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# Sustainable Afterglow Room-temperature Phosphorescence Emission Materials Generated Using Natural Phenolics

Keliang Wan,[a] Yingxiang Zhai,[a] Shouxin Liu,[a] Jian Li,[a] Shujun Li,[a] Bernd Strehmel,[d] Zhijun Chen*[a] and Tony D. James[b,c]

[a]   Keliang Wan, Yingxiang Zhai, Shouxin Liu, Jian Li, Shujun Li, Zhijun Chen
     Key Laboratory of Bio-based Material Science and Technology of Ministry of Education
     Northeast Forestry University
     Harbin 150040, P. R. China
     **E-mail**: Chenzhijun@nefu.edu.cn
[b]   Tony D. James
     Department of Chemistry
     University of Bath
     Bath BA2 7AY, United Kingdom
[c]   Tony D. James
     School of Chemistry and Chemical Engineering
     Henan Normal University
     Xinxiang 453007, P. R.China
[d]   Bernd Strehmel
     Department of Chemistry, Institute for Coatings and Surface Chemistry
     Niederrhein University of Applied Sciences
     Adlerstr. 1, 47798 Krefeld, Germany

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**Abstract:** Long-lived afterglow room-temperature phosphorescence (RTP) from natural phenolics has seldom been reported yet this is essential for the development of sustainable afterglow RTP materials. With this research, we have prepared sustainable afterglow RTP materials (GA@SA) with a lifetime of up to ~934.7 ms by embedding gallic acid (GA) within a $Ca^{2+}$-crosslinked sodium alginate (SA) matrix. Theoretical simulations indicate that the restricted carbonyl moieties of the GA and H-type aggregates of GA in a SA matrix promoted the spin orbit coupling (SOC) of GA and induced afterglow emission. Moreover, afterglow RTP emission could be produced by embedding different types of natural phenolics such as, tannic acid, caffeic acid and chlorogenic acid into $Ca^{2+}$-crosslinked networks of SA. As an illustration of potential applications, GA@SA was used to prepare anti-counterfeit afterglow clothing and paper. This work provides an innovative method for the activation of long-lived afterglow RTP from sustainable phenolics.

## Introduction

Largely found as secondary plant metabolites, natural phenolics play a pivotal role in a plants' defence mechanism. The intrinsic properties of natural phenolic compounds, such as metal chelation, hydrogen bonding, pH responsiveness, accessible redox potential, radical scavenging and polymerization ability, have made them powerful building blocks for functional materials.[1] Specifically, attributed to the incorporated aromatic units, natural phenolics exhibit interesting luminescent emission properties, enabling their potential application for bioimaging and sensing applications.[1b, 2] Nevertheless, producing afterglow RTP materials from natural phenolics has been seldomly reported even though they contain an aromatic carbonyl scaffold making them suitable afterglow RTP chromophores.

Afterglow RTP emission is defined as emission lasting for more than 100 ms after removal of the excitation source and can typically be detected by the naked eye.[3] Materials with afterglow RTP emission exhibit long lifetimes, large Stokes shifts, and significant signal-to-noise ratio, enabling their use for a broad selection of applications, such as, optical sensing, biological imaging and information encryption.[4] Amongst all the afterglow RTP materials, organic afterglow RTP materials derived from natural sources are of particularly interest since they are abundant, sustainable, flexible and biocompatible.[5] There are two main strategies for fabricating sustainable afterglow RTP materials. The first approach is to convert natural materials to carbon dots with efficient SOC, which are subsequently confined in an organic matrix in order to stabilize the triplet excitons and generate afterglow RTP emission.[6] The second strategy is to directly use untreated natural sources, such as lignin, gelatin and cellulose as chromophores for afterglow RTP emission within a rigid matrix.[7] The second method is particularly attractive since it is convenient, energy saving and significantly more sustainable. Nevertheless, the as-obtained afterglow RTP materials obtained from the second method suffer from short lifetimes, preventing their practical application.

Motivated by these observations, we embedded natural phenolic, gallic acid (GA), into a natural matrix, $Ca^{2+}$-crosslinked sodium alginate (SA) in order to generate sustainable afterglow RTP materials (GA@SA) (**Figure 1**). In the crosslinked SA matrix, GA formed H-type aggregates. Additionally, the carbonyl moieties of GA formed intermolecular hydrogen bonds, restricting vibration. All these aspects promoted SOC and enabled the afterglow RTP emission of GA@SA. Moreover, we determined that our method was general, since other natural phenolics, such as, tannic acid (TA), caffeic acid (Cafa) and chlorogenic acid (CA) could be converted into afterglow RTP materials by embedding them in crosslinked SA polymer matrixes (**Figure 1**). To demonstrate the

applicability of our approach, GA@SA was used to prepare afterglow materials, that exhibited potential as anti-counterfeiting reagents for clothing and paper. To the best of our knowledge, this is the first example where natural phenolics have been used to generate afterglow RTP emission.
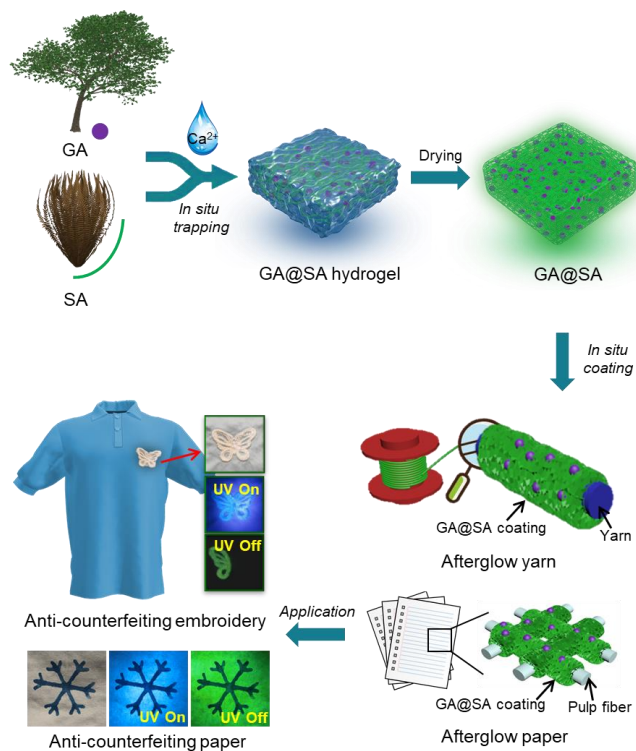


**Figure 1.** Schematic illustrating the production of sustainable afterglow RTP materials from natural phenolics.

## Results and Discussion

GA, as a representative natural phenolic, was used for preparing sustainable afterglow RTP materials. A polymeric network formed between SA and $Ca^{2+}$ was used as the crosslinked matrix.[8] As expected, *in situ* trapping of GA in the crosslinked SA network to produce GA@SA triggered strong afterglow RTP emission centred at 500 nm (**Figures 2a**). As a control, pure GA did not exhibit afterglow emission (**Figure S1**). Time-resolved spectroscopy indicated that the GA@SA had a long-lasting and stable afterglow emission and retained weak phosphorescence emission at the same emission wavelength for as long as ~1000 ms (**Figure 2b**). The intensity and lifetime of GA@SA afterglow emission decreased when the temperature was increased from 77 K to 277 K (**Figure 2c and Figure S2**), in keeping with the expected reduction in phosphorescence at elevated temperatures because of increased non-radiative decay. The effect of environmental humidity on the phosphorescence lifetime of GA@SA was also investigated. The phosphorescence was found to be sensitive to humidity with simultaneous reduction of lifetime when the humidity was gradually increased. In particular, the phosphorescence lifetime dropped rapidly when the humidity reached 70% (**Figure 2d**). Interestingly, the lifetime recovered after the samples were dried (**Figure 2d**). Moreover, the lifetime of GA@SA was tuneable. Increasing the concentration of $Ca^{2+}$ enhanced the crosslinking

density and rigidity of the SA matrix, which eventually increased the lifetime of GA@SA. The lifetime of GA@SA increased up to ~ 934.7 ms when the $Ca^{2+}$ content was ~7.8 w/w% (**Figure S3**). The lifetime remained stable upon further increasing the $Ca^{2+}$ content up to ~11.7 w/w%, which might be attributed to a "saturated" crosslinking density (**Figure S3**). Comparison between the lifetime of GA@SA and some reported sustainable afterglow RTP materials confirmed that GA@SA exhibited the longest lifetime.[6-7, 9] In addition to a long lifetime, the GA@SA also exhibited several advantages. For example, the preparation process did not require heating or the use of toxic chemicals, which is both energy saving and environmentally friendly. In addition, both GA and SA are naturally occurring, abundant and cheap, enabling their facile use on a large scale. Moreover, the convenient tuneable lifetime indicates that GA@SA could be tailored to meet any requirements. The as-prepared GA@SA powder was dispersed in organic solvents including ethanol, acetonitrile, and ethyl acetate. Surprisingly, the afterglow RTP was not quenched by these solvents, and a very long lifetime afterglow could be observed (~ 780 ms, 720 ms and 710 ms in ethanol, acetonitrile, and ethyl acetate, respectively) (**Figure S4a**). The lifetime of GA@SA was also investigated at different pH values (**Figure S4b**). The lifetime of GA@SA was ~884.25 ms and ~774.50 ms when treated by an aqueous solution at pH 3 and 11, respectively. The decreased lifetime is probably due to the acidic/basic environment partially breaking the crosslinked network of SA.
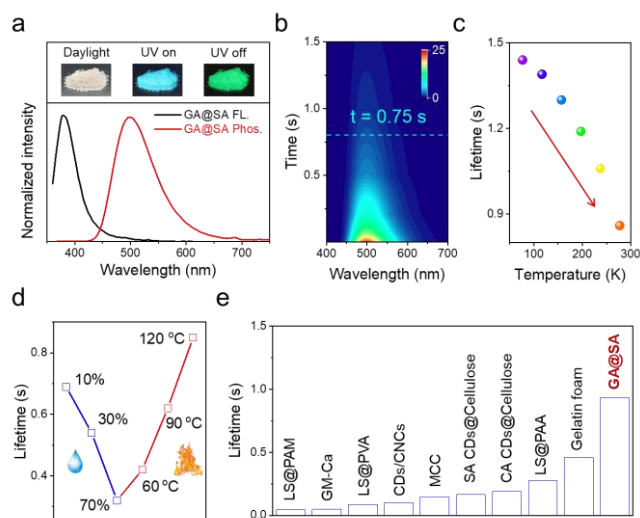


**Figure 2.** Afterglow RTP emission of GA@SA. a) Fluorescence and RTP emission of GA@SA, excitation wavelength = 365 nm, inset: Images of bright field, fluorescent and RTP emission of GA@SA upon UV irradiation (365 nm); b) Time-resolved RTP emission of GA@SA, excitation wavelength = 365 nm; c) RTP lifetime of GA@SA at different temperatures. d) RTP lifetime of GA@SA upon treatment of humidity and drying. e) Comparison of RTP lifetime between LS@PAM,[7a] GM-Ca,[9] LS@PVA,[7a] CDs@CNCs,[6b] MCC,[7c] SA CDs@Cellulose,[6a] CA CDs@Cellulose,[6a] LS@PAA,[7a] gelation foams[7b] and GA@SA.

To better understand the mechanism of the long afterglow emission, theoretical simulations of GA@SA were conducted. The results indicated that GA tended to form multiple hydrogen bonds with the SA chains (**Figure 3a**). Especially, the carbonyl moieties of the GA tended to form intramolecular hydrogen bonds (**Figure 3a**). Such conformationally constrained carbonyl moieties are particularly beneficial for SOC and RTP emission.[10] This result was also confirmed using control experiments. In the control

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group, pyrogalloic acid (GA without carboxylic acid) was confined in a crosslinked SA matrix and only exhibited afterglow emission with a short lifetime of ~ 267.4 ms (**Figure S5**). Moreover, the simulation results for GA@SA indicated that the average center-center distance between ~37% adjacent GA (the total number of statistic aromatic units was 36) was less than ca. ~0.4 nm, which enabled the formation of π - π interactions between the interlayer phosphors (**Figure 3b**). The relative orientation of two neighboring GA was populated over a range from ~60° to 100° with an optimal angle of ~ 90°, indicating H-type dimers of GA formed in GA@SA. Such dimers can help stabilize the lowest excited triplet state, and prolong the RTP lifetime (**Figure 3c**).[11] Subsequently, the excitation state energies, spin-orbit couplings (ξ) of GA and GA dimers were obtained from the calculations. Significantly, the spin orbit coupling (SOC) ξ ($S_1$, Tn) of the GA dimers (0.92, 0.53 and 0.83 cm$^{-1}$, n = 1, 2 and 3, respectively) was larger than that of GA (0.03, 0.02 and 0.02 cm$^{-1}$, n = 1, 2 and 3, respectively), which is favourable for phosphorescence (**Figure 3d** and **Figure S6**). Additionally, urea, as a hydrogen bond breaker, was added to GA@SA to reduce the interaction between GA and SA. The lifetime of GA@SA decreased from ~742.5 ms to ~354.1 ms when the fraction of urea went up from 3.8% to 37.5% (**Figure S7**). Taking all above results together, the mechanism for the long afterglow emission was attributed to the intermolecular hydrogen bonding, restricted vibration of the carbonyl moieties and formation of H aggregates of GA trapped in a crosslinked SA matrix. These factors promoted SOC and stabilized the triplet excitons, resulting in the enhanced long-lifetime afterglow emission of GA@SA.
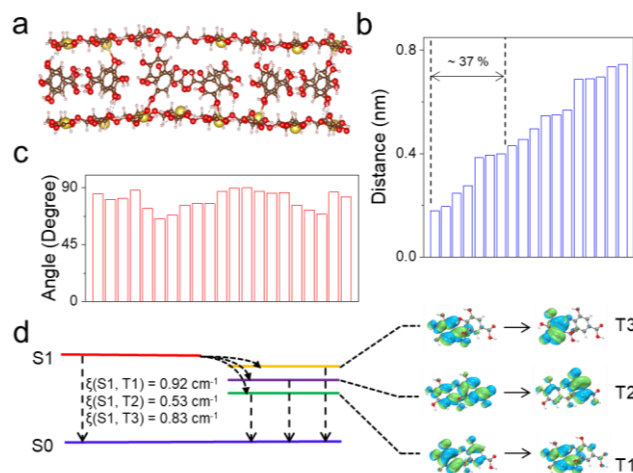


**Figure 3**. Theoretical simulation of GA@SA. a) Schematic illustration of the molecular interactions between the GA and SA molecules. b) Distance between GA in GA@SA. c) The relative orientation of two neighboring GA in GA@SA. d) Calculated excitation energies, spin-orbit couplings (ξ) and orbitals for GA dimers.

Furthermore, this method can easily be expanded to other molecular matrices. Polyacrylic acid (PAA) network, polyacrylamide (PAAM) network, and poly (vinyl alcohol) (PVA) were used to prepare GA@PAA, GA@PAAM and GA@PVA, respectively. The three materials all emitted blue fluorescence when irradiated at 365 nm and yellow long phosphorescence, which could be observed by the naked eye, when a UV lamp was switched off (**Figures 4a-4c**). The afterglow RTP lifetime of GA@PAA, GA@PAAM and GA@PVA were ~ 499.9 ms, ~386.5 ms and ~

380.9 ms, respectively (**Figures S8-S10**), demonstrating that GA can be embedded in a wide range of matrices to produce sustainable RTP materials. Moreover, to further illustrate the generality, several natural phenolics including tannic acid (TA), caffeic acid (Cafa) and chlorogenic acid (CA) were embedded into a crosslinked SA network to produce TA@SA, Cafa@SA and CA@SA, respectively. Specifically, the UV-Vis absorbances of the three new materials were all located in the UV region, which was comparable to the corresponding natural phenolics (**Figure S11**). Significantly, TA@SA, Cafa@SA and CA@SA all emitted blue fluorescence when irradiated at 365 nm and yellow afterglow phosphorescence (**Figure 4d-4f**). The lifetime of TA@SA, Cafa@SA and CA@SA were ~ 705.8 ms, ~ 284.5 ms and ~ 322.32 ms, respectively (**Figure S12-S14**).
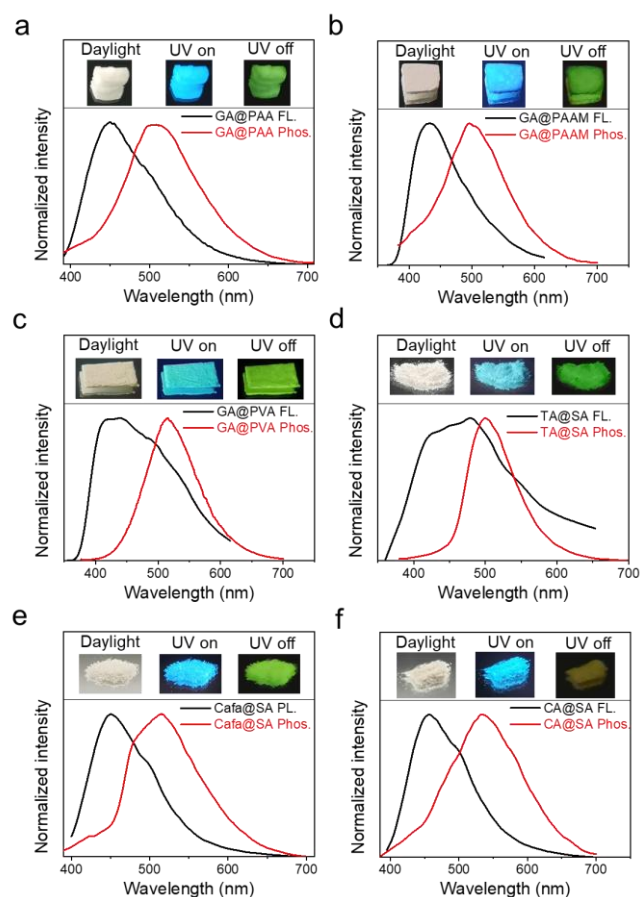


**Figure 4**. General afterglow RTP emission of natural phenolic@polymer matrix. a-c) Fluorescence and Phosphorescence spectra of GA@matrix at room temperature (inset photographs show GA@matrix taken before (left) and after (right) turning off 365 nm UV lamp); d-f) Fluorescence and Phosphorescence spectra of natural phenolic@SA at room temperature (inset photographs show natural phenolic@SA taken before (left) and after (right) turning off 365 nm UV lamp).

Since the all the components in GA@SA are natural and exhibit good biocompatibility, we decided to explore the practical utility of GA@SA in the development of an anti-counterfeiting logo for clothing. To this end, GA@SA was used to prepare flexible afterglow yarns. An automated apparatus comprising a dip-coating tank, collection roller and heating plate was designed for fabrication of the afterglow yarns. Cotton yarns were passed through the coating tank filled with SA/GA solution, collected, and then

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crosslinked *in situ* and dried using a heating plate (**Figure 5a and Video S1**). Afterglow yarns were obtained by further drying at 120 °C for 1 h (**Figure 5b**). The afterglow yarns exhibited good stability and retained their afterglow RTP emission after soaking in ethanol, acetonitrile, ethyl acetate, n-hexane and acetone for 1 h (**Figure 5c**). Encouraged by the excellent stability, we then used the afterglow yarns and fluorescent yarns (made from pure GA) to create a time-resolved logo embroidered on clothing using a commercial machine. Upon excitation with a 365 nm UV lamp, a white-blue butterfly became clearly visible. When the lamp was turned off, the portion of the embroidery made from fluorescent yarns immediately became invisible because of the short lifetimes. However, afterglow emission originating from the afterglow yarns could be clearly seen by the naked eye (**Figure 5d**). The embroidery also exhibited good stability. The time-resolved logo was still observed after 20- and 30-days storage (**Figure S15**). Moreover, the embroidery exhibited time-resolved emission after washing in water (**Figure S16**). These observations clearly indicate that our GA@SA exhibits great potential as an anti-counterfeiting logo for clothing. In addition, GA@SA was used to fabricate afterglow paper. Standard   paper was first spayed with a mixed solution (GA/SA). Then, $Ca^{2+}$ was sprayed on to the paper to enable the *in situ* generation of GA@SA within the paper matrix. As expected, the as-obtained paper exhibited afterglow emission following UV excitation (**Figure 5e**). Moreover, the afterglow paper could be printed on normally and exhibited afterglow emission after UV excitation. As a control, paper without GA@SA did not exhibit afterglow emission (**Figure S17**). These results indicate that paper modified with GA@SA has the potential to be used for anti-counterfeiting purposes.
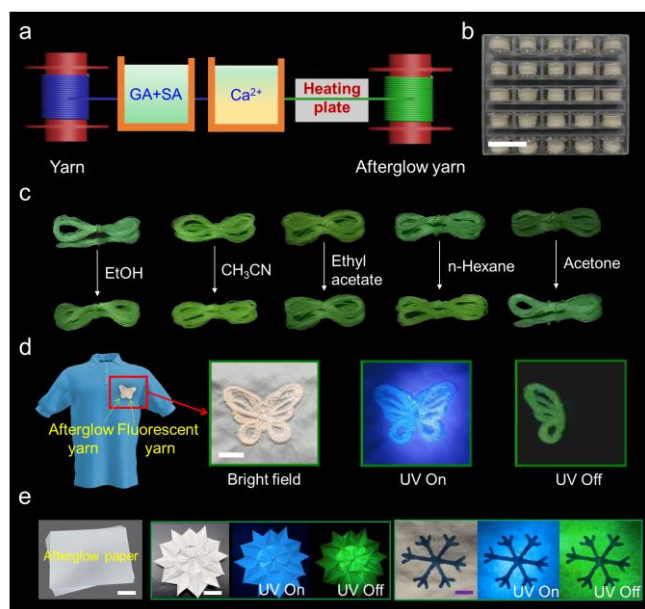


**Figure 5.** Application of GA@SA. (a) Schematic illustration showing preparation of afterglow yarns using custom built apparatus; (b) Digital images of afterglow yarns in bright field, scale bar = 1.5  cm; (c) Afterglow RTP emission of yarns before and after immersion in different solvents for 1 h (photographs were taken after drying the treated yarns at 120°C for 0.5 h); (d) Digital images of logo embroidered on clothing (left part made from GA@SA and right part made from GA) in bright field, under UV irradiation and after switching off the UV lamp, scale bar = 1 cm; (e) Digital images of afterglow paper (left), snow-shape afterglow paper (middle) and printed afterglow paper (right), scale bar = 2 cm.

## Conclusion

With this research we have developed sustainable afterglow RTP materials exhibiting long lifetime, which was achieved by embedding GA into crosslinked SA matrices. The restricted vibration of the carbonyl moieties and formation of H aggregates of GA enhanced SOC, promoting ultra-long afterglow emission. More interestingly, our method exhibited excellent generalization. Other natural phenolics including tannic acid (TA), caffeic acid (Cafa) and chlorogenic acid (CA) could be used to generate afterglow RTP emission after being embedded in to a SA matrix. To demonstrate the potential practical applications of our new and sustainable GA@SA materials, we prepared a yarn with afterglow RTP, using a custom-built apparatus. We then used the as-prepared yarns as part of anti-counterfeiting logos for clothing. In addition, GA@SA could be used to prepare anti-counterfeit paper. Considering the excellent sustainability, convenient preparation, long lifetime easy processability, of the as-developed GA@SA materials they represent attractive materials for use in OLEDs,[12] flexible display textiles[13], photocatalyst[14] and for bioimaging applications.[15]

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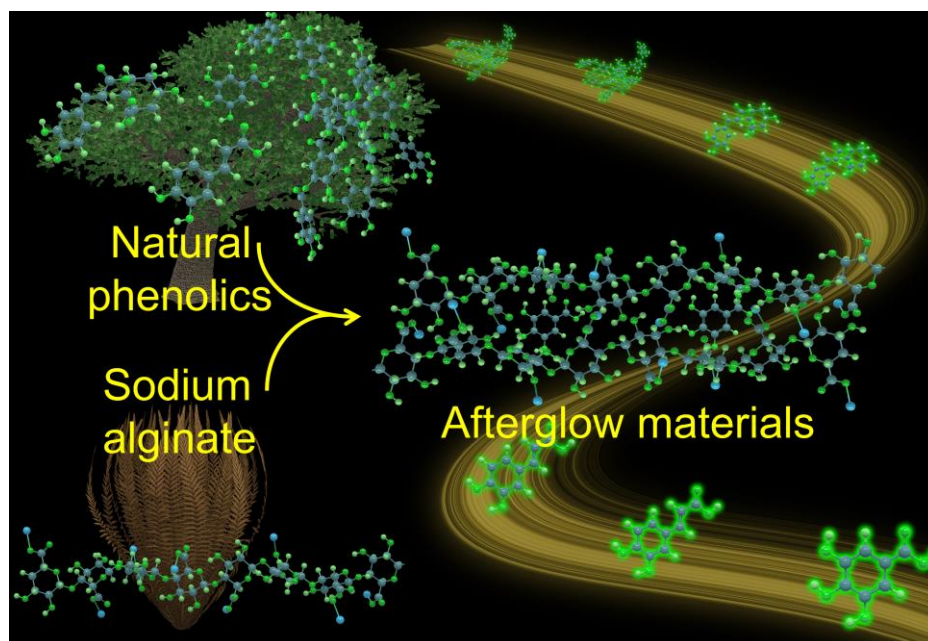


Sustainable organic afterglow room-temperature phosphorescence (RTP) with long lifetime is a particularly attractive phenomenon but remains difficult to achieve. Here, we prepared sustainable afterglow RTP materials (GA@SA) with a lifetime up to 934.7 ms by embedding gallic acid (GA) within a $Ca^{2+}$-crosslinked sodium alginate (SA) matrix.