ELECTRO-BIO-FABRICATION: DIVERSE ROUTES TO FUNCTIONAL FILMS/HYDROGELS

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Key Words: Electrobiofabrication, Collagen molten fibrils, Co-deposition, Mediated oxidation

Vision. We believe electrochemistry provides unique opportunities to couple top-down and bottom-up assembly methods for the fabrication of films and hydrogels with complex microstructures and advanced functionality.[1] We highlight several different routes for conferring function through electro-bio-fabrication.

Controlling the Emergence of Hierarchical Structure. Electrical inputs imposed at an electrode result in the "transmission" of both chemical signals and electrical fields. The chemical signals often result from electrolysis reactions that cause localized changes in pH that can induce electrodeposition through the self-assembly of pH-responsive film-forming biopolymers. The electric fields can apply forces on charged polymers that can: induce chain migration (i.e., electrophoresis); alter chain conformation (i.e., extended vs collapsed); and align the assembled chains. One recent study showed that the protein collagen can be electro-assembled through a pH-responsive self-assembly mechanism. The results show that the electro-assembled collagen films exist as an intermediate molten fibril state in which collagen fibrils are partially aligned while higher-order structure features are absent (e.g., no fibers or D-banding are observed). Importantly, these molten fibril collagen films are dynamically-responsive and can be further processed to guide the formation of higher-ordered structural features that recapitulate native collagens.[2] We envision that electro-assembly of collagen molten fibrils could become an exciting route for tailoring the structure and properties of collagen matrices for diverse applications in regenerative medicine.

Creating Functional Composites. A variety of electrofabrication methods are available to create films/hydrogels with diverse functional properties. One approach to confer function is by co-deposition in which function-conferring particles (e.g., graphene) are blended into the deposition solution (e.g., a solution of the pH-responsive film-forming polymer chitosan). Upon deposition the added particles are entrapped within the deposited polymer matrix. A second approach to confer function is oxidative-assembly in which a diffusible chemical (e.g., catechol) is purposefully added.[3] Upon anodic oxidation a reactive oxidant is generated (e.g., the electrophilic quinone) that covalently conjugates to the deposited film (i.e., grafts onto the deposited chitosan). Using this two-step electrofabrication method we prepared a catechol-graphene-chitosan composite. Spectroelectrochemical characterization indicates that this composite has both conducting and redox properties that can offer benefits for energy and information processing applications.

Mediated Oxidation to Control Functionalization. Biology often uses oxidation mechanisms to induce protein matrix crosslinking and functionalization, and these mechanisms are often residue-specific (i.e., different mechanisms are used to induce crosslinking through cysteine thiols, lysine amines and tyrosine phenols). We used mediators (e.g., ferrocene dimethanol) to induce electrodeposition of a four-armed thiolated PEG through an oxidative crosslinking mechanism. Partially oxidized moieties (e.g., -S-OH) on the deposited hydrogel could then be used to assemble proteins through accessible cysteine residues. We are using this method to create protein functionalized hydrogel films for various applications in biotechnology (e.g., as a platform for antibody-based biosensing).[4,5]

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