# Recent progress of fuel-driven temporary materials

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#### Abstract

Fuel-driven dissipative self-assembly, which is a well-established concept in recent years, refers to out-of-equilibrium molecular self-assembly initiated and supported by the addition of active molecules (chemical fuel). It widely exists in nature since many tempo-rary, active micro- or nanostructures in living bodies are generated by the dissipative self-assembly of biomolecules. Therefore, the study on dissipative self-assembly provides a good opportunity to have an insight into the microscopic mechanism of living organisms. In the meantime, dissipative assembly is thought to be a potential pathway to achieve dynamic, temporary supramolecular materials. Recently, a number of temporary materials have been developed with the aid of strategies for realizing dissipative self-assembly. Some of their properties, including solubility, stiffness, turbidity, color, or self-healing ability, change upon the addition of chemical fuel but spontaneously restore with chemical fuel consumption. The dynamic of these materials brings them various unprecedented functions. In this review, the principles of fabricating a fuel-driven temporary material are first reviewed and subsequently, recent examples of fuel-driven temporary materials are emphatically summarized, including gels, self-erased inks, nanoreactors, self-healing materials, and nanochannels. Finally, the challenges of developing fuel-driven temporary materials are discussed.

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## Keywords

Chemical fuel | Dissipative self-assembly | Temporary material | Non-equilibrium | Hydrogel Comprehensive Summary

Fuel-driven dissipative self-assembly, which is a well-established concept in recent years, refers to out-of-equilibrium molecul

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- 1. Introduction

Molecular self-assembly is one of the important bridges that connect chemical science and life science. Living organisms actually consist of delicate structures formed by the self-assembly of biomolecules. Thus, a great effort has been made to investigate the self-assembly of various natural or artificial molecules. Plenty of functional materials on the basis of molecular self-assembly have been successfully constructed. [1-5] However, the functionality of the present examples of artificial self-assembly is still far from those in living organisms, because most of the reported artificial self-assembled structures, including the micelles, vesicles, membranes, etc. are static under thermodynamic equilibrium. While the *in vivo* self-assembly is usually out-of-equilibrium, dynamic, temporary, and varied by the drive of external energy. Hence, a class of special self-assembly named "dissipative self-assembly" (DSA), which refers to the self-assembly that is driven by external energy input, has drawn extensive attention in recent years. [6-9] Unlike spontaneous self-assembly under thermodynamic equilibrium, the ordered structure formed by DSA is usually temporary and decays with energy dissipation. A large number of self-assemblies in living organisms can be classified as DSA. For example, DSA of actin networks and microtubules driven by adenosine triphosphate (ATP) or its analogs. It plays an essential role in various cellular processes, such as the formation of the cytoskeleton, intracellular transportation, and cell motility. [10-12].



Figure 1 The scheme of the reaction network for creating chemical fuel-driven temporary materials.

Meanwhile, the concept of DSA has been also applied to designing functional fuel-driven temporary materials. Unlike the permanent materials of which stability was considered as their advantage, temporary (transient) materials can spontaneously collapse without external destruction. The time-dependent variety brings more opportunities to realize new functions and applications. The external energy that drives the formation of temporary materials can be from light, [13-15] sound, [16-18] mechanical forces, [19] or chemical fuels, etc. However, chemical fuel-driven temporary materials are the most frequently reported among them. The principle to realize artificial fuel-driven DSA provides an effective strategy to prepare a fuel-driven temporary material. As shown in Figure 1, a well-designed precursor reacts with chemical fuel to yield an aggregated or cross-linked molecular structure which can result in the formation of a bulky material. However, the aggregation or crosslink is thermodynamically unstable in presence of a deactivator. The reaction between the material and the deactivator led to the gradual dissociation of the aggregation or cross-linking, as well as the disintegration of the material.

In recent years, a great effort has been made to investigate chemical fuel-driven temporary materials. A number of such type of materials have been reported. In this review, we will provide a brief overview of the reaction networks that can be applied to construct fuel-driven temporary materials, then systemically discuss recent examples of all kinds of fuel-driven temporary materials, such as gels, inks, nanoreactors, self-healing materials, and nanochannels. Finally, the challenges of investigating fuel-driven temporary materials and some perspectives on the function and application of such kind of materials will be discussed.

2. Chemical fuel-driven reaction networks

The key to constructing a fuel-driven temporary material is to find a reaction network (Figure 1) that contains a temporally existent intermediate product, which is usually fast produced by the reaction between the chemical fuel and the precursor in the material, then spontaneously decomposes or be consumed by the reaction with other components. [9, 20] The formation and decomposition of the temporary material rely on the existence of the intermediate product. The lifetime of the temporary material depends on the duration of the existence of the intermediate product. Recently, with the continual report on fuel-driven DSA, a number of such reaction networks have been established. They were listed in Table 1 with the relative reference.

Table 1 Reaction networks that were applied for realizing artificial DSA and fuel-driven temporary materials

No	Chemical Fuel	Precursor	Product	Deactivat
1	CH <sub>3</sub> I	-COOH	-COOCH <sub>3</sub>	OH-
2	$(CH_3)_2SO_4$	-COOH	-COOCH <sub>3</sub>	OH-
3				$H_2O$
4	OH-	pH-responsive groups	deprotonated counterpart	ester
5	$\mathrm{H}^+$	pH-responsive groups	protonated counterpart	urea and
6	Cl <sub>3</sub> CCOOH	pH-responsive groups	protonated counterpart	base
7	ATP and its analogs	organic cations	electrostatic complex of ATP and cations	apyrase
8	Na2S2O4			$O_2$
9	Na2S2O4			а
10	$I_2$			$CS(NH_2)_2$
11	$H_2O_2$	Reductive state of redox-active species	oxidative state of redox-active species	reductant

<sup>*a*</sup> (Slowly produced by hexamethylenetetramine and glucono- $\delta$ -lactone)

3. Fuel-driven temporary materials

## 3.1. Fuel-driven temporary gels

Temporary gels are the earliest and most frequently reported fuel-driven temporary materials. Thus far, more than one type of temporary gel has been presented. The majority of temporary gels are formed upon the addition of the chemical fuel and gradually collapse with fuel exhaustion. While some other temporary gels, on the contrary, carry out a "gel-sol-gel" cycle by the drive of the chemical fuel. They dissolve with the fuel feeding and slowly regelation as the consumption of the chemical fuel. Additionally, there are still a few gels that can temporarily swell or deswell as the reaction network proceeds. They will be potential candidates for developing a fuel-driven gel actuator. In this section, we will demonstrate fuel-driven temporary gels systemically and try to summarize some principles of fabricating such a kind of material.



**Figure 2** (a) Temporal hydrogel driven by  $CH_3I$ . Copyright (2010) John Wiley and Sons. (b) Temporal hydrogel driven by  $(CH_3)_2SO_4$ . Copyright (2015) American Association for the Advancement of Science.

**3.1.1. Temporary gels based on carboxyl group.** Early in 2010, J. van Esch and J. Boekhoven et al applied a carboxyl-containing low-molecular-weight precursor to successfully fabricate a temporary hydrogel. [21] As shown in Figure 2a, the precursor was formed by coupling two dibenzoyl-(l)-cystine with two carboxyl groups on both sides. Thus, it is well-soluble after being mixed into an alkaline buffer. Then the chemical fuel, iodomethane, was added, and it quickly methylated the carboxyl groups in the precursor, producing the less soluble gelator, which can self-assemble into fibrous nanoaggregates. Hydrogel formed subsequently once the gelator increased to a critical concentration. However, unlike the static hydrogels under thermodynamic equilibrium, it spontaneously dissolved in the following days since the methyl carboxylate groups were slowly hydrolyzed by the OH<sup>-</sup>encapsulated in the hydrogel. Five years later, J. Boekhoven and J. van Esch et al used dimethyl sulfate, another highly active methylation agent, to realize a fuel-driven temporary hydrogel using carboxyl-containing gelators with a similar structure (Figure 2b). [22] The experimental results displayed that the lifetime, stiffness, and self-regenerating capability can be controlled by the amount of the chemical fuel or deactivator (OH<sup>-</sup>). It can be found that iodomethane and dimethyl sulfate are quite effective chemical fuels for initiating the temporal gelation of wide-range carboxyl-containing precursors because they are highly active and the methylation of the carboxyl group can remarkably decrease the hydrophilicity, which is conducive to the formation of the hydrogel. Meanwhile, the resulting methyl ester is unstable in the presence of OH<sup>-</sup> and can spontaneously revert back to the carboxyl groups, leading to a non-equilibrium self-decayed hydrogel. However, such highly active methylating agents show significantly poisonousness. It severely restricts the further development of the temporal material driven by them. Thus, to avoid the high toxicity, carbodiimide, for example, 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDC), was used to replace the iodomethane or dimethyl sulfate to initiate the temporary gelation of precursors containing carboxyl groups. [23, 31-37] As shown in Figure 3a, D. Haldar and coworkers presented a temporary hydrogel of which the precursor was benzyloxycarbonyl-L-phenylalanine (ZF). [35] Upon the addition of EDC, two ZF molecules rapidly condensed to an anhydride gelator, yielding a self-supporting, translucent gel. Due to the instability of the anhydride in the presence of water, the gel slowly redissolved after a period of time. Similar to the temporary gel formed by the drive of dimethyl sulfate, the author found that increasing the concentration of chemical fuel remarkably delayed the spontaneous dissolution of the gel. It exhibited once more that the lifetime of such kind of temporary gel is well-tunable. Additionally, the author also illustrated that the temporary gel was regeneratable by the refueling of EDC. In the same year, C. S. Hartley and D. Konkolewicz et al reported a polymeric temporary gel fabricated formed by the drive of EDC. [36] The precursor was the random polymer (Am-r-AA) formed by acrylic acid and acrylamide. (Figure 3b) The EDC-catalyzed condensation of carboxyl groups on the Am-r-AA chains resulted in an anhydride crosslinked polymer network, producing a yellow polymer hydrogel, which can slowly self-degrade. Unsurprisingly, many parameters, such as the concentration of EDC, temperature, the molecular weight of Am-r-AA, and the ratio of Am/AA units, can significantly affect the lifetime and stiffness of the temporary hydrogel. Besides the above fuel-driven "sol-gel-sol" processes, it was also reported that the carboxyl-containing hydrogel can also temporally deform with the addition of chemical fuel. In 2022, F. Xuan, Y. Wang, and coworkers demonstrated an EDC-driven hydrogel actuator based on poly(acrylic acid) (PAA). [37] As shown in Figure 3c, the addition of the EDC led to the deswelling of the PAA hydrogel, which can self-relax with the slow hydrolysis of the anhydride linkage. The temporary deformation is repeatable by the refueling of the EDC. It can be found that the mechanism of the temporary deformation was quite close to natural muscles, of which temporal contraction was driven by the energy from ATP or its analogs. Therefore, such fuel-driven temporarily-deformed hydrogel exhibited a potential application in developing artificial muscles and the manufacture of the soft robot.

Figure 3. (a) An EDC-driven temporal non-covalent hydrogel by a supramolecular gelator. Copyright (2021) Royal Society



**Figure 4** (a) An alkali-driven temporal organogel. Copyright (2019) John Wiley and Sons. (b) A KOHdriven temporal supramolecular chiral G-quadruplex hydrogels. Copyright (2021) John Wiley and Sons.

**3.1.2.** Temporary gels based on pH-responsive gelator.pH-responsive gels are a sort of typical stimuliresponsive material which has been widely reported in recent decades. [38-41] They are thought to be good candidates for controlled drug delivery [42,43] or gel actuators. [42, 44-46] The key to fabricating a pHresponsive gel is to introduce a group, which is a weak acid (or base) or can be broken in presence of  $H^+$  (or OH<sup>-</sup>), to the 3D molecular network of the gel. It is therefore expected that combining a pH-responsive gel with a fuel-driven reaction network in which the pH value can temporarily change is an applicable strategy for creating a non-equilibrium temporary gel material. According to this hypothesis, some temporary gels based on pH-responsive gelators have been reported. In 2019, D. J. Adams and coworkers presented a temporary supramolecular gel by applying an amino-containing gelator. [47] As shown in Figure 4a, the hydrochloride of the gelator was well-soluble in water. To initiate the gelation, uncase, and uncase added.  $NH_3$ yielded by their autocatalytic ureolysis rapidly enhanced the pH to 9.1–9.2, resulting in the deprotonation of the gelator. A semitransparent hydrogel can be obtained within 5 min. However, the increase in pH triggered the base-catalyzed saponification reaction of methyl formate, which was added together with the urease and urea. The formic acid generated by the saponification led to a slow decrease of pH to 6 or even 4. It will redissolve the gelator and destroy the hydrogel. The stiffness, viscosity, and lifetime can be enhanced by both increasing the concentration of urea and decreasing the amount of methyl formate. This work provided a simple example of pH-regulated temporal gel. Similarly, J. Li and coworkers reported a temporary supramolecular chiral G-quadruplex hydrogel realized by another pH-feedback reaction network. (Figure 4b) [48] Herein the pH was enhanced by directly adding KOH. It combined the guanosine and 5fluorobenzoxaborole, yielding a benzoxaborolate complex that can self-assemble into a helical G-quadruplex, ultimately leading to the formation of a highly transparent hydrogel. The recovery of pH in this work was achieved by the hydrolysis of 1,3-propanesultone. It decomposed the gelator and damaged the temporary hydrogel. In addition to the alkalis such as NH<sub>3</sub> and KOH, acid-induced temporal pH decrease has also been used to promote the formation of temporary gels. For example, A. Walther and coworkers applied citric acid as a chemical fuel to initiate the DSA of a pH-responsive dipeptide precursor. [24] (Figure 5a) The precursor immediately self-assembled into twisted nanofibrils and thereafter gelation occurred. The automatic pH recovery is caused by urase and urea premixed with the precursor. The rapid pH drop activated the urease that can catalyze the hydrolysis of urea into  $CO_2$  and  $NH_3$ , resulting in the disassembly of the nanofibrils and the collapse of the hydrogel. Furthermore, the acid-driven temporal deformation of hydrogel based on the same principle has also been reported recently. X. Wang et al. developed a bilayer hydrogel actuator consisting of a tertiary amine-containing, pH-responsive layer, and a urease-containing non-responsive layer. [49] (Figure 5b) Upon the addition of acidic urea solution, a significant bend can be observed due to the swelling of the pH-responsive layer. Meanwhile, urease in the other layer would catalyze the hydrolysis of the urea. The resulting  $NH_3$  led to the deswelling of the automatic relaxation of the actuator. It can be found that the key to constructing the above temporary gel material is to find a deactivator that can slowly and spontaneously self-decompose to neutralize the pH jump caused by the addition of alkali or acid. However, in some special cases, the pH can also be recovered by direct decomposition of the acidic/alkaline chemical fuel itself. For example, A. Quintard and coworkers presented a temporary gel that formed under the drive of CCl<sub>3</sub>COOH. [50] CCl<sub>3</sub>COOH protonated the precursor and led to its self-assembly and gelation. While the basic moieties in the reaction mixture, as a deactivator, catalyzed the decomposition of CCl<sub>3</sub>COOH into volatile chloroform and carbon dioxide. Unsurprisingly, the temporary gel gradually dissolved as the CCl<sub>3</sub>COOH was consumed.



Figure 5 (a) Temperal hydrogel driven by acid. Copyright (2015) John Wiley and Sons. (b) Acid-driven bilayer hydrogel actuator. Copyright (2022) American Chemical Society.

**3.1.3.** ATP-driven temporal gels. As a medium for energy exchange, ATP and its analogs widely exist in living organisms. Plenty of microscopic vital movements are directly driven by the energy provided by ATP or its analogs. In recent years, artificial ATP-driven dissipative molecular self-assemblies have been widely reported. [26, 51-55] The reaction network for such a kind of DSA has been successfully built. [26,53] However, temporary gel formation ("sol-gel-sol" cycle) driven by ATP or its analogs seems to be seldom reported. The possible reason is that the electrostatic attraction is a weak and non-oriented interaction which is detrimental to a long-range ordered aggregation or robust crosslinked structure. However, contrary to the temporary formation of the gel, the temporary "gel-sol-gel" conversion driven by ATP has emerged. As shown in Figure 6a, Q. Yan and coworkers reported a polymer gel that was prepared by mixing two linear polymers that contained  $\beta$ -cyclodextrin ( $\beta$ -CD) and adamantine (ADA) as side groups, respectively. [56] The host-guest interaction between the two side groups crosslinked the polymer chains to yield a highly transparent gel. However, ATP, which was the chemical fuel as well as a competitive guest, can displace the ADA group in the  $\beta$ -CD ring because it has a higher binding affinity with  $\beta$ -CD. (Association constant:  $K_{\beta-\Delta/AT\Pi}$  [?] 10<sup>6</sup> M<sup>-1</sup>,  $K_{\beta-\Delta/A\Delta A}$  [?] 10<sup>4</sup> M<sup>-1</sup>) The competition interrupted the crosslinked structure and led to the dissolution of the gel. Meanwhile, the potato apyrase preloaded in the hydrogel slowly hydrolyzed ATP to AMP. Since the  $K_{\beta} - \Delta/AM\Pi}$  ([?] 10<sup>2</sup>M<sup>-1</sup>) is much lower than  $K_{\beta} - \Delta/A\Delta A$ , the ADA reoccupied the β-CD ring causing the regeneration of the hydrogel. Furthermore, Q. Yan et. al also achieved ATP-driven temporary swelling of a microgel by slightly modifying the molecular design. As shown in Figure 6b, the β-CD-ADA supramolecular interaction was partially replaced by spiropyran-based linkers to avoid total dissolution of the hydrogel. The addition of ATP destroyed the  $\beta$ -CD-ADA interaction. The electrostatic repulsion between the ATP molecules enlarged the distance of the polymer chains and pull the spiropyran ring open. It can be found that the microgel significantly swelled and the color of the colloidal dispersion visibly changed. Finally, the ATP was totally hydrolyzed by the potato appase, leading to the recovery of the microgel.



**Figure 6** (a) Temperal gel-sol-gel cycle driven by ATP. (b) ATP-driven gel temperoal swelling. Copyright (2021) Chinese Chemical Society.

**3.1.4.H\_2O\_2-driven temporary gels.**  $H_2O_2$  is a highly active and strong oxidant. Redox-active species such as thiol and ferrocene can be rapidly oxidized by  $H_2O_2$  and then gradually reduced by some stronger reductants. Thus, it can create a reaction network that is able to drive dissipative molecular self-assembly or create temporary materials. For example, Z. Guan and coworkers presented a H<sub>2</sub>O<sub>2</sub>-driven temporary hydrogel formed by a thiol-containing precursor. [57] (Figure 7a) The  $H_2O_2$  oxidation resulted in a disulfidelinked dimmer (CSSC). It self-assembled into the fiber-like structure in aqueous solution, yielding a highly transparent hydrogel. A stronger reductant, dithiothreitol was used as the deactivator. It slowly decomposed the CSSC into CSH and destroyed the temporary hydrogel. Similarly, B. J. Ravoo and coworkers realized a  $H_2O_2$ -driven temporary gel-sol-gel process. [58] As shown in Figure 7b, the hydrogel was formed via the supramolecular crosslink between two grafted polyacrylic acids which are grafted with  $\beta$ -cyclodextrin ( $\beta$ -CD) and ferrocene (Fc), respectively. Upon the catalysis of horseradish peroxidase (HRP), H<sub>2</sub>O<sub>2</sub>destroyed the supramolecular interaction by oxidizing Fc into ferrocenium ion  $(Fc^+)$ , dissolving hydrogel quickly. D-glucose was chosen as a deactivator in this reaction network. It reduced  $Fc^+$  to Fc in the presence of GOx. The enzymatic reduction restored the supramolecular crosslink and rebuilt the hydrogel within a few hours. It can be found that the addition and consumption of  $H_2O_2$ , an active oxidant, creates a transient oxidizing environment that allows the redox-responsive precursor to temporally aggregate or crosslink to form material. Correspondingly, the reaction network driven by the reactant has also been successfully constructed. The reductant-driven temporal materials will be introduced in the following sections.



Figure 7 (a)  $H_2O_2$ -driven transient organogel. Copyright (2020) John Wiley and Sons. (b)  $H_2O_2$ -driven

transient gel-sol-gel process. Copyright (2021) John Wiley and Sons.

**3.1.5.** Other fuel-driven temporary gels. Besides the above typical reaction networks, there are some unusual strategies for constructing a fuel-driven temporary gel. In 2015, A. K. Das prepared a temporary hydrogel that could be used for human umbilical cords via a lipase-catalyzed reaction network. [59] As shown in Figure 8a, a peptide bolaamphiphile (HO-WYSuc-YW-OH) reacted with p-hydroxy benzylalcohol in the presence of lipase forming an activated diester building block (BHO-WYSuc-YW-OHB). It self-assembled to produce nanofibrillar thixotropic hydrogel. The subsequent hydrolysis of BHO-WYSuc-YW-OHB resulted in the dissipation of energy and collapse of the hydrogel. The author found that the hydrogel displayed a thixotropic behavior due to the dynamicity of hydrogen bonding interaction and other noncovalent interactions between the gelators. Hence, it was facially used as a supreme scaffold for human umbilical cord stem-cell proliferation. MTT, XTT, and DNA leaching experiments revealed that the hydrogel promoted the proliferation and survival of the stem cells. Later on, D. Das and coworkers demonstrated a simple fatty acid-based system that could temporarily gelate upon the addition of dimethylaminomethyl ferrocene (Fc-NMe<sub>2</sub>).As shown in Figure 8b, Fc-NMe<sub>2</sub> acted as a counteraction to access unique hexagonal compartments resulting in the formation of a self-supporting gel. [60] However, an oxidizing environment created by preadding  $Fe(ClO_4)_3$  contributed to the dissipation of energy by converting Fc-NMe<sub>2</sub> to its oxidation products and the gel autonomously undergoes a transition to a sol. Furthermore, the authors also found that the temporary hexagonal nanostructures were able to host hemin and temporarily tune its peroxidase-mimicking activity up to an order of magnitude. Temporary enzyme regulation through compartmentalization is a feature seen in extant biology, therefore, this work indicated that fuel-driven temporary materials have the potential in mimicking the special function in living bodies. In 2020, T. M. Hermans and coworkers reported a "gel-sol-gel" temporary cycle driven by a reaction network initiated with dithionite (DT), glucono- $\delta$ -lactone (GdL), and hexamethylenetetramine (HMTA). [61] As shown in Figure 8c, the aldehyde saccharide hydrogelator (SachCHO) was converted to a negative-charged  $\alpha$ -hydroxy sulfonate (SachSO<sub>3</sub><sup>-</sup>) by DT. Thus, SachCHO gels rapidly disassemble due to the electrostatic repulsion of SachSO<sub>3</sub><sup>-</sup> to give a clear solution. The gradual re-gelation was achieved by the formaldehyde produced in situ by the slow reaction between GdL and HMTA which were added together with DT. Hence, it is understandable that the authors can control the lifetime of the sol state by modulating the concentration of GdL. Similarly, the "gel-sol-gel" temporary process was also realized by a thiuram disulfides-driven reaction network. As reported by Y. J. Zheng and coworkers [62], the hydrogel was synthesized by crosslinking a 4-armed, star-like, branched PEG terminated with a thiol group. As shown in Figure 8d, the addition of thiuram disulfides (chemical fuel) can break the disulfide linkages via dynamic disulfide exchange. It will soften the hydrogel and finally lead to its dissolution. However, the thiuram terminal group was unstable. Its automatic hydrolysis-coupling reaction will restore the disulfide crosslinking and cause the regelation. Finally, the author gave an interesting example of this fuel-driven "gel-sol-gel" cycle. As shown in Figure 8d, they encrypted an invisible hydrophilic image of "nature" on a hydrophobic aluminum substrate, while an "SHTU" made from the hydrogel was put on the substrate. Upon the addition of chemical fuel, the SHTU gel self-turned into a sol state. The liquid would wet the hydrophilic area and the excessive aqueous solution was automatically removed due to the hydrophobic interaction. Thus, the left solution spontaneously reformed a stable gel showing "nature", the encrypted information, indicating that this cycle might have potential in anticounterfeiting applications.

#### **3.2.** Self-erased inks

Self-erased ink can be used for transmitting confidential messages, as the information written by such kind of ink can spontaneously disappear within a controllable period of time due to the consumption of chemical fuel. The key to developing self-erased ink is to find a material of which the color or fluorescent emission can change significantly as the reaction network proceeds. In 2017, J. Boekhoven and coworkers immobilized an aspartate-based precursor (Figure 9a) in a polyacrylamide polymer hydrogel to produce a transparent gel substrate. [31] High concentration of EDC, the chemical fuel, was applied as an ink to spread on the gel surface with a spray coater through a three-dimensional (3D) printed mask. The formation of insoluble anhydride made the exposed portion of the gel substrate turbid, yielding a clear trace. (Figure 9b) However, the anhydride was unstable and spontaneously hydrolyzed, resulting in the slow disappearance of the trace. The visibility of the traces decreased over time and was completely erased after roughly 10 h. (Figure 9b) Notably, the lifetimes of the visible traces could be tuned from roughly 200 to 500 min by changing the concentration of EDC, indicating that the availability of the presented information can be controlled. Similarly, S. J. George et al. presented a hydrogel of which color could be temporarily changed from red to purple by adding chemical fuel. [63] It made the writing more observable compared with the turbidity change. They designed a charge transfer (CT) system containing coronene salt (CS) and dodecyl methyl viologen (DMV). The CT interaction between CS and DMV produced a supramolecular amphiphile with red color. Once the concentration of the amphiphile reached 8 mM, it would undergo hydrogenation to yield red-colored CT gels. As shown in Figure 10a, sodium dithionite (SDT) was applied as chemical fuel to reduce the DMV to its cor-

Figure 8. (a) Temporal hydrogel that can be used for human umbilical cord stem-cell via a lipase-catalyzed reaction network

responding free radical, DMV<sup>+</sup>. It would destroy the CT complex and lead to the formation of aggregate consisting of DMV<sup>+</sup> itself, turning the color from red to purple. However, DMV<sup>+</sup> was unstable in the atmosphere and spontaneously oxidized by  $O_2$  under the catalysis of glucose oxidase (GOx), resulting in the recovery of the color. Thus, a temporary pattern can be obtained by "writing" or "drawing" with SDT on the red-colored CT gels. More importantly, the temporary pattern is well repeatable and its lifetime can be modulated by the concentration of SDT, GOx, or glucose. Similarly, A. Quintard and coworkers prepared a self-erased writing by using a trichloroacetic acid (TCA)-driven reaction network. [64] Upon the addition of TCA, the NH<sub>2</sub>-containing organogelators were immediately protonated, converting the green gel into a yellow sol. (Figure 10b) Meanwhile, the alkaline amine groups of organogelators can catalyze the decarboxylation of TCA, yielding volatile  $CO_2$  and  $CCl_3$ . The decrease of acidity induced the recovery of the green gel without any residual. Hence, temporary words or patterns can be repeatedly written on the surface of the green gel by the addition of TCA. Furthermore, except for writing on the gel surface, it was reported that the gel itself can be applied as self-erased ink as well. J. Jiang and L. Wang et al. presented a writable temporary gel, the precursor of the temporary gelator was a star-shaped molecule containing four carboxyl groups. [65] (Figure 11a) The addition of EDC crosslinked the precursor by catalyzing the condensation of the carboxyl groups. yielding a pulpous and plastic hydrogel. After a while, the anhydride bridges formed by the condensation of carboxyl groups slowly hydrolyzed, causing the collapse of the crosslinking network structure as well as the hydrogel. Due to its good plasticity, the hydrogel showed a good application in 3D printing. Materials in which fluorescence can be temporarily changed by the drive of chemical fuel are also potential self-erased inks. Therefore, the temporary fluorescent emission aggregate reported by D.-S. Guo and coworkers should also be noted. [66] The AIE gens shown in Figure 11b can generate significant fluorescent emission after co-assembly with DNA. However, the DNase I that existed in the solution led DNA to slowly decompose to oligonucleotides, bringing about the disappearance of the fluorescence. Although the author did not provide direct experimental evidence to illustrate its application in self-erased ink. It is still to be expected that this solution can be used in transferring confidential information.



Figure 9 (a) The reaction network of EDC-driven temporal pattern. (b) Photographs of EDC-driven temporal pattern over time. Copyright (2017) Springer Nature Limited.

Figure 10 (a) an SDT-driven transient pattern written on a hydrogel. Copyright (2020) American Chemical Society. (b) a

### 3.3. Temporary nanoreactors

The cell membrane system provides a specific local environment in living cells to protect some chemical reactions against external interference. The synthesis efficiency of the biomolecules was significantly improved. The well-organized and efficient biosynthesis resulted from the cell membrane system encourages chemists to develop synthetic nanomaterials that can provide a mesoscopic chamber with special polarity and stereo hindrance to change the yield and selectivity of the chemical reaction. In recent decades, a large number of such materials, called nanoreactors, were reported. [67-70] The yield and selectivity of many organic reactions in the nanoreactor were remarkably improved compared with the reaction in the homogeneous phase. In addition, nanoreactors were also used for controlling the growth of inorganic nanoparticles. The size of the nanoparticles synthesized in the nanoreactors was restricted because the amounts of the reactants encapsulated in each nanoreactor are limited. Therefore, it is an effective approach to obtaining nanoparticles with a uniform size. However, removing the nanoreactor after the completion of the synthesis remains a quite critical challenge. It greatly constraints the collection and purification of the product. Hence, it will be ideal to find a nanoreactor that can spontaneously disintegrate after the reaction completes. In 2016, L. J. Prins and coworkers attempted to fabricate a conceptual self-dissociable nanoreactor with the aid of fuel-driven DSA. They found a cationic surfactant,  $C_{16}TACN \cdot Zn^{2+}$ , can be micellized with the addition of ATP. [26] (Figure 12a) The micelles formed created a nonpolar microdomain that promoted the reaction between two hydrophobic reactants (C<sub>8</sub>-SH and NBD-Cl) in aqueous solution. Furthermore, the potato apyrase in the solution slowly decomposed ATP to AMP and phosphoric acid, resulting in the dissociation of the micellar nanoreactor. The lifetime of the nanoreactor can be well controlled by the amount of ATP added. The increase in the ATP concentration enhanced the yield of the reaction between C<sub>8</sub>-SH and NBD-Cl. The similar temporary nanoreactor can also be realized by the DSA of polymers. In 2021, A. Walther, J. Boekhoven et al. applied the EDC, as the chemical fuel, and poly(ethylene glycol) - b - poly(styrene-alt-maleic acid) (BCP1),as the precursor, to fabricate a polymeric temporary nanoreactor. [71] (Figure 12b) The reaction network was the same as their previous work. [34] As an example, a Diels-Alder reaction between two hydrophobic reactants successfully proceeded in this temporary nanoreactor. It was also found that the larger fuel concentrations resulted in higher reaction yields due to the longer sustained encapsulation of the nanoreactor. In the meantime, H. Zhao and coworkers presented another EDC-driven polymeric temporary nanoreactor. [72] The reactor was formed by the DSA of poly(ethylene glycol)-b-polyacrylate (PEG-PAE), which yielded by the EDC-catalyzed esterification of poly(ethylene glycol)-b-polyacrylic acid at pH 6.5. While the ester slowly hydrolyzed in such a weakly acidic environment resulting in the dissociation of the nanoreactor. The authors employed UV-induced anthracene dimerization as a model to study the nanoreactor. They not only found that the nanoreactor significantly increased both the yield and rate of the dimerization in aqueous solution but also provided evidence that the fuel-driven temporary nanoreactor could effectively prevent the product from being trapped, further enhance the inversion of the reactants and the utilization of the reactor.

#### 3.4. Temporary Self-healable materials

In the above discussion, it can be found that the concept of fuel-driven DSA or temporary material can be extended to improve the properties of existing functional materials. Another example is self-healing materials. The kinetic stability of intrinsic self-healing materials was usually unsatisfactory since the existence of dynamic cross-linking. It will lead to the undesired merging of intact materials. However, the dynamic bonds or non-covalent interactions between the polymer chains are essential for self-healing, making it difficult to develop a synthetic material that has excellent dynamic stability and self-healing ability simultaneously. In 2020, X. Wang and coworkers provided a strat egy to create kinetically stable hydrogels with self-healing ability enlightened by the concept of fuel-driven temporary material. [73] As shown in Figure 13a, the hydrogel was synthesized by crosslinking 4-armed histidine-modified polyethylene glycol with Co<sup>3+</sup>. A small amount of GOx was mixed during the preparation of hydrogel. It was found that the  $Co^{3+}$  cross-linked hydrogel has high kinetic stability without the undesired fusion due to the strong coordinate interaction. But it cannot spontaneously heal after cutting into two completely separated pieces. However, healing can be realized by bringing the damaged surfaces together with the addition of a mixture of ascorbic acid and glucose. The healing efficiency can reach 90% after 24 h. It is because that  $Co^{3+}$  was rapidly reduced to  $Co^{2+}$  by ascorbic acid, weakening the coordinate interaction and causing a local dissolution on the fracture surfaces. It will facilitate the recombination of the two separated pieces. More importantly, the dissolution was temporary since the production of  $H_2O_2$  by GOx-catalytic glucose oxidation. The regeneration of  $Co^{3+}$  would solidify the combination resulting in a high self-healing efficiency. This work exhibited that replacing permanent self-healing with fuel-driven temporary self-healing smartly avoided the aporia of maintaining kinetically

stability.







Figure 11 (a) an EDC-driven writable transient gel (b) Fuel-driven transient fluorescence emission of an AIEgen. Copyright (2017) Royal Society of Chemistry.

With this strategy, X. Wang and coworkers developed another two kinetically stable self-healing materials. In the same year, they reported a temporary self-healing hydrogel via the crosslinking of ketone-type acylhydrazone bonds. [74] (Figure 13b) Such bonds show a dynamic feature in an acidic environment but are kinetically locked under alkaline conditions. Thus, the temporary self-healing ability of the hydrogel was achieved by the urea/urease-containing reaction network which can result in a temporary pH increase. [24] Another example is an acylhydrazone-based hydrogel containing NaHCO<sub>3</sub>. [75] (Figure 13c) The alkalinity of NaHCO<sub>3</sub> made the hydrogel kinetically stable and inert, but incapable of spontaneous self-healing. However, applying a small amount of acidic buffer on the fracture surfaces created a temporary pH decrease, allowing the fast exchange of the acylhydrazone and the temporary self-healing of the severed hydrogel. Additionally, it is noteworthy that compared with the two examples above, this temporary self-healing hydrogel was achieved without using enzyme, consequently, the material has a better tolerance to various harsh treatment conditions including organic solvents, high ionic strength, drying, and extreme temperatures.



Figure 12 (a) ATP-driven transient nanoreactor. Copyright (2016) Nature publishing group. (b) EDCdriven transient polymeric nanoreactor. Copyright (2020) American Chemical Society.

#### 3.5. Temporary nanochannels

Besides the above examples, there are also some sorts of fuel-driven temporary materials with other attractive functions that are worth to be mentioned. Although they have not been

## Figure 13 (a) A H<sub>2</sub>O<sub>2</sub>-driven transient self-healable hydrogel. Copyright (2020) American Chemical Society. (b) A H<sup>+</sup>-dri

frequently reported, they should also be discussed owing to their probability to be further developed. Early in 2014, T. M. Fyles and co-workers applied the intermolecular thioester exchange reaction to fabricate a fueldriven temporary channel on a bilayer membrane. (Figure 14a) [74] The permeability of the membrane can temporarily enhance upon the addition of chemical fuel. S. J. George et al. demonstrated a solid fuel-driven temporary nanochannel by modifying the wall of the pores of mesoporous silica spheres with pH-responsive groups, such as carboxyl and amino groups. [75] With the aid of the typical OH<sup>-</sup>-ester reaction network (Table 1), the electric field in the 1D nanochannel temporary inversed from positive to negative. As a result, the alkaline chemical fuel would lead a positively charged guest molecule, crystal violet, to be temporarily locked in the 1D channel. Subsequently, with the consumption of the chemical fuel by esterase-catalyzed hydrolysis of ethyl acetate, it was found that the crystal violet was gradually released due to the recovery of the electric field in the 1D channel. (Figure 14b) Considering that temporary regulation of mass transport across the membrane is a vital feature of living organisms, the above works provided a good approach to developing biomimicking membrane materials.



Figure 14 (a) The reaction network of the temporal nanochannel on a bilayer membrane. Copyright (2014) Royal Society of Chemistry. (b) The temporal switch of the 1D channel on the silicon particle. Copyright (2019) Royal Society of Chemistry

#### 4. Conclusions and Perspectives

Since the first report in 2010, a number of artificial fuel-driven DSAs have been proposed, and various temporary, ordered molecular aggregates have been obtained. It greatly promoted the study of supramolecular chemistry from thermodynamic statistics to non-equilibrium states. Recently, the concept of fuel-driven DSA has been extended to create non-equilibrium temporary materials. Some materials, of which the solubility, color, fluorescence, self-healable abilities, adsorption capacity, etc. can be altered by the addition and spontaneous consumption of the chemical fuel, were successfully prepared. In this review, we firstly summarized the recently reported reaction networks which are possible to be used for realizing artificial dissipative self-assemblies and creating temporary materials in recent years, and then demonstrated the latest advances in fuel-driven temporary materials, including gels, nanoreactors, self-erased inks, temporary self-healable materials, etc. The mechanisms of their temporary behaviors and potential applications were carefully discussed. It can be found that compared with static materials under thermodynamic equilibrium, fuel-driven temporary materials provide more opportunities to create new functions and applications due to their controllable time-dependent variability.

However, as a new type of material, fuel-driven temporary materials are very far from well-developed. Firstly, the vast majority of present fuel-driven temporary materials are organic or polymeric materials. Their stiffness, robustness, and heat/cold resistance restrict their availability in some harsh conditions. However, the report on fuel-driven temporary inorganic materials, such as ceramics, alloys, or carbon materials, is still rare. Although the temporary formation or deformation of an inorganic bulky material remains a challenge, temporary alteration of the wettability of inorganic particles is not difficult to be achieved. It may offer great convenience for the flotation of inorganic nanoparticles. Secondly, the repeatability of the fuel-driven cycles remains to be enhanced. Most fuel-driven temporary materials were so far conducted under the experimental condition of batch-wise addition of fuel, which often results in poor recyclability due to the accumulation of the waste. Thus, it is expected to find more reaction networks in which the waste can automatically evaporate or precipitate. [25] Moreover, developing a special continuous reactor that can quantitively feed the chemical fuel and discharge the waste is another path to solving this problem. [78] Finally, the new functions and applications of fuel-driven temporal materials are still to be explored. The motivation for studying DSA is the curiosity to have an insight into molecular self-assembly in living bodies. The similitude in mechanism suggests that fuel-driven temporary materials are possible candidates for constructing bionic equipment. For example, a fuel-driven temporarily-deformed hydrogel is potentially used as a new type of artificial muscle in the manufacturing of soft robots since the contraction of the natural muscle is also driven by chemical fuel (ATP). Meanwhile, fuel-driven temporary gating of a 1D nanochannel is probably used in producing semipermeable membranes that can modulate the transmembrane mass transportation like cytomembrane. Besides, fuel-driven temporary hydrogels may also achieve other applications such as controlled drug delivery systems, temporary implantable cell scaffolds, and controllable adhesives. Since the continuous accumulation of successful examples, we do believe that the above applications will be realized in the near future with the smart molecular design of the precursor and the suitable selection of the reaction network. In the meantime, it can be expected that more fuel-driven temporary materials with other novel properties will be created to meet the increasing demands of daily life, medicine, or industry.

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