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Electrically Fueled Active Supramolecular Materials

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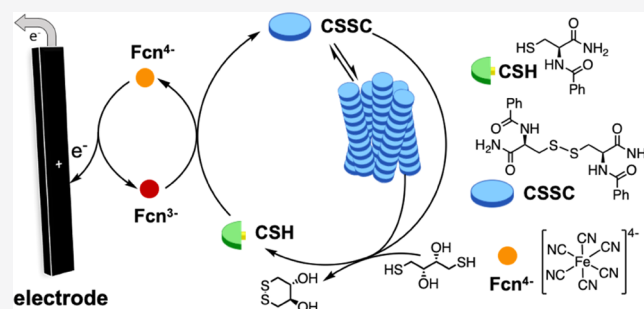
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ABSTRACT: Fuel-driven dissipative self-assemblies play essential roles in living systems, contributing both to their complex, dynamic structures and emergent functions. Several dissipative supramolecular materials have been created using chemicals or light as fuel. However, electrical energy, one of the most common energy sources, has remained unexplored for such purposes. Here, we demonstrate a new platform for creating active supramolecular materials using electrically fueled dissipative self-assembly. Through an electrochemical redox reaction network, a transient and highly active supramolecular assembly is achieved with rapid kinetics, directionality, and precise spatiotemporal control. As electronic signals are the default information carriers in modern technology, the described approach offers a potential opportunity to integrate active materials into electronic devices for bioelectronic applications.



INTRODUCTION

Fuel-driven dissipative supramolecular assemblies in biology, such as actin filaments and microtubules, contribute to the formation of complex, dynamic structures in living organisms and give rise to emergent functions such as motility, homeostasis, self-healing, and camouflage.^{1,2} Such out-of-equilibrium active supramolecular systems in living systems exhibit important emergent properties that are controlled spatiotemporally by the kinetics of fuel consumption.³ Over the past decade, several synthetic dissipative assembly systems have been developed using chemicals^{4–7} or light^{8–10} as the major fuel sources. Chemical fuels, such as alkylating agents,⁴ carbodiimides,^{11,12} ATP/GTP,^{13–17} and oxidants,^{18–20} have been used to drive dissipative assemblies of various building blocks, including organic molecules,^{4,11,12,19,21} peptides,^{11,22,23} DNAs,^{17,24} and nanoparticles.²⁵ Light has also been used to drive the dissipative assembly of small molecules,^{26,27} proteins,⁹ and particles.^{8,28} These two main types of fueled active material systems complement each other with their respective advantages and limitations.^{5,10} Chemical fuels are versatile and have relatively high efficiency in generating the activated state but face the challenge of generating waste in closed systems and are inherently limited in achieving spatiotemporal control of the dynamic assemblies.⁵ Light, on the other hand, is a cleaner fuel with no waste generation and can be delivered spatiotemporally to control the assembly process; however, it is limited in penetration depth and has lower efficiency in generating the activated state.¹⁰

Another major energy form, electrical energy, has remained mostly unexplored for fueling active supramolecular assembly. Electrical energy offers several advantages as a fuel: it is readily

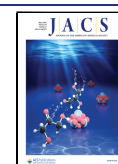
available, clean, and can be modulated spatiotemporally. Electrical fields have been used to actuate electroactive polymers²⁹ and liquid crystalline materials,³⁰ control particle assembly,³¹ and power particle motions through various forms of electrostrictive hydrodynamics.³² Electric potential has also been shown to polymerize organic monomers^{33,34} and modulate supramolecular interactions.^{35,36} Nevertheless, no prior study has reported electrically fueled (e-fueled) dissipative self-assembly of active supramolecular materials in bulk solution.

RESULTS AND DISCUSSION

Designing e-Fueled Dissipative Assembly System. To achieve our e-fueled dissipative self-assembly system, we designed an electrochemical redox reaction network that converts a cysteine derivative (CSH) into its corresponding cystine derivative (CSSC), which self-assembles into fibers (Figure 1a).³⁷ Ferrocyanide ($[\text{Fe}(\text{CN})_6]^{4-}$), a safe and biologically tolerated reagent,³⁸ was used as a homogeneous electrocatalyst because it could be easily oxidized electrochemically to ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-}$), which could further oxidize cysteine to the cystine.³⁹ The disassembly half of the redox reaction network was accomplished using the chemical reductant dithiothreitol (DTT). When a positive electric

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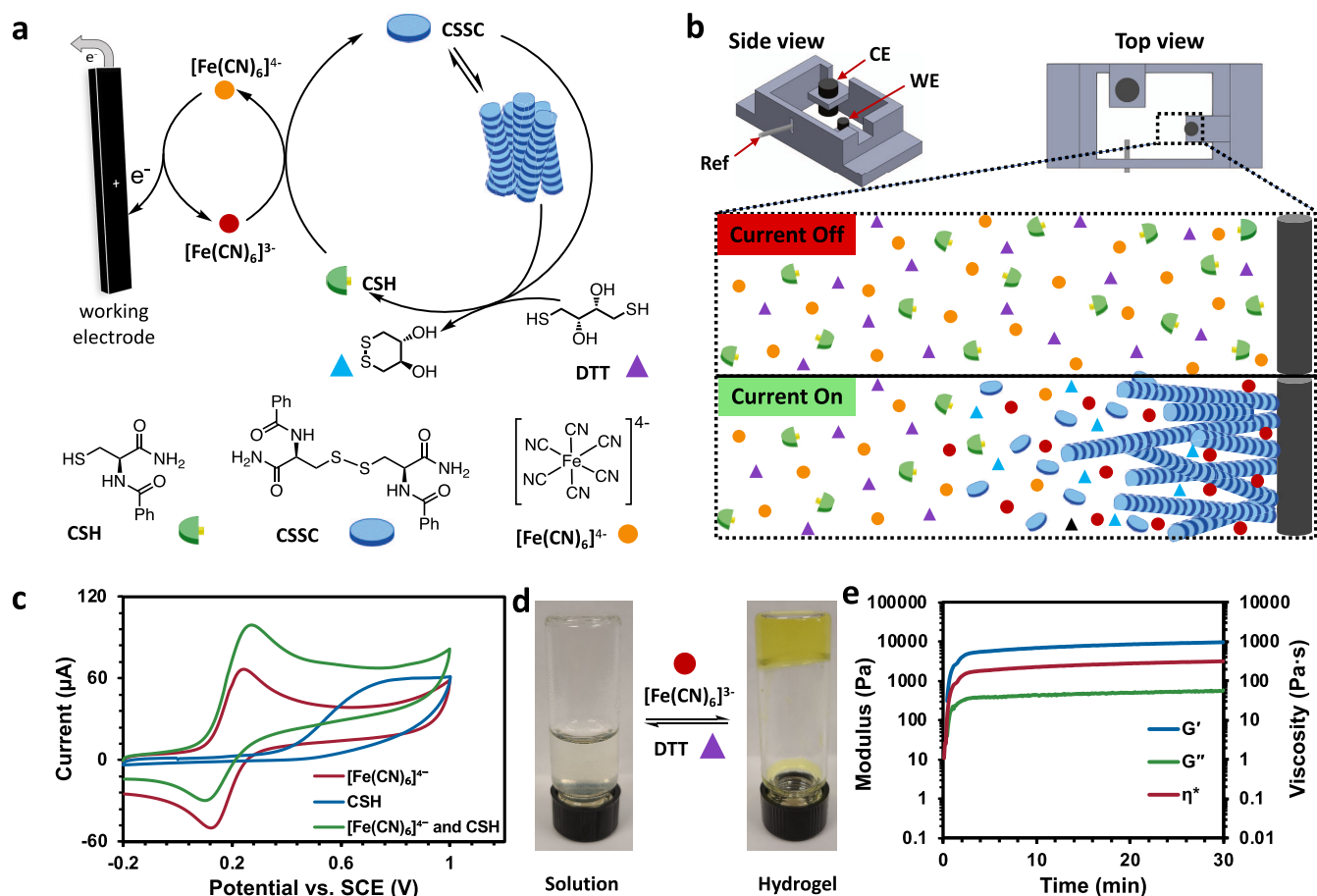


Figure 1. Design of electrically fueled active materials. (a) Schematic representation of the dissipative self-assembly process fueled by electricity. (b) Side and top view of the electrochemical cell used in the study (CE = glassy carbon counter electrode, WE = glassy carbon working electrode, Ref = silver wire pseudo-reference electrode) and schematic representation of species distribution in the cell when current is turned on and off. (c) Cyclic voltammogram showing electrocatalytic oxidation of CSH by ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-}$) generated *in situ*. (d) Images showing the reversible fiber assembly and dissolution upon addition of $[\text{Fe}(\text{CN})_6]^{3-}$ or DTT to the solution ($[\text{CSH}]_0 = 5.0 \text{ mM}$, $\text{pH} = 8$). (e) Rheology measurements showing the formation of hydrogel upon addition of $[\text{Fe}(\text{CN})_6]^{3-}$ to CSH solution (same condition as (d)).

potential is applied to the working electrode, $[\text{Fe}(\text{CN})_6]^{4-}$ near the electrode surface is oxidized to $[\text{Fe}(\text{CN})_6]^{3-}$ via electron transfer to the electrode, which subsequently oxidizes CSH into CSSC, initiating fiber growth from the surface (Figure 1b). As the potential is removed, DTT present in solution reduces CSSC back to CSH, resulting in the spontaneous dissolution of the fibers.

To test the feasibility of our design, we first confirmed that $[\text{Fe}(\text{CN})_6]^{4-}$ acts as a homogeneous electrocatalyst for CSH oxidation. Cyclic voltammograms (CV) of $[\text{Fe}(\text{CN})_6]^{4-}$ and CSH in an aqueous buffer (Figure 1c) show that the former was easily and reversibly oxidized with a $E_{1/2} = 200 \text{ mV}$ vs Ag/Ag^+ , whereas CSH was oxidized at 600 mV vs Ag/Ag^+ irreversibly. When $[\text{Fe}(\text{CN})_6]^{4-}$ was added to CSH solution, the CV became electrochemically irreversible, as shown by the cathodic current being significantly smaller in magnitude than the anodic current, indicating that $[\text{Fe}(\text{CN})_6]^{4-}$ was participating in the electrocatalytic oxidation of CSH. The kinetics for the redox reactions involved in the system were quantified through a combination of stopped-flow UV–Vis spectroscopy and ultra-performance liquid chromatography (UPLC) (see the Supporting Information for details). Based on the kinetics, we demonstrated that $[\text{Fe}(\text{CN})_6]^{3-}$ could oxidize CSH to form CSSC gel, which could be dissolved by DTT, as was visualized by vial inversion (Figure 1d) and confirmed by rheology (Figures 1e, S14, and S15).

e-Fueled Transient and Directional Assembly. To demonstrate e-fueled dissipative self-assembly, we fabricated a custom glass-bottom, three-electrode bulk electrochemical cell (Figures 1b and S1) in which e-fueled dissipative assembly could be monitored *in situ* using confocal laser scanning microscopy (CLSM). We screened the experimental parameters to determine conditions for fast fiber growth and dissolution. We began by identifying the minimal $[\text{CSH}]_0$ and maximal $[\text{DTT}]_0$ that allowed for fiber formation at relatively low potential ($<1 \text{ V}$ vs Ag/Ag^+). Then, several experimental parameters were iteratively varied, including pH, $[\text{CSH}]_0$, $[\text{DTT}]_0$, and electrical current. As expected, increasing the current led to faster and more vigorous fiber growth (Figure S3), while increasing $[\text{DTT}]_0$ accelerated the dissolution (Figure S4). The kinetics of fiber dissolution were pH-dependent, with higher pH resulting in faster dissolution (Figure S5), in agreement with previous studies.¹⁹ The concentration of CSH within the range of 2–5 mM did not significantly impact growth and dissolution kinetics (Figure S6). On the basis of these observations, the dissipative self-assembly was conducted in a pH 8 buffer with 2.5 mM CSH, 20 mM DTT, 150 mM ferrocyanide, and 25 μM Nile red (as an intercalation dye for CLSM)¹⁹ by applying a potential of 430 mV between the glassy carbon working electrode and silver wire pseudo-reference electrode (Figure 1b).

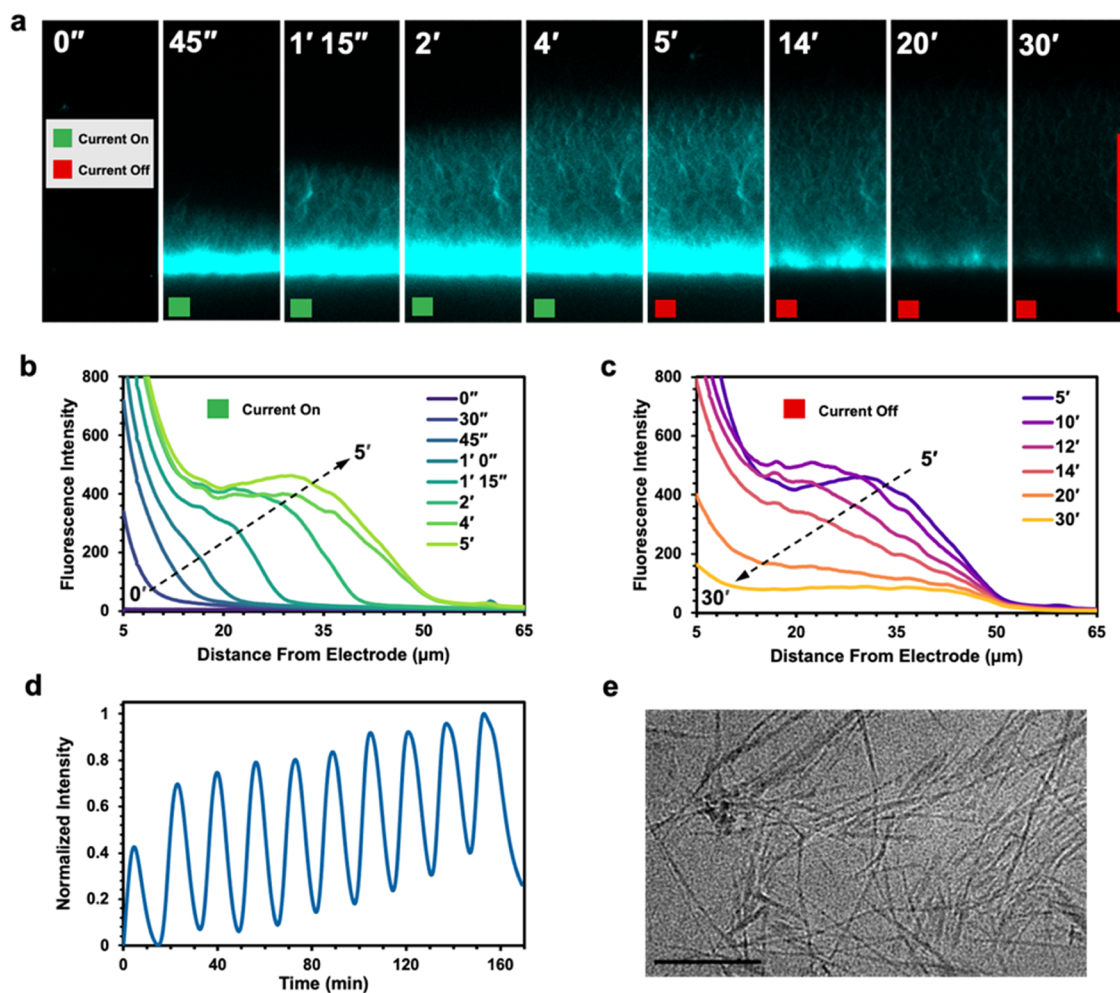


Figure 2. e-Fueled transient supramolecular assembly. (a) CLSM snapshots showing directional fiber growth when current was applied (green square) and dissolution when current was turned off (red square) (pH 8, $[\text{CSH}]_0 = 2.5 \text{ mM}$, $[\text{DTT}]_0 = 20 \text{ mM}$, $[[\text{Fe}(\text{CN})_6]^{4-}]_0 = 150 \text{ mM}$, scale bar = $50 \mu\text{m}$, 175% hue saturation, electrode at bottom). (b, c) Fluorescence intensity at varying distances from the electrode surface observed over time during fiber growth with current on (b) and dissolution with current off (c). (d) Ten cycles of fiber growth and dissolution by repetitively switching current on and off (600 mV vs Ag/Ag⁺ for 16 s followed by 24 min current off, under the same condition as (a)). (e) Cryo-TEM micrograph of self-assembled fibers formed by e-fueled assembly (scale bar = 200 nm).

Shortly after applying the potential, fibers began to grow directionally perpendicular to the surface of the working electrode, which continued to grow outward when the potential was maintained (Figure 2a and SI Movie 1). When the current was turned off at 5 min, the fibers began to disassemble and eventually disappear. This is consistent with the fact that as the ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-}$) is generated at the electrode, it transports away from the electrode and oxidizes CSH into CSSC at the fiber front, enabling fibers to grow outward (Figure 1b). Upon depletion of the ferricyanide when the current is turned off, the DTT in the bulk solution will diffuse back into the gel, initially reducing fibers at the front and then the body of the gel. The electrochemical generation of $[\text{Fe}(\text{CN})_6]^{3-}$ results in the formation of two regions in our system. The region closest to the electrode is rich in oxidant as the generated $[\text{Fe}(\text{CN})_6]^{3-}$ depletes the DTT, and the remainder of the bulk solution is a reducing region rich in DTT. The fiber morphology of the e-fueled assembly was confirmed by cryo-TEM imaging, showing fibers with an average diameter of $\sim 12 \text{ nm}$ and an average length of $\sim 412 \text{ nm}$ (Figures 2e and S17). The fibers were observed to stack and coil together, creating larger micron-sized assemblies (Figure S16). The fluorescence histograms of the images reveal

that during the fiber growth with the current on, they grew outward as a front while steadily increasing in fluorescence intensity throughout the body of the gel (Figure 2b). Conversely, when the fibers began to disassemble with the current off, the fiber front gradually receded toward the electrode while the fluorescence intensity dropped across the whole gel (Figure 2c). The fluorescence disappearance suggests two possible modes of fiber assembly, both governed by reduction with DTT. The fibers can shrink and disassemble from their ends through monomer dissociation and reduction leading to the receding fluorescence front. They can also be eroded along their width by direct reduction resulting in an overall decrease in fluorescence intensity. The gel was grown as far as 1.5 mm from the electrode surface through continual application of current for 30 min (SI Movie 2). Furthermore, the transient fibers could be grown and dissolved repetitively by turning the current on and off (Figure 2d). These experiments clearly demonstrate the transient nature, directional growth, and precise temporal control of the e-fueled dissipative self-assembly.

Several control experiments were conducted to confirm that there was no appreciable photobleaching under experimental

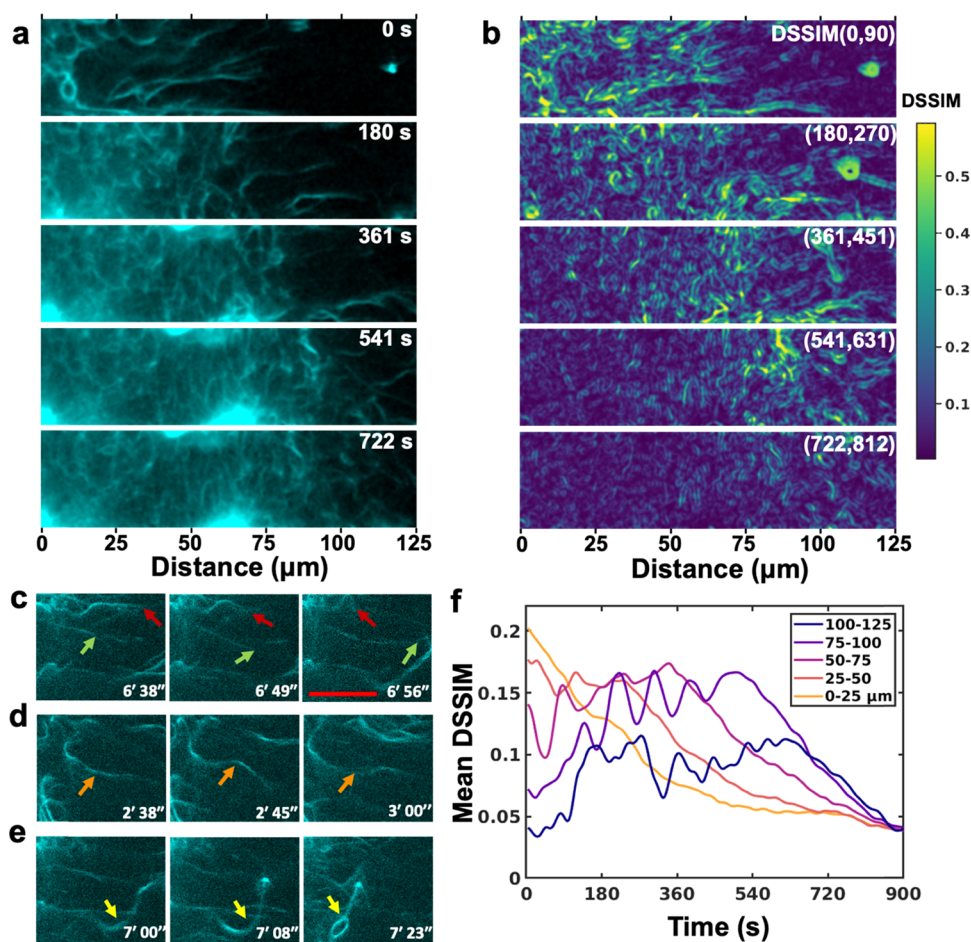


Figure 3. Active dynamic self-assembly fueled by electricity. (a) Processed CLSM snapshots highlighting the high dynamics for self-assembly at the gel front (details in Supporting Information). (b) Structural dissimilarity frame series generated by calculating the DSSIM of CLSM frames taken 90 s apart. Bright pixels represent regions of high structural dissimilarity between local areas in frames of comparison, which corresponds to fiber dynamics. (c–e) Snapshots showing different active fiber movements: simultaneous fiber growth and shrinkage ((c) green arrow for growing fiber and red for shrinking), waving (d), and curling/looping (e) (CLSM images rendered with $\gamma = 0.45$ and 150% hue saturation for fiber visualization). (f) Mean DSSIM in each region seen in (b). (The working electrode for (a–e) is out of frame on the left. Scale bar = 20 μm for (c–e).).

conditions (SI Movies 3 and 5), and the observed fluorescence changes were due to intercalation of the Nile Red dye into self-assembled fibers rather than simple electrochemical activation or physical attraction of the dye (SI Movies 4 and 5). Without DTT in the solution, the static fibers formed by electrochemical oxidation of CSH did not show any appreciable change in fluorescence intensity over 1 h period after the current was turned off (SI Movie 3), indicating no significant photobleaching under experimental conditions. In the full system, the observed fluorescence decrease with the current off (Figure 1a and SI Movie 1) was indeed due to fiber disassembly caused by DTT-induced reduction of CSSC. In the absence of the CSH precursor in the solution, no fibers were observed at all despite repeated application of an electrical potential (600 mV) (SI Movie 4), confirming that electrochemical oxidation of CSH to CSSC led to the fiber assembly. Lastly, without ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-}$) as the electrocatalyst, repeated application of an electrical potential to a solution containing static fibers formed by chemical oxidation by H_2O_2 did not cause any appreciable change to the fluorescence intensity (SI Movie 5), further confirming that the observed fluorescence changes in the full system were due to fiber assembly and disassembly rather than simple electrochemical activation or physical attraction of the dye.

Active and Dynamic Self-Assembly. Next, we investigated the active, dynamic self-assembly for the CSH/CSSC system fueled by electricity. To observe the dynamics on a shorter time scale, we replaced DTT with a more efficient reductant, (tris(2-carboxyethyl)phosphine) (TCEP).⁴⁰ The e-fueled system provides a convenient way to tune the kinetics of the reaction in real time by modulating the potential applied to the system. After applying an initial potential of 2 V vs Ag/Ag^+ for 11 s to grow a layer of fibers from the electrode surface, the potential was reduced to 600 mV to slow down the fiber growth for observing dynamics at the fiber front. The CLSM video shows highly complex active, dynamic processes for the system (SI Movie 6), especially at the fiber–water interface (Figure 3a,b). The selected snapshots highlight different modes of activity for the self-assembly of fibers, including simultaneously growing and shrinking (Figure 3c), waving (Figure 3d), and curling and looping (Figure 3e). Another observation is that as new fibers form at the front, they collapse onto the body of the fibers already formed (SI Movie 6). The complexity of the observed active behavior is tentatively attributed to multiple processes potentially ongoing in the system. In addition to the anticipated dissipative assembly/disassembly, several physico-chemical processes may influence the active behavior. The electrochemical reaction should create concentration gradients

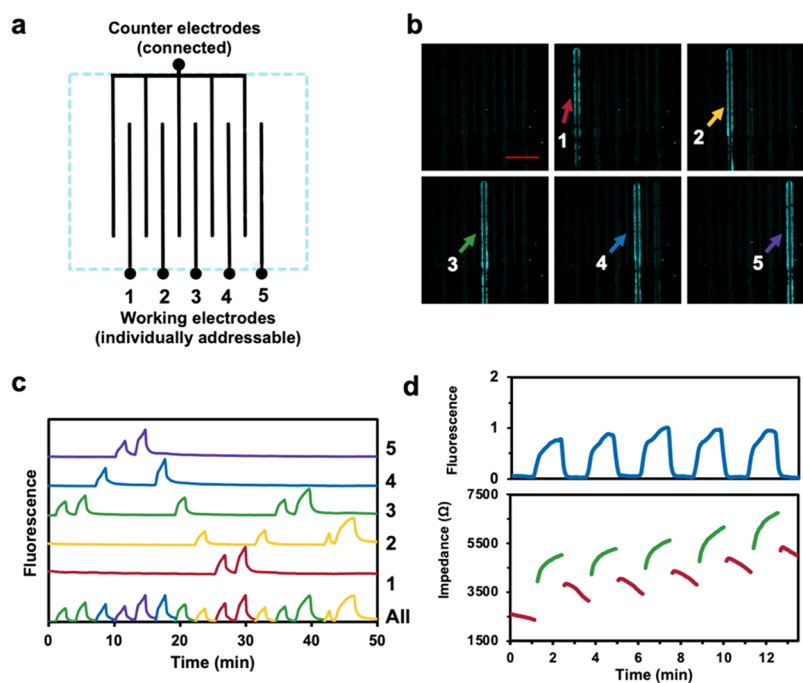


Figure 4. Spatiotemporal control of the e-fueled dissipative assembly. (a) Schematic representation of the individually addressable interdigitated gold microelectrodes. (b) Growth of fibers at each of the working electrodes by selectively applying an electric potential at different times (CLSM images rendered at 150% hue saturation). (c) Normalized fluorescence intensity measured around each working electrode to monitor fiber growth pattern after selectively applying an electric potential to each electrode at different times for varying durations. Each line corresponds to the working electrode of matching number and color in (b). The bottom trace superimposes 1–5 into one. If placed on a treble staff with the red graph on middle C, the pattern mimics that of the first four measures of Beethoven’s “Ode to Joy” (see Figure S7 and SI Movie 8). (d) Fluorescence and impedance changes in the system upon cycling fiber growth at 2.4 V and fiber dissolution at 0 V over 5 cycles.

for both the redox-sensitive species and electrolytes near the working electrode surface (Figure 1b), which may cause liquid–liquid phase separation of the growing fibers into a gel phase.⁴¹ In addition, various electrostrictive hydrodynamics, such as electrohydrodynamics and/or electro-osmosis,^{42,43} may also contribute to the complex dynamic behavior. A control experiment without DTT in the solution (SI Movie 3) showed only static fiber formation without any of the dynamics observed in the active system, confirming that the observed dynamic behavior is indeed due to the dissipative self-assembly process.

The self-assembly dynamics observed in CLSM (SI Movie 6) were quantified using the structural dissimilarity index measurement (DSSIM) (Figure 3b,f).⁴⁴ DSSIM is a standard measure of the difference between two images, which compares variation in the mean, variance, and cross-correlation between local regions of two images (see Supporting Information for details). DSSIM images were obtained by comparing two frames taken 90 s (Figures 3b and S9 and SI Movie 7) or 4 s (Figures S9 and S10 and SI Movie 7) apart in a sliding-window calculation. The 90 s sliding-window calculation quantifies dynamics occurring over a large time window, while the 4 s sliding-window calculation captures the high temporal resolution dynamics. Each of the 240 DSSIM images was divided into five equally spaced regions with increasing distance from the working electrode, and the average DSSIM in each region is plotted for every frame (Figures 3f and S10d and SI Movie 7).

The results show that the dissipative self-assembly system is highly dynamic, with the most dynamic changes at the fiber–water interface, which is seen for both the 90 and 4 s intervals. The dynamics decrease with distance from the fiber front, as can be seen with the time-delayed decline in DSSIM values starting with the 0–25 μm region, which is then echoed in the 25–50

and 50–75 μm regions. The 75–100 and 100–125 μm regions start with low DSSIM values, which steadily increase as the fiber–water interface progresses further from the electrode until a peak is reached and then gradually decline. The data also shows that the dynamics at the fiber–water interface are highest in the early stages and gradually decrease over time.

Spatiotemporal Control of Active Assembly. Spatiotemporal control is a hallmark of biological dissipative self-assembly systems, which is critical for their emergent functions.^{1,2} To demonstrate spatiotemporal control of the e-fueled active material system, we designed an array of interdigitated gold microelectrodes for use in a two-electrode configuration (Figures 4a and S2). Each of the five bottom electrodes is an individually addressable working electrode, whereas the top five are connected as a single counter/reference electrode. By placing the sample solution (2.5 mM CSH, 150 mM ferrocyanide, 60 mM DTT, pH 8 buffer) on the interdigitated microelectrodes and applying 2.4 V vs ref for 90 s, fibers were grown at each individually addressed electrode (Figure 4b). When the current was turned off, it took roughly 90 s to fully dissolve the fibers and return to baseline fluorescence. By selectively applying an electric potential to different working electrodes over time while also varying the duration for current on and off, the first four measures of Beethoven’s “Ode to Joy” were “played” on the microelectrode array (Figures 4c and S7 and SI Movie 8). This experiment clearly demonstrates precise spatiotemporal control and fast assembly/disassembly kinetics for the e-fueled dissipative system.

We also demonstrated that the e-fueled dissipative self-assemblies could dynamically transduce electronic inputs related to sensing, actuation, and computation. Single-frequency electrochemical impedance spectroscopy (SFEIS) was used to

probe the impedance changes of the e-fueled dissipative assembly system on carbon-coated interdigitated gold microelectrodes (Figure S2) at 8 kHz. The impedance of the system increased sharply upon application of $2.4 \text{ V} \pm 10 \text{ mV}$ vs ref for 1 min, resulting from the growth of fiber networks between electrodes, and dropped after the potential was returned to $0 \text{ V} \pm 10 \text{ mV}$ vs ref (Figure 4d). The fiber growth was concurrently monitored using CLSM during SFEIS measurements, confirming that the impedance changes correlate with fiber assembly and disassembly, as indicated by changes in fluorescence intensity (Figure 4d). In contrast, the control system without CSH in the solution only showed minimal changes of impedance under identical conditions (Figure S13). The increase in impedance is attributed to the inhibition of ionic currents between electrodes due to diminished ionic transport through the self-assembled fiber network.

Conclusions and Outlook. In summary, here we have demonstrated a new platform for dissipative self-assembly of active materials using an electric current as the fuel. Electrical inputs are able to rapidly and repetitively fuel the dissipative self-assembly of fibers with directionality, high dynamics, and precise spatiotemporal control. These combined features would be difficult to achieve with either chemical- or light-fueled dissipative systems. Furthermore, the system operates in mild aqueous buffers, uses electrical energy as a clean fuel, and works at relatively low voltage. These features make this design potentially suitable for developing sustainable dissipative self-assembly systems as well as applying this design to other redox-sensitive assembling building blocks and/or microelectrode arrays. Currently, we are working toward a complete electrically fueled dissipative self-assembly system, where both oxidation and reduction proceed electrochemically, with the aim to achieve a waste-free and sustainable dissipative self-assembly system for further study. As electronic signals are at the heart of many modern technologies, the described e-fueled active material platform may find potential applications in bioelectronics.^{45,46}

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c01884>.

Materials, electrode design, experimental details and data for confocal laser scanning microscopy, kinetic data, DSSIM process and characterization, rheology data, and cryo-TEM characterization (PDF)

SI Movie 1: video depicting the transient growth and disassembly of the e-fueled supramolecular fibers; accompanies Figure 2 (MP4)

SI Movie 2: video depicting the growth of gel upon continuous application of a 600 mV electrical potential; the stage is moved throughout the experiment to follow the gel growth (MP4)

SI Movie 3: video depicting the growth of gel in the absence of reductant (MP4)

SI Movie 4: video depicting the repeated application of an electrical potential to a sample that lacks the redox active CSH building block precursor (MP4)

SI Movie 5: video depicting the repeated application of an electrical potential to a sample of chemically grown gel fibers in the absence of both reductant and electrochemical mediator ferrocyanide (MP4)

SI Movie 6: video depicting the active dynamic behavior of the e-fueled dissipative self-assembly fibers; accompanies Figure 3 (MP4)

SI Movie 7: real-time generation of DSSIM plots based on 90 and 4 s sliding-window calculations; accompanies Figure 3 (MP4)

SI Movie 8: spatiotemporally controlled dissipative self-assembly of fibers at an interdigitated gold microelectrode junction synced with the tune of Beethoven's "Ode to Joy"; accompanies Figure 4 (MP4)

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Notes

The authors declare no competing financial interest.

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