

Nanostructured Electroactive Polymeric Composites for Energy Storage and Separation Applications

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Submitted to the Department of Chemical Engineering
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in Chemical Engineering

Electroactive polymeric materials have garnered considerable interest due to their potential applications in advancing electrochemical energy storage, sensing, catalysis, and separations systems. Electroactive polymers include conducting polymers with π -conjugated backbones and redox polymers with localized redox-responsive moieties. The electro-responsive property of both conjugated and redox polymers is highly impacted by the efficient transport of counter-ions within polymers to maintain charge neutrality. The interactions at the molecular interface between the polymer and target entities ultimately dictate the performance of electroactive materials in the aforementioned applications. Nanostructures provide a shortened diffusion path for the transport of electrolyte ions or target molecules during a reversible redox process. The large interfacial area arising from an improved morphology allows efficient utilization of polymeric materials. Consequently, the union of nanostructures and electro-responsiveness has proven to be a powerful strategy to enhance the merit of electroactive polymers in the design of next generation energy storage devices, sensors, catalysts and separation platforms.

In this thesis, we focused on developing novel synthesis strategies for nanostructured electroactive polymeric composites. Two different synthesis approaches for the polymeric component were realized by exploiting the inter-molecular interactions between monomeric units and other entities during an electrochemical polymerization process. In the first approach, a nanostructured polyvinylferrocene /polypyrrole hybrid was fabricated via a co-deposition method as a result of the π - π stacking interactions between the aromatic pyrrole monomers and the metallocene moieties of polyvinylferrocene. The hybrid has a highly porous morphology with a significantly increased surface area compared to its bulk counterpart. The synergistic effects between polyvinylferrocene and polypyrrole lead to enhanced ionic and electronic conductivity and, consequently, a higher specific capacitance as a supercapacitor electrode material.

The second approach was a diffusion-controlled electrochemical method facilitated by the interactions between pyrrole monomers and the carbamate groups in CO₂-bound polyamines. As a result, a porous polypyrrole coating consisting of nanofibrous structures was synthesized and deposited on a carbon microfiber substrate. This composite material demonstrated enhanced electrochemical properties and adsorption capability towards aldehydes as a result of its porous morphology and high surface area. We later applied this composite material in achieving electrochemically modulated adsorption of polynucleotides. The adsorption process was found to have a strong dependence on the oxidation states of the composite due to the electrostatic

interactions between positively charged polypyrrole backbones and negatively charged phosphate groups in DNAs.

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