Persistent luminescent nanoparticles: Challenges and opportunities for a shimmering future

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Victor Castaing, Encarnación Arroyo, Ana I. Becerro, Manuel Ocaña, Gabriel Lozano, Hernán Míguez, et al.

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Victor Castaing,a) Encarnación Arroyo, Ana I. Becerro, Manuel Ocaña, Gabriel Lozano,b) and Hernán Míguez

AFFILIATIONS
Institute of Materials Science of Sevilla, Consejo Superior de Investigaciones Científicas—Universidad de Sevilla (CSIC-US), Américo Vespucio 49, 41092, Sevilla, Spain

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Email: victor.castaing@icmse.csic.es
b)Author to whom correspondence should be addressed: g.lozano@csic.es

ABSTRACT
Persistent phosphors are luminescent sources based on crystalline materials doped with rare-earth or transition metal cations able to produce light after the excitation source vanishes. Although known for centuries, these materials gained renewed interest after the discovery of Eu²⁺,RE³⁺ co-doped aluminates and silicates in the late 1990s due to their unprecedented afterglow properties. In contrast, persistent nanophosphors have emerged only recently as a nanoscale alternative to their bulk counterparts, offering exciting opportunities of particular relevance for in vivo imaging, optical data storage, or unconventional light generation. However, taking advantage of the avenues opened by nanoscience demands developing new synthetic strategies that allow precise control of the morphology, surface, and defect chemistry of the nanomaterials, along with a profound understanding of the physical mechanisms occurring in the nanoscale. Besides, advanced physicochemical characterization is required to assess persistent luminescence in a quantitative manner, which allows strict comparison among different persistent nanophosphors, aiming to propel their applicability. Herein, we revisit the main phenomena that determine the emission properties of persistent nanoparticles, discuss the most promising preparation and characterization protocols, highlight recent achievements, and elaborate on the challenges ahead.

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I. INTRODUCTION
Smart utilization of light-generating tools enabled the extension of social and economic activities when sunlight did not reach, being the development of light-emitting materials and devices that are both efficient and environmentally friendly the cornerstone of lighting technologies nowadays. In particular, the widespread use of light-emitting diodes (LEDs) during the last decade has changed the way we light up the world.1 With main efforts devoted to improve the efficiency of LED chips and tune the properties of the photoluminescent materials employed for color conversion in general lighting, there is significant interest to develop materials with unconventional emission properties. In stark contrast with conventional phosphors in which defects are detrimental for photoluminescence efficiency, devised structural defects are key in persistent phosphors since they allow energy storage and controlled release by charge trapping. For this reason, defect engineering is essential to find the balance between large storage capacity, persistent luminescence kinetics, and emission efficiency. Although persistent materials have fascinated not only researchers but also artists for centuries,2,3 they gained their widest scientific and technological interest with the discovery of green emitting SrAl₂O₄:Eu²⁺,Dy³⁺.4 Due to their unprecedented long and intense persistent luminescence (Pers. Lum.), Eu²⁺,RE³⁺ co-doped aluminates and silicates have been thoroughly investigated since then.5–7 In the same context, researchers have pursued the demonstration of similar properties in alternate materials,8–15 which include yttrium- and gadolinium-based garnets (Y₃Al₂O₉:Ce³⁺,Cr⁳⁺, Gd₃Al₂Ga₃O₁₂:Ce³⁺,Cr⁳⁺),20–22 perovskite-type niobates and titanates (NaNbO₃:Pr⁴⁺, CaTiO₃:Pr⁴⁺),23–25 zinc
gallates and derivatives (ZnGa₂O₄:Ce³⁺, Zn₁₋ₓGa₁ₓGeO₃:O₂Ca³⁺, Zn₁₋ₓGa₂Sn₁₋ₓO₄:O₂Ca³⁺, Zn₁₋ₓGa₂SnₓO₄:O₂Ca³⁺), 37,38 germanates (MgGeO₃: Mn²⁺, Dy³⁺), 39 phosphates [Ca₃(PO₄)₂:Mn²⁺, Dy³⁺, YPO₄:Pr³⁺, Ho³⁺], 32,33 or sulfides (Ca₃Eu²⁺,Tm³⁺, Ca₃Eu²⁺, Dy³⁺). 3,4,5 In their bulk form, persistent phosphors already found commercial applications as they are routinely used for adornment in toys or watch needles or signaling. Besides, these materials are widely employed for security usage as they are present in night safety panels and dials to ensure information reading in the absence of light during night or during an electricity cutoff (see Fig. 1). In these cases, powdered persistent phosphors are used embedded in paints or resins. Coming out of this successful use as indoor safety signs, persistent phosphors have been proposed for jogging and cycling paths, 36 or even for road markings. 37 However, limited storage capacity combined with a reduction of the release rate associated with temperature drop at night prevent the usage of these materials for outdoor applications. 38

In addition to their applicative concern, bulk persistent phosphors also retain purely scientific interest from a fundamental point of view since they allow studying the effect of variations in the chemical composition on the optical properties in a simple way. 39 Finally, we refer the reader to recent review articles authored by Li et al. and by Poelman et al. for in-depth discussions on these materials. 39,40

Herein, we focus on persistent nanophosphors, specifically in persistent luminescence nanoparticles (PLNPs): the opportunities they offer and the main challenges ahead in terms of their morphology, initial brightness, and afterglow duration. PLNPs have been in the spotlight during the last decade mainly motivated for their prospect for in vivo imaging applications. 27,41–43 a field in which both their nanometric size and their colloidal stability in water are key since these features enable proper biodistribution but also superior imaging resolution. Unique delayed emission of PLNPs prevents living-tissue damage associated with the simultaneous excitation with UV light required for most phosphors 24,45 and minimizes the interferences produced by the autofluorescence of tissues, hence leading to an unprecedented high signal over noise ratio. 27,46 Although bioimaging drove the field in its infancy, PLNPs have proven interesting for a wide variety of applications that may benefit from the higher resolution brought by size reduction, as it is the case for anticounterfeiting, optical data storage or displays, in which PLNPs can be used as PLNP-based converters of AC-driven micro-LEDs. 37,48 While the research in bulk persistent phosphors is principally focused nowadays on composition optimization to improve afterglow properties, PLNPs have posed new fundamental challenges that we seek to discuss. Indeed, PLNPs generally suffer from poor persistent luminescence properties due to the small size and low crystalline quality that nanophosphors typically feature: (i) large surface to volume ratio associated with nanometric size leads to a higher concentration of surface defects and (ii) most synthetic routes avoid high temperature processing to prevent the nanoparticles (NPs) from aggregation, which leads to more defective crystal lattice structures compared to their bulk counterparts, resulting in uncontrolled trapping states, all of which can be highly detrimental for Pers. Lum. Consequently, increasing the initial persistent brightness and optimizing persistent decay kinetics appear as the main challenges of the field. In Sec. II, we discuss the most promising strategies to design efficient PLNPs. Also, as we address in Sec. III, it is central to develop preparation methods to attain PLNPs with tailor-made physical dimensions: uniform particle shape and narrow size distribution, along with colloidal stability, especially in biological media, without compromising the luminescence properties of the nanomaterials. In order to tackle this, it is necessary to attain a profound understanding on the physical mechanisms involved in Pers. Lum. generation in the nanoscale. For this reason, in Sec. IV, we discuss the main phenomena involved in afterglow: charging (A), storage (B), release (C), and finally light emission (D), along with the most relevant characterization techniques employed to study the abovementioned processes. So, in order to boost the next generation of Pers. Lum. nanomaterials ready to be integrated into applications that can benefit from them, as highlighted in Sec. V, it is primordial to develop means to control not only the initial brightness but also the charging and release efficiencies that determine the afterglow duration, along with the chromaticity of the Pers. Lum.

II. DESIGN STRATEGIES OF PERSISTENT LUMINESCENCE NANOPARTICLES

The elaboration of PLNPs with bright, long, and tailor-made Pers. Lum., satisfying application specifications, appears as one of the main challenges in the field. In Sec. II, we elaborate on the most relevant and innovative design aspects to consider in developing efficient persistent nanomaterials with devised properties.

A. Composition engineering

In general, dispersed PLNP preparation methods (see Sec. III) do not allow a strict control over the particle composition and doping ion distribution, being challenging to elaborate optimized host compositions with the proper doping agents and contents for bright and long Pers. Lum with tailor-made spectral characteristics. Therefore, composition engineering appears as the current main route to tune the properties of PLNPs.
On the other hand, similarly to what has already proven useful in bulk persistent phosphors, playing with the host composition and dopants is the most commonly used strategy to tune the spectral characteristics of the Pers. Lumin. in PLNPs from UV to near infrared (NIR). In fact, devised co-doping strategies have enabled an afterglow color tuning through a persistent energy transfer mechanism, as first demonstrated in ZnGa$_2$O$_4$:Cr$^{3+}$,Yb$^{3+}$ PLNPs embedded in glass, in which both Cr$^{3+}$ and Yb$^{3+}$ emissions can be monitored after excitation stoppage,\textsuperscript{49} and then applied to dispersed PNLPs with similar composition.\textsuperscript{49} Dopant exchange from Cr$^{3+}$ to Co$^{2+}$ and Ni$^{2+}$ in ZnGa$_2$O$_4$ nanophosphors has also proven effective to tune the afterglow emission from deep red (at 696 nm) to NIR (at ca. 1000 and 1275 nm, respectively).\textsuperscript{51} Finally, as rigorously demonstrated in bulky ZnGa$_2$O$_4$,\textsuperscript{30} host matrix modification of PLNPs can lead to an afterglow color change, through the spectral shift of Cr$^{3+}$ $\rightarrow$ A$_2$ emission band.\textsuperscript{52} Careful chemical engineering has proven effective to yield green persistent nanophosphors in zinc-based spinel type nanoparticles by doping with Mn$^{2+}$ and moving from gallate to germanate host.\textsuperscript{53} It is worth mentioning that a similar behavior is expected for Eu$^{2+}$-based PLNPs, as Pers. Lumin. from blue to red has been observed using different hosts in bulk.\textsuperscript{18,54}

Interestingly, spectral dependence of Pers. Lumin. charging can be tuned as well via composition engineering. In a meaningful example, partial substitution of two Ga$^{3+}$ ions by Zn$^{2+}$ and Sn$^{4+}$ or Zn$^{2+}$ and Ge$^{4+}$ ions results in a red shift of the Pers. Lumin. charging along with an increased efficiency.\textsuperscript{26,30,52}

On the other hand, slight modifications of persistent phosphor composition may induce variation of the persistent dynamics. As we will discuss in Sec. IV, afterglow dynamics is driven by trap energy states. For instance, shallow traps lead to faster decays with higher initial intensity whereas deep ones yield long persistency. The creation of efficient traps in phosphors generally remains in the trial-and-error stage. However, chemical engineering is known to provide efficient ways for trap depth engineering in bulk phosphors. Interestingly, in most cases, compositions optimized for bulk materials are targeted in the nanoscale. An effective route to achieve trap depths engineering consists in the addition of trivalent rare earth (RE$^{3+}$) dopants, which act as electron trapping centers (becoming RE$^{2+}$ filled trap).\textsuperscript{55} As a matter of fact, the usage of RE$^{3+}$ as potential electron traps has been facilitated by works done by Dorenbos, introducing a semi-empirical model to predict RE relative energy levels positions in different hosts.\textsuperscript{56,57} The same model enables the estimation of the relative energy levels of another RE co-dopant, being possible to predict the position of the RE$^{2+}$ ground state level with respect to the conduction band, i.e., the energy depth of the filled trap.\textsuperscript{58,59} In particular, it has been found that Sm$^{3+}$ is the best RE$^{3+}$ co-dopant for efficient electron trapping (0.91 eV depth) in La$_2$O$_3$:Cr$^{3+}$ bulk phosphor,\textsuperscript{60} which has been extended to PLNPs design.\textsuperscript{61} Likewise, the modification of the RE$^{3+}$ co-dopant appears to be efficient to tune the trap depth in Ca$_3$Zn$_2$Mg$_6$Si$_8$O$_{24}$:Eu$^{3+}$, Mn$^{3+}$, RE$^{3+}$ PLNPs, as shown in Fig. 2(a).\textsuperscript{62} Other strategies, as the inclusion of a dopant that does not belong to the RE family\textsuperscript{63-66} or the manipulation of the host composition,\textsuperscript{67-71} also allowed as bandgap engineering, have been employed to tune the energy difference between the energy levels of the activator and those of the traps in bulk phosphors. The interest of the combination of these two strategies is perfectly illustrated in Ce$^{3+}$-doped yttrium aluminum gallium garnet persistent phosphors, in which Cr$^{3+}$ acting as electron trap and an Al:Ga ratio of 2:3 have been demonstrated as optimum for persistent luminescence,\textsuperscript{63,68} and then extrapolated to PLNPs, as displayed in Figs. 2(b)–2(d).\textsuperscript{72,73}

### B. Nano-architecture engineering

Nanoparticles feature larger surface to volume ratios compared with bulk phosphors, increasing the interaction between optically active cations and the environment (ligands, solvent, etc.). At the surface, atoms are largely exposed, requiring defects for charge balance. Therefore, the particle size reduction leads to a critical increase in surface defects density, which play a critical role in the brightness and storage capacity of the nanomaterials. In general, surface defects have a deleterious effect on the photoluminescence quantum yield of light nano-sources, as it is well known for down-shifting nanophosphors.\textsuperscript{74} Surface defects in PLNPs are often...
related to inefficient shallow trapping states, making size and nano-architecture engineering methods of prime interest to limit surface quenching effects in order to maximize PLNPs initial luminescence intensity and detection time. Fu et al. have recently demonstrated that mild thermal treatment and protective shell coverage enable surface passivation without nanoparticle growth nor crystalline quality improvement, which yield a dramatic effect on Zn$_{1.2}$Ga$_{1.6}$Ge$_{0.2}$O$_4$:Cr$^{3+}$ Pers. Lum. intensity and afterglow duration, which show the influence of surface defects on properties of PLNPs. Panels republished with permission from Mandl et al., Nanoscale 12, 20759–20766 (2020). Copyright 2020 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center, Inc.

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In addition to the potential interest of surface defects for energy storage, nanoscale offers the unique opportunity to prepare core/shell architectures to endow nano-object or nano-platforms with multifunctionalities and tailor-made properties. Core/shell architectures may allow studying basic principles of energy storage at the nanoscale. In particular, unconventional Pers. Lum. charging and storage properties have been shown by coating PLNP core with an upconversion shell or clustering upconversion nanoparticles. As it has been demonstrated already for upconversion nanoparticles, broad spectra of nano-architecture combinations can be imagined for shimming PLNPs.

C. Photonic engineering

An alternative route to achieve specific properties without changing the morphological properties nor the composition of the nanophosphors consists of providing PLNPs with a devised optical environment. In fact, the combination of very recently developed scattering-free PLNP-based films with nanophotonic architectures, whose potential to improve the properties of down-shifting or upconversion nanophosphors has been demonstrated, offers new opportunities that are fully unexplored. As it has been demonstrated in a wide variety of fields from energy harvesting to sensing or light emission, nanophotonics provides enhanced light–matter interaction, which can be of interest to improve trap charging or alter afterglow dynamics. Indeed, resonant nanostructures have proven effective to tailor the emission of nanophosphor thin films for color conversion. Photonic architectures can also assist in improving the emission process in persistent materials, enabling faster radiative decay rates or an effective outcoupling mechanism to maximize the fraction of the generated light that escapes from the nanophosphor layer in a given direction, as illustrated in Fig. 4. A broad range of new PLNP functionalities can be expected by combining persistent nanophosphors and nanophotonic materials.

III. FABRICATION

A precise control of the physical dimensions of PLNPs demands novel preparation methods. In what follows, we list a number of synthetic routes with their benefits and potential limitations. In general, elaboration methods of nanosized objects can be divided according to two distinct approaches: (i) those based on a top-down strategy, in which the size is decreased from the micro scale and (ii) those based on a bottom-up strategy, in which the nano-object is grown from precursors.

The most popular top-down method aiming at elaborating PLNPs is based on the downsizing of a bulk phosphor prepared by conventional solid-state reaction (SSR) through ball milling. Despite the large number of persistent materials obtained following this approach, it provides little control on morphology or dimensions, with an average particle size within the submicrometer range rather than within the nanometric one. As a result, this technique...
is mainly inappropriate to develop nanoparticles. Alternatively, pulsed laser ablation methods combining top-down and bottom-up processes have been explored to elaborate dispersed PLNPs.\(^{89-91}\) Focusing a pulsed laser on a persistent phosphor pellet prepared by SSR leads to the production of highly reactive species that recombine to form a nanophosphor material. However, this technique generally leads to reduced amounts of material with limited size control. Besides, it is worth to mention that it has not been demonstrated yet the preparation of nanoparticles that are colloidally stable using this approach.\(^{92,93}\)

Current limitations of top-down strategies make bottom-up techniques the most widespread to attain persistent nanophosphors. Among these methods, the combustion procedure for the preparation of PLNPs was first investigated.\(^{94-97}\) This method is interesting because it typically features short reaction times and high processing temperatures, which limit the presence of surface quenchers in the nanophosphors. However, the lack of reaction control and the poor reproducibility have hindered its extended use. The glass-ceramic method was then introduced to elaborate PLNPs embedded in a transparent glassy matrix, as illustrated in Fig. 5(a).\(^{98}\) Although this method provides materials with excellent optical properties due to the high crystallization temperatures employed and a precise control of the PLNP size, it does not allow fabricating dispersed PLNPs, which limits its applicability. However, researchers find this method useful to demonstrate properties associated with specific nanophosphor size and composition, relevant for proof of principle purposes.\(^{99}\)

Nowadays, wet chemistry methods are becoming the preferred choice to elaborate PLNPs. This originates from the high homogeneity of the nanoparticles attained with a precise morphology control, the ease of tailoring the surface chemistry, which allows obtaining nanophosphors that are colloidally stable in water, and the added benefit of lower power consumption compared to previous methods. For all these reasons, sol-gel,\(^{100-102}\) hydrothermal co-precipitation\(^{51,101,103-109}\) and solvothermal methods\(^{100-118}\) represent some of the most promising synthetic routes currently under development to prepare PLNPs. Some work has also been carried out using the thermal decomposition method with high boiling point solvents at atmospheric pressure.\(^{117}\) Figures 5(b)–5(f) show few demonstrations of monodisperse PLNPs synthesized through the wet chemistry methods described above. It is important to mention, however, that the vast majority of examples reported so far do not render monodisperse PLNPs, but give rise to either nanoparticle aggregates or nanoparticles with a non-uniform shape or with a broad size distribution. Therefore, there is still plenty of room to design synthesis methods that yield tailor-made PLNPs. Wet chemistry methods allow fine adjustments of PLNP size and morphology through modifications of the nucleation and particle growth kinetics. For instance, the precipitation rate can be efficiently modified via pH adjustment, variation of the doping concentration and regulation of reactive cation release speed using complexing agents or changing the cation salt precursor.\(^{118}\)
whereas increasing reaction medium temperature or aging times can also favor the growth of nanoparticles.\textsuperscript{110} However, modifying these parameters to tune PLNPs size may also have detrimental effects on the final PLNPs composition, doping ions content, and distribution or crystalline quality. Hence, novel smart methods to solely induce particles size increase such as seed-mediated growth are currently under development.\textsuperscript{119} In general, due to the relatively low temperature employed to prevent particle growth and coalescence, wet chemistry methods fail to render nanoparticles with high crystalline quality, leading to uncontrolled defect states that are detrimental for the luminescence. Controlled subsequent thermal treatments are frequently considered to overcome this issue,\textsuperscript{117} which usually involves particle sintering resulting in non-homogeneous particles. To keep the initial nanoparticles well separated during calcination, a silica protecting shell can be deposited on the NPs surface which is further removed by etching thus keeping the initial nanometric size.\textsuperscript{108} Despite the possibility to control the morphology and the surface chemistry of the nanoparticles to improve their colloidal stability, it is challenging to find the right reaction conditions to scale up the process, which might be key to develop commercial applications.

Finally, templated growth methods deserve attention. They recently gained interest as they enable the preparation of nanoparticles with several functionalities. In these methods, mesoporous silica nanospheres (MSNs) are first prepared and the PLNPs are directly grown and calcined within the nanopores, crystal size being governed by the dimensions of the pores.\textsuperscript{120} However, the initial brightness of such persistent phosphor-loaded MSNs is somehow limited due to the reduced amount of active materials compared to PLNPs with similar size.

IV. PHYSICAL PROCESSES BEHIND PERSISTENT LUMINESCENCE

As any other photoluminescent process, Pers. Lum. occurs when an activator that has been excited by the absorption of a high-energy photon relaxes to the ground state emitting a photon with lower energy. Interestingly, persistent phosphors feature lattice defects in which the excitation energy can be stored for some time. Indeed, defects enable the energy exchange between trapped and excited states. It is important to remind that depending on the material, the energy storage can take place under the form of electron, hole, or exciton trapping. For the sake of simplicity, we will now refer to charging (or charge trapping) in the general case. External stimuli in the form of thermal energy allow trap release, which eventually leads to electron radiative de-excitation some time after the excitation source was removed. Afterglow is thus governed by: charging (A), storage (B), release (C), and light emission (D), as schematized in Fig. 6. In what follows, we provide some keys to study these phenomena and to understand the way in which they are altered in the nanoscale, which determine the distinct features of PLNPs.

A. Charging

All the physical processes involved in PLNPs leading to persistent emission are initiated by photon absorption. In most cases, relatively high energy sources such as UV lamps are used to excite PLNPs through the host bandgap to ensure a sufficiently large number of trapped charges to yield a certain level of brightness. However, for certain application purposes, different light sources may be appealing (see Sec. V). In any case, it is relevant to reveal the most efficient pathways to put energy in the traps, as this will impact the number of trapped charges and therefore the initial brightness of the materials. The spectral dependence of charge trapping is typically extracted from Pers. Lum. excitation spectra in which Pers. Lum. decays or thermoluminescence glow curves are recorded as a function of the photoexcitation wavelength. Pers. Lum. excitation spectra were used to demonstrate the charging of ZnGa$_2$O$_4$ PLNPs directly through living tissues (in the deep red range), crucial from the application point of view.\textsuperscript{27} Also, in the case of more complex systems with multiple persistent emission centers, this method can help unravelling charging mechanism, as for the persistent energy transfer in Cr$^{3+}$,Yb$^{3+}$ co-doped ZnGa$_2$O$_4$.\textsuperscript{49} In addition to the excitation wavelength, temperature and excitation intensity have an influence on the charging efficiency and need to be systematically studied to optimize the performance of PLNPs. Since the effect of these parameters on charging has only been reported and analyzed for bulk persistent phosphors, it will be necessary to study their relevance in nanomaterials. As a matter of fact, it has been reported a significant variation in the charging efficiency depending on the temperature at which the material is illuminated, as it happens when charging Eu$^{2+}$-doped persistent phosphors through the Eu$^{2+}$ lowest 5d excited state below room temperature.\textsuperscript{24} Similarly, the excitation intensity needs to be considered as well in the optimization process. Despite the number of filled traps is known to increase with the number of photons employed to excite, charging dynamics is far from trivial due to the simultaneous occurrence of optical release of the stored energy.\textsuperscript{125,126}
B. Storage

Energy storage by charge trapping through optical excitation is a key process in the evaluation of the persistent luminescence properties. A genuine understanding of energy storage requires not only to know (i) the nature of the defects related to the trapping but also (ii) their trapping properties. Indeed, the identification of trapping-related defects enables further engineering while trapping characteristics, such as energy depth and energy distribution (ΔE and δE in Fig. 6, respectively), govern the afterglow dynamics of the phosphors. Specifically, shallow traps lead to high initial brightness and fast afterglow, whereas deeper ones may lead to longer emission times after light exposure, or even storage without release at room temperature for the deepest ones (trap depth >1 eV). In what follows, we discuss the most relevant techniques to characterize energy storage properties in nanophosphors.

1. Trap nature

Understanding the physical origin of charge trapping and energy storage is challenging, as perfectly illustrated by the long-debated nature of this mechanism in canonical Eu²⁺,RE³⁺ co-doped aluminates and silicates.10,12,16,127–129 As we have already discussed, defects are central to this process, being their precise characterization one of the most difficult tasks ahead. As it happens for their bulk counterparts, defects associated with Pers. Lum. in nanomaterials are of vastly different nature, and they can be both intrinsic to the host lattice (oxygen vacancies, antisites,…) or induced by an extrinsic doping agent. Generally, state-of-the-art structural characterizations such as x-ray and synchrotron diffraction or doping ion valence state studies through x-ray absorption spectroscopies are used in bulk persistent phosphors to unravel the origin of energy storage and then, similar trapping centers are assumed for PLNPs.6,9,20,30,61,130 However, as introduced in Sec. II, new trap states appear in persistent nanophosphors. Indeed, (i) a higher number of crystalline defects in the core of the nanoparticle can be expected from the low temperature synthetic routes typically associated with nanomaterial preparation and (ii) a large surface to volume ratio yields the emergence of surface defects, being arduous to isolate the effect of each of these. This highlights the need of developing techniques specifically devoted to this aim. In the meantime, Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR) have proven useful to study structural defects in standard ZnGa₂O₄:Cr³⁺ PLNPs, and correlate structural and optical properties. Efficient trapping is related to antisite defect pairs (GaZn°) in Cr³⁺ neighborhood.131 Also, Ga NMR, which enables the quantification of Ga inversion in the spinel structure (Ga occupying a Zn tetrahedral site, i.e., GaZn°), helped to show the impact of thermal treatment to rearrange Ga cations within the structure of the nanophosphors.108 EPR has also proven useful to probe Cr³⁺ local environment and to quantify Cr³⁺ neighboring antisite defects, which are effective to analyze charge trapping in standard ZnGa₂O₄:Cr³⁺ PLNPs.108,129 EPR has shown the positive effect of thermal annealing on the local environment of Cr³⁺ in ZnGa₂O₄:Cr³⁺ nano glass-ceramics.79 The widespread use of a shell coverage to enable annealing and further processing of the nanophosphors without aggregation or to endow them with multifunctional properties highlights the need to study surface defect states and the related trap structures in nanomaterials. However, nanophosphor size tuning generally comes from different preparation conditions which also has an influence on the crystallinity and/or composition of the nanoparticles, making particularly challenging to study and evaluate the potential of surface defects for efficient Pers. Lum. storage.73,75,76

2. Trap depth and distribution

Unravelling the nature of traps is not sufficient to understand and eventually improve persistent decay dynamics. In order to study storage dynamics, the central piece of information to characterize defects is related to the depth and distribution of the involved traps. Indeed, midrange trap depths of typically 0.4–1 eV, ideally around 0.65 eV are commonly accepted as suitable for room temperature persistent emission, whereas shallower traps might lead to rapid afterglow decays and deeper ones to energy storage without release at room temperature. To study the depth and distribution of traps in persistent phosphors, thermoluminescence (TL) is the most employed method and has been proven very effective to analyze bulk persistent phosphors. This technique is based on the gradual heating of the phosphor after being charged using light or x rays. Specific thermal energy triggers charge recombination at an active cation, hence leading to thermally stimulated luminescence. Position and width of the glow peaks provide information on the energy depth and distribution of traps. Shedding light on traps’ characteristics appears to be more complex in nanomaterials, owing to the very different nature of defects. This is generally reflected in poorly resolved and abnormally large TL glow curves, as observed for ZnGa₂O₄:Cr³⁺ and La₂Al₂O₆:Cr³⁺,Sm³⁺ nanoparticles.61,107,134,135,136 Nevertheless, the TL comparison of dispersed ZnGa₂O₄:Cr³⁺ PLNPs with nano glass-ceramic and bulk versions of the same persistent material has allowed to link surface defects to inefficient shallow traps.136 On top of this, TL results combined with EPR measurements indicate that improving crystalline quality leads to less distributed trap states (antisite defect pairs) with an increased energy depth, more suitable for room temperature Pers. Lums.29,136 Similarly, systematic TL glow curve shape analyses of co-doped Y₃Al₅Ga₁₂O₃₅ PLNPs elaborated with different particle size and crystalline quality enable the association of shallow traps to surface defects in these compounds.73 Pushing TL analyses with combined heavy-going “Tmax − Tmin” TL measurements137 and Randal and Wilkins calculations138,139 allow to unravel the complex trap structure (traps number, distribution, and depth) and explain the afterglow dynamics, as demonstrated in SmO₂:Eu³⁺ PLNPs.140 Finally, it is important to mention that TL measurements depend on numerous experimental parameters (excitation characteristics, heating rate, initial T), hence not allowing a direct comparison between the storage capabilities of PLNPs obtained in different works. For this particular purpose, it is noteworthy to highlight a recently developed method based on absolute photon counting that enables universal comparison of the absolute storage capacity of persistent phosphors.141

C. Release

Once the optical energy is stored, several pathways enable its release and recombination, leading to delayed photon emission.
Among others, thermal and optical releases have attracted the attention of the scientific community. Indeed, thermal energy brought by ambient temperature acts as the external stimulus to trigger the delayed emission in most PLNP applications. TL is a good technique to study this process. Recently, the optimal temperature for most efficient photon release has been carefully investigated and a connection with experimental TL glow curves has been established. On a different note, charge de-trapping can also be triggered by light, leading to optically stimulated luminescence (OSL) after charge recombination on the active cation but also due to charge redistribution within traps. Recently, this optical stimulation is getting increased attention in the community. It may bring about new opportunities for the application of PLNPs, as NIR stimulation enables the redistribution of charges from deep traps (trap depth >1 eV) toward efficient traps for room temperature Pers. Lum. as illustrated in Fig. 7(a). Also, optical stimulation could work as a novel readout tool for data storage. However, light-induced charge de-trapping highlights that, during charging, energy storage and release occur simultaneously, thus limiting trap filling. This has been experimentally demonstrated in bulk Eu\(^{2+},\)Dy\(^{3+}\)-co-doped strontium silicates and aluminates due to the relatively high absorption cross sections of the involved filled traps, as shown in Fig. 7(b). Consequently, one of the main challenges to go one step further toward PLNPs applicability relays on acquiring a better understanding of the properties of filled traps, aiming to control energy storage and release dynamics. Up to now the importance of this effect has only been studied and proven critical for applications in bulk persistent phosphors. Transient absorption spectroscopy, which has already demonstrated potential to study intermediate excited states of organic films, represents a promising tool to investigate generated metastable filled trap states with the same goal in mind.

**D. Light emission**

After trapped charges release, the last step of the process is the radiative de-excitation, leading to the observed delayed photon emission. As in any other photoluminescent material, this final step drives the afterglow chromaticity, but it is also the last process determining the resulting Pers. Lum. efficiency through the ratio between radiative and total rate of the transition. The spectral characterization of the afterglow provides important clues on the doping ion environment involved in the process, as the N2 line in the Pers. Lum. spectrum of Cr\(^{3+}\) in ZnGa\(_2\)O\(_4:\)Cr\(^{3+}\) PLNPs demonstrated the role of neighboring antisite defects. In addition, the radiative rate of the transition, which is directly related to the photoluminescence quantum yield (PLQY) of the material, is somehow complex to measure for Pers. Lum. materials since their optical excitation induces PL, charge trapping, and release simultaneously. Before measuring the PLQY, a certain time should be waited to ensure reaching the equilibrium state between all the involved processes. In addition to this time dependence, a significant drop of the PLQY with excitation intensity, from 71% to 54%, has been demonstrated for bulk SrAl\(_2\)O\(_4:\)Eu\(^{2+},\)Dy\(^{3+}\) materials, explained by the high absorption cross section of the filled trap, leading to the increase in the absorption strength of the material while charging, in stark contrast with conventional trap-free PL phosphors. Similar characterization on PLNPs is yet to be done.

The use of novel PLNPs is often motivated because of their longer persistent decay. However, quantitative characterization of the afterglow is not as straightforward as it looks, due to the difficulty to use absolute units, being difficult to establish a rigorous comparison between materials prepared in different laboratories. Afterglow radiance or luminance should be respectively measured in radiometric (W/m\(^2\)/sr) or photometric...
units (cd/m²), the latter considering human eye sensitivity in low intensity conditions. Besides, the absolute comparison of persistent decays requires certain material specifications related to the amount of excited material, the number of doping agents, and the number of trapping center or radiative rate of the transition. As demonstrated for bulk persistent phosphors, these pieces of information might be difficult to attain in powder samples or opaque ceramics. Therefore, the processing of PLNPs as persistent transparent (scattering-free) thin films or persistent micro-powders embedded in transparent matrices to avoid scattering losses and control light propagation throughout the layer brings new opportunities to enable comparative Pers. Lum. studies.

Finally, the ultimate tool for the precise characterization of Pers. Lum. should allow measuring the fraction of stored energy that results in the emission of light, i.e., the Pers. Lum. efficiency. It will steer research and development of efficient persistent materials. As introduced by Botterman et al., the same quantity can be also referred to as “afterglow quantum efficiency,” and defined as the ratio between emitted photons and trapped charges. Its estimation requires a genuine understanding of all the processes ruling the luminescence intensity measurements and has been only performed for standard SrAl₂O₄:Eu²⁺,Dy³⁺ being a challenge to the determination of afterglow efficiency in nanomaterials.

V. OPPORTUNITIES OF PERSISTENT LUMINESCENCE NANOPARTICLES

PLNPs are interesting for a wide variety of applications. In order to select a specific Pers. Lum. nanomaterial for a particular application, it is important to establish the source employed for charging and the targeted delayed emission chromaticity and dynamics. In what follows, a few examples are presented together with the added value that PLNPs provide, highlighting the most suitable nanophosphor for each application. Finally, recent advances along with future directions are mentioned.

FIG. 8. (a) Comparison of mouse in vivo imaging using PLNPs and QDs, highlighting the unprecedently high imaging signal to noise ratio enabled by PLNPs utilization. (b) Comparison of the PL/PLE spectra (black) with the Pers. Lum. charging and emission spectra (green) illustrating the possible in vivo activation of ZnGa₂O₄:Cr³⁺ PLNPs. Reprinted with permission from Maldiney et al., Nat. Mater. 13, 418–426 (2014). Copyright 2014 Springer. Schematic of the fabrication (c), therapy and multimodal imaging (d) of multifunctional nanospheres. High resolution SEM (e) and TEM (f) images (scale bars: 100 nm) of the multifunctional nanomaterials. Reprinted with permission from Zou et al., ACS Appl. Mater. Interfaces 13, 9667–9680 (2021). Copyright 2021 American Chemical Society.
A. Theranostics

The initial interest of PLNPs for \textit{in vivo} imaging arises from their unique delayed emission properties, preventing both UV light-induced tissue damage\cite{114,115} and living-tissue autofluorescence,\cite{116} hence leading to unprecedented detection sensitivity [Fig. 8(a)].\cite{117} However, to go from the green afterglow of bulky \textit{SrAl}_{12}O_{19}:Eu^{2+},Dy^{3+} PLNPs to suitable PLNPs actually usable for \textit{in vivo} applications, both morphological and spectral specifications needed must be carefully designed.\cite{118} Particle size has a critical influence on important processes that take place after intravenous administration in the organism such as their circulation, biodistribution, and excretion pathways. It is accepted that the diameter of nanoparticles for \textit{in vivo} intravenous use should be in the range of 10–100 nm although the upper threshold size is not yet well defined.\cite{119} After introduction into the bloodstream, the particles travel to the organs through the blood vessels. Retention of the NPs in the circulatory system should then be long enough as to allow them to reach the region of interest either for visualization through bioimaging or for therapy. Since the kidney is the first site where NPs can be eliminated, the lower size bound has been established based on the glomerular filtration: particles smaller than 10 nm will be filtered and cleared from the blood.\cite{120} Therefore, it is important to use NPs bigger than 10 nm for successful evasion of the renal elimination. The upper size limit is determined on the basis of the clearance action of the mononuclear phagocytic system (MPS). The MPS is a component of the immune system whose function is to capture and eliminate inert particles, bacteria, viruses, old cells, and other substances that generate a direct or indirect toxic load in the body. The MPS consists of phagocytic and Kupffer cells located in the spleen, lymph nodes, and liver. Particles with a diameter greater than 200 nm will activate the MPS and be quickly removed from the bloodstream.\cite{121} Within the 10–200 nm interval, the optimum NPs size is not yet clear although a diameter lower than 100 nm is usually preferred based on biodistribution studies.\cite{122} In fact, about 50 nm has shown the greatest cellular uptake in most experimental analyses.\cite{123,124,125} However, experiments from animal models also suggest that 150 nm, neutral or slightly negatively charged entities show good biodistribution\cite{126} and can well move through tumor tissue.\cite{127} It is likely, therefore, that the ideal NP size will be diagnosis- or disease-specific. As for the persistent emission wavelength, green Pers. Lum. of \textit{SrAl}_{12}O_{19}:Eu^{2+},Dy^{3+} is not suitable for \textit{in vivo} imaging due to the low penetration depth of visible light in living tissues. For this reason, persistent emission wavelength must be located within one of the three partially transparent biological windows, i.e., BW-I (650–950 nm), BW-II (1000–1350 nm), or BW-III (1500–1800 nm).\cite{128,129,130} In their pioneer work, le Masne de Chermont \textit{et al.} defined these specifications and elaborated \textit{Ca}_{0.1}\textit{Zn}_{0.9}\textit{Mg}_{0.6}\textit{Sb}_{0.4}\textit{O}_{6}Eu^{2+},Dy^{3+},Mn^{2+} PLNPs by sol-gel. They also injected the PLNPs in a mouse after UV excitation, enabling imaging through the living tissues 1 h after the excitation of the nanoparticles.\cite{131} This pioneering work opened the door to the development of a number of novel nanophosphors aiming at increasing the afterglow brightness and duration, and thus expanding the detection window of the small quantity of nanoprobes injected inside the living body.

Among others,\cite{132,133,134,135,136,137,138,139,140} \textit{ZnGa}_{2}O_{4}:Cr^{3+} PLNPs have raised particular interest, not only due to their long Pers. Lum. in the deep red range, within BW-I, but mainly due to the unprecedented possibility of Pers. Lum. direct activation—see Fig. 8(b)—and reactivation (\textit{via} NIR-induced trap stimulation) through living tissues.\cite{141,142,143,144,145} Even though several other materials have been proposed for these applications,\cite{146,147} since its discovery most contributions focused on (i) finding routes to prepare \textit{ZnGa}_{2}O_{4}:Cr^{3+} nanophosphors of controlled size and morphology, which are colloidaly stable, and (ii) the understanding and optimization of \textit{ZnGa}_{2}O_{4}:Cr^{3+} Pers. Lum. properties. As discussed in Sec. III, wet chemistry syntheses are the preferred fabrication methods for this purpose. Synthetic conditions such as the pH, the precursors nature, the doping content, the reacting temperature, or the presence of surfactants are still being explored aiming at reaching a better control on the uniformity of the nanoparticles and their stability in water. For now, the main advancements regarding the optimization of the properties have been made by composition engineering through matrix modification and co-doping. Indeed, isovalent substitution have been shown to provide efficient tuning of the trap depths. For instance, substituting \textit{Ga}^{3+} by \textit{Al}^{3+} increased the trap depths, hence slowing down the decay kinetics and favoring light-induced Pers. Lum. reactivation.\cite{148} Moreover, aliovalent substitutions, such as two \textit{Ga}^{3+} by one \textit{Zn}^{2+} and one \textit{Sn}^{4+} (or Ge^{4+}) appeared as effective strategies to both enhance the storage capacity and shift both the excitation and emission wavelength toward longer wavelengths in the deep red/NIR region.\cite{149,150,151} In their pioneer work, le Masne de Chermont \textit{et al.} showed interesting for increasing the initial brightness (\textit{Bi}^{3+})\cite{152} and to shift the Pers. Lum. wavelength toward the NIR (\textit{Yb}^{3+}).\cite{153,154} Although most results have been attained on bulk materials, and presented as proofs of concept, working in the nanoscale is essential, as pointed out recently.\cite{155,156,157,158,159}

Next challenges ahead in the field could be summarized as follows: (i) reaching Pers. Lum. deeper in the NIR range, (ii) designing PLNPs with imaging multimodality, and (iii) designing PLNPs that allow simultaneous imaging and therapy. Indeed, persistent NIR emission within BW-II or BW-III would allow to reduce further the scattering, absorption, and autofluorescence. To this end, change of the transition metal (\textit{Ni}^{2+}) cations doping,\cite{160,161} specific RE (\textit{Yb}^{3+}, \textit{Er}^{3+}, \textit{Nd}^{3+}) co-doping and persistent energy transfer,\cite{162,163,164,165,166,167} and host modification\cite{168,169,170,171,172,173,174,175,176,177} approaches have been proposed. In order to increase the spatial resolution of PLNPs probes, while keeping the high sensitivity of optical imaging, multimodal imaging \textit{via} simultaneous magnetic resonance imaging (MRI) appeared as a promising strategy.\cite{178} \textit{Gd}^{3+} retained the attention as the MRI probe and its functionality has been incorporated through co-doping,\cite{179} functionalizing surfaces,\cite{180} or using shell coverage with \textit{Gd}^{3+}-based species.\cite{181} Finally, the combination of imaging and therapy through devised drug release or direct photothermal and/or photodynamic therapy is being explored, using multifunctional nanospheres containing PLNPs, MRI contrast agents for imaging but also radioactive \textit{Ga} and chemotherapy drugs for therapy, as illustrated in Figs. 8(c) and 8(f).\cite{182,183,184,185,186}

\textit{In vivo} imaging is by far the most accomplished application field of PLNPs. In what we discuss next, proof of concepts for the bulk persistent phosphors have been demonstrated but a full development at the nanoscale remains elusive.
Next-generation information storage technologies are sought after to enable a fast processing of information. The ability of persistent phosphors to store and emit back optical energy after external stimulation makes them interesting to develop materials for optical data storage. Due to exceptional re-writability and high storage capacity, which come with low ecological impact, persistent phosphors are being investigated as optical information storage materials. Devised external stimulation allows juggling between two optical states in these materials. Recording is performed using a high energy source that leads to charge separation and trapping, whereas reading is through light emission triggered by thermal, optical, or mechanical stimulation. Depending on the conditions of utilization, such as the temperature at which the information need to be stored and read out, charge trapping characteristics will strongly vary and require careful adjustments. In the general case of stable information storage at room temperature and readout by an optical stimulus at room temperature, deep traps engineered for efficient OSL are desired.

Nanophosphors enable optical data storage below the light-diffraction limit and data multiplexing, which place these nanomaterials in the forefront of the race toward achieving high storage densities. The main challenge in this field of application is related to the preparation of PLNPs with sufficiently high crystalline quality and low density of surface defects to avoid trap distribution broadening, which prevents the spontaneous de-trapping at room temperature that would result in information loss.

C. Anticounterfeiting

The growing worldwide exchanges of money and valuables have undoubtedly led to an increased circulation of counterfeits, making the development of anticounterfeiting agents a priority in the bank security field. UV fluorescent inks are well known for this security purpose, as, for example, present in the form of glowing stars and threads in Euro and US dollar currencies, to limit their illegal reproduction. The security they offer is though limited due to their widespread usage and the single UV fluorescence check mode. Using persistent phosphor-based anticounterfeiting agents enables a supplementary time-gated security check mode, which is the continuous light emission once the UV excitation is stopped. Combining persistent phosphor-based anticounterfeiting agents with regular UV fluorescent ones can significantly increase the security, as displayed in Fig. 9.

Optical specifications of PLNPs will be linked to requirements of the anticounterfeiting inks. In the case of bill anticounterfeiting, for instance, codes need to be efficiently read out by the eye after a rapid passing under a UV lamp. For this reason, the preferred choice materials would be those with high initial brightness and emission in the spectral region where eye sensitivity peaks. Up to now, developments on Pers. Lum. phosphors size down to the nanoscale would enable printing motifs with higher resolution. However, printing motifs invisible by naked eyes under daylight using translucent inks requires the use of reduced amount of materials and therefore a reduced number of emitted photons compared to bulk persistent phosphor-based resins used for night signalization, being a challenge to the elaboration of bright PLNPs in the visible range.

D. AC-LEDs

Most domestic lighting is currently provided by white LEDs, combining a blue LED chip to a YAG:Ce3+ color converting phosphor layer. The widespread usage of these systems comes from their low power consumption, their low production cost, and their long lifespan. However, current LEDs need to work in DC mode, requiring AC to DC conversion that inevitably led to a 30% electric power loss. AC-LEDs, that can be powered directly by urban power supply and therefore further reduce both production cost and power losses, have recently been proposed. Nevertheless, powering LED chips with alternating current inevitably produces successive light and dark stages that can be perceived as flickering and lead to users discomfort, thereby limiting their potential use. Taking advantage of the unique delayed emission persistent phosphors provide, they have been proposed as potential converting layers to minimize the intensity gap between light and dark stages, hence reducing the perceived flickering. Among the physical processes involved in persistent emission, those that are more critical for AC applications are (i) the charging and release dynamics, which should match the light and dark periods induced by AC frequency (50–60 Hz) powering, being fast decays in the 10 ms range and shallow traps targeted and (ii) charging must be triggered by LED chip emission, which occurs in the blue spectral range.
range. Complex cerium doped garnets recognized for their possible Pers. Lum. blue activation through cerium absorption bands\textsuperscript{43} have been engineered to have Pers. Lum. decays matching the alternating frequency, resulting, for instance, in Mg\textsubscript{2}Y\textsubscript{2}Ge\textsubscript{2}Si\textsubscript{5}O\textsubscript{14}:Ce\textsuperscript{3+} and Gd\textsubscript{3}Al\textsubscript{2}Ga\textsubscript{3}O\textsubscript{12}:Ce\textsuperscript{3+},Cr\textsuperscript{3+} persistent phosphors with flickering reducing powers up to 40%.\textsuperscript{28} Despite these results are promising, further research is needed to bridge the gap between material development and device integration in commercial applications. PLNPs might be of interest to develop scattering-free conversion layers, which may offer opportunities to design devices with new functionalities.

VI. SUMMARY

As a result of the success of the afterglow properties of persistent luminescence bulk emitters, and the global growing interest in nanotechnologies, PLNPs are an attractive platform to realize further achievements in this field. Herein, we present most recent advances in the design of strategies—involving size, composition, and photonic engineering, fabrication techniques, and applications of PLNPs, ranging from the most established in vivo imaging to other more exploratory and unconventional ways of generating light. In addition, the physical processes of persistent luminescence, from charging to light emission through energy storage and release, are explained in detail for a better understanding of the afterglow mechanism. Although substantial and rapid progress has been made in both the design and fabrication fronts, there are still a number of constraints that need to be overcome, including the development of colloidally stable nanoparticles of controlled size, shape, and composition, in which structural defects can be engineered to provide efficient persistent luminescence. Besides, issues related to large-scale synthesis, aiming at maximizing production yield while limiting by-products, are expected to have a major economic and environmental impact. Advanced physical and chemical characterization is also required to study the processes involved in persistent emission, to comprehend how they are altered in the nanoscale and further demonstrate the potential of persistent nanophosphors. A precise understanding of the nature and role of defects in persistent nanomaterials remains also elusive. For bioimaging applications, new compositions are required for the design of multifunctional PLNPs, and more efforts need to be devoted to analyzing their toxicity or their potential in the diagnosis and treatment of diseases. Finally, the implantation of PLNPs in other fields, such as information storage, ant-counterfeiting, or AC-LEDs, requires significant work related to both material and device integration. In short, persistent nanomaterials hold great promise as nanobatteries for light, but further development is still required to unleash their full potential.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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