Photo-induced Afterglow of Carbon Dots for Dynamic Patterning

Yanfeng Liu

School of Chemistry & Chemical Engineering, Nanjing University, No. 163 Xianlin Rd, Nanjing, Jiangsu, China.

Xin Huang

Nanjing University

Zuoji Niu

Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials

Dongni Wang

School of chemistry and chemical engineering, Nanjing University

Huilin Gou

Nanjing University

Qiaobo Liao

Nanjing University

Kai Xi (✉ xikai@nju.edu.cn)

School of chemistry and chemical engineering, Nanjing University <https://orcid.org/0000-0002-8770-5956>

Zhongfu An

Key Laboratory of Flexible Electronics & Institute of Advanced Materials, Nanjing Tech University

<https://orcid.org/0000-0002-6522-2654>

Xudong Jia

Nanjing University <https://orcid.org/0000-0002-0144-1209>

Article

Keywords: room temperature phosphorescence, long afterglow, carbon dots, photo-induced optical memory, smart materials

Posted Date: September 3rd, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-56109/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Flexible materials with afterglow feature have received considerable attention in the field of flexible electronics. To date, it is still a formidable challenge to develop flexible materials with dynamic long afterglow for practical applications. Herein, we report for the first time photo-induced long afterglow in a flexible solid composite film made of luminescent carbon dots (CDs) and the oxygen-permeable poly pyrrolidone (PVP). The phosphorescent afterglow of the film can be reversibly activated by photo-irradiation and de-activated by thermal treatment. Impressively, the photo-activation leads to a significant luminescence lifetime enhancement with a factor of over 3900, and editable afterglow patterns with fine resolution exceeding 1280 dpi are readily achieved by masking and lithography. Furthermore, the retention time of such memorized optical patterns can be tuned from minutes to days by varying temperature, enabling the unique time-temperature indicating function. These findings not only enrich both the library of the afterglow materials vastly, but also extend the scope of the potential applications of CDs materials.

Introduction

Light for material processing plays a critical role in the non-contact manufacturing of structures and patterns with high precision¹⁻⁴. Photo-irradiation may cause the variations of regional optical features, which therefore lead to photo-induced optical memory (PIOM) effects for designable patterning³⁻⁷. Such phenomena have found practical applications in various fields, such as data recording^{6,7} and display.^{3-5,7} In particular, PIOM materials capable of “write-read-erase” cycling are of most interest for their capability of reversible edition⁷⁻¹⁷. Utilizing these materials, programmable graphic data edition has been achieved and applied in various fields including optical storage^{7,8,12}, anti-counterfeiting¹⁴, bio-imaging¹⁵, and patterning^{9,11,13,16,17}. Typically, the visualization of recorded optical data involves the regional change of photophysical properties including absorption⁷⁻¹⁰, reflection^{9,10}, or photoluminescence (PL)^{8,11-17}. Unlike others, the PL signal requires specific excitation, which therefore guarantees advanced data confidentiality in anti-counterfeit and optical encryption applications. Among all reported PL materials, the materials with long afterglow features show very unique persistent luminescence with significantly prolonged lifetimes (ms~s), which enables naked-eye observation of their delayed emission with enhanced signal-to-noise ratio¹⁸⁻²⁴. Despite their fascinating properties, long afterglow materials with PIOM characters are still rarely reported. Recently, dynamic ultra-long phosphorescence has been realized by manipulating intermolecular interactions with photo-irradiation in organic crystals^{14,15}. Furthermore, Gmelch et al developed transparent coating layers made of polymers and organic molecules with programmable photo-induced afterglow^{16,17}. These inspiring achievements have demonstrated the possibility of constructing materials with photo-induced afterglow by rational design. Up to now, luminescent materials with such advanced properties are still urgently needed.

Since its first discovery in 2006²⁵, carbon dots (CDs), an emerging class of luminescent nanomaterials, have drawn massive research interest for their fascinating PL properties, advanced stability and low-

toxicity nature. Based on that, the vast applications of CDs in different fields, including bio-imaging, theranostics, illumination/display, and energy conversion have been explored²⁶⁻²⁹. Particularly, CDs materials with room temperature long afterglow have recently become a new research hotspot³⁰⁻⁴⁰, showing superiority in applications compared to the traditional fluorescent CDs. For example, time-resolved data encryption and anti-counterfeit patterns have been manufactured, taking advantage of their prolonged emission lifetime³⁵⁻⁴⁰. Despite the ever-growing interest in these novel materials, to the best of our knowledge, researchers have yet to find a type of CDs-based long afterglow materials with photo-induced optical memory (PIOM) characteristics.

We herein propose, for the first time, a flexible CDs/PVP film showing photo-induced long afterglow with PIOM effect. In this specific design, triplet oxygen, a well-known quencher of triplet excitons^{41,42}, is intentionally introduced to mediate the phosphorescent afterglow. Upon photo irradiation, CDs embedded in the oxygen-permeable PVP host continuously generate triplet excitons that remove the triplet oxygen through an *in situ* photodynamic process (Process I and II in **Fig. 1a**). After that, the irradiated region gradually becomes anoxic and resultantly allows the room temperature phosphorescence (RTP) emission of CDs (Process III in **Fig. 1a**). The photo-induced phosphorescent long afterglow character remains in the pre-irradiated region for a considerable duration, before environmental oxygen permeates the film again and causes RTP quenching, erasing the PIOM effect. Notably, the oxygen permeability can be tuned through thermal treatment, resulting in variable retention time of the evoked long afterglow feature (Process IV in **Fig. 1a**).

Results

Material design and fabrication

To validate our hypothesis, we firstly synthesized a type of CDs containing abundant heteroatoms (N, O) through a solvothermal method (I in **Fig. 1b**). N, O-containing functional groups can benefit the RTP afterglow of CDs in two major ways. Firstly, N and O atoms contain lone-pair electrons that can facilitate $n\text{-}\pi^*$ transitions and enhance the intersystem crossing (ISC)^{43,44}, promoting the generation of triplet excitons. Secondly, these functional groups can serve as “anchor spots” for hydrogen bonding fixation, which can efficiently reduce non-radiative energy loss.^{30,35} As was validated by structural analysis (**Supplementary Figs. 1~3, Supplementary Table 1**), the as-prepared CDs were highly functionalized with amine, imine, hydroxyl, carboxyl and enamine groups, in agreement with our design principle. At this point, the CDs showed only short-lived fluorescence with a lifetime of 3.3 ns in solution (**Supplementary Fig. 4**); meanwhile in the powdery state, there was no visualized PL emission whatsoever. However, significant long afterglow occurs in a transparent CDs/PVP composite film prepared by solvent-casting (II in **Fig. 1b**). In this specific composite, PVP acts as a hydrogen-bonded matrix with abundant lactam groups which provide solid fixation that suppresses the non-radiative energy loss and benefits the RTP emission of CDs. Importantly, as a bio-compatible hydrophilic polymer, PVP features excellent oxygen

permeability⁴⁵, which fundamentally enables the PIOM design. Furthermore, PVP is reductive and capable of scavenging the generated singlet oxygen¹³, thereby enabling rapid removal of molecular oxygen and a fast responding rate.

Reversible photo-induced long afterglow

The resultant CDs/PVP composite film initially emitted bright cyan light upon 400 nm excitation, which instantly disappeared as the irradiation switched off. As expected, the first short irradiation (<0.5 s) did not evoke any observable afterglow in the film. Impressively, an intense orange phosphorescent afterglow that lasts for several seconds appeared after the film was continuously irradiated by a 365 nm UV lamp (III in **Fig. 1b** and **Fig. 2a**). The photo-activation of afterglow significantly prolonged the luminescence lifetime of the material by a factor of 3932 (from 148 μ s to 582 ms. **Fig. 2b** and **Supplementary Table 2**). It is worthy to note that the afterglow feature aroused by the photo-induced anoxia naturally last for more than 1 h at room temperature, before it gradually disappeared due to oxygen penetration. Within this time, the orange afterglow could be evoked at will by short irradiation. In addition, the photo-induced afterglow feature could be executed by applying thermal treatment shortly. Such an on-off switch could be repeated for multiple cycles without significantly losing the original RTP characteristics (**Fig. 2c** and **Supplementary Fig. 5**).

In a further set of experiments, the responding behavior of the photo-induced afterglow was studied. From **Fig. 2d**, it was found that the time required to turn-on the afterglow clearly decreased with increasing irradiation power density. Specifically, the time required to achieve half-maximal RTP intensity ($t_{1/2}$) was inversely proportional to the irradiation power density (**Supplementary Fig. 6**). Estimated from that, with an irradiation power density of 10 mW/cm², the RTP intensity would reach 50% maximum within 4 s and 90% maximum within 20 s under continuous irradiation, allowing the rapid recording of optical information. Meanwhile, it was found that the disappearing speed of the photo-induced afterglow feature was evidently temperature-dependent due to the enhancement of oxygen permeation under higher temperature. For instance, the afterglow feature quickly vanished at 373 K within 15 min, but remained detectable at 253 K even after 48 h (**Fig. 2e**). Because the disappearing speed of the afterglow feature was fundamentally determined by oxygen permeability, higher temperature could induce faster oxygen permeation, causing the potential long afterglow to perish within a shorter period of time. Additionally, we also found that the retention time could be tuned by further adjusting the molecular weight of the PVP host material, or simply applying surface barrier layers with different thickness (**Supplementary Fig. 7**).

Verification of the oxygen-mediated mechanism

To further illustrate the oxygen-mediated regulation of such a photo-induced long afterglow, a set of control experiments were conducted. A different composite film was prepared using polyacrylamide (PAM) instead of the PVP polymer. Different from the oxygen-permeable PVP, PAM features minimal oxygen permeability⁴⁶, which leads to a constant anoxia environment in the composite film. The emission wavelength and decay profiles of the CDs/PAM composite are similar to those of the CDs/PVP

composites with photo-induced afterglow (**Supplementary Fig. 8** and **Table S3**). The difference occurred, however, when the delayed emission properties of two different composite films were examined under intermittent irradiations with a regular “on-off” switching pattern (**Fig. 3a**). In this case, the CDs/PVP composite film showed a gradually accumulating RTP intensity with evident memory effect, while the CDs/PAM composite film showed a constant RTP intensity that almost instantly reached its maximum as the irradiation switched on. A more straight-forward demonstration was shown in **Fig. 3b** and **Supplementary Video 1**, where the CDs/PAM composite showed intrinsic long afterglow nature, but CDs/PVP clearly showed memory effect and only emitted long afterglow in the photo-activated region. The above-mentioned results validated that adequate oxygen permeability of the material was crucial to achieving the unique photo-induced long afterglow. In both composite films, the host polymers provided hydrogen bonding fixations, which suppressed non-radiative transitions and enabled long afterglow. However, only the CDs/PVP composite demonstrated the dynamic long afterglow mediated by a photodynamic oxygen removal process (**Fig. 3c**). This process was further confirmed by monitoring the characteristic near-infrared (NIR) luminescence of singlet oxygen at 1268 nm⁴⁷. As revealed in **Fig. 3d**, evident NIR emission was detected from the CDs solution under 400 nm irradiation. The emission intensity, however, dramatically decreased in the presence of PVP, indicating the consumption of the generated singlet oxygen by the PVP macromolecules¹³.

Notably, the photo-induced afterglow was always distinctly localized in the pre-irradiated region, showing promising potential for graphic information processing (**IV** in **Fig. 3b**). Based on that, we further applied masking and lithography methods to create designable afterglow patterns on the film. From **Supplementary Fig. 9**, we found that the limiting resolution of such patterns was up to 1280 dpi with a standard USAF-1951 target, which equaled to a limiting line resolution of <20 μm . As demonstrated in **Fig. 4a**, reversible writing-reading-erasing of afterglow patterns could be readily achieved by applying pre-designed masks for optical printing (**Supplementary Video 2**). It's also worth mentioning that the optical printing and afterglow read-out process could be accomplished with a commercial white light LED lamp (**Supplementary Fig. 10** and **Supplementary Video 3**). During this process, the transmittance, morphology, and steady-state PL emission of the film remained almost unchanged (See **Supplementary Figs. 11~12**), which altogether made this material naturally suitable for practical applications (See **Supplementary Fig. 13**).

Applications for dynamic patterning and time-temperature indication (TTI)

The transportation of many thermal-sensitive cargos like vaccines and medicines relies firmly on the cold-chain. Occasionally, cold-chain failures may occur, causing not only financial loss, but also potential public hygiene hazard⁴⁸. To avoid such issues, time-temperature indicating (TTI) tags like Warmmark (SpotSeeTM) were used to visualize the potential thermal abuse of cargos during storage and transportation. Herein, taking advantage of the editable long afterglow of CDs/PVP composite and its thermal-sensitive retention, a multi-use smart TTI tag carrying renewable logistics data was realized. Following the procedure illustrated in **Fig. 4b**, editable TTI tags were facily fabricated. And a conceptual multi-stop cold chain transportation monitored by the CDs/PVP TTI tags was illustrated in **Fig. 4c**. Herein,

a hypothetical 6-stop transportation route was set up, with the logistics datas updated daily. For usage demonstration, two tags were prepared, referring to sample A (well preserved) and sample B (thermally abused), respectively. During the transportation, logistics datas were optically printed upon departure and inspected upon arrival at each stage. The delayed emission photographs of the two tags upon departure and arrival were captured and listed in **Fig 4c**. In the first three transport segments (NJ→JZ, JZ→CZ, and CZ→WX), both tags were well-preserved at 253 K. At this stage, all graphic information could be readily recognized upon arrival. At the fourth segment between WX and SZ, while sample A was constantly kept at 253 K, sample B was exposed to room temperature (298 K) for 1 h during this process. As a result, upon arrival at SZ, only the sample A tag retained recognizable barcode pattern. Meanwhile, no information could be read from the sample B tag after multiple attempts (**Supplementary Fig. 14** and **Supplementary Video 4**), which indicated the potential deterioration of the cargoes. Such a result demonstrated that the CDs/PVP composite could be used as editable TTI tags for niche application.

Discussion

In summary, we presented a rational design of flexible composite materials with photo-induced phosphorescent afterglow based on the combination of the CDs phosphor and an oxygen-permeable PVP host. We found that the phosphorescent afterglow can be reversibly switched on-off by light and thermal treatment within seconds. Impressively, the photo-activation aroused a significant luminescence lifetime enhancement with a factor of over 3900. With lithography method, editable patterns on this material showed fine resolution (> 1280 dpi), excellent writing-erasing reversibility, and tunable memory retention with thermal sensitivity. Additionally, potential applications of this material were demonstrated in dynamic optical patterning, encryption and time-temperature indication. To the best of our knowledge, this is the first example of a CDs-based long afterglow material with PIOM effect, which not only opens up a new field of CDs-based smart optical materials, but also provides novel ideas for the production of flexible stimuli-responsive materials with long afterglow.

Methods

Synthesis of CDs:

Briefly, 648 mg (6 mmol) of PBQ was dissolved in 200 mL of ethanol under agitation to form a homogeneous solution. To that solution was added 480 mg (8 mmol) of EDA in one portion to form a hazel dispersion, which was further sealed in an autoclave and maintained at 120 °C for 10 h. Afterward, the reaction was naturally cooled down to room temperature. The crude product was collected and concentrated by rotary evaporation under reduced pressure before further purified by dialysis (Cutoff Mw: 5000 D. Crude product was dialyzed against DI water for 48 h with water renewed every 12 h) and silica column chromatography (eluent: 90% dichloromethane and 10% methanol). As a result, about 200 mg powdery product was finally obtained.

Preparation of the CDs/PVP composite film

To prepare a CDs/PVP composite film, 1 g of PVP was fully dissolved in 19 mL of deionized water under agitation at 328 K (55 °C). Next, 1 mL of ethanol solution containing 5 mg CDs was added to the PVP aqueous solution quickly. The solution was further magnetically stirred for 30 min to ensure a homogeneous dispersion.

Afterward, onto a standard 9 cm x 9 cm square polystyrene petri dish was poured 17.5 g of the CDs/PVP solution. Transferred to a flat heater previously adjust to 313 K (40 °C), the solution was left for solvent evaporation for 10 h. The resultant film was then heated at 393 K (120 °C) under reduced pressure (~ 0.1 mbar) for another 2 h for complete drying. The thickness of such as-prepared film was 80 µm (measured with a micrometer screw gauge). Commercially available PET lamination films (purchased from Jiwen lamination film Co. Ltd. Wuxi, China) with different thicknesses (50, 80, 100, 125, 150 µm) were applied to protect the film from scratch and adjust its oxygen permeability. In this work, typical photophysics data of the material were acquired from a sample coated with 80 µm-thick PET, unless otherwise specified.

Declarations

Acknowledgements

We thank Professor Fei Xu and PhD. candidate Yifeng Xiong for technical assistance. This work is supported by the National Key R&D Program of China (No.2017YFA0700503), the Fundamental Research Funds for the Central Universities (No. 14380221) and the National Natural Science Foundation of China (No. 21875102, 21875104).

Author contributions

Y.L, K.X, Z.A. and X.J initiated, managed and planned the overall project. Y.L, X. H and Z.N were primarily responsible for the experiments. Y.L and X.H prepared and characterized the carbon dots and the composite materials. Y.L and Z.N measured the photophysical properties of the materials. Y.L conceived and performed the applications. Y.L, K.X and Z.A. prepared the paper. All authors contributed to data analysis, manuscript refinement and preparation.

Data availability.

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

References

1. Kelly, B. E. *et al.* Volumetric additive manufacturing via tomographic reconstruction. *Science* **363**, 1075–1079 (2019).
2. Lee, J. *et al.* Universal process-inert encoding architecture for polymer microparticles. *Nat. Mater.* **13**, 524–529 (2014).

3. Ito, M. M. *et al.* Structural colour using organized microfibrillation in glassy polymer films. *Nature* **570**, 363–367 (2019).
4. Han, T. *et al.* Photoresponsive spiro-polymers generated in situ by C–H-activated polyspiroannulation. *Nat. Commun.* **10**, 5483 (2019).
5. Su, Y. *et al.* Ultralong room temperature phosphorescence from amorphous organic materials toward confidential information encryption and decryption. *Sci. Adv.* **4**, eaas9732 (2018).
6. Nozaki, K. *et al.* Ultralow-power all-optical RAM based on nanocavities. *Nat. Photonics* **6**, 248–252 (2012).
7. Jiang, G. *et al.* Highly Fluorescent Contrast for Rewritable Optical Storage Based on Photochromic Bisthiénylene-Bridged Naphthalimide Dimer. *Chem. Mater.* **18**, 235–237 (2006).
8. Zhang, C. *et al.* Luminescence modulation of ordered upconversion nanopatterns by a photochromic diarylethene: Rewritable optical storage with nondestructive readout. *Adv. Mater.* **22**, 633–637 (2010).
9. Qin, L., Gu, W., Wei, J. & Yu, Y. Piecewise Phototuning of Self-Organized Helical Superstructures. *Adv. Mater.* **30**, 1704941 (2018).
10. Chen, P. *et al.* Chirality invertible superstructure mediated active planar optics. *Nat. Commun.* **10**, 2518 (2019).
11. Fukaminato, T. *et al.* Single-Molecule Fluorescence Photoswitching of a Diarylethene – Perylenebisimide Dyad: Non-destructive Fluorescence Readout. *J. Am. Chem. Soc.* **133**, 4984–4990 (2011).
12. Zheng, K. *et al.* Rewritable Optical Memory Through High-Registry Orthogonal Upconversion. *Adv. Mater.* **30**, 1801726 (2018).
13. Lin, J., Wan, S., Liu, W. & Lu, W. Photo-writing self-erasable phosphorescent images using poly(N - vinyl-2-pyrrolidone) as a photochemically deoxygenating matrix. *Chem. Commun.* **55**, 4299–4302 (2019).
14. Gu, L. *et al.* Dynamic Ultralong Organic Phosphorescence by Photoactivation. *Angew. Chem. Int. Ed.* **57**, 8425–8431 (2018).
15. Yang, J. *et al.* The influence of the molecular packing on the room temperature phosphorescence of purely organic luminogens. *Nat. Commun.* **9**, 840 (2018).
16. Gmelch, M., Thomas, H., Fries, F. & Reineke, S. Programmable transparent organic luminescent tags. *Sci. Adv.* **5**, eaau7310 (2019).
17. Thomas, H. *et al.* Aromatic Phosphonates: A Novel Group of Emitters Showing Blue Ultralong Room Temperature Phosphorescence. *Adv. Mater.* 2000880 (2020) doi:10.1002/adma.202000880.
18. An, Z. *et al.* Stabilizing triplet excited states for ultralong organic phosphorescence. *Nat. Mater.* **14**, 685–690 (2015).
19. Tian, S. *et al.* Utilizing d–p π Bonds for Ultralong Organic Phosphorescence. *Angew. Chem. Int. Ed.* **58**, 6645–6649 (2019).

20. Gu, L. *et al.* Colour-tunable ultra-long organic phosphorescence of a single-component molecular crystal. *Nat. Photonics* **13**, 406–411 (2019).
21. Li, D. *et al.* Amorphous Metal-Free Room-Temperature Phosphorescent Small Molecules with Multicolor Photoluminescence via a Host–Guest and Dual-Emission Strategy. *J. Am. Chem. Soc.* **140**, 1916–1923 (2018).
22. Ogoshi, T. *et al.* Ultralong Room-Temperature Phosphorescence from Amorphous Polymer Poly(Styrene Sulfonic Acid) in Air in the Dry Solid State. *Adv. Funct. Mater.* **28**, 1707369 (2018).
23. Cai, S. *et al.* Enabling long-lived organic room temperature phosphorescence in polymers by subunit interlocking. *Nat. Commun.* **10**, 4247 (2019).
24. Al-Attar, H. A. & Monkman, A. P. Room-Temperature Phosphorescence From Films of Isolated Water-Soluble Conjugated Polymers in Hydrogen-Bonded Matrices. *Adv. Funct. Mater.* **22**, 3824–3832 (2012).
25. Sun, Y. P. *et al.* Quantum-Sized Carbon Dots for Bright and Colorful Photoluminescence. *J. Am. Chem. Soc.* **128**, 7756–7757 (2006).
26. Yuan, F. *et al.* Bright high-colour-purity deep-blue carbon dot light-emitting diodes via efficient edge amination. *Nat. Photonics* (2019) doi:10.1038/s41566-019-0557-5.
27. Kim, D. *et al.* Graphene quantum dots prevent α -synucleinopathy in Parkinson's disease. *Nat. Nanotechnol.* **13**, 812–818 (2018).
28. Ge, J. *et al.* A graphene quantum dot photodynamic therapy agent with high singlet oxygen generation. *Nat. Commun.* **5**, 4596 (2014).
29. Liu, J. *et al.* Metal-free efficient photocatalyst for stable visible water splitting via a two-electron pathway. *Science* **347**, 970–974 (2015).
30. Deng, Y. *et al.* Long lifetime pure organic phosphorescence based on water soluble carbon dots. *Chem. Commun.* **49**, 5751 (2013).
31. Green, D. C. *et al.* Controlling the fluorescence and room-temperature phosphorescence behaviour of carbon nanodots with inorganic crystalline nanocomposites. *Nat. Commun.* **10**, 206 (2019).
32. Liu, J. *et al.* Carbon dots in zeolites: A new class of thermally activated delayed fluorescence materials with ultralong lifetimes. *Sci. Adv.* **3**, e1603171 (2017).
33. Li, Q. *et al.* Efficient room-temperature phosphorescence from nitrogen-doped carbon dots in composite matrices. *Chem. Mater.* **28**, 8221–8227 (2016).
34. Li, Q. *et al.* Induction of long-lived room temperature phosphorescence of carbon dots by water in hydrogen-bonded matrices. *Nat. Commun.* **9**, 734 (2018).
35. Jiang, K. *et al.* Triple-Mode Emission of Carbon Dots: Applications for Advanced Anti-Counterfeiting. *Angew. Chem. Int. Ed.* **55**, 7231–7235 (2016).
36. Tao, S. *et al.* Design of Metal-Free Polymer Carbon Dots: A New Class of Room-Temperature Phosphorescent Materials. *Angew. Chem. Int. Ed.* **57**, 2393–2398 (2018).

37. Li, W. *et al.* A Universal Strategy for Activating the Multicolor Room-Temperature Afterglow of Carbon Dots in a Boric Acid Matrix. *Angew. Chem. Int. Ed.* **58**, 7278–7283 (2019).
38. Tian, Z. *et al.* Multilevel Data Encryption Using Thermal-Treatment Controlled Room Temperature Phosphorescence of Carbon Dot/Polyvinylalcohol Composites. *Adv. Sci.* **1800795**, 1800795 (2018).
39. Long, P. *et al.* Self-Protective Room-Temperature Phosphorescence of Fluorine and Nitrogen Codoped Carbon Dots. *Adv. Funct. Mater.* **28**, 1800791 (2018).
40. Jiang, K., Wang, Y., Cai, C. & Lin, H. Conversion of Carbon Dots from Fluorescence to Ultralong Room-Temperature Phosphorescence by Heating for Security Applications. *Adv. Mater.* **30**, 1800783 (2018).
41. Zhang, G., Palmer, G. M., Dewhirst, M. W. & Fraser, C. L. A dual-emissive-materials design concept enables tumour hypoxia imaging. *Nat. Mater.* **8**, 747–751 (2009).
42. Vanderkooi, J. M., Maniara, G., Green, T. J. & Wilson, D. F. An optical method for measurement of dioxygen concentration based upon quenching of phosphorescence. *J. Biol. Chem.* **262**, 5476–5482 (1987).
43. Zhao, J., Wu, W., Sun, J. & Guo, S. Triplet photosensitizers: from molecular design to applications. *Chem. Soc. Rev.* **42**, 5323 (2013).
44. Li, Q., Tang, Y., Hu, W. & Li, Z. Fluorescence of Nonaromatic Organic Systems and Room Temperature Phosphorescence of Organic Luminogens: The Intrinsic Principle and Recent Progress. *Small* **14**, 1801560 (2018).
45. Higa, O., Rogero, S. ., Machado, L. D. ., Mathor, M.. & Lugão, A.. Biocompatibility study for PVP wound dressing obtained in different conditions. *Radiat. Phys. Chem.* **55**, 705–707 (1999).
46. Jang, W.-S., Rawson, I. & Grunlan, J. C. Layer-by-layer assembly of thin film oxygen barrier. *Thin Solid Films* **516**, 4819–4825 (2008).
47. Khan, A. U. & Kasha, M. Direct spectroscopic observation of singlet oxygen emission at 1268 nm excited by sensitizing dyes of biological interest in liquid solution. *Proc. Natl. Acad. Sci.* **76**, 6047–6049 (1979).
48. Weir, E. Preventing cold chain failure: vaccine storage and handling. *Can. Med. Assoc. J.* **171**, 1050–1050 (2004).

Figures

Figure 1

Schematic illustration for the design and fabrication of the CDs/PVP composite film with reversible photo-induced long afterglow. **a** Diagram of the processes to achieve photo-induced long afterglow. The CDs/PVP composite film initially showed no afterglow due to oxygen quenching (I). Upon irradiation, the permeated triplet oxygen was gradually converted to singlet oxygen through a photodynamic process (II), eventually creating an oxygen-free area in the exposed region that showed RTP afterglow (III). Afterward, the regional anoxia would last for a certain duration before oxygen replenishment through diffusion (IV), which could be accelerated by thermal exposure. **b** The preparation of the CDs/PVP composite film and demonstration of its PIOM. The CDs synthesized from molecular precursors through solvothermal method (I) were blended with PVP in an aqueous solution and cast into a transparent, flexible film (II). The as-prepared film initially showed no afterglow after being shortly irradiated (400 nm, 10 mW/cm², <0.5 s), however, intense afterglow occurred after prolonged irradiation was applied (30 s).

Figure 2

Photophysical properties of the CDs/PVP film. **a** The steady-state PL emission (solid blue line) and the delayed emission spectra (dotted and solid red line) of a CDs/PVP composite film. The PL emission of the film peaked at 470 nm, slightly blue-shifted compared with solution phase emission (Supplementary Fig. 4). The delayed emission intensity of the composite was initially low (dotted red line), then significantly increased after being continuously irradiated with a 400 nm flashlight for 30 s (solid red line). The fully evoked RTP afterglow peaked at 580 nm. **b** The PL decay profile of the film before (blue dots) and after (red dots) photo-activation. **c** Photographs of the film with and without long afterglow feature at different on-off switch cycles. **d** Delayed emission intensity plotted against irradiation time under different power density. **e** Delayed emission intensity plotted against storage time under different temperatures. Inserted: photographs of the film's long afterglow examined after gradually extending storage time under different temperatures.

Figure 3

Mechanistic investigation of the oxygen mediated photo-induced long afterglow. **a** The normalized RTP intensity of CDs/PVP and CDs/PAM films against time upon intermittent irradiation (0.8 mW/cm², 30 s irradiation followed by 10 s darkness) cycles. The RTP intensity of CDs/PVP clearly showed gradual accumulation, while the RTP intensity of CDs/PAM is almost constant in each irradiation window. **b** Photographs of CDs/PVP (☒) and CDs/PAM (☒) films upon photo-activation and excitation. The two films were placed side by side for demonstration (I). After shortly irradiated by a 400 nm lamp, only ☒ showed observable afterglow (II). A mask was applied to cover the lower half of both films (III) before applying continuous irradiation (IV). Afterward, the mask was removed, no significant morphological change occurred when inspected under ambient light (V). Another short irradiation revealed the change of afterglow feature in film ☒ after continuous irradiation, as its uncovered part showed intense afterglow (VI). **c** Schematic illustration of the reversible dynamic RTP realized by light-induced oxygen removal and oxygen diffusion. **d** The NIR luminescence of singlet oxygen in D₂O solutions containing neat CDs (0.25 wt%) and CDs + PVP (CDs: 0.25 wt%, PVP: 5wt%) under continuous 400 nm irradiation.

Figure 4

Photo-induced long afterglow patterning and its unique applications thereof. **a** Illustration of the Ink-free optical printing of dynamic afterglow patterns by masking and lithography. Emblem and Chinese characters (RTP pattern-1 and pattern-2) were created with different masks successively on the same film after the previous pattern was erased by thermal exposure. Bending the flexible film did not affect the display quality. **b** Schematic illustration for the use of editable smart tags with thermal sensitive long afterglow memory. Firstly, the logistics data was filed and encrypted into a 2D barcode using the Micro-PDF147 format (I). Then, the barcode was printed onto a transparent PET membrane using a commercial static printer to obtain a temporary mask (II). By applying that mask for optical printing (III), a long afterglow pattern containing logistics data was created on the tag (IV). The edited tag was then packaged with the cargo, being regularly inspected, erased, and updated at each stop during the delivery. **(c)** Flowchart: a hypothetical multi-stop cold-chain transportation route through which thermal-sensitive cargos (sample A and B) were delivered. Photographs: RTP afterglow patterns of tags referring to sample A (top) and sample B (bottom) upon departure and arrival at each stop.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementaryInformation.docx](#)
- [SupplementaryVideo1.mp4](#)
- [SupplementaryVideo2.mp4](#)
- [SupplementaryVideo3.mp4](#)
- [SupplementaryVideo4.mp4](#)