Engineering Electroresponsive Layer-by-Layer Thin Films

By
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Electroresponsive layer-by-layer (LbL) polymer films and polymer nanocomposite films were investigated as model systems for electrically triggered drug delivery applications and “mechanomutable” surface coating applications. Two strategies were implemented in the design of these electroresponsive films: the use of redox-active, charge-shifting nanoparticles and the control over local pH utilizing the electrochemical reduction of dissolved oxygen. These strategies and the multiple materials systems explored are described below.

Redox-active Prussian Blue (PB) nanoparticles exhibit multiple, stable oxidation states and can shift their charge in response to mild electric potentials. The inherently negatively charged particles may be self-assembled into LbL films along with positively charged polyelectrolytes. When the PB in an LbL film is oxidized to its neutral state, dissolution of the film occurs as cohesive ionic crosslinks are broken and excess charge in the film brings in ions and water for electroneutrality, which solubilize the film components. The release of the polyanion dextran sulfate and the small molecule antibiotic gentamicin sulfate were precisely controlled with an electric potential. When PB is reduced, the negative charge on the particle is doubled, which results in film swelling and a decrease in stiffness. In films comprising PB and linear polyethyleneimine, reversible thickness changes on the order of 5-10% and reversible elastic modulus changes on the order of 50% (between 3.40 GPa and 1.75 GPa) were observed.

Employing the second strategy mentioned above, the local pH near an electrode surface may be increased to more basic values when dissolved oxygen is electrochemically reduced to hydroxide ions. In the first model system explored, hydrogen bonded (H-bonded) films comprising polyvinylpyrrolidone (PVPON) and tannic acid (TA), were dissolved at constant bulk pH by applying mild potentials (-0.25 V to -1.00 V vs. Ag/AgCl). The dissolution mechanism and kinetics could be tuned with the magnitude of the applied voltage and the concentration of dissolved oxygen. In the second model system explored, films comprising polyallylamine hydrochloride (PAH) and sulfonated polystyrene (SPS) were found to undergo reversible and dramatic swelling/deswelling transitions on the order of roughly 300 vol% and mechanical transitions on the order of 600-800% (shear modulus between 230 kPa and 1.9 MPa and loss modulus between 90 kPa and 620 kPa).

This thesis contributes to the applied materials science branch of chemical engineering. New polymer and polymer nanocomposite thin films were developed that can be further engineered and incorporated into implantable drug delivery devices for electrically triggered drug delivery or incorporated into MEMS and microfluidic systems for flow control or biomedical applications. Furthermore, the model systems presented here open doors for fundamental work on the transport of electrons, ions, and water through these electroresponsive films and the implications of transport phenomena on the control over film dissolution and swelling responses.

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