Microstructural Manipulation and Architecture Design of Carbon-Based Electrochemical Systems

Xianwen Mao

Abstract

Carbon materials are important in electrochemistry. The often cited advantages of carbonaceous materials for electrochemical applications include wide potential working windows, tunable electrocatalytic activity for a variety of redox species, and ease of modifications either by covalent or by noncovalent functionalization. My thesis aims at elucidating the structure-property relationships of carbon-based electrochemical systems, to realize several important applications including electrochemical sensing, catalysis, and energy storage. Specifically, I have examined two classes of carbon-based electrochemical systems: electrospun carbon nanofibers (ECNFs) and redox polymer/carbon hybrid systems.

For the first type of material system, I have studied the effects of synthesis condition, architecture design, and post-treatment of ECNFs on their electrochemical properties of ECNFs, and explored the applications of ECNFs in electrochemical sensing and energy storage. I have studied the effects of the carbonization condition of ECNFs on their densities of electronic states (DOS) and electrochemical activities for a wide range of redox-active molecules. Additionally, I have demonstrated ultrawide-range electrochemical sensing using substrate-supported continuous high-DOS ECNFs. Furthermore, I have examined microwave-assisted controlled oxidation of high-DOS ECNFs for tailoring their electrocapacitive performance.

For the second type of material system, I have investigated the assembly methods and structural manipulation of redox polymer/carbon hybrid systems, and explored their applications in energy storage and catalysis. I have demonstrated that a redox-responsive polymer, polyvinylferrocene (PVF), is useful for noncovalent dispersion and redox-controlled precipitation of pristine carbon nanotubes (CNTs) in nonaqueous media. Moreover, using the stable PVF/CNT dispersion, I have demonstrated solution-based fabrication of PVF/CNT hybrids with controlled nanostructures for supercapacitor applications. Furthermore, I have demonstrated local oxidation-induced deposition of PVF onto a carbon fiber matrix for electrochemical control over heterogeneous catalysis.