Materials Letters 355 (2024) 135497

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Featured Letter

# Electronic inputs to cue the emergence of hydrogel structure and to confer function

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ARTICLE INFO

*Keywords:*
Chitosan
Electrodepositon
Electrobiofabrication
Hydrogel
pH-responsive

ABSTRACT

Electrode-imposed electronic inputs can generate various cues that can control the emergence of hierarchical structure and confer function to hydrogel systems. Here we describe three such top-down cues. Electrolytic reactions can create pH cues that can induce the electrodeposition of pH-responsive self-assembling polymers (e.g., chitosan and alginate). The electric field provides a long-range cue that can induce polymer chains to migrate toward (or away from) the electrode and can align the polymer chains within the assembling hydrogel network (e.g., collagen). The electrochemical generation of diffusible oxidants provides a molecular cue that can induce oxidative assembly - typically through the formation of covalent bonds (e.g., disulfide bonds). Here, we review recent results on the use of these three cues for the electrofabrication of hydrogels and we illustrate how complementary capabilities from biotechnology allow the creation of functional hydrogel systems. Overall, we envision that electro-bio-fabrication could emerge as a scalable additive manufacturing method as well as a flexible approach for distributed manufacturing in public maker spaces.

## 1. Introduction

Research over the last couple decades has shown that electrodeposition provides unique opportunities for the fabrication of hydrogels with controlled structures and functions for various applications in biotechnology, medicine, and information processing. Often, biology serves as the source of materials, mechanisms, or inspiration for such hydrogel electro-fabrication. Specifically, biology provides many examples of how information is encoded into polymers that enable them to be "cued" to organize over a hierarchy of length scales. Here, we describe three top-down cues that can be imposed by electrodes to organize hydrogels with complex internal structure. We also illustrate how function-conferring components can be integrated into these hydrogels especially through biotechnological methods.

## 2. pH cues

Biological polymers often contain weakly acidic and/or basic substituents (carboxylates and amines) that can be (de)protonated at near-physiological pHs. In some cases, such changes in the polymer's charge can switch the balance of intermolecular interactions allowing individual dissociated chains to self-assemble through the formation of interchain associations. For instance, the aminopolysaccharide chitosan can be cued to undergo a reversible sol–gel transition by raising the pH near its pKa (6.3). This sol–gel transition is a type of self-assembly in which deprotonation eliminates electrostatic repulsions between isolated

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https://doi.org/10.1016/j.matlet.2023.135497
Received 14 June 2023; Received in revised form 4 October 2023; Accepted 28 October 2023
Available online 30 October 2023

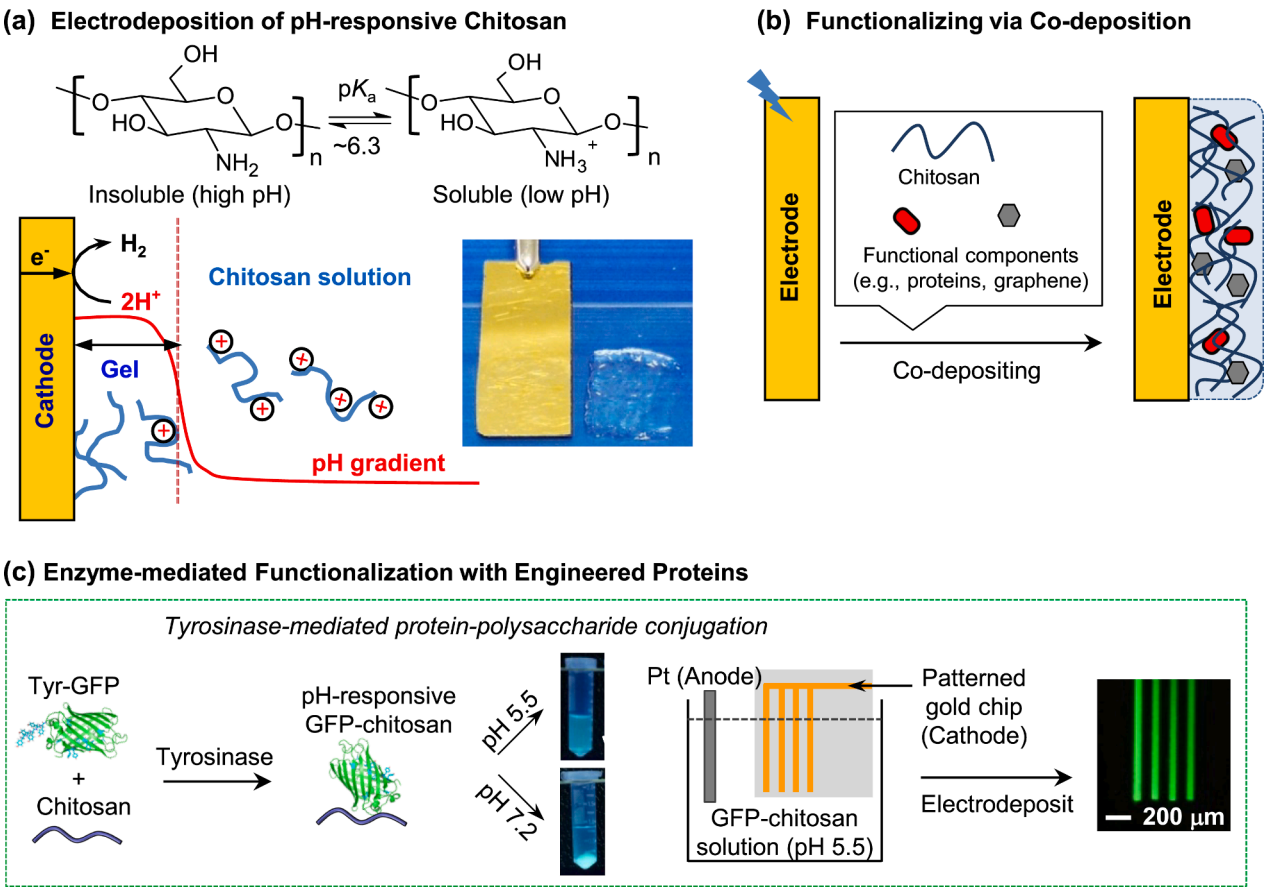


**Fig. 1.** (a) Chitosan's electrodeposition in response to a pH cue, adapted from [18]. (b) Creating functional hydrogels by co-depositing chitosan with function-conferring components that become entrapped in the hydrogel, adapted from [19]. (c) Enzymatic conjugation (by tyrosinase) of a protein engineered with accessible amino acid residues (e.g., tyrosines) and electrodeposition of the protein-chitosan conjugate, adapted from [16].

chitosan chains and allows the formation of a network of inter-chain hydrogen bonds characteristic of crystalline regions. These crystalline regions serve as the gel's network junctions (i.e., physical crosslinks) that can be reversibly formed or broken by shifting the pH.

Fig. 1a shows that electrolytic reactions can generate the pH cue that induces chitosan's electrodeposition at a cathode surface through a pH-neutralization mechanism. Specifically, the electrical input generates a region of high pH adjacent to the cathode and chitosan chains in this region are deprotonated and self-assemble to form a hydrogel. Both the high pH front and chitosan gelation front continue growing while the electrical input is imposed, and the rate of growth is controlled by the imposed electrical current. To our knowledge, chitosan was the first polysaccharide to be electrodeposited through a pH neutralization mechanism [1,2], and a few years later the acidic polysaccharide alginate was reported to undergo anodic electrodeposition through a pH neutralization mechanism [3–5]. Similarly, electrodeposition of pH-responsive low molecular weight hydrogelators have also been reported [6–9].

The electrodeposition of chitosan has been extensively investigated and these studies have demonstrated several important points that are presumably generalizable to other pH-responsive polymers. Chitosan's electrodeposition from aqueous solution is simple, rapid (i.e., minutes), safe (<5 V) and reagentless. Compared to other additive manufacturing methods, chitosan's electrodeposition can be performed in a covered solution (i.e., within a microfluidic channel) without the need for line-of-site (required by photolithography) or direct contact (required for printing) [10]. Also, if patterned electrodes are used, chitosan can be electrodeposited with spatial selectivity, and deposition can be performed either serially (to functionalize individual electrodes), or in parallel (to pattern all electrodes simultaneously). Further, electrodeposition scales with the electrode surface area (i.e., large surface area films can be generated by electrodeposition with a large electrode), and electrodeposition allows the conformal coating of complex surfaces [11,12]. Finally, Fig. 1b shows that function-conferring components that can be blended with chitosan in a deposition solution can often be co-deposited and entrapped within chitosan hydrogel films [13–15].

Chitosan also has the unique feature that its primary amines are nucleophilic and thus it is possible to use simple coupling chemistries to graft function-conferring components (e.g., proteins) to chitosan. This is illustrated in Fig. 1c which shows the enzymatic grafting of a model protein (green fluorescent protein; GFP) to chitosan [16,17]. Specifically, this protein was genetically engineered to have a short sequence of tyrosine residues to form an unstructured region capable of reacting with the oxidative enzyme tyrosinase. This enzymatic reaction generates quinone residues which are reactive and spontaneously conjugate the protein to chitosan. This GFP-chitosan conjugate retained both chitosan's functionality (i.e., pH responsiveness) and the protein's functionality (i.e., fluorescence). As a result, Fig. 1c shows that the GFP-chitosan conjugate could be electrodeposited onto a patterned electrode.

## 3. Electric field cues

While the pH cue is essential for chitosan's electrodeposition, the electric field plays an important role in organizing the hydrogel's emergent microstructure. Specifically, the electric field can provide a driving force for chain migration toward the electrode and may also provide a driving force for the chains to change conformation and alignment. Importantly, the effects of the electric field are not well

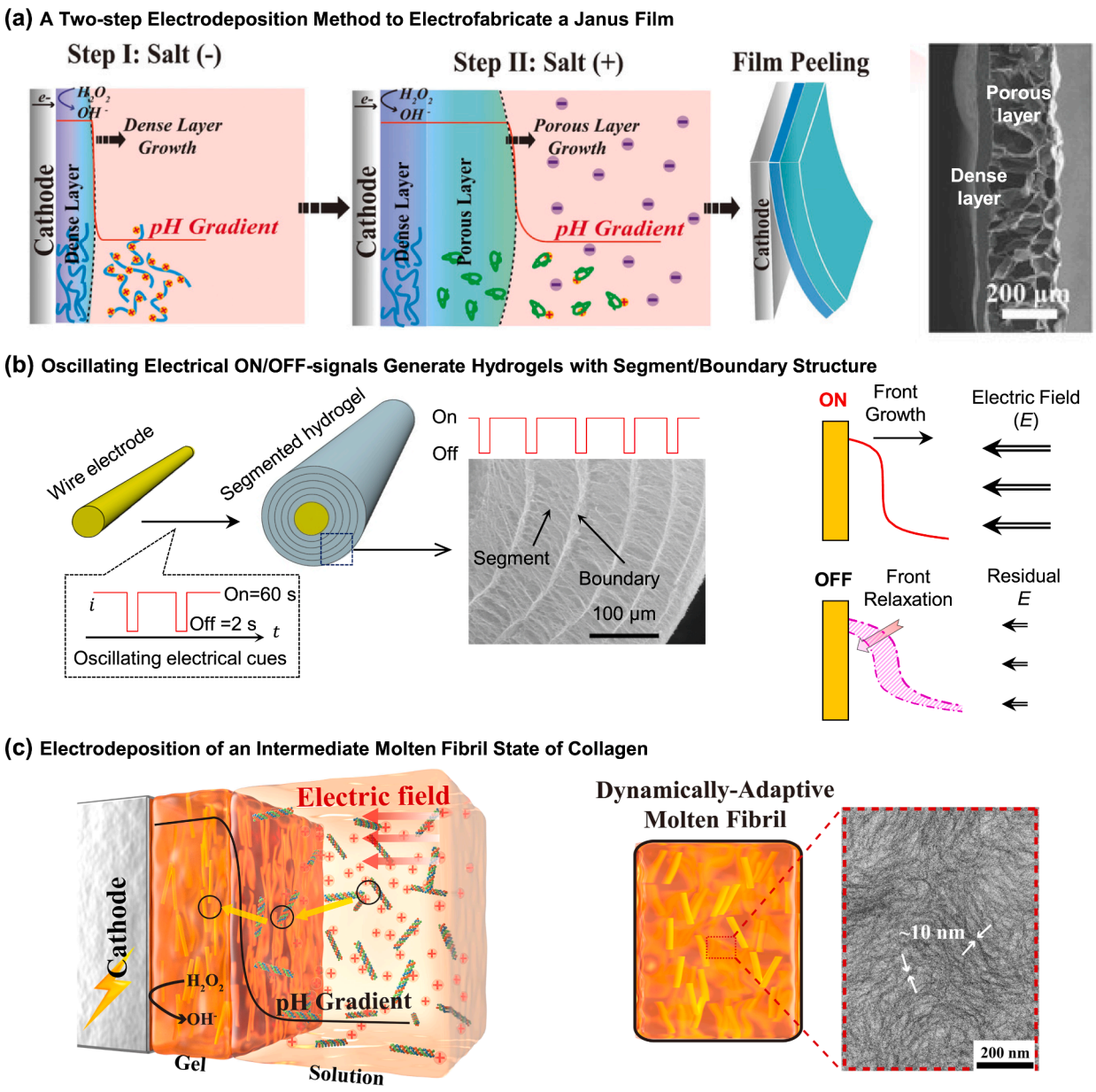


**Fig. 2.** (a) Janus film generated by a two-step electrodeposition process, adapted from [20]. (b) Segmented structure generated by oscillating electrical inputs, adapted from [21]. (c) Collagen's cathodic electrodeposition of a molten fibril state, adapted from [22].

understood but the field does not seem to be able to induce deposition directly (i.e., chitosan must be deprotonated to self-assemble while the field imposed during deposition can control the emergent microstructure). Initial evidence for the importance of the electric field were observations that chitosan's electrodeposition was markedly different in the presence or absence of salt that can screen the electrode-imposed electric field and screen inter-chain electrostatic repulsions [18]. When high levels of salt were added to the deposition solution, deposition was more rapid, but the deposited films were less dense (i.e., contained more water) and mechanically weak.

This salt effect was used to generate a Janus film in a two-step electrodeposition process illustrated in Fig. 2a [20]. In the first step, the dense "face" was electrodeposited from a chitosan solution with no added salt. Next, this film-coated electrode was transferred to a deposition solution containing salt, and the "porous" face was electrodeposited onto the dense face. This Janus chitosan film has been tested for guided bone regeneration.

Less direct evidence of the importance of the electric field on the emergent structure were results from a study in which electrodeposition was performed using an oscillating electrical input by stepping between a constant ON current and an OFF (current = 0). Fig. 2b shows that when a wire was used as the electrode, a segmented structure was generated by these oscillating inputs [21]. The segments grew during the ON steps while the boundaries were formed during the OFF steps. Subsequent studies indicated that during the OFF step, the open circuit potential was sufficient to "recruit" chitosan chains toward the interface, and this appears to explain the formation of the dense boundary regions [23].

In addition to chitosan, other biological polymers have been electrodeposited. To our knowledge, collagen was the first biologically-derived polymer to be electro-assembled although there seemed to be a gap of four decades between the initial report [24] and subsequent reports [25,26]. For collagen's electroassembly, both the pH and electrical field are believed to be important. In a recent study, illustrated in Fig. 2c [22], collagen was electrodeposited from an acidic solution and was observed to form a partially aligned hydrogel that was described as a "molten fibril state". This molten fibril state could be dissipated by re-

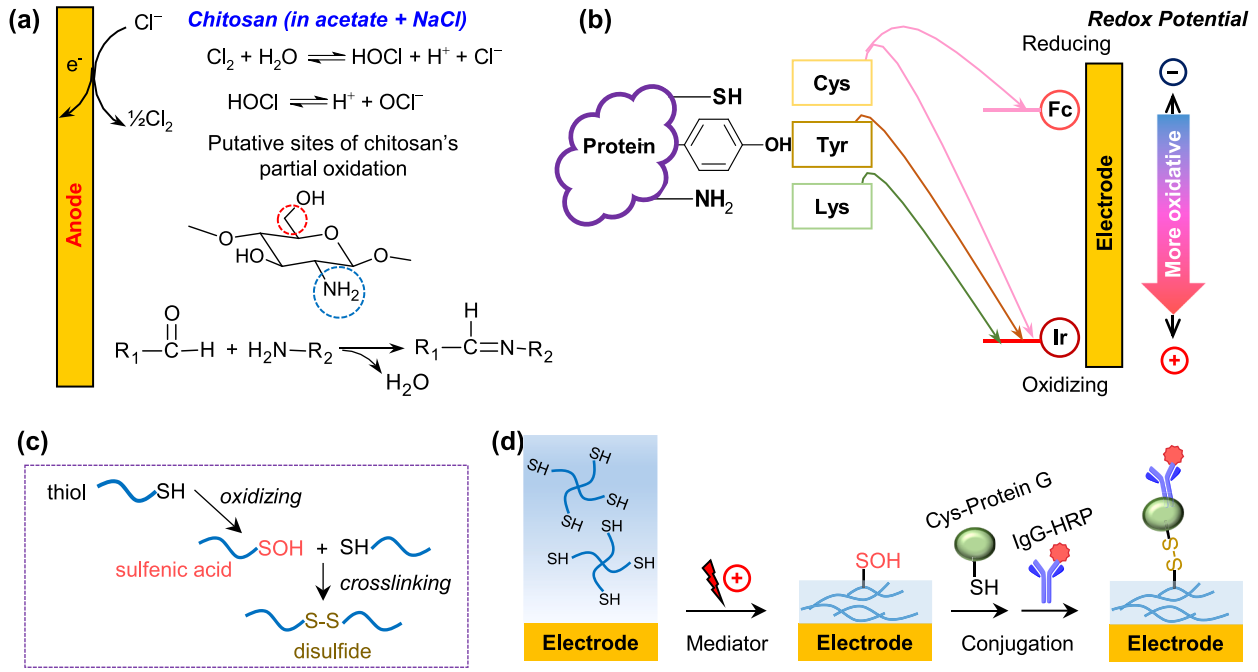


**Fig. 3.** (a) Anodic oxidation can generate HOCl that can oxidize amine-containing polymers (e.g., chitosan or gelatin) to induce crosslinking or conjugation reactions. (b) Some amino acid residues can be selectively oxidized based on the redox potential of the mediators (i.e., the electrochemically-generated diffusible oxidants). (c) Oxidative crosslinking of thiols to form disulfides. (d) Electrofabricating an antibody-presenting hydrogel using mediators to oxidatively crosslink a 4-armed PEG-SH (as shown in (c)) that allows the subsequent conjugation of an antibody-binding Protein G that was genetically engineered with accessible cysteine residues.

dissolving in acid or could be further organized/aligned by mechanical stretching and covalent crosslinking. Depending on subsequent processing, these molten collagen fibrils could be organized to offer structural features and functional properties similar to the collagen found in the cornea [27,28] or in tendons [29].

## 4. Oxidant cues

While the electric field cue can be imposed instantaneously and appears to operate over a relatively long distance, the pH cue is molecular in nature requiring diffusion from the electrode and this limits the speed and distance over which this cue can operate. Other molecular cues can be generated at an electrode, and these have been described as "morphogens" [30,31] by analogy to the historical work of Alan Turing to explain how complex patterns could be generated by the diffusion and reaction of structure-inducing molecules [32]. We are focused on the electro-generation of molecular oxidants that can serve as cues for electrodeposition.

Biology uses various oxidative mechanisms for materials fabrication (e.g., for crosslinking) and these include; the oxidative deamination of lysine to yield collagen crosslinks [33]; the conversion of thiols (e.g., cysteines) to a disulfide [34]; the tyrosinase-based oxidative setting of the mussel glue and hardening of the insect cuticle [35]; and the peroxidase based formation of dityrosine crosslinks that is being extended into technological applications (e.g., silk-tropoelastin gels) [36]. A common oxidant that biology generates as part of its immune reaction is HOCl, which can also be electrochemically generated by anodic oxidation in an NaCl-containing solution as illustrated in Fig. 3a. When HOCl is anodically generated in the presence of either the aminopolysaccharide chitosan or the protein gelatin, a hydrogel is observed to form on the anode surface. The presumptive gelation mechanism for this anodic deposition involves an oxidative deamination that forms an "active" aldehyde moiety that can react with available amines. This coupling between electrochemically-generated aldehydes and amines has been used to form crosslinked hydrogels either from chitosan [37] or gelatin [38] and to graft proteins to these hydrogels.

Fig. 3b illustrates that mediators can be used as oxidants and can exert some selectivity to electro-assembly [39]. For instance, the oxidized ferrocene mediator (Fc) is a weak oxidant and can oxidize the cysteine residues of proteins but not the lysine or tyrosine residues. In contrast, the oxidized iridium mediator is a stronger oxidant and can oxidize cysteine, lysine, and tyrosine residues [39,40].

Fig. 3c shows that the underlying chemical mechanism associated with mediated oxidation (with Fc) of thiols to form disulfide bonds [41]. Fig. 3d illustrates a mediator-based deposition mechanism for a 4-armed thiolated polyethylene glycol (PEG). Importantly, after deposition, some of the hydrogel's residues are in a sulfenic acid state and thus activated for disulfide bond formation. As illustrated, a protein (i.e., Protein G) that was genetically engineered to have a short sequence of accessible cysteine residues could be readily conjugated to the electrodeposited PEG hydrogel. Protein G is a useful protein in biotechnology since it can bind to the constant region of IgG antibodies [39]. Together, the combination of mediated electrodeposition and protein engineering allowed the facile fabrication of an "antibody-presenting" hydrogel for applications in biotechnology. In addition, it is important to note that mediated oxidative assembly can be sufficiently mild that it allows living cells to be electroassembled and immobilized within the hydrogel matrix [39].

## 5. Conclusions and perspectives

The electrodeposition of hydrogels uses externally-imposed electrical inputs to induce the bottom-up formation of hierarchical structure (e.g., to induce polymer chains to assemble into a hydrogel). As noted, the electrode can impose various cues that enable the electrofabrication of hydrogels with controlled internal microstructures. While it has generally been easier to understand/control the mechanisms associated with the molecular-based cues (pH and oxidant), the role of the electric field has been more difficult to understand. Recent results suggest the opportunity to tailor the imposed electric field not only to guide chain movement, but also to adjust the relative positions of the monomer units within a chain (i.e., the polymer conformation) and between chains (i.e., the chain alignment). The speed, simplicity, and versatility of

electrodeposition, as well as the ability to integrate alternative assembly methods (e.g., bio-based mechanisms) suggests significant benefits in a manufacturing setting. Thus, we envision electro-bio-fabrication could emerge as a new approach to additive manufacturing [11,12].

## CRediT authorship contribution statement

**Yi Liu:** Conceptualization, Investigation, Data curation, Writing – original draft. **Miao Lei:** Conceptualization, Investigation, Data curation. **Jinyang Li:** Conceptualization, Investigation, Data curation. **Eunkyoung Kim:** Conceptualization, Investigation, Data curation. **Kun Yan:** Conceptualization, Investigation, Data curation. **William E. Bentley:** Funding acquisition, Supervision. **Xiaowen Shi:** Funding acquisition, Supervision. **Xue Qu:** Investigation, Supervision. **Gregory F. Payne:** Writing – review & editing, Conceptualization, Funding acquisition, Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

## Acknowledgments

We are grateful for continued funding through the US National Science Foundation (e.g., MCB 2227598, SemiSyn and CBET 1932963), the Defense Threat Reduction Agency (HDTRA1-19-0021), and the Betty and Gordon Moore Foundation.

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