Single-Molecule Interfacial Electron Transfer Dynamics

H. Peter Lu
Email: hplu@bgsu.edu
Bowling Green State University, Department of Chemistry and the Center for Photochemical Sciences, Bowling Green, OH 43403

We apply single-molecule high spatial and temporal resolved techniques to study the complex reaction dynamics associated with electron and energy transfer rate processes.\(^1\)\(^-\)\(^5\) The complexity and inhomogeneity of the interfacial ET dynamics often present a major challenge for a molecular level comprehension of the intrinsically complex systems, which calls for both higher spatial and temporal resolutions at ultimate single-molecule and single-particle sensitivities. Combined single-molecule time resolved spectroscopy, femtosecond ultrafast spectroscopy, and electrochemical atomic force microscopy (E-Chem AFM) approaches are unique for heterogeneous and complex interfacial electron transfer systems because the static and dynamic inhomogeneities can be identified and characterized by studying one molecule at a specific nanoscale surface site at a time.\(^1\)\(^-\)\(^5\) The physical nature of the observed multi-exponential or stretched-exponential ET dynamics in the ensemble-averaged experiments, often associated with dynamic and static inhomogeneous ET dynamics, can be identified and analyzed by the single-molecule spectroscopy measurements. Single-molecule spectroscopy reveals statistical distributions correlated with microscopic parameters and their fluctuations, which are often hidden in ensemble-averaged measurements. The interfacial ET activity of individual dye molecules showed fluctuations and intermittency at time scale of milliseconds to seconds. The fluctuation dynamics were found to be inhomogeneous from molecule to molecule and from time to time, showing significant static and dynamic disorders in the dynamics. The inhomogeneous electron transfer rate due to the interaction between a dye molecule and the semiconductor surface depends on the chemical and physical nature of both dye molecule and the semiconductor.

Reference