Functionalized two-dimensional membranes and materials for solar-to-fuel devices: a multiscale computational approach

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Summary

In the current global context, there is a pressing need to address sustainable energy supplies to safeguard our Planet and its ecosystems. The choices made by human society have a significant impact on genetic evolution and climate. To ensure a better future for all, it is crucial to exercise foresight, foster collaboration across various sectors, and reach agreements based on fair and ethical principles. Science plays a pivotal role in advancing energy conversion, offering the potential for significant scientific breakthroughs that contribute to the protection and respect of our World. Specifically, the development of solar-to-fuel devices holds promise for achieving this transition to green energy. This Ph.D. dissertation centers on the development and functionalization of 2D membranes and materials, which constitute integral components of these conversion devices. The optimization of functionalized 2D materials necessitates a comprehensive computational design approach. This involves the adoption of a multiscale computational framework for the thorough design of these materials and the precise prediction and understanding of molecular processes, encompassing molecular self-assembly, ion transport, and catalytic surface reactions.

Chapter 3 of this dissertation focused on a computational study of two distinct molecular systems, namely hexa(2,2’-dipyridylamino) hexabenzocoronene (HPAHBC) and 2,2’:6’,2’’-terpyridine (TPY), illustrating how minor differences in molecular structure can significantly impact the aggregation process. Employing a classical Molecular Dynamics (MD) method and combining it with Density Functional Theory (DFT) and DFTB methods, the study accurately described the molecular interactions driving the self-assembly process, highlighting the roles of π-π stacking, hydrogen bonds, and steric hindrance.

Chapter 4 delved into the molecular aggregation of two specific systems, decacyclene, and B, B’, B’’-trianthryl-N, N’, N’’-tri(i-propyl) arylborazine, under Langmuir-Blodgett-like compression conditions. By replicating experimental settings, the research revealed the formation of ordered monolayers on the water surface driven by molecular symmetry, steric hindrance, and non-covalent intermolecular forces. Compression induced a reorganization process, resulting in bilayer formation for the decacyclene system and monolayer formation for the B, B’, B’’-trianthryl-N, N’, N’’-tri(i-propyl) arylborazine system. The computational analysis closely aligned with experimental data on compression isotherms and accurately estimated photochemical

properties such as absorption and fluorescence spectra, demonstrating the successful integration of DFT and classical MD techniques for the *de novo* design of 2D materials.

In order to advance the innovation of two-dimensional Proton Exchange Membranes (PEMs), a comprehensive understanding of proton transport through graphene nanopores appears crucial. In **Chapter 5**, a sophisticated computational approach was undertaken, employing a combination of ReaxFF Molecular Dynamics, metadynamics, and Density Functional Theory (DFT), to explore and enhance proton transport properties within a graphene nanopore. This enhancement was achieved through the introduction of a covalent benzenesulfonic functionalization to the graphene nanopore. The computational analysis consistently revealed significant improvements in proton permeability and selectivity of the benzenesulfonic functionalized graphene nanopore with respect to the hydrogenated graphene nanopore system. In the case of the benzenesulfonic functionalized graphene nanopore, the activation barrier for proton transport is ≈ 0.15 eV, and it exhibits proton selectivity over water molecules and sodium cation. This benzenesulfonic functionality played a dynamical role as a proton shuttle, fostering a favorable hydrogen-bond network and establishing an efficient proton transport pathway through the nanopore. An important outcome of the study was the identification of an optimal equilibrium between proton permeability and selectivity, a crucial factor in designing effective proton exchange membranes. Remarkably, the benzenesulfonic functionalized graphene nanopore system demonstrated a theoretically estimated proton diffusion of the order of 10^{-10} m^2 s^{-1}, comparable to or even surpassing the current state-of-the-art PEM, Nafion. As a result, the introduction of benzenesulfonic functionalization emerged as a highly promising approach for future developments of graphene-based membranes in energy conversion devices. The findings from Chapter 5 provide valuable insights and pave the way for further advancements in the field of 2D-PEMs and their role in new clean and renewable energy technologies.

The oligomeric ruthenium-based catalyst $Ru(bda)_n$ has been observed to attach to graphitic surfaces through CH-π stacking interactions. This anchoring method offers precise control over molecular coverage and enhances the catalytic efficiency of water oxidation, resulting in high current density at pH 7. The oligomeric nature of $Ru(bda)_n$ provides multiple anchoring sites, significantly bolstering the stability of the hybrid catalyst-graphitic surface anode through dynamic bonding. However, the precise influence of this dynamic anchoring on the overall catalytic mechanism is still under debate. To address this question, **Chapter 6** presents a computational study that utilizes DFT-based molecular dynamics simulations. The study focuses on investigating the rate-limiting proton-coupled electron transfer (PCET) event in the catalytic cycle of a Ru(bda)$_n$ oligomer anchored on a graphitic surface. The CH-π stacking anchoring not only stabilizes the catalyst-graphitic surface system but also facilitates the proton-coupled electron transfer through a suggested vibronic couplings. Additionally, the computational assessment uncovers a disparity between the spin configuration of the resulting product and the literature experimental data. Specifically, the product quartet spin state is determined to have a higher Kohn-Sham (KS) potential energy compared to the experimentally observed product doublet spin state. An analysis of constant potential energy shows that the KS potential energy of the product doublet spin state is equivalent to that of the reactant triplet spin state, offering new insights into understanding the catalytic mechanism. This chapter significantly contributes to our understanding of the anchoring and catalytic behavior of the oligomeric ruthenium-based water oxidation catalyst (WOC) on graphitic surfaces. The integration of computational methods and experimental data sheds light on the intricate interactions and mechanisms involved, paving the way for future advances in heterogeneous catalysis and water oxidation technologies.

In **Chapter 7**, the Ph.D. dissertation concludes with ongoing investigations. Two significant advancements are highlighted in this chapter, namely the development of an electron reactive force field (eReaxFF) for a dye-RuWOC molecular system and the creation of a Martini 3.0 Coarse-Grained parametrization for hexabenzocoronene (HBC). The eReaxFF force field aims the study of proton-coupled electron transfer (PCET) events within the dye-RuWOC molecular system, offering a pseudoclassical computational approach that allows for longer timescale simulations compared to traditional DFT-based molecular dynamics. This work holds tremendous potential for understanding complex electron transfer processes and catalytic reactions in various chemical systems. On the other hand, the Martini 3.0 Coarse-Grained parametrization of HBC empowers researchers to investigate molecular aggregation at the water-to-air interface at an extended timescale. This Coarse-Grained approach reduces the computational complexity and resources required for studying large molecular systems, such as HBC-based nanowires, offering insights into their behavior and interactions that were previously computationally prohibitive at the atomistic level. The incorporation of these advanced techniques and methodologies in computational chemistry and material science research opens new avenues for exploring complex molecular phenomena and designing novel functional materials.