Abstract

Currently, there is a significant and ongoing effort to replace fossil fuels with more sustainable, environmentally friendly, and cost-effective alternatives. Using solar energy to synthesize fuels appears to be a valuable option because of the large availability and affordability of sunlight. In this context, photocatalytic technologies are promising solutions for solar fuel production. In this thesis, we focus on the use of soap films as fundamental component of a future prototype for solar fuel generation. Soap films are expected to be interesting for their potential use as soft, self-assembled and recyclable membranes. The intrinsic possibility of tuning their properties via tailored underlying chemistry makes them flexible enough for a wide range of different physico-chemical applications. Soap films can be regarded as a continuum mean separating two gas volumes and are stabilized by surfactant molecules that self-assemble at the gas-liquid interfaces, lowering surface tension. The envisioned photoreactive soap film consists of two opposite monolayers composed of photoactive molecules that allow the two half reactions of water oxidation and carbon dioxide reduction. The latter two half reactions are part of the desired overall photochemical reaction that will ultimately convert carbon dioxide into fuel using solar energy.

For the sake of simplicity, we start analysing separately the several involved phenomena. Initially, we focus on gas transport through a single membrane realized in the form of soap-film since the gases must be generated and kept separated for both safety and storage purposes. To this end, while diffusion phenomena in the water core and surfactant monolayers are described by a continuum model, molecular dynamics is used to compute static and dynamical properties of water, gases and surfactants in the surfactant monolayers. The obtained atomistic details are incorporated in a drift-diffusion model for consistently extracting a boundary condition for the above continuum model describing transport phenomena at a larger scale. The developed model is used to estimate the characteristic time for disparate gas mixing when initially separated by soap film membranes. In this respect, we make use of a novel

device for the detailed experimental characterization of the soap film permeability to gases. Additionally, we analyzed the process of spraying photoactive molecules on the two surfactant monolayers of a single soap film with the aim of generating a dissymmetric self-assembled structure. The latter approach is a novel and crucial strategy for producing oxygen and fuel in two separated compartments.

Finally, we elaborate a multi-scale and multi-physics model to describe the relevant phenomena other than gas transport occurring in a single photosynthetic membrane. We present a macro scale continuum model, which now accounts also for the transport of ionic species within the soap film, the chemical equilibria and the two involved photocatalytic half-reactions of the CO_2 reduction and water oxidation at the two gas-surfactant-water interfaces of the soap film. Then, we introduce a mesoscale discrete Monte Carlo model, to deepen the investigation of the structure of the functional monolayers. The model is validated both for soluble and insoluble surfactants. The morphological information obtained at the mesoscale level is integrated into the continuum model through a properly redefined reaction constant of the two half-reactions. The developed tools are then used to perform sensitivity studies in a wide range of possible experimental conditions to provide scenarios on fuel production by such a novel approach.

In conclusion, we analysed the physical and chemical phenomena envisioned in a new kind of self-assembled photosynthetic membrane based on soap films. In particular, we aim at providing a multi-scale and multi-physics perspective in order to provide valuable insight on the photocatalytic production of fuels in soap films and possible device optimization strategies.