Fabiana Ciocchetti, 03/2023

Waste-Free Fully Electrically Fueled Dissipative Self-Assembly System

Dipankar Barpuzary, Zhibin Guan et al. JACS.2c13140, 2022,

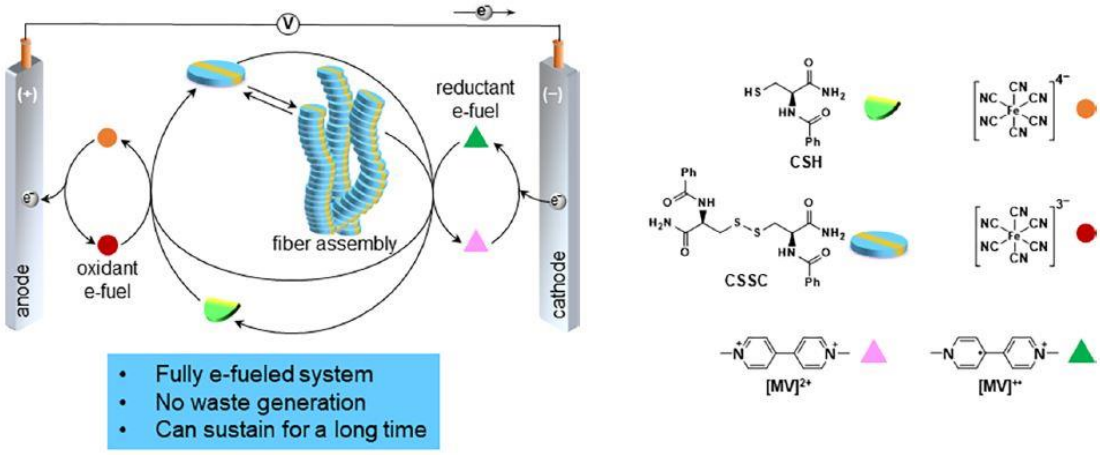

Figure 1: Illustration of the design of fully e-fueled dissipative self-assemblies of CSH/CSSC system mediated by dual electrocatalytic cycles. Under applied electrical potential, at the anode, $[Fe(CN)_6]^{4-}$ is electrochemically oxidized to $[Fe(CN)_6]^{3-}$ that further oxidizes CSH into CSSC for fiber assembly. Simultaneously, at the cathode, $[MV]^{2+}$ is electrochemically reduced to produce $[MV]^{+\bullet}$, which further reduces CSSC to CSH and induces disassembly.

Who are the corresponding authors and what are their research areas?

Zhibin Guan (Center for Complex and Active Materials, University of California Irvine).

Zhibin heads a group called:" Bioinspired design of dynamic soft materials and biomaterials with chemistry". The group generates a plethora of supramolecular assemblies and polymers that are active, adaptive, malleable, and self-healing. In addition, they develop multifunctional biomaterials for the cellular delivery of various biomacromolecules, for CRISPR-Cas gene editing, and for immunomodulation. An overarching theme for their research is to build direct links between molecular structures and material properties, with the aim to rationally design soft materials from the bottom-up and control material properties at the molecular level.

What is the main claim of the article?

Here, they developed a fully electrically fueled (e-fueled) active self-assembly material that can be sustained for an extended period of time by electrical energy.

Until nowadays, many synthetic active materials have been developed, but several limitations remain to be addressed *i.e.* the accumulation of chemical waste during the process, the lack of precise spatiotemporal control and the unsustainable active behavior.

To overcome these limitations, they used an electrochemical setup with dual electrocatalysts, the anodic oxidation of one electrocatalyst (ferrocyanide, $[Fe(CN)_6]^{4-}$) creates a fuel that activates the self-assembly, while

simultaneously, the cathodic reduction of the other electrocatalyst (methyl viologen, $[MV]^{2+}$) generates a fuel triggering fiber disassembly.
The generated system is completely waste-free, with a good spatiotemporal control and can perform several cycles.

How is it demonstrated?

They used a combination of several techniques:

- Cyclic Voltammetry (CV) experiments in order to confirm the viability of the design, and so the oxidation and reduction of CSH and CSSC in the presence of $[Fe(CN)_6]^{4-}$ and $[MV]^{2+}$,
- UPLC and UV-vis spectroscopy to monitor the formation and decay of the disulfide species,
- Confocal laser scanning microscopy (CLSM) to observe the growth and depletion of the fibers,
- Electrochemical impedance spectroscopy (EIS) to probe the impedance changes in the system.

What are the typical experimental conditions?

Reactions in deoxygenated phosphate buffer at pH 7, millimolar concentration range.

Which are the key related papers?

1. *Selmani, S.; Schwartz, E.; Mulvey, J. T.; Wei, H.; Grosvirt- Dramen, A.; Gibson, W.; Hochbaum, A. I.; Patterson, J. P.; Ragan, R.; Guan, Z. Electrically Fueled Active Supramolecular Materials. J. Am. Chem. Soc. 2022, 144, 7844−7851*