Out-of-equilibrium supramolecular self-assembling systems driven by chemical fuel

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INTRODUCTION

In biological systems, building blocks (such as peptides) self-assemble into large architectures to perform sophisticated functions so that these systems are able to be self-regulating, adaptive, and communicating.\(^1\)\(^1\) Inspired by nature, chemists have developed supramolecular assembling systems with great complexities and multiple functionalities by using those synthesized molecular building blocks via the supramolecular self-assembly strategy involving noncovalent interactions (hydrogen bonds, hydrophobic interactions, electrostatic interactions).\(^2\)\(^-\)\(^4\) The noncovalent interactions enable assembling structures and properties to be dynamic and controllable, which give rise to smart materials. Prominent examples of such materials include molecular machines,\(^5\)\(^-\)\(^8\) controllable, which give rise to smart materials. Prominent examples of such materials include molecular machines,\(^5\)\(^-\)\(^8\) controllable, which give rise to smart materials. 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at the local minimum energy landscape, but with different energy barriers.\textsuperscript{[30]} The energy barrier of metastable assembly is on the same order of magnitude as $k_B T$ (where $k_B$ is the Boltzmann constant, and $T$ is the temperature). In this situation, the assembling structures are metastable, and are converting to more stable states with time. In contrast, if the energy barrier is higher than $k_B T$, systems would not be able to escape from the local minimum, resulting in a longer lifetime than the experimental observation (kinetic trap). External stimuli are thus necessary to help the assembly systems escape from the trap. After understanding these processes, chemists can manually regulate building blocks between different states with the facilitation of external stimulus, and create stimuli-responsive materials with more controllable properties and functions.\textsuperscript{[31–33]} In this way, the microtubules’ function could be demonstrated is as follows: Tubulin-dimers are bound to GTP by forming active building blocks (tubulin-GTP), which is then self-assembled into microtubules. Along with this assembling process, GTP is hydrolyzed into guanosine diphosphate (GDP) and Pi, the resulting GDP-rich microtubules are unstable and spontaneously disassembled into tubulin-GDP. Following that, other GTPs within the system replace the GDP, forming active building blocks (tubulin-GTP) again. This whole process is repeated for another cycle. Therefore, the formation of microtubules is reversible upon the consumption of the GTPs. Owing to this dynamic dissipative nature, sophisticated
functions and adaptive behaviors could be achieved in living organisms. To develop advanced smart materials, for example, life-like materials, chemists have been keen on designing them based on the strategies close to those used in biological environments, that is, integrating building blocks within chemical reaction networks driven by energy consumption, and therefore, drive it away from the previous equilibrium state.\(^{39–40}\)

By following these strategies, the first synthetic out-of-equilibrium system driven by chemical fuel was introduced by van Esch and co-workers\(^{41}\) in 2010 (Figure 1C). In this work, a simple hydrogelator, dibenzoyl-(L)-cystine (DBC), was chosen as the building block. Above the \(\mathrm{pK}_a\) value, monomeric DBC existed in solution owing to the intermolecular repulsion between the carboxylate groups. Upon introducing methyl iodide (\(\text{MeI}\)) to the solutions (fuel input), the esterification of carboxylate groups occurred and the intermolecular repulsion was therefore eliminated, leading to the activation of the building blocks (in a form of DBC-\(\text{OMe}_2\)). These activated building blocks self-assembled into transient fibers and the formation of hydrogen gel was observed. The reverse process of this activated self-assembling is the hydrolysis of esters, which took place in an alkaline environment, resulting in a disassembling of the transient fibers. When all the fuel (\(\text{MeI}\)) was consumed, the fibers would deconstruct due to dissipation of the energy. Such systems could be redriven by further injection of the chemical fuel. Although the concentrations of ester were equal, difference between fiber formation was observed in the refueled process, which was attributed to the products (waste) of the reaction. In this case, the activation and self-assembly rate were usually higher than the deactivation rate, that is, fuel consumption rate must be higher than energy dissipation rate. Otherwise, self-assembly process could not be triggered.

Since the pioneered chemical-fuel-driven system was successfully developed, various fuel-driven systems with its fuel sources in forms of light,\(^{39}\) biomolecules,\(^{42–43}\) chemical reactants,\(^{44}\) and ultrasound\(^{45}\) have been developed in recent years. In this review, we have attempted to present the artificial out-of-equilibrium systems driven by chemical fuel, and to categorize the existing systems in terms of the class of the fuel including adenosine triphosphate (ATP),\(^{46}\) carbodi-imide reagents,\(^{47}\) acid/base,\(^{48}\) as well as redox signals.\(^{49}\)

**ATP**

ATP, a high-energy molecule, is the major energy source in biological systems.\(^{50}\) By consuming the energy of ATP, living systems keep at an out-of-equilibrium state, being adaptive to the environment. In living organisms, one of the most efficient strategies to use the energy stored in ATP is coupling ATP to chemical reaction network. Using strategies similar to this, ATP-triggered assembling systems have been developed. Among these strategies, two particular types are commonly used to develop ATP-triggered out-of-equilibrium supramolecular systems: i) ATP binds to the building blocks directly through either covalent or noncovalent interactions (Figure 2A); ii) either the phosphate groups or the energy is transferred from ATP to the building blocks during the ATP hydrolysis process (Figure 2B,C). Both strategies will activate the building blocks and therefore assemble to those architectures with desired functionalities. The difference between two strategies is the way of energy input and dissipation. For the former, “energy” is input by the interactions and is dissipated though the hydrolysis of ATP, both in building blocks and architectures. However, the hydrolysis of ATP supplies energy later and energy dissipation is achieved through other enzymatic reactions.

Following these strategies, a variety of out-of-equilibrium supramolecular assembly systems have been successfully developed in recent years.\(^{51–55}\) Prins and co-workers fabricated transient vesicular nanoreactors by coassembling ATP with the surfactant \(\text{C}_{16}\text{TACN-Zn}^{2+}\) (Figure 2D).\(^{56}\) In their work, ATP was reported to act as a template to stabilize the vesicle formed by \(\text{C}_{16}\text{TACN-Zn}^{2+}\) as well as the chemical fuel to drive the supramolecular assembly towards out-of-equilibrium. The transient vesicles formation process could be demonstrated as: upon co-injecting a mixture solution of ATP and potato apyrase, \(\text{C}_{16}\text{TACN-Zn}^{2+}\) instantly combined with ATP to form active building blocks and then assembled into vesicle with an approximate diameter of 70 nm. With the presence of the potato apyrase enzyme, ATP was gradually hydrolyzed to adenosine monophosphate (AMP) and \(\Pi\), resulting in the disassembly of the vesicles. Such process could be refueled by introduced ATP again. In this process, the kinetic of coassembly was fast than that of hydrolysis. If hydrolysis occurred at a higher rate relative to the coassembling, ATP would be directly hydrolyzed after the addition rather than activating the building blocks, and the transient assembly could consequently not be observed. The lifetime of the transient assembly could be controlled by the rate of ATP hydrolysis, that is, controlling the concentrations of the enzyme and ATP was essential. The out-of-equilibrium systems were suggested to have an interesting application, transient nanoreactors. The apolar environment created during the assembling could enrich the apolar reactant and thereby speed up the reaction. In addition, Prins’s group has extended their systems to regulate the chemical reactivity,\(^{57}\) transient fluorescence signaling,\(^{58–59}\) as well as cooperative catalysts.\(^{60}\)

By using similar coassembly approach, George and co-workers have successfully developed a serious of transient helical conformational switch supramolecular polymers driven by chemical fuel (Figure 2E).\(^{61}\) The pioneered example was based on naphthalenediimide dipicolylethyleneamine (NDPA) molecules. Their previous work has demonstrated that the NDPA molecules formed supramolecular P-helices polymers with the presence of ATP whereas M-helices were formed when coassembling with adenosine diphosphate (ADP) or AMP.\(^{62}\) Therefore, the helical conformational switch of polymers could be controlled by an external addition of ATP or ADP. Based on that, fuel-driven transient helicity supramolecular polymers were constructed by introducing hexokinase (HK) and its corresponding substrate glucose (\(\text{G}\)), to drive the system away from a previous equilibrium state.\(^{63}\) Upon the addition of ATP, the chemical fuel, activated building blocks were formed by coassembling between the ATP and the NDPA molecules, and then self-assembled to P-helices supramolecular polymers (P-NDPA-ATP). ATP gradually hydrolyzed to ADP with time in the presence of HK, resulting in the \(\text{P} \rightarrow \text{M}\) stereomutation. Thus, fuel-driven transient helical supramolecular polymers were successfully developed and such system could be refueled by ATP. Furthermore, more complex out-of-equilibrium
Figure 2 (A–C) Schematic representations for three types of ATP-driven out-of-equilibrium supramolecular systems: (A) Building blocks were activated by the ATP coassembly and then assembled into larger structures, which would disassemble with the decreasing concentration of ATP. The ATP hydrolysis process occurred for free ATP, activated building blocks, and even the coassembled structures. (B) Phosphate activated building blocks. Phosphate group transferred from ATP to building blocks under enzyme catalysis, resulting in the change of building blocks’ charge balance and following by assembly. The assembly structures will degrade with time owing to the enzyme catalytic deactivation (dephosphorylation) process. (C) Building blocks activated by the energy of ATP. The deactivation process was triggered by another type of enzyme and such process only took place at high-energy assembled structures. (D) ATP-regulated self-assembly of vesicular nanoreactors. Reproduced with permission.[56] Copyright 2016, Springer Nature. (E) A schematic representation of fuel-driven transient conformational switch supramolecular polymers. Reproduced with permission.[61] Copyright 2017, Wiley-VCH

A system could be constructed by introducing two types of the enzymes simultaneously. In this system, the reversible conversion process between ATP and ADP occurred simultaneously after the addition of chemical fuel phosphocreatine (PCr). The concentration of ATP increased on account of the catalyzed reaction rate of CPK being higher than that of HK, that is, \( \nu_{\text{ATP generation}} > \nu_{\text{ATP hydrolysis}} \), enabling \( M \to P \) stereomutation; while the concentration of ATP decreased with time due to the entire consumption of the chemical fuel, leading to \( P \to M \) stereomutation.

The other strategy to construct out-of-equilibrium systems was by transferring phosphate groups to activate building blocks. One prominent example was reported by Hermans and co-workers (Figure 3A).[64] The building block in their work was based on a derivative of 3,4,9,10-perylene diimide (PDI) conjugated with a peptide sequence (LRRASL), which can be phosphorylated in the presence of enzyme protein kinase A (PKA) and also dephosphorylated by another enzyme phosphatase (\( \lambda \text{PP} \)). Precursors were self-assembled into P-helical fibers in aqueous solutions due to the \( \pi-\pi \) stacking and the hydrophobic effect. Two phosphate groups were introduced into the peptides during the phosphorylation process, resulting in a change of molecules’ charge and \( P \to M \) stereomutation. Whereas, the dephosphorylation process removed the phosphate groups from peptides, leading to \( M \to P \) stereomutation. Thus, transient M-helical...
supramolecular polymers could be realized and their lifetime was controlled by the kinetics of phosphorylation and dephosphorylation process. Moreover, a membrane device was designed to keep a continuing influx of ATP and to remove the waste that would stop the reaction cycle by competitively combining to the enzyme, enabling the system to maintain at the out-of-equilibrium steady state.

Other than activating precursors by transferring phosphate groups, out-of-equilibrium system that was fueled by the energy generated by ATP hydrolysis was also developed by Walther’s group (Figure 3B).[65] The system involved a transient DNA polymerization, which was driven by ATP via a chemical reaction network consisting of DNA catalytic enzymes, T4 DNA ligase and BamHI. The building blocks were DySS DNA with self-complementary ends. With the absence of T4 DNA ligase, DySS DNA stays in monomeric states in solution instead of polymer owing to its self-complementary ends being too short to stably connect the DNA monomers together. In the presence of T4 DNA ligase, enzyme-catalyzed polymerization occurred on account of the phosphodiester bond formation upon the consumption of ATP; subsequently, BamHI catalytic cleavage happened at the ligation site, leading to a depolymerization. Therefore, by injecting ATP to the mixture solution of DNA monomers and two enzymes, both the enzyme-catalyzed ligation and cleavage occurred simultaneously, resulting in the formation of dynamic covalent bonds and also the transient polymers. The formation of DNA polymers was governed by the kinetics of enzyme-catalyzed reactions and their lifetime could be manipulated by the concentrations of ATP as well as enzymes. Unlike other ATP-fueled systems, this type of system was fueled by the energy originated from hydrolyzing ATP. The waste had little effect on the reaction cycle, enabling a good reactivation. Moreover, the intermolecular
CARBODIIMIDE REAGENTS

Carbodiimides have been widely used as the dehydrating agent in chemical reactions, converting dicarboxylates into anhydrides, which are unstable in water and easily hydrolyzed back to their dicarboxylate states. Therefore, a type of transient dynamic covalent interactions could be achieved upon adding carbodiimides to aqueous solutions of dicarboxylates. In other words, carbodiimide reagents serve as the chemical fuel to activate dicarboxylate groups (precursors). The activation is driven by the high reactivity of the fuel in the presence of the specific building block (dicarboxylate groups) (Figure 4A), and the assembly is caused by the conversion of a charged to an uncharged building block. Moreover, transient covalent bond could associate two components together, providing a new approach to extend the diversity of artificial out-of-equilibrium systems.

The first example for these out-of-equilibrium systems was reported by Boekhoven and co-workers in July 2017 (Figure 4B). These supramolecular materials with tunable lifetime were comprised by the coupling of fluorenyl-methyloxycarbonyl (Fmoc)-protected amino acid and tripeptides in chemical reaction networks driven by carbodiimide reagents. For example, precursors, Fmoc-protected aspartic acid (Fmoc-D) could not be assembled into larger structures owing to the intermolecular repulsion generated by the negatively charged carboxyl groups (COO⁻). Therefore, Fmoc-D stayed in monomeric state in aqueous solution and a transparent solution initially turned turbid due to the light scattering effect of these large spherulites and was then reverted to a clear solution with a full consumption of fuel. Based on these results, self-erasing materials could therefore be developed by immobilizing the precursors in a polycrylamide polymer hydrogel. Temporal messages can be written with a spray coater through a mask using fuel as ink. In addition, different assembly behaviors were observed by changing the molecular structures of precursors. Fmoc-protected glutamic acid (Fmoc-E) could assemble into colloids while Fmoc-protected tripeptides formed fibers first and then assembly into hydrogels. Most importantly, a feed-back regulation, a significant feature of these systems, was highlighted, that is, the formation of colloids shielded anhydride from water, showing a negative effect on the hydrolysis reaction. This mechanism inhibited from reaching the nonequilibrium state; the activated building blocks were assembled, but no assembly of nonactivated precursors was achieved.

Another out-of-equilibrium system fueled by carbodiimides (EDC) was reported by Hartley’s group in August, 2017 (Figure 4C). According to their work, oligo(ethylene glycol) diacids (precursors) were introduced into the chemical reaction networks to develop the EDC fueled supramolecular system, synthesizing transient hosts and crown ethers. In addition, the negative templation effect of cations on intramolecular anhydride formation was discussed. They proposed that the precursor coupling of carbodiimides driving chemical reaction networks is a new strategy to developed out-of-equilibrium systems involving dynamic and transient covalent bonding. Based on this approach, more transient covalently bonded compounds such as macrocycles were synthesized by Hartley and co-workers. This approach was also applied to the design of polymeric materials, developing transiently covalent-crosslinked and higher storage moduli supramolecular gels.

Another transiently covalent crosslinked gel was reported by Wang and co-workers (Figure 4D). The precursor (MCTPE 1) was a derivative of tetraphenylethylene modified with four m-benzenedicarboxylic acids, which could then form carboxylic anhydrides in the presence of EDC. Upon adding EDC to the precursor solution, hydrogel could be formed at a low concentration (0.45 wt%) due to the formation of intermolecular covalent bond. The hydrogel slowly reverted to aqueous precursors when the hydrolysis of anhydride occurred. For this to happen, the kinetic of deactivation process (hydrolysis) was needed to be slower than activation process (anhydride formation). Consequently, a type of writable and self-erasing material can be successfully achieved by injecting a MCTPE 1 aqueous solution into the EDC aqueous solution.

EDC fueled chemical reactions are able to associate two kinds of components together. Taking advantage of this feature, Das and co-workers designed a chemically fueled dissipative self-assembly system that mimicked a nature out-of-equilibrium system (the microtubule filament formation), using histidine derivates (C18-H) and 4-nitrophenol (NP) as the precursors (Figure 4E). Introducing EDC to a mixture solution of C18-H and NP, the esterification was triggered, resulting in the formation of C18-F-NP. The coassembly of C18-H and C18-F-NP was then taken place and a hydrogel was therefore obtained. However, the histidine that was not esterified in its assembly state has a cooperative catalytic effect on breaking the ester bonds, accelerating the disassembly process. Consequently, the hydrogel formed was transient.
and eventually reverted back to a solution containing C_{18}F-NP precursors over time. In summary, such system exhibited similar behaviors to those in organisms, where the fuel-driven transient assembly facilitated the disassembly process and the degradation of fuel. This work has provided a good example for how to design life-like out-of-equilibrium system in a fine way.

Another example for such reciprocal coupling chemically fueled assembly system using peptide as the building block has also been developed by Boekhoven and co-workers recently (Figure 5A). In this system, the property that assembly structure accelerated deactivation and activation was demonstrated by comparing the influence of assembly of Fmoc-AVD and Ac-FAVD. The first one could be assembly to fibers after activation whereas the latter one did not, and the first one resulted in a faster degradation of fuel and anhydride, which affected the rate of activation and deactivation, respectively. Moreover, the mechanisms of accelerated activation and deactivation were investigated. In the activation process, the activated building blocks assembled into fibers, creating a more hydrophobic microenvironment, also resulting in the change of activation pathway from step-wise to faster concerted proton transfer. The acceleration of deactivation may be attributed to the β-sheet hydrogen-bonding interactions.
Additionally, the catalytic efficiency can be tuned through controlling the assembly state ($\beta$-sheet) by molecular design of the peptide sequence.

Peptide sequence has positive effect on assembly process whereas the dicarboxylate groups prevent its assembly. Therefore, the assembly behavior can be regulated by controlling the ratio of peptide sequence and dicarboxylate groups. For example, introducing the chemical fuel, carbodiimide reagents could convert dicarboxylate groups into anhydride, leading to the decreased negative effect of the dicarboxylates and resulting in the assembly of peptide. Designing different peptide sequence to regulate attractive interactions was another approach to control molecular assembly behaviors. Such design rules that can toggle assembly behaviors between no assembly, out-of-equilibrium self-assembly, thermal equilibrium assembly have been reported by Boekhoven’s group recently (Figure 5B).[76] Additionally, by changing the peptide sequence to alkyl chain, a dissipative assembly with a self-inhibition feedback mechanism was developed and used as hydrogel in drug delivery.[77]

Taking the advantage of structure-independent, various EDC fueled out-of-equilibrium systems have been developed.[77–80] These examples have provided an inspiring starting point to design advanced materials with self-regulation properties. Among them, feedback regulation[78] and even reciprocal coupling mechanisms[75] were designed. Such mechanisms may be exploited to create life-like materials.

ACID/BASE

One of the approaches to control molecular assembly behaviors is regulating their charge, which generates electrostatic attraction or repulsion to affect assembly. Such regulation can be achieved upon introducing the Ox/Red reactants,[81] acid/base,[82] and other reagents.[83] Among them, the acid/base reactants have been widely used to modulate molecular behaviors through pH-responsive groups.[11] To date, various pH-responsive materials including hydrogel,[84] nanoparticles,[85] as well as light-emitting materials[86–87] have been constructed. More recently, Walther and co-workers reported a concept to program the time domain of self-assemblies and successfully drove pH-responsive out-of-equilibrium materials out-of-equilibrium.[52]

As proof-of-concept, they developed a pH out-of-equilibrium system by introducing rapid promoters (acid/base) that were able to activate building blocks ($v_1$) and dormant deactivators (DDs) simultaneously (Figure 6A).[88] The dormant deactivators would delay and converted to deactivators with time ($v_*$), resulting in the deactivation of the building blocks ($v_2$) and disassembly of the system. Unlike other out-of-equilibrium systems in which the system’s kinetic was mainly controlled by the activation rate ($v_1$) and deactivation rate ($v_2$), its kinetic controlled rate was $v_*$ and the corresponding kinetic boundary condition was $v_1 \gg v_*$. Therefore, the lifetime of the transient nonequilibrium state could be regulated from minutes to days by controlling the delay process of dormant deactivators. Moreover, the environment was gradually changed (pH value increased or decreased) with the generation of deactivators, which further influenced the delay process, leading to a positive or negative feedback mechanism.

Following this concept, Walther’s group was the first to develop the program transient alkaline states by combining an alkaline activator with three types of esters, acid δ-lactone (δ-GL), methyl formate (MF), and ε-caprolactone (ε-CL) as dormant deactivators (Figure 6B).[88] Upon injecting base into the solution, the esters gradually hydrolyzed and furnished the acid, resulting in a decrease of pH. The lifetime of transient pH could be programmed by controlling the concentration and structure of the DD. Lowering DD’s concentration at a constant promoter strength or using it with slower hydrolysis kinetics resulted in a longer lifetime. The lifetime...
FIGURE 6 (A) A schematic illustration of nonequilibrium self-assembly. A transient pH profile was achieved by simultaneously introducing both promoters and dormant deactivators (DDs). Notably, the kinetic boundary conditions were $v_1 \gg v^*$.

(B) Building blocks self-assembled under dissipative acid or basic conditions. Addition of promoters resulted in larger assembly structures, which degraded in the presence of deactivators. Schematic representations of temporally programmable nanoreactors (C) and fluidic system (D). Reproduced with permission. Copyright 2018, American Chemical Society. Reproduced with permission. Copyright 2020, Wiley-VCH. (E) Transient crystallization of a cucurbit[8]uril-based supramolecular self-assembling system driven by TCA. Such revisable changes can be performed for 18 cycles. Reproduced with permission. Copyright 2019, Wiley-VCH.

could therefore be regulated from minutes ($\delta$-GL), hours (b-BL), to days ($\varepsilon$-CL). Moreover, the ester hydrolysis process was able to be catalyzed by acid or base, that is, the transient pH resulting from ester hydrolysis process would affect its hydrolysis process, showing a feedback mechanism. After getting a fairly deep understanding about this hydrolysis process, they then applied it to block copolymers, nanoparticles, and peptides, driving the pH-switchable self-assembly materials out-of-equilibrium.

Additionally, Walther and co-workers programed the transient pH state in acid regime, which was achieved following a similar strategy of combining acid promoter with the dormant deactivator urea (Figure 6B). In the presence of urease, urea was gradually hydrolyzed and liberated an active deactivator, $\text{NH}_3$, resulting in an increase of pH. This rate of hydrolysis process was dependent on the urease activity, which performed a bell-shaped pH-dependent curve, that is, low activity at high and low pH values ($\text{pH} < 3.5$ or $\text{pH} > 9$) whereas high at $\text{pH} = 3.5–9$ and most active at $\text{pH} = 7$. Therefore, hydrolysis process influenced the enzyme activity in a way that it further accelerated itself, showing self-regulation and feedback mechanisms. Eventually, time-programmed hydrogels that can be used as drug delivery device were developed by coupling this transient system to dipeptides.

It is worth highlighting that the assembly of building blocks in transient acid/alkaline systems was self-assembly...
under dissipative conditions instead of dissipative self-assembly, because the chemical fuel-to-waste conversion was not involving any building blocks. In other words, the dissipative conditions drove stimuli-responsive systems out-of-equilibrium. Moreover, such conditions were influenced by the activator and deactivator instead of the building blocks, enabling generically and widely usages in a range of applications.

van Hest and co-workers developed a time-programmed nanoreactor by functioning pH-sensitive polymersomes loaded with two type of enzymes, horseradish peroxidase (catalyzed substrates reaction) and urease under transient acid conditions (Figure 6C). Dispersing the nanoreactor to an alkaline solution, the polymers deprotonated and shrunk, leading to the impermeability of the nanoreactor. Thus, such reactor exhibited “OFF” state because substrates could not pass the polymer membranes and enzyme-catalytic reaction was inactive. Introducing the acid resulted in an increased permeability, therefore, the substrates were able to pass the membranes and the nanoreactors turned to “ON” state. Adding the chemical fuel (HCl and urea) to an alkaline solution led to the creation of a transient acid environment. This dissipative condition caused the reactivity of nanoreactor to turn to “ON” state at first and then gradually to return to “OFF” state with time. Such change was reversible and could be refueled by the continuous addition of the chemical fuel. Moreover, the lifetime of the reactivity could be regulated by controlling the concentrations of urea.

Additionally, a non-Newtonian polymeric fluid system with a switchable nonlinear rheological property was designed by Yang and co-workers based on the urea/urease reaction (Figure 6D). This system was grounded on the polyelectrolytes consisting of N,N-dimethylacrylamide (DMA), N,N-dimethylaminoethyl methacrylate (DMAEMA), nacycloxsuccinimide (ASM), and octadecyl bromide (C18Br), followed by immobilization of urease. The polymers were pH-sensitive and exhibited a shear thinning when pH was equal or greater than 7.5, otherwise exhibited a shear thickening at lower pH. Introducing the chemical fuel into the initial polymer solution showed a shear thinning property at high pH (9.0), pH then decreased fast and subsequently the polymers exhibited a shear-gel behavior. The dormant deactivator, urea, was gradually hydrolyzed by urease with time, leading to the decrease of pH. In this situation, gel slowly reverted to sol with the switch of shaking character. This study has provided a good example of how to use chemical-fueled reaction to design smart fluid system.

Besides the chemical reaction process, base-promoted decarboxylation organic acids have provided another approach to construct acid–base fueled out-of-equilibrium systems. Kim and co-workers developed a transient crystallization of a cucurbit[8]uril-based host–guest system using trichloroacetic acid as the chemical fuel (Figure 6E). The building block was formed by the complexation of L-tryptophan methyl ester (TrpE) and CB[8], which was highly water soluble without the presence of trichloroacetic acid (TCA). The addition of trichloroacetic acid resulted in an extensive hydrogen-bonding network between complexes, facilitating the formation of TrpE@CB[8] crystals. Therefore, the transparent solution turned turbid. The crystals were transient because trichloroacetic acid underwent thermal decarboxylation with time. When acid was used up, the hydrogen bonding interactions between the complexes were eliminated, leading to the degradation of the crystals. The turbid solution subsequently reverted back to transparency. In this work, it is worth highlighting that the waste, generated from the decarboxylation of the trichloroacetic acid, could be easily removable. Therefore, the accumulation and poisoning due to a large amount of waste could be prevented and such system was able to perform for 18 cycles.

OTHER CHEMICAL SIGNALS

Besides the chemical fuel discussed, other types of fuel such as redox reactants and even chemical oscillators have also been used to fabricate out-of-equilibrium systems. Recently, Hermans and co-workers have developed a transient dis-assembly of a hydrogelator (i.e., gel–sol–gel) by coupling an oxidizing reagent, dithionite (DT), and the catalytic-conversion fuel (formaldehyde) to building blocks (aldehyde saccharide hydrogelator (SachCHO)) (Figure 7A). SachCHO was self-assembled forming hydrogel in water and the addition of DT resulted in the oxidation of SachCHO turning into α-hydroxy sulfate (SachSO3−), thereby generating intermolecular electrostatic repulsion. As a result, the disassembly process was triggered and gave a clear solution. Simultaneously, the other fuel (formaldehyde) was generated by the catalytic conversion of the prefuel (hexamethylenetetramine) leading to the reduction of SachSO3−. When DT was fully consumed, SachCHO was accumulated and hydrogel was then reformed. Hence, the transient transition of gel–sol–gel was accomplished by introducing a combination of chemical fuel (DT, GdL, and HMTA) simultaneously and the lifetime of the disassembly could be regulated by controlling the rates of catalytic fuel production. Moreover, they also developed a simple device to remove the waste, which was accumulated after each cycle and resulted in poisoning of the system. Taking this advantage, this system was able to be refueled for 13 cycles with minimal kinetics changes during the process.

By coupling redox-responsive charge-transfer complexes to chemical reaction network driven by sodium dithionite (SDT) and glucose, a transient supramolecular gel with chemochromism properties was developed by George and co-workers (Figure 7B). The building blocks consisted of a donor, coronene salt (CS), and an amphiphile acceptor, dodecyl methyl viologen (DMV), CS and DMV self-assembled to cylindrical micellar with a high aqueous association constant resulted in red color hydrogel. By introducing the strong reducing agent, SDT, DMV was reduced to the radical cation (MV+), which was accumulated once formed. As a consequence, the CT complexes was disassembled and a solution with typical color of the MV+ was observed. The solution was transient and converted back to gel due to the oxidation induced by hydrogen peroxide, which was originated from a controllable enzymatic reaction, catalytic glucose oxidation using glucose oxidase (GOX). On the basis of this process, a self-erasing hydrogel with multiple rewrite times was obtained.

Out-of-equilibrium system can also be generated by coupling building blocks with chemical oscillators in
FIGURE 7  (A) A schematic representation for the transient disassembly of hydrogel driven by a redox reagent. Reproduced with permission.[100] Copyright 2020, American Chemical Society. (B) The scheme of the SDT-fueled reaction cycle for transient disassembly of CS and DMV followed by formation of CT complexes in the presence of oxidant, resulting in regelation. Reproduced with permission.[101] Copyright 2019, American Chemical Society. (C) A schematic illustration of a dissipative supra-amphiphile system based on IO₃⁻–NH₃OH⁺–OH⁻ chemical oscillators. Reproduced with permission.[102] Copyright 2016, Royal Society of Chemistry. (D) A graphic illustration of dissipative aggregation-induced emission system realized by a TPE-based fluorescent molecule coupled with a chemical oscillator. Reproduced with permission.[103] Copyright 2020, Royal Society of Chemistry. (E) A schematic representation of the transient assembly cycle of color-tunable fluorescence system. Time-dependent multicolor luminescence could be achieved by treating with γ-CDs. Based on dynamic properties of the system, a self-erasing material was developed. Reproduced with permission.[98] Copyright 2020, Springer Nature

which the reactant concentrations changed periodically. For example, Zhang and co-workers fabricated a dissipative supra-amphiphile system by using PEG double-hydrophilic copolymers as building blocks and coupled them with the IO₃⁻–NH₃OH⁺–OH⁻ chemical oscillators (Figure 7C).[102] The PEG copolymers were dispersed in discrete states in aqueous solution but self-assembled to spherical nanoparticles after coordination with iodine produced by the chemical oscillators in a periodic fashion. The noncovalent coordination between iodine and PEG was reversible and dependent on the concentration of iodine. Therefore, decreasing the concentration of iodine resulted in a disassembly of iodine and copolymers and subsequently a redispersion of the polymer. In addition, the waste was able to be remove by a continuous stirred tank reactor (CSTR) so that the oscillation could perform more than four times.

Recently, Tang and co-workers have reported a pH oscillating dissipative self-assembled system by coupling a typical
aggregation induce emission (AIE) fluorophore, tetrakis(4-
aminophenyl)ethylene (TPE-4N), with a pH oscillator (Fig-
ure 7D). TPE-4N was used as the pH-responsive units owing to its pH-dependent solubility and AIE properties. Under acidic condition, the amino moiety was protonated and the solubility of molecules was increased, leading to a great dispersion with weak fluorescence of TPE-4N in solution. Consequently, the quaternary supramolecular complexes were disassembled into the monomeric state under dilute aqueous conditions with a blue fluorescence while self-assembled to vesicles, which exhibited green-yellow fluorescence in concentrated solution owing to the assembly of the pyrene units. Addition of γ-CD resulted in the formation of 2:2 supramolecular complexes, enabling further red-shift of the fluorescence and therefore a yellow luminescence was observed. Therefore, the tunable fluorescence emission ranged from blue to yellow, including a pure white-light emission, which could be regulated by controlled the γ-CD concentrations. Considering the highly γ-CD-dependent fluorescence properties, we introduced α-
amylase, which can hydrolyze γ-CD under mild conditions to develop out-of-equilibrium system and to make the flu-
orescence programmable. Upon the addition of the γ-CD, molecule was assembled and the host–guest complexes were formed, leading to a yellow fluorescence. Overtime, a gradual decrease in the γ-CD concentration occurred through the enzymatic hydrolysis reaction. Consequently, the quater-
nary supramolecular complexes were disassembled into the monomers, and reverted the fluorescence from yellow to blue. Moreover, the lifetime of the supramolecular complexes can be controlled by the concentration of γ-CD, for instance, 5 eq γ-CD resulted in a relatively shorter lifetime (1.5 h) while a longer lifetime was observed at γ-CD = 50 eq. On the basis of this assembly encoded emission system, a self-erasing mate-
rail that could be rewritten over four times was achieved by transferring the system from a solution to a hydrogel.

CONCLUSION AND OUTLOOK

In summary, we have presented some representative exam-
pl es of artificial out-of-equilibrium systems and categorized them with regards to the chemical fuel type. The involv-
ing self-assembling systems have been summarized as fol-
lo ws: ATP-triggered transient systems driven by coassembly, phosphorylation, as well as energy transferring. In particu-
lar, systems fueled by energy transferring have the advantage of integrating energetic events within structural transitions, which was similar to the dissipative process in living-systems. Another type of chemical fuel, carbodiimide reagents, pro-
vided a new approach by combining two types of building blocks through dynamic covalent bonding to generate a new form of activated building blocks and to further diversify the out-of-equilibrium systems. Three features should be high-
lit ed here: (1) The fuel used is commercially available. (2) A common and easy to prepare functional group, carboxyl, is involved. (3) Activation process is structure-independent and therefore different types of building blocks could be com-
bined together. In addition, integrating pH-responsive build-
ing blocks within a dissipative pH environment is also proven to be an efficient strategy to develop out-of-equilibrium sys-
tems. The dissipative environment is created by combining a fast activator with the dormant deactivator, but does not involve building blocks. Therefore, the systematic nonequ-
ilibrium pH is decoupled from the building block structures, enabling the general applicability to other self-assembling systems. Moreover, out-of-equilibrium systems could also be achieved by using metastable organic acids as the chemical fuel, taking the advantage of removing waste in an easy manner. Among these out-of-equilibrium systems, chemical oscil-
lation, a specific system, should be noticed for periodic fluc-
tuation of its reactant concentrations and its ability of per-
foming multiple cycles once triggered. Such artificial sys-
tem offers inspiring insights for how oscillators with similar functions in living organism could be developed.

For these transient assembly systems, their lifetime is determined by the different kinetics of the activation and deactivation processes. These processes can be controlled by regulating the amount of fuel initially added, the precursor concentration, pH, and temperature, which enables the life-
time to be programmed from minutes to days. For exam-
ple, by varying the fuel (ATP) concentration, the lifetime of transient DNA polymer systems can be regulated from hours to days. Such long-lifetime (days) assemblies can be observed in those systems with a slow deactivation, such as the decarboxylation of TCA, and the hydrolysis of a phospho-
diester linkage. In contrast, the systems having a fast deact-
viation process, such as some EDC-fuel assemblies, chemical oscillations, usually exhibit short lifetime (minutes). More-
over, the lifetime can also be influenced by the assembly morphology. Among the EDC-fuel transient systems, those whose active building blocks assembly to micrometer-sized droplet exhibited a longer lifetime, comparing to that of those without assembly, owing to the negative effect of the deact-
ivation process. Notwithstanding, many out-of-equilibrium systems have been fabricated in recent years, developing life-like systems remains challenging. A concerning challenge is to use such system for performing functions or even work. That is, building blocks harvest energy from either the chemical fuel or the chemical reaction networks, and then assemble into larger, more ordered structures, generating power to perform functions like the living examples, actin network, which gener-
ates force in muscles through out-of-equilibrium assembly. Another challenge is to remove the accumulative waste, which resulted in poisoning of the system so that the reaction cycle can be performed in multiple cycles. Up to now, several systems have been explored, including the one using external devices and the one in which the accumulated waste was gas (escaped from the system once generated), while the ideal
situation, converting the waste to fuel or others desirable products, is still difficult to achieve. Additionally, how to cooperatively program systems by using multiple fuels is also a challenge.

To solve these challenges as well as to extend the library of the out-of-equilibrium systems, developing new type of chemical fuel is necessary. For example, Lee and co-workers developed a transient substrate-driven nanoreactors, which is fueled by chemicals.[104] Idle was selected because it reverted developed a transient substrate-driven nanoreactors, which is chemical fuel is necessary. For example, Lee and co-workers also a challenge.

Out-of-equilibrium systems take advantages of temporal programming and self-regulating behaviors that would be difficult to obtain in thermodynamic equilibrium systems. Integrating synthetic building blocks within chemical reaction networks has been proven to be an efficient strategy to fabricate out-of-equilibrium systems owing to the dissipative environment that was generated by photochromic process.[135] Moreover, spiropyran, a type of photochromic molecules, is also a potential future fuel candidate to fabricate out-of-equilibrium systems owing to the dissipative environment that was generated by photochromic process.[135]

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Conflict of interests

The authors declare no conflict of interest.

Data availability statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Ethics statement

This review does not involve any human investigation and animal experiment.

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