



 Cite this: *RSC Adv.*, 2025, 15, 37074

# Application of photoluminescent materials in cultural relics protection

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At present, issues such as counterfeiting of cultural relics, damage to cultural relics, and difficulties in the restoration and detection of cultural relics are urgent problems to be solved in cultural relics protection. Therefore, it is necessary to develop protective materials for cultural relics to prevent their counterfeiting, delay their damage, and achieve visual detection. Photoluminescent materials match well with the requirements of protecting cultural relics and have become a research hotspot in cultural relics protection due to their advantages of rich optical properties, low damage potential, high chemical stability, and safety. This study firstly introduces the luminescence mechanisms and main synthesis strategies of photoluminescent materials. Then, the research status of the photoluminescent materials in cultural relics protection in recent years is elaborated in detail, and four types of applications of photoluminescent materials in cultural relics protection (anticounterfeiting of cultural relics, anti-aging of cultural relics, damage monitoring of cultural relics, and restoration detection of cultural relics) are summarized and concluded. Finally, the problems and challenges faced in the application of photoluminescent materials in cultural relics protection are pointed out, and future development directions are proposed.

 Received 14th August 2025  
 Accepted 17th September 2025

DOI: 10.1039/d5ra05991g

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## 1. Introduction

In recent years, many countries like China, the United Kingdom, India, and France have placed an increasingly greater emphasis on cultural heritage.<sup>1,2</sup> Cultural heritages can be divided into tangible cultural heritages and intangible cultural heritages. The core component of tangible cultural heritages is the cultural relics.<sup>3</sup> Cultural relics embody splendid civilization, history and culture, serving to maintain cultural diversity,

enhance the country's cultural soft power, promote tourism development, and strengthen national cultural confidence.<sup>4</sup> Therefore, protecting cultural relics is an important prerequisite for promoting national cultural development.<sup>5,6</sup> However, many cultural relics are currently facing various kinds of damage and hazards, such as cultural relics forgery,<sup>7-9</sup> imperfect preservation environments that lead to aging and damage of cultural relics,<sup>10-12</sup> and difficulties in detecting the effect of cultural relics restoration.<sup>13,14</sup> Therefore, various types of functional materials are usually used to verify the authenticity of cultural relics, delay their damage and enable visual detection.<sup>14-17</sup> Luminescent materials represent a class of

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materials with a wide range of applications. The protection of cultural relics with the help of luminescent materials, which possess rich optical properties, low damageability, high chemical stability and safety, is presently one of the hotspots in the field of cultural relics protection.<sup>18–22</sup>

Luminescent materials, just as their name implies, is a type of material that can absorb energy in a certain way and convert the energy into light radiation.<sup>22</sup> In recent years, the types of luminescent materials that have been widely studied mainly include photoluminescent materials,<sup>23,24</sup> mechanoluminescent materials,<sup>25,26</sup> electroluminescent materials,<sup>27,28</sup> thermoluminescent materials,<sup>29,30</sup> and chemiluminescent materials.<sup>31,32</sup> Among these, photoluminescent materials have received the most extensive research attention. Transition metal element-doped luminescent materials and rare earth element-doped luminescent materials are typical research representatives in photoluminescent materials due to their abundant optical properties. Due to the differences in the doped elements of the two types, they have significant differences in their optical properties. The light excitation range of transition metal element-doped luminescent materials (such as  $\text{Mn}^{4+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Mn}^{2+}$ ) is usually located in the UV-Vis light region, which is wide. Their luminescence comes from the strong coupling of the d electron energy levels and is thus greatly affected by the crystal field environment, resulting in broadband emission. Meanwhile, rare earth element-doped luminescent materials (such as  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Er}^{3+}$ ) have a larger light excitation range, with the excitation range spanning from the UV to NIR light region. Their luminescence mainly comes from the localized 4f electron energy levels, and the 4f orbitals are shielded by the  $5s^2$  and  $5p^6$  outer orbitals which are completely filled. Therefore, the luminescence is less affected by the external chemical environment (matrix lattice) and has sharp-line emission. In addition, the luminescence color, luminescence intensity, and luminescence lifetime of the two can be adjusted by changing the doped elements and the matrix.<sup>33–37</sup> Therefore, through specific structure design and controllable synthesis, the optical properties of photoluminescent materials can be precisely

regulated in multiple dimensions, such as the color of luminescence, luminescence intensity, and luminescence lifetime.<sup>23,24,38</sup> More importantly, based on the physical and chemical properties of cultural relics and their protection requirements, suitable photoluminescent materials with specific luminescent properties can be designed and synthesized.

Over the past decade, optical anticounterfeiting traceability, optical preventive protection technologies, and optical imaging visualization detection based on photoluminescent materials have been widely reported, demonstrating significant application potential in the protection of various cultural relics. This study firstly provides an overview of the luminescence mechanisms and synthesis strategies of photoluminescent materials, and focuses on summarizing the research status of photoluminescent materials in cultural relics protection in recent years. Four types of applications of luminescent materials in cultural relics protection are summarized, namely anticounterfeiting of cultural relics (the fundamental protection of cultural relics), anti-aging of cultural relics (preventive protection of cultural relics), damage monitoring of cultural relics (protective measures during the damage process of cultural relics), and restoration detection of cultural relics (protective measures during the restoration process after damage to cultural relics). Finally, the review analyzes and looks ahead to the problems, and challenges existing in the application of photoluminescent materials in cultural relics protection.

## 2. Luminescence mechanisms of photoluminescent materials

Photoluminescence refers to the process where a material is excited by absorbing photons (ultraviolet, visible or infrared light) and then releases photons through radiative transition.<sup>23,24,38,39</sup> So far, researchers have conducted extensive studies on various photoluminescent materials, mainly divided into inorganic photoluminescent materials and organic phosphorescent materials.<sup>40–43</sup> Different types of photoluminescent



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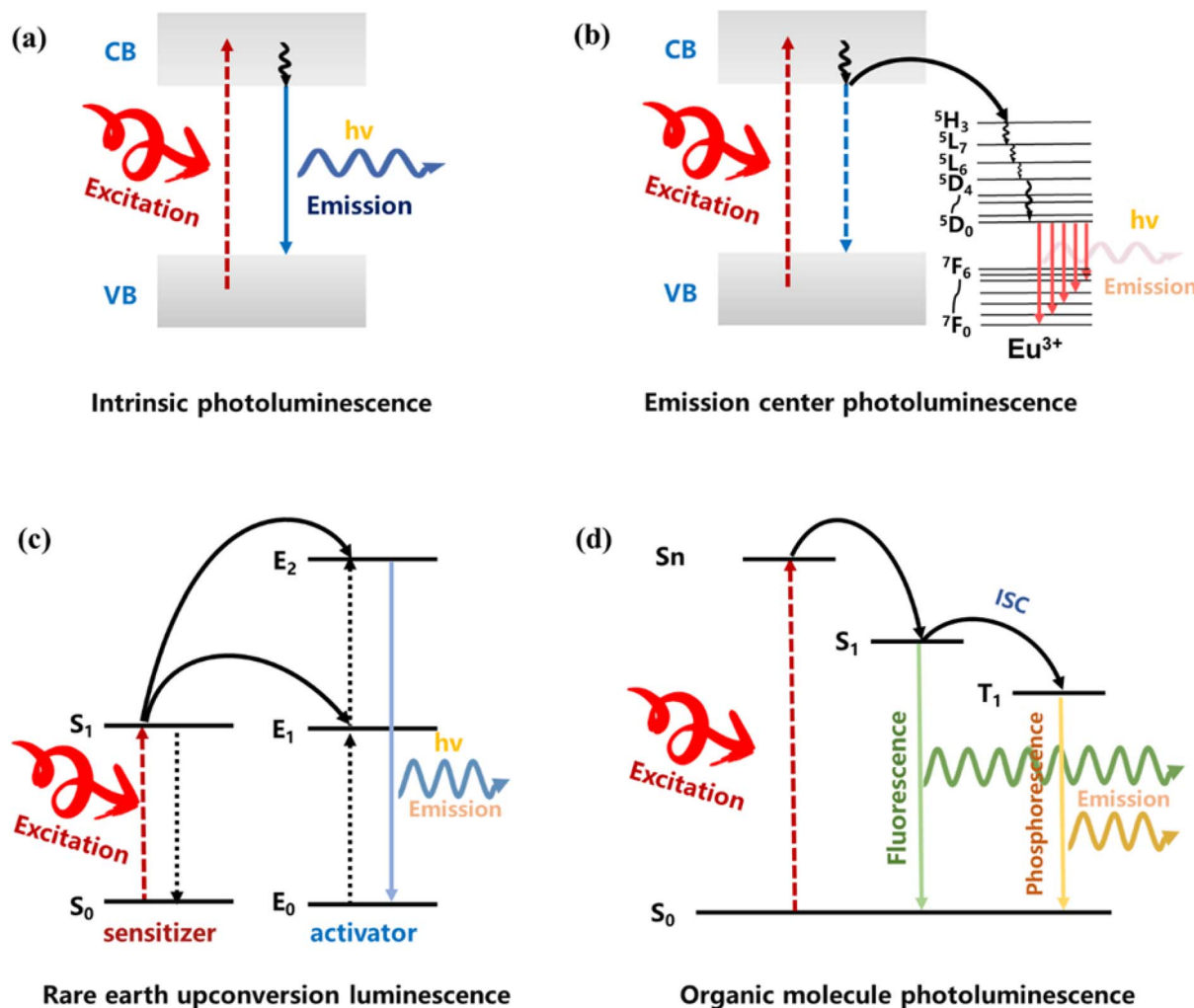


Fig. 1 Luminescence mechanism of (a) intrinsic photoluminescence; (b) emission center photoluminescence; (c) rare earth upconversion luminescence; and (d) organic molecule photoluminescence.

materials have different luminescence mechanisms, mainly including intrinsic photoluminescence,<sup>39</sup> emission center (impurities, defects, dopants) photoluminescence,<sup>44</sup> rare earth upconversion photoluminescence,<sup>45–47</sup> and organic molecule photoluminescence.<sup>42,43,48</sup> A thorough understanding of the luminescence mechanisms of each type of photoluminescence materials is also a prerequisite for their rational structure design, controllable synthesis, and subsequent application in cultural relics protection. This chapter will provide an overview and discussion of the luminescence mechanisms of the photoluminescence materials.

### 2.1. Luminescence mechanism of intrinsic photoluminescence

Intrinsic photoluminescence refers to the luminescence phenomenon that occurs in pure semiconductor or insulator materials when their intrinsic electronic structure (rather than impurities or defects) is excited by light.<sup>39,49–51</sup> The luminescence mechanism mainly involves the intrinsic electronic

structure and energy band characteristics of the materials. The specific mechanism is as follows: after absorbing the energy (photons) from light radiation, electrons in the valence band transition to the conduction band, while leaving holes in the valence band. If the absorbed photon energy is much greater than the band gap, the electrons may transition to a higher energy level and then return to the conduction band bottom through non-radiative relaxation (thermal relaxation, phonon scattering, *etc.*), and the holes relax to the valence band top. Moreover, in low-temperature or high binding energy materials, electrons and holes may form bound states (excitons) due to Coulomb interaction and be excited to transition to the conduction band. Finally, the electrons transition from the bottom of the conduction band (or exciton state) back to the top of the valence band, releasing the energy difference as photons, known as photoluminescence (Fig. 1a). Common photoluminescent materials with such luminescence mechanism include semiconductor quantum dots,<sup>49</sup> carbon quantum dots,<sup>50</sup> and two-dimensional materials.<sup>51</sup>



## 2.2. Luminescence mechanism of the emission center photoluminescence (impurities, defects, dopants)

The light absorption process of the emission center (impurities, defects, dopants) in photoluminescence is similar to that of intrinsic photoluminescence, while the light emission process is achieved by transferring energy to the emission center and the radiative transition of the emission center (impurities, defects, dopants).<sup>44,52–54</sup> The specific luminescence mechanism is as follows: the material absorbs the energy under light irradiation, and electrons transition from the valence band to the conduction band, or form electron–hole pairs (excitons) through an indirect transition. Then, the electrons (excitons) transfer the energy to the excited energy level of the emission center (impurities, defects, dopants) through non-radiative transitions (such as phonon scattering) and energy transfer (resonance energy transfer, Dexter transfer or carrier capture). Finally, the excited-state electrons return to the ground state through radiative transitions and release photons (Fig. 1b). Common photoluminescent materials with such luminescence mechanisms include fluorescent powders (such as rare earth doped:  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ , transition-metal doped:  $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ ),<sup>52,53</sup> and doped semiconductor quantum dots (such as  $\text{CdSe}:\text{Mn}^{2+}$ ).<sup>54</sup>

## 2.3. Luminescence mechanism of rare earth upconversion luminescence

Rare earth upconversion luminescence is a nonlinear anti-Stokes emission process that emits high-energy photons (visible light or ultraviolet light) after absorbing multiple low-energy photons (typically near-infrared light). The entire luminescence process is completed by rare earth ions, including sensitizer ions and activator ions.<sup>45–47,55</sup> The specific mechanism of luminescence is as follows: the sensitizer ions in the material absorb light energy (photons) and transfer the energy to the activator ions, causing the activator ions to transition to an intermediate energy level. Subsequently, the activator ions accept energy from the sensitizer ions again and transition to a higher energy level, repeating this process (with non-radiative relaxation occurring in between). Finally, the activator ions rise to the excited state energy levels and transition to the ground state through radiative relaxation with the release of high-energy photons (Fig. 1c). Common photoluminescent materials with rare earth upconversion luminescence mainly include rare earth upconversion luminescent nanomaterials (such as  $\text{NaYF}_4:\text{Yb},\text{Er}$ ),<sup>55</sup> *etc.*

## 2.4. Luminescence mechanism of organic molecules photoluminescence

The luminescence process of organic molecules mainly involves the excitation state relaxation process with emitting photons after the molecules absorb light energy. It mainly consists of two types: fluorescence and phosphorescence.<sup>42,43,48,56–60</sup> The specific luminescence mechanism is as follows: after absorbing photons, the ground state ( $S_0$ ) electrons of organic molecules transition to higher-energy excited singlet states ( $S_1, S_2 \dots S_n$ ) first, usually corresponding to  $\pi \rightarrow \pi$  or  $n \rightarrow \pi$  transitions.

Then, the high-energy excited state (such as  $S_n$ ) rapidly relaxes to the lowest excited singlet state ( $S_1$ ) through non-radiative transitions (internal conversion) or loses vibrational energy to reach the lowest vibrational energy level of  $S_1$  (vibrational relaxation). Finally, the excited electron state transitions to the ground state ( $S_0$ ) and emits fluorescence; if there is spin–orbit coupling (such as molecules containing heavy atoms or carbonyl groups), some electrons may transfer from  $S_1$  to the triplet state ( $T_1$ ) (intersystem crossing, ISC) with a change in the spin state to triplet, and then transition to the ground state ( $S_0$ ) and emit phosphorescence (Fig. 1d). Common organic molecules that emit fluorescence include traditional fluorophores (such as rhodamine)<sup>57</sup> and aggregation-induced emission molecules (such as tetraphenylethene),<sup>58</sup> *etc.* In addition, organic molecules that emit phosphorescence include carbazole derivatives (such as  $\text{CzBN}$ )<sup>59</sup> and aromatic carbonyl compounds (such as diphenyl ketone),<sup>60</sup> *etc.*

## 3. Synthesis strategies of photoluminescent materials

The synthesis strategies for photoluminescent materials are diverse, and the structures, luminescence mechanisms, and luminescent properties of the materials obtained through different synthesis strategies vary. Generally, an appropriate synthesis method needs to be selected based on the type of the target materials (fluorescent powders, quantum dots, upconversion luminescent nanomaterials, organic molecules, *etc.*), the luminescence mechanism (intrinsic luminescence, upconversion, *etc.*), and the application requirements (optical anti-counterfeiting traceability, fluorescence labeling imaging, and optical preventive protection technologies, *etc.*). The synthesis methods can be mainly divided into two categories: the synthesis of inorganic photoluminescent materials and the synthesis of organic photoluminescent materials. The synthesis strategies for inorganic photoluminescent materials mainly include solid–state reaction method,<sup>61–64</sup> sol–gel method,<sup>65,66</sup> hydrothermal/solvothermal method,<sup>67,68</sup> and co-precipitation method.<sup>69,70</sup> The preparation of organic photoluminescent materials mainly relies on designing molecules with specific luminescent properties and synthesizing.<sup>71,72</sup> Different synthesis strategies have their own unique characteristics and target materials (Table 1). This chapter will provide an overview and discussion of these synthesis strategies.

### 3.1. Solid-state reaction method

The traditional solid–state reaction method involves mixing two or more solid substances (with the constituent elements' precursor compounds mixed in a stoichiometric ratio) and heating them to form a solid product through the diffusion interaction between the solids. During the heating process, the mixture undergoes four stages: diffusion, reaction, nucleation, and growth. During this reaction process, a large number of chemical bonds are broken, and then a new crystal structure undergoes reorganization (Fig. 2a). The solid–state reaction method has some inherent advantages, such as a simple



Table 1 Synthesis strategies of luminescence materials, their characteristics and target materials

Synthesis strategy	Characteristics	Type of target materials
Solid-state reaction method	A simple synthesis process, readily available raw materials with low cost, large-scale production capability, products with a large surface area, "clean" reactions (without involving other elements), and especially easy introduction of defects into the host lattice	Fluorescent powders, <sup>61–63,73,74</sup> nanomaterials <sup>64</sup>
Sol-gel method	Good product uniformity, controllable particle size, lower hardness, higher purity, difficult to control the morphology, high temperature calcination is required	Fluorescent powders <sup>65,66,75,76</sup>
Hydrothermal/solvothermal method	Low synthesis temperature, mild conditions, small oxygen content, insignificant defects, stable system, special reaction equipment is required, and organic additives are usually required to control the form	Quantum dots, <sup>67</sup> MOFs, <sup>68</sup> fluorescent powders <sup>77,78</sup>
Co-precipitation method	Low cost, environmentally friendly, convenient synthesis, generally requires subsequent calcination treatment	Nanomaterials, <sup>69,79,80</sup> quantum dots <sup>70</sup>
Organic synthesis method	High selectivity and controllability, diverse reaction types, flexible strategy design, good product machinability, high purification cost, poor product stability	Organic molecules <sup>71,72,81,82</sup>

synthesis process, readily available raw materials with low cost, large-scale production capability, products with a large surface area, "clean" reactions (without involving other elements), and especially easy introduction of defects into the host lattice. Therefore, the solid-state reaction route is one of the most commonly used methods for preparing polycrystalline solids. However, due to its unique chemical reaction mechanism, solid-state reactions conducted by heating usually require high temperatures and long reaction times to overcome diffusion barriers. Inevitably, some problems arise such as undesirable aggregation phenomena, larger particle diameters at the random micrometer scale, the formation of phase impurities, and difficulty in controlling the uniformity of the morphology. According to the synthesis characteristics of the solid-state reaction method, it is mainly applicable to the preparation of various inorganic phosphors. The structure and luminescent properties of the phosphors can be controlled by changing the reaction conditions. Zhao *et al.* used sodium carbonate as a fluxing agent and prepared a Gd<sub>2</sub>Mo<sub>3</sub>O<sub>9</sub>:Eu red phosphor through the solid-state reaction method.<sup>73</sup> Then, the effects of different flux contents and sintering temperatures on the luminescent properties were investigated. By comparing the emission spectra and excitation spectra under different synthesis conditions, it was proved that the optimal flux content was 3% and the optimal sintering temperature was 800 °C. Pan *et al.* thoroughly explored the effects of different types of flux (NH<sub>4</sub>Cl, H<sub>3</sub>BO<sub>3</sub>, and Li<sub>2</sub>CO<sub>3</sub>) and reaction atmospheres (air and carbon monoxide) on the photoluminescent properties of the Y<sub>3</sub>A<sub>15</sub>O<sub>12</sub>:Ce (YAG:Ce) phosphor.<sup>74</sup> Compared with products without flux, the luminescence intensity of Ce<sup>3+</sup> increased after adding NH<sub>4</sub>Cl, while it was weakened after adding H<sub>3</sub>BO<sub>3</sub> or Li<sub>2</sub>CO<sub>3</sub>. Moreover, all three types of flux caused a blue shift in the emission wavelength of Ce<sup>3+</sup>. Additionally, the carbon monoxide produced by incomplete combustion of activated carbon

(atmosphere) helped reduce Ce<sup>4+</sup> and induced them into the host lattice, while the formation of CeO<sub>2</sub> by Ce<sup>4+</sup> and oxygen in air atmosphere led to a decrease in the luminescence intensity of Ce<sup>3+</sup>.

### 3.2. Sol-gel method

To address the challenges faced by solid-solid reactions, mild chemical synthesis methods are typically employed. The sol-gel method usually uses compounds containing highly chemically active components as precursors, including metal alkoxides, inorganic salts or complexes. These raw materials are uniformly mixed in a liquid environment and undergo reactions, such as hydrolysis, polymerization, condensation, gel dissolution, gelation, drying, and thermal decomposition, to form a stable transparent sol system in the solution. Subsequently, the gel particles in the sol cross are slowly linked and aggregated into a three-dimensional spatial network structure gel. Finally, the gel is dried, sintered, and solidified to produce crystalline molecular or nano-structured luminescent materials (Fig. 2b). The sol-gel method can precisely control the chemical composition, particle size, and morphology of luminescent materials, and can improve the luminescent performance of the materials. Additionally, it allows the incorporation of auxiliary ions and modifiers to regulate the optical properties of the luminescent materials. The Guckan group studied the effects of different calcination temperatures (800, 900, 1000, 1100, and 1200 °C) on the structural and photoluminescent properties of the luminescent powders during the synthesis of ZnO:Eu nano fluorescent powders by the sol-gel method.<sup>75</sup> Results showed that with higher calcination temperatures and larger material sizes, the concentration of defects (Eu<sup>3+</sup> concentration) and zinc vacancies (oxygen interstitials) decreased, resulting in a reduction in the overall emission intensity. Lu *et al.* prepared nanometer to



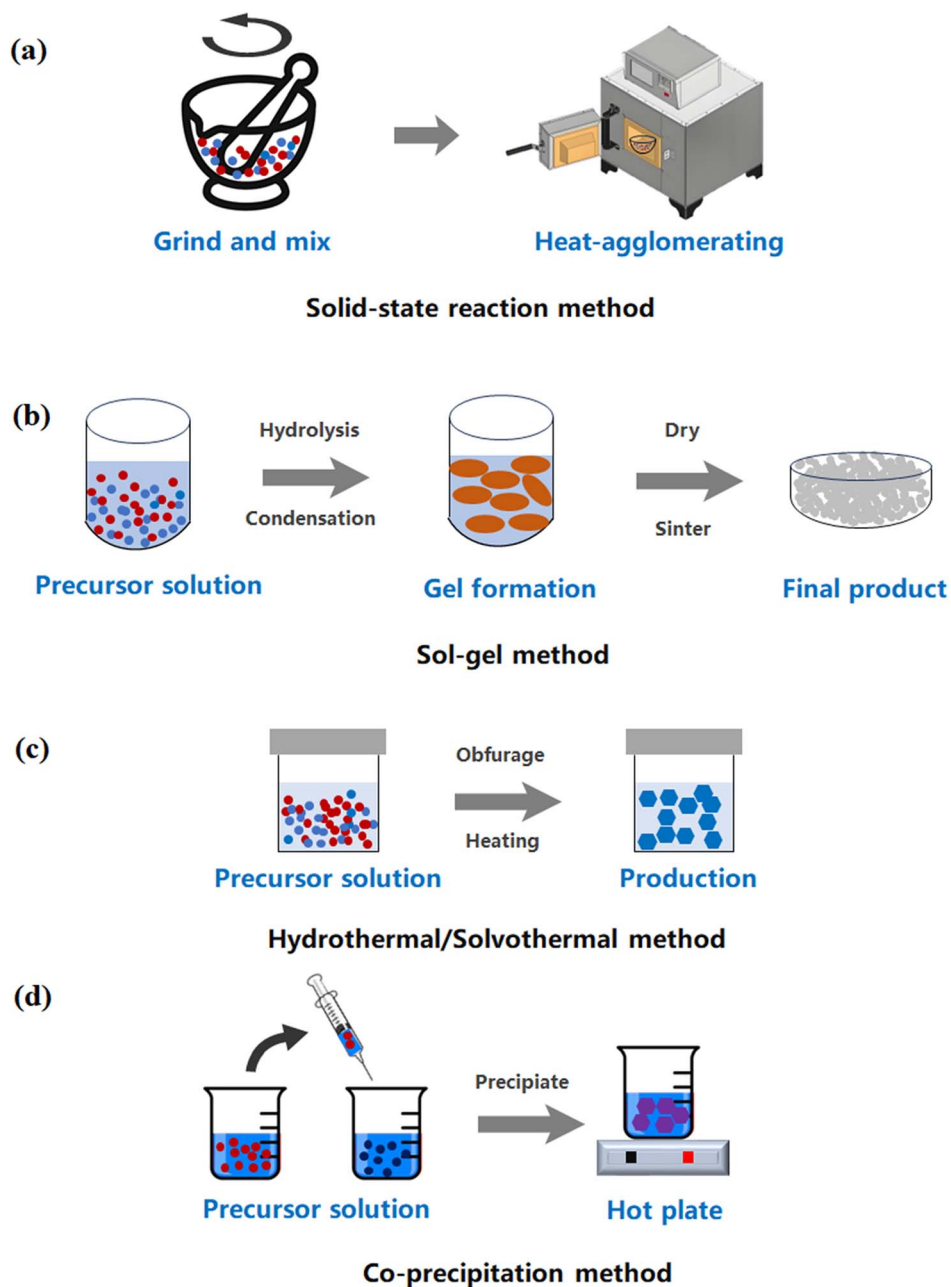


Fig. 2 Device diagram and synthesis flow chart of the (a) solid-state reaction method; (b) sol-gel method; (c) hydrothermal/solvothermal method; and (d) co-precipitation method.

micrometer-sized  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$  (YAG:Ce) luminescent ceramic powders with single-crystal features using a new sol-gel pyrolysis method by introducing the combined fuel system of urea and poly(vinyl alcohol).<sup>76</sup> Moreover, using only urea as the fuel, the luminescent yield of the YAG:Ce samples prepared at a lower temperature (1000 °C) was higher than that of the samples prepared by the traditional solid-state reaction method at 1450 °C.

### 3.3. Hydrothermal/solvothermal method

In the mid-1990s, scientific researchers began to use hydrothermal/solvothermal methods to prepare various

luminescent materials because of their advantages such as low synthesis temperature, mild conditions, simple operation, stable system, and low energy consumption. Specifically, the hydrothermal/solvothermal method proceeds as follows: in a closed system that uses water solution/organic solution (or non-aqueous solvent) as the medium, the substances in the system undergo chemical reactions when the system is heated to a certain temperature under the pressure generated by the solution itself, resulting in the formation of new phases or new substances. The closed system and heating conditions can create a high-pressure environment, which can increase the solubility of almost all solid reactants in the solution and enhance the reactivity, also accelerating the migration and



diffusion of ions within the substance, thereby speeding up the reaction rate and efficiency. Moreover, reactions that do not easily occur under normal pressure heating conditions can be achieved in the hydrothermal/solvothermal method (Fig. 2c). Currently, the synthesis reactions of photoluminescent materials are mostly carried out under low-temperature and medium-temperature hydrothermal/solvothermal conditions. These conditions are suitable for preparing luminescent materials with high purity, high crystallinity, good dispersion, regular morphology, and uniform size. Yan *et al.* synthesized calcite type and vaterite type  $\text{LuBO}_3:\text{Eu}$  nanocrystals/microcrystals with various morphologies by controlling the pH value of the precursor solution (7, 8, 8.7 and 9) using the hydrothermal method.<sup>77</sup> It was found that as the pH increased from 7 to 9, the structure of  $\text{LuBO}_3:\text{Eu}$  would change from calcite type to vaterite type, and the size would gradually increase. The Gan research group successfully prepared lanthanide-ion-doped fluoride phosphors  $\text{LuF}_3:\text{Ln}^{3+}$  ( $\text{Ln}^{3+} = \text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Dy}^{3+}$ ) with different morphologies and sizes *via* the solvothermal method and using different solvents (anhydrous ethanol, ethylene glycol, isopropanol and deionized water), fluoride sources ( $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{BF}_4$ , and 1-octyl-3-methylimidazolium hexafluorophosphate ( $\text{OmimPF}_6$ )), and synthesis temperatures (140, 150, and 180 °C).<sup>78</sup> The research results showed that compared with the other two solvents, pure rhombic nanocrystals  $\text{LuF}_3$  could be prepared under the anhydrous ethanol medium conditions. Similar morphology and uniform-sized pure rhombic nanocrystals  $\text{LuF}_3$  could be obtained by using  $\text{NH}_4\text{F}$  or  $\text{OmimPF}_6$  fluoride sources. In addition, the size of pure rhombic nanocrystals would gradually increase as the synthesis temperature increased.

### 3.4. Co-precipitation method

The co-precipitation method plays a crucial role in the preparation of photoluminescent materials. The main process of the co-precipitation method is as follows: firstly, two or more metal ions are mixed in the aqueous solution. Then, an appropriate precipitating agent is added to the mixture. When the product of the concentration of the ions that form the precipitate exceeds the solubility product under the given conditions, different metal ions can be precipitated out from the solution (Fig. 2d). The co-precipitation method is one of the most convenient strategies for preparing small-sized and narrow-distributed luminescent materials. This precipitation reaction can directly produce many luminescent materials, but the luminescence intensity of the luminescent materials obtained directly by precipitation (precursors) is relatively weak, due to the mild reaction conditions and low crystallization degree of the precipitate. Therefore, post-treatment reactions and calcination crystallization (or changing the crystal phase) are usually required. Yi *et al.* synthesized the narrow-sized cubic phase  $\text{NaYF}_4:\text{Yb},\text{Er}$  ( $\alpha\text{-NaYF}_4$ ) through the co-precipitation method under the control of ethylenediaminetetraacetic acid (EDTA) for crystal growth.<sup>79</sup> Due to the low quantum efficiency of  $\alpha\text{-NaYF}_4$ , it can only emit very weak upconversion luminescence under near-infrared excitation. However, the cubic phase  $\text{NaYF}_4$  transformed into the hexagonal phase  $\text{NaYF}_4$  after annealing at temperatures between 400 and

600 °C, and the luminescence intensity was enhanced by up to 40-fold. Meanwhile, the morphology and size of the particles remained basically unchanged after annealing. In addition, the additives added to the reaction mixture would greatly affect the particle size, particle size uniformity, and luminescence properties of the nanofluorescent materials. Kang *et al.* studied the synthesis of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles by using oleic acid as a surfactant and adding sodium chloride or ethylenediaminetetraacetic acid as additives under the co-precipitation method.<sup>80</sup> The result showed that the sizes of the synthesized nanoparticles increased and decreased respectively (compared with those without additives), and the luminescence intensities of the nanoparticles also significantly increased and decreased, respectively.

### 3.5. Organic synthesis method

The preparation of photoluminescent materials (such as organic fluorescent dye molecules, phosphorescent materials, thermally activated delayed fluorescence materials, *etc.*) by organic synthesis usually involves designing molecular structures with specific luminescent properties, and regulating the luminescent performance (such as luminescent color, efficiency, lifetime, *etc.*) through molecular design. The design strategies for molecular structures mainly include the following: expanding the conjugated system to increase the  $\pi$  conjugation length, thereby red-shifting the luminescence wavelength (from blue light to red light); introducing rigid structures to reduce non-radiative transitions caused by molecular vibration/rotation, and improving the fluorescence quantum yield; and regulating the push-pull electron groups to adjust the energy levels (HOMO/LUMO), resulting in changing the luminescent color and efficiency. Then, the designed photoluminescent materials are synthesized through organic synthesis methodologies (such as Suzuki coupling, Heck reaction, Knoevenagel condensation, *etc.*). Wang *et al.* synthesized six new diacetoxyboron complexes of the bis- $\beta$ -diketones linked thienothiophene moiety using acetylacetone as the raw material.<sup>81</sup> The synthesized diacetoxyboron complexes exhibited blue luminescence in DMF solution, and emitted a greenish-yellow emission in powders and polymethyl methacrylate films. The Lee research group synthesized several new 1*H*-pyrazolo[3,4-*b*]quinoxaline derivatives and studied their photoluminescence properties in different solvents.<sup>82</sup> The results showed that these compounds exhibited emission at 520–540 nm in moderately polar solvents with a fluorescence quantum yield close to unity. Furthermore, the absorption and emission maxima shifted to red with the increase in the solvent polarity. The fluorescence quantum yield also increased with the increase in the solvent polarity (from non-polar to moderately polar solvents), and then slightly decreased with a further increase in the solvent polarity, indicating that both “positive” and “negative” solvatokinetic effects exist simultaneously.

## 4. Application of photoluminescent materials in cultural relics protection

Cultural relics are important carriers of human civilization which carry historical memories, cultural traditions and artistic



achievements. In addition, cultural relics from different periods reflect the development process of society, economy, technology and art. Therefore, the protection of cultural relics is not only the preservation of historical relics, but also an important guarantee for the continuation of human civilization, the inheritance of national spirit and social development. Up to now, there are many problems that urgently need to be solved in the protection of cultural relics, such as the theft and smuggling of cultural relics, the aging and damage of cultural relics, and the incompatibility and aging of protection and restoration materials, *etc.* To address these problems, in recent years, researchers have developed various types of tunable luminescent photoluminescent materials and used optical means for the scientific protection of cultural relics.<sup>17,83–91</sup> Below, this chapter classifies the photoluminescent materials and their applications in the protection of cultural relics reported in recent years, followed by summarizing and generalizing four types of cultural relics protection applications: anticounterfeiting of cultural relics (the most fundamental protection of cultural relics), anti-aging of cultural relics (preventive protection of cultural relics), damage monitoring of cultural relics (protective measures during the process of cultural relics damage) and restoration detection of cultural relics (protective measures during the restoration process after cultural relics damage).

#### 4.1. Anticounterfeiting of cultural relics

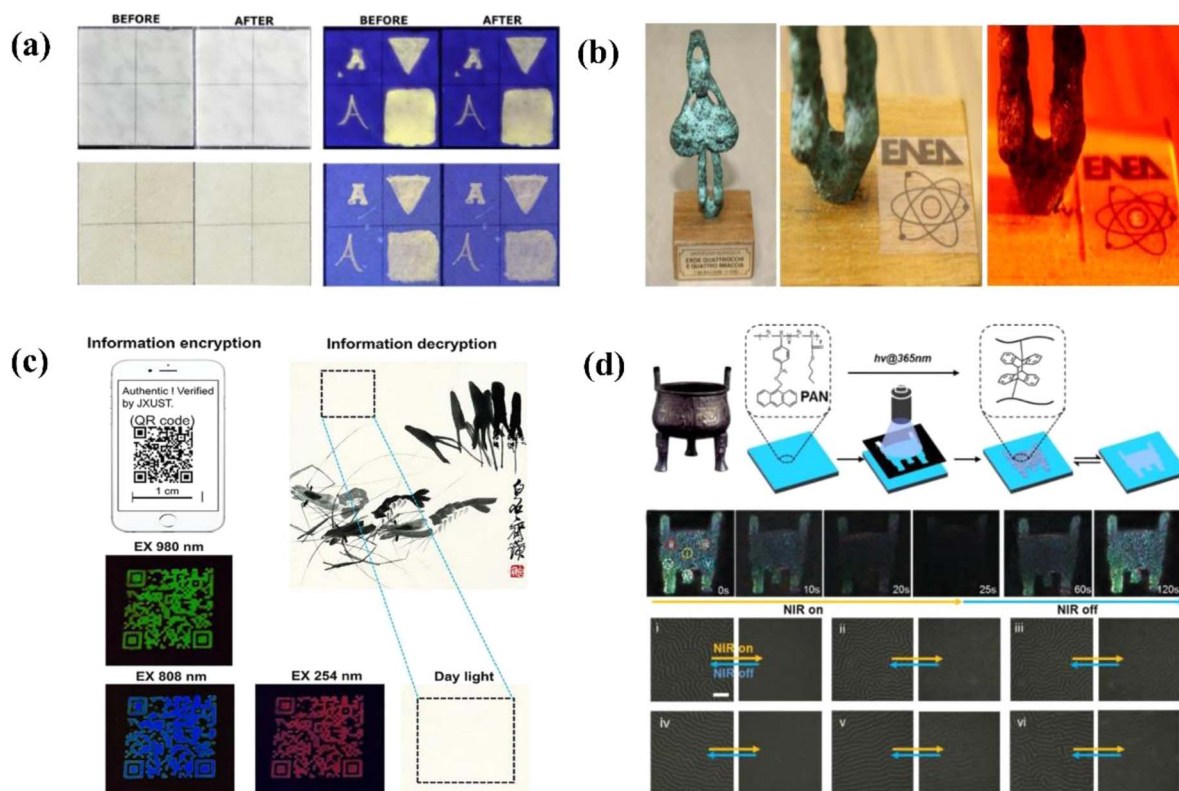
The acts of counterfeiting, theft, and illegal trafficking of cultural relics are still currently on the rise. Criminal organizations are constantly developing new strategies to evade existing security measures. Thus, the demand for intervention and protection through new technologies is also increasing. The use of markers on these cultural relics is of crucial importance for crime prevention and evidence-based verification. Optical anticounterfeiting is one of the very promising technical methods. The luminescent anticounterfeiting labels are generally undetectable with the naked eye, but can be revealed under light stimulation, providing a hidden protective layer for the cultural relics to prevent fraud and serving as key identifiers for identification, authentication, and tracking.<sup>92–95</sup> Rodorico Giorgi's research group designed and fabricated a photoluminescent anticounterfeiting ink using silanized-ZnO quantum dots as the fluorescent agent and cellulose ether as the binder.<sup>92</sup> This ink has long-term optical stability and can be compatible with various common cultural heritage substrate surfaces. It is invisible under daylight, but becomes sharply readable as a yellow label under ultraviolet light, providing an innovative and effective method for cultural relics anticounterfeiting (Fig. 3a). P. Di Lazzaro *et al.* used extreme ultraviolet radiation to write an invisible pattern "E" on a label based on an alkali LiF film and stuck it on the wooden base of a bronze statue replica.<sup>93</sup> The pattern is invisible under daylight, but shows the "E" pattern under UV radiation. This invisible marking can effectively combat the counterfeiting of cultural relics (Fig. 3b). Zhou Bo's research group designed and synthesized a kind of orthogonal three excitation wavelength-

responsive (980/808/254 nm) upconversion nanomaterials NaGdF<sub>4</sub>:Yb,Ho,Ce@NaYF<sub>4</sub>:Eu@NaYF<sub>4</sub>:Yb,Tm@NaYF<sub>4</sub>:Nd,Yb and made it into an anticounterfeiting ink.<sup>94</sup> Then, they printed a luminescent anticounterfeiting QR code with encrypted information on the replica of the cultural relic (a painting by Qi Baishi) through screen printing technology. This QR code can emit green light under 980 nm excitation, blue light under 808 nm, and red light under 254 nm, resulting in greatly increasing the complexity and diversity of the anticounterfeiting security mode (Fig. 3c). Due to the mismatch between the modulus of the hard skin layer (PAN) and the modulus of the soft carbon nanotube-polydimethylsiloxane (CNT-PDMS), selective wrinkles are generated. Xie *et al.* combined PAN and CNT-PDMS, and reported a NIR-driven dynamic pattern memory surface material similar to fingerprints, which does not damage the original wrinkles after 1000 NIR on/off cycles and still has excellent pattern memory performance.<sup>95</sup> Then, a tripod pattern label was made for the identification of tripod cultural relics (ancient sacrifices) by using the material. The tripod pattern gradually disappears under NIR light irradiation and reappears after NIR light removal, which provides dynamic non-copyable anticounterfeiting characteristics. Furthermore, the wrinkles of the tripod pattern have good stability, with the detail distribution and dynamic characteristics remaining almost unchanged even after three months (Fig. 3d).

#### 4.2. Anti-aging of cultural relics

Organic material cultural relics are prone to rapid aging due to their chemical structure characteristics when exposed to external environments (such as light, humidity, oxygen, *etc.*). Among them, paper-based cultural relics (including ancient books, historical documents, calligraphy, paintings, *etc.*) are more likely to be affected by external destructive factors (photo-degradation, hydrolysis, oxidation degradation) during transportation, preservation and exhibition, thereby leading to age and deterioration. After absorbing sufficient light energy (with wavelengths ranging from 340–350 nm or shorter), cellulose will break its main chemical bonds (C–C and C–O bonds), resulting in a photo-degradation reaction. Therefore, the photochemical decomposition of cellulose (the main component of paper) is an important reason for the aging of paper. Obviously, photoluminescent materials can delay or avoid the aging of paper from the perspective of light, thereby providing preventive protection for paper-based cultural relics.<sup>96–99</sup> The Guo research group prepared a kind of carbon quantum dots with excellent ultraviolet absorption ability by a hydrothermal reaction using polyvinyl alcohol as the carbon source and ethylenediamine monohydrate.<sup>96</sup> With the help of dissolving the carbon quantum dots in water and soaking it with bamboo paper, they prepared anti-aging bamboo paper. After conducting the UV aging experiment, the degree of pH acidity decrease in the carbon quantum dot-treated bamboo paper was significantly slower than that of ordinary bamboo paper (photo-degradation reactions produce acidic substances), and the degree of paper yellowing was also smaller than that of ordinary bamboo paper, proving that the excellent ultraviolet shielding performance and





**Fig. 3** (a) Sample photographs of ink applications under D65 and 365 nm UV light before and after weathering tests on Carrara marble (top) and Lecce stone (bottom).<sup>92</sup> (b) Copy of an archaeological bronze statue (left). A transparent and adhesive tag based on an LiF film stuck on the wood base of the statue (middle). The letter 'E' patterned by EUV radiation on the film appears when using the patented reading technique (right).<sup>93</sup> (c) Demonstration of information encryption and decryption in cultural relics protection filed by using Gd-YbHoCe(low)@Eu@YbTm@NdYb core-triple-shell nanocrystals as an anticounterfeiting ink to print the optical QR code. Luminescence photographs in daylight or under the excitations of 980 and 808 nm lasers and 254 nm handheld Xe lamp, respectively.<sup>94</sup> (d) Identity tags with NIR-responsive dynamic wrinkles for anticounterfeiting of cultural relics.<sup>95</sup>

light stability of carbon quantum dots can effectively reduce the damage caused by ultraviolet radiation to paper. Additionally, the luminescent property of carbon quantum dots enables the protected paper to emit blue light under ultraviolet light and phosphorescence at room temperature, serving as a security function. Therefore, the carbon quantum dots provide dual-function protections for paper-based cultural relics (Fig. 4a). Subsequently, due to the Mg-Al layered double hydroxides also having an anti-aging effect on papers, the research group combined polyethyleneimine as the carbon source with magnesium nitrate and aluminum nitrate to *in situ* prepare carbon dot-layered double hydroxides nanosheets (CDs/Mg-Al LDH).<sup>97</sup> Subsequently, they dissolved the nanosheets in water and soaked it with bamboo paper to prepare CDs/Mg-Al LDH synergistic anti-aging bamboo paper. Under UV aging and dry heat aging conditions, the synergistic anti-aging protection paper (CDs/LDH-BP) exhibits the lowest oxidation and acidic degradation rates compared to ordinary bamboo paper and LDH-BP (bamboo paper doped with Mg-Al LDH) (Fig. 4b). Moreover, they prepared carbon dot films (CDFs) by combining carbon dots with PVA. While ensuring that the content on the paper was clear and legible, the carbon dot films were covered on the bamboo paper or Xuan paper, which has the function of

ultraviolet radiation absorption and paper anti-aging.<sup>98</sup> At the same time, the CDFs can be easily removed from the paper without leaving residues. Furthermore, the ultraviolet transmittance of the CDFs can be precisely controlled according to the content of carbon dots (Fig. 4c). Tao's research group modified polyvinyl alcohol (PVA) using the Hansch reaction to generate a PVA derivative with 1,4-dihydropyridine (1,4-DHP) side chains, and prepared a series of water-soluble anti-UV PVA films due to the excellent UV-blocking capability of 1,4-DHP groups.<sup>99</sup> Then, the best-performing PVA film (F-30) was used to protect a Chinese peony painting from fading caused by ultraviolet radiation. The experiment results showed that after 168 hours of ultraviolet exposure, the red color in the area covered by the F-30 film only showed slight changes, and the transparency remained good; while the red color in the unprotected area or the area covered by the PVA film faded significantly, and in some places even disappeared. Therefore, it was proved that the modified anti-UV PVA films outperformed the existing ultraviolet-blocking films available in the market in terms of their ultraviolet protection effect and high transparency, making them a kind of powerful protective material for preventing the fading of cultural relics and artworks (Fig. 4d).



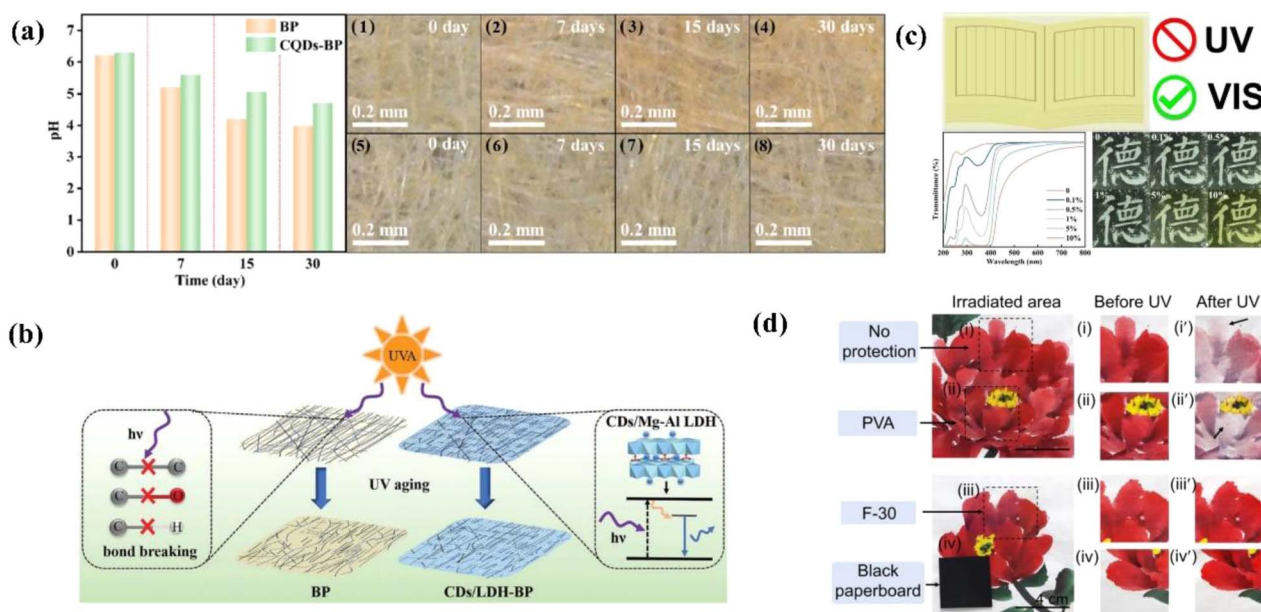


Fig. 4 (a) pH values of BP and CQD-BP before and after UV aging for 7, 15, and 30 days. Optical images of BP and BP after UV aging (1–4) and CQD-BP and CQD-BP after UV aging (5–8) for 7, 15, and 30 days.<sup>96</sup> (b) Illustration of the mechanism of CDs/LDH-BP protection against UV degradation.<sup>97</sup> (c) High-security and efficient method utilizing CD films (CDFs) for the preventive protection of paper against UV damage while preserving its visual appeal.<sup>98</sup> (d) Enlarged experimental areas of a treated Chinese painting. Without protection (i), PVA film (ii), F-30 (iii), and black (iv) paperboard before UV irradiation. Photographs of (i)–(iv) after 168 h of UV exposure (i'–iv').<sup>99</sup>

### 4.3. Damage monitoring of cultural relics

There are various forms of damage to cultural relics, such as cracks in murals, aging (acidification) and cracking of paper-based cultural relics, and corrosion of metal cultural relics under external environmental destructive factors (photodegradation, hydrolysis, oxidation degradation, wind erosion, etc.). If the damage to cultural relics is not dealt with, the damage will continue to expand and even lead to the destruction of the entire relics. Therefore, damage monitoring of cultural relics is helpful for the timely detection of damages and maintenance and restoration of cultural relics.<sup>100–105</sup> He *et al.* brushed a photochromic 1,1,2,2-tetrakis(4-nitrophenyl)ethene (TPE-4N) coating on a mural model.<sup>100</sup> During the cyclic accelerated aging (temperature/humidity) process, the pigment layer developed micro-cracks and gradually expanded, causing the TPE-4N coating to be damaged. Through photography analysis under ultraviolet light, micro-crack fluorescence (micron level) that was invisible to the naked eye could be observed. Therefore, TPE-4N can be used as a tracer for micro-damage of the pigment layer, which provides visualization, quantification, and monitoring (Fig. 5a). The salt corrosion damage and oxygen corrosion damage of metal cultural relics are two common corrosion problems that urgently need to be solved by researchers. Therefore, Zhao's research group used rhodamine-ethylenediamine with strong fluorescence response and specificity for copper ions to monitor the salt corrosion of copper cultural relics under epoxy coating protection.<sup>101</sup> The results showed that the fluorescence of the epoxy coatings area on copper cultural relics gradually increased with the increase of the soaking time in a 3.5% sodium chloride solution, proving

that the copper ions in the fluorescent area gradually increased and the salt corrosion damage of the fluorescent area intensified. Therefore, this strategy can effectively determine and monitor the early salt corrosion areas of copper metal cultural relics, which is helpful for the timely maintenance of cultural relics (Fig. 5b). The oxygen corrosion of metal cultural relics is due to the presence of oxygen. Based on this, Matthiesen designed an optical oxygen electrode sensor, in which the oxygen-sensitive compound is a ruthenium complex that can be excited under 505 nm and emit light at 600 nm.<sup>102,103</sup> Since the energy of the excited molecule of the ruthenium complex will be dissipated through collision with oxygen, its emission intensity and lifetime are negatively correlated with the concentration of oxygen. Therefore, the sensor is used to monitor the oxygen content around the metal cultural relics and protect them (Fig. 5c). Paper-based cultural relics often acidify due to aging during long-term storage; hence, the accurate monitoring of the acidity of paper is of great significance for evaluating the aging condition and extending the preservation period of paper-based cultural relics. Wang *et al.* prepared CdZnSeS quantum dots modified with *p*-aminothiophenol (*p*-ATP), which emitted green light under 365 nm ultraviolet light, and their brightness decreased with the increase of acidity.<sup>104</sup> Therefore, the quantum dots solution was dropped onto four different types of paper by using a pipette for acidity detection. The results showed that the pH of the newspaper from 1922 was about 3.14, the pH of bamboo paper from the 19th-century was about 3.89, the pH of Mianlian paper from the 19th-century was about 5.33, and the pH of the filter paper was about 6.5, which also proved the superiority of ancient Chinese handmade paper (Fig. 5d).



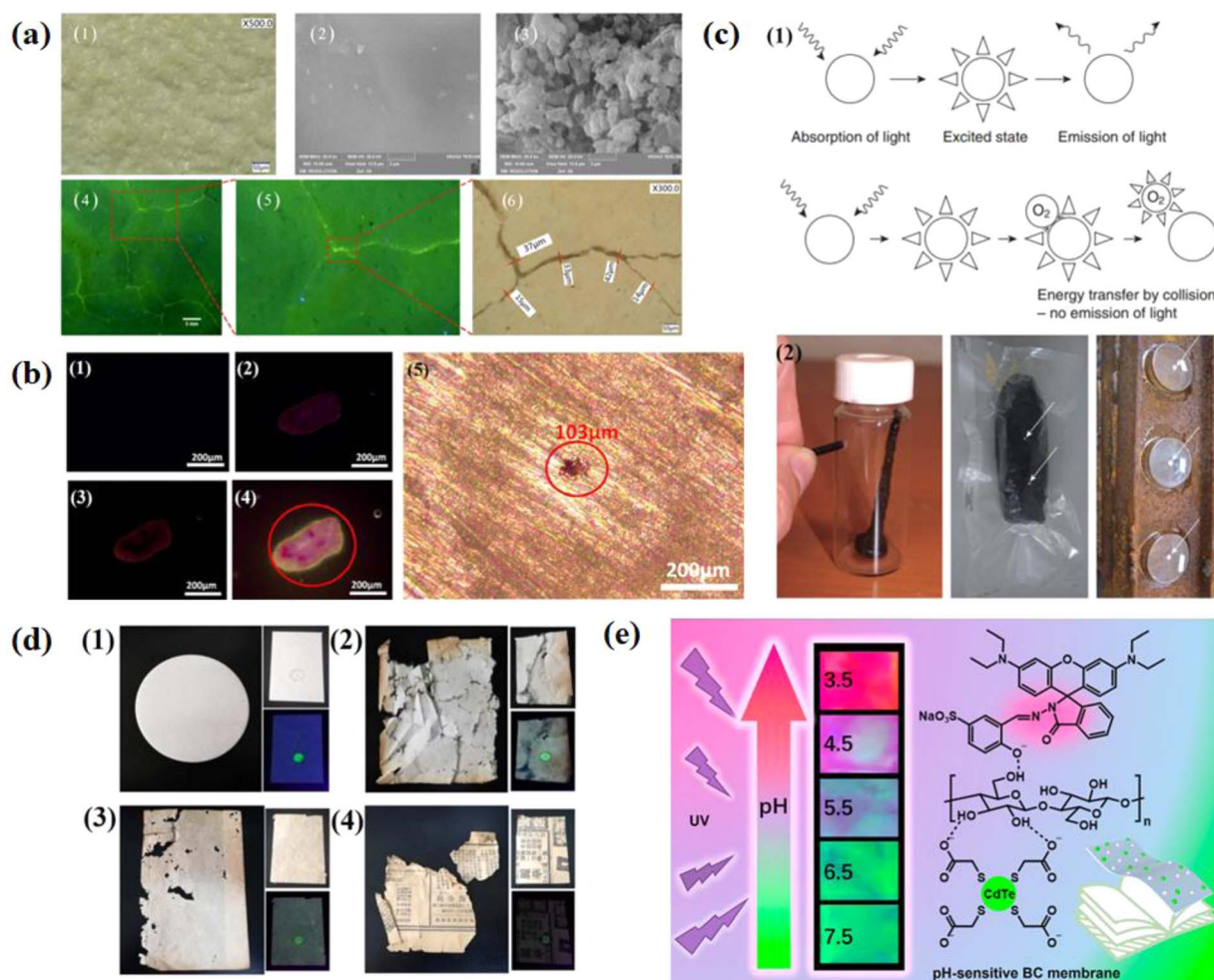


Fig. 5 (a) Images of the sample surface: TPE-4N coating after fumigation under an optical microscope (1), intact TPE-4N under a SEM microscope (2), fracture surface of the TPE-4N surface (3), microcracks under ultraviolet light (4, 5), and microcracks under an optical microscope (6); Copyright 2025, with permission from Springer Nature.<sup>100</sup> (b) Fluorescence microscopy images of a bronze sample coated with epoxy resin containing 0.8 wt% rhodamine-ethylenediamine after being soaked in a 3.5% NaCl solution for different times (1–4) and superficial corrosion morphology of the bronze sample after removal of the protective coating (5); Copyright 2020, with permission from the American Chemical Society.<sup>101</sup> (c) Working principle behind the optical oxygen electrodes (1), and three different respirometers used for corrosion measurements: fixed volume, flexible volume using a transparent oxygen barrier film, and *in situ* measurements of oxygen consumption on large artifacts (2).<sup>102</sup> (d) Photographs of four paper samples: filter paper (1), ancient book title page of Mianlian paper from the 19th century (2), ancient book title page of bamboo paper from the 19th century (3), and newspaper from 1922 (4). Upper-right and lower-right corners show the photographs of paper samples containing CdZnSeS-pATP QDs under daylight and a 365 nm UV light, respectively; Copyright 2021, with permission from MDPI.<sup>104</sup> (e) Nanofibers of a bacterial cellulose (BC) membrane doped with pH-sensitive cadmium telluride (CdTe) quantum dots (QDs) and rhodamine B (RB) for enabling the visual acidity detection of paper.<sup>105</sup>

Using fluorescence probes is a typical strategy to directly detect the acidity of paper-based cultural relics, but this strategy will cause the fluorescence probe to directly contact the surface of the paper, which poses a risk of damage to the cultural relics. Based on this issue, the Yan's research group synthesized pH-sensitive cadmium telluride quantum dots (CdTe) and rhodamine B (RB) fluorescent probes, and incorporated them onto the nanofibers of bacterial cellulose (BC) membranes.<sup>105</sup> Due to the complementary pH detection ranges of CdTe quantum dots and RB probes, the composite BC membrane exhibited a clear pH response (from red to green) in the acidic to neutral range (pH 3.0–7.5) under 365 nm ultraviolet light, which enabled the visual detection of paper acidity while avoiding direct contact of

the fluorescent probes with the paper. Moreover, common metal ions in most paper fillers, inks, pigments, as well as some sugars and amino acids, had little interference with the pH response of the composite BC membrane. Therefore, it is highly suitable for the acid content monitoring of paper-based cultural relics (Fig. 5e).

#### 4.4. Restoration detection of cultural relics

In the field of culture relics restoration, there is a principle known as “restore as old as the original”. This means that only the damaged parts will be restored after restoration, and the appearance after restoration should be exactly the same as



before. Therefore, considering the effect and appearance of culture relics restoration, the restoration materials used in the restoration process are preferably colorless and transparent to reduce the traces of restoration and increase the aesthetic appeal. However, colorless and transparent restoration materials are difficult to rejudge for restoration and detect the location of the restoration (especially for minor damages) in the later stage, while luminescent materials can precisely visualize the location and effect of restoration due to their luminescent properties, which can solve this problem. Therefore, it is necessary to design restoration materials with luminescent properties. The main ideas can be divided into two parts: one is to directly design and prepare restoration materials with luminescent functions; the other is to add some luminescent materials to the restoration materials. Thus, the location and effect of restoration can be precisely and visually displayed in real time in the process of culture relics restoration.<sup>106–108</sup> Zhang *et al.* designed and synthesized random hyperbranched polyamide-amide hot melt adhesives using 1,8-octanediamine and *N,N'*-methylene diacrylamide as raw materials.<sup>106</sup> The hot melt adhesives not only have good adhesion (maximum bonding strength is about 11.4 MPa), but also can emit blue light under 365 nm ultraviolet light (with photoluminescence properties). Subsequently, the hot melt adhesives were used to repair a broken ceramic bowl. After the repair, the ceramic bowl could withstand a weight of 500 g, which proved the practicality of the hot melt adhesives for cultural relics restoration. At the same time, the restored ceramic bowl did not show any traces of restoration under daylight, while obvious cracks could be seen

under ultraviolet light, thereby achieving the function of visual positioning. Additionally, the adhesives can be dissolved in green solvents such as ethanol after drying and curing, and can be effectively peeled off from the surface of the cultural relics without causing pollution or damage, for meeting the requirement of being able to reprocess the restored cultural relics (Fig. 6a). Moreover, Lu *et al.* successfully prepared a eugenol-based epoxy resin (EBER) with excellent bonding and photoluminescence properties.<sup>107</sup> Due to its dark green appearance, it can be applied to the restoration of bronze cultural relics of the same dark green color. To prove this application, EBER was used to bond the broken replicated bronze cultural relics fragments together. The restored bronze handicraft after curing did not show any bonding traces under daylight, while obvious green restoration traces could be clearly seen under ultraviolet light irradiation, which achieved the function of visual positioning. Becerra's research group added the luminescent ZnO quantum dots to nanolimes ( $\text{Ca}(\text{OH})_2$  nanoparticles), and the fluorescence properties of the nano-composite material could show the actual penetration of nanolimes into the stone matrix after the reinforcement and restoration of the stone cultural heritage.<sup>108</sup> Furthermore, the affinity between nanolimes and the solvents used in the application was studied in order to select the best solvent for each type of stone, thereby improving the penetration effect of the treatment process on the stone. In addition, the blue-violet fluorescence of ZnO quantum dots can serve as an indicator mark for the reinforcement and restoration area in cultural heritage applications (Fig. 6c).

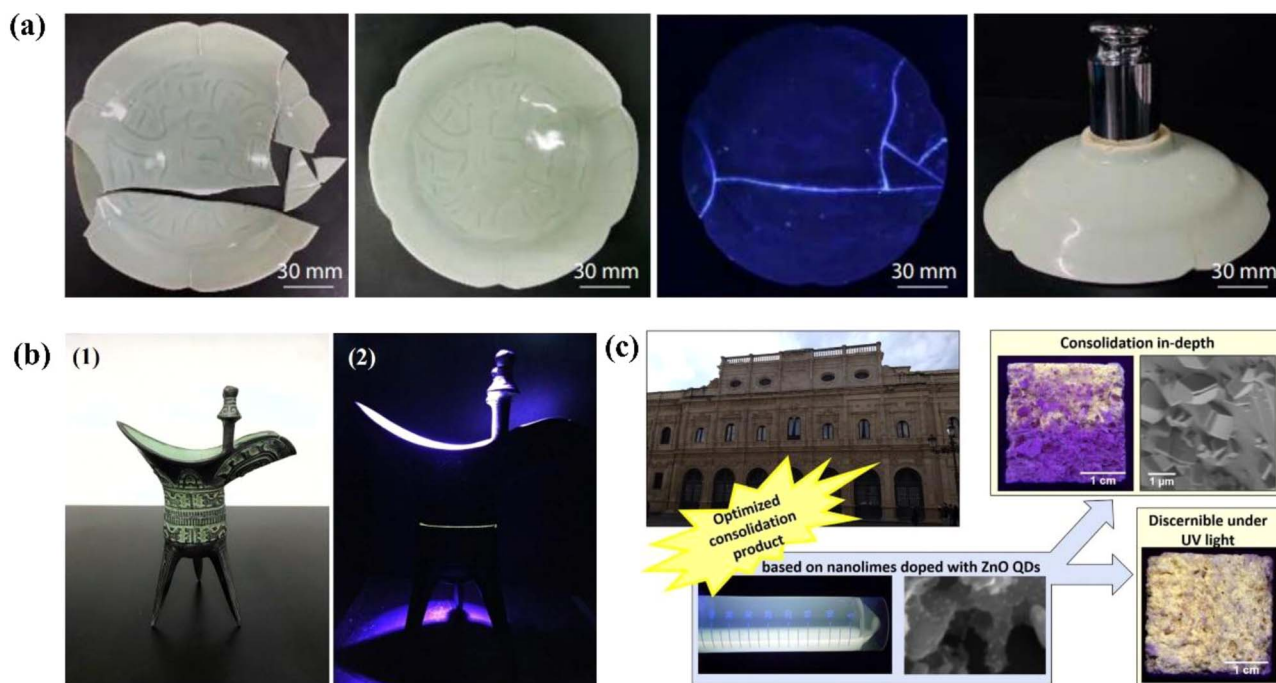


Fig. 6 (a) Photographs of the broken ceramic bowl and repaired ceramic bowl by ODA-RHP under daylight and a UV lamp;<sup>106</sup> (b) photographs of the repaired bronze ware under natural light (1) and UV (2);<sup>107</sup> (c) new nanocomposite based on  $\text{Ca}(\text{OH})_2$  nanoparticles doped with ZnO quantum dots whose fluorescence shows the real penetration of the nanomaterial into the stone matrices, allowing for studying the affinity between the nanolimes and the solvent used in the application in order to improve the penetration of the treatment into stones.<sup>108</sup>



## 5. Conclusions and outlook

Due to the rich optical properties, low damage potential, high chemical stability and safety of photoluminescent materials, they show great application potential in many fields. In addition to their wide application in traditional optical display and optical anticounterfeiting fields by leveraging the optical properties, they hold significant research value in some cross-disciplinary areas such as cultural relic protection, which has received extensive attention and research from scientific researchers. This study first discusses the luminescence mechanisms of photoluminescent materials and summarizes the main synthesis strategies of current photoluminescent materials. Then, the application directions in the field of cultural relics protection are analyzed and discussed. At the same time, four types of applications of luminescent materials in cultural relics protection (anticounterfeiting of cultural relics, anti-aging of cultural relics, damage monitoring of cultural relics, and restoration detection of cultural relics.) are summarized.

Although photoluminescent materials have achieved certain development and progress in their application in cultural relics protection, there are still many problems and challenges in truly applying the materials reliably for the same: (1) firstly, many photoluminescent materials such as rare earth upconversion luminescent materials have low luminescence efficiency. Therefore, improving and enhancing the luminescence intensity and efficiency of photoluminescent materials themselves is a prerequisite for expanding their application scope and practicality, and is also one of the current research focuses of photoluminescent materials. Currently, strategies to enhance the luminescence intensity of photoluminescent materials mainly include material composition and structure optimization, morphology and size control, surface and interface engineering design, and excitation condition optimization. However, the effects of these optimization strategies on different types of photoluminescent material structures are not the same, and their reference value is limited. The implementation of these strategies to a specific material generally still requires specific conditions screening and optimization. (2) When photoluminescent materials are applied to cultural relics protection, there are compatibility and safety issues between the materials. Firstly, photoluminescent materials (such as rare earth doped fluorescent materials, quantum dots, *etc.*) may react with the original material of the cultural relics (such as organic dyes, metal oxides, ceramic glazes, *etc.*), causing a color change or degradation (the chemical compatibility problem); secondly, some fluorescent materials may decompose under light or environmental humidity, which results in generating harmful by-products (such as acidic substances) to accelerate the aging of the cultural relic (the long-term stability problem); thirdly, the fluorescent markers used for detection may be difficult to completely remove, and the long-term residue may affect the appearance or chemical properties of the cultural relics (the residue risk). (3) There are some limitations when using photoluminescent materials for detection in cultural relics. The composition of cultural relics is a relatively complex (such as

mixed pigments, rust layers), and the fluorescence signal is easily interfered by the background, thereby affecting the accuracy of detection and monitoring results. In addition, the excitation source of the detection and monitoring equipment, such as ultraviolet or strong laser, may trigger photo-oxidation aging reactions of organic cultural relics (such as paper and silk) during the excitation process. Therefore, strict control of the light source parameters (such as wavelength, excitation power, and exposure time) is required, and a risk of light damage is expected. (4) Some excellent photoluminescent materials such as ligand-protected metal nanoclusters have complex preparation processes, and the cost of some materials is also high. As a result, they are difficult to be widely applied in the field of cultural relics protection, which limits their further promotion and use. (5) With the rapid development of science and technology, the requirements for cultural relics protection materials are also constantly increasing. Multifunctional materials are more favored by cultural relics protectionists. Therefore, future material structure designs should focus on making photoluminescent materials with multiple functions rather than a single luminescence function. Thus, in addition to meeting the luminescent properties requirements for the cultural relics protection, the materials need to possess other protective functions such as fire resistance, waterproofness, heat resistance, thereby further improving the position of photoluminescent materials in the field of cultural relics protection application.

In general, the application of photoluminescent materials in cultural relics protection is still in the initial research stage at present. There are still complex challenges in optimizing photoluminescent materials and exploring their other potential applications in cultural relics protection. As cultural relics protection is an interdisciplinary field, researchers from various disciplines need to closely collaborate and jointly overcome difficulties. It is believed that photoluminescent materials with unique luminescent properties and photocatalytic stability will be able to carve out their own space in the field of cultural relics protection.

## Author contributions

Yang Wang: writing – original draft preparation, review and editing, visualization, conceptualization; Shiqiang Fang: supervision, visualization; Xueqiang Chen: supervision, visualization; Sheng Chen: writing – review and editing. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Data availability

This study is a review article, and no new data were generated or analyzed during the course of this research. All data discussed



and referenced are available in the publicly accessible sources cited within the article. Further information can be provided upon reasonable request from the corresponding author.

## Acknowledgements

This work was supported by the National Social Science Foundation of China (Grant No. 21CKG019) and Zhejiang Provincial Administration of Cultural Heritage (2022019).

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