Chapter 1

Introduction

1.1 Purpose and Scope

This dissertation describes my research efforts in the field of photoelectrochemistry in the Lewis group between January 2011 through December 2015. It has been written in part to fulfill the requirements of a doctoral degree in chemistry from the California Institute of Technology. It has also been written with the hope that future researchers in the fields of photoelectrochemistry and solar fuels find its contents useful in furthering their own work; it also serves as an archive of the research that I was unable to publish during my time at Caltech and as a mechanism by which I hope to convey my opinions on the strengths and well as weaknesses of the work that I have performed.

Chapter 1 serves as a brief overview of the rest of this dissertation and includes a discussion of the work described in Chapters 2-5 from a personal viewpoint.

Chapters 2 and 3 describe my efforts to address controversial topics in the field of photoelectrochemistry. Chapter 2 focuses on defining nomenclature and taxonomy sufficient to differentiate solar fuels generator devices into two groups:

1. Those that are essentially photovoltaic devices whose electrochemical properties are independent of the electrolyte with which they operate.
2. Those that are photoelectrochemical devices whose properties and efficiency actively depend on the nature of the electrolyte environment in which they operate.

Because these different devices have varying advantages as well as research challenges associated with them, identifying a device as such allows researchers to quickly understand the context in which new systems of either variety should be viewed. Chapter 3 discusses methods necessary to determine the efficiency of a hypothetical solar fuels generator device without requiring that the device of interest actually be constructed. Because actual device construction entails significant engineering efforts, the ability to determine the efficiency of a hypothetical system facilitates comparison of the efficacy of new components in solar fuels generating devices to previously reported components without concern that inconsistent engineering may prevent a one-to-one comparison. The bulk of the work in both chapters was published in 2015 in *Energy and Environmental Science*.

Chapters 4 and 5 describe my efforts to understand the photoelectrochemical activity of graphene-covered silicon photoelectrodes. In particular, chapter 4 discusses the activity of pristine graphene monolayers on n-Si electrodes and demonstrates that stability in aqueous electrolyte is imparted to n-Si electrodes by the presence of a graphene protective layer. However, this stability is only demonstrated over 1,000 seconds, as demonstration of further stability was hindered by inconsistent results.

Chapter 5 discusses the related photoelectrochemical behavior of fluorinated graphene (F-Gr) on n-Si electrodes. The fluorination of graphene was found to improve the stability of the photoelectrochemical activity of F-Gr-covered n-Si surfaces in aqueous electrolyte to over 100,000 seconds, representing a two order-of-magnitude increase over pristine graphene. The bulk of the work described in chapter 4 was published in *The Journal of the American Chemical Society* in 2013 and the work in Chapter 5 is currently prepared for submission to peer review as of January 2016.

Chapter 6 reviews a number of additional efforts that I undertook that, because of incompleteness or lack of reproducibility, have yet to be prepared for peer review. These efforts include the following: work to understand the effect of multilayer graphene at Si interfaces, demonstration of the use of pristine graphene monolayers to prevent silicide formation, a survey of efforts to understand the impurities left behind by different graphene transfer methods, and a brief foray into the use of ALD to modify pristine graphene surfaces. I believe each of these, with sufficient care, are worthy of future efforts, and I hope chapter 6 can serve as a starting point for other researchers in this regard.

1.2 Personal Summary

The vast majority of the experimental work that I have performed in the Lewis group has related to understanding the chemical and photoelectrochemical behavior of n-type silicon photoanodes covered by monolayer sheets of graphene. The idea for this project was originally formulated by Nate just prior to my arrival at Caltech, and I began work on it in conjunction with a postdoc in the Lewis group and a graduate student at Columbia University, Matt Bierman and Nick Petrone, in May of 2011 after four months of work on measuring the kinetics of the surface reaction on silicon surfaces.

This project immediately proved to be promising, as n-Si electrodes covered by monolayer graphene showed significantly improved stability in aqueous electrolytes relative to uncovered n-Si electrodes. Furthermore, it was clear that the graphene did not fully pin the Fermi level of the silicon surface relative to nonaqueous redox couples. This was particularly exciting, as it suggested that graphene might be an ideal protective layer for a range of semiconductors in a photoelectrochemical motif since the graphene Fermi level could be modified by modification of the electrochemical potential of the electrolyte solution. With this in mind, another postdoc in our group, Fan Yang, began working on understanding the photoelectrochemical behavior of graphene-covered GaAs surfaces in aqueous electrolyte. While graphene did also inhibit deleterious reactions at the GaAs surface in contact with aqueous electrolyte, the protective ability of graphene on GaAs was limited in comparison to Si due to corrosion of GaAs at graphene imperfections leading to undercutting and eventual loss of graphene from the surface. This was in comparison to the passivation of Si that occurred at graphene imperfections.

However, despite the success that we found using graphene as a protective layer for silicon surfaces, problems existed. Specifically, the stability imparted by graphene to the Si was inconsistent from batch-to-batch of CVD grown graphene. This made further study of this interface challenging as the fabrication time per electrode was high. I tried a number of avenues to solve this issue. Among them, Ron Grimm and I built our own CVD chamber to grown graphene in an attempt to control the quality of the graphene employed in these experiments. Additionally, extensive effort was poured into understanding the nature of impurities and imperfections at the Si/graphene interface using Raman and XP spectroscopy. Unfortunately, in spite of these efforts, inconsistent results, particularly with regard to the imparted stability by graphene coverage on Si, is the major limiting factor in further studying graphene/Si interfaces in photoelectrochemical devices. This is perhaps not surprising as we are working with single-atom thick sheets of material in a non-cleanroom environment; however, based on the promising results that I have observed, I believe that these limitations are purely practical in nature. In retrospect, focusing on fabrication of micro- or ultramicroelectrodes of graphene-on-silicon surfaces via lithographic methods in an attempt to isolate a pristine, defect-free, impurity-free, graphene/silicon interface would have been a rational decision.

Concurrently with this work, I embarked on understanding the details of the field of photoelectrochemistry, which eventually led to my collaboration with Nate, Matt Shaner, and Rob Coridan, on the work that is discussed in chapters 4 and 5. Writing these papers was extremely satisfying as it forced us to carefully evaluate our understanding of the underpinnings of our field as well as provide a guide for researchers new to the field to orient themselves with.

Meanwhile, two enterprising graduate students, Chris Roske and Annelise Thompson, came up with the idea that perhaps fluorination of the graphene surface would improve its performance both in terms of protection of silicon from oxidation as well as the quality of rectification and charge separation at the interface. As related in chapter 5, we found that fluorination of graphene that otherwise was ineffective as a protective layer for Si allowed for protection of underlying silicon in aqueous solution. This relieved some, but not all, of the problems associated with the inconsistencies we had found with graphene. Furthermore, Jackie Maslyn demonstrated that these fluorinated graphene surfaces were capable of acting as physical barriers to prevent other deleterious reactions at the semiconductor surface as well, including the formation of metal silicides during evaporation of metals onto Si surfaces. As of January 2016, Annelise is continuing to try and understand the advantages and limitations, as well as the fundamental properties, of 2D materials at semiconductor/electrolyte interfaces.