-earth-doped nanophosphors for practical bioimaging and clinical applications where biocompatible optical probes with high photostability and specific targeting are critical. Such research directions require interdisciplinary knowledge or close collaboration between different fields. Given advances in information technology, one may look for ways to integrate earlier rare-earth technologies into new smart gadgets. The development of biometric sensors or devices that monitor environmental conditions such as the concentration of metal ions or acidity can benefit significantly from rare-earth-doped nanomaterials. At the same time, it is worth exploring new data processing protocols for nanomaterial applications that facilitate material design and device integration. For applications in catalysts, the potential contribution of the surface charge of rare-earth ions to catalytic substrates could increase interest in surface-mediated catalysis. Moreover, doping of nanomaterials with rare-earths in a single-atom format could provide more reactive sites for catalytic conversion, which clearly requires more research attention.

The future will envision the integration of multidisciplinary knowledge and technologies to explore new functions of rare-earth-doped nanomaterials in rapidly growing research areas. This development will further drive the discovery of optical nanomaterials for breakthrough applications in diverse fields, such as photodetectors, optogenetics, immunotherapy, super-resolution imaging, optoelectronics, and many others.^{562,1111}

AUTHOR INFORMATION

Corresponding Authors

Juan Wang – Institute of Environmental Health, MOE Key Laboratory of Environmental Remediation and Ecosystem Health, College of Environmental & Resource Sciences, Zhejiang University, Hangzhou 310058, China; orcid.org/0000-0002-1340-9011; Email: wjuan@zju.edu.cn

Feng Wang – Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong SAR 999077, China; orcid.org/0000-0001-9471-4386; Email: fwang24@cityu.edu.hk

Renren Deng – State Key Laboratory of Silicon Materials, Institute for Composites Science Innovation, School of Materials Science and Engineering, Zhejiang University,

Hangzhou 310027, China; orcid.org/0000-0001-8213-6304; Email: rdeng@zju.edu.cn

Xiaogang Liu – Department of Chemistry, National University of Singapore, Singapore 117543, Singapore; orcid.org/0000-0003-2517-5790; Email: chmlx@nus.edu.sg

Authors

Bingzhu Zheng – State Key Laboratory of Silicon Materials, Institute for Composites Science Innovation, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China

Jingyue Fan – Department of Chemistry, National University of Singapore, Singapore 117543, Singapore; orcid.org/0000-0003-4987-7025

Bing Chen – Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong SAR 999077, China; orcid.org/0000-0002-0663-1343

Xian Qin – Department of Chemistry, National University of Singapore, Singapore 117543, Singapore

Complete contact information is available at:

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Notes

The authors declare no competing financial interest.

Biographies

Bingzhu Zheng earned her B.S. degree in Materials Science from Central South University in China in 2017. She is currently a Ph.D. student at the School of Material Science and Engineering, Zhejiang University, under the supervision of Prof. Renren Deng. Her research interests include energy transfer processes between organic molecules and inorganic rare-earth-doped nanocrystals and exploring potential applications of hybrid nanomaterials for catalysis, drug delivery, and therapy.

Jingyue Fan received her B.S. degree in Chemistry (Hons) from the National University of Singapore in 2017, and she is currently a Ph.D. student in the group of Prof. Xiaogang Liu. Her research focuses on the fundamental study of rare-earth-doped luminescent nanomaterials and their surface interaction properties.

Bing Chen was born in Zhejiang, China. He received his B.E. (2012) and Ph.D. (2017) degrees in Materials Science and Engineering from Zhejiang University. Currently, he is a postdoctoral researcher in Prof. Feng Wang's group at City University of Hong Kong. His research interest is on the development of luminescent micro/nanomaterials containing lanthanide ions.

Xian Qin earned her B.S. degree (2007) in Mechanical Engineering from Sichuan University. She received her Ph.D. degree from Harbin Institute of Technology, P. R. China, in 2013 under the supervision of Prof. Qingyuan Meng. She subsequently carried out postdoctoral training in the Chemistry Department of National University of Singapore and also the Institute of Materials Research and Engineering (IMRE) of A*STAR, Singapore. Her current research focuses on molecular optoelectronics, energy conversion, and nanocatalysis, as well as developing quantum and classical methodologies to understand the photophysical processes of luminescent nanomaterials.

Juan Wang is a professor at the College of Environment and Resources Science, Zhejiang University. She received her Ph.D. from the National University of Singapore in 2012. She then worked as a consultant at EnviroSolutions. Pte. Ltd. followed by postdoctoral studies at Nanyang Technological University between 2013 and 2016.

Her research interests include photocatalysis, photothermal catalysis, photothermal conversion materials, and devices for wastewater and seawater treatment.

Feng Wang is a professor in the Department of Materials Science and Engineering at the City University of Hong Kong. He obtained his B.E. and Ph.D. degrees in Materials Science and Engineering from Zhejiang University, China. He then carried out postdoctoral research at the National University of Singapore and the Institute of Materials Research and Engineering of A*STAR. His current research focuses on the synthesis, spectroscopic investigation, and application of micro/nanostructured luminescent materials.

Renren Deng is a professor at the School of Materials Science and Engineering, Zhejiang University, China. He received his B.S. degree in Chemistry from Zhejiang University, China, in 2009 and his Ph.D. in Chemistry from the National University of Singapore (NUS) in 2014. From 2014–2016, he worked as a postdoctoral researcher at NUS and Cavendish Laboratory at Cambridge University. His research interests focus on developing luminescent nanomaterials for applications in photovoltaics and biomedicine and understanding energy transfer through organic molecule–inorganic nanocrystal hybrid systems.

Xiaogang Liu received his B.E. degree in Chemical Engineering from Beijing Technology and Business University, China. He received his M.S. degree in Chemistry from East Carolina University and his Ph.D. degree from Northwestern University. He then worked as a postdoctoral researcher at the Massachusetts Institute of Technology for two years before moving to the National University of Singapore in 2006. He is currently an associate editor of *Nanoscale* and serves on the editorial boards of *Research*, *Nanoscale Horizons*, *Chemistry: An Asian Journal*, *Advanced Optical Materials*, *Analysis and Sensing*, *Journal of Luminescence*, and *Journal of Physical Chemistry Letters*. His research areas include catalysis, molecular sensing, and biomedicine, as well as the development of luminescent nanomaterials for optogenetic neuromodulation, cancer immunotherapy, assistive technologies, and X-ray imaging.

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ABBREVIATIONS AND LIST OF ACRONYMS

ACC	atom confinement and coordination
BDC	1,4-benzendicarboxylate
BPDC	biphenyl dicarboxylate
BTB	1,3,5-tris(4-carboxyphenyl)benzene
BTC	1,3,5-benzenetricarboxylic acid
CB	conduction band

ChR	channelrhodopsins	PLQY	photoluminescence quantum yield
CN	coordination numbers	PMMA	poly(methyl methacrylate)
CR	cross-relaxation	PSC	perovskite solar cell
CRISPR-Cas9	clustered regularly interspaced short palindromic repeats-associated protein 9	PTT	photothermal therapy
CRR	carbon dioxide reduction reaction	QD	quantum dot
CT	computed tomography	RBS	Roussin's black salt
CVD	chemical vapor deposition	RGO	reduced graphene oxide
DEF	<i>N,N'</i> -diethylformamide	ROS	reactive oxygen species
DFT	density functional theory	RRAM	resistive random-access memory
DMA	dimethylammonium	SEM	scanning electron microscopy
DMBDC	2,5-dimethoxy-1,4-benzenedicarboxylate	SPECT	single-photon emission computed tomography
DMF	<i>N,N</i> -dimethylformamide	SPR	surface plasmon resonance
DMSO	dimethyl sulfoxide	STED	stimulated-emission depletion
DOX	doxorubicin	STEM	scanning transmission electron microscopy
DSSC	dye-sensitized solar cell	STM	scanning tunneling microscopy
DTE	diarylethene	TEM	transmission electron microscopy
DTT	dithiothreitol	TMS-Br	trimethylbromosilane
EDS	energy dispersive spectroscopy	TMS-Cl	trimethylchlorosilane
EDTA	ethylenedinitrilo-tetraacetic acid	UCNP	upconversion nanoparticle
EELS	electron energy loss spectroscopy	UV	ultraviolet
eNpHR	enhanced Natronomonas halorhodopsin	VB	valence band
FA	formamidinium	VE	vacancy-engineered
FIR	fluorescence intensity ratio	VIS	visible
FRET	Förster resonance energy transfer	VOC	volatile organic compounds
FT-EXAFS	Fourier-transformed extended X-ray absorption fine structure	WGM	whispering gallery mode
fwhm	full width at half-maximum	XAFS	X-ray absorption fine structure
GO	graphene oxide	XPS	X-ray photoelectron spectroscopy
HAADF-STEM	high-angle annular dark-field image scanning transmission electron microscopy	XRD	X-ray diffraction
HCR	hybridization chain reaction	Xr-LEI	X-ray luminescence extension imaging
hfa	hexafluoro acetylacetonato		
HHTP	2,3,6,7,10,11-hexahydroxytriphenylene		
HMM	hyperbolic meta-material		
HRTEM	high-resolution transmission electron microscope		
ICP-AES	inductively coupled plasma–atomic emission spectroscopy		
ICP-OES	inductively coupled plasma–optical emission spectroscopy		
IoT	internet of things		
LMCT	ligand-to-metal charge transfer		
LRH	layered rare-earth hydroxide		
MA	methylammonium		
MASR-CVD	matrix-assisted sustained-release chemical vapor deposition		
MB	Methylene Blue		
MMT	montmorillonite		
MN	motor neuron		
MOF	metal–organic framework		
MRI	magnetic resonance imaging		
NIR	near-infrared		
NP	nanoparticle		
OA	oleic acid		
ODE	1-octadecene		
OM	oleylamine		
OSC	oxygen storage capacity		
PAA	polyacrylic acid		
PCE	power conversion efficiency		
PDMS	polydimethylsiloxane		
PDT	photodynamic therapy		
PET	positron emission tomography		

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