Abstract

This dissertation describes efforts over the last five years to develop protective layers for semiconductor photoelectrodes based on monolayer or few-layer graphene sheets. Graphene is an attractive candidate for a protective layer because of its known chemical inertness, transparency, ease of deposition, and limited number of electronic states. Monolayer graphene was found to effectively inhibit loss of photocurrent over 1000 seconds at n-Si/aqueous electrolyte interfaces that exhibit total loss over photocurrent over 100 seconds. Further, the presence of graphene was found to effect only partial Fermi level pinning at the Si/graphene interface with respect to a range of nonaqueous electrolytes. Fluorination of graphene was found to extend the stability imparted on n-Si by the monolayer sheet in aqueous $Fe(CN)_6^{3-/4-}$ electrolyte to over 100,000 seconds. It was demonstrated that the stability of the photocurrent of n-Si/fluorinated graphene/aqueous electrolyte interfaces relative to n-Si/aqueous electrolyte interfaces is likely attributable to the inhibition of oxidation of the silicon surface.

This dissertation also relates efforts to describe and define terminology relevant to the field of photoelectrochemistry and solar fuels production. Terminology describing varying interfaces employed in electrochemical solar fuels devices are defined, and the research challenges associated with each are discussed. Methods for determining the efficiency of varying photoelectrochemical and solar-fuel-producing cells from the current-voltage behavior of the individual components of such a device without requiring the device be constructed are described, and a range of commonly employed performance metrics are explored.