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Recent advances and prospects of persistent luminescent materials as inner secondary self-luminous light source for photocatalytic applications

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**ABSTRACT**

Nowadays, materials with persistent luminescence (MPLs) have attracted growing attention in the catalytic field because they can act as an inner light source to irradiate the photocatalytic materials (PCMs) and sustain their photocatalytic activities in the absence of the external irradiation source. The motivation of the present work is to provide a review of the MPL@PCM composites that are of interest for both photocatalytic and lighting fields. In terms of the unique luminescence of MPLs and the principal optical properties of PCMs, the review is organized as follows: first, we categorize and discuss a number of rare-earth (RE)/non-RE-doped MPLs and bulk MPLs, along with their emission/persistent ranges and potentially-coupled PCM counterparts. Then, we present and discuss the intrinsic nature of the photocatalytic properties and the working principles of the MPLs that have been coupled with the PCMs. In the 4th section, we summarize the principal synthesis strategies that are reported for the MPL@PCM composites. At last, by taking advantages of some reported works, we exhibit the photocatalytic applications of the MPL@PCM composites, and give a summary, perspectives, potential challenges and future development directions to this review. With the profound impact of the persistent luminescence, we believe that this review will be not only of particular interest to the scientists in the lighting field, but can also attract those with backgrounds in the fields of the environmental science, materials and physics, chemistry, energy fuels, and their coupling subdivisions to jointly address some of the major environmental issues like degradation of organic waste, removal of gas-phased materials, etc.

**Key words:** persistent luminescence; inner light source; self-luminous; rare-earth (RE); non-RE; photocatalysis.
1. Introduction

Photocatalytic materials (PCMs) are a type of important materials that enable addressing a number of world-wide environmental problems such as organic degradation and water waste purification. Normally, these PCMs need to be exposed to an external irradiation source (e.g., UV [1-2], visible [1-3], artificial solar [4-5], near infrared (NIR) light [6]), so long to sustain their photocatalytic activities continuously by absorbing the incoming photon energy from the irradiation source. In the past years, more than tens of thousands of PCMs are discovered, such as Er$^{3+}$-Yb$^{3+}$-TiO$_2$ [7], La$^{3+}$-doped TiO$_2$ [8], Mn$^{2+}$-Co$^{2+}$ co-doped TiO$_2$ [9], Ag$_3$PO$_4$:Bi$^{3+}$ [10], metal-organic frameworks (MOFs) [11], graphene quantum dots (GQDs) [12], carbon dots (CDs) [13], CdS-based molecular Ni catalyst [14], two-dimensional (2D) nanomaterials (e.g., WS$_2$ / MoS$_2$ nanocluster [15], MoS$_2$ / graphene cocatalysts [16]), perovskite CsPbBr$_3$ QDs / graphene oxide [17], semiconductors (e.g., TiO$_2$ [18], ZnO [19], ZnS [20], BiVO$_4$ [21-22], and BiOCl [23]), and the coupled nano- and micro-composites (e.g., perovskite CsPbBr$_3$ QDs / graphene oxide [17], Ag-AgCl [24], MoS$_2$-TiO$_2$ [25], TiO$_2$-MOFs [26], TiO$_2$-Au [27], and BiVO$_4$-BiOCl [28]). However, they can continuously show the photocatalytic activity only as long as an external irradiation source is on. Once the irradiation source is off, the photocatalytic process terminates immediately. Thus, an external irradiation source that enables providing the continuous irradiation energy is the primary factor to preserve the photocatalytic process. In the context of how to alleviate the environmental pollution and energy crisis, keeping a photocatalytic reaction under an electrically-powered irradiation source is not a sustainable option due to the continuous consumption of energy. This is particularly crucial in the under-developed and poor regions that frequently face the shortage of electric power. In this concern, exploring alternative strategies that can sustain the photocatalytic reaction but do not need the external irradiation source have been focused in the past years, and they have led to great concerns to those materials with persistent luminescence and the relevant self-luminous MPL@PCM associations. In fact, the self-luminous working principle of these MPL@PCM composites is mainly based on the storage capacity of the MPLs and its correlated persistent luminescence as an inner light source for the PCMs, making it possible to generate a continuous self-induced photocatalytic activity when the external irradiation source is off. Moreover, it generally only needs to charge the MPLs in a short time (i.e., usually limited to a few seconds or minutes), by use of either x- [29-32], α- [32], β- [32], and γ-ray [32-33], UV [34-37], visible
The persistent luminescence, which is also called long-lasting or afterglow luminescence [42-45], can be traced back more than one thousand years ago. In ancient China (about Tang dynasty), the legendary glow-in-the-dark pearl was the most famous natural persistent material frequently used for fabricating artworks and ornaments like the paintings and luminous wine cups [42-43, 46-47]. Nowadays, with the continuous progresses in chemical- and physical-synthesis routes and in-depth understanding on the persistent working principle (i.e., the involved physics), we can easily design and manufacture numerous inorganic and organic MPLs with the persistent durations broadly ranging from several seconds up to several hours and even to several days in few special cases and the persistent spectral regions spreading from UV, visible, and to NIR light. Because of these unique persistent properties, a number of application opportunities in diverse fields have been discovered, including the photocatalysis [48-49], security and anti-counterfeiting purposes [50-51], solar energy [52], biosensing [53], information data storage [54], biological imaging [55-56] etc. Noteworthy is the recent design demonstration — highly efficient photocatalytic reaction for the organic pollutants degradation and hydrogen evolution from the water through the self-activated (i.e., also called the external irradiation-free self-luminous) plasmonic photocatalyst composite g-C3N4@Ag@SrAl2O4:Eu2+,Dy3+ [57].

During the last decade (i.e., 2009-2019), more than 40,000 articles (including the review and research articles), retrieved from Web of Science by tracing the key words “photocatalysis” or “photocatalyst”, have been published. In particular, all the mainstream publishers indexed by Web of Science have reported the review articles (> 2,000). To the best of our knowledge, however, among these publications, there are only 6 review papers that have involved the progress of the MPLs that are of interest for the photocatalytic fields, whose amounts are very few compared to “> 2,000” volumes of the reviews dedicated “photocatalysis” or “photocatalysts”. More Specifically, Liu et. al. [48] reviewed the light-conversion phosphor-based composites for photocatalysis (i.e., up-conversion-, downconversion-, and afterglow-based phosphor composites), but they only listed four types of MPLs (CaAl2O4:Eu2+,Nd3+; SrAl2O4:Eu2+,Nd3+; BaAl2O4:Eu2+,Nd3+; BaZrO3:Mg2+); Sakar et. al. [58] in 2018 summarized the photocatalytic materials and the relevant reaction mechanisms under light and dark conditions and used the “long-afterglow phosphor” as a key word, but they just considered a type of long-persistent phosphors as an example (Sr2MgSi2O7:(Eu,
Dy)) to illustrate the photocatalytic reactions and did not go through the working principles of “persistent-photocatalytic” composites; Huo et al reviewed the design, synthesis, and applications of phosphorescent cyclometalated platinum complexes [59], but they restricted to this category of organic and briefly commented on the photocatalysis (by using less 300 words); Li et al [60-61] showed the persistent photocatalysis of continuously flowing gas-phase nitric oxide based upon the CaAl$_2$O$_4$:(Eu,Nd)@rutile TiO$_2$N$_2$ composites, but they only gave one type of MPLs; Qiu and his coworkers [44] reviewed the fundamentals and general applications of MPLs based on the archival literatures prior to 2016, with focusing on the synthesis methods, persistent mechanism, measurement characterization, classification of the MPLs, but only seven MPLs were introduced in correlation with the photocatalytic applications. Obviously, these reviews confine either to a specific type of photocatalytic compound or to limited MPLs, thus failing to account satisfactorily either for the latest progresses and achievements on the “persistent-photocatalytic” composites or for the prospects of other MPLs that can potentially act as an inner irradiation source to sustain the photocatalytic activity. This is one of the major motivations for us to undertake the present review whose synoptic organization is illustrated in Figure 1.

We start by reviewing in Section 2, with disclosing the most attractive MPLs for fabricating the MPL@PCM composites and their photocatalytic application. These MPLs are classified based on the nature of their dopants, irradiation wavelength, emission spectral regions and peak positions, as well as persistent duration. As we can see, most of MPLs have not yet been tested for photocatalytic purposes, opening a wide field of study in the matter. Then, we dedicate to review the mainstream PCMs and reported MPL@PCM composites, with paying special attention to the working principles and mechanistic models involved in the self-luminous MPL@PCM composites (Section 3), and to some selected synthesis methodologies of relevant MPL@PCM counterparts (Section 4). Meanwhile, in Section 4, we also select 29 SEM / FESEM / TEM / HRTEM images of the MPLs, PCMs, or MPL@PCM system to illustrate the design consideration. In Section 5, some typical examples of the MPL@PCM composites, which are applied for, e.g., degradation of organic molecules, removal of poisonous gas-phased materials, and water splitting into H$_2$ and O$_2$, and so forth, are reviewed. Then, in Section 6, we summarize this review and, from the side of our logical thinking, disclose some perspectives, insights, potential challenges and future directions of the use of the MPL@PCM composites for other emerging applications, including but not limited
to the lighting and photocatalytic fields.

2. Principal MLs and relevant optical properties

According to the database from the Web of Science database, more than 20,000 articles associated with the key word of “long persistent luminescence”, “afterglow luminescence”, and/or long-lasting luminescence” have been reported. In this case, it is impossible for us to list all in this review; instead, we have chosen to review the MPLs that have been reported to work with the PCMs or feature potentially attractive contributions for the “persistent-photocatalytic” purpose. Along with those materials featuring the up-converted persistent luminescence, the MPLs are classified based on the category of their emitting species, including the rare-earth (RE)-doped MPLs, transition metal (TM) ions doped MPLs, ns²-type cation-doped MPLs, self-activated bulk MPLs and NIR-converted MPLs.

2.1 RE-doped MPLs

In RE-doped MPLs, the persistent luminescence mainly originates either from d-f transition RE ions (i.e., Eu³⁺, and Ce³⁺) [31, 33-34, 42, 44, 49, 57, 60-106], well-shielded 4f (e.g., Eu³⁺, Pr³⁺, Tb³⁺, Sm³⁺, Tm³⁺, Gd³⁺, and Dy³⁺) [35-37, 51-52, 107-142], or from the coupling arrangements of these RE ions [33-34, 38, 42, 44, 52, 57, 64, 67-69, 72-77, 79-82, 85-89, 92-94, 96-99, 101, 103, 105-107, 118, 120, 125, 127, 134]. Besides, with the purposes of creating the defects, modifying the trap depths, or constructing the energy transfer paths, the non-RE (e.g., Bi³⁺ [91, 130, 141], Mn²⁺ [90, 92], Ce³⁺ [40, 56, 84, 87]), or some of other RE (e.g., Nd³⁺ [49, 61, 70-71, 142], Pr³⁺ [38, 56, 98, 101, 107], Ho³⁺ [95, 125] etc) are also often used as the co-dopants for RE-doped MPLs.

The d-f RE (i.e., Eu³⁺, and Ce³⁺) doped MPLs (Table 1, and Figure 2) can exhibit a broad range of fluorescent and persistent luminescence, and the spectral edge can start either from the visible or from the UV, and end to the NIR region, depending on the nearby chemical microenvironment that the d-f RE ions have experienced. Although the d-f RE-doped MPLs usually feature broad emission bands (Figure 2a), they could also show multiple bands (i.e., including the emission and persistent bands) if the related crystal contains multiple crystal sites (Figure 2a(iii)) or in case of inefficient energy transfer from the host or the co-doping ion to the d-f transition RE ion [77-78, 82-85, 87, 96-98]. In addition, accessing the d-f RE MPLs needs a reductive atmosphere such as the N₂ + H₂, and N₂ + CO atmosphere, so as to reduce the europium and cerium ion with the high valence, i.e., from Eu³⁺ and Ce⁴⁺ to Eu²⁺ and Ce³⁺, respectively. Considering different persistent
spectral ranges and their potentially-matched PCMs, in Table 1, we summarize not only the $d$-$f$ RE emission or persistent positions but also relevant persistent durations, although many of them use the same $d$-$f$ RE ion as the emission or persistent activator.

Unlike the $d$-$f$ RE MPLs, the well-shielded $4f$ RE-doped MPLs are characterized by the persistent lines analogous to their respective fluorescent lines and colors (Table 2, and Figure 3). Different $4f$ RE ions show their own spectral properties (i.e., the fixed spectral shape and peak positions, sharp lines and narrow band width), independent of the crystal lattice. The persistent luminescence is then confined to the given spectral regions, which limits the spectral overlap with the absorption of PCMs. This is one of the major reasons why the $d$-$f$ RE ions are often used to design the “persistent-photocatalytic” MPL@PCM composites rather than the $f$-$f$ RE ions (next section). In the cases of some $4f$ RE ions like Dy$^{3+}$ [129, 144-146], Tb$^{3+}$ [144-145, 147-148], and Eu$^{3+}$ [145, 148-149] ions, the dominant persistent lines usually appear beyond 450 nm (Figure 3a, Figure 3b(iii)) and overlap only very weakly the optical absorption of a few PCMs. However, we still can find the $4f$ RE like Tb$^{3+}$ or Tm$^{3+}$ have a wide range of emissions individually distributed in the visible region, and some of their emission lines fall in the UV region. Thus, their energy can be easily re-absorbed by the PCMs, such as the Sr$_4$Al$_4$O$_{25}$:Tb$^{3+}$ [114], Ca$_3$Ga$_2$Ge$_2$O$_{12}$:Tb$^{3+}$,Tm$^{3+}$ [118], CdSiO$_2$:Tb$^{3+}$ [115, 150], and Ca$_2$SnO$_4$:Tm$^{3+}$ [132]. As a result, narrow emission lines of the $4f$ RE ions can allow unique coupling with a given specific absorption band of PCMs with which the $d$-$f$ RE ions cannot have. That is to say, in principle, they could be used for coupling some specific PCMs if the MPL@PCM designer wants the dominant emission lines of the $f$-$f$ RE ions to couple with the strongest absorption of the PCMs. For example, the Eu$^{3+}$-dominant line of 616 nm matches with one of the surface plasmon resonance (SPR) absorption peaks (~615 nm) of Ag nanoparticles (NPs) in the ZnO:Co/Ag PCMs [68]. Although this is based on the spectra-selective characteristics and still has not been proved by previous works, such MPLs also show the potential desirable for the photocatalytic reactions in the absence of external irradiation source.

2.2 Transition metal (TM)-doped MPLs

Previous research works dedicated to TM-doped MPLs mostly concern 3$d$ ions like Mn$^{4+}$ [142, 151-157], Cr$^{3+}$ [39, 55-56, 158-197], and Mn$^{2+}$ (Table 3) [53, 90, 92, 194, 198-235]. Among them, Mn$^{4+}$-doped MPLs are still undeveloped, the number and type of which are limited. Generally, in an oxidic environment, exciting with the UV and visible light, the Mn$^{4+}$ MPLs exhibit an
excitation range broadly covering the whole UV and part of the visible light (usually ≤ 550), but a relatively fixed and narrow persistent spectral band in the range of 600-800 nm (Figure 4). In many reports [142, 150-155, 157], the red Mn$^{4+}$ luminescence is also referred to the NIR or deep red, because its emission range (or part of the emission wavelength) falls precisely in the NIR optical window (i.e., 650-1350 nm). Because of the site occupancy preferential issue or the crystal field strength change, however, the Mn$^{4+}$ enables showing different dominant emission positions (Figure 4a(iii-iv)), but basically sustains in the range of 600-800 nm, allowing the persistent range of Mn$^{4+}$-doped MPLs to match those PCMs with the absorption wavelength larger than 600 nm. Similar to the Mn$^{4+}$-doped case, the spectra of Cr$^{3+}$ ion also feature a relatively narrow and fixed deep red or NIR persistent range whose edge usually starts from ~600 nm but, relying on the crystal hosts, ends to different positions (Figure 5). The excitation range of Cr$^{3+}$ ion can cover the whole UV and visible region (Figure 5a(iii-iv)), showing much broader when compared to that of Mn$^{4+}$ ion. In several cases (e.g., Zn$_{2-x}$Al$_{2-x}$Sn$_{1-x}$O$_4$:Cr$^{3+}$[164], Sr$_4$Al$_{12}$O$_{25}$:Cr$^{3+}$,Eu$^{2+}$,Dy$^{3+}$[174], SrAl$_2$O$_4$:Cr$^{3+}$,Eu$^{2+}$,Dy$^{3+}$[179], and CaGa$_2$O$_4$:Cr$^{3+}$,Yb$^{3+}$[183]), the persistent luminescence of Cr$^{3+}$ can be generated. Normally, the Cr$^{3+}$ ion shows not only broad spectral range (Figure 5) but also ultralong persistent luminescence (Figure 5b). Thus, the Cr$^{3+}$ MPLs can be used for coupling with the PCMs with the absorption in the range of 600-900 nm. Moreover, the Cr$^{3+}$ ion can also feature the tunable red/NIR positions like in Zn$_{2-x}$Al$_{2-x}$Sn$_{1-x}$O$_4$:Cr$^{3+}$ (Figure 5a(i-ii)) [164], thus providing multiple choices for the practical need of photocatalytic purposes to achieve the desirable persistent wavelength and intensity maxima. For Mn$^{2+}$-doped MPLs, they often exhibit bandlike persistent band whose intensity maxima, band width, persistent duration and color largely depend on the chemical environment the Mn$^{2+}$ ion experienced (Table 3, and Figures 6-7). Moreover, co-doping with other RE/non-RE ions usually broadens the persistent range owning to the integrated contributions of all involved emitting species. For example, the spectral range of co-ZnGa$_2$O$_4$:Mn$^{2+}$,Eu$^{2+}$ MPLs is composed of the Mn$^{2+}$ and Eu$^{2+}$ bands, showing a persistent range broader than that of single Mn$^{2+}$-doped cases. In other situations, the Mn$^{2+}$ ion can also act as a sensitizer for RE (e.g., Ce$^{3+}$[232], Eu$^{3+}$[236], Tb$^{3+}$[237], Pr$^{3+}$[238], Sm$^{3+}$[233, 239], Dy$^{3+}$[90, 220, 240], Tm$^{3+}$[241], Eu$^{2+}$[90, 92, 241, 242]), multiple RE/non-RE [92, 240-241, 243-248], and non-RE co-dopants (e.g., Bi$^{3+}$[234-235, 249-253], Cr$^{3+}$[194, 254], Mn$^{4+}$[255] etc), which is a relevant strategy for broadening and harvesting the emission spectral range as well as enhancing
the spectral intensity and realizing the tunable fluorescence for the solid-state lighting technology such as phosphor-converted white LEDs. With these spectral properties, the Mn\textsuperscript{2+} MPLs, similarly to one previous work that uses the fluorescent Zn\textsubscript{4}GeO\textsubscript{4}:Mn\textsuperscript{2+} (noted that it is not MPL) as photocatalyst [256], can couple with the PCMs to form the MPL@PCM composites.

2.3 \textit{ns}\textsuperscript{2}-type cation-doped MPLs

Bandlike persistent luminescence can also be achieved in MPLs doped with \textit{ns}\textsuperscript{2} cations like Bi\textsuperscript{3+} [141, 149, 234, 257-269] or Pb\textsuperscript{2+} ion [270-273] (Table 4). Unlike the Mn\textsuperscript{4+} and Cr\textsuperscript{3+} ions yet similar to the Eu\textsuperscript{2+}, Ce\textsuperscript{3+}, and Mn\textsuperscript{2+} ions, single Bi\textsuperscript{3+} ion, depending on different crystal hosts, can exhibit the fluorescence broadly spanning from UV, blue, yellow and to reddish/red [45, 274-285]. In many cases, the Bi\textsuperscript{3+} ion also can be used as an efficient sensitizer for the RE or non-RE co-dopants (e. g., Mn\textsuperscript{2+} [234-235, 249-250, 253]. Eu\textsuperscript{3+} [91, 130, 149, 286-288], Tb\textsuperscript{3+} [150, 287], Dy\textsuperscript{3+} [288-289], Pr\textsuperscript{3+} [290], Sm\textsuperscript{3+} [291-292], 3d Mn\textsuperscript{4+} [293-296], and Cr\textsuperscript{3+} ions [189, 297]), and multiple RE/non-RE co-dopants [288, 298-301] to improve or influence the fluorescent properties of these co-dopants. Sometimes, the Bi\textsuperscript{3+} can spread the persistent potentialities toward the short wavelength region, allowing the persistent range being broader than that with single RE and TM dopant. This, as we will discuss further, is of particular interest and importance for the MPL@PCM composites design. In addition, the up-converting optical properties of the RE ions like the Yb\textsuperscript{3+} [183, 302], Er\textsuperscript{3+}/Yb\textsuperscript{3+} [303], and Er\textsuperscript{3+}/Tm\textsuperscript{3+}/Yb\textsuperscript{3+} [304] can sometimes be modified by Bi\textsuperscript{3+} ion. Although the number and type of Bi\textsuperscript{3+} MPLs are also not plentiful as compared to those RE-based MPLs, they are desirable for the photocatalytic purposes due to the broad and host-dependent persistent range (Figure 8). Besides, the Pb\textsuperscript{2+} ion is also found to have the persistent phenomenon, but its number is much more limited as regard to its severe toxicity. As some works have indicated, however, the intensity maxima of Pb\textsuperscript{2+} ion strongly depends on crystal host, excitation wavelength, doping concentration and external temperature [269-273, 305-309], but its emission and persistent regions are usually located in the UV region (Figure 8c). Thus, this UV persistent feature allows the Pb\textsuperscript{2+} ion to have the potential to couple with the absorption region of many PCMs. In fact, all the \textit{ns}\textsuperscript{2}-type MPLs feature broad spectral range, with a full width at half maxima (fwhm) value larger than 50 nm (in some cases, the fwhm value like in CaGa\textsubscript{2}O\textsubscript{4}:Bi\textsuperscript{3+} [269] can nearly reach 200 nm). As for \textit{ns}\textsuperscript{2}-type cations, they have a significant contribution in the UV region (Table 4, and Figure 8), which may couple with the PCMs in the MPL@PCM
composites. These UV features are unique for $ns^2$-type ions that other ions like the $f$-$f$ and $d$-$f$ RE and 3$d$ ions do not have.

2.4 Self-activated bulk MPLs

Unlike the above RE and non-RE MPLs that require at least an external RE or non-RE ion as the luminescent center, interesting to mention here is that the bandlike persistent luminescence are also observed frequently in some self-activated compounds, where the luminescence is assigned to the complex groups and/or defects [168, 170, 177, 199, 215, 225, 310-342]. In general, the emitted spectra are ultra-broad and excitation / temperature-dependent (Table 5, and Figure 9). However, the self-activated MPLs usually sustain a relatively short persistent duration and low intensity when compared to the RE and non-RE MPLs, although a few MPLs (e.g., Zn$_3$Al$_2$Ge$_2$O$_{10}$ [177], Mg(Mg,Sn)O$_4$ [323]) are able to sustain their duration for several hours (Table 5). Although the emission and persistent bands of the self-activated MPLs can match with the absorption region of a variety of photocatalysts (even at some conditions at a given temperature) and some of them like ZnGa$_2$O$_4$ [310, 325], and Zn$_4$Ga$_2$O$_{3+x}$ [342]) have been tested as photocatalysts to decompose the Rhodamine B (PhB), most of them have not yet been explored for the photocatalytic purpose.

2.5 NIR-converted MPLs

The last category of MPLs involves the conversion of NIR radiation (typically 800 - 1000 nm) to the visible / UV persistent luminescence. These compounds are referred to the up-converted MPLs (UC-MPLs), and they are mostly activated with the 808 nm and 980 nm NIR light. In this case, to realize the UC process in UC-MPLs, it generally needs an Yb$^{3+}$ ion that efficiently absorbs the 980 nm NIR photons or an Nd$^{3+}$ ion that can absorb the 808 nm NIR photons [40, 135, 143, 193, 302-304, 343-359].

To access the UC NIR, UC visible or UCPL light, except for Nd$^{3+}$ and/or Yb$^{3+}$ ions, it also needs other RE and/or non-RE ions like Cr$^{3+}$ [40, 178, 183, 193, 343-344, 346-347, 349-350], Pr$^{3+}$ [125], Ce$^{3+}$ [347, 351], Mn$^{2+}$ [352-353, 355, 359], Tb$^{3+}$ [301], Eu$^{2+}$ [359-361], Eu$^{3+}$ [183, 301], Tm$^{3+}$ [144, 249, 301, 304, 350, 358, 359], and Er$^{3+}$ [40, 144, 178, 303-304, 346, 349, 354, 359] (Table 6, Figures 10-11), or to construct the hybrid composite consisting of the NIR-to-visible UC nanocrystals aggregated onto the MPLs so as to activate the persistent luminescence through re-absorbing the UV or visible photons that are emitted from the UC nanomaterials (e.g., the core / shell β-NaYF$_4$:Yb,Er/NaYF$_4$@CaS:Eu$^{2+}$,Tm,Ce [343], NaYF$_4$:Yb,Tm@CaAl$_2$O$_3$:Eu$^{2+}$,Nd [360],
Attempts to result smaller the photon of W Band gap of the semiconductor important role in the photo reaction, the chemical potential by means of a redox process to molecules adsorbed on hole In a semiconductor 3.1 3. PCMs future in the photocatalytic field provide the photon energy. c ZnGa degradation materials (PTM) if (based on the phonon 11 from the Ga 2+ the co-dopants like the yellow, red or NIR light from the Cr3+ (Figure 10a,d, and Figure 11c), Mn2+ (Figure 10c, and Figure 11a), and Ce3+ ions (Figure 11b)). Note that the UC-MPLs based on the phonon-assisted UC charging are also reported in some Cr3+-doped crystal systems (e.g., Zn3Ga2GeO8:Cr3+, Figure 10d) [362], and ZnGa2O4:Cr3+ [363]), although the cases are rare.

At last, it is worth noting that the MPLs could sometimes act as the photocatalysts by themselves if their persistent spectra have overlapped with the absorption range of the photocatalytic-toward materials (PTM). Attempts based on the MPLs have made for the H2 production or RhB degradation, such as Sr2MgSi2O7:Eu2+,Dy3+ [66], Sr3Al14O25:Eu, Dy, Bi [66], ZnGa2O4:Cr3+ [197], ZnGa2O4 [310, 325], Zn3Ga2O5+4 [342], Ga2O3:Cr3+,In2+ [364], Ga2O3:Cr3+,Zn2+ [365]. However, the photocatalytic efficiency of such MPLs taken alone is always lower than that under the corresponding MPL@PCM composites when there is no external light source to continuously provide the photon energy. All in all, from the above summarization, the MPLs exhibit a bright future in the photocatalytic field.

3. PCMs, MPLs, and MPL@PCM composites: working principles and design consideration

3.1 Consideration of PCMs

In a semiconductor photocatalyst, the photocatalysis is based on the photon-induced electrons and holes separation, followed by their migration to the surface of PCMs. Thus, the carriers provide a chemical potential by means of a redox process to molecules adsorbed onto the materials [366-367]. Except for the photon-induced charge separation which is a beginning of photocatalytic reaction, the two major aspects, i.e., the band gap of semiconductor and charge migration, play an important role in the photocatalytic efficiency in its following processes.

Band gap of the semiconductor

Whether the photons can or not induce the electron-hole pairs strongly depends on the comparison of how the photon energy scales respective to the optical bandgap of a semiconductor. Only the photons with the energy larger than the optical bandgap can induce the electron-hole pairs, i.e., the smaller the optical bandgap the longer the wavelength of the incoming absorbed photons. As a result, the optical window available for photocatalysis should be broader than the photon energy
of an external irradiation source. However, a smaller optical bandgap is equivalent to a smaller redox potential, showing that it is not advantageous to decompose the stable chemical bonds of the associated organic matter. In Figure 12, we can see, for instance, that the anatase form of TiO₂ (α-TiO₂) has an optical bandgap of 3.2 eV that corresponds to ~387 nm photons [367-368]. Its oxidation energy level (i.e., the bottom of the conduction band) is lower than the O₂/H₂O level, while the reduction energy level (i.e., the top of the conduction band) is higher than H₂/H⁺ (SHE) [369]. This makes the α-TiO₂ particularly relevant to produce the radicals for small organic dyes molecules decomposition [370], water splitting [371], CO₂ reduction [372] etc. Although the small optical bandgap could extend the optical window for the photon-induced photocatalysis process, it does not favor the degradation of chemical bonds with high reduction or low oxidation energy levels. For example, Bi₂O₃ has an optical bandgap smaller than TiO₂, but its reduction energy is insufficient to the H₂ - H⁺ photocatalytic reaction.

**Charge migration**

Charge migration of photon-induced electrons and holes to the surface of PCMs is the second critical issue. In fact, this step is usually affected by recombination of the charge carriers or by defects that both contribute to lower the number of reactive charge carriers from PCMs [366, 369, 371]. Thus, the number of reactive carriers contributing to the photocatalysis is determined by: (i) the distance separating, where the charge carriers generated to the PCM surface must be as small as possible while the mean free path of charge carriers in the host fundamental bands must be as large as possible, and (ii) the distance that the charge carriers can transport in the conduction band. Thus, to achieve (i), small particle diameter is often required so as to confine the carriers in a small region [373]; but for (ii), the transportation distance of the carriers is directly determined by the lifetime of the carriers in the conduction band that usually inverses proportional to the recombination rate, thus the inhibition of electron-hole recombination is advantageous to the charge migration and improve the photocatalytic efficiency [374]. However, controlling the electron-hole recombination rate is still now a difficult issue because it seems to be only determined by the band structure of materials rather than the external condition, although the change of band structure can be controlled in atomic scale by using the doping method, such as doping of TiO₂ with Fe³⁺ or Nb⁵⁺ ions [375]. Furthermore, the stacking of particles is usually not advantageous to the light penetration, thus the desirable photocatalytic particles should distribute
homogeneously and the thickness should be controllable, with the aim of optimizing the photon absorption and enhancing the photocatalytic efficiency. In this case, we have summarized in Table 7 several mainstream PCMs and corresponding synthesis treatment route, along with their average particle size and optical characteristics.

3.2 Consideration of MPLs

The consideration of MPLs is mainly based on the ability of their photon management. That is the quantum efficiency (QE) of the photon emission, which includes the photoluminescence (PL) and persistent luminescence simultaneously [105]. On one hand, in an MPL@PCM system consisting of PCMs deposited onto the surface of MPLs, we expect first that the MPL can absorb the excess photons that pass through the PCM layer and then generates a secondary luminescence to excite the PCMs again. On the other hand, the MPL is also expected to store the incoming photon energy by trapping carriers for a desirable time. With the aid of the thermal release, these trapped carriers gradually return to the luminescent centers and generate the persistent luminescence, continuously acting as the photon resource for the PCMs after switching off the external excitation source. In this frame, both the PL and persistent luminescence contribute to the photocatalytic process and, thus, can optimize the incoming of photon energy and the resulting photocatalytic efficiency [61, 106]. With these considerations, a MPL with stronger PL and persistent intensity as well as longer persistent duration is more desirable for providing the photons to the PCM when there is no external excitation source. In addition, the persistent spectral region should lie in a spectral region where the PCMs also lie in, for instance, those MPLs (Tables 1-6) with the spectral regions that can match with the absorption range of the PCMs (e.g., Ag-AgCl [63], g-C₃N₄ [65], BiVO₄ [72], and Ag₃PO₄ PCMs [64, 376], whose optical bandgap fall in the range of 2.5~3.0 eV). So far, the PCMs that meet the above conditions include, such as, aluminates like MAI₂O₄:Eu³⁺,Dy³⁺/Nd³⁺ (M: alkaline) [60-62, 64, 67, 70-71], and silicates like M₂MgSi₂O₇:Eu³⁺,Dy³⁺ [66, 72, 376-379].

Moreover, another working principle of the MPLs we need to consider is the physicochemical stability, typically in presence of moisture. For this aspect, aluminate-based MPLs are not stable in water or moisture environment for a long time [75], because they can decompose easily and cause loose luminescence. As a matter of comparison, silicate-based MPLs are, in this context, largely preferred because they can sustain the persistent luminescence in water for a relatively long term, with persistent intensity degradation in an acceptable range. In fact, the MPLs we listed in Table 8...
confirm the conclusion, in which almost all of the MPLs@PCMs composites that are proved for the photocatalytic degradation of aqueous phase pollutant are now those silicate-based MPLs.

**3.3 Consideration of MPL@PCM composites**

The first basic requirement for the design of “persistent-photocatalytic” MPL@PCM composites is that the persistent spectrum of the MPLs overlaps the absorption region of the PCMs (Figure 13) so that the reabsorbed photons can generate the electron-hole pairs continuously when the external irradiation source is off. Looking back Section 2, however, the MPLs do not have equivalent attributes, because those showing a persistent duration shorter than a few tens of minutes and/or having a persistent band lying out of the absorption range of PCMs or narrow un-tunable spectra are, in practice, no use for the current purpose, except for some specific situations where a specific persistent line of the MPLs for the PCMs is wanted. Conversely, the MPLs featuring broad band and long persistent duration, especially for those showing a spectral contribution extending to the UV spectral range, are privileged. For example, the melilite-type Ce³⁺-doped Ca₂MgSi₂O₇ whose persistent band peaks at 380 nm is suitable for a TiO₂ PCM that presents an absorption cut-off at 387 nm, whereas other types of PMLs like CaAl₂O₄:Eu²⁺,Nd³⁺ with emission peaking at ~440 nm [49, 60-61, 71], SrAl₂O₄:Eu²⁺,Dy³⁺ with ~520 nm emission [64, 379], and Sr₂MgSi₂O₇:Eu³⁺,Dy³⁺ with ~465 nm emission [66, 72] are unsuitable. With this logical thinking, the TiO₂ is usefully associated with MPLs, as proved by the Sr₄Al₁₂O₃₅:Eu²⁺,Dy³⁺,Bi³⁺@TiO₂ for the MB degradation [69], BaAl₂O₄:Eu²⁺,Nd⁵⁺@TiO₂ for the benzene decomposition, Ca₂MgSi₂O₇:Ce@TiO₂ [366] and Mg₃Y₃Ge₄O₁₂:Bi@TiO₂ [380] for the MO degradation, etc. Noteworthy, the absorption efficiency of PCMs can be boosted by widening or adapting their absorption range to the persistent range of MPLs by using some appropriate strategies. For example, the absorption efficiency of TiO₂ can be improved by doping with nitrogen [60, 106, 378], building the hybrid photocatalysts [16, 25-27], or attaching onto its surface a certain type of noble metal nanoparticles with suitable fermi-level from which the hot electrons can be extracted and transferred, like TiO₂-Ag [367] and Ag-BiOBr [381] (Figure 12). In particular, there is no band gap in metal, but in theory an electron at low energy level could be excited to high level when the photon is adsorbed by nano-metal particles. Then a hole is induced in a low level. An instantaneous charge separation is induced at that time. Hence, this process involves the excitation of an electron located in low energy levels to high energy levels of the noble metal nanoparticles, leaving a hole in low energy levels. An
instantaneous charge separation follows at this time. The electron at high level (i.e., hot electron) then travels through in noble metal and thus has some probability to migrate to the surface of the nano-particle. Here, the hot electron can be transferred to the conduction band of another material that has close contact to the metal, subject that the Fermi-level of the two associated materials have the suitable energy. With this process, the hot electron can contribute to the photocatalytic activity if it is located at the surface of the relevant materials. For example, introducing the Ag nanocrystals in the ZnO:Co-Ag composite leads to three additional absorption bands in the range of 500-700 nm in superimposition with the UV-vis absorption of the ZnO:Co catalyst [68]. Thus, in general, enlarging the absorption range can improve the corresponding photocatalytic ability.

The MPL@PCM composite structure typically consists of fine particles of the PCMs attached onto the MPL with a coating process that depends strongly on the specific type of the PCMs, the synthesis strategies, and the post- or after-treatment routes. For instance, BiVO₄ and g-C₃N₄ can be in-situ grown onto the surface of the Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ by using hydrothermal [72] and sintering methods [379], respectively; while nano-TiO₂ particles are preferably deposited onto the surface of CaAl₂O₄:Eu³⁺,Nd³⁺ [61, 71] or Ca₂MgSi₂O₇:Ce²⁺ [366] particles rather than grown. Thus, constructing a suitable type of “persistent-photocatalytic” MPL@PCM composite actually is a process of constructing PCMs coating or loading MPLs structure.

3.4 Mechanistic models

An ideal mechanistic model established for illustrating the “persistent-photocatalytic” process needs to meet at least the two requirements, i.e., efficient photon utilization and effective charge separation. Upon irradiation with a suitable light, both the MPLs and PCMs in the MPL@PCM composites can be excited if this irradiation light is located either in the excitation range of MPLs and the absorption range of PCMs, or only in the the excitation range of MPLs but the emission range from MPLs overlaps with the absorption range of PCMs. In the PCMs, the absorbed energy can be converted to charge carriers; while in the MPLs, it is partly stored in traps and partly converted to photoluminescence (PL). Upon a continuous light irradiation, the PCMs can be sensitized from both sides, namely, the photons directly emitted from the external irradiation source, and the photons emitted from the MPLs. When the external light is cut off, the thermal release of the traps allows MPLs to generate the persistent luminescence [105] that can act as the inner light resource for the PCMs until the MPL@PCM composite is recharged again. Once the
PCMs are irradiated, separation and transport of charge carriers to the surface of PCMs must be achieved with minimum losses. Besides, if PCMs and MPLs have a very close contact (i.e., a clean interface, and a suitable band structure) [366], the charge separation, which is confirmed by recording a photocurrent, can be achieved via a charge transfer process. In this concern, the formation of a hybridized hetero-junction within the MPL@PCM composite is highly desired, because it can have efficient charge separation (Figure 14). In such a hybridized hetero-junction, the electrons would tend to migrate to MPLs with a low energy (more oxidative) location, while the holes tend to migrate to PCMs with a high energy (more reductive) location. If the MPLs and PCMs have band alignment, the above migrations happen simultaneously, leading to the accumulation of holes and alignment in the two respective materials and the formation of the reduction and oxidation centers accordingly. As a result, the charge recombination is inhibited.

However, since it requires a clean interface (i.e., without other impurity materials such as the excessive chemical reagents) and suitable structures of both components, we find, for instance, in Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$,Dy$^{3+}$@Ag$_3$PO$_4$ [377] (Figure 15), that the band-to-band transition in the PCMs is often followed by the transfer of an electron to the conduction band of the MPLs. The better photon utilization by the inner light photons from Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$,Dy$^{3+}$, along with a charge separation between the Ag$_3$PO$_4$ and the MPL, improve the catalytic efficiency of this hybridized hetero-junction composite substantially.

4. Synthesis strategies of “persistent-photocatalytic” MPL@PCM composites

The photocatalytic performance of “persistent-photocatalytic” MPL@PCM composites can be influenced by various factors such as the particle size and morphology, microstructure, persistent intensity and duration of MPLs and PCMs, and the photocatalytic efficiency of PCMs. All these factors are initially determined by the synthesis methods. Once a given synthesis route is selected to fabricate the MPL@PCM composite, the corresponding photocatalytic behavior is usually determined unless other factors like the oxygen and moisture in the air, the variation of external temperature and post-synthesis route appear. Based upon the previous works [60-73, 107, 310-312, 342, 364-366, 376-385], we show the synthesis methods of the reported MPL@PCM composites (Table 8). The synthesis consideration of the MPL@PCM composites is more complicated than that of singly achieving the MPLs and PCMs, because it needs to take into a joint consideration all the possible properties of both materials. Except for the MPLs that are directly used as
photocatalyst (e.g., Sr₂MgSi₂O₇:Eu³⁺,Dy³⁺ [66], Sr₂Al₄O₂₃:(Eu³⁺,Dy³⁺,Bi³⁺) [69], ZnGa₂O₄:Cr³⁺ [197], ZnGa₂O₄ [310], ZnₓGa₂O₄₋ₓ (0.8 ≤ x ≤ 1.0) [342], Ga₂O₃:Cr³⁺,In³⁺ [364], Ga₂O₃:Cr³⁺,Zn²⁺ [365], and ZnGa₂O₄:Ti [382]), the synthesis method generally contains three step processes, and it usually uses the powder reagents as the starting materials, i.e., first the MPLs are synthesized basing upon a nominal stoichiometric chemical ratio of MPLs, then the PCMs are bought (if commercially available, such as TiO₂), or specifically processed (e.g., the hydrothermal, chemical, or sol-gel methods) for the optimization of the photocatalytic properties (e.g., TiO₂:N and BiVO₄), and at last the two components are assembled to form the MPL@PCM composite. Because of the powder-typed mixtures, different synthesis strategies can be applied for achieving the MPCs, depending on the desired processing cost, production scale, and targeted particle size. Normally, the solid-state reaction method is used for micro-sized MPLs, while the sol-gel and hydrothermal routes are used for nanoscale MPLs. We summarize in Tables 7-8 the principal routes that are used for the synthesis of MPLs, PCMs, and MPL@PCM composites, and show in Figures 16-17 representative SEM, FESEM, TEM, and HRTEM images revealing the structural organization of the MPLs, PCMs, and MPL@PCM composites. We focus below on reviewing the solid-state reaction, sol-gel, hydrothermal, combustion, mechano-chemical, and chemical vapor deposition (CVD) synthesis routes for MPL@PCM composites.

4.1 Solid-state reaction & combustion routes

The solid-state & combustion reaction routes are the most frequently used. The synthesis process is relatively simple, low-cost, and quite suitable for large-scale production. However, they easily lead to distortions and imperfections of MPLs crystals, including various kinds of “bad, and ugly” defects (e.g., surface and interstitial cation and anion vacancies, point defects [44]), which affect the persistent luminescent properties. The two routes are especially desirable for producing the MPL@PCM composites with micro-size particles, such as the ZnGa₂O₄:Cr³⁺ [197], BaZrO₃:Mg²⁺@TiO₂ [311], Ca₂MgSi₂O₇:Ce³⁺@TiO₂ [366], Sr₂MgSi₂O₇:Eu²⁺,Ce³⁺@g-C₃N₄ [379], (3ZnO:Ga₂O₃:2GeO₂):Cr³⁺@TiO₂ [383], as depicted in Figures 12a-f. To better make the PCMs being individually deposited onto the surface of the MPLs, the PCMs should feature nano-sized particles, such as Ag₃PO₄ [377], g-C₃N₄ [379], and TiO₂ [311, 383] (Figures 16f-h). Taking the Ca₂MgSi₂O₇:Ce³⁺@TiO₂ composite for example, Wu et al [366] synthesized the Ca₂MgSi₂O₇:Ce³⁺ MPL at 1300 °C and then compressed into a pellet. Followed by sintering at a temperature of 900
°C, the pellet was transformed into a ceramic substrate that immobilizes the nano-sized TiO$_2$ (P25, Macklin) particles onto its surface. After dropping the TiO$_2$ powder onto the surface of the MPL ceramic substrate and sintering again at 400 °C, the Ca$_2$MgSi$_2$O$_7$:Ce$^{3+}@$TiO$_2$ composite features the persistent luminescence and the photocatalytic properties simultaneously. Such strategies are also applied for the MO degradation using the Mg$_3$Y$_2$Ge$_2$O$_{12}$:Bi$^{3+}@$TiO$_2$ composite [380].

4.2 Sol-gel and hydrothermal approaches
Unlike the solid-state & combustion reaction routes, the hydrothermal and sol-gel methods are popular for the synthesis of MPL@PCM nanocomposites with regular particle size and smooth particle surface, as proved by the Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$,Dy$^{3+}$ [66], CaAl$_2$O$_4$:(Eu,Nd)@Fe$_2$O$_3$-SrTiO$_3$ [70], and Sr$_2$MgSi$_2$O$_7$:Eu$^{2+}$,Dy$^{3+}@$BiVO$_4$ [72]. Although they sometimes can make the composites featuring irregular micro-size particles and rough surfaces (e.g., Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}@$Ag-AgCl [63], Sr$_4$Al$_4$O$_{12}$:Eu, Dy@g-C$_3$N$_4$ [65], MgAl$_2$O$_4$:(Pr$^{3+}$,Dy$^{3+}$)@Cr-TiO$_2$ [107], and GP@Fe-N-TiO$_2$ [384], Figures 17a-d), the particle size and surface morphology of the MPLs after being loaded or coated with the PCMs do not change significantly. If the whole synthesis processes were based on the sol-gel or hydrothermal route, the chance of achieving irregular micro particle size and rough surface becomes less, such as the GP@Fe-N-TiO$_2$ achieved by a hydrothermal approach [382].

4.3 Chemical vapor deposition (CVD) route
Compared to the above approaches, the CVD route is infrequently used. So far, to the best of our knowledge, only Kim et al in 2015 [71] and 2016 [73] have used the CVD method to prepare the CaAl$_2$O$_4$:Eu,Nd@TiO$_2$ and Sr$_4$Al$_4$O$_{12}$:Eu, Dy@TiO$_2$ composites by deposition of the TiO$_2$ onto the surface of the solid-state processed CaAl$_2$O$_4$:Eu$^{2+}$,Nd$^{3+}$ and Sr$_4$Al$_4$O$_{12}$:Eu$^{2+}$,Dy$^{3+}$ particles, respectively. In the synthesis process, the Ti[OC(CH$_3$)$_2$]$_4$ was used as the TiO$_2$ precursor and the oxygen gas was used as reaction gases under a very low-pressure condition (i.e., at 1 Torr).

4.4 Others
As for any composite system, the quality of the interfacial contact between the MPLs and PCMs is essential to yield a synergistic coupling between the two constituents of “persistent-photocatalytic” MPL@PCM composites. In this purpose, in-situ growth of the PCMs onto the surface of the MPLs, such as directly coating the photocatalytic precursors onto the surface of the MPLs [379], is preferred. The PCMs can be also synthesized firstly, and then load on the surface of MPLs directly [60, 73], but this process usually needs a hydrophilic surface to attract the MPLs and PCMs via
chemical bonding. Thus, it often needs to modify the surface of PCMs or MPLs using some type of materials such as kaolin [366, 380, 386-387] to favor the grafting. However, the surface chemical functional groups of the PCMs or MPLs are often instable and even can be eliminated easily when the synthesis process is at high temperature, leading to a clean surface of PCMs or MPLs. That is, there is no PCMs and/or MPLs components in the targeted MPL@PCM composites. Obviously, although the “a clean interface” mentioned here is different from the case of “a clean interface” mentioned in “3.4 Mechanistic models” section, both lead to a bad photocatalytic activity.

Furthermore, a single synthesis route can also be used for directly obtaining the MPL@PCM composites, but some hybridized MPL@PCM composites generally need a coupling arrangement of multiple approaches to achieve an optimized photocatalytic property. Hence, such MPL@PCM composites needs to explore and develop other approaches. Typically, an in-depth study on the energy transfer from the MPLs to the PCMs is necessary. For example, Li et al [62] in 2010 used the sol-gel method to prepare the BaAl2O3:Eu,Dy@TiO2 composite by deposition of the TiO2 onto the surface of BaAl2O3:Eu,Dy and adjustment of the TiO2 loading content, but the photocatalytic efficiency is not desirable because of a low utility of persistent energy by the PCMs, owning to the interface gap between MPLs and PCMs.

5. Photocatalytic application of self-luminous MPL@PCM composites

Until now, a number of materials, composites, and hybrids, such as the Ag-TiO2[1, 71], TiO2[16, 49, 71, 388], Ag-AgCl[24, 63], MoS2-TiO2 [25], TiO2-MOF [26], Au-TiO2 [27], BiOCl-BiVO4 [28], Ag3PO4[64, 374-375, 390], ZnO:Co-Ag [68], g-C3N4[379], COF [389], AgBr-Ag3PO4[391], YFeO3 [392], g-C3N4-Cs2WO3 [393], g-C3N4-Bi2WO6 [394], Co3O4-g-C3N4 [395], ZnO-SnO2 [396], BiOCl [23, 397], BiOCl-rGO [398], M2Sb2O7 (M = Ca, Sr) [399], CNTs/P-TiO2 [400], BiFeO3 [401], and AgBr-WO3 [402], are reported to have the photocatalytic properties, and they have been suggested for use in, e.g., photocatalytic elimination of bacterial pathogens [9], degradation of methyl orange (MO) [63, 68, 391, 396, 403-405], methylene blue (MB) and RhB [141, 311, 342, 376, 381, 406-407], removal of gas-phased materials [61, 67, 70, 385, 408-413], production of hydrogen (H2) and oxygen (O2) and splitting of water [57, 66, 414-423], degradation of pesticide atrazine and antibiotic oxytetracycline [384], reduction and oxidation of gas such as CO2 [424], cleavage and amination of chemical bonds such as the C-C bond [425], etc. However,
only a tiny of these PCMs have been reported to couple with the MPLs to fabricate the hybrid MPL@PCM composites (Table 8). Attempts made for other PCMs still have not been tried in previous works, leaving a big room of investigation for this research subject in the future. Until now, the photocatalytic applications of the hybrid MPL@PCM composites are mainly focused on the degradation of MO, MB, and RhB dyes, removal of poisonous gas such as nitric oxide (NO) and benzene, and photocatalytic production of hydrogen (H₂) and oxygen (O₂).

5.1 Methyl orange (MO) degradation

The MO is a relevant and widely used model organic dye to qualify the photocatalytic degradation performances of a PCM and it, under different conditions (e.g., at different pH values, temperature, external irradiation intensity and duration), can be conveniently monitored by using UV-visible spectroscopy. Normally, in distilled water, the MO shows two absorption bands with the intensity maxima peaking at 270 nm and 465 nm [403-404], as shown in Figure 18a. The intensity and position of the latter band are in general used to monitor the degradation rate upon continuous irradiation with an external sources such as sunlight [388], UV [389], arc lamp [391], and NIR light [304, 358]. When the MO is placed in presence of the Sr₂MgSi₇O₁₇:Eu²⁺,Dy³⁺@Ag₃PO₄ [377] (Figure 18b), and Mg₃Y₃Ge₃O₁₂:Bi³⁺@TiO₂ [380], its photocatalytic degradation persists for a relatively long time after removal of the UV light source. In the cases of Ca₂Al₃SiO₇:Ce³⁺ MPL (curve 1), Ag-AgCl PCM (curve 2), and Ca₂Al₃SiO₇:Ce³⁺@Ag-AgCl composite (curve 3) [63] (Figure 18c), it is found that after putting in dark for 30 min (i.e., with light off), the MO concentration, corresponding to the Ca₂Al₃SiO₇:Ce³⁺, Ag-AgCl, and Ca₂Al₃SiO₇:Ce³⁺@Ag-AgCl composite, respectively, is reduced from 1.0 to ~0.93, ~0.98, and ~0.99 (Figure 18c). This indicates that the MO can be decomposed even though there is no external UV light source. Such experimental observations can also be found in other PCMs like Ag-AgCl [63], and TiO₂ [369, 371, 375, 426], which are attributed to the self- or/and photocatalyst-sensitized MO degradation [426]. Hence, the self-sensitized degradation issue should attract significant attention in the future research. Under a simulated solar light irradiation for 5 min, the residual MO in the Ag-AgCl PCM and Ca₂Al₃SiO₇:Ce³⁺@Ag-AgCl composite is decreased dramatically; the photocatalytic activity of the Ag-AgCl PCM being above that of the Ca₂Al₃SiO₇:Ce³⁺@Ag-AgCl composite. Moreover, the MO concentration in Ca₂Al₃SiO₇:Ce³⁺, along with its next process with the light off (35-55 min), does not change, indicating that Ca₂Al₃SiO₇:Ce³⁺ does no longer decompose the MO
when the MPL-sensitized MO degradation is finished. This Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}$-sensitized MO degradation, as this work reveals, is independent of whether the light source is off or on. Besides, despite the Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}$@Ag-AgCl composite can continue the MO degradation with the light off (curve 3, 35-55min), its final MO concentration is lower than that of the Ag-AgCl PCM alone (curve 2, 35-55min). This may be because the MPL can partially block the light reaching the PCM and thus induce the decrease of the overall MO degradation content. As a result, the light filtering effect of the MPL and/or the decrease of the active surface of the PCM (which is due to its binding to the MPL) is more significant than the possible decrease in the electron-hole recombination due to the migration of the generated conduction band electron to MPL. As for the continuous MO degradation within 35-55min, it can be assigned to the gradual release of the stored photon energy from the Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}$ followed by transferring to the Ag-AgCl. As a result, when compared to the photocatalytic effect of the Ag-AgCl alone, ~15% of the retained MO content is decomposed further in the Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}$@Ag-AgCl composite after removal of the light for 20 min (Figure 18d). Hence, the above findings reveal that the persistent luminescence of the Ca$_2$Al$_2$SiO$_7$:Ce$^{3+}$ (its duration can last several days after instantly pre-exciting and removal of a 254 nm UV source [63, 406]) plays an essential role in sustaining the photocatalytic activity of the Ag-AgCl for MO degradation. Such results are confirmed by other MPL@PCM composites like Sr$_4$Al$_{14}$O$_{25}$:Eu,Dy@ZnO:Co-Ag [68], Sr$_2$MgSi$_2$O$_7$:Eu,Ce@Ag$_3$PO$_4$[377] (Figure 18b), and Mg$_3$Y$_2$Ge$_3$O$_{12}$:Bi$^{3+}$@TiO$_2$ [380].

5.2 Methylene blue (MB) and Rhodamine B (RhB) degradation

Similar to the MO, the MB and RhB are also two frequently-used aqueous-phase organic dyes for modeling the photocatalytic activity of a PCM, but the absorption position and shape are different from the MO. The MB organic dye features a broad absorption band in the red spectral region (i.e., 550-720 nm) with the maxima intensity at 663 nm and ~608 nm (shoulder), and it can be degraded using the PCMs like Ag–In–Ni–S nanocomposites upon irradiation with the sunlight and 100 W tungsten lamp [406], or by the β-NaYF$_4$:Yb$^{3+}$,Er$^{3+}$@BiOCl-rGO composites under UV irradiation [398]. The RhB dye features a substantially absorption range similar to that of the MO, but its absorption band is shifted to the range of 450-600 nm with two intensity maxima at 554 nm and ~520 nm (shoulder). The RhB dye can be degraded well using the ZnO-Au nanocomposites [427]. Both the MB and RhB dyes as the irradiation time goes on experience a gradual increase of
degradation. Typically, when the irradiation light source is off, they can be also decomposed (see Figure 19a (in dark condition, -1–0 min), Figure 20a (in dark condition, -0.5–0 min), and Figure 20d (in dark condition, -60–0 min)), independent of whether or not they are placed in the presence of PCMs, MPLs, and MPL@PCM composites. These observations are analogous to the case of the MO decomposition [369], and they are also assigned to the self- and/or photocatalysts-sensitized RhB degradation. Although the MPLs, such as the oxygen vacancy-rich Zn$_2$Ga$_2$O$_{3+x}$, whose persistent spectral band matches the absorption region of RhB dyes [342], sometimes can be directly used as the PMC for the RhB decomposition and its decomposition effect is higher than the RhB self-sensitized degradation (Figure 19c), it needs a continuous UV light source to sustain this photocatalytic activity. This is because the persistent luminescent intensity and duration (about 10 min) of the Zn$_2$Ga$_2$O$_{3+x}$ is not enough to efficiently degrade the RhB dye. Conversely, the degradation efficiency of the MB and RhB dyes can be continued for a relatively long time in the MPL@PCM composites where the MPLs can show the persistent duration for several hours, e.g., SrAl$_2$O$_4$:Eu,Dy@g-C$_3$N$_4$@Au [57], SrAl$_2$O$_4$:Eu,Dy@Ag$_3$PO$_4$ [64], Sr$_2$MgSi$_2$O$_7$:Eu,Dy@Ag$_3$PO$_4$ [376], Sr$_2$MgSi$_2$O$_7$:Eu,Dy@g-C$_3$N$_4$ [379], and NL-PA@BiOBr [381]. Besides, for instance, the BiOBr@NL-PA under a 300 W Xe lamp shows the improved photocatalytic RhB decomposition compared to the BiOBr PCM alone [381] (Figure 19d), which directly proves that the use of MPL@PCM composite is beneficial to the photocatalysis. Although the NL-PA may partially block the light reaching the BiOBr, the effect seems not to make the final RhB concentration being lower than that of the BiOBr alone, which is different from some of the MO degradation [369].

Although it is well known that in the heterogeneous photocatalysis the dependence of pollutants degradation rate ($r$) on the photon flow ($p$) features a linear relationship when the irradiation photon flow is low (i.e., $r = k \times p$, where $k$ is the constant) and show an independent form at high photon flow [428], but all the reported works involving the use of MPL@PCM composites for photocatalysis still have not studied this relationship. Li et al [376] studied the influence of the persistent duration on RhB degradation by using the Ag$_3$PO$_4$@Sr$_2$MgSi$_2$O$_7$:Eu,Dy and Ag$_3$PO$_4$@Sr$_2$Al$_2$O$_{35}$:Eu,Dy,Er composites in dark condition, and found that the photocatalytic activity keeps excellent stability after ten cyclic experiments (Figure 19b). Furthermore, previous works also reveal that other external environmental factors, such as the added content of MPLs and PCMs, and the persistent spectral position and duration of MPLs, have significant impact on the
photocatalytic MB degradation when the light source is off (Figure 19c, Figures 20a-d). Along with “5.1 Methyl orange (MO) degradation” section and the following sections, we can notice that different works sometimes use different irradiation or pre-irradiation light as the main photon source for the photocatalysis. As revealed by several previous works that only involve the PCMs, we can realize further that the light source is also a very important factor affecting the final photocatalytic results. A given PCM under different light sources can sometimes show different photocatalytic activities, but so far it still lacks a systematic study on how different light sources influence on the photocatalytic activities of the MPL@PCM composites, leaving an open room for future research.

5.3 Removal of gas-phased nitric oxide (NO) and benzene

In addition to the soluble organic molecules or dyes degradation, the PCMs are also widely used for removing poisonous gas-phased materials such as TiO$_2$ for photocatalytic oxidation of NO$_x$ gas [61, 67, 70, 408-410], TiO$_2$-polyacrylonitrile nanofibers for photocatalytic desulfurization and denitification of flue gas [411], TiO$_2$-Y-zeolite for photocatalytic removal of toluene and benzene gas [412], and TiO$_2$-aluminum silicate fiber for removal of SO$_2$, NO and mercury gases [413]. However, all the removal process analogous to traditional photocatalytic process is performed under a continuous external irradiation. These PCMs terminate their photocatalytic activity after cutting-off irradiation source unless they are coupled with a type of suitable MPLs or directly using the MPLs as the PCMs. For example, Li et al [385] used the Ti-contained materials (i.e., SrTiO$_3$ and Cr$^{3+}$-doped SrTiO$_3$) featuring the visible light-responsive activity as the PCMs to model the removal of NO gas under various LED lamps irradiation. They found that both the SrTiO$_3$ and Cr$^{3+}$-doped SrTiO$_3$ under red, green, blue, and UV LEDs have good photocatalytic activities in the shorter wavelength light regions, but only the Cr$^{3+}$-doped SrTiO$_3$ exhibits the photocatalytic performance in the longer wavelength regions (i.e., 627 nm, and 530 nm) (Figure 21a). Further analysis reveals further that the former is due to the presence of the oxygen vacancies in nonstoichiometric SrTiO$_3$ (Sr/Ti = 1.67), while the latter is attributed to formation of new donor levels by doping SrTiO$_3$ with Cr ion. Moreover, in this work, the authors revealed that doping with the external Cr$^{3+}$ ion is a good strategy to extend the photocatalytic wavelength range. The drawback is, however, that once the irradiation UV light in the range of >290 nm is off, the Ti-contained materials stop their photocatalytic process. Even though they are coupled with the
CaAl₂O₄:(Eu²⁺,Nd³⁺) MPL, this situation cannot be changed (i.e., in the range of 0-5 min, Figure 21b). Although the SrTiO₃ under the UV irradiation (λ > 290 nm) removes the NO gas more effective than that with the Cr-doped SrTiO₃ (i.e., in the range of 5-45 min, Figure 21b), it can sustain the superiority of NO removal in the CaAl₂O₄:(Eu,Nd)@Cr-doped SrTiO₃ composite after removal of the irradiation light (i.e., the range of 45-200 min, Figure 21b). Specifically, the CaAl₂O₄:(Eu²⁺,Nd³⁺)@Cr-doped SrTiO₃ composite retains 8.2% of NO removal at 180 min, higher than 3.4% of that in the CaAl₂O₄:(Eu²⁺,Nd³⁺)/SrTiO₃ composite. Moreover, Li et al found that the light irradiation intensity also influences the photocatalytic removal of NO gas in the above composite systems significantly. To verify whether other MPL@PCM composites could be used for removing the NO gas, Li et al also tried the CaAl₂O₄:(Eu,Nd)@TiO₂₃Nₓ (curves 1-2) and CaAl₂O₄:(Eu,Nd)@TiO₂ (curves 3) (Figures 21c-d) [61], CaAl₂O₄:(Eu,Nd)@TiO₂/Fe₂O₃:/(Ta,N) [67], and CaAl₂O₄:(Eu,Nd)@SrTiO₃/Fe₂O₃ [70]. They also found that all of the composites under UV irradiation can remove the NO gas efficiently. The removal process is basically the same, but differs from that involved in the CaAl₂O₄:(Eu,Nd)@SrTiO₃ composite in the time range 5-45 min (Figure 21b). After turning off the UV irradiation, these MPL@PCM composites also keep highly efficient removal of NO gas in the time range 45-200 min. However, the final photocatalytic effects in the absence of the external light source are different from each other due to the coupled PCMs, although all of them use the persistent luminescence of the CaAl₂O₄:Eu²⁺,Nd³⁺ as the same inner irradiation source. In addition to the NO gas, a few years ago, Kim et al found that the CaAl₂O₄:Eu²⁺,Nd³⁺ [71] and SrₓAl₁₄O₂₅:Eu²⁺,Dy³⁺ [73] can relevantly combine with TiO₂ and TiO₂-Ag PCMs to remove the benzene gas for more than 20 h after cutting off the light source. In particular, the TiO₂ or TiO₂-Ag PCMs under UV and visible light efficiently remove the benzene gas, but fail to remove the benzene gas without the light irradiation. Meanwhile, they found that the photocatalytic efficiency is reinforced by co-coupling the TiO₂ with Ag NPs, which is because the Ag NPs retard the electron-hole pairs recombination.

Although the previous works, based on the use of MPLs and PCMs to fabricate the MPL@PCM composites, are still not widely reported for removing or filtering poisonous gas-phased materials, the above-mentioned works prove that this design idea can broaden the application range of the MPL@PCM composites, providing some insights into removing other poisonous gas in the absence of available external irradiation source.
5.4 Hydrogen (H₂) and oxygen (O₂) production

Recently, Liu et al [57] used the SrAl₂O₄:Eu²⁺,Dy³⁺ MPL in association with pristine g-C₃N₄-xAu PCM composites to design a novel self-luminous visible-light plasmonic photocatalyst composite (*i.e.*, g-C₃N₄-Au@SrAl₂O₄:Eu²⁺,Dy³⁺) for photocatalytic hydrogen (H₂) evolution ([Figure 22]). In this multiscale composite, the gold nanocrystals were introduced to expand the absorption range of g-C₃N₄ to the visible region in order to better overlap the emission band of the SrAl₂O₄:Eu²⁺,Dy³⁺ ([Figure 22a]). Despite the introduction of g-C₃N₄@Au, the persistent spectral position and shape of the SrAl₂O₄:Eu²⁺,Dy³⁺ do not vary. By using a 300 W Xe lamp as continuous irradiation source, the optimal g-C₃N₄@0.6%Au composite produces 4.5 times more H₂ compared to the pristine g-C₃N₄ ([Figure 22b]), indicating the positive role of a suitable Au NPs amount on the H₂ production. For those systems without the pristine g-C₃N₄, however, there is no photocatalytic H₂ generation in the SrAl₂O₄:Eu²⁺,Dy³⁺ and SrAl₂O₄:Eu²⁺,Dy³⁺@Au under the same visible light ([Figure 22b, red line]), indicating the role of the pristine g-C₃N₄ in the photocatalytic H₂ generation. When the light is off, those systems without the SrAl₂O₄:Eu²⁺,Dy³⁺ cannot show the photocatalytic H₂ generation. This is different from the MO, MB and RhB degradation cases where the three aqueous phase dyes can be decomposed slightly in the absence of the external irradiation source owing to the self- and/or photocatalyst-sensitized degradation. Thus, Liu et al proved the synergistic effect of the Au SPR in the g-C₃N₄-Au composite and the persistent luminescence in the SrAl₂O₄:Eu²⁺,Dy³⁺, where only the g-C₃N₄@Au@SrAl₂O₄:Eu²⁺,Dy³⁺ can sustain the photocatalytic H₂ evolution from water in a sunless environment (*i.e.*, in the absence of external irradiation light).

Unlike the above work reported by Liu et al, Cui et al [66] demonstrated that the brick-like and micrometer-sized Sr₂MgSi₂O₇:Eu²⁺,Dy³⁺ MPLs could be directly used as a PCM for producing H₂ by the photocatalytic methanol reforming method under UV, visible light and dark conditions. The results reveal that the solar-to-hydrogen (STH) conversion efficiency under UV irradiation can be up to ~5.2%, which is slightly more than the highest STH conversion efficiency of 5 % for a particulate photocatalyst system [429-431]. In particular, the STH value can still be up to ~0.2 % in dark after removal of the UV light for 8 h. Moreover, the research conducted by Liu [57] and Cui et al [66] demonstrated that there are other factors that influence the photocatalytic efficiency of H₂ and O₂ production, among which the chemical nature and amounts of MPLs, PCMs, and
MPL@PCM composite, the assistance of surface plasmonic effect for spectral adaptation, the photocatalytic cycles, chemical and thermal stability of MPLs, PCMs and MPL@PCM composite, the external photocatalytic working conditions such as the PH value, temperature, and irradiation conditions (Figure 23). These factors provide insights into directing the future photocatalytic works by use of MPLs as an inner excitation light source to keep the photocatalytic activity. Since the persistent intensity of MPLs, such as SrAl2O4:Eu2+,Dy3+ [57] and NL-PA [381], can be gradually decreased in the absence of the external irradiation light, intermediately recharging the storage energy by re-exciting the MPL is a feasible approach to keep the persistent intensity at a certain intensity, leading to a new concept, i.e., “around-the-clock” photocatalytic activity.

6. Conclusions, challenges, and perspectives

Looking back on this review, we disclosures the recent advances and prospets of the MPLs as inner secondary excitation light for photocatalytic application. We first compile the MPLs attractive for coupling with the PCMs to form the self-luminous MPL@PCM composites, including the MPLs doped with RE ions such as the d-f transition ions (i.e., Eu2+, and Ce3+) and the well-shielded 4f ions (e.g., Eu3+, Pr3+, Tb3+, Sm3+, Er3+, Tm3+, Gd3+, Dy3+), non-RE ions (i.e., Bi3+, Pb2+, Mn2+, Cr3+, Mn4+), and the coupling arrangements of these RE and non-RE ions, as well as bulk MPLs. In the meanwhile, other RE and non-RE(e.g., Nd3+, Ho3+, Li3+ etc) ions that do not act as the luminescent centers but can be used to create the defects or modify the trap depth are also listed in this work. The persistent spectral region of these MPLs broadly covers the visible light, and/or parts of UV and NIR region. We hope that this summarization can promote the discovery of more novel MPLs, PCMs and self-luminous MPL@PCM composites for addressing some of the major photocatalytic challenges, i.e., the continuously supplied energy problem required in the photocatalytic activity. Then, we review the already-reported MPL@PCM composites. Along with the persistent spectral positions, excitation and photoemission spectra of MPLs and the absorption regions of PCMs, we discuss how to select a MPL to couple with a PCM to design the “persistent-photocatalytic” MPL@PCM composites. The major working principles and relevant mechanistic models are also discussed. In addition, we disclose the principal methods used for achieving the MPL@PCM composites, including the solid-state reaction, combustion route, CVD approach, hydrothermal and sol-gel methods. These methods are expected to promote the discovery of new synthesis routes, typically those needing to couple with different methods. At last, we take some examples
to illustrate the photocatalytic application of the MPL@PCM composites, including degradation from MO, MB and RhB dyes, removal of poisonous gas-phased materials, splitting of water, H₂ and O₂ production, decontamination of waste water, drugs and industrial waste etc.

As we have discussed and highlighted in the main text, the design and use of the self-luminous MPL@PCM composites for photocatalysis is still an open field, but will be of great significance for forthcoming future investigations. When compared to those photocatalytic activities that only involve the use of the PCMs or heterogeneous photocatalysts, the MPL@PCM composites have many in-depth issues needing to be resolved and explored, in terms of the fundamental research and technical-economic spin offs. At the current stage, all of the studies are still in academic study and thus waiting for the full-scale (or even bench-scale) practical applications in the future, but the potential challenges we shown below would be a great help for any researcher working in the photocatalytic field. On the whole, through the review, we realize: (i) how important number of possible combinations of MPLs and PCMs that have still to be tested to produce the self-luminous MPL@PCM composites; (ii) the strategic importance of chemistry in this concern, in terms of micro-, nano- and multiscale organization of materials, MPL-PCM interface engineering for an optimized synergy, adjustment of the persistent spectral range of MPLs through appropriate doping and/or co-doping, control of the persistent luminescent duration of the MPLs through careful management of the defects, adaptation of the absorption spectra of PCMs for an optimized overlap at the MPL@PCM composite interface, light extraction by surface texturation; (iii) the importance of how to widen the research logical thinking, not just limited to the current state, for example, the dependence of pollutants degradation rate (r) on the photon flow (p) is a very important influence factor in the heterogeneous photocatalysis [428], which, together with some theoretical calculations (e.g., DFT modeling), can be used to qualitatively analyze and discuss the in-depth photocatalytic principles behind the MPL@PCM and then confirm whether or not the use of a MPL@PCM composite could be beneficial to the overall rate of photocatalytic degradation, and to establish some reliable models to explain the photocatalytic activity. Moreover, although the MPL@PCM composites can sustain the photocatalytic activities in the absence of an external irradiation source, they still need an external pre-irradiation step. When the pre-irradiation step is finished, the persistent intensity and duration as the delay time goes on are decreased gradually, resulting in the weakening of photocatalytic reaction. Fortunately, with the assistance of the
regular decrease of the persistent intensity, the delay process of a given MPL can be easily parametrized. As a result, it is possible for us to design an automatic “round-the-clock” procedure that can allow for recharging the MPL@PCM composites repeatedly once the persistent intensity is low to a certain value or dose. Hence, the persistent duration and intensity problems of the MPLs, which are a first order lock in the context of the self-luminous MPL@PCM composites, can be intermittently and continuously renewed and complemented by using the same irradiation light source once the persistent intensity of MPLs is decreased to a given level. Unfortunately, however, except for the observation of the improved photocatalytic performance that is due to the improved photon utilization, it still lacks relevant study on how to monitor the photon efficiency of the persistent irradiation (i.e., how many photons at a given excitation wavelength are required to obtain the afterglow photons). For this concern, since the emission of a MPL can be quenched by means of photon absorption and scattering or somehow internal filtering effect and the quenching process can be presented by the decrement of luminescent intensity which is also estimated by the quantum efficiency [375], the energy transfer efficiency from a MPL to a PCM can be deduced to depend strongly on the contact or the distance between the MPL and PCM, and their matching (i.e., overlapping) spectral area between the emission spectra of MPL and the absorption spectra of PCM. Besides, as we have mentioned in the “5. Photocatalytic application of self-luminous MPL@PCM composites” section, in different works, the light sources used for the photocatalytic application of MPL@PCM composites are not the same. Some works use the sunlight as main photon source, while others would like to use the artificial light. Since the emission wavelength and the photon flux of the artificial light source, together with the PCMs and the reactor geometry, can be optimized while the emission wavelength and intensity of sunlight are relatively fixed, the use of different light source may lead to different photocatalytic results. Thus, a systematic study on how different light sources influence on the photocatalytic activities of the MPL@PCM composites should also attract more attention. As shown in Table 6, most of the MPLs successfully used nowadays for coupling with the PCMs for the photocatalytic application are aluminates- and silicate-based MPLs that address well the continuous persistent duration and intensity issues and meet different practical applications. Nevertheless, this situation encourages us to continue to explore new compositions of MPLs with longer persistent duration, stronger intensity and higher structural, thermal, chemical and moisture-resisted stability, as well
as more desirable persistent spectral region that can match the absorption range or the optical bandgap of the PCMs. In this case, engineering a suitable optical band gap in a given PCM is a very important thing if there are no suitable MPLs. Because of this consideration, we present in Figure 24 a graph that summarizes the persistent positions (i.e., the dominant positions from RE and non-RE ions doped MPLs and bulk MPLs we exhibited in this review), from which we can identify easily the most desirable positions of MPLs for the PCMs. Furthermore, we should also notice that when the light source is used for irradiating to the PCMs, only one side of the MPLs continuously emits the photons if the thicknesses of the MPL@PCM composites were too thick. Last but not the least, we point out the interesting perspectives that may also follow the use of the NIR light as a pre-irradiation light source to promote the MO degradation, H₂ evolution and RhB/phenol degradation, as done recently by Huang et al [304], Shi et al [393], Kang et al [405] who used the oxide nanocrystal-coupled PCMs (i.e., NaY(WO₄)₂-TiO₂-YF₃:Er³⁺,Tm³⁺,Yb³⁺,Bi³⁺, g-C₃N₄@Cs₃WO₃, g-C₃N₄@F-doped (NH₄)₀.₃(WO₄)₃) as the NIR-converting PCMs, although the photocatalytic activities were still under the continuous NIR irradiation. In fact, these perspectives are also the motivations of this review.

Looking forwards to the future, with the profound impact of the persistent luminescence in the photocatalytic field, allowing the MPLs to act as an inner excitation source for sustaining the photocatalytic process will be very attractive. Although more new self-NIR-luminous MPL@PCM systems are still waiting to be invented, we should treat the MPL@PCM composites like baby or like something new just appeared, bringing more of the scientists’ attention to them and let them grow up. In the end, we believe that this topic will promote the significant development of the MPL@PCM composite for addressing some of the major environmental challenges we are facing, and attract more and more attention of the scientists from different disciplines and fields, typically those with the backgrounds in chemistry, energy fuels, materials, physics environmental science, and optoelectronics, as well as the relevant subdivisions and multidisciplinary. In future, a number of new experimental observations, along with corresponding new physicochemical mechanisms and other previously-unnoticed applications, may appear. On the whole, this review contains many core points and implicactions, including but not limited to those we mentioned above. Disclosing this review can allow to understanding better the use of MPL@PCM composite for photocatalysis.
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Figure captions

Figure 1 Schematic organization of this review work along with each section heading and its subdivision headings. Meanwhile, seven pictures are also selected to illustrate the core point and the logical thinking of this review, including the persistent luminescence of MPLs whose colors broadly span from blue to green (top), photocatalytic degradation of Rhodamine B (RhB) and its mechanism (left), TiO2-BiVO4-ZnO catalysts (bottom), CaAl2O4:(Eu,Nd)@TiO2-Ni composite and its mechanism (right), and the photocatalytic mechanism of Ag-BiOBr PCM coupled blue NL-PA MPL composite with the external irradiation source on and off (center). These pictures can reflect that a suitable combination of MPLs and PCMs enables us to sustain the photocatalytic activity in the absence of the external irradiation source.

Figure 2 (a) (i) Normalized emission spectra of Y2.96Se2Ga3.4Al12.004Ce3+ [78], (ii) emission spectra of (Ca1.99Eu0.002)BO2Cl and (Ca1.99Eu0.002Dy0.002)BO2Cl and phosphorescence (persistent) spectra of (Ca1.99Eu0.002Dy0.002)BO2Cl [81], (iii) emission spectra of BaEu(Si3O8)2:Eu3+ and BaEu(Si3O8)2:Eu3+,Dy3+ [88], and (iv) persistent spectra of Ca4(PO4)2:Eu2+,Y3+ measured at 10 min, 30 min, and 2 h after removal of the excitation source [93]; (b) (i) Digital emission images of Y3Al2Ga3O12:Ce3+Cr3+ and SrAl2O4:Eu2+-Dy3+ under a white LED irradiation (upper), and 5 min after ceased the white LED light (middle), as well as Ce-Cr-doped Lu3Al2Ga3O12, Y3Al2Ga3O12, and Gd3Al2Ga3O12 after ceased the white LED (bottom) [84], (ii) digital emission images of Sr2+x,yAl2SiO4:xCe3+,yDy3+ (x = 0.005, y = 0, A; x = 0.005, y = 0.03, B; x = 0, y = 0.03, C) [89], and (iii) digital images of body, and emission of BaCaSiO4:Eu2+,Mn2+ under 254 nm UV lamp via different YF3 addition, together with the persistent colors measured at 30 s and 60 s after removing the 254 nm UV source [90]. In the figure, the irradiation or pre-irradiation sources are given.

Figure 3 (a) Persistent spectra of (i) Ca2+SnO2-xPr3+ (x=0.3%) [111], (ii) Sr2+Al2O2Cl2:0.02% Tb3+ [117], (iii) Sr2SiO4:Dy3+ [124], and (iv) Sr2SnO4:Sm3+ [131]; (b) (i) CIE chromaticity diagram under UV light excitation (A-C) and persistent luminescent chromaticity coordinates (D-F) of Lu2O3:R3+,M (R, M =Pr, HfIV; Eu; and Tb, Ca2+) [121], (ii) persistent spectra of CdSiO3:R3+ (R = Pr3+, Sm3+, Gd3+, Tb3+, and Dy3+) and their corresponding CIE chromaticity coordinates [133]; (c) Photographs of 4f RE emissions, from the left to right are Dy3+ in Gd2O3 [144], Tm3+ and Dy3+ in Ca9La6(GeO4)4O2 [145], Dy3+ in LiLaP2O12 [146], Tb3+ in KNaCa2(PO4)2:Na+ [147] and Ca9La6(GeO4)4O2 [145], Sm3+ in KNaCa2(PO4)2:Na+ [147], Eu3+ in Ca9La6(GeO4)4O2 [145], Pr3+ in (Ca,Zn)TiO2 [128], Eu3+ in X2-type Y2SiO5:Bi3+ [149].

Figure 4 (a) (i) Emission and excitation spectra of LaAlO3:Mn4+,Ge4+ [151], (ii) persistent spectra of Mg2GeO4:MN4+ co-doped with and without Re3+ (Re = Pr, Er, Nd, Yb) ions [155], and emission spectra of LaAl1.5Ga0.5O3 (iii) and La1.5Gd0.5AlO3 solid solutions (iv) [156]; (b) (i) Persistent imaging patterns of GdAlO3:Mn4+,Ge4+ and LaAlO3:Mn4+,Ge4+ under 325 nm pre-irradiation for 10 min (A) and recorded at the post-irradiation time of 1 min (B), 10 min (C), 30 min (D), 2 h (E), and 20 h min (F) [151], and (ii) GdAlO3:Mn4+,Ge4+@Au (A), GdAlO3:Mn4+,Ge4+@SiO2 (B), and GdAlO3:Mn4+,Ge4+ (C) from 0 min to 24 h [154].

Figure 5 (a) (i) Normalized photoluminescence and (ii) long-persistence phosphorescence spectra (λex = 320 nm) as a function of Al concentration in the Zn2xAl2Sn1-xO4 (x = 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, and 0.4, corresponding to ZS4-ZS10) [164], (iii) excitation and emission spectra of Zn4Al2Ge2O10:0.01Cr3+ [177], and (iv) excitation and emission spectra of ZnGa2O4:Cr3+,Bi3+ and ZnGa2O4:Cr3+ pellets [196]; (b) (i) Digital photos and NIR images of Zn3Ga2GeO8:Cr3+ (left) and
Zn$_3$Ga$_2$SnO$_6$:Cr$^{3+}$ (right) powders after being acquired at different time intervals (from 5 min to 300 h) [160], (ii) persistent imaging of SrAl$_2$O$_3$:Cr$^{3+}$,Ti$^{4+}$ (right), SrAl$_2$O$_3$:Cr$^{3+}$ (middle), and SrAl$_2$O$_3$:Cr$^{3+}$ powders (left) recorded from 3 min to 5 h [182], and (iii) NIR persistent images of Zn$_3$Ga$_2$Ge$_2$O$_{10}$:Cr$^{3+}$ ceramic disks (right row) and LumiNova-G pills (left row) taken from 2 min to 50 h after irradiated by a 365 nm UV lamp (left column) and direct sunlight (right column) for 5 min [39].

Figure 6 Persistent spectra of (a) CaZnGe$_2$O$_6$:Mn$^{2+}$ recorded from 1 min to 8 min [199], (b) γ-Zn$_3$(PO$_4$)$_2$:Mn$^{2+}$,Ga$^{3+}$ [203], (c) LiGaSiO$_4$:xMn$^{2+}$ [206], (d-f) (89-x)GeO$_2$-11Al$_2$O$_3$-xCaO-1MnO (x = 10) from 30 s to 24 h [208], (g) Li$_2$ZnGeO$_4$ (LZGO) and Li$_2$ZnGeO$_4$:xMn$^{2+}$ (LZGO:Mn) after removal of 254 nm excitation and the corresponding photos (inset) taken under sunlight and 254 nm irradiation, and after removal of 254 nm excitation [215]; (h) Photoluminescence spectra of (Mg,Zn)Ge$_2$O$_3$:Mn$^{2+}$,Yb$^{3+}$ [228]; (i) photoluminescence (PL) and persistent luminescence (PersL) spectra of CaMg$_2$Ge$_2$O$_6$:Mn$^{2+}$ [233].

Figure 7 (a) (i) Fluorescent (upper) and afterglow (bottom) images of Ca$_2$Sn$_2$Al$_2$O$_9$:Mn$^{2+}$ [210], (ii) persistent images (0-180 s) of the 8Na$_2$O·12Ga$_2$O$_3$·8GeO$_2$:Mn$^{2+}$ glass prepared upon different crystallization times (0.5 h) at removal of 254 nm UV light [222], and (iii) photographs of (89-x)GeO$_2$-11Al$_2$O$_3$-xCaO-1MnO (x = 10) placed on different patterns of mesh paper and taken at the persistent time of 40 s after removal of 254 nm illumination [208]; (b) (i) CIE chromaticity coordinates of γ-Zn$_3$(PO$_4$)$_2$:1%Mn$^{2+}$,y%Ga$^{3+}$ (y = 1-8) [203], and (ii) LiGaSiO$_4$:xMn$^{2+}$ and their relevant photographs (inset) [206].

Figure 8 (a) (i) Persistent spectra of KGaGe$_2$O$_4$:xBi$^{3+}$ and the relationship between the persistent intensity and the Bi$^{3+}$ content (inset) [260], (ii) intensity-normalized photoluminescence (PL), long-lasting (LPL), and photostimulated (PSL) spectra of CaGa$_2$O$_4$:Bi$^{3+}$ and a photo (inset) [269], and (iii) persistent spectra of Sr$_2$:99Bi$_{0.01}$Ga$_4$O$_9$ from 30 s to 246 min [261]; (b) Photographs of (i) Sr$_2$:985Bi$_{0.015}$Ga$_4$O$_9$ taken within the range of 0-600s after removal of 254 nm UV lamp [261], and (ii) LiYGeO$_4$:Bi$^{3+}$ in the range of 24-300 h and its relevant PSL luminescent images under 980 nm, 808 nm, and a LED irradiation and taken after 300 h (bottom row) [265]; (c) (i) Persistent spectrum of CdSiO$_3$:Pb$^{2+}$ [270], (ii) fluorescence spectra of CaO:Pb$^{2+}$ (A) and SrO:Pb$^{2+}$ (B) and persistent spectrum of SrO:Pb$^{2+}$ (C) [271], (iii) persistent spectra of Sr$_2$MgGe$_2$O$_7$:Pb$^{2+}$ [273].

Figure 9 (a) (i) Excitation, photoluminescence (PL) and persistent spectra of SrZrO$_3$ [319], (ii) PL (1) and the persistent (PerL) spectra of SrZrSi$_2$O$_7$ sintered in reducing atmosphere (2) and air (3), the insets are persistent (left) and PL images (right) of the sample [328], (iii) persistent spectra of Na$_2$(Zn$_{1.6}$Ga$_{2.4}$)GeO$_4$ and the image of Na$_2$(Zn$_{0.8}$Ga$_{0.2}$)GeO$_4$ after removal of femtosecond laser (inset) [329], (iv) normalized PL and persistent spectra of ZrO$_2$ [331]; (b) Persistent images of (i) Mg$_2$SnO$_4$ [320], and (ii) MgGa$_2$O$_4$ [322], (iii) PL colors of bauxite-type BaZr$_1$,Ti$_x$Si$_3$O$_9$ under 254 nm and 312 nm light and persistent images of a pabstite-type BaSn$_1$,Ti$_y$Si$_3$O$_9$ [327].

Figure 10 (a) Upconverting persistent spectrum of Zn$_3$Ga$_2$Ge$_2$O$_8$:Cr$^{3+}$,Yb$^{3+}$,Er$^{3+}$ phosphor and its decay curve monitored at 700 nm peak (inset, upper right) and NIR images (inset, upper left) [40]; (b) Upconversion fluorescent spectra of the β-NaYF$_{4}$:Yb,Er/NaYF$_{4}$ membrane achieved with different 980 laser powers [343]; (c) Emission spectra of NaCa$_2$Ge$_2$O$_6$F:0.2%Mn$^{2+}$,xYb$^{3+}$ [345]; (d) Phonon-assisted upconversion persistent spectra of Zn$_3$Ga$_2$Ge$_2$O$_8$:Cr$^{3+}$ recorded at 20 °C and 70 °C and the corresponding decay curves acquired within 60 min [362].
Figure 11 (a) Photographs of the KCDf3:Yb3+,Mn2+, KCDf3:Yb3+,Mn,Er3+, KCDf3:Yb3+,Mn,Ho3+, and KCDf3:Yb3+,Mn,Sm2+,Ti3+ (from bottom to upper) with the dynamic radiation of a 980 nm laser and luminescence images of a printed plantlet (the bottom left, inset) [355]; (b) Persistent images of Y3Al5,Ga2O12:Ce3+,Cr3+ (YAGG:Ce-Cr) and Y3Al5,Ga2O12:Nd3+,Ce3+,Cr3+ (YAGG:Nd-Ce-Cr) [347]; (c) Upconversion persistent decay images of Zn3Ga2GeO6:Yb3+,Er3+,xCr3+ (x = 0.2%, 0.5%, 0.8%) recorded from 5 min, 10 min, 30 min, and 120 min [356].

Figure 12 Energy positions of some mainstream semiconductors and noble metal photocatalysts [369].

Figure 13 (a) UV-vis diffuse reflectance spectra of Sr2MgSi2O7:Eu2+,Dy3+ (M, orange curve) phosphor coupled with different Ag3PO4 (A, black curve) contents (M:A = 20:1 (blue curve), 15:1 (green curve), 10:1 (violet curve), and 5:1 (red curve) [377], where the inset is the persistent images of Sr2MgSi2O7:Eu2+,Dy3+ before and after dispersed in CH3OH [66]; (b) Persistent spectra of (a) samples of recorded at 10 s after removal of 360 nm UV light [377], where the curve colors are related that of (a); (c) Excitation (λem = 320 nm) and emission spectra (λex = 380 nm) of Ca1.993MgSi2O7:0.005Ce3+ powder (solid), mixture of Ca1.993MgSi2O7:0.005Ce3+ and kaolin with compression (dash), and after 900 °C sintering (dot), and after depositing with TiO2 in 6.3 mg/cm² [366]; (d) Transmission spectrum of TiO2-deposited glass (●), and absorption spectrum of TiO2-deposited Ca2MgSi2O7:Ce3+ ceramic (●), where the photographs (inset) of the light penetration (●), the ceramic substrate made from the Ca1.995MgSi2O7:Ce3+0.005-kaolin with 6.3 mg/cm² of TiO2 deposition (●), and the ceramic substrate under UV irradiation (iii) [366].

Figure 14 Mechanism for the improved photocatalysis of Ag3PO4 by better photon utilization and charge separation with Sr2MgSi2O7:Eu2+,Dy3+ [377].

Figure 15 Schematic model of persistent Sr2MgSi2O7:Eu2+,Dy3+ phosphor-assisted photocatalytic reaction with light on and off [377].

Figure 16 (a) SEM image of Ca2MgSi2O7:Ce3+ substrate (i), and Ca2MgSi2O7:Ce3+@TiO2 composite (ii) [366]; (b) Field emission SEM images of Ca2MgSi2O7:Eu2+,Ce3+ (i), g-C3N4 (ii), Ca2MgSi2O7:Eu2+,Ce3+@g-C3N4 (iii), and (iv) high-magnification FESEM image of (ii) [379]; (c) SEM image of ZnGa2O4 [310]; (d) SEM image of (2ZnO:Ga2O3:2GeO2):Cr@TiO2; [383]; (e) SEM images of ZnGa2O4 (i) and ZnGa2O4:Cr3+ (ii) [197]; (f-g) TEM (i) and HRTEM (ii) images of Sr2MgSi2O7:Eu2+,Ce3+@g-C3N4 [379] and BaZrO3:Me2+@TiO2 composites [311]; and (h) SEM images of Ag3PO4 (i), Sr2MgSi2O7:Eu2+,Ce3+ (ii), and Sr2MgSi2O7:Eu2+,Ce3+@Ag3PO4 (iii) [377].

Figure 17 (a) Field emission SEM (i) and TEM (ii) images as well as EDX spectrum (inset) of Ca2Al2SiO7:Ce3+@Ag-AgCl (10:1) composite [63]; (b) SEM images of MgAl2O4:Pr3+,Dy3+ (i), and MgAl2O4:Pr3+,Dy3+@Cr-TiO2 (ii) [107]; (c) TEM images of g-C3N4 (i) and SrAl14O25:(Eu,Dy) MPL coupled with 60% wt of g-C3N4 (ii), and SEM images of SrAl14O25:(Eu,Dy) (iii) and Sr2Al14O25:(Eu,Dy) MPL coupled with 60% wt of g-C3N4 (iv) [65]; (d) SEM images of GP MPL (i-ii) and GP@Fe-N-TiO2 prepared with PEG 200 (iii) and 400 (iv) [384]. Noted that GP MPL is denoted as a alumina-based persistent phosphor ((provided by DB-Chemic).

Figure 18 (a) UV-Vis absorption spectra of MO degraded using UTSA-38 photocatalyst [404]; (b) C/C0 of MO degradation placed in xSr2MgSi2O7:Eu2+,Dy3+@yAg3PO4 (curves 1-5 are x:y = 5:1, 10:1, 15:1, 10:1, 1:0, respectively) and recored in the persistent step as a function of time [377]; (c) Time-dependent MO degradation process placed in the Ca2Al2SiO7:Ce3+ (curve 1), Ag-AgCl
(curve 2), and Ca$_{2}$Al$_{5}$Si$_{7}$O$_{21}$:Ce$^{3+}$:Ag-AgCl (curve 3), and recored in dark, under light irradiation and in the absence of light [63]; (d) Expanded persistent MO degradation step (i.e., after-light-off) of (c) with the ordinate expressed by C/C$_{0}$ [63].

**Figure 19 (a-b)** Persistent photocatalysis degradation of RhB in the Ag$_{3}$PO$_{4}$:Sr$_{2}$MgSi$_{2}$O$_{7}$:Eu,Dy, Ag$_{3}$PO$_{4}$:Sr$_{4}$Al$_{12}$O$_{25}$:Eu,Dy,Er, Ag$_{3}$PO$_{4}$:SrAl$_{2}$O$_{4}$:Eu,Dy, and Ag$_{3}$PO$_{4}$@silicone-acrylic-emulsion coating systems in dark condition [376], where the Sr$_{2}$MgSi$_{2}$O$_{7}$:Eu,Dy is denoted as “SMSOED”; (e) Photocatalytic degradation of RhB in bulk ZnGa$_{2}$O$_{4}$ (S1), Zn$_{0.95}$Ga$_{2}$O$_{3.95}$ (S2), Zn$_{0.9}$Ga$_{2}$O$_{3.9}$ (S3), Zn$_{0.85}$Ga$_{2}$O$_{3.85}$ (S4), and Zn$_{0.8}$Ga$_{2}$O$_{3.8}$ (S5) [342]; (d) Photocatalytic degradation of the RhB dye on different BiOBr films with and without long-afterglow phosphor [381], where the photocatalytic process is divided into two steps, i.e., the light on (0-60 min) and light off (60-120 min).

**Figure 20 (a)** Photocatalytic decomposition of MB dye in the Sr$_{4}$Al$_{12}$O$_{25}$:(Eu,Dy), g-C$_{3}$N$_{4}$, and various Sr$_{4}$Al$_{12}$O$_{25}$:(Eu,Dy)@g-C$_{3}$N$_{4}$ composites in dark condition (-0.5-0 h) and in the presence of visible-light irradiation (0-5 h); (b) Persistent luminescence assisted MB decomposition in dark with the the same reaction conditions of (a) [65]; (c) Decomposition curves of MB dye placed in CdSiO$_{3}$:Gd$^{3+}$,Bi$^{3+}$:TiO$_{2}$ composite (curve 1), pure TiO$_{2}$ (curve 2) and CdSiO$_{3}$:Gd$^{3+}$,Bi$^{3+}$ (curve 3) in dark (iv) [141], (d) Photocatalytic decomposition of MB dye placed in BaZrO$_{3}$:Mg$^{2+}$:TiO$_{2}$ composite, pure TiO$_{2}$ and BaZrO$_{3}$:Mg$^{2+}$ in dark without the UV light irradiation [311].

**Figure 21 (a)** Photocatalytic activity of NO destruction placed in Cr-doped SrTiO$_{3}$ (curve 1) and nonstoichiometric SrTiO$_{3}$ (curve 2) under UV, blue, green and LED irradiation [385]; (b) DeNO$_{x}$ process placed in CaAl$_{2}$O$_{3}$:(Eu,Nd)@Cr-doped SrTiO$_{3}$ and CaAl$_{2}$O$_{3}$:(Eu,Nd)@nonstoichiometric SrTiO$_{3}$ with and without the UV LED irradiation ($\lambda > 290$ nm) [385]; (c-d) Photocatalytic deNO$_{x}$ activity placed in CaAl$_{2}$O$_{3}$:(Eu,Nd)@TiO$_{2}$,N$_{2}$ (curve 1), brookite-phase TiO$_{2}$,N$_{2}$ (curve 2), and CaAl$_{2}$O$_{3}$:(Eu,Nd)@undoped TiO$_{2}$ (curve 3) under and without the UV LED irradiation [61].

**Figure 22 (a)** UV-vis diffuse reflectance spectra of pristine g-C$_{3}$N$_{4}$, g-C$_{3}$N$_{4}$@xwt%Au composites, and g-C$_{3}$N$_{4}$@Au@SrAl$_{2}$O$_{4}$:Eu,Dy composite, along with the absorption spectra of Au nanoparticle stock solution and persistent spectra of the SrAl$_{2}$O$_{4}$:Eu,Dy and g-C$_{3}$N$_{4}$@Au@SrAl$_{2}$O$_{4}$:Eu,Dy; (b) Time course for H$_{2}$ evolution of the g-C$_{3}$N$_{4}$, SrAl$_{2}$O$_{4}$:Eu,Dy, SrAl$_{2}$O$_{4}$:Eu,Dy@Au, g-C$_{3}$N$_{4}$@Au, g-C$_{3}$N$_{4}$@SrAl$_{2}$O$_{4}$:Eu,Dy, and g-C$_{3}$N$_{4}$@Au@SrAl$_{2}$O$_{4}$:Eu,Dy composite with and without visible light irradiation; (c) Time course for H$_{2}$ evolution of the g-C$_{3}$N$_{4}$, g-C$_{3}$N$_{4}$@xwt%Au composites, the inset shows the photocatalytic activities as a function of the embedded Au content; (d) Time course for H$_{2}$ evolution of g-C$_{3}$N$_{4}$@Au@xSrAl$_{2}$O$_{4}$:Eu,Dy composites with different mass ratios of g-C$_{3}$N$_{4}$@Au and SrAl$_{2}$O$_{4}$:Eu,Dy with and without visible light irradiation [57].

**Figure 23** Dependence of pH reactive mediums (a), time course (b), irradiation duration (c), and temperature (d) on photocatalytic performance of Sr$_{2}$MgSi$_{2}$O$_{7}$:Eu$^{2+}$,Dy$^{3+}$ in dark [66].

**Figure 24** A distribution pattern of the persistent intensity maxima of the RE- and non-RE-doped MPLs, and bulk MPLs we exhibited in this review. Noted that there are 300 points but some of them are overlapped with each other.
Recent advances and prospects of persistent luminescent materials as inner secondary self-luminous light source for photocatalytic applications

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**Key words:** persistent luminescence; inner light source; self-luminous; rare-earth (RE); non-RE; photocatalysis.

**TOC figure**

A suitable combination of MPLs and PCMs enables sustaining the photocatalytic activities when there is no external light irradiation source.
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6. Prof. Jian Lu

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