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Photodarkening, Photobrightening, and the Role of Color Centers in Emerging Applications of Lanthanide-Based Upconverting Nanomaterials

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Keywords

lanthanide-doped upconverting nanoparticles, color centers, photon avalanching, photoswitching, X-ray detection, optical patterning

Abstract

Upconverting nanoparticles (UCNPs) compose a class of luminescent materials that utilize the unique wavelength-converting properties of lanthanide (Ln) ions for light-harvesting applications, photonics technologies, and biological imaging and sensing experiments. Recent advances in UCNP design have shed light on the properties of local color centers, both intrinsic and controllably induced, within these materials and their potential influence on UCNP photophysics. In this review, we describe fundamental studies of color centers in Ln-based materials, including research into their origins and their roles in observed photodarkening and photobrightening mechanisms. We place particular focus on the new functionalities that are enabled by harnessing the properties of color centers within Ln-doped nanocrystals, illustrated through applications in afterglow-based bioimaging, X-ray detection, all-inorganic nanocrystal photoswitching, and fully rewritable optical patterning and memory.

Ln: lanthanide

UCNP: upconverting nanoparticle

NIR: near-IR

Vis: visible

PD: photodarkening

AGNP: afterglow nanoparticle

ANP: avalanching nanoparticle

1. INTRODUCTION

Lanthanide (Ln)-based upconverting nanoparticles (UCNPs) are luminescent nanocrystals that absorb multiple photons in the near-IR (NIR) and emit at higher energies in the NIR or visible (Vis) spectral regions. Their development has been informed by decades of research on bulk glass or crystalline upconverting materials originally designed for use in IR quantum counting devices and short-wavelength solid-state lasers (1–3). Because of their upconverted, or anti-Stokes emissions, UCNPs exhibit no overlap with cellular autofluorescence, and their wavelength-converting efficiencies are orders of magnitude higher than those of the best two-photon fluorophores (4–7). They present several advantages over other luminescent probes, such as dye molecules, fluorescent proteins, and quantum dots, and thus are finding their way into applications as diverse as bioimaging (8, 9), photovoltaics (10–12), light-based therapeutics (13–15), deep-tissue optogenetics (16, 17), miniature lasers (18–22), molecular sensing (14, 23), and security printing (7, 24, 25).

A defining feature of standard UCNPs has been their robust photostability, a feature that separates them from other luminescent probes. Even under intense optical illumination conditions (26), UCNPs showed no notable signs of photodegradation, photobleaching, photodarkening (PD), or photoblinking (27, 28). While point defects are certainly present within UCNPs (extended defects are rare in the high-quality nanocrystals now widely available) (3), the influence of these defects is often viewed as relatively minor based on the reliable UCNP emission under widely varying operating conditions. This, combined with difficulties in directly characterizing subsurface atomic scale structures, meant that point defects within UCNPs garnered relatively little attention, particularly during the early stages of the UCNP field.

However, the advent of afterglow (or persistent luminescence) (29–31) and, more recently, the realization of photon-avalanching upconversion within Ln-doped nanoparticles (32–36) have cast a new light on optically active defects (color centers) within these materials. In particular, the long-lived, rechargeable, persistent phosphorescence in afterglow nanoparticles (AGNPs) and the light-stimulated PD and photobrightening responses observed in avalanching nanoparticles (ANPs)—all originating from optically active defects—offer promise for new applications while also raising fundamental questions about defect properties in this class of nanomaterials.

In this review, we begin with a brief summary of color centers commonly found in Ln-doped materials, highlighting several key attributes within the context of upconversion. This is followed by a discussion on color-center-induced PD of upconverted luminescence in these material systems, as well as experimental strategies for mitigating PD and even reversing it (photobrightening). We then present three emerging application spaces that are harnessing the properties of color centers in upconverting nanomaterials: afterglow luminescence imaging, X-ray detection, and optical patterning. We round out our discussion with a brief outlook for new material designs and color-center-enabled optical functionalities in UCNPs.

2. COLOR CENTERS

Color centers naturally exist in a variety of crystals. They are responsible for the smokey shade in quartz (37–39) (**Figure 1a**), the blue and yellow colors in sapphire (40), and the wide-ranging hues in topaz (41) (**Figure 1b**).

The color centers in these and many other crystals have been extensively studied for more than a century, ever since the discovery of the color change of sodium chloride with heat treatment (44). Early on, the origin of the color centers was proposed to be related to charges trapped in the potential well of an ion defect (45). This has proven to be true in general, though characterizing and identifying optical properties associated with specific defect states are often challenging due to their atomic size and diversity (46).

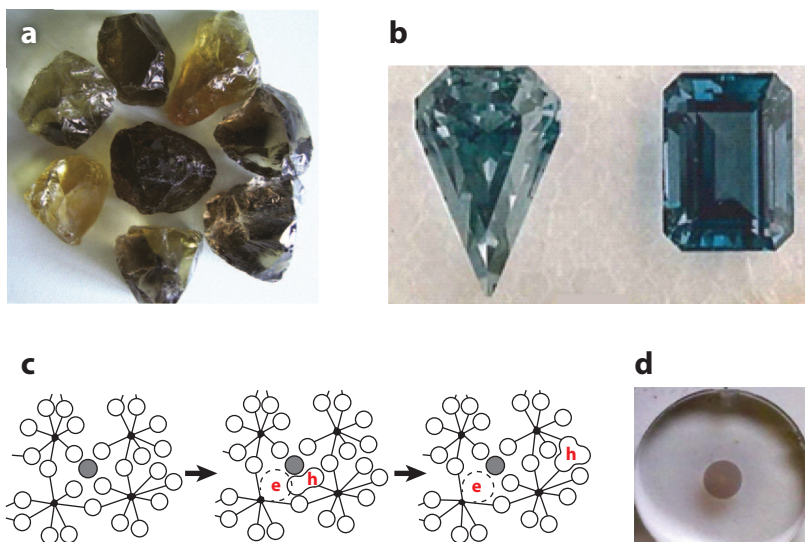


Figure 1

(a) Photograph of various colored quartz crystals. Photo provided by Rainer Schultz-Güttle. Panel *a* reproduced with permission from Reference 39; copyright 2012 The Gemmological Association of Great Britain. (b) Photograph of natural (*left*) and electron-irradiated (*right*) topaz. Panel *b* reproduced with permission from Reference 41; copyright 1985 The Gemmological Institute of America. (c) A schematic of the paramagnetic point defect formation in heavy-metal fluoride glass. Panel *c* reproduced with permission from Reference 42; copyright 1993 Elsevier. (d) Photograph of a Yb-doped aluminosilicate preform core and the surrounding silica cladding after X-ray irradiation. The core became less transparent due to color center formation. Panel *d* reproduced with permission from Reference 43; copyright 2010 Optica. Abbreviations: e, electron; h, hole.

2.1. Color Centers in Lanthanide-Doped Materials

A veritable zoo of optically active and inert defect species exists within any crystal, and the Ln-hosting materials are no different. For example, in silica (amorphous SiO_2), there are trapped-hole centers (e.g., the E' center, the nonbridging-oxygen center, the peroxy radical, and self-trapped holes) and trapped-electron centers, with many centers related to the deficiency and excess of oxygen atoms (46). In halide glasses [e.g., zirconium barium lanthanum aluminum sodium fluoride (ZBLAN) and NaYF_4], electron- and hole-trap-related color centers, known as F-centers and H-centers (**Figure 1c**), respectively, have been studied (42). Such defects can form naturally, but high-energy irradiation, including X-ray photon or neutron irradiation, also generates them (**Figure 1d**). In some cases, however, optical pumping with relatively low-energy Vis and NIR photons can also induce the formation of certain color centers (47) (see Section 3.2).

Ln ions themselves can play important roles in color-center-generating processes. Their $4f$ energy states are located between the valence and conduction bands of host materials according to an empirical model (48, 49) (**Figure 2a**). The ground states of trivalent and divalent states offer trap sites for holes and electrons, respectively (50) (**Figure 2b**). In addition, the Ln ions can act as optically activated sources of charge, where, for example, photons can excite an electron from the Ln ion into the conduction band of the host material either by single-photon absorption if the photon energy is sufficient or via multiphoton upconversion mediated by the Ln energy levels (see Section 3.2).

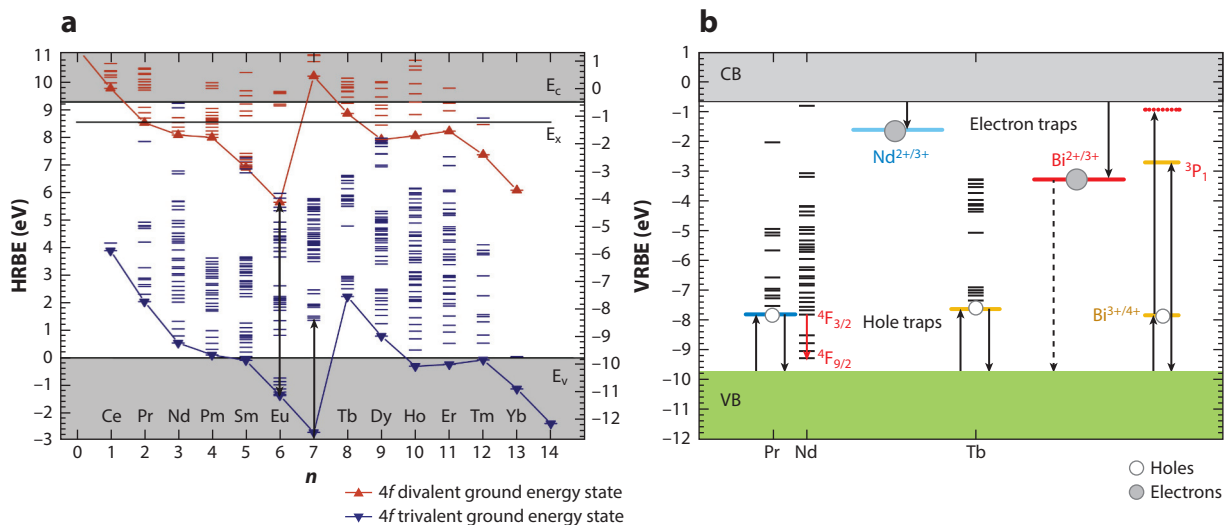


Figure 2

(a) The 4*f* energy states of Ln ions in YPO₄. The left-hand and right-hand scales are the HRBEs and the VRBEs, respectively. Panel *a* reproduced with permission from Reference 49; copyright 2013 Elsevier. (b) A schematic of a charge trapping mechanism with divalent and trivalent Ln ions. Panel *b* reproduced with permission from Reference 51; copyright 2019 American Chemical Society. Abbreviations: CB, conduction band; HRBE, host-relative binding energy; Ln, lanthanide; VB, valence band; VRBE, vacuum-related binding energy.

2.2. Characterization of Color Centers in Insulators

Correlating specific defect structures with observed optical and electronic properties is a challenge, due in large part to the difficulties inherent in structural imaging of individual subsurface atomic scale point defects within a material (52). This challenge has motivated the development and use of other powerful, though less direct, spectroscopic methods for probing defect properties.

Electron spin resonance (ESR) spectroscopy combined with atomic scale modeling provides insight into the nature of charged color centers, many of which are paramagnetic (46). ESR spectroscopy monitors the magnetic-field-dependent Zeeman and hyperfine interactions (Figure 3a) of unpaired electrons in the color centers by observing the absorption of microwave irradiation under the application of a magnetic field (Figure 3b). These interactions are influenced by the chemical and steric natures of the atoms surrounding the charged color center. By comparing the ESR spectrum with theoretical calculations based on point defect models, one can ascertain the local arrangement of the unpaired electron and the surrounding atoms (53).

X-ray photoelectron spectroscopy (XPS) is another powerful technique, revealing chemical compositions, oxidation states, and bonding environments within a material (54, 55, 58, 59). The presence of defects introduces new peaks in the XPS spectrum of a sample (Figure 3d), which are specific to binding energies associated with the defect structure (Figure 3c). Because X-ray irradiation is required for this method, however, it generally cannot detect color centers located more than 10 nm below the surface of the crystal.

While ESR spectroscopy and XPS tend to offer chemical and structural information, thermoluminescence measurements are effective at elucidating the electronic energy levels of color centers, when the energy levels are located close to the conduction band or valence band of the crystal materials (30, 31, 56, 57, 60, 61). In thermoluminescence experiments, trapped electrons (holes) are excited to the conduction (valence) band by phonon absorption and then relax to the valence

ESR: electron spin resonance

XPS: X-ray photoelectron spectroscopy

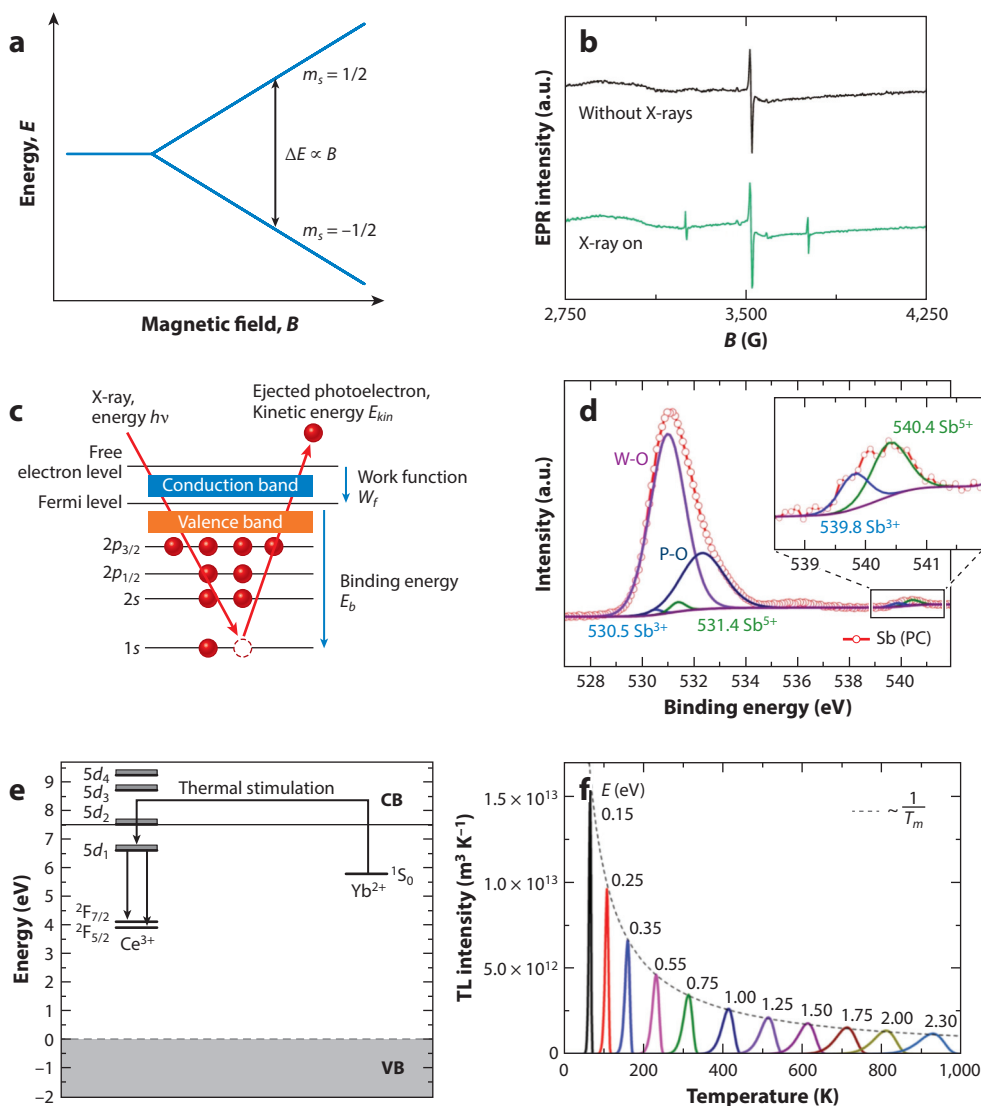


Figure 3

(a) A schematic of the Zeeman interaction for a single unpaired electron. (b) EPR spectra of Tb-doped NaLuF₄ nanocrystals before and after X-ray irradiation. Panel b reproduced with permission from Reference 31; copyright 2021 Nature Publishing Group. (c) A schematic of the photoionization process. Panel c reproduced with permission from Reference 54; copyright 2022 Elsevier B.V. (d) An XPS spectrum of Eu³⁺-doped tungsten phosphate glass after 473-nm laser irradiation. An XPS peak of Sb⁵⁺ is observed after PC. Panel d reproduced with permission from Reference 55; copyright 2021 Nature Publishing Group. (e) An energy level diagram of Y₃Al₅O₁₂ (YAG):Ce³⁺, Yb³⁺. Panel e reproduced with permission from Reference 56; copyright 2011 IOP Publishing. (f) Thermally stimulated luminescence peaks derived from the Randall–Wilkins equation. A constant heating rate of 1 K/s is applied. Panel f reproduced with permission from Reference 57; copyright 2017 MDPI. Abbreviations: CB, conduction band; EPR, electron paramagnetic resonance; PC, photochromism; TL, thermoluminescence; VB, valence band; XPS, X-ray photoelectron spectroscopy.

(conduction) band, emitting photons (30, 31, 56, 60, 61) (**Figure 3e**). Analysis of the thermoluminescence spectra versus temperature allows one to deduce the size of the energy gap between the energy level of the charged color center and the nearest band edge using the thermal decay model or the Halperin–Branner method (57, 60) (**Figure 3f**). Combining the thermoluminescence analysis with density functional theory models that estimate the energy level structure of specific defect chemistries enables the match of thermoluminescence to a variety of color centers (29, 31).

3. PHOTODARKENING

PD describes the phenomenon in which the luminescence or emission power from a medium decreases when the medium is irradiated with certain wavelengths of light (62). It is sometimes called photochromatic damage or photoinduced absorption because the loss of emission power results from absorption or scattering of the emission wavelengths that increases with pump irradiation time, as shown, for example, by time-resolved numerical simulations of a fiber laser (63) (**Figure 4a**). The PD effect has generally been considered unfavorable due to its negative impact on the performance of some Ln-based devices such as fiber lasers (64–67). The impact of

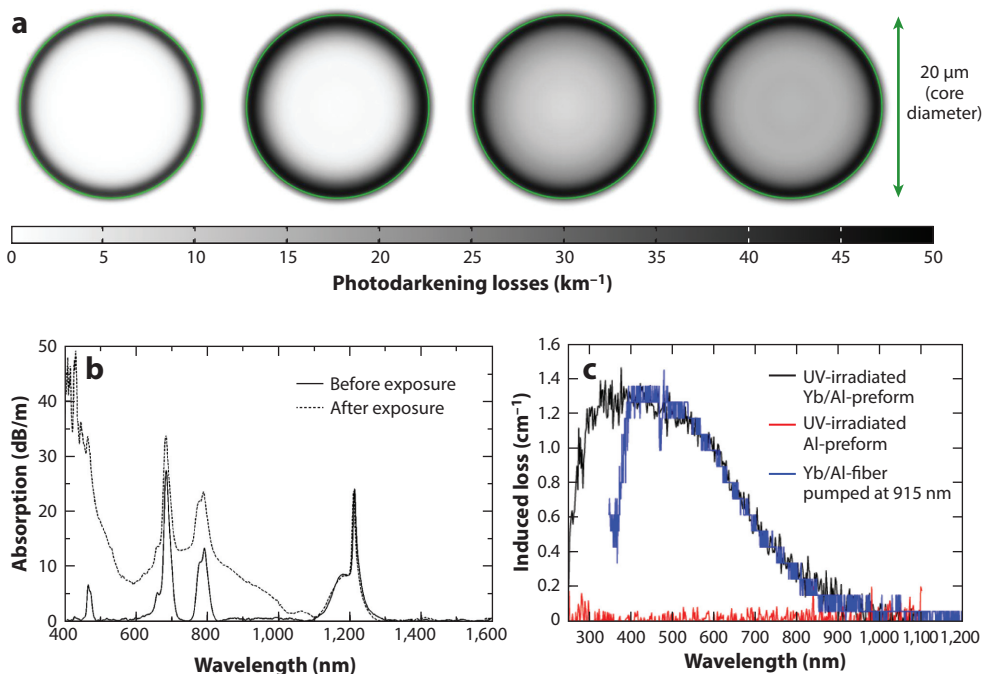


Figure 4

(a) Simulation results of the spatial distribution of photodarkening-induced losses in a fiber cross section after 10, 100, 1,000, and 10,000 h of excitation. The green circles represent the boundary of the fiber core. Panel *a* reproduced with permission from Reference 63; copyright 2018 SPIE. (b) Absorption spectra of a Tm-doped ZBLAN (zirconium barium lanthanum aluminum sodium fluoride) fiber before and after 1,120-nm laser irradiation. Panel *b* reproduced with permission from Reference 74; copyright 1995 Optica. (c) Absorption spectra of Yb-doped silica fibers after 915-nm laser (blue) and UV irradiation (black). The red plot represents an absorption spectrum of an undoped silica fiber after UV irradiation. Panel *c* reproduced with permission from Reference 75; copyright 2008 Optica.

PD is further exacerbated by the fact that it worsens over time, shortening the operation lifetime of lasers, and is exaggerated with increasing pumping power (64, 68–70). In addition to the loss of laser power, lasing mode instability increases, degrading the beam quality. Also, temporal fluctuations of laser beam intensity can surge with PD, inducing an additional heat load (71–73).

Still, although often viewed as a negative effect, the possible usefulness of PD was recognized when it was first discovered (76). Notably, periodic gratings within a material, formed by modification of the refractive index induced by the PD effect, were demonstrated. This and similar demonstrations suggested potential applications in optical switching, storage, and phase conjugation, which are now being realized in Ln-doped nanomaterials (see Section 4.3).

3.1. Photodarkening and Color Centers

In many cases, the mechanism underlying PD involves the formation of color centers within the material (for the purposes of this review, we include a change in charge state of an ion within our definition of color center). Within Ln-doped materials, the absorption band of an induced color center often overlaps with the emission band of the Ln ions, resulting in loss of Ln luminescence (Figure 4b,c).

In the case of Ln-doped silica, self-trapped-hole color centers have absorptions ranging from 0.7 to 1.2 eV (47), which can quench emission from, for example, the $^2F_{5/2}$ state of Yb^{3+} ions, the 3F_4 and 3H_4 states of Tm^{3+} ions, and the $^4I_{13/2}$ and $^4I_{11/2}$ states of Er^{3+} ions. Other color centers in silica, such as the nonbridging-oxygen center and peroxy radicals, can absorb energies from higher-lying Ln^{3+} energy levels (47), including the 3H_4 state of Tm^{3+} ions, the $^4S_{3/2}$ state of Er^{3+} ions, and the 5D_0 state of Eu^{3+} ions. For halide materials, F-centers and H-centers have relatively low energies (42). For example, the F-centers in NaYF_4 have absorption peaks near 0.9 eV (30, 60, 61), which can quench the 3F_4 and 3H_5 states of Tm^{3+} ions. Other than those color centers, there are a variety of color center candidates for PD behaviors such as Frenkel and Schottky defects, whose energy states in $\alpha\text{-NaYF}_4$ were calculated by a density functional theory simulation to have absorption bands in the Vis to NIR regions (Figure 5).

More generally, absorption spectra measurements on Tm^{3+} -doped silica (67, 77) and fluoride (74, 78) fibers and on Yb^{3+} -doped silica fiber (43, 75, 79, 80) showed that broad absorptions in the Vis regions correlate directly with the onset of PD. This finding implies that light-induced color centers in the silica and fluoride fibers underlie PD, with the overlapping of the induced absorption and Ln emission bands explaining the luminescence decay in photodarkened materials.

3.2. Upconverting Processes for Photodarkening

An interesting feature of PD is that it occurs under optical irradiation using photons with much lower energies compared with other color-center-generating processes, which often require, for example, gamma ray or electron beams. Notably, several works reported that color centers generated by low-photon-energy optical pumping show optical characteristics similar to those induced by high-energy particle irradiation (47) [though unique features of laser-induced defects, including anisotropic spatial orientation (81, 82) and spectrally selective damage (83), have also been reported]. This photodarkening of Ln-doped materials with low-energy illumination can be explained by the occurrence of photon upconversion within the sample, in which the energies of several pump photons are combined, leading to one high-energy excitation. The link between PD and photon upconversion is supported by the following observations: (a) The rate of luminescence decay during PD, that is, the rate at which luminescence intensity decreases under constant optical pumping, is dependent on the pumping power (74, 84, 85). When the decay rate as a function of pump laser power is evaluated, it becomes clear that the absorption of multiple pumping photons is

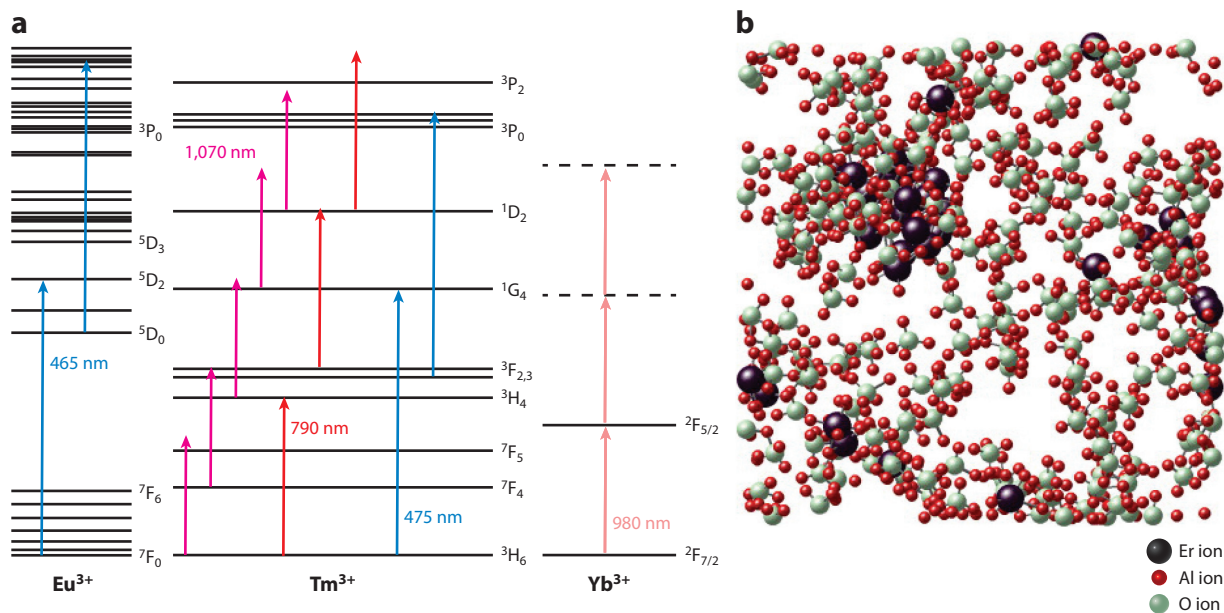


Figure 6

(a) A diagram of the 4f energy level for Eu^{3+} , Tm^{3+} , and Yb^{3+} with optical pumping (colored arrows). (b) An Er-Al codoped silica structure from a molecular dynamics simulation. Panel b reproduced with permission from Reference 91; copyright 2004 Elsevier.

The existence of Ln ion clusters, nanoscopic regions with dense Ln^{3+} concentration, within the material can greatly increase the probability of multiphoton upconversion that ultimately results either in the excitation of a Ln electron (host crystal hole) to an energy above the host crystal conduction band (Ln electronic state) energy (and thus Ln photoionization) or in charge-transfer state excitation that induces electron transfer from neighboring ligand ions to Ln ions (50). Indeed, the clustering of various Ln ions in glasses has been predicted and demonstrated (91). For example, molecular dynamics simulations predict the presence of Eu^{3+} clustering in silica glasses (Figure 6b). Time-resolved 786-nm luminescence of Tm^{3+} -doped silica glasses under 1,586-nm pumping fiber showed that ETU is a main energy transfer pathway even for low Tm concentrations, proving that Ln clusters are present (92). Also, PD in Tm^{3+} - and Yb^{3+} -doped materials worsens with increased active-ion concentration (68, 74, 90, 93). This finding is consistent with enhanced ETU from ion clustering, with the probability of cluster formation increasing as dopant content increases.

PD in Yb^{3+} -doped glasses has also been extensively reported. However, a Yb-Yb ETU mechanism does not explain PD effects in Yb^{3+} -doped materials under NIR irradiation because Yb^{3+} has only one 4f-4f state within the UV/Vis/NIR regime (7). Thus, sequential absorption and up-conversion of low-energy pump photons are not possible. Rather, to explain PD of Yb^{3+} -based materials under NIR excitation, Morasse et al. (93) suggested a collective emission of coupled Yb^{3+} ions. In this case, neighboring Yb^{3+} ions create a single dimer or trimer state (Figure 6a). Calculations based on a first-principles multielectron method show that a Yb^{3+} dimer possesses an energy state at $\sim 20,000 \text{ cm}^{-1}$ (94). Experimentally, Vis luminescence of Yb^{3+} -doped calcium aluminosilicate glass and Y_2O_3 crystals under 980-nm excitation shows that this cooperative dimer state plays a role as an intermediate state for upconversion (93, 95, 96). Furthermore, UV emission of Yb^{3+} -doped CaF_2 at 343 nm under 915-nm excitation was reported, demonstrating the cooperative state of the Yb^{3+} trimer (97).

In addition to sequential multiphoton absorption, the simultaneous absorption of multiple photons in an ultrashort laser pulse can also achieve upconversion without the need for the real $4f$ - $4f$ (or Yb dimer or trimer) intermediate transitions (98). This simultaneous multiphoton absorption has also been observed, for example, in Eu^{3+} - and Ce^{3+} -doped materials under femtosecond laser irradiation (98, 99).

3.3. Photodarkening and the Effects of Optical Avalanching Processes

As noted above, PD behavior in Ln-doped fiber during laser operation has been widely reported. Lasing, in which coherent luminescence is amplified within an optical cavity designed to trap photons of certain wavelengths (100), is an example of an optical avalanching process. In avalanching phenomena, chain reactions of events are triggered by relatively small system changes, resulting in highly nonlinear behavior and disproportionately large output responses (1, 101–103). This has two important ramifications for PD. First, it implies that a considerable amount of energy is present within the lasing system, which leads to increased probability of color center generation. Second, avalanching tends to amplify small perturbations exponentially; therefore, the generation of even a low concentration of absorbing color centers can dramatically affect lasing. Because of the highly nonlinear optical response near the lasing threshold, even a small shift of the lasing threshold can yield a steep decline of laser performance. Experimentally, researchers have shown that PD in fiber lasers increases the lasing threshold intensity (64, 69) and decreases lasing efficiency (104–106). The PD-induced absorption in the fibers overlaps with the amplified stimulated emission (64, 69, 104), affecting the stimulated radiation process.

The connection between PD and optical avalanching processes is noteworthy in light of recent observations of photon-avalanching upconversion within Ln-doped nanocrystals (32–34, 36). PD in these ANPs is now being reported, showing spectral and Ln-content-dependent PD characteristics similar to those of the Ln-doped fiber lasers (see Section 4.3) and suggesting new potential applications (see Section 5).

3.4. Suppression of Photodarkening

Motivated by the negative impact of PD on device performance, several strategies have been investigated and employed for alleviating PD effects (sometimes termed decolorizing the glass) (107), which we discuss briefly here.

3.4.1. Aluminum codoping. Al codoping is widely used in silicate glass for purposes such as precise control of refractive index profiles, reduction of background loss, and enhancement of absorption and emission cross sections of Ln ions (108). Importantly, for PD considerations, Al doping also improves the homogeneity of Ln^{3+} doping in silicate glasses by increasing the solubility of the Ln^{3+} ions (109). Doping homogeneity results in less Ln^{3+} ion clustering, hence a reduction in locally enhanced ETU events that can induce PD. Ln^{3+} luminescence line narrowing has confirmed the influence of Al^{3+} codoping on homogeneous Ln^{3+} distribution (91). More directly, decreased PD-induced loss in Yb-doped fibers was reported when the Al dopant concentration was increased from 0.5 to 3.0 wt% (68). In other studies, Al codoping showed negligible PD-induced loss in the wavelength range of 700 to 1,300 nm (93, 110), in contrast to Yb^{3+} -doped fibers codoped with Ge^{3+} and Er^{3+} . Time-resolved measurements revealed that the absolute Al concentration rather than the Al/Yb^{3+} ratio determines the degree of PD. This finding supports the suggestion that the solvation shell formed by Al around the Yb ions does not coordinate directly with the Yb^{3+} , unlike the case with P codoping (91). The total Al doping concentration is limited by the glass or fiber fabrication process. But recent work has shown that

a high Al concentration above 11 mol% is achievable using the molten core method and that PD is dramatically reduced with the exceptionally high dopant concentration (108).

Although Al codoping is an effective approach for suppressing PD behavior, it also increases the refractive index of the fiber, degrading the laser beam quality (108, 111). To resolve this disadvantage, one can use fibers with a pedestal design of the index profile to decrease the numerical aperture of the laser fiber (112). Codoping of Al and P can also result in smaller increases of the refractive index while reducing PD and has led to the realization of a fiber laser with an output power of >100 W (111).

3.4.2. Lanthanide codoping. Research has shown that La^{3+} codoping suppresses PD-induced absorption in Tm^{3+} -doped aluminosilicate. The effect has been attributed to the inhibited formation of Tm^{3+} ion clusters, which promotes photoionization via ETU (90) (see Section 3.2). Er^{3+} codoping also reduced PD in Yb^{3+} -doped fibers by moderating Yb^{3+} cluster formation that enhances UV cooperative emission (93). The idea that Ln codoping inhibits cluster formation is further supported by the dependence of PD reduction on increased codoping concentrations in Yb^{3+} - and Tm^{3+} -doped fibers (112, 113), suggesting that an increased average distance between optically active Ln ions is related to the PD mitigation effect.

Additionally, Ce has long been known to decolorize glasses (114), with Ce^{3+} and Ce^{4+} ions playing an important role in redox reactions of trapped-hole and trapped-electron color centers. Using Ce codoping, Engholm et al. (112) dramatically reduced PD-induced emission loss at 600 nm for Yb^{3+} -doped aluminosilicate fibers without affecting performance of the fiber laser. Mechanistically, it was shown that while most Ce ions are initially present as Ce^{3+} ions in Yb-doped aluminosilicate fibers, the number of Ce^{3+} ions in the fibers reduces during 969-nm pumping (113). This observation confirmed that holes generated under intense NIR pumping are trapped by Ce^{3+} ions, creating either Ce^{4+} ions or Ce^{3+} -hole pairs, inhibiting formation of photochromic hole color centers and reducing PD. An optimum $\text{Ce}^{3+}/\text{Yb}^{3+}$ ratio between 0.5 and 0.6 was suggested for aluminosilicate fibers to achieve effective PD suppression. Ce^{3+} codoping also suppresses PD-induced emission absorption of Tm^{3+} -doped aluminosilicate fibers (90). Because electron-related color centers induce PD in these Tm^{3+} -doped fibers, it was proposed that Ce^{4+} ions play the key role in PD suppression by reducing trapped-electron color centers and converting to Ce^{3+} . Furthermore, additional optical effects of the Ce ions were suggested to mitigate PD in the Tm^{3+} -doped fibers. Specifically, high-lying energy states such as the $^3\text{P}_0$ state in Tm^{3+} can be effectively quenched by energy transfer processes related to Ce ions, yielding an electron- Ce^{4+} ion pair or excitation from the Ce^{3+} ground state to the $\text{Ce}^{3+} 5d$ state.

There are two drawbacks to Ce^{3+} codoping of fibers. The first is that the fiber numerical aperture increases due to the increased refractive index of Ce^{3+} -doped glass (112). As with the case of Al codoping, a pedestal design to compensate the refractive index increases has been recommended to alleviate this issue. The second is the extreme heating of Ce-doped glass when pumped, which affects mode instabilities in laser fibers (113). Here, temperature surges are observed to correlate with increased Ce ion concentration even though PD-induced losses decrease, suggesting that the PD inhibition with Ce codoping somehow acts as a heat source.

3.4.3. Hydrogen and deuterium loading. Because it can alleviate the formation of trapped-hole color centers, H_2 loading has been utilized as an approach to reduce PD behavior. In this case, an H_2 molecule reacts with a hole and an oxygen ligand, forming a hydroxyl group. Indeed, absorption spectra of H_2 -loaded Yb^{3+} -doped fibers that have undergone 925-nm pumping show less PD-induced loss in the Vis region compared with Yb^{3+} -doped fibers without H_2 loading, demonstrating a reduction of hole-related color centers (115). Similarly, D_2 loading effectively

reduced PD in Yb^{3+} - and Tm^{3+} -doped silica fibers (116, 117). The preexisting PD-induced loss can also be relieved by D_2 loading.

3.5. Photobrightening

Researchers previously discovered that color centers in topaz generated under X-ray irradiation are reversibly deactivated with thermal or optical treatment, changing the color of topaz (41). Equivalently, color centers generated or activated during PD processes can also be deactivated by thermal and optical stimulation. Often, the color-center-trapped charges are excited to the conduction or valence band of the host matrix. These charges can then recombine with opposite charges, resulting in thermally stimulated or photostimulated luminescence signatures of the deactivation. The color center deactivation is accompanied by a recovery of emission from the material, here referred to as photobrightening.

Photobrightening of Tm^{3+} -doped materials has been widely reported. For Tm^{3+} -doped ZBLAN, PD-induced absorption is recovered by Vis laser illumination at 481 and 514 nm (64–66). In addition, studies found that PD in Tm^{3+} :ZBLAN is effectively mitigated by thermal annealing at 49°C (78) and $\sim 100^\circ\text{C}$ (64). For Tm^{3+} -doped silica fibers, it was revealed that optical irradiation at 514 (89) or 793 nm (118) alleviates the PD effect. Notably, photobrightening is now being observed in Tm^{3+} -doped nanocrystals, specifically in ANPs that have experienced PD after intense 1,064-nm excitation.

In Yb^{3+} -doped silica, 355- (104), 543- (79), and 633-nm (109) optical pumping can reduce PD-induced absorption. Further, Yb^{3+} -doped fibers photodarkened under NIR irradiation were photobrightened by thermal annealing at temperatures ranging from 237°C to 625°C (119–122). In Eu-doped silicate and phosphate glasses photodarkened under 466-nm irradiation, photobrightening was achieved via thermal annealing at ~ 390 , 420, and 520 K depending on the glass composition (76).

A coillumination approach that illuminates the sample with two wavelengths simultaneously has proven effective at combating PD in real time (123). Yb^{3+} -doped aluminosilicate fibers under 976- and 550-nm coillumination showed no noticeable PD even with a high Yb dopant concentration, enabling the high population inversion for lasing.

Beyond the simple recovery of optical performance following degradation, harnessing the ability to photobrighten opens avenues for new applications. These include high-density optical memory (124–126) and photoswitchable nanocrystals for superresolution imaging and sensing (127), which are described in more detail in Section 4.3.

4. APPLICATIONS OF COLOR CENTERS IN LANTHANIDE-DOPED NANOMATERIALS

4.1. Persistent Luminescence (Afterglow)

Persistent luminescence, also known as afterglow, is a phenomenon in which a material, after being pumped by a high-energy source, emits photons in the UV to NIR range for seconds to even months without any additional pumping (128). It is enabled by the storage of charge carriers (electrons and holes) photoionized by the high-energy pump (e.g., X-ray, gamma-ray, and UV excitation). Because the charges are trapped in defect states (often color centers) with deep potential wells relative to thermal energy, they can be stored for long periods before they are released by thermal fluctuation, optical stimulation, or quantum tunneling. The release is followed by recombination with the opposite charge, resulting in photon emission.

The presence of various chemical species ranging from transition metals and posttransition metals to Ln ions enables afterglow capabilities in numerous host materials (128). Among them, Ln

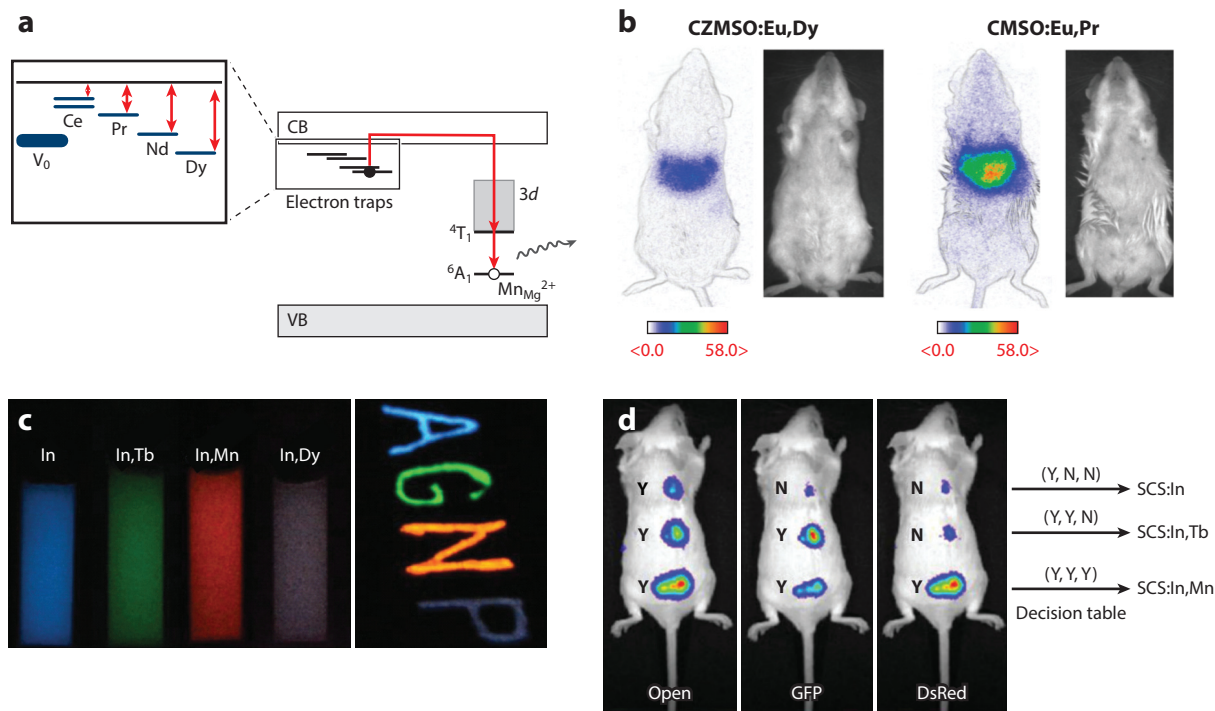


Figure 7

(a) Schematic of an electron-trapping mechanism in lanthanide (Ln)-doped CMSO. (b) In vivo imaging of CZMSO:Eu²⁺, Mn²⁺, Dy³⁺ (left) and CaMgSi₂O₆:Eu²⁺, Mn²⁺, Pr³⁺ (right) nanocrystals. Panels a and b reproduced with permission from Reference 134; copyright 2011 American Chemical Society. (c) Photograph of afterglow of SCS:In³⁺, Ln³⁺ nanocrystal colloidal dispersion (left) and writing (right) after UV excitation (254 nm, 5 min). (d) In vivo imaging of SCS:In³⁺, Ln³⁺ nanocrystals with different optical filters. Panels c and d reproduced with permission from Reference 135; copyright 2020 Wiley-VCH. Abbreviations: CB, conduction band; CMSO, CaMgSi₂O₆; CZMSO, Ca_{0.2}Zn_{0.9}Mg_{0.9}Si₂O₆; GFP, green fluorescent protein; SCS, SiO₂/CdSiO₃; VB, valence band.

ions are widely chosen to achieve afterglow due to their unique optical properties. Ln ions support a broad range of emission bands from their ladder-like energy level structure, leading to afterglow that spans the UV (129, 130) to short-wave IR (51) regions. The fact that the 4*f*-4*f* transitions of Ln ions are less affected by host materials and environments [due to shielding by outer shells of electrons (131)] facilitates the straightforward engineering of afterglow properties via codoping of various Ln ions and a variation of host materials (51). This enables the modulation of energy transfer paths and depths of trapped charge states. Also, the energy levels of many Ln dopants are spread throughout the energy gap of host materials, providing additional sites (beyond defect color centers) to capture charge carriers generated by photoionization (132, 133) (**Figure 7a**).

A surge in recent work has highlighted the potential of afterglow in Ln-based materials for a variety of applications (128). When afterglow was first discovered, its use for self-sustained light-up displays was immediately recognized and widely applied in industry for use in safety signs and watch dials (136). In the years since, researchers have shown that afterglow is sensitive to environmental temperature, high-energy photon irradiation, and mechanical forces; thus, afterglow-supporting materials can be used as sensors to detect temperature, external force and pressure, and X-ray exposure (128).

Now realized in nanoparticle form, the self-sustained luminescent behavior of afterglow has become an even more powerful tool (30, 31, 61, 135). Because AGNPs do not need simultaneous

optical pumping and can emit photons in the NIR spectral windows of biological transparency, they have proven beneficial as new contrast agents for bioimaging (135). For example, recent work demonstrated in vivo imaging of Pr-doped $\text{CaMgSi}_2\text{O}_6$ AGNPs (134), in which the AGNP design was engineered so that the Pr^{2+} ground state was placed close to the conduction band of the host material (**Figure 7a**). This resulted in thermally stimulated luminescence afterglow peaks in the NIR that were optimized for operation at physiological temperature and were brighter than particles doped with other Ln ions (**Figure 7b**). In other work, 5-nm-sized ZnSn_2O_4 nanoparticles doped with Cr and Er ions emitted 800-nm afterglow, which is known to penetrate through tissue (137), allowing in vivo imaging of mice with high signal-to-noise ratios. More recently, multicolor in vivo imaging was realized in $\text{SiO}_2/\text{CdSiO}_2$ AGNPs codoped with a variety of Ln ion species, enabling design-tunable afterglow emission bands (135) (**Figure 7c,d**). Complementary to the NIR emission suitable for bioimaging, afterglow in the UV region is being utilized for photodynamic therapy applications (138). As a proof of concept, UV afterglow from X-ray-irradiated Tb^{3+} -doped $\beta\text{-NaYF}_4$ AGNPs demonstrated photodynamic inhibition of *Pseudomonas aeruginosa* bacterial growth (30). In this study, reactive oxygen species were generated from the photocatalyst g- C_3N_4 , activated by the UV afterglow emission, which then prevented growth of the bacteria due to the strong oxidation properties of the reactive oxygen species.

In a different context, AGNPs can easily be combined with existing printing systems for facile optical patterning of AGNPs deposited onto paper or other substrates. For example, optical patterning of afterglow in AGNP films printed using an inkjet printer and multicolor luminescent inks was reported (61). Multicolor AGNPs were fabricated with various Ln dopants supporting different emission bands. The inkjet printing with AGNP-based inks can enable high-density optical patterning by printing different patterns with the multicolor persistent luminescence inks on the same area.

4.2. X-Ray Detection

X-ray detection has been achieved by leveraging the color-center-generating and color-center-charging processes in Ln-doped materials induced by X-ray irradiation (139). The Ln-based materials convert absorbed or scattered X-rays to UV/Vis light, which is highly favorable for, for example, X-ray photon counting, using afterglow or phosphorescence as the readout. Relatedly, modifications of Ln spectral properties upon change of valency can be exploited to measure the X-ray dose levels. For example, the conversion of Sm^{3+} ions to Sm^{2+} ions in SrBPO_5 crystals is X-ray dose dependent (140). Changes in the luminescence spectrum followed by the valency conversion can enable development of high-sensitivity X-ray dosimeters using Sm^{3+} -doped crystals.

Recently, an advance in AGNP design has resulted in a potential breakthrough in X-ray imaging technologies. Liu and colleagues (31) engineered new AGNPs for long-lived X-ray-pumped luminescence (radioluminescence) that persists for more than 30 days (**Figure 8a,b**). The authors demonstrated the fabrication of flexible, solution-processable nanoscintillators that can enable high-resolution 3D X-ray imaging (31) (**Figure 8c,d**). They leveraged two key innovations in their nanoparticle design: First, Tb^{3+} -doped NaLuF_4 nanocrystals were used, taking advantage of the very low phonon energies of the host matrix. Second, they exploited long-lived deep trap states that allow for the recombination of trapped charge carriers only via quantum tunneling, not thermal stimulation. Combining nanoscale materials engineering with their new insights into the mechanisms that underlie X-ray energy conversion clears a path for the development of wearable, highly sensitive X-ray detectors for imaging-guided therapies and point-of-care radiography.

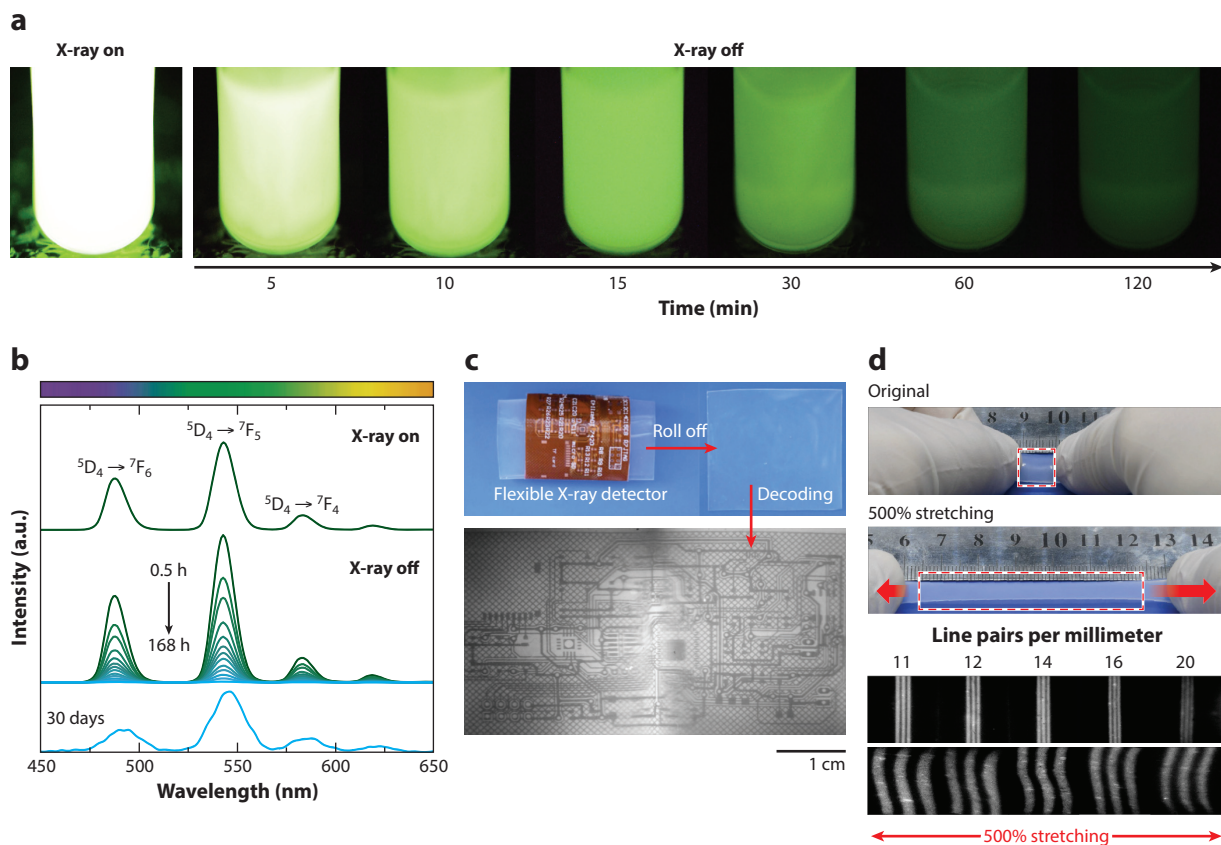


Figure 8

(a) Photograph of afterglow of a 1-mL NaLuF₄:Tb (15 mol%)/NaYF₄ nanocrystal colloidal dispersion. (b) Emission spectra of the core-shell nanocrystals during X-ray irradiation and after cessation of the irradiation. (c) X-ray luminescence imaging of a flexible X-ray detector embedded with core-shell nanocrystals after X-ray irradiation through a 3D electronic board. (d) Photograph of a stretchable X-ray detector (*top*) and high-resolution luminescence imaging of the stretched detector (*bottom*). Figure reproduced with permission from Reference 31; copyright 2021 Nature Publishing Group.

4.3. Optical Patterning

As might be expected from the name, color center generation that leads to PD is often accompanied by changes in color of the host material (76). This photochromism is attractive for applications, including optical storage and photoswitching (76, 81, 141). Combining PD with photobrightening strategies (see Section 3.5) results in reversible PD and/or photochromism behavior that is particularly useful in those applications, enabling optical patterns to be written repeatedly.

One of the first applications of laser-induced PD in a Ln-doped material was a demonstration of optical patterning. Researchers utilized the fact that PD results in a refractive index change of the material to optically write laser-induced refractive index gratings (76). Gratings, for example, have been generated in Eu³⁺-doped silicate and phosphate glasses under 466-nm excitation. The same concept was also exploited in Ge-doped optical fibers, where periodic PD fabricated distributed feedback reflectors (81). More recently, reversible color changing of ceramics between

gray and pink by PD and photobrightening $\text{Yb}^{3+}/\text{Tb}^{3+}$ -doped BaMgSiO_4 under 254-nm and 473-nm pumping, respectively, has been reported (142) (**Figure 9a**). In that work, the authors suggested such behavior has possible applications in anticounterfeiting.

Importantly, the multiphoton absorption properties of Ln ions allow not only optical patterning with low-energy photons but also high-density optical writing in which the nonlinearity of the PD process leads to improved resolution and 3D addressability. Because the pump photons induce PD only in regions of high pump intensity, a focused pump spot can be scanned in three dimensions to write arbitrary patterns, as recently reported (55). In that work, Eu^{3+} -doped tungsten phosphate glasses were irradiated under 473 nm for optical writing, and optical patterns were erased by thermal stimulation (**Figure 9b**). A key advantage general to these materials systems is that the high upconversion efficiency afforded by Ln ions allows for 3D optical writing without the need for a femtosecond pulsed laser, unlike 3D optical patterning with other materials (143–145) for which the expensive pulsed laser system is required.

Very recently, PD-photobrightening-based reversible photoswitching in Ln-doped nanoparticles has been realized, enabling ultrastable all-optical read-write capabilities in a nanomaterial system (**Figure 9c**). Pushing this functionality into nanomaterials allows researchers to move beyond bulk crystal media, which have size and geometric limitations as well as strict processing requirements. Nanoparticle-based systems offer an avenue for simple, fully solution-processed fabrication and assembly (that is also complementary metal-oxide semiconductor compatible) into a wide variety of photonic structures, products, and device platforms.

5. FUTURE OUTLOOK AND CONCLUSIONS

Extensive studies have contributed to our understanding of PD phenomena in Ln-doped materials. However, the precise correlations of specific color center species to particular PD behaviors, color center precursors, and color-center-generating mechanisms are in many cases still under debate. Perhaps the most important factor contributing to the existing knowledge gap is the difficulty in directly imaging an atomic scale point defect and also probing its optical properties while minimizing contributions and background signals from surrounding optically active material and emitting sites (e.g., other nearby color centers). The challenging aspects of such studies are exacerbated by the dynamic, often unstable, nature of many color centers, which are easily affected by both environmental stimuli (e.g., local temperature) and possible perturbations from high-spatial-resolution characterization probes (e.g., electrons, X-rays, and scanning probes). The continued development of nondestructive multimodal techniques and capabilities that combine atomic resolution and optical spectroscopy such as next-generation nano-optical scanning tunneling microscopies (146–150) should lead to new breakthroughs.

Here, we have highlighted several existing and future applications that exploit color center properties in Ln-based nanomaterials. A primary theme is the realization of all-inorganic photoswitchability, with Ln-doped nanoparticles providing a new framework for such capabilities. Notably, this material system overcomes the innate drawbacks of existing organic photoswitches such as photoinstability and photobleaching and is now leading to, for example, single-molecule localization imaging with subangstrom localization accuracies and high-density optical data storage (127). Looking forward, we expect that the robust reversibility and optical controllability offered by PD and photobrightening should enable other uses, particularly when combined with recent advances in UCNP synthesis strategies. Such advances now allow for narrow size distributions, tunable surface chemistries, and precision heterostructuring of multilayer compositions that can effectively manipulate energy propagation pathways. Marrying these cutting-edge abilities with an increased understanding of color center properties in UCNPs will lead to new functionalities and an ever-broadening scope of applicability.

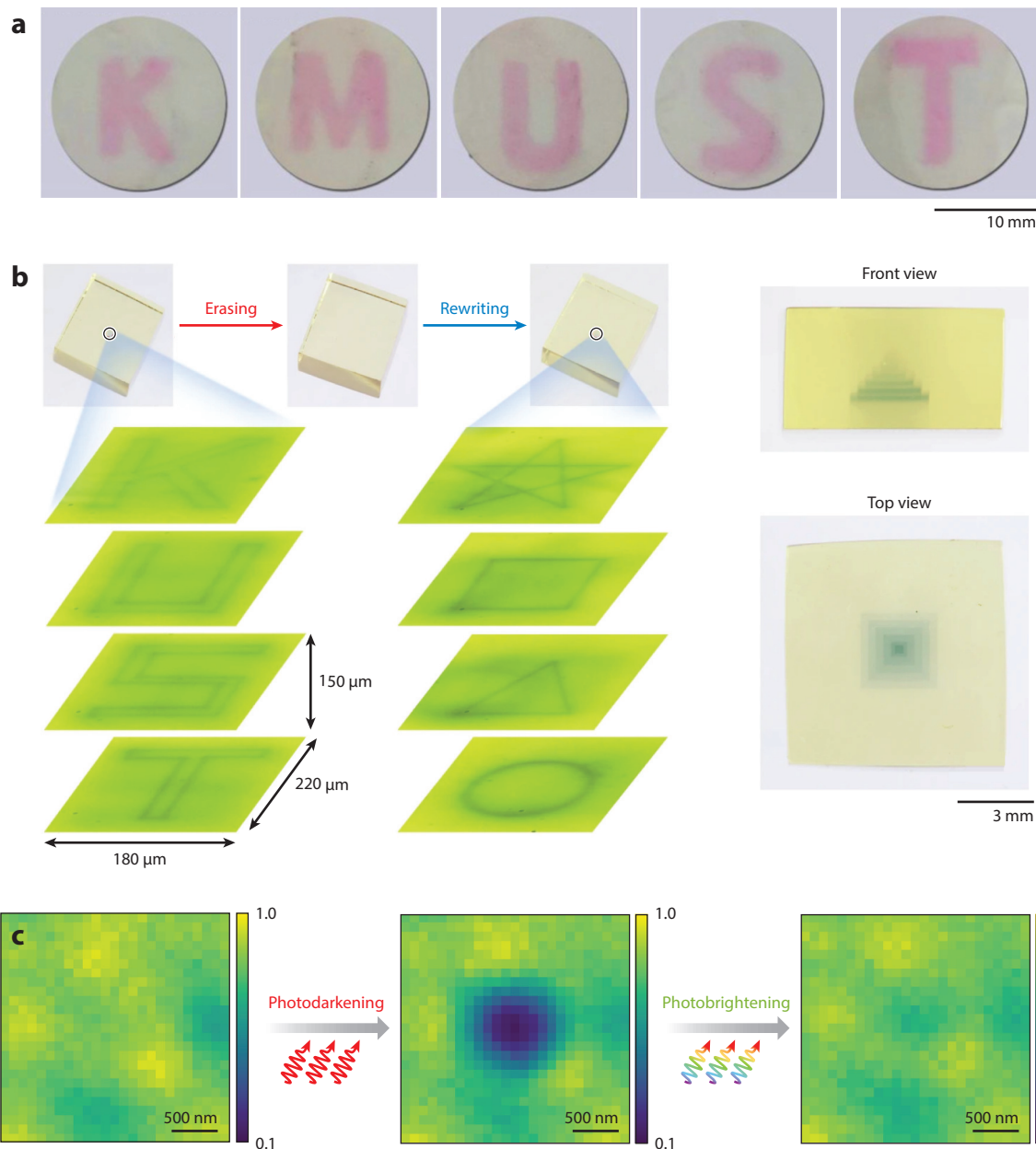


Figure 9

(a) Photograph of K, M, U, S, T patterns on the $\text{BaMgSiO}_4:\text{Yb}^{3+}, \text{Tb}^{3+}$ ceramics irradiated by 254-nm UV light. Panel *a* reproduced with permission from Reference 142; copyright 2019 Wiley-VCH. (b) Reversible 3D optical patterning on a Eu-doped tungsten phosphate glass medium. Panel *b* reproduced with permission from Reference 55; copyright 2021 Nature Publishing Group. (c) Reversible optical patterning on a nanocrystal ensemble film ~ 100 nm thick, exploiting photodarkening and photobrightening effects. Three images are measured by 2D laser confocal scanning with optical pumping before and after photodarkening (left and middle, respectively) and after photobrightening (right). The center of the film was exposed to focused laser beams for photodarkening and photobrightening.

SUMMARY POINTS

1. The unique optical characteristics of lanthanide (Ln) ions provide upconverting nanoparticles (UCNPs) with several advantageous properties as luminescent nanostructures, including high anti-Stokes emission efficiencies and photostability.
2. As in other crystals, color centers are present in UCNPs, often in the form of charges trapped in a local defect state or on an ion. The electronic states of activated color centers can be resonant with other absorptive and emissive transitions in UCNPs, leading to color changes when the centers are activated.
3. Activation of color centers is widely linked to photodarkening (PD). Additionally, Ln ions play important roles in the initiation of PD, enabling efficient upconversion that accelerates photoionization processes and activates color centers.
4. PD can negatively affect material performance, resulting in photochromism and heat generation that yield optical losses and instability in the systems. Several approaches, including Al/P codoping, Ln codoping, and H₂/D₂ loading, can mitigate PD effects by reducing Ln clusters or color center precursors.
5. PD processes are not irreversible. The recovery of emission intensity, also called photobrightening, can be achieved by thermal, optical, or mechanical stimulation. Such stimulation can release trapped charges at defect sites, deactivating color centers.
6. Color centers provide new functionalities in UCNPs. These include afterglow, which enables, for example, in vivo imaging without simultaneous optical pumping, and high X-ray sensitivity, which allows for solution-based fabrication of versatile nanoscintillators.
7. Combining PD with photobrightening offers a novel approach for reversible optical manipulation and patterning of photochromic properties of crystals, including UCNPs using low-energy visible/near-IR photons. In nanoscale materials, combining PD and photobrightening results in photoswitchable inorganic constructs with advantages over existing organic photoswitches.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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