

Clarkson University  
Department of Chemical and Biomolecular Engineering  
**Ph.D. Dissertation Defense**

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**“Fundamental Studies of Interfaces and Heterointerfaces of Photovoltaic Materials from  
Molecular-level Simulations”**

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Solar energy is increasingly becoming a significant contributor to renewables for powering portable devices, residential and commercial buildings. Highly efficient yet cost-effective photovoltaic materials are required to meet future demands for solar energy affordably. One of the strategies for making solar cells cheaper and solar energy more utilized is reducing the manufacturing cost of narrow band-gap substrates (e.g., silicon) for solar cells by employing an efficient single-crystalline silicon wafering technique like horizontal ribbon growth (HRG). Another strategy is developing solar cells, like dye-sensitized solar cells (DSSCs), based on cheaper broad band-gap substrates (e.g., titanium dioxide) that can sustainably power redox-mediated desalination of brackish water. However, the growth physics at the solidification front of HRG at fast growth rates desirable for commercialization is not well-understood. Also, DSSCs based on aqueous solvents are required to minimize contamination of the product stream from the desalination process. But the aqueous-based DSSCs show poor performance relative to traditional organic-based DSSCs, with no consistent explanation for the observed disparity.

In the first part of this dissertation, solidification models based on molecular dynamics (MD) simulations were developed to (1) provide a molecular-level understanding of fundamental growth processes occurring at the silicon crystal-melt interface (CMI) at high growth rates and (2) determine coefficients such as kinetic, diffusivity, segregation, needed for modeling and optimizing the HRG process. Results from the growth on the smooth silicon (111) surface showed mixed mechanisms of island nucleation, merger, and expansion accounted for the layer-by-layer growth of a silicon (111) facet. The nucleation rate was determined as a function of CMI undercooling temperature, from which a new two-dimensional (2D) nucleation kinetic coefficient is derived. Simulation of crystal growth on rough silicon surfaces showed a kinetics-dependent CMI instability at high growth rates. A surface with low interfacial kinetics was found to promote the growth of grain-boundary grooves and parallel twins and the transition of growth mode from single-crystalline to polycrystalline. Furthermore, silicon-carbon interactions were systematically modeled for application in solidification simulations to determine carbon diffusivity and segregation at the CMI and identify probable carbon incorporation sites.

In the second part of this dissertation, (1) time-dependent density functional theory (TD-DFT) calculations were performed to model the effects of implicit water and acetonitrile solvents, on the optoelectronic properties of two photosensitizers, ruthenium N719, and indoline D149 dyes and (2) MD simulations were performed to model dye-TiO<sub>2</sub> interface exposed to water and acetonitrile in the presence of co-adsorbents and electrolyte ions. The TD-DFT calculation of UV-vis spectra, lowest unoccupied molecular orbital (LUMO), and highest occupied molecular orbital (HOMO) energy levels showed that molar absorptivity and LUMO-HOMO energy levels for both dyes are weakly dependent on solvating media. From MD simulations, the water- and acetonitrile-based dye-electrolyte-TiO<sub>2</sub> heterointerfaces were compared using adsorbate conformations, number density distributions, and trajectory visualizations for the dye, solvent, and ions. Based on these comparisons, dye desorption, commonly believed to cause performance deterioration in aqueous DSSCs, is not the primary factor affecting photoanode efficiency. The redox potential and transport behaviors of electrolyte ions, and their direct access to anatase, are plausible factors. Insights from this work offer additional knowledge for guiding the rational design of more efficient aqueous DSSCs.

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Victor Fabiyi is a Ph.D. candidate in the Department of Chemical and Biomolecular Engineering under the supervision of Drs. Eunsu Paek and Sitaraman Krishnan. His atomistic and molecular modeling and simulation research provide insights for improving processes and rationally designing materials for photovoltaic applications. Victor earned his bachelor's degree in chemical engineering from Ahmadu Bello University, Nigeria.