Summary of the Ph.D. thesis

Title: "Thin films of functional redox materials for solar energy conversion, electrocatalysis, and energy storage".

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The present Ph.D. thesis describes research on preparation and characterization of thin films of organic functional materials based on the [C_{60}]fullerene, Co porphyrin, and Zn phthalocyanine derivatives as well as on carbon nanotubes, for solar energy harvesting, dioxygen electrocatalytic reduction, and electric energy storage.

The first part of the thesis is composed of three chapters devoted to electron donor-acceptor dyads. The first chapter describes preparation and characterization of the electron donor-acceptor dyad of uracil-appended [C_{60}]fullerene and 2-aminopurine, C_{60}ur-(2-AP). The dyad was self-assembled in a Langmuir film on the water-air interface by the Watson-Crick nucleobase paring. The second chapter describes investigations of the Langmuir and Langmuir-Blodgett (LB) films of the electron donor-acceptor dyad of (alkylether-appended Zn phthalocyanine)-(imidazole-derivatized [C_{60}]fullerene), Zn(TPPE)-C_{60}im. The third chapter presents results of the research of an electron donor-acceptor dyad composed of a polymer of triphenylamine-appended Zn porphyrin as the donor moiety and C_{60}im axially self-assembled to the Zn central atom, [$(Ph_3N)_4$ZnP polymer]-C_{60}im. Structure of the dyads was optimized with the DFT computing. Formation of dyads in Langmuir films and the film morphology were unraveled by Brewster angle microscopy imaging. Multilayer LB films of dyads and the [$(Ph_3N)_4$ZnP polymer]-C_{60}im construct were prepared on different solid substrates and characterized with the UV-vis, PM-IRRAS, and femtosecond transient absorption spectroscopic as well as electrochemical measurements, and AFM imaging. Finally, photoelectrochemical behavior of the multilayer LB film of the Zn(TPPE)-C_{60}im dyad and the [$(Ph_3N)_4$ZnP polymer]-C_{60}im construct was examined.

The second part of the thesis presents investigations of an electrocatalytic material for dioxygen reduction based on a polymer of Co porphyrin appended with triphenylamine peripheral substituents. A bidentate templating organic ligand was used to form a face-to-face dimer of two monomer molecules prior to electropolymerization. This templating enhanced electrocatalytic activity towards dioxygen reduction of the resulting polymer film. The film was characterized with different electrochemical and spectroscopic techniques as well as by AFM imaging.

The third part of the thesis describes electrochemical performance of an electric charge storage material composed of the electropolymerized ferrocene adduct of [C_{60}]fullerene immobilized over an electrophoretically deposited film of non-covalently modified single-wall carbon nanotubes. The electrophoretic deposition procedure was optimized and a charge storage device, composed of two identical Au disk electrodes coated with the composite films, was assembled. Then, electrochemical stability of the films in galvanostatic multi-cycle charging and discharging was evaluated. Finally, power of the fully or partially charged device was determined.