ABSTRACT

CONDUCTIVE POLYMERS AND THEIR APPLICATIONS IN ELECTROCHEMISTRY, BIO-SENSING AND ENVIRONMENTAL ANALYSIS

By

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This dissertation involves the fundamental electrochemical study of conductive polymers’ properties and their application in electrochemistry, bio-sensing and environmental analysis. Conductive polymers are a class of versatile smart materials that conduct electricity and have found widespread applications for constructing chemical, environmental and bio-sensors. Two complementary methods are typically utilized to improve conductive polymers’ properties: doping and substituent variation. Ionic liquids, as a series of environmentally-friendly solvents and electrolytes, are ideal as the dopants for optimizing conductive polymers’ properties. Different imidazolium-based ionic liquids have been used as the electrolytes and dopants for aniline electro-polymerization to give the polyaniline/ionic liquid composites. Among these composites, polyaniline that is doped by the hydrophobic ionic liquid [Bmim][PF₆] is electroactive in the biologically important MOPS (3-(N-Morpholino)-propanesulfonic acid) solution, with a pH of 5, extending the working pH range of polyaniline, which is typically electroactive in solutions with pH values less than 3. This novel doping of conductive polymer by ionic liquids offers the novel idea and opportunity to develop more versatile materials.
Substituent variation is another approach for modifying conductive polymers. Methoxy and methyl substituents on aniline are able to introduce the significant difference in sensing performances of the resulting poly (2-methoxy aniline) and poly (2-methylaniline) for environmental analysis of sulfur dioxide pollutant. Poly (2-methoxyaniline) can also function as an adsorbing material for removal of SO$_2$ and a unique gas storage reservoir for this pollutant. Another quinone substituent was also installed on polyaniline to evaluate the resulting substituent influences. It was observed that the electrochemical responses from polyaniline backbone in this unique polymer have been “shielded” by quinone pendant. This unique poly (aniline quinone) showed a quasi-reversible redox process from the redox behavior of the pendant quinone and performed excellently as a reference electrode in aqueous and non-aqueous media, being useful under both non-zero current and zero-current conditions.

Besides polyaniline, polythiophene and its derivatives have also been investigated. A glycosylated lactose-functionalized polythiophene biosensor has been constructed. The disaccharide lactose was grafted on polythiophene via CuBr-mediated click chemistry. The resulting polythiophene-lactose biosensor was applied for detecting *Erythrina Cristagalli* lectin by differential pulse voltammetry, which enabled evaluation of the changes of polythiophene’s electrochemical properties induced by the carbohydrate-protein recognition event. This biosensor can be easily prepared and quite promising for developing a label-free, reagent-less protein sensor based on the conductive polymeric substrates.

Lastly, poly (hydroxymethyl 3, 4-ethylenedioxythiophene), another substituted polythiophene derivative, was doped by molybdenum disulfide (MoS$_2$) nanomaterial to form a binary composite, which has been applied for environmental analysis of the bisphenol A pollutant. The formed poly (EDOT-OH)/MoS$_2$ composite showed synergistic electro-catalytic
response towards bisphenol A oxidation. A linear range of 0.5 to 100 \( \mu \)M was obtained. A favorable hydrogen bonding interaction between hydroxymethyl of polythiophene and bisphenol A’s phenol hydroxyls was supported by the quantum mechanical calculation, providing a reasonable explanation for this environmental sensor’s enhanced electro-catalytic sensing behavior.