FUNCTIONALIZED GRAPHENE SHEETS IN
DYE-SENSITIZED SOLAR CELL
COUNTER ELECTRODES

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Abstract

The use of thermally exfoliated graphite oxide, commonly referred to as functionalized graphene sheets (FGSs), was investigated as a catalytic counter electrode material in dye-sensitized solar cells to substitute for platinum nanoparticles traditionally used in devices. A catalyst’s activity depends both on the material’s intrinsic activity as well as on its surface area accessible for reaction. Thus, this work aimed i) to determine the intrinsic activity of FGSs with various chemical compositions and structures, and ii) to create high surface area networks of FGSs to use as catalytic electrodes in dye-sensitized solar cells.

Monolayers of FGSs were fabricated and electrochemically tested to determine the intrinsic catalytic activity for a common dye-sensitized solar cell redox mediator, cobalt bipyridine. It was found that lattice defect rich, oxygen-site poor FGSs catalyze the reduction of the cobalt complex as well as platinum does, exhibiting a rate constant of $\sim 6 \times 10^{-3}$ cm/s. This rate is an order of magnitude faster than exhibited with oxygen-site rich graphene oxide, and over two orders of magnitude faster than found with the basal plane of graphite (as a surrogate for pristine graphene).

FGSs are less catalytic towards the iodide/triiodide redox mediator, thus larger surface areas must be used for effective catalysis. In this work, conductive, high surface area networks of FGSs were produced by first tape casting surfactant-stabilized aqueous suspensions of FGSs and then thermolyzing the surfactant materials. Iodide/triiodide mediated dye-sensitized solar cells using these FGS electrodes exhibited power conversion efficiencies within 10% of devices using platinum nanoparticles. Furthermore,
to interpret the catalytic activity of FGSs towards the reduction of triiodide, a new electrochemical impedance spectroscopy equivalent circuit was proposed that matches the observed spectra features to the appropriate phenomena.

Lastly, improved catalytic performance was achieved through better control of electrode morphology. By using ethyl cellulose as a sacrificial binder, and partially thermolyzing it, electrodes were created which exhibited lower effective charge transfer resistance (< 1 Ω-cm$^2$) than the traditional platinum electrodes for the iodide/triiodide, the cobalt bipyridine, and a sulfur-based redox couple. Dye-sensitized solar cells using these FGS electrodes had power conversion efficiencies equal to or greater than those using platinum nanoparticles with each of the three major redox mediators.
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4. US61696565 Nano-Graphene and Nano-Graphene Oxide, Preliminary Application

3. US61391668 Graphene Electrodes for Solar Cells, Full Application

2. US12949448 Graphene Tapes, Full Application

1. PCT/US2010/57201 Semiconductor Coated Microporous Graphene Scaffolds, Full Application
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1 Introduction

In this chapter how current energy practices are contributing to climate change is presented, followed by a discussion of how photovoltaics have been advancing to mitigate emissions of warming agents.

1.1 Climate Change and Energy

Parts of this section are adapted from work coauthored with Ilissa Ocko and submitted to the Woodrow Wilson School of Public and International Affairs for a certificate in Science, Technology and Environmental Policy.¹

Although humans have always adapted their environment to better meet their needs, with industrialization and a population surpassing seven billion, these environmental changes are now global in scale. Many of these changes are driven by energy consumption. Primary energy use stands at a global average of over 15 TW, having increased almost 10% since the beginning of this thesis, and energy demand is projected to increase by 50% over the next 25 years, primarily in less developed countries.² Our current energy generation system relies extensively on the combustion of fossil-fuels – oil, gas, and coal. Although vast reserves can be extracted to meet our demand for the foreseeable future, the supply is finite, and accessing these resources will continue to become more complex. Furthermore, the immediate (e.g., the Deepwater Horizon oil spill)
and the long-term consequences (e.g., climate change) of these technologies range from disruptive to devastating.

![Figure 1.1: Emissions of warming agents from 1850 to 2010. This analysis does not include cooling agents such as sulfate or organic carbon, nor does it take into account secondary effects such as chlorofluorocarbons destroying stratospheric ozone. Montreal Protocol Gases include the major ozone depleting substances regulated by the treaty. See Appendix A for details. Adapted from Roy-Mayhew and Ocko.](image)

Climate change is an unintended consequence of our current energy system due to the emission of large quantities of greenhouse gases (GHGs) and warming aerosols, the most prevalent being carbon dioxide. Anthropogenic emissions, the vast majority from the energy sector, are changing the composition of Earth’s atmosphere, thereby altering how much energy is absorbed, reflected, and radiated by Earth. Figure 1.1 shows
anthropogenic emissions since 1850, normalized to carbon dioxide, using the integrated radiative forcing for each warming agent over a hundred years (100-year global warming potential, GWP\textsubscript{100}). These emissions are projected to grow concomitant with the rise in energy demand.

By altering the global radiative balance, emitted warming agents contribute to atmospheric temperature rise as well as a host of other effects which have the potential to disrupt ecosystems and induce regional conflicts. Although precise changes are not clear, a plethora of evidence suggests that continuing to emit large quantities of warming agents – such as would occur if we are to meet our surging energy demand with fossil fuels – will lead to a much warmer planet.\textsuperscript{3} Figure 1.2 shows predicted global average temperature increases as a function of atmospheric GHG concentration. The current atmospheric concentration of carbon dioxide is almost 400 ppm (up from ~270 ppm preceding the industrial revolution).\textsuperscript{4} Adding to this value concentrations from methane, nitrous oxide and the other warming agents in the atmosphere, current concentrations are already pushing into region III. Thus we can expect temperatures to increase 2-4.5 °C from preindustrial levels, and even more as emissions continue.

In addition to global warming, we can expect continued sea level rise and ocean acidification, as well as more frequent and more intense storms.\textsuperscript{3} Many of these changes will not occur evenly over the planet. It is predicted that the extra energy in the atmosphere and ocean with lead to a shift toward the extremes, with arid regions becoming drier and tropical regions getting wetter.\textsuperscript{3}
Many governments are beginning to understand and address these risks. Since 2009, over 130 nations—including all major emitters—have declared that a 2 °C increase in global average temperatures represents “dangerous anthropogenic interference with the climate system,” as described in the Framework Convention on Climate Change. To limit warming to only ~ 2 °C without resorting to geoengineering, emissions must be drastically reduced in the near future.

Precedents exist for rapid changes at large scale. For instance, a swift decline in emissions can be seen as a result of international agreement. The Montreal Protocol phased out ozone depleting – and climate warming – substances, reducing their emissions by 85% in a few years (see Figure 1.1). A second example can be seen to be a result of a
CHAPTER 1

disruptive technology. In France, nuclear fission became the dominant source of electricity in less than 15 years (see Figure 1.3). With failures in Copenhagen, Cancun, and Durban to solidify binding global agreements to mitigate greenhouse gases, and the ending of the first commitment period of the Kyoto Protocol in 2012, attention has increasingly focused on the development and deployment of reduced emission technologies that can compete without global regulatory frameworks in order to mitigate emissions. In particular, disruptive energy technologies such as those for natural gas (primarily made up of methane), wind, and solar are sought.

![Electricity generation in France from 1971-1989. Data ascertained from an International Energy Agency figure.](image)

**Figure 1.3:** Electricity generation in France from 1971-1989. Data ascertained from an International Energy Agency figure.7

Solar energy is one of the few sources which can meet the global energy demand (notable others include nuclear fission and fusion). Radiating more power to the Earth’s
surface every hour than the world uses each year, the sun provides an abundant and
available resource around the globe. Effectively harnessing this energy is one of the main
challenges of the 21st century. Photovoltaic solar cells (PV) can do so with low emissions
of warming agents. No emissions are generated during the use of PV, but there are
emissions associated with the production of current technologies – particularly long-lived
fluorinated gases for the fabrication of silicon and thin film devices.8,9 Governments and
the private sector have looked to affordably harness this abundant resource; however, the
high cost, intermittency, and low power density of PV have kept them from being
competitive. Rapid advancements in the technology have taken place over the last decade
(discussed further in Section 1.2), but even so, more cost reductions and performance
improvements must be made for PV to become a major energy player and displace more
polluting technologies.

1.2 Photovoltaic Solar Cells

The PV landscape looks very different now than it did when work on this thesis
began. Over the past five years, PV went from being an expensive, niche energy source to
a mainstream commodity that can compete with conventional energy generation at some
locations. For instance, it was recently announced that First Solar plans to sell electricity
for less than $0.06/kWh from a utility-sized solar installation in New Mexico.10 Due to
sharp cost reductions as well as from government incentives, especially in Europe, PV
installations grew rapidly, as can be seen in Figure 1.4. In 2011 alone, almost
30 gigawatts of peak capacity (GWp) were added worldwide. Assuming the industry
average capacity factor of about 20%,\textsuperscript{11} this addition represents 6 GW of production capability, enough to displace about six large nuclear plants or twelve average sized coal-fired power plants.\textsuperscript{12} PV module (and balance of system) prices are predicted to continue to decrease, and installations are predicted to continue to grow with China and the United States becoming increasingly important players.\textsuperscript{13} Although this growth is impressive, total capacity (~ 70 GW\textsubscript{P} in 2011) is still a miniscule fraction of the rate that energy is consumed in the world today (> 15 TW). Further improvements in device efficiency and reductions in system costs will be required for PV to play a major role in meeting future energy demand with reduced environmental impact.

![Global average PV module price and capacity additions since 2008](image)

**Figure 1.4:** Global average PV module price and capacity additions since 2008. Capacity additions for 2012 are a projection with error bars based on mid-year data.\textsuperscript{14} Costs are from the National Renewable Energy Laboratory.\textsuperscript{15} Capacity values are from BP,\textsuperscript{16} though they align with data from the European Photovoltaic Industry Association.\textsuperscript{13}

All PV technologies aim to convert solar energy to electricity and they do so by i) absorbing photons to excite electrons in the material, ii) separating these electron from their holes, and iii) transporting these charges to the device’s anode and cathode, respectively. In the following sections, we discuss the make-up of technologies currently
Chapter 1

in the market and describe their basic characteristics (1.2.1), and then we introduce two emerging technologies: organic solar cells and dye-sensitized solar cells (1.2.2).

1.2.1 Current Technologies

Crystalline silicon has been the dominant PV technology since its commercialization. Nevertheless in 2010, for the first time, polycrystalline devices edged out monocrystalline ones for the top market share, 48% to 37%, as can be seen in Figure 1.5. Cadmium telluride cells, currently the cheapest modules to manufacture, comprise the third largest segment, followed by other emerging thin-film technologies.

Figure 1.5: Global annual PV module production by technology from 1999 to 2010. Thin film technologies include copper indium gallium selenide and copper indium selenide (CIGS/CIS), cadmium telluride (CdTe), and amorphous silicon (α-Si). Crystalline silicon technologies include single crystals created by the ribbon process (Ribbon Si) and the Czochralski method (Cz) as well as polycrystalline silicon (PxSi). This figure is originally from the Navigant Consulting Photovoltaic Service, and reproduced by the National Renewable Energy Laboratory.11
In crystalline silicon devices, relatively thick layers (150+ µm) of silicon are used to absorb photons, as well as to separate and transfer charge.\textsuperscript{17} To prevent electron and hole recombination, high purity silicon (> 99.999995%) is used and doped to create a p-n junction (\textit{i.e.}, an internal electric field) in the device.\textsuperscript{18} Currently, as can be seen in Figure 1.6, the record power conversion efficiency ($\eta$, defined as the ratio of power incident on the solar cell to the maximum power produced by the solar cell) of monocrystalline research cells at 1 sun illumination is 25%, close to the theoretical Shockley-Queissser limit for silicon devices (\textasciitilde 30%).\textsuperscript{19}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_6.png}
\caption{Record research PV cell efficiencies from 1976 to 2012. Reproduced from the National Renewable Energy Laboratory.\textsuperscript{20}}
\end{figure}
Polycrystalline films are less expensive to produce than large single crystals; however, grain boundaries reduce the $\eta$ of the solar cells. Although silicon is abundant, the processing techniques required to use the material in solar applications are energy intensive and costly. Thin film technologies have several advantages based on the fact that they use materials which absorb much more strongly than silicon. This quality allows for the creation of thinner devices which use much less material, and which can be created via high throughput deposition schemes such as solution processing, chemical vapor deposition, and sputtering. Nevertheless, these solar cells have low efficiencies (e.g., amorphous silicon), or use rare (e.g., indium, tellurium) or toxic (e.g., cadmium) elements.

Due to the tradeoffs of current technologies, combined with the rapid reduction in manufacturing costs and increases in module efficiencies of the past four years, it is no surprise that the PV landscape has changed considerably. For example, in 2010, the top five producers of solar cells in the United States were Solar World (251 MW$_p$, U.S. production, mono- and polycrystalline silicon), First Solar (222 MW$_p$, cadmium telluride), Suniva (170 MW$_p$, monocrystalline silicon), Evergreen Solar (158 MW$_p$, monocrystalline silicon), and United Solar Ovanic (120 MW$_p$, amorphous silicon).$^{11}$ Of these, Evergreen Solar and United Solar Ovanic has since filed for bankruptcy, and Solar World may follow suit as its stock has lost over 98% of its value. With the large potential market for solar energy and the continued development of new technologies, the shake out is likely to continue.$^{21}$
1.2.2 Emerging Technologies

Even with the dramatic cost reductions of the past few years, several emerging technologies could prove disruptive from either a cost or functionality standpoint. Organic solar cells use polymers or small molecules to absorb light and separate charge. Rather than an electron-hole pair, an exciton is created, which has a diffusion length on the order of 10 nm. Thus, interfacial engineering is of paramount importance in these devices. Organic solar cells are generally ~100 nm thick, and can be made through solution processing or thermal evaporation of acceptor and donor molecules. By stacking multiple cells in a tandem structure, each with a different absorption range, devices exhibiting $\eta$ over 11% have been fabricated (see Figure 1.6). For organic solar cells to compete in the marketplace, long-term stability concerns must be addressed and low-cost manufacturing, as suggested by the large-scale processing techniques, must be realized.

Another promising technology is a hybrid organic-inorganic device called a dye-sensitized solar cell (DSSC). This cell type combines the frugal material use of thin film devices, the flexibility provided by organic chemistry, and the stability and $\eta$ of inorganic devices by employing specialized materials for specific cell functions such as photon absorption, charge separation, and charge transport. Details on how DSSCs operate can be found in Section 2.1. By 1997, efficiencies over 10% were achieved; however, little progress in this area has been made since then. Nevertheless, research has focused on ways to reduce the material and processing costs, and several companies have been formed to commercialize the technology. Although DSSCs originally aimed to displace
conventional PVs based on an economy of scale price point of around $0.5/W_p, due to the reduced price of silicon and cadmium telluride solar modules, the market entry for DSSCs has shifted to niches where the technology excels, such as in low light conditions, in portable electronics, and in flexible applications. To become competitive at the utility scale and have an impact on meeting future energy demand in an environmentally sensitive way, further efficiency improvements and cost reductions are needed. One way to contribute to this goal is to replace the traditional cathode, which requires platinum and high temperature processing, with an inexpensive, yet effective alternative. Investigating the use of carbon materials for this purpose is the focus of this dissertation as detailed in the next section.

1.3 Goals and Outline of this Dissertation

In this dissertation, the role of functionalized graphene sheets (FGSs) in DSSC counter electrodes is explored. This work focuses on creating a scalable, low cost, and highly active catalytic electrode to use as a device cathode. An electrode’s catalytic activity is dictated by its intrinsic activity and the surface area available for catalysis. Thus, the main goals of this work are to: i) understand the intrinsic activity of pristine graphene and graphene defect sites towards DSSC redox couples, ii) fabricate high surface electrodes using highly active FGSs, and iii) develop stand-alone electrodes which are both conductive and catalytic. Underlying all of these goals is the need to explore and better understand the link between the material’s structural, electronic, and catalytic properties.
Chapter 2 provides a background on both DSSCs and graphene materials, focusing on FGSs which are created through the simultaneous exfoliation and reduction of graphite oxide. The production of FGS and techniques to characterize the physical and electrical properties of our electrodes are elaborated upon in Chapter 3. This section includes specific experimental details which are general to each of the subsequent chapters. Study specific experimental methods, such as electrode preparation techniques, are discussed in the beginning of the chapters which detail the studies that they are used in. Studies to determine the intrinsic catalytic activity of graphene defect sites toward a common cobalt-based DSSC redox couple are presented in Chapter 4. These studies employ monolayers of FGSs which have undergone different heat treatment processes and they correlate electrochemical performance with FGS chemical makeup and structure. A manuscript detailing this work has been prepared. In Chapter 5, the processing and properties of a tape-cast porous FGS electrode and its use in a DSSC are discussed. A new electrochemical impedance spectroscopy model for porous carbon electrodes is also presented. These results have been published in two papers appearing in *ACS Nano*. A second generation electrode, created through partial decomposition of a polymer-FGS composite, is presented in Chapter 6. The improved catalytic performance of the second generation electrode – matching or exceeding that of platinum nanoparticles – is investigated. The electrode’s use in multiple redox systems is also explored. This work has been published in *ACS Materials & Interfaces*. Lastly, Chapter 7 summarizes the conclusions drawn from the work presented and provides recommendations for future research.
Appendix A

Emissions data for warming agents

Climate forcers considered in this analysis are carbon dioxide (CO$_2$), nitrous oxide (N$_2$O), chlorofluorocarbons and hydrochlorofluorocarbons (herein Montreal Protocol Gases), perfluorocarbons (PFCs), sulfur hexafluoride (SF$_6$), nitrogen trifluoride (NF$_3$), black carbon (BC), methane (CH$_4$) and hydrofluorocarbons (HFCs). The majority of emissions data presented in Figure 1.1 were obtained by analyzing data from three main sources: The Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4),$^3$ the Representative Concentration Pathways (RCP) emissions database,$^{27}$ and the U.S Energy Information Administration Emissions of Greenhouse Gases Report.$^{28}$ These databases are compilations of data from various sources, and details of the original sources can be found below. Where data were incomplete, we used individual references from peer-reviewed literature. Specific calculations and data, with their respective sources can be found in the following. GWPs can be calculated from Equation 1:

$$GWP(\alpha, t) = \frac{\int_0^t F_\alpha e^{-t/\tau_\alpha} dt}{\int_0^t F_{CO_2} \times r(t) dt},$$ (1)

where $\alpha =$ agent of interest,

$t =$ time horizon (years),

$F_\alpha =$ specific radiative forcing of agent $x$, $\frac{W}{m^2 \times kg}$,

$\tau_\alpha =$ atmospheric lifetime of forcer $\alpha$, (years),
r(t) = 0.217 + 0.259 \times e^{-t/172.9} + 0.338 \times e^{-t/18.51} + 0.186 \times e^{-t/1.186},

derived from the atmospheric lifetime of CO$_2$ from the Bern Carbon Cycle Model for the decay of CO$_2$ as a function of time.\textsuperscript{3, 29}

Values for $F_x$ and $\tau_x$ are provided in Table 1.1.

**Table 1.1:** Specific radiative forcing, atmospheric lifetime, and select GWPs for warming agents. Specific radiative forcings compiled from Table 2 in Fuglestvedt et al.\textsuperscript{30} unless otherwise noted. Lifetimes and 20-, 100- and 500-year GWPs compiled from Table 2.14 in Forster et al.\textsuperscript{31} GWP$_1$ calculated using equation (1). a: Lifetime of CO$_2$ calculated from the Bern Carbon Cycle Model.\textsuperscript{3, 29} b: Specific radiative forcing back-calculated using equation (1) for agents not listed in the IPCC AR4.

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<tr>
<th>Agent</th>
<th>Specific Rad. Forcing (Wm$^{-2}$kg$^{-1}$)</th>
<th>Atmospheric Lifetime (years)</th>
<th>GWP$_1$</th>
<th>GWP$_{20}$</th>
<th>GWP$_{100}$</th>
<th>GWP$_{500}$</th>
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<td>1</td>
<td>1</td>
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An approximation that goes into the GWP calculations is that we always use a background CO$_2$ concentration of 378 ppm similar to the IPCC AR4.\textsuperscript{3} We deemed this the clearest way to compare the emissions over time. However, using actual CO$_2$ concentrations from 1850 to 2000, and projected CO$_2$ values to 2050, would change the values reported. For instance, when background CO$_2$ concentrations are lower, the denominator in Equation 1 will become larger for a given time horizon, resulting in a smaller GWP for each forcer. This is due to a saturation effect of light absorption in the atmosphere resulting in a slight reduction in radiative forcing for each additional CO$_2$ molecule added to the atmosphere. In the future, when the background CO$_2$ concentration is larger, the denominator would become smaller and the GWP for any warming agent would become larger.

The emissions data used for Figure 1.1 are presented in Tables 1.2, 1.3, and 1.4. The historical emissions data are from the 2009 RCP Database unless otherwise mentioned.\textsuperscript{27} This database is a compilation of data from various sources, including Bond \textit{et al.},\textsuperscript{32} Buhaug \textit{et al.},\textsuperscript{33} Eyring \textit{et al.},\textsuperscript{34} Hurtt \textit{et al.},\textsuperscript{35} Lamarque \textit{et al.},\textsuperscript{36} Lee \textit{et al.},\textsuperscript{37} Mieville \textit{et al.},\textsuperscript{38} Schultz \textit{et al.},\textsuperscript{39} and Van der Werf \textit{et al.}\textsuperscript{40}
Table 1.2: Historical annual emissions (1850-1920) in kilotonnes for agents used in this study, compiled from the RCP Database,\textsuperscript{27} except where noted. a: Emissions from Weiss et al.\textsuperscript{41}

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<th>1870</th>
<th>1880</th>
<th>1890</th>
<th>1900</th>
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Table 1.3: Historical annual emissions (1930-2000) in kilotonnes for agents used in this study, compiled from RCP Database\(^2\) except where noted. a: Emissions from Weiss \textit{et al.}\(^4\)

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\(\text{BC}\): Bottoming agents; \(\text{HFCs}\): Hydrofluorocarbons; \(\text{PFCs}\): Perfluorocarbons; \(\text{CF}_{\text{4}}\): Carbon tetrafluoride; \(\text{C}_{\text{2}}\text{F}_{\text{4}}\): Dichlorodifluoromethane; \(\text{C}_{\text{2}}\text{F}_{\text{6}}\): Dichlorodifluoromethane; \(\text{SF}_{\text{6}}\): Sulfur hexafluoride; \(\text{NF}_{\text{3}}\): Nitrogen trifluoride.
Table 1.4: Projected annual emissions (2010-2050) in kilotonnes for agents used in Figure 1.1 compiled from SRES A1B scenario, except where noted. a: Emissions from Velders et al.; b: Emissions from an exponential decay fit of data from 1990 to 2005 as provided by the RCP Database; c: Emissions from assumption of 5% per year increase after 2000. This rate is similar to projections for CF$_4$ and C$_2$F$_6$ and matches the rate of increase over the past 10 years for NF$_3$ in the United States.

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CHAPTER 1

References


CHAPTER 1


2 Background

This chapter is adapted from a manuscript to be submitted to Chemical Reviews coauthored with Ilhan Aksay.¹

This chapter first provides an introduction to DSSCs, and then gives an overview of graphene materials, focusing on FGSs which are created through the simultaneous exfoliation and reduction of graphite oxide. Lastly, the use of graphene materials in DSSCs is briefly reviewed.

2.1 Dye-Sensitized Solar Cells

DSSCs have taken up broad interest as a promising low-cost PV technology since they were first reported on in 1991.² DSSCs use specialized materials for specific cell functions such as photon absorption, charge separation, and charge transport. Figure 2.1 depicts a simple energy diagram of how these devices function. A photon can enter the solar cell and be absorbed by a sensitizer, exciting an electron (a). Then this electron can be injected into the conduction band of a neighboring semiconductor (b) and diffuse to the current collector (c). The electron can perform work and flow to the cathode (d) where it is transferred to an electrolyte or hole conductor (e). This material can then transfer an electron to the sensitizer (f), regenerating it, and completing the circuit. To optimize these devices and achieve respectable η researchers have looked at ways to
Chapter 2

i) maximize light harvesting, and ii) minimize losses due to parasitic electron transfer pathways (v-z in Figure 2.1b) while also minimizing the overpotentials required to drive the electron transfer in the desired direction (colored bands in Figure 2.1b).

Figure 2.1: Energy diagram for a DSSC. CB and VB refer to the conduction band and valance band, respectively. \( E_F \) represents the Fermi level of the semiconductor, and is represented near CB due to a high level of electronic doping. The LUMO and HOMO levels are the least unoccupied, and highest unoccupied molecular orbitals of the sensitizer. For traditional DSSC architectures, at least one current collector must be a transparent electrode to allow light into the cell. a) Desired electron pathway. Colored arrows a-f represent some of the energy transfer steps as described in the main text. b) Recombination pathways. Colored arrows v-z represent some of recombination pathways. Voltage drops for different charge transfer steps are represented by the colored bands.

Towards these ends, the archetypical DSSC Figure 2.2 uses a fluorine-doped tin oxide (FTO) transparent electrode with a sintered titania nanoparticle scaffold sensitized with organo-metallic dye molecules as the photoanode, an iodide/triiodide redox couple dissolved in acetonitrile as the electrolyte, and a platinized FTO cathode. The nanoparticles provide a high surface area film (~1,000x roughness for 10 \( \mu \)m thick) for increased dye loading, while the sintering ensures high connectivity of the particles for fast electron transport and mechanical stability. DSSC dyes absorb strongly in the visible, they have extended excited state lifetimes, and they bind to the titania scaffold for
Figure 2.2: Schematic of typical DSSC. The primary particle diameter of TiO$_2$ used is 10-20 nm, and the phase is anatase. Void space is about 50%. FTO generally has a sheet conductivity of ~ 15 $\Omega$/sq and transmittance in the visible of ~ 85%. Platinum nanoparticles typically have diameter of ~5 nm and are created through the thermolysis of chloroplatinic acid.

Stability and improved charge transport. For instance, a ruthenium bipyridyl dye, N719, absorbs wavelengths up to ~ 800 nm, has an extinction coefficient of ~ $1.5 \times 10^4$ M$^{-1}$·cm$^{-1}$ (at 535 nm), and has carboxylic acid groups that can chemisorb to the titania scaffold. In the electrolyte, acetonitrile has been the solvent of choice for high efficiency cells due to its low viscosity (0.34 mPa·s at 25 °C), facilitating ion transport, and for its high electrochemical stability. However, the low boiling point, and thus high volatility, of the solvent inhibits the long term stability of devices. To improve device stability, higher viscosity solvents are commonly mixed with acetonitrile (i.e., valeronitrile) or used on their own (i.e., methoxypropionitrile). The iodide/triiodide redox mediator was used in the original DSSC and has remained the dominant mediator for the past 20 years. In a
simplistic view of this system, iodide regenerates the dye forming triiodide. Triiodide then diffuses to the cathode and is reduced back to iodide, which in turn can diffuse back to the photoanode and continue the cycle.

A primary reason for the success of the iodide/triiodide mediator is that electron transfer from the photoanode to triiodide is slow (recombination pathway $y$), reducing recombination in the solar cell. Nevertheless, at the cathode, triiodide must be reduced fast (i.e., with a minimum overpotential) dictating the necessity of a catalyst. Cathodes comprised of platinum nanoparticles deposited on FTO have been widely used due to their facile fabrication, high activity towards triiodide reduction, and sufficient corrosion resistance to iodo species present in the electrolyte.\(^5\)\(^-\)\(^8\) However, since platinum is a precious metal, there is economic incentive to develop DSSC counter electrodes using cheaper, abundant materials which can be easily processed. Transition metal compounds,\(^9\)\(^,\)\(^10\) conducting polymers,\(^11\) and carbon materials\(^12\),\(^13\) have all been introduced as alternatives catalysts to platinum. Of particular interest to this dissertation, extensive research has been performed on using carbonaceous nanomaterials for the counter electrode because they are low-cost, corrosion resistant, and electrically conductive.\(^8\),\(^14\)\(^-\)\(^21\) While graphite has poor catalytic activity towards the reduction of triiodide, its high surface area analogs such as carbon black and carbon nanotubes have shown promise, and in some cases have been reported to exceed the performance of platinum.\(^12\),\(^21\),\(^22\) At the beginning of this dissertation work, graphene composites had just emerged as potential catalysts for DSSC cathodes, due to graphene’s exceptional surface area and conductivity.\(^23\)\(^-\)\(^25\) Hong \textit{et al.}, for example, used a chemically reduced graphene
oxide/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) composite and achieved \( \eta \) of 4.5\%, comparable to their platinum control cell at 6.3\%. Improving catalyst performance, and understanding why improvement occurs provided motivation for this dissertation work.

Recently, alternative redox mediators have challenged the dominance of the iodide/triiodide system. The redox potential of the iodide/triiodide redox couple (~ 0.35 V vs. normal hydrogen electrode) is significantly more negative than is required for dye regeneration, limiting the voltage obtainable and hence \( \eta \) of the device (this voltage loss is represented by the red band in Figure 2.1b).\(^{26}\) Furthermore, the triiodide itself absorbs light, reducing \( \eta \) of the device. To overcome these limitations, alternative redox couples have been explored\(^{27}\) including cobalt-,\(^{28}\) sulfur-,\(^{29}\) and iron-based\(^{30}\) compounds. Recently, Yella \textit{et al.} reported a new power conversion efficiency record of 12.3\% for a DSSC using a zinc porphyrin dye, co-sensitized with an organic dye, in conjunction with a cobalt-based redox mediator.\(^{31}\) While platinum is very effective for catalyzing the reduction of triiodide, it is less effective as a catalyst in the cobalt redox system, and particularly poor with sulfur-based mediators.\(^{29,32}\) Until this thesis work, there were no reports of an alternative catalyst to platinum that can match – or exceed – this precious metal’s performance with multiple redox couples.

### 2.2 Graphene Materials

The term graphene has been used loosely in the literature to represent pristine graphene as well as many other materials with some similar characteristics, all of which
we include under the umbrella of graphene materials. Depending on how they are
produced, these materials can have vastly different chemical structures and thus
properties. Ideally, we should be able to identify each material by its exact chemical
makeup or at least by its properties. However, currently there are no standard criteria to
evaluate graphene materials with, and information provided by authors is understandably
incomplete. Rather, readers often have to sense what the structure and properties of the
graphene materials used in the literature are based on basic information on the fabrication
 technique, with the idea that materials produced in similar ways will have similar
properties. A comprehensive description of graphene materials production techniques and
properties can be found in numerous reviews,\textsuperscript{33-46} with a brief outline provided in this
section.

Pristine graphene is an atomic planar layer of hexagonal $sp^2$ hybridized carbon.
Many of the advantages of the material come from quantum effects prominent when it is
present in its single atomic layer – and to lesser extent, few layer – form. Preventing
aggregation and stacking is a main challenge of working with the material due to
attractive van der Waals interactions. Staggered stacks of graphene, which have an
interlayer spacing of 0.34 nm, make up graphite. Studies which aim to use pristine
graphene are currently limited to low throughput production techniques such as
mechanical exfoliation (“Scotch Tape” method),\textsuperscript{47, 48} liquid exfoliation,\textsuperscript{49, 50} epitaxial
growth,\textsuperscript{42, 51-53} and chemical vapor deposition (CVD).\textsuperscript{40, 42, 54, 55} These methods result in
monolayers of the material on a substrate (~ 0.8 mg/m$^2$), or very dilute suspensions
(~ 0.01 mg/mL).\textsuperscript{49}
Both liquid exfoliated graphene and CVD derived graphene have been used in DSSC applications. Liquid exfoliation involves the sonication of graphite in the presence of a solvent (e.g., N-methyl-pyrrolidone) which has a surface energy close to that of graphite (ideally it would match) with the idea that the interfacial energy between the solvent and graphene would be minimized as would the van der Waals forces between graphene sheets. The resulting suspension is a mixture of single, few, and multi-layered graphene sheets. The concentration can be increased by additional sonication and recycling of the sediments. For CVD, a gaseous carbonaceous precursor (e.g., methane) is flowed at high temperatures (~ 1000 °C) over a metal substrate. The most common metals used are copper and nickel, which were chosen in part due to their catalytic activity toward hydrocarbon decomposition, and in part due to the low solubility of carbon in them, both of which are important to facilitate the production of atomically thin films. As detailed in the reviews, much research is ongoing to reduce the number of defects and grains in CVD derived graphene, and to improve the concentration of single sheet liquid exfoliated graphene so that the materials behave more like pristine graphene.

We report briefly on the properties of pristine graphene, but much more information can be found in the aforementioned reviews. The intrinsic room temperature mobility for pristine graphene has been reported to be as high as 200,000 cm²/(V·s), but most reported values fall between 3,000 and 15,000 cm²/(V·s). This value is highly influenced by the substrate and whether any grain boundaries are present. Although mobility is high, due to the low intrinsic charge carrier concentration, the sheet resistance ($R_{sh}$) of a single layer of graphene is ~ 6.45 kΩ/sq. Electronic doping can reduce the
Pristine graphene has been shown to exhibit strength and modulus of 130 GPa and 1.0 TPa, respectively. The material also has very high optical absorption properties (~2.3% of light is captured per sheet); however, due to the other exceptional properties, its absorption per unit modulus, or mobility, is low, presenting it as a strong candidate for transparent applications. Furthermore, being only an atom thick, the material has a specific surface area calculated to be 2,630 m$^2$/g.

Currently, for bulk production of graphene materials, graphite is first oxidized using strong oxidants and intercalating compounds by methods that date back to 1859 (e.g., H$_2$SO$_4$, HNO$_3$, KMnO$_4$, KClO$_3$, NaClO$_2$). Fully oxidized graphite has a molar carbon to oxygen ratio (C/O) of ~ 2 (though recent ab initio results suggest that C/O as low as 1.14 can be obtained) and is called graphite oxide. This material can be exfoliated in water through ultrasonic agitation producing suspensions of graphene oxide, which disperse readily in water. Detailed reviews of the properties and proposed structure of graphene oxide can be found in the literature, though we note that specific oxygen groups and their locations on the lattice will vary by oxidation method. Two model structures are presented in Figure 2.3.

**Figure 2.3:** Proposed structures of graphene oxide. a) The Lerf-Klinowski model. b) A model proposed by Gao et al. Figure adapted from Loh et al.
Graphene oxide can be reduced by chemical, electrochemical, or thermal means. The resulting material has structure and properties somewhere along a spectrum between graphene oxide and pristine graphene, depending on the degree of reduction and starting structure of the graphene oxide. We term this class of materials as FGSs, however we recognize that a plethora of other acronyms are currently in use in the literature (FLG, GNP, GP, RGO, TEGO, etc.). A schematic of an FGS with a sampling of the functional groups and lattice defects can be seen in Figure 2.4.

The most prevalent means of chemical reduction of graphene oxide is through hydrazine vapor; however, many other reducing agents have been used. Both deoxygenation and dehydration reactions can take place, which partially restore the aromatic carbon lattice. Nevertheless, C/Os are limited to ~13 in this approach, confining the size of the pristine graphene domains \( (L_A) \) in the material and the associated mobility.

Thermal treatment of graphene oxide – on a substrate, as a powder, or in suspension – will also reduce the material, with higher temperatures and longer durations resulting in higher degrees of reduction. Alternatively, rapid heating of graphite oxide \((i.e., \text{putting the material into a furnace heated to 1100 } ^\circ \text{C})\) can simultaneously exfoliate and reduce the material, resulting in a black fluffy powder with specific surface areas above 800 m\(^2\)/g measured by nitrogen adsorption and greater than 1,750 m\(^2\)/g measured in suspension. Although heating in a furnace is most often employed for thermal reduction, other techniques have been explored, including microwave heating, flash photoreduction, and heating in suspension \((i.e., \text{solvothermal reduction})\).
Figure 2.4: Schematic of functional groups and lattice defects on an FGS. Epoxides and hydroxyls are on both sides of the graphene plane, while carboxyl and hydroxyl groups are at the edges. Carbon atoms are gray, oxygen atoms are red, and hydrogen atoms are white. (a) Top view emphasizing a 5-8-5 defect (green) and a 5-7-7-5 (Stone-Wales) defect (yellow). (b) Side view emphasizing the topography of the sheet. These schematics are representative of the functionalities on FGSs but not an actual sheet which would measure on the order of 1 µm across.

Thermal treatment of graphene oxide removes oxygen from the material through the evolution of CO, CO$_2$, H$_2$O, and O$_2$, leaving behind lattice defect sites when carbon is removed from the lattice.$^{62, 76, 83-88}$ Nevertheless, at elevated temperatures the lattice diffusion rate of carbon is enhanced, and between 1100 °C and 1500 °C annealing of the lattice (i.e., increasing $L_A$) is observed$^{89}$ resulting in large increases in conductivity.$^{59, 90}$ Some researchers use a two-step process of chemical reduction followed by thermal reduction.$^{73}$ The idea is to first remove as many oxygen sites without disrupting the lattice as possible, and then remove the remaining groups thermally, resulting in a final material with fewer lattice defects than those treated only thermally.
As can be expected from the different structures, various graphene materials have distinct properties. One of the most prominent transitions is the conductivity between graphene oxide (an insulator) and graphene (a semi-metal). Conductivity (inverse of resistivity) of a material is equal to the product of its mobility, charge carrier density, and the elementary charge. Thus a material’s $R_{sh}$ is inversely proportional to its mobility and the number of charge carriers. Figure 2.5 show the experimentally-derived correlations between $L_A$ and mobility (a), and between C/O and $R_{sh}$ (b) for FGSs.

![Figure 2.5: Relations of structural and electrical properties of FGSs. a) Mobility as a function of $L_A$. Figure adapted from Su et al.\textsuperscript{75} b) $R_{sh}$ as a function of C/O. Figure reproduced from Punctk et al.\textsuperscript{59}]

Although mobility increases as graphitic domains grow and become percolated, the number of charge carriers is likely reduced as functional sites are eliminated. At the highest C/O, $R_{sh}$ is similar to that measured for pristine graphene; however, it is likely that the mobilities are higher and charge carriers are lower in the latter case. Thus, one of the most straightforward identifiers of FGSs is their C/O and we differentiate between FGSs we produce through the nomenclature FGS$_x$ where $x$ is the C/O. Thus, graphene
oxide is also referred to as FGS₂ using our terminology. More recently, through work initiated by Michael Pope, the Ceramic Materials Laboratory has started to also identify the material with its defectiveness as measured by Raman spectroscopy (discussed further in Chapter 4).

![Figure 2.6: Production of graphene materials. The triangle qualitatively represents the material space encompassed by FGSs.](image)

Figure 2.6 summarizes the production methods for graphene materials. Pristine graphene can be isolated by the exfoliation of graphite or grown on substrates. It should be reiterated that FGSs are not pristine graphene, but rather highly defective sheets decorated with oxygen groups (epoxides, hydroxyls, carbonyls, etc.) and lattice defects, whose make up are highly dependent on the starting material and reduction parameters. The interior of the triangle represents a phase diagram for FGSs, and depicts the
progression of oxygen content and defectiveness (i.e., \( L_A \)) for different reduction techniques.

### 2.3 Graphene Materials in Dye-Sensitized Solar Cells

Graphene, with its exceptional electrical, optical, and mechanical properties has been incorporated into each aspect of a DSSC (see Figure 2.7). It was first used in 2008 as a transparent electrode to replace FTO at the photoanode, and has since been used to harvest light, to improve transport through both the titania layer and the electrolyte, and, as elucidated in this work, to supersede platinum at the cathode. An ISI Web of Knowledge search, Figure 2.8, shows the rapid increase in the number of publications on graphene, DSSCs, and graphene in DSSCs.

![Schematic of a DSSC incorporating graphene materials in each part of the device.](image)

**Figure 2.7:** Schematic of a DSSC incorporating graphene materials in each part of the device.
Although, graphene materials can be used to improve DSSCs in a variety of roles, particular functions are best performed by specific graphene materials. Pristine graphene, followed by highly reduced FGSs, have the best prospects for transparent conductors, though, by themselves, the materials are not sufficient to meet application demands. These materials will either have to be electrically doped, or as a part of a metal hybrid system. In the photoanode, graphene materials have resulted in improved photocurrent; however, it is unclear whether the advantages will persist in optimized devices. Additionally, whether FGS$_2$, or chemically or thermally reduced FGS$_2$ are processed with the titania is unlikely to matter significantly, as heat treatment is generally required to sinter the titania layer, which will thermally reduce the graphene material as well. Graphene materials can be used as a sensitizer in solar cells and

![Figure 2.8: Number of studies with keywords of “Graphene” or “Dye Solar Cell” published since 2000. Inset shows yearly publications for “Graphene” and “Dye Solar Cell.”](image)
quantum effects, in particular, hot injection, could allow cells to exceed the Shockley-Queisser efficiency limit. Nevertheless, current optimization processing of graphene quantum dots has brought the material closer to current organic dye structures. Furthermore, FGS$_2$ could be a useful gelling agent in the electrolyte, whereas thermally reduced FGS$_2$ in this role would likely catalyze recombination and reduce DSSC $\eta$. At the cathode, two approaches have shown they can equal or surpass the performance of platinum nanoparticles: i) high surface area electrodes, and ii) high activity materials (see Figure 2.9). In both approaches FGSs are advantageous as pristine graphene is

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**Figure 2.9:** Comparison of DSSC $\eta$ for graphene materials and their platinum control counter electrodes. Color is indicative of technique used. Triangles: Generation 1 FGS electrodes (see Chapter 5); Diamonds: Generation 2 FGS electrodes (see Chapter 6). Circles: Other published studies. Adapted from Roy-Mayhew and Aksay.

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relatively inert (see Chapter 4). In the first case, care must be taken to prevent restacking of sheets (see Chapters 5 and 6), while in the second case, either a highly active nanoparticle composite can be formed, or a redox mediator for which FGSs are highly active for (e.g., cobalt bipyridine) can be used (see Chapters 4 and 6).

References


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CHAPTER 2


3 Experimental Methods

In this chapter, a brief description of materials, measurement techniques, and equipment common to Chapter 4, 5, and 6 is presented.

3.1 Production of Functionalized Graphene Sheets

FGSs used for this dissertation were either produced by Michael Pope or obtained from Vorbeck Materials. A brief description of the typical fabrication procedure follows. To synthesize FGS$_2$, a modified Hummer’s method$^{1,2}$ was carried out. A slurry of 0.5 g of graphite, 0.5 g of NaNO$_3$, and 23 mL of H$_2$SO$_4$ was prepared under constant stirring in an ice bath. Subsequently, 3 g of KMnO$_4$ was added and the slurry was heated to 35 °C and stirred for 1 h. 400 mL of water was then added and the resulting suspension was stirred for 30 min during which time the reaction temperature increased to ~ 90 °C. Still under stirring, 100 mL of water was then added, followed by 3 mL of H$_2$O$_2$ (30%). The reaction mixture was then centrifuged to separate FGS$_2$ from the soluble components of the reaction mixture. Reduced FGS$_2$ (e.g., FGS$_7$, FGS$_{48}$, FGS$_{68}$) was produced by thermal exfoliation$^{3,4}$ and, for FGS with C/O > 100, a subsequent annealing step was completed. Thermal exfoliation took place in a tube furnace (Blue M, SPX Thermal Products) at temperatures between 300 °C (FGS$_7$), and 1100 °C (FGS$_{68}$) for ~ 60 s under argon.
Annealing consisted of heating thermally exfoliated powder for 2 h in a resistively heated graphite furnace (Astro-1000, Thermal Technologies) at 1300 °C (FGS$_{324}$) and 1900 °C (FGS$_{353}$) under argon. FGS$_{48}$ was supplied by Vorbeck Materials (Vor-x®, batch RC-213).

3.2 Physical Characterization

This section describes techniques used to examine the morphology and structure of samples in the subsequent chapters.

3.2.1 Scanning Electron Microscopy

The morphology of the samples was investigated by scanning electron microscopy (SEM; Tescan 5130MM) under 20 kV accelerating voltage. For cross sectional images, samples were secured to 45° sample holders using carbon adhesive tabs.

3.2.2 Energy Dispersive X-ray Spectroscopy

Elemental analysis of samples was determined through energy dispersive X-ray spectroscopy (INCA x-act, Oxford Instruments) at 10 kV accelerating voltage in the SEM described above and these results were confirmed with combustion-based analysis (Atlantic Microlab). For measurement of C/O, thick layers of FGS powders were deposited onto conductive SEM sample holders. For each sample, multiple areas were sampled (at 500 – 1000x magnification) and the results were averaged. Although only a single C/O is reported for each FGS type used, individual sheets may be more or less oxidized, as the reported value represents an average of the bulk material.
3.2.3 Powder X-ray Diffraction

To analyze FGS spacing and the degree of graphitization in samples, X-ray diffraction (XRD) patterns were obtained using a desktop diffractometer (Rigaku MiniFlex II, Cu K$_\alpha$ radiation at $\lambda = 1.54$ Å) sampling at $2^\circ$/min, 30 kV and 15 mA. Graphitic spacing (0.34 nm) is indicated by a diffraction peak at $2\theta = 26.4^\circ$ with larger spacing indicated by peaks at lower angles.

3.2.4 Surface Area Analysis

Surface area was determined from nitrogen adsorption by the Brunauer, Emmett, and Teller (BET) method$^5$ using a surface area analyzer (Gemini V, Micromeritics Instrument Corporation). 11 data points were taken for each fit from a relative pressure of 0.05 to 0.30, with an equilibrium time of 5 s, an evacuation rate of 100 mmHg/min (13.3 kPa/min) and an evacuation time of 2 min. Samples were dried for 3 h at 160-200 °C under vacuum before measurement. This technique is limited to providing information on N$_2$ gas accessible surface area, which may not be indicative of the surface area available to a particular species of interest. For instance, triiodide in solution is larger than a N$_2$ molecule and thus pores that are large enough for N$_2$ penetration may not be accessible to triiodide.

3.2.5 Simultaneous Thermal Analysis

Decomposition profiles of samples were examined by simultaneous thermal analysis (STA; 449 C Jupiter, Netzsch) incorporating a thermogravimetric analyzer (TGA) and a
differential scanning calorimeter (DSC). Aluminum pans were used and STA measurements were done either under flowing dry nitrogen (40 mL/min) or under flowing dry air (40 mL/min). The DSC was calibrated using a set of standards (In, Sn, Bi, Zn, CsCl) with well-known temperatures and enthalpies of phase transitions.

3.3 Electrochemical Characterization

This section describes the electrochemical techniques and analysis common to the subsequent chapters. Unless otherwise noted, all electrochemical characterization was carried out with a potentiostat (SP-150, Biologic).

3.3.1 Linear Sweep Voltammetry (the “I-V curve”)

A standard technique to measure solar cell performance is a current-voltage (I-V) or current density-voltage (J-V) curve. By performing a voltage sweep with a device that can uptake load, such as a potentiostat, or by running a current through a solar cell at variable external resistances, one can generate a J-V curve. By applying light with a well-defined spectra and intensity (e.g., AM1.5G solar simulation) to a solar cell and then measuring its J-V response, several solar cell parameters can be deduced as demonstrated in Figure 3.1. The open circuit voltage ($V_{OC}$) is the potential difference of the cell when no current is drawn (e.g., when $I = 0$, resistance $\rightarrow \infty$). The short circuit current ($I_{SC}$) is the current produced through the cell when no external load is applied (e.g., when $V = 0$, resistance $\rightarrow 0$). A device’s fill factor ($FF$) is the ratio of the maximum power ($P_{Max}$) that can be obtain from the solar cell to the product of $V_{OC}$ and $I_{SC}$ (i.e., the ratio of area.
Figure 3.1: A sample DSSC J-V curve obtained under 1,000 W/m² AM1.5G solar simulation. The $J_{SC}$, $V_{OC}$, and $P_{Max}$ points are highlighted, and solar cell characteristics tabulated under the curve. The FF can be determined as the ratio of the area enclosed by the gray dotted lines, to the area enclosed by the blue dotted lines.

bounded by the gray dotted line to the area bounded by the blue dotted line in Figure 3.1). Higher resistance and more recombination in a solar cell reduce the device’s FF. The $\eta$ of a solar cell is defined as the ratio of $P_{Max}$ to the power incident on the solar cell ($P_{In}$) per area. Often current density ($J$) is reported rather than current as the former normalizes the value with respect to electrode area. To prevent stray light from influencing the measurements and to control the active area for testing, an opaque mask with a predefined window area is used. The relations describing common solar cell parameters are summarized in Equation 2:

$$
\eta = \frac{P_{Max}}{P_{In}} = \frac{FF \cdot J_{SC} \cdot V_{OC}}{P_{In}}.
$$

(2)
3.3.2 Cyclic Voltammetry

To study the electrocatalytic properties of electrodes with respect to specific redox couples, cyclic voltammetry (CV) was used. For these measurements a three electrode electrochemical cell was used, as depicted in Figure 3.2. In this technique, the potential of the working electrode (i.e., electrode of interest) is ramped linearly with time until it reaches a set potential, whereupon the potential ramp is inverted. The ramp rate (potential change per time) is known as the measurement’s scan rate, \( \nu \). A reference electrode (for our studies 0.01 M Ag/Ag\(^+\) and 0.1 M LiClO\(_4\) in acetonitrile) is used to provide a baseline for our potential values. For the studies detailed in Chapter 5,
ferrocene was also used as an internal standard. The counter electrode for these measurements was a platinum wire.

Figure 3.3: Interpreting a cyclic voltammogram. Curves are for an electrode made of platinum nanoparticles on a conductive substrate with electrolytes containing cobalt-bipyridine redox mediator with a supporting electrolyte (solid), and containing supporting electrolyte only (dashed). The dashed line represents the capacitive charging, and the width is equal to twice $I_C$. With high surface area electrodes, the peak currents cannot be measured directly from the plots, rather the contribution of the anodic or cathodic current (represented by colored dashed lines) and $I_C$ must be taken into account. $E_{pp}$ is the difference between the potential of the cathodic and anodic peaks as represented by the thickness of the gray band. $E_{red}$ is the potential value midway between the two peaks.

A typical CV curve for a one electron reaction is shown in Figure 3.3. As the potential is increased, the reaction rate increases as expected due to Butler-Volmer kinetics, resulting in an increasing current. However, the curve peaks due to limited supply of analyte near the electrode surface. As the potential is increased, the analyte
depletion layer grows and the system becomes diffusion limited. Several electrochemical parameters can be determined from these curves such as peak-to-peak separation ($E_{pp}$), peak height of the cathodic and anodic current ($I_{pc}$ and $I_{pa}$), capacitive current ($I_C$), and the redox potential ($E_{Red}$) of the electrolyte. By analyzing how these parameters depend on $v$, the reaction rate constants and whether or not the reaction is reversible can be deduced as discussed further in Chapters 4 and 5, respectively.

### 3.3.3 Electrochemical Impedance Spectroscopy

To obtain information about interfacial phenomena, electrochemical impedance spectroscopy (EIS) is used. In this technique, a small alternating current perturbs the electrochemical system and the opposition to electronic flow (i.e., the impedance, $Z$) is measured for a range of frequencies. Impedance is often represented in complex notation and it is calculated by Equation 3,

$$Z(\omega) = Z'(\omega) + j \times Z''(\omega) = \frac{V_A(\omega)}{I_A(\omega)},$$  \hspace{1cm} (3)

where $\omega$ is the frequency, $j = \sqrt{-1}$, and $V_A$ and $I_A$ are the alternating voltage and current, respectively. A common interface in an electrochemical cell is the electrode-electrolyte interface, where an electron is transferred to (or from) the electrode from (or to) the electrolyte. This process can often be described as a resistor in parallel with a capacitor (RC) and an equivalent circuit can be used to analyze the system. For a resistor, the impedance is equivalent to the resistance ($R$), i.e., $Z_R = R$, while for a capacitor the impedance is inversely proportional to $\omega$ and the capacitance ($C$) in the complex plane,
\[ Z_C = \frac{1}{j \times \omega \times C} \]. In parallel, impedances add inversely, i.e., \( \frac{1}{Z_{RC}} = \frac{1}{Z_R} + \frac{1}{Z_C} \), while in series impedances simply add together. One representation of impedance data is the Nyquist plot, where the real and imaginary parts of the impedance are plotted on separate axes. For the RC circuit in a Nyquist plot, as seen in Figure 3.4, a semicircle is formed with the diameter equal to \( R \), and \( \omega \) at the 90° position corresponding to \( \frac{1}{R \times C} \).

\[ Z = \frac{R}{1 + j \times \omega \times R \times C} \]

\[ \omega = \frac{1}{R \times C} \]

**Figure 3.4:** Interpreting EIS data. Nyquist plot for sample RC circuit.

Some common EIS equivalent circuit units are included in Table 3.1. The constant phase element (CPE) is used to fit non-ideal systems, and is sometimes referred to as a “leaky capacitor,” or used to account for rough surfaces with uneven current density distributions. Depending on the exponent, \( \beta \), the unit can behave from an ideal capacitor to an ideal resistor. Warburg diffusion employs infinite boundary conditions, and arises as a line with a 45° angle on a Nyquist plot. Nernst diffusion impedance uses semi-infinite boundary conditions, and reduces to the Warburg case when the diffusion layer, \( \delta \), becomes infinite. At finite \( \delta \), Nernst diffusion can appear as a semicircle on a Nyquist
plot. Different phenomena respond at different frequencies, and thus several effects can be distinguished using this technique. EIS was first used with DSSCs in 2002, and greatly expanded upon in 2005.

Table 3.1: EIS equivalent circuit components.

<table>
<thead>
<tr>
<th>Component</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>( Z_R = R )</td>
</tr>
<tr>
<td>Capacitor</td>
<td>( Z_C = \frac{1}{j \times \omega \times C} )</td>
</tr>
<tr>
<td>Constant Phase Element (CPE)</td>
<td>( Z_{CPE} = \frac{1}{(j \times \omega)^{\beta} \times C_s} )</td>
</tr>
<tr>
<td>Warburg diffusion</td>
<td>( Z_W = \varphi \times \omega^{-0.5} \times (1 - j), \text{ where} )</td>
</tr>
<tr>
<td></td>
<td>( \varphi = \frac{R \times T}{n^2 \times F^2 \times A \times \sqrt{2}} \times \left( \frac{1}{C_O \times \sqrt{D_O}} + \frac{1}{C_R \times \sqrt{D_R}} \right) )</td>
</tr>
<tr>
<td>Nernst diffusion</td>
<td>( Z_N = Z_W \times \omega^{-0.5} \times \text{tanh} \left( \delta \times \left( \frac{j \times \omega}{D} \right)^{0.5} \right) )</td>
</tr>
</tbody>
</table>

References


4 Electrocatalytic Activity of Functionalized Graphene Sheets towards the Cobalt Bipyridine Redox Mediator

This chapter is adapted from work to be submitted to the Journal of the American Chemical Society coauthored with Michael A. Pope, Christian Punckt, and Ilhan Aksay.¹

M. Pope fabricated the FGS used in this study unless otherwise stated and he helped with experimental design. C. Punckt created a base Matlab analysis code for the electrochemical experiments and ran simulations to determine appropriate fitting parameters.

The effectiveness of a catalyst depends on both the intrinsic activity of the material and the surface area available for reaction. In this chapter, we focus on determining the intrinsic activity of FGSs with different structural compositions by using monolayers of the material processed in different ways, with the goal that which sites are active can be elucidated. This knowledge would allow for the better engineering of FGSs for use as a DSSC catalyst.

We demonstrate that FGSs, rich with lattice defects but lean with oxygen sites, catalyze the reduction of Co(bpy)₃(III), where bpy = 2,2′-bipyridine, as well as platinum does, exhibiting a rate constant, \( k_0 \), of \( \sim 6 \times 10^{-3} \) cm/s. We show this to be an order of
magnitude faster than oxygen site-rich FGS$_2$ (i.e., graphene oxide), and over two orders of magnitude faster than the basal plane of graphite (as surrogate for pristine graphene). Furthermore, DSSCs using these monolayers perform similarly to those using platinum nanoparticles as the catalyst.

4.1 Introduction

Carbonaceous materials are capable of matching or even exceeding the performance of platinum electrodes for a variety of redox mediators; but the sites that are responsible for catalysis have not yet been identified. Some previous studies have hypothesized that oxygen functionalities may be the primary agents of catalysis, while others suggest dangling bonds at lattice vacancies and edges are responsible. While the apparent electrochemical activity of a catalyst can be determined through CV and EIS, the intrinsic activity of a material, particularly high surface area carbon materials, is obfuscated by morphology. Both theoretical and experimental studies have shown that porosity can increase peak current ($I_p$) and decrease $E_{pp}$ in cyclic voltammograms and thus affect the extracted electrochemical parameters. Furthermore, the high electronic resistance that exists in networks of poorly conducting particles (i.e., FGS$_2$) can decrease or even eliminate the observed catalytic activity of a material.

Herein, using CV and EIS, we test monolayers of FGSs to determine the intrinsic catalytic activity of oxygen functional groups and lattice defect sites towards the Co(bpy)$_3$(II/III) redox system. By using a Langmuir-Blodgett (LB) trough approach, wherein we disperse sheets at the air-water interface and compress them to a densely tiled
FGS film,\textsuperscript{11, 12} we form patchwork monolayers of FGSs which have negligible surface roughness, as seen in Figure 4.1. Through this approach, we eliminate the role of morphology, as recently demonstrated by Pope \textit{et al.}\textsuperscript{13} Additionally, electronic losses, especially important with insulating FGS\textsubscript{2} films, are minimized due to the mosaic of single layer sheets in direct contact with the conducting substrates.

![Figure 4.1: SEM images of FGS\textsubscript{1} monolayers on silicon. (a) FGS\textsubscript{2} and (b) FGS\textsubscript{68} layers. Silicon substrates (lightest regions) are shown as they provide greater contrast with the darker FGSs. Surface coverage is greater than 90%, and a few instances of overlapped sheets are observed.](image)

Cobalt-based redox mediators were first shown to be viable replacements for the iodide/triiodide system in 2001.\textsuperscript{14} They involve only a single electron transfer and have a lower redox potential energy than the iodide/triiodide system allowing for smaller voltage drops and greater \textit{V}_{OC} in devices.\textsuperscript{14, 15} However, these traits also contributed to a greater recombination with electrons in the photoanode and limited DSSC performance in early devices.\textsuperscript{14, 15} By modifying the dye and using bulky cobalt complexes to sterically reduce recombination, in 2010 Feldt \textit{et al.} created Co(bpy)\textsubscript{3}(II/III) mediated DSSCs with \(\eta\) greater than 7%.\textsuperscript{16} Yella \textit{et al.} expanded upon this work, setting the current record DSSC
efficiency using the cobalt mediator.\textsuperscript{17} The cobalt mediator is used in this work due to its first class performance and – even more pertinent – because the complex involves a single electron transfer. This simplicity facilitates a clear interpretation of electrochemical data and assessment of catalytic activity.

4.2 Experimental Methods

Experimental details specific to this chapter are included below. In particular, the preparation of both monolayers and DSSCs for this study is discussed, as is how the electrochemical measurements were obtained and analyzed. General experimental techniques can be found in Chapter 3.

4.2.1 Preparation of Monolayers

Monolayers were prepared similarly to Pope \textit{et al.}\textsuperscript{13} In brief, aqueous suspensions of FGS\textsubscript{2} were mixed with methanol (Fisher) at a 1:5 volume ratio. FGSs with C/O of 7 and above were suspended in residue-free 1,2-dichloroethane (Acros) at a concentration of \(~0.33\) mg/mL, and the resulting suspensions were tip sonicated (150 W, Branson Ultrasonics) for 30 min at 40\% amplitude in an ice bath. Aggregates were removed by centrifugation at 2000 g for 60 min. The suspensions were spread out on the air–water interface of an LB trough (Nima Technology) using a syringe pump set at a flow rate of 0.2 mL/min. A sufficient coverage of FGSs was attained after the addition of 0.5 – 3 mL of suspension. The FGS\textsubscript{2} coverage was observed with a Brewster angle microscope (BAM2plus, Nanofilm Technologie GmbH), and the surface tension was monitored using a Wilhelmy plate cut from filter paper. LB films of reduced FGSs could be observed by
eye as a faint film. Movable Teflon barriers were used to condense the film by reducing the area at a rate of 20 cm$^2$/min. The LB films were transferred to highly ordered pyrolytic graphite (HOPG, freshly cleaved, Grade 2, Structure Probe), FTO (TEC 8, Hartford Glass), and silicon (from 4 inch 100 test grade wafer) substrates by the horizontal deposition method. In this method, the substrates were placed in the water subphase in the absence of the LB film. Once the LB film was under compression, it was lowered onto the various surfaces by removing water from the trough. Coated samples were air-dried for 10 min and then placed on a hot plate at 80 °C until use.

### 4.2.2 Preparation of DSSCs

DSSCs were constructed similarly to Feldt et al. FTO glass (TEC15, Hartford Glass) was cleaned in an ultrasonic bath overnight in ethanol (Fisher). A titania underlayer was formed by pretreating the glass at 70 °C in 40 mM TiCl$_4$ solution for 30 min. The films were then subsequently washed with water and ethanol. Titania films, 0.5 × 0.5 cm$^2$, were prepared by screen printing two layers of a colloidal TiO$_2$ paste (Dyesol DSL 18 NR-T). Two layers of a scattering paste (PST-400C, received from JGS Catalysts and Chemicals) were then screen printed on top of the TiO$_2$ nanoparticle film. Resulting films had a thickness of ~ 18 µm. The electrodes were heated (Nabertherm Controller P320) in an air atmosphere at 180 °C (10 min), 320 °C (10 min), 390 °C (10 min), and 500 °C (30 min). A final TiCl$_4$ treatment was performed similar to above, and the electrodes were sintered again using the above protocol. Before use, electrodes were heated to 300 °C to remove water, and allowed to cool to 80 °C, at which point they...
were placed in a dye solution (0.2 mM D35 dye in ethanol) overnight. The films were then rinsed with ethanol and dried. Platinum counter electrodes were prepared by depositing a 4.8 mM chloroplatinic acid solution in ethanol onto the FTO glass substrate (10 µL/cm²) and then heating the electrode to 400 °C for 30 min before use. FGSₓ counter electrodes were prepared by depositing a LB monolayer onto the FTO glass substrate, as described above. Electrolyte (0.22 M Co(bpy)₃(PF₆)₂, 0.033 M Co(bpy)₃(PF₆)₂, 0.1 M lithium perchlorate 0.2 M 4-tert-butylpyridine in acetonitrile) was added by via vacuum filling through holes in the counter electrode. A 50 µm Surlyn thermoplastic film was used to separate the photoanode and the counter electrode and to seal the cell after electrolyte was added.

4.2.3 Measurements

CV measurements were taken from 5 to 1000 mV/s. The electrolyte solution resistance was measured before CV tests and compensated for (85%) during the measurements. EIS measurements were taken at 0 V, the magnitude of the alternating signal was 10 mV, and the frequency range was 1 Hz to 100 kHz. ZFit (Biologic) and Matlab code was used to analyze the impedance spectra. For measurements, a homemade electrochemical cell was designed to hold block-type electrodes as described in Pope et al. (see Figure 4.2). This device is a slightly modified version of the electrode holder described by Randin and Yeager¹⁹ and later modified by Compton’s group.²⁰ The electrodes are spring-loaded against an O-ring that is used to isolate the electrochemically active surface area. The screw-on Teflon lid features ports for a platinum wire counter
electrode, a Ag/Ag$^+$(0.01 M AgNO$_3$, 0.1 M LiClO$_4$) reference electrode, and a Teflon hose for nitrogen purging.

**Figure 4.2:** Schematic of electrochemical test cell. CE: counter electrode; RE: reference electrode; PTFE: polytetrafluoroethylene. Adapted from Pope et al.$^{13}$

Data values presented are the average of three identically prepared samples, while figures are representative of individual runs.

### 4.2.4 Rate Constant Determination

Determination of rate constants in electrochemical systems has matured with several techniques in widespread use.$^{21-23}$ For our measurements, three techniques were used, two based on CV and one on EIS. In the first technique, often called the Nicholson method, the separation between oxidation and reduction peak (*i.e.*, $E_{pp}$) of a one electron reaction...
as a function of \( \nu \) was determined.\(^{21}\) Under the assumption of a symmetric reaction and negligible ohmic losses, a dimensionless number, \( \Lambda \), can be backed out from \( E_{pp} \), see Table 4.1. This number, obtained for a particular \( \nu \), corresponds to a reaction rate (\( i.e., k_0 \)) which can be calculated as

\[
k_0 = \frac{\Lambda \times D_0^{0.5} \times F \times \nu}{(D_0^{D_R})^{\nu} \times R \times T},
\]

where \( \alpha \) is the reaction transfer coefficient, \( D_0 \) and \( D_R \) are the diffusion coefficients of the oxidized and reduced species, \( F \) is the Faraday constant, \( R \) is the universal gas constant, and \( T \) is temperature (298 K). We assume that the oxidized and reduced species have the same diffusion coefficient, \( D \), due to their similar size. This simplifies the equation to

\[
k_0 = \frac{\Lambda \times D^{0.5} \times F \times \nu}{R \times T}.
\]

The variation of \( \Lambda \) with \( E_{pp} \) was determined by running simulations of the reaction-diffusion system, as described in electrochemistry textbooks, with \( \alpha = 0.5 \), and a scan window of 600 mV.\(^{21,22}\) A polynomial interpolation between the data points shown in Table 4.1 is used to obtain \( \Lambda \) from \( E_{pp} \).

**Table 4.1:** Nicholson Method - Variation of \( E_{pp} \) (in mV) with \( \Lambda \).

<table>
<thead>
<tr>
<th>( \Lambda )</th>
<th>( E_{pp} )</th>
<th>( \Lambda )</th>
<th>( E_{pp} )</th>
<th>( \Lambda )</th>
<th>( E_{pp} )</th>
<th>( \Lambda )</th>
<th>( E_{pp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 6.38 \times 10^3 )</td>
<td>57.7</td>
<td>( 4.47 \times 10^0 )</td>
<td>67.7</td>
<td>( 4.47 \times 10^{-1} )</td>
<td>144</td>
<td>( 4.47 \times 10^{-2} )</td>
<td>358</td>
</tr>
<tr>
<td>( 3.19 \times 10^3 )</td>
<td>58.4</td>
<td>( 3.19 \times 10^0 )</td>
<td>71.8</td>
<td>( 3.19 \times 10^{-1} )</td>
<td>168</td>
<td>( 3.19 \times 10^{-2} )</td>
<td>393</td>
</tr>
<tr>
<td>( 2.24 \times 10^3 )</td>
<td>59.1</td>
<td>( 2.24 \times 10^0 )</td>
<td>77.9</td>
<td>( 2.24 \times 10^{-1} )</td>
<td>198</td>
<td>( 2.24 \times 10^{-2} )</td>
<td>430</td>
</tr>
<tr>
<td>( 1.28 \times 10^3 )</td>
<td>60.7</td>
<td>( 1.28 \times 10^0 )</td>
<td>92.3</td>
<td>( 1.28 \times 10^{-1} )</td>
<td>251</td>
<td>( 1.28 \times 10^{-2} )</td>
<td>488</td>
</tr>
<tr>
<td>( 8.94 \times 10^0 )</td>
<td>62.3</td>
<td>( 8.94 \times 10^{-1} )</td>
<td>106</td>
<td>( 8.94 \times 10^{-2} )</td>
<td>287</td>
<td>( 8.94 \times 10^{-3} )</td>
<td>525</td>
</tr>
<tr>
<td>( 6.39 \times 10^0 )</td>
<td>64.5</td>
<td>( 6.39 \times 10^{-1} )</td>
<td>122</td>
<td>( 6.39 \times 10^{-2} )</td>
<td>321</td>
<td>( 6.39 \times 10^{-3} )</td>
<td>560</td>
</tr>
</tbody>
</table>
In this study, $D$ was determined to be $3.0 \pm 0.6 \times 10^{-6} \text{ cm}^2/\text{s}$ through diffusion limiting current (see Figure 4.3) and EIS measurements. For both methods, two sandwich cell electrodes (spacing thickness, $l$, of 37 and 49 µm, respectively) with different concentrations, $C_{Co}$, of Co(bpy)$_3$(PF$_6$)$_2$, 2 mM and 10 mM, were used. In the first case, the limiting current, $i_{lim}$, was found and then $D$ was determined from

$$D = \frac{i_{lim} \times l}{2 \times A \times C_{Co} \times F \times n^2},$$

where $A$ is the electrode area, and $n$ is the number of electrons transferred in each reaction (in our cobalt system $n = 1$). For the latter case, EIS fitting software was used to solve for the Warburg parameter, $\varphi$, which relates to the diffusion coefficient through

$$\varphi = \left(\frac{R \times T}{\sqrt{2} \times A \times F^2 \times n^2}\right) \left(\frac{1}{D_0^{0.5} \times C_0} + \frac{1}{D_R^{0.5} \times C_R}\right).$$
Again, we assume $D_O = D_R = D$. Also, before EIS measurements, the system was held at the $E_{Red}$ of the mediator for 2 min, to bring the system towards equilibrium in which the $C_O = C_R = 0.5 \times C_{Co}$ near the electrode. Thus the equation simplifies to

$$D = 8 \times \left(\frac{R \times T}{A \times C_{Co} \times F^2 \times \varphi}\right)^2. \quad (8)$$

$D$ obtained in this study is greater than that found by Tsao et al. using macroscopic electrodes, smaller than that found by microelectrode studies, and is similar to that determined for related cobalt compounds.

For large values of $E_{pp}$, and in particular where peaks are not present in the scan window, Tafel slopes were used to determine $k_0$. The Tafel slope is the slope of the linear region of the logarithm of $I$ vs. overpotential plot, where the back reaction is negligible and mass transfer is not limiting. This region can be extrapolated to zero overpotential to determine the exchange current $i_0$ and thus $k_0$ as described by

$$k_0 = \frac{i_0}{A \times C_{Co} \times F \times n}. \quad (9)$$

For both CV methods, values of $k_0$ were obtained at scan rates of 1000, 500, 100, 50, 20, and 5 mV/s, and averaged. An exception was made for very fast reactions in which $\Lambda > 5$, as $\Lambda$ is very sensitive to $E_{pp}$ in this range. In these cases only faster scan rates, with larger $E_{pp}$, were used. Data obtained for all measurements were analyzed with Matlab.

EIS derived rate constants (i.e., $k_0$) were obtained using Equation 9, by fitting EIS spectra to an RC equivalent circuit to determine the charge transfer resistance, $R_{CT}$, which is related to $i_0$ according to Equation 10:

$$i_0 = \frac{R \times T}{n \times F \times R_{CT}}. \quad (10)$$
4.3 Results and Discussion

To determine the catalytic role of oxygen groups, we varied their presence on the sheets over two orders of magnitude, as measured by C/O (from ~ 0 to 33 at.% oxygen) through thermal treatment as seen in Figure 4.4. The basal plane surface of HOPG is used as a surrogate for the surface of pristine graphene (C/O → ∞). Although oxygen content is a convenient identifier, it is not a unique one, as for a given value of C/O there can be different compositions of oxygen groups (epoxides, hydroxyls, carbonyls, etc.) and lattice defects (topological defects, lattice vacancies, etc.) on the sheets, which can affect the chemical and electrical properties of the material.

Figure 4.4: FGS₄ properties. Oxygen content (■) and defectiveness as measured by I_D/I_G (○). Oxygen content calculations do not take into account the contribution of hydrogen. Raman data from Pope and Aksay.²⁷

Thermal treatment of FGS₂ removes oxygen from the material through the evolution of CO, CO₂, H₂O, and O₂, leaving behind lattice defect sites when carbon is removed from the lattice.²⁸-³⁰ However, at elevated temperatures, as the lattice diffusion rate of carbon is enhanced, the lattice defects can heal³¹ and the structure moves towards a more
pristine graphene state as suggested by a decrease in the Raman spectroscopy D-band to G-band peak intensity ratio (I_D/I_G), as shown in Figure 4.4.\textsuperscript{32,33}

The G-band is due to vibrations of pairs of sp\(^2\)-bonded carbon atoms and thus its intensity scales with the number of sp\(^2\)-bonded carbon atoms in the material. The D-band, on the other hand, is due to the breathing oscillation of aromatic six-membered rings of carbon atoms and its intensity scales with number of edge-site dangling bonds, functional groups, and lattice defects whose presence and distribution define the lateral crystallite size of graphitic domains (\textit{i.e.}, \(L_A\)) within the material.\textsuperscript{34,35} The D-band shows non-monotonic behavior because the intensity grows with number of 6-member aromatic rings but the oscillation is dampened when \(L_A\) exceeds \(\sim 2\) nm.\textsuperscript{36} The processing conditions for the samples used in this work are tabulated in Table 4.2.

\textbf{Table 4.2:} Material processing conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt foil</td>
<td>Polished</td>
</tr>
<tr>
<td>GC</td>
<td>Polished, Oxygen plasma 5 min at 500 mTorr</td>
</tr>
<tr>
<td>FGS(_{32})</td>
<td>Ultrasonic exfoliation of GO in ammoniated water (pH 10)</td>
</tr>
<tr>
<td>FGS(_{7})</td>
<td>Exfoliation of GO at 300 °C 60 s</td>
</tr>
<tr>
<td>FGS(_{48})</td>
<td>Vor-x®, supplied by Vorbeck Materials Corp.</td>
</tr>
<tr>
<td>FGS(_{68})</td>
<td>Exfoliation of GO at 1100 °C 300 s</td>
</tr>
<tr>
<td>FGS(_{324})</td>
<td>Exfoliation of GO at 1100 °C 60 s, anneal at 1300 °C 2 hr</td>
</tr>
<tr>
<td>FGS(_{393})</td>
<td>Exfoliation of GO at 1100 °C 60 s, anneal at 1900 °C for 2 hr</td>
</tr>
<tr>
<td>HOPG</td>
<td>Freshly cleaved</td>
</tr>
</tbody>
</table>
From Figure 4.5, it is evident that these different materials exhibit different intrinsic catalytic activities for the Co(bpy)$_3$(II/III) redox couple. As C/O increases, the catalytic activity (as indicated by $E_{pp}$ and $I_p$) first increases and then decreases.$^8$ HOPG shows negligible activity, consistent with previous reports for the low activity of this material.$^2$. $^4, 37$ We see FGS$_2$ performing significantly better than HOPG, in contradiction to results of Kavan et al.$^2$ The electrodes used in their work were formed through drop casting, spin coating, and airbrush coating – all techniques that form films of multiple layers. FGS$_2$ films even a few nanometers thick prevent electron transfer due to the insulating properties of the material. Our own attempts to make thin FGS$_2$ layers on conductive substrates using drop casting and spin coating techniques also resulted in inactive electrodes, thus contributing to our use of LB monolayer electrodes.

**Figure 4.5:** Cyclic voltammograms of the Co(bpy)$_3$(II/III) redox couple with FGS$_x$ monolayer electrodes. $v = 1$ V/s.

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The dependence of catalytic activity on the degree of FGS reduction is clearly observed through the comparison of heterogeneous reaction rate constants \((i.e., k_0)\) (Figure 4.6) which we determined using several techniques. CV data were analyzed by employing both Nicholson’s method and by determining Tafel slopes. EIS data were fit to an equivalent circuit model to determine \(R_{CT}\) and from this \(k_0\). These different approaches for reaction rate determination yielded analogous results. Rate constants measured with FGS\(_2\) are over 15 times larger than those with HOPG, supporting the claim that oxygen functional groups act as catalytic sites on FGSs, and by extension, other carbonaceous materials. Nevertheless, thermally reducing FGS\(_2\) improves the reaction rate further. In fact, FGS\(_{68}\) and its industrially-produced counterpart, FGS\(_{48}\), have activities that match that of platinum \((k_0 \sim 6 \times 10^{-3} \text{ cm/s})\). Additional thermal treatment above 1100 °C decreases activity, correlating with a decrease in FGS defectiveness.

**Figure 4.6:** Reaction rate constants for the Co(bpy)\(_3\)(II/III) redox couple. FGS\(_x\) monolayers were tested on both HOPG and FTO substrates.
Highly active lattice defects, moderately active oxygen sites, and poorly active pristine graphene domains are consistent with the observations from Figure 4.6. As moderately active oxygen sites on FGS\(_2\) are thermally reduced, CO\(_2\) and CO is evolved, removing carbon atoms from the lattice. This process results in vacancies or other highly active defect sites which improve the overall activity of the material. At high temperatures, the lattice defects can migrate and are effectively replaced by pristine graphene domains, reducing the activity. This study does not distinguish which lattice defect sites are most active; however, literature suggest some to be relatively inert (\textit{i.e.}, Stone-Wales, 5-7-7-5, topological defects) and some to be more active (\textit{i.e.}, carbon vacancies).\(^{38,39}\) We also acknowledge that specific oxygen sites likely have different activities as well, and a small number of highly active oxygen sites may be responsible for the perceived activity of oxygen rich FGS. Additionally, some oxygen sites can be created during the reduction process,\(^{40,41}\) and we cannot rule out the possibility that these sites are highly active and responsible for the increased activity.

Although we could not control for each type of oxygen site, we did find that FGS\(_2\) monolayers formed from large (\(~ 200 \mu m^2\)) and small (\(~ 20 \mu m^2\)) sheets had similar activity, as did oxidized glassy carbon whose structure is proposed to have a high proportion of edge atoms.\(^{8,42}\) Large sheets (\(~ 200 \mu m^2\)) of FGS\(_2\) were primarily used in this study due to the ease in forming monolayers from the material. The large surface facilitates the aggregation at the air-water interface. Smaller sheets, which can be obtained by sonicating suspensions of larger FGS\(_2\) sheets, tend to sink into the water phase of the LB trough and much more material must be used to obtain an acceptable
monolayer, such as that seen in Figure 4.7. Drop casting and spin coating techniques were also attempted to form a monolayer of smaller sheets, however, large area (1 cm²) uniformity was unable to be achieved.

Samples from large and small sheets behaved similarly in electrochemical measurements, and correcting for area coverage, both types exhibit statistically equivalent performance. Rate constants for large FGS₂ are $3.1 \pm 2.2 \times 10^{-4}$ cm/s, and small FGS₂ are $2.2 \pm 2.2 \times 10^{-4}$ cm/s (sample size of 10 and 8, respectively). Accounting for surface coverage, $k_0$ for small FGS₂ samples is $3.2 \pm 2.2 \times 10^{-4}$ cm/s. These results suggest that sheet edges, with their carbonyl and other oxygen functional groups, may not be the dominant reactive site for the cobalt mediator, as is often suggested for other systems.⁴⁴,⁴⁵

To further support the results of Figure 4.6, we made FGS₂ monolayers on FTO substrates and then heated these samples in air at 150, 250, and 350 °C, resulting in FGSs with C/Os of 2.9, 4.5, and 6.9, as estimated from the heating of bulk powder and
subsequent measurement by energy dispersive X-ray spectroscopy. A trend of increasing activity was observed, with the data falling between the FGS\textsubscript{2} and FGS\textsubscript{48} samples ($k_0 \sim 0.7 \times 10^{-3}$, $2.5 \times 10^{-3}$, and $3.6 \times 10^{-3}$ cm/s respectively). As the samples matched or outperformed FGS\textsubscript{7} at lower C/O, the partial thermolysis of the material in the presence of oxygen may have increased the density of catalytic lattice defect sites.

We also electrochemically reduced FGS\textsubscript{2} monolayers, a technique that is suggested to remove oxygen (to a C/O of ~ 22) without disrupting the carbon lattice.\textsuperscript{46} This technique was carried out both in aqueous (as detailed by Zhou et al.) and in acetonitrile electrolyte by applying sufficiently negative potentials to the electrode (see Figure 4.8a). Unlike thermal reduction, electrochemical reduction resulted in a material with decreased activity compared to FGS\textsubscript{2} ($k_0 \sim 2 \times 10^{-4}$ cm/s), which is consistent with it losing active oxygen functionalities and yielding a less defective form of graphene. No change in FGS\textsubscript{2} activity was observed after scanning in our normal scan window (-0.6 to 0.6 V vs. Ag/Ag\textsuperscript{+}); however, at mild reduction conditions (scan to -0.8 V vs. Ag/Ag\textsuperscript{+}) the activity increased almost 100 percent, before declining at higher degrees of reduction as seen in Figure 4.8b. This result could be explained by the tradeoff between the increase of conductivity which facilitates electron transfer, and the loss of active sites, both due to the removal of oxygen groups.
Figure 4.8: Electrochemical reduction of FGS$_2$. (a) Description of parameters used for reduction levels in (b). (b) Rate constant progressing during electrochemical reduction of FGS$_2$. Activity increased through a -0.9 V vs. Ag/Ag$^+$ reduction cycle, and then decreased through reduction cycles of up to -1.3 V where we approached the stability limit of our electrolyte. Additional reduction cycles at -1.1 V have little effect, with the resultant electrode performing similarly to those reduced in water.
Table 4.3 presents a summary of rate constant averages and standard deviations.

**Table 4.3:** Compiled $k_0$ data.

<table>
<thead>
<tr>
<th>Bulk Samples</th>
<th>Average $k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt Foll</td>
<td>$5.95 \pm 1.71 \times 10^{-3}$</td>
</tr>
<tr>
<td>GC</td>
<td>$7.58 \pm 4.05 \times 10^{-3}$</td>
</tr>
<tr>
<td>HOPG</td>
<td>$2.49 \pm 1.31 \times 10^{-5}$</td>
</tr>
<tr>
<td>FTO</td>
<td>$8.05 \pm 8.15 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Monolayers</th>
<th>Average $k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FGS$_2$</td>
<td>$3.93 \pm 3.43 \times 10^{-4}$</td>
</tr>
<tr>
<td>FGS$_7$</td>
<td>$2.17 \pm 0.74 \times 10^{-3}$</td>
</tr>
<tr>
<td>FGS$_{48}$</td>
<td>$6.10 \pm 1.82 \times 10^{-3}$</td>
</tr>
<tr>
<td>FGS$_{69}$</td>
<td>$5.22 \pm 2.40 \times 10^{-3}$</td>
</tr>
<tr>
<td>FGS$_{323}$</td>
<td>$1.77 \pm 1.35 \times 10^{-3}$</td>
</tr>
<tr>
<td>FGS$_{353}$</td>
<td>$6.78 \pm 4.65 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Monolayers reduced in-situ</th>
<th>Average $k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemically</td>
<td>$1.93 \pm 1.01 \times 10^{-4}$</td>
</tr>
<tr>
<td>Thermally (150 °C)</td>
<td>$6.87 \times 10^{-4}$</td>
</tr>
<tr>
<td>Thermally (250 °C)</td>
<td>$2.48 \times 10^{-3}$</td>
</tr>
<tr>
<td>Thermally (350 °C)</td>
<td>$3.57 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

| Pt Nanoparticles on FTO     | $1.97 \pm 1.16 \times 10^{-2}$ |

DSSCs similar to those employed by Feldt *et al.* were fabricated using the cobalt mediator, D35 dye, and the various counter electrodes. The J-V curves (Figure 4.9) support the CV and EIS findings, with FGS$_{48}$ performing similarly to the standard thermolyzed platinic acid platinum nanoparticle catalyst, followed by FGS$_{353}$ and FGS$_2$. Of note, the platinum nanoparticles have a high surface area, and thus higher activity ($k_0 \sim 2 \times 10^{-2} \text{ cm/s}$) than their planar counterpart. Due to the higher concentration of the cobalt mediator in the DSSC, an $R_{CT}$ of 1 $\Omega$ can be achieved at the cathode with a $k_0$ of $8 \times 10^{-3} \text{ cm/s}$. Thus, a faster reaction rate than what we achieve with FGS$_{48}$ samples has little advantage in a device, as is seen. The high $R_{CT}$ from low catalytic activity is
noticeable, however, in the poor $FF$ of the FGS$_2$ device.

**Figure 4.9:** J-V curves for DSSCs using thermolyzed chloroplatinic acid (Pt) and FGS$_x$ monolayer counter electrodes. Inset shows average device characteristics measured for three cells. Cells were measured under AM 1.5G (1000 W/m$^2$) illumination. Active area is 0.25 cm$^2$.

### 4.4 Conclusions

In summary, using a tunable FGS surface, we determined the relative efficacy of various functional sites on defective graphene towards the Co(bpy)$_3$(II/III) mediator. The basal plane of HOPG, as surrogate for pristine graphene, shows low activity ($k_0 \sim 2.5 \times 10^{-5}$ cm/s), while FGS$_{48}$, a functionalized graphene with high lattice disorder and low oxygen content, shows activity $\sim$ 245 times greater. The relative performance is conserved in DSSCs as cells using a single layer of FGS$_{48}$ as the catalyst perform as well as those using thermolyzed platinic acid. This work represents an important step forward
in understanding carbon nanomaterials by determining the intrinsic catalytic activity of FGSs with different oxygen contents and degrees of defectiveness.

References


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45. Banks, C. E.; Davies, T. J.; Wildgoose, G. G.; Compton, R. G., Electrocatalysis at graphite and carbon nanotube modified electrodes: edge-plane sites and tube ends are the reactive sites. *Chemical Communications* **2004**, *7*, 829-841.

5 Networks of Functionalized Graphene Sheets and Their Use as a Catalytic Counter Electrode for Dye-Sensitized Solar Cells (Generation 1)

This chapter is adapted from two works published in ACS Nano, one coauthored with Sibel Korkut (first author), Daniel M. Dabbs, David L. Milius, and Ilhan A. Aksay, and the other coauthored with David J. Bozym, Christian Punckt, and Ilhan A. Aksay. S. Korkut performed conductivity and density measurements, created FGS pellets, determined the glass silane treatment conditions and helped with experimental design, rheological measurements, thermal analysis, XRD measurements, and stabilization studies. S. Korkut and D. Dabbs helped with data analysis. D. Milius fabricated FGS tapes. D. Bozym helped with the CV study and imaging samples. C. Punckt helped with electrochemical data analysis.

Chapter 4 discussed the intrinsic catalytic activity of FGSs for the cobalt mediator. Although a monolayer may be sufficient to effectively catalyze this reaction, more of the material is required for other redox couples such as the iodide/triiodide mediator. Furthermore, the LB through approach is not a highly scalable manufacturing technique, a necessity for low cost, large area solar cells. Thus, in this chapter, we discuss a scalable
method for producing continuous graphene networks by tape casting surfactant-stabilized aqueous suspensions of FGSs and then thermolyzing the surfactant materials. When cast on FTO and heat treated, FGS tapes perform comparably to platinum as a DSSC counter electrode with the iodide/triiodide redox couple (conversion efficiencies of 5.0 and 5.5%, respectively, at 1000 W/m$^2$ AM1.5G simulated light). To interpret the catalytic activity of FGSs towards the reduction of triiodide, we propose a new electrochemical impedance spectroscopy equivalent circuit that matches the observed spectra features to the appropriate phenomena. Furthermore, we demonstrate that a FGS-based ink can serve as a catalytic, flexible, electrically conductive counter electrode material.

5.1 Introduction

Although LB trough derived monolayers are useful for fundamental studies, and may have select applications (such as being an effective Co(bpy)$_3$(II/III) catalyst), high surface area networks of highly connected FGSs offer significantly improved performance for a wide-range of devices including batteries,$^3, 4$ sensors,$^5$ supercapacitors,$^6$ and as we will discuss in detail in this chapter, DSSCs. Commercialization of these technologies requires large scale manufacturing techniques that permit the simultaneous control of the surface area, degree of functionalization, electrical conductivity, and mechanical properties of the network. Current methods for fabricating interconnected graphene networks are limited to batch processes best suited for applications at the laboratory scale. Films of layered networks of graphene materials are assembled layer-by-layer from monolayers formed in an LB trough$^7$ or made by filtering graphene suspensions across a
Nevertheless, the LB trough is impractical for fabricating films thicker than a few layers, and although filtration can produce dense and mechanically robust FGS networks, fabricating an FGS film of sufficient size for testing and evaluation can take over a week. We have circumvented the limitations of these small-scale processes by using tape casting to produce polymer-FGS composite tapes from which the polymer is subsequently removed by thermolysis, resulting in large-area, highly connected graphene networks. The resulting tapes combine high surface area with high electrical conductivity making them good candidates for a DSSC catalyst.

Figure 5.1: FGS tape casting schematic. The FGS schematic shows its defective and wrinkled structure. Oxygen functionalities are shown in red, a 5-8-5 defect in pink and a 5-7-7-5 defect in yellow. Image reproduced from Korkut et al.1

Tape casting is the controlled casting of a colloidal suspension through a slit by the motion of a substrate relative to a doctor blade Figure 5.1).10 As it is a high throughput technique, tape casting requires large quantities of FGSs. Because of this, we used FGSs supplied by Vorbeck Materials (batch Bk86x, C/O ~ 13), a company which has
industrialized production of FGSs via the simultaneous thermal exfoliation and reduction of graphite oxide.

In the following sections, we first describe how FGS tapes were produced and discuss their general structure. We analyze their specific surface area and electrical properties by focusing on the structural changes caused by different heat treatments, and then we compare these properties to those of other carbonaceous materials. Finally, we provide a thorough analysis of DSSC cathodes based on networks of FGSs created through the tape casting method showing that FGSs can function as the catalytic counter electrode material in a fully assembled DSSC with a performance similar to that of platinum.

5.2 Experimental Methods

Experimental details specific to this chapter are included below. General experimental techniques can be found in Chapter 3.

5.2.1 Preparation of FGS Tapes and Pellets

The fabrication of FGS tapes began with the production of FGS/surfactant/organic binder composite tapes, which were cast from a suspension of FGSs stabilized with a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (EO₁₀₆PO₇₀EO₁₀₆) triblock copolymer surfactant (F-127, Pluronic®) in an aqueous poly(ethylene oxide) (PEO, Mₜ 600,000) binder solution. To produce the FGS suspensions, we first prepared an EO₁₀₆PO₇₀EO₁₀₆ surfactant solution with equal amount of surfactant (by mass) to that of the FGSs to be added in deionized water. The equal mass of surfactant to FGS
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corresponded to adequate coverage of FGS by surfactant to ensure a stable dispersion for the duration of the tape casting process. Then, over a period of 1 h, the FGS suspension was slowly added to the surfactant solution under continuous stirring and ultrasonication at 30% power (Vibra Cell, Sonics & Materials) while it was kept in an ice bath to prevent heating. The suspension was then centrifuged at 900 g for 10 min to remove any remaining agglomerates, and the supernatant was decanted. The FGS concentration of this supernatant was typically ~ 1.6 wt.%, measured using UV-Vis spectroscopy (Model 9430, IBM). These refined suspensions were then transferred to a vacuum chamber and stirred under slight vacuum to remove entrained air.

Binder solutions of 4.5 wt.% PEO were prepared by first adding the PEO powder to absolute ethanol under continuous stirring at 65 ºC and then adding an equal volume of water. Pre-mixing the PEO with ethanol prevents the formation of clumps and facilitates the homogeneous dispersion of the PEO. Stock PEO solutions were then added to the FGS/surfactant suspensions to obtain FGS/surfactant/PEO tape casting suspensions having the desired weight ratios. The tape casting suspensions were stirred for at least 2 h prior to casting.

Rheological measurements (Fluid Spectrometer RFS-II, Rheometrics) were done using a parallel plate fixture (diameter: 5 cm). The temperature of the fixture and the sample was kept constant at 25 ºC using a temperature controlled water bath (Environmental Control Circulator, Rheometrics).

The glass plates on which the tapes were cast were prepared by first cleaning their surfaces using detergent followed by 1 M KOH (Acros) aqueous solution. After rinsing
and drying, the surfaces were treated with a mixed silane solution (a mixture of 6.6 mM octadecyltrichlorosilane and 3.3 mM aminopropyltriethoxy silane in hexane (Acros)) then dried to reduce the adhesion between the glass and the composite tape. Without this silane treatment, the tapes could not be peeled cleanly off the glass.

The FGS/surfactant/PEO suspensions were cast on the silane-coated glass plate using a doctor blade assembly (Model SDBA, Richard E. Mistler) with a 1.5 mm blade gap in a class 1,000 soft wall clean room (Model DFE1214-7 Atmos-Tech Industries). The tapes were dried in the clean room at ambient temperature for several days and then removed from the glass templates to obtain large, free standing tapes.

The thermolysis of the binder and surfactant from these composite tapes was done in a graphite-element furnace (Model 1000, Thermal Technology). In order to heat many samples in each batch, composite tapes were stacked alternating with Grafoil® sheets (GTB grade, 5 mil thick, Union Carbide). The pressure in the furnace chamber was first reduced to 100 mTorr and then backfilled with dry nitrogen to atmospheric pressure in order to decompose the organics in a non-oxidizing atmosphere. Thermolysis runs were done under flowing nitrogen at 2 SCFM (3.4 m³/h). The furnace chamber was heated to 90 °C at 5 °C/min, held for 1 h to remove volatiles, then heated to 315 °C at 5 °C/min and held at the higher temperature for 10 h. When higher temperatures were used for subsequent processing, the furnace temperature was raised at 10 °C/min to the target temperature. For heat treatments above 1000 °C argon was used in the furnace chamber as the inert atmosphere.
FGS pellets, comprised only of compacted FGSs, were used to distinguish between the contributions of FGSs, the thermolyzed surfactant, and the thermolyzed PEO to the conductivity of FGS tapes and reduced FGS tapes. By compressing ~100-150 mg of FGSs using a cylindrical stainless steel die with inner diameter of 2.9 cm and height of 4.4 cm under a hydraulic press (Model-C Laboratory Press, Fred. S. Carver) brittle FGS pellets were formed. The density of the pellets was adjusted by varying the load between 40 and 150 MPa. Subsequent heat treatments for the pellets were done under the same conditions used for the thermolysis of the composite tapes and reduction of FGS tapes.

To probe the effect of solvent evaporation on the graphitization of FGSs, freeze dried samples were prepared. In order to freeze dry an FGS suspension that has been sonicated, de-aired, and classified as previously described, the suspension was added drop wise to the ultrasonicator probe at 60% power. When the drop reached the tip of the probe it was broken up into a spray of smaller drops and settled into a bath of liquid nitrogen stirred by propeller creating a frozen suspension. This frozen suspension was then placed in an insulating container and freeze dried (Virtis AdVantage) at 50 mTorr for 96 h.

5.2.2 FGS Tape Characterization

The density of the tapes was determined by measuring the dimensions and weight of rectangular pieces. The densities for three samples were measured for each FGS concentration and the average density was reported. The volume fraction of the FGSs in the tapes was determined assuming an FGS density of 2.2 g/cm$^3$, the density of graphite
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as calculated from the hexagonal carbon lattice with an interlayer graphitic spacing of 0.34 nm.

TGA runs of composite tapes were performed to determine the onset of decomposition and the required duration of the heat treatment. Two runs of thermal analysis were done: in the first run the temperature was increased at a rate of 1 °C/min and the decomposition temperature was determined; in the second run, the sample was held at the decomposition temperature and the time required for complete decomposition of the polymer was determined. Based on the information from STA, the thermolysis procedure described in the preceding section was chosen.

Electrical conductivity measurements were made similarly to the described ISO3915 standard procedure. Copper tapes (3M) were attached to the two sides of a rectangular piece of graphene tape or compressed pellet and a constant current of 2-10 mA was applied. For compressed pellets, carbon paste (Electron Microscopy Sciences) was applied between the sample and the copper tape in order to ensure equipotential cross sectional areas. Potential difference between two points along the direction of the current flow was simultaneously recorded for 20 s. The average potential drop and the applied current were used to calculate the conductivity, σ, of the samples using the formula:

\[ \sigma = \frac{I}{V} \cdot \frac{w}{A_x}, \]

where \( w \) is the distance between the two points that the potential difference is measured and \( A_x \) is the cross sectional area for the current flow.
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5.2.3 Preparation of Counter Electrodes

For electrodes used in EIS and DSSCs, FGS counter electrodes were prepared on FTO (TEC8) in a similar manner as described for free standing tapes. FGS-surfactant suspension (1.66 wt.% FGS, 1.66 wt.% F127 in water) was mixed in a PEO solution (0.6 g in 10 mL water, 10 mL ethanol) in a 1:4 FGS:PEO weight ratio and stirred overnight. The resulting suspension was spin coated onto clean FTO substrates at given speeds for 4 min. The resulting film was dried at room temperature and then the surfactants were thermally decomposed in an ashing furnace at 350 °C in air for 2 h. Thermally treated chloroplatinic acid electrodes were prepared as described by Papageorgiou et al.\textsuperscript{12} Briefly, 2 µL of 5 mM chloroplatinic acid in isopropanol were drop cast on an FTO electrode with a 0.39 cm\textsuperscript{2} mask. The sample was then heated to 380 °C for 20 min before use. Vor-ink\textsuperscript{TM} films based on FGSs were cast on mylar by Vorbeck Materials\textsuperscript{13} and used as received.

Electrodes for CV were prepared by drop casting a pH 11 aqueous suspension of FGS\textsubscript{13}, on the tips of titanium rods (grade 2, diameter = ⅛ inch, McMaster). Thermally treated chloroplatinic acid electrodes were also prepared using titanium rods. Titanium was selected as the electrode bulk material due to its high electrical conductivity, high corrosion resistance in the iodine-based electrolyte solution, and low catalytic activity for the redox reaction of interest.
5.2.4 Preparation of DSSCs

DSSCs were constructed similarly to as described by Nazeeruddin et al.\textsuperscript{14} 2 g of P25 titania nanoparticles (Evanonik Industries) were suspended with 66 µL of acetylacetone and 3.333 mL deionized water. Titania films, four layers thick, were cast on TiCl\textsubscript{4} treated FTO glass using a scotch tape mask and a glass rod via the doctor blade technique. These films were then heated to 485 °C for 30 min in air before being placed in a 0.2 M TiCl\textsubscript{4} solution for 12 h and heated to 450 °C for 30 min. The resulting electrode was immersed in a 0.3 mM N3 dye/ethanol solution for 20 h to form the sensitized photocathode. Platinum and FGS counter electrodes were formed as described above. A 25 µm Surlyn film (Solaronix) was used to separate the photocathode and counter electrode and seal the cell after electrolyte (Iodolyte AN-50 from Solaronix) was added. For the Vor-in\textsuperscript{TM} data series, TiCl\textsubscript{4} treatments were not performed. Also, due to the flexible nature of the Vor-in\textsuperscript{TM} films, to prevent short-circuiting of the cells, the electrodes were separated by 100 µm thick laboratory tape (Fisher) and clamped together using binder clips. Cells were tested immediately after fabrication.

5.2.5 Counter Electrode Measurements

The CV study was performed in a single compartment, three-electrode setup using an acetonitrile solution containing 0.1 M lithium perchlorate, 5 mM lithium iodide, and 0.5 mM iodine. A Ag/Ag\textsuperscript{+} reference electrode (0.01 M AgNO\textsubscript{3} in acetonitrile) was used and the cells were normalized to an external ferrocene reference. EIS was performed using a sandwich cell configuration with symmetric films in an acetonitrile electrolyte.
containing 0.5 M lithium iodide and 0.05 M iodine unless otherwise noted. A 25µm Surlyn film was used to separate the films and seal the cells. EIS measurements were taken from 0 V to 0.8 V, the magnitude of the alternating signal was 10 mV, and the frequency range was 1 Hz to 400 kHz. ZFit, with the appropriate equivalent circuit, was used to analyze the impedance spectra. I-V characteristics of DSSCs were taken under AM1.5G light, simulated at 1000 W/m² with a 16S solar simulator (SolarLight) using the potentiostat to apply various loads. Data values presented are the average of 2-6 identically prepared samples, while figures are representative of individual runs unless otherwise noted.

5.3 Results and Discussion

5.3.1 FGS Tape Production and Properties

Fabrication of high surface area tapes begins by preparing highly dispersed suspensions of FGSs. To disperse FGSs in water, we used a triblock copolymer surfactant, \( \text{EO}_{100}\text{PO}_{65}\text{EO}_{100} \). This surfactant is compatible with the binder polymer, PEO, and does not leave any metallic residues upon carbonization. The amount of surfactant needed to disperse the sheets was determined by measuring the FGS concentrations in the supernatant of suspensions containing different amounts of surfactants and comparing that to the initial overall suspension concentration (Figure 5.2a). The amount of FGSs in supernatant was observed to increase with increasing surfactant concentration, indicating improved suspension stability, until the FGS concentration plateaued at the initial concentration near a surfactant-to-FGS ratio of 1 (g/g). This behavior is typical for a
sterically stabilized suspension,\textsuperscript{15} where increased surface coverage of the particles increases the suspension stability.\textsuperscript{16} EO\textsubscript{100}PO\textsubscript{65}EO\textsubscript{100} adsorbs on carbon surfaces through its hydrophobic PO chain and extends its hydrophilic EO chains into water.\textsuperscript{17} Since water
is a good solvent for EO, the interaction between EO chains provides a repulsive barrier preventing the aggregation of FGSs. If coverage of FGSs by surfactants is not complete, the FGSs can aggregate due to van der Waals forces. Therefore, a plateau in the dispersion concentration implies saturation of FGS surfaces by surfactant molecules. The decrease in supernatant concentrations over time indicates sedimentation of FGSs from aged suspensions. This result suggests aggregation of FGSs. Although this process is not fully understood, it could take place through van der Waals interactions upon desorption of weakly adsorbed surfactant.\textsuperscript{18, 19} However, as both tape casting and drying were complete within two days, the adsorption of the triblock copolymer on FGSs was found to be adequate for effective tape casting.

In addition to maintaining a sufficient degree of dispersion for the duration of the casting process, tape casting suspensions need to flow easily through the gap between the blade and substrate under shear, and maintain the shape and thickness of the cast tape once shearing is removed after exiting the blade. This type of behavior is typically achieved by tape casting shear thinning suspensions. The tape casting suspensions used for this study exhibited shear thinning behavior under the shear rates used in their casting, ~ 100 s\textsuperscript{-1} (Figure 5.2b). The viscosities of the FGS tape casting suspensions varied within one order of magnitude at a fixed strain rate, with suspensions having the highest FGS content exhibiting the lowest viscosity. The viscosity of the suspension increased with increasing PEO content; the PEO solution with comparatively higher viscosity acted as a thickening agent and was used to tune the suspension viscosity. When the shear rate was decreased from 100 to 1 s\textsuperscript{-1}, the viscosity of the cast suspension took 1-2 s to return to the
viscosity exhibited under a shear rate of 1 s$^{-1}$. Therefore, the viscosity of the suspensions rose substantially within a few seconds of being cast. However, when cast on non-wetting substrates on which the contact line was not sufficiently pinned, the suspension pulled away from the substrate and cohered into a formless puddle, demonstrating that the zero shear viscosity of the suspensions was not high enough to maintain the shape of the cast tape. Casting the suspension on a wetting substrate on which the contact line was pinned overcame this difficulty, maintaining the tape’s shape during solvent evaporation.

The cast and dried tapes were easily removed from the substrate, producing free standing, continuous composite tapes up to 15 cm wide (Figure 5.2c). The size of these tapes was limited only by the width of the doctor blade and the width and length of the substrate; hence, even larger composite tapes are feasible using this approach. Subsequent heating of the composite tapes at 315 °C removed most of the polymer and surfactant (see Table 5.1) and the resulting FGS tape remained flexible and mechanically robust (Figure 5.2d,e). Elemental analysis showed that the C/O increased from 13 in the as-received FGSs to 17, 247, and 371 after heat treatments of 315 °C, 1000 °C, and 2250 °C respectively.

<table>
<thead>
<tr>
<th>Component</th>
<th>FGS Tape</th>
<th>Reduced FGS Tape*</th>
<th>Annealed FGS Tape*</th>
</tr>
</thead>
<tbody>
<tr>
<td>FGS</td>
<td>0.93</td>
<td>0.82</td>
<td>0.76</td>
</tr>
<tr>
<td>PEO</td>
<td>0.06</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>Surfactant</td>
<td>0.04</td>
<td>0.03</td>
<td>0.01</td>
</tr>
</tbody>
</table>

*Relative to the amount of the component in the composite tape prior to heat treatment.
FGS tapes exhibited uniform thickness and a defect-free microstructure (Figure 5.3). The absence of microscale cracks within the FGS tapes suggests that thermolysis was done slowly enough to allow the evolved gases to escape from the tape without creating structural defects.

The structure of the tapes changed with the FGS concentration in the initial composite tape. An anisotropic structure was observed in the cross-section of the denser tapes (i.e., higher FGS concentration in the composite tape), with striations parallel to the tape surfaces running along the long axis of the tape (Figure 5.3a). At lower densities this structure was lost and the cross-section of the low density tape appeared more isotropic (Figure 5.3b). The anisotropy is most likely caused by the alignment of the FGSs, which could take place due to the constrained rotational motion with increasing FGS content.  

Figure 5.3: Microstructure of FGS tapes. SEM images of FGS tapes with a) 0.40 g/cm$^3$ and b) 0.15 g/cm$^3$ density. Insets show increased magnification of the tape cross section. The scale bars show 50 µm for the main images and 5 µm for the insets. Figure reproduced from Korkut et al.$^1$
Alignment of FGS due to shear during the tape casting process is also expected since the rotary Peclet number is large (Pe ≈ 10^4-10^5 even when the rotary diffusivity is calculated based on dilute conditions). However, as there was sufficient time during solvent evaporation for rotational Brownian motion to randomize the orientation of FGSs after shearing, the anisotropic structure of the tapes is most likely not due to shear during the casting process. Horizontal alignment of FGS may inhibit the flow of electrolyte, effectively reducing the assessable surface area for redox species, and thus may be undesirable for a catalyst material.

The degree of graphene restacking in our FGS tapes was monitored through XRD analysis (Figure 5.4), the presence of graphite being indicated by the appearance of a
diffraction peak centered at an angle of 26.4°. The amount of scattering was very low for powders formed by freeze-drying suspensions of FGSs. The graphitic peak was seen to be higher for the composite tape, implying that FGSs partially reassembled into stacked structures during solvent evaporation. Further, the little difference that was seen to exist between the diffraction intensities of the composite and thermolyzed FGS tapes showed that removing most of the polymer and surfactant from the composite tape (Table 5.1) had little effect on the degree of graphitization.

A degree of graphene restacking is required to fabricate self-supporting, three-dimensional graphene networks, but stacks of FGS containing more than a few sheets must be avoided to more fully exploit graphene’s properties. Therefore, the amounts of graphitic and graphene regions need to be balanced to combine a mechanically robust tape with more graphene-like properties, such as high surface area and electrical conductivity. Even though some graphitization occurred during their preparation, the surface area of FGS tapes was significantly higher than the values reported for FGS networks formed by evaporative drying of suspensions of flatter graphene sheets (44 m²/g). Our conjecture is that the crumpled structure of FGSs limits the contact area between adjacent sheets, whereas flattening the sheets increases the degree of overlap and results in a lower surface area.

FGSs can be flattened and the spacing between the sheets reduced through thermal treatment. XRD patterns from FGS tapes heated to 1000 °C (“reduced FGS tapes”) did not appear to be significantly affected by the higher temperature treatment (Figure 5.4), indicating that the FGSs were not significantly flatter than those in the FGS tapes.
Although the oxygen content of the sheets was lowered, the apparent density and surface area of the tapes were only slightly different from those of the FGS tapes treated at 315 °C (Figure 5.5). However, heating the tapes to 2250 °C (“annealed FGS tapes”) had a significant effect on the intensity of the XRD peaks. The higher temperature of annealing partially restored the $sp^2$ network within the sheets causing the sheets to flatten. The flatter sheets then stacked more readily (Figure 5.4), increasing the apparent density by 17 to 49% when compared to FGS tapes and decreasing the surface area to ~ 200 m$^2$/g (Figure 5.5). Increased stacking, with the lower surface area, is undesirable for catalysis. Furthermore, the annealing likely results in a less catalytic material as discussed in Chapter 4.

**Figure 5.5:** FGS tape surface areas. BET surface area of FGS tapes, reduced FGS tapes, and annealed FGS tapes as a function of FGS concentration in the composite tapes. Figure reproduced from Korkut et al.\textsuperscript{1}
The electrical conductivity of the FGS tapes changed by two orders of magnitude, from 130 to 24,000 S/m depending on the FGS concentration and the heat treatment protocol (Figure 5.6a). Increasing the FGS concentration in the tapes increased the number of conductive paths in the sample and resulted in higher conductivities. We separated the effect of heat treatment on FGSs from that on the polymer and surfactant by comparing the electrical properties of the tapes with those of pellets formed by compressing FGS without any binders (“FGS pellets”). At a given FGS concentration, the conductivity of the tapes doubled following the removal of the polymer and the surfactant at 315 °C and increased another order of magnitude when reduced at 1000 °C (Figure 5.6a). The pellets’ conductivity also increased when heated at 315 °C, but to a smaller extent. These observations suggest that a significant part of the increase in the FGS tape’s conductivity during first heat treatment was due to decreasing the contact resistance between the FGSs simply by removing the polymer and surfactant. A smaller effect resulted from changes in the FGSs themselves, seen as an increase in C/O from 13 to 17.28 A further 8 to 10-fold increase in conductivity was exhibited by both the reduced (1000 °C) tapes and reduced pellets. Since the pellets did not contain any material other than FGS; we conclude that the conductivity of the tapes was strongly affected by the changes in FGS, particularly the drastic increase in C/O, but not so much by changes in the polymer and surfactant residues upon reduction.

Extrapolating the measured relationships between conductivity and the density for reduced and annealed FGS tapes (Figure 5.6a) to the density of graphite (1.84 g/cm³)29 gives values of 1.0×10⁵ S/m and 1.2×10⁵ S/m, respectively. These are very close to the
Figure 5.6: Comparison of carbonaceous materials. a) and b) compare conductivity and surface area of our tapes with the corresponding properties of other carbonaceous films, tapes and monoliths. The diagonal lines in (b) represent constant values for the multiplication of conductivity with surface area and are plotted to guide the eye. Both high conductivity and high surface area are desirable for electronic applications. Although the relative importance of each attribute is device specific, we assume an equal weighting to conductivity and surface area, thus the higher the diagonal, the better device performance. Standard deviations are calculated from three or more identically prepared samples. (1) FGS tapes, (2) reduced FGS tapes, (3) annealed FGS tapes, (4) carbon monoliths containing 30 wt.% carbon nanotubes, (5) carbon monoliths without carbon nanotubes, (6) carbon monoliths with 8 wt.% double-walled carbon nanotubes, (7) carbon monoliths, (8) carbon nanotube paper using Triton-X as dispersant, (9) carbon nanotube paper using DNA as dispersant, (10) carbon nanotube paper using chitosan as dispersant, (11) carbon nanotube ribbons, (12) Grafoil foam, (13) ZYX (Grafoil-like material produced from HOPG), (14) Grafoil, (15) ZYX, (16) Grafoil, (17) Grafoil, (18) graphene intrinsic conductivity (calculated from carrier density of 10^{12} cm^{-2} and mobility of 200,000 cm^{2}/(V·s)), (19) graphene intrinsic conductivity (no charge carriers), (20) HOPG, (21) carbon fibers. Figure adapted from Korkut et al. 1

conductivity of polycrystalline graphite (1×10^5 S/m) but lower than the conductivity of HOPG or single graphene sheets (Figure 5.6a), indicating that the contact resistance between the sheets played a significant role in the conductivity of the tapes. Annealing at 2250 °C resulted in a 50 to 300% increase in conductivity over that of the reduced FGS tapes, and the conductivity reached a maximum measured value of 24 kS/m. This improved tape conductivity may have resulted from increasing FGS conductivity due to
removing defects and increasing C/O (from 247 to 371), as well as from decreasing contact resistance. Both the decrease in separation between sheets, caused by the removal of oxygen-containing functional groups and the increase in contact area, due to flatter sheets, contributed to a lower contact resistance.

The FGS tapes had lower density compared to those of other carbonaceous networks, while exhibiting high surface area and good electrical conductivity (Figure 5.6a,b). We attribute this combination of features to the consolidation of FGSs during tape casting and thermolysis that resulted in a “patch-quilt” structure. In this model, crumpled graphene sheets are randomly interwoven and stitched together by overlapping, graphitic junctions. The resulting graphene-graphite hybrid contains regions of single wrinkled sheets, enhancing the overall surface area, plus graphitic regions composed of partially overlapping sheets for structural integrity. This structure allows for high surface area to be maintained, and the FGS tapes exhibited values an order of magnitude higher than those measured for Grafoil® tapes with equivalent densities (Figure 5.6a,b).

5.3.2 Photovoltaic performance of DSSCs with FGS Tape Based Counter Electrodes (Generation 1)

To determine the catalytic properties of FGS networks, we decided to cast films on FTO glass and use low temperature thermolysis to remove the polymer. We term electrodes created in this way as Generation 1 FGS electrodes. There are several reasons for this approach. First, we identified surface area as a key characteristic, and higher temperatures resulted in lower surface area materials. Second, low temperature
processing reduces fabrication costs, a high priority for next generation solar cell devices. Lastly, as we test liquid based solar cell devices, a non-porous substrate must be used, and few substrates are stable at temperatures at or above 1000 °C.

In Figure 5.7, we show the $J-V$ curves and summarize the device characteristics for DSSCs with Generation 1 FGS network and thermally decomposed chloroplatinic acid counter electrodes. DSSCs employing FGS reach an $\eta$ of 4.99% which is more than 90% that of platinum-based cells ($\eta = 5.48\%$). Both types exhibit a $V_{OC}$ of 0.64 V and a similar $J_{SC}$ of about 13 mA/cm$^2$. The $FF$ is lower for the Generation 1 FGS cells accounting for their lower $\eta$. In view of these encouraging results with FGS as the counter electrode, below, we analyze our electrodes electrochemically to quantify their catalytic activity and determine how the material could be processed or further modified to improve device efficiency.

![Figure 5.7: J-V curve characteristics of Generation 1 DSSCs thermally decomposed chloroplatinic acid (Pt) and Generation 1 FGS counter electrodes (FGS). Electrolyte is Iodolyte AN-50. Active area is 0.39 cm$^2$.](image-url)
5.3.3 Quantifying FGS Catalytic Activity by Electrochemical Impedance Spectroscopy

EIS has been widely used to study the reduction of triiodide on platinum electrodes.\textsuperscript{12,44-46} Specifically, a well-supported equivalent circuit has proved a valuable tool in understanding the platinum counter electrode in DSSC operation. This equivalent circuit has also been applied to measurements performed with carbon-based electrodes without a robust understanding of its appropriateness,\textsuperscript{47-50} as we demonstrate below with our results on FGS-based counter electrodes.

![EIS of Generation 1 FGS electrodes. (a) Impedance spectra for a symmetric cell at various applied biases. (b) An expansion of the high frequency region. The legend in (b) is for (a) as well. At low bias the spectra have two semicircles. As bias is increased a third semicircle becomes more prominent.](image)

Figure 5.8: EIS of Generation 1 FGS electrodes. (a) Impedance spectra for a symmetric cell at various applied biases. (b) An expansion of the high frequency region. The legend in (b) is for (a) as well. At low bias the spectra have two semicircles. As bias is increased a third semicircle becomes more prominent.
Figure 5.8 shows EIS data of FGS electrodes in a symmetric sandwich cell configuration at various applied biases. As bias is applied, the high frequency semicircle remains unchanged, while the lower frequency semicircle shrinks until eventually three semicircles are visible.

![Nyquist plot with two semicircles offset from the origin as shown in Figure 5.9a (blue diamonds) and Figure 5.9b. Accordingly, the ohmic series resistance ($R_s$) can be determined from the onset of the first semicircle ($\sim 100$ kHz). Charge transfer resistance ($i.e., R_{CT}$) and double layer capacitance ($i.e., C$) of the electrode surface give rise to the

We use the traditional equivalent circuit for a sandwich cell configuration detailed by Hauch and Georg to interpret our impedance spectra.\textsuperscript{44} This equivalent circuit is a resistor in series with an $RC$ pair and a Nernst diffusion element which results in a Nyquist plot with two semicircles offset from the origin as shown in Figure 5.9a (blue diamonds) and Figure 5.9b. Accordingly, the ohmic series resistance ($R_s$) can be determined from the onset of the first semicircle ($\sim 100$ kHz). Charge transfer resistance ($i.e., R_{CT}$) and double layer capacitance ($i.e., C$) of the electrode surface give rise to the
first semicircle (mid-frequency: 100-1 kHz). Diffusion of electrolyte species which is affected by the separation between the electrodes causes the second semicircle (low frequency: less than 10 Hz). This phenomenon is described by the Nernstian diffusion element ($N$).

Based on this approach, we find that $R_{CT}$ should be $0.64 \pm 0.07 \, \Omega \cdot \text{cm}^2$ for a Generation 1 FGS electrode, whereas the $R_{CT}$ for a platinum electrode should have a value of $0.79 \pm 0.02 \, \Omega \cdot \text{cm}^2$. The lower $R_{CT}$ would imply a greater $FF$ and higher $\eta$ in solar cell operation for the FGS electrode. However, our device performance data (Figure 5.7) shows the opposite effect, suggesting that the EIS interpretation based on platinum electrodes may not be appropriate for our system.

To further demonstrate the inappropriateness of the model, we analyze impedance spectra recorded under bias. We expect that, as bias is applied to the system, the diffusion impedance increases, corresponding to a depletion of triiodide at the cathode.\textsuperscript{44} Furthermore, we expect that the catalytic $R_{CT}$ decreases exponentially until a diffusion limited region is reached, as predicted by simple Butler-Volmer kinetics.\textsuperscript{51} These effects have been previously demonstrated for platinum\textsuperscript{44} and reproduced by us. However, our FGS electrodes do not follow this behavior, providing additional evidence towards the inappropriateness of applying the traditional equivalent circuit to our system. As deviation from the traditional equivalent circuit is only evident under applied bias, it is possible that researchers have misinterpreted their data in previous studies and have underestimated the $R_{CT}$ associated with their carbon electrodes. This misinterpretation could explain inconsistencies between device performance and EIS derived $R_{CT}$ data.
To more accurately explain our results, we propose a model for porous FGS electrodes (and likely other porous carbon electrodes) seen in Figure 5.9c in which we attribute the high frequency semicircle (100-2.5 kHz) to a second Nernst diffusion impedance resulting from diffusion through the electrode pores ($N_{\text{pore}}$). The middle semicircle (2,500-25 Hz) represents the $R_{\text{CT}}$ and the “capacitance” of the FGS/electrolyte interface (using $CPE$). As in the traditional approach, the low frequency semicircle is determined by bulk Nernst diffusion ($N_{\text{bulk}}$) while the high frequency offset determines $R_s$.

To further analyze the validity of our model, we performed studies varying the FGS layer thickness, applied bias, electrolyte concentration, and electrolyte viscosity. To create FGS electrodes of varying thicknesses, FGS tape casting suspensions were spin coated on conductive glass substrates at three different spin rates. These electrodes were then assembled in a symmetric sandwich cell configuration and the impedance measurements were taken at biases from 0 to 0.8 V. As seen in Figure 5.8, $R_{\text{CT}}$ initially decreases exponentially with increasing bias as expected due to faster kinetics at higher overpotential. The thicker the FGS network, the lower the $R_{\text{CT}}$ at low bias; however, the impedance for all thicknesses collapses to a single curve at high voltages. Meanwhile, $N_{\text{pores}}$ decreases only slightly with bias since iodide and triiodide are similar in size and carry equal charge.

To further prove the diffusive nature of the first and the third semicircles in our impedance data, we varied two parameters, as shown in Figure 5.10: (i) the viscosity, by adding a gelling agent, and (ii) the concentration of the electrolyte species. Both
increasing viscosity and decreasing electrolyte concentration should increase $N_{\text{bulk}}$ and $N_{\text{pore}}$. A higher viscosity leads to a lower $D$, and reducing the species concentration would reduce the electrolyte conductivity, placing the system in a regime in which depletion of triiodide could be significant. Using our EIS interpretation, these effects are indeed observed as a large increase in impedance of the low frequency semicircle is visible with the high viscosity (PEG) electrolyte, and $N_{\text{pore}}$ even dominates over $R_{\text{CT}}$ in the low species concentration sample. A similar effect is seen with the high-frequency semicircles as well.

In order to confirm the symmetrical nature of our cells, and, in particular, to confirm that the mid and low frequency semicircles each do not represent a contribution from

![Figure 5.10: $R_{\text{CT}}$ and $N_{\text{pore}}$ for symmetric Generation 1 FGS electrodes of different thicknesses at various applied biases. Open symbols use left axis, closed square uses right axis. Cells spun at higher rates have less material, and thus, less surface area than those spun at slower rates.](image)
individual electrodes which behave differently due to an unequal distribution of applied bias in the sandwich cell, we performed experiments in a classical three electrode configuration, thus only analyzing one half cell. A silver wire was used as a reference between the two symmetric cells, with Celgard 2320 membranes used as spacers between the electrodes. In this setup, only the impedance associated with one electrode \( R_{CT}, N_{pore} \) and about half of \( N_{bulk} \) and \( R_s \) would be measured. At all frequencies, the impedance in this three electrode setup was about half that for the same cell connected in the traditional two electrode setup. This result dismisses the possibility that the mid frequency semicircle represents one electrode while the low frequency semicircle represents the other electrode, and further supports our model. Due to the corrosive nature of the electrolyte and complications arising from trying to prevent the reference from contacting the electrodes, this setup was only used for this comparative purpose and not for our quantitative measurements.

Figure 5.11: Effect of electrolyte composition on impedance spectra. Impedance spectra at 0.5 V for Generation 1 FGS electrode symmetric cells with (i) Low Concentration Electrolyte: 0.05 M LiI, 5 mM \( I_2 \), (ii) Unmodified Electrolyte: 0.5 M LiI, 0.05 M \( I_2 \), (iii) PEG Electrolyte: 0.5 M LiI, 0.05 M \( I_2 \), 25 mM poly(ethylene glycol) 8000 in acetonitrile.
Using the appropriate equivalent circuits for platinum and our porous FGS samples, we determined $R_{CT}$ associated with the redox couple. At zero bias, the charge transfer resistance of a thermally decomposed chloroplatinic acid cell is 0.79 $\Omega \cdot \text{cm}^2$ which agrees well with literature values (0.5-1.8 $\Omega \cdot \text{cm}^2$) and is well below the 10 $\Omega \cdot \text{cm}^2$ level needed for high performance cells.\textsuperscript{3, 44, 50, 52} At zero bias, the FGS-based counter electrodes performed relatively poorly, with $R_{CT} \sim 9.4 \Omega \cdot \text{cm}^2$ recorded for cells spun at 1000 rpm. These values are based on the geometric surface area of the electrode and not the accessible surface area due to the porosity of the material. However, at applied bias, the $R_{CT}$ approaches that of platinum. For instance at a 0.5 V bias, $R_{CT}$ of thermally decomposed chloroplatinic acid was measured to be 0.78 $\Omega \cdot \text{cm}^2$ while that of the FGS cell spun at 1000 rpm was 1.2 $\Omega \cdot \text{cm}^2$. The greater $R_{CT}$ for FGS compared to platinum, especially at low bias, is consistent with the decrease in the $FF$ and $\eta$ of DSSCs using FGS electrodes. However, based on the EIS data alone, we cannot determine whether the greater $R_{CT}$ is due to an intrinsically lower catalytic activity for the material or to inadequate accessible surface area.

### 5.3.4 Investigating Catalytic Activity of FGS using Cyclic Voltammetry

To distinguish between specific catalytic activity and surface area effects, we obtained cyclic voltammograms for FGS and platinum-modified titanium electrodes (Figure 5.12). To probe exclusively the catalytic contribution of FGSs, we analyzed films created from drop casting an ammoniated water ($\sim$ pH 11) FGS suspension onto an inert
polished titanium rod. Additionally, to resolve the peaks, we used an electrolyte concentration ten times lower than that used in a DSSC.

Figure 5.12: Cyclic voltammograms of the iodide/triiodide redox mediator obtained at a scan rate of 50 mV/s using polished titanium rod electrodes loaded with 12 µg of platinum and FGS. The voltammogram for a blank polished titanium rod is also shown. A\textsubscript{ox} and A\textsubscript{red} indicate the oxidative and reductive peaks for the I\textsubscript{2}/I\textsubscript{3}– couple while B\textsubscript{ox} and B\textsubscript{red} indicate the oxidative and reductive peaks for the I\textsubscript{2}/I\textsubscript{3}– couple.

Scanning from −0.5 to 0.75 V vs. Ag/Ag\textsuperscript{+} (for ferrocene, the redox potential is 55 ± 5 mV on all samples) two pairs of peaks are observed for both materials, similar to what has been reported for comparable systems in the literature.\textsuperscript{53-55} Although the exact charge transfer mechanisms are not fully understood, literature attributes peaks A\textsubscript{ox} and A\textsubscript{red} to the oxidation and reduction of iodine/triiodide and peaks B\textsubscript{ox} and B\textsubscript{red} to the oxidation and
reduction of iodide/triiodide.\textsuperscript{56-58} Since the counter electrode of a DSSC is responsible for catalyzing the reduction of triiodide to iodide, the characteristics of peaks B\textsubscript{ox} and B\textsubscript{red} are at the focus of our analysis.

The standard electrochemical rate constant of a redox reaction is negatively correlated with \(E_{pp}\).\textsuperscript{59} Thus, with CV, we rely mostly on \(E_{pp}\) between B\textsubscript{red} and B\textsubscript{ox} to gauge the catalytic activity of the modified electrodes. For electrodes modified with platinum and FGS, we measure \(E_{pp}\) values of 90 and 150 mV, respectively. The platinum-modified electrode is thus more catalytic toward the reaction due to a lower \(E_{pp}\), which supports our EIS model and can explain the higher device efficiencies using a platinum-based counter electrode material.

### 5.3.5 Impact of FGS Electrode Morphology on Apparent Catalytic Activity

From Figure 5.12, it is clear that our FGS electrodes have significant \(I_C\) and thus surface area. This observation is consistent with previous work which shows that our electrode coating process results in FGS films that are highly porous.\textsuperscript{60} Theoretical studies suggest that porosity can significantly affect the apparent catalytic properties of an electrode.\textsuperscript{61-63} Thus to further analyze the role of this porosity for our system, we use CV to look at the apparent catalytic activity for various loadings of FGSs. Furthermore, to characterize the effect of electrode morphology on the apparent catalytic activity of the FGS, we have examined the dependence of \(I_p\) on \(v\) and performed CV measurements with coatings of varying thickness.
The $I_p$ for the oxidation and reduction of iodide/triiodide measured as a function of $\nu$ deviates slightly from the ideal behavior expected for semi-infinite diffusion of the involved redox species ($I_p \propto \nu^{1/2}$) as shown in Figure 5.13. The deviation is prominent for low $\nu$ where the magnitude of both the oxidation and the reduction peaks decreases considerably. Electrode porosity might account for this since for small $\nu$ the electrolyte can become depleted of the involved redox species.\textsuperscript{59} The effect is more pronounced for the reduction peak since the concentration of triiodide is considerably lower than the concentration of iodide.

![Normalized $I_p$ response versus the square root of $\nu$ for oxidation and reduction of the iodide/triiodide redox couple.](image)

**Figure 5.13:** Normalized $I_p$ response versus the square root of $\nu$ for oxidation and reduction of the iodide/triiodide redox couple.

An additional indication for an impact of electrode morphology is the dependence of $E_{pp}$ and $I_p$ on the thickness of the electrode coating (Figure 5.14). The geometric areas of all tested electrodes are identical. Therefore, higher loadings correspond to thicker films. As seen in the insert of Figure 5.14, $E_{pp}$ of the iodide/triiodide redox reaction is much
larger for the electrode with 2 µg FGS than for those with higher loadings. The reduction potential (peak B_{red}) experiences a significant positive shift as the FGS loading increases.

At the same time, I_{p} (and also the I_{C}) increases indicating a higher accessible surface area. Since we do not know the exact relation between electrode loading and accessible surface area, we cannot analyze the data quantitatively. However, the observed behavior is reminiscent of cyclic voltammograms simulated for electrodes of varying porosity.\(^{63}\) We then conclude that the observed differences in the apparent catalytic activity of the tested electrodes are probably in part affected by differences in electrode morphology. This is of particular importance when comparing electrode materials as different materials may result in different electrode porosity and, thus, different apparent catalytic activities.

Figure 5.14: Thickness effect on cyclic voltammograms obtained at a scan rate of 50 mV/s. Electrodes are polished titanium rod electrodes loaded with 2, 6, 12, and 24 µg of FGS. \(E_{pp}\) for the oxidation and reduction of the iodide/triiodide redox couple for each loading is given in the insert.
Figure 5.15: Morphology of FGS, electrodes. SEM images of 12 µg films of (a) FGS₇, (b) FGS₁₃, (c) FGS₄₈ and (d) FGS₃₅₀ drop cast from ammoniated water suspensions on polished titanium substrates. The scale bar in (a) applies to all images.

The aforementioned results are for FGS₁₃ electrodes due to the availability of the material. Yet, in Chapter 4, we showed that C/O is correlated with intrinsic catalytic activity, and FGS₁₃ might not be optimal. In any case, C/O could also affect electrode performance through affecting electrode morphology. To test this hypothesis, we examine the morphology of films of FGS with varied C/O using SEM. As seen in Figure 5.15, adjusting the number of oxygen-containing functional groups on FGSs alters
the drying dynamics of the material and results in different FGS packing. At low C/O, the material forms an open, layered structure with pores on the micron scale. As C/O increases, the FGSs form coarser films as a result of increased agglomeration. Thus, in addition to differences in intrinsic activity discussed in Chapter 4, it is reasonable to expect that FGSs films made from different types of FGSs may exhibit different apparent activities due to how they pack into porous structures. Development of a more optimized film morphology is discussed in Chapter 6.

5.3.6 Flexible Counter Electrodes via FGS-based Inks

Although Generation 1 FGS electrodes exhibit high catalytic activity, the mild heat treatment results in films which are too resistive to be used in DSSCs without a conducting substrate. However, as demonstrated in Table 5.2, in addition to replacing platinum, FGS-based counter electrodes can be printed onto a variety of substrates, including those which are insulating, heat sensitive, and flexible. Cells produced using counter electrodes made from FGS-based conductive inks (Vor-ink™) cast onto mylar (Figure 5.16) exhibit efficiencies within 10% of cells using platinized FTO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$FF$</th>
<th>η (%)</th>
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<tbody>
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<td>0.66</td>
<td>3.75</td>
</tr>
<tr>
<td>Vor-ink™ P10</td>
<td>0.71</td>
<td>7.77</td>
<td>0.70</td>
<td>3.83</td>
</tr>
<tr>
<td>Pt on FTO</td>
<td>0.73</td>
<td>7.89</td>
<td>0.72</td>
<td>4.16</td>
</tr>
</tbody>
</table>

Table 5.2: Photovoltaic characteristics of DSSCs with Vor-ink™ and platinized FTO counter electrodes.
Both Vor-ink™ P3 and the FTO electrodes have a resistivity of \( \sim 10 \, \Omega/{\text{sq}} \) while Vor-ink™ P10 has a resistivity of \( \sim 5 \, \Omega/{\text{sq}} \).\textsuperscript{64} This difference does not appear to have a large effect on the tested cells (active area 0.39 cm\(^2\)); however, the lower resistivity films could have significant benefit for larger cells where \( R_s \) is prominent. Although more work is needed to look at the stability of these films, we emphasize that highly conductive, catalytic, low-cost materials for flexible DSSCs which use FGS are already commercially available.

![Vor-ink™ P10 film cast on mylar.](image)

**Figure 5.16:** Vor-ink™ P10 film cast on mylar.

### 5.4 Conclusion

Tape casting of FGS-polymer composites followed by thermolysis of the polymer provides an industrially scalable way of producing large, free-standing, conductive, and high surface area FGS tapes. DSSCs using the iodide/triiodide mediator and FGS networks as a catalyst had efficiencies \( \sim 10\% \) lower than cells using platinum. To explain this observation, we rigorously examined the catalytic activity of FGS using electrochemical techniques. A new EIS equivalent circuit for porous carbon electrodes is
proposed that relates the observed impedance semicircles to their associated phenomena. Using this model, we determined that the $R_{CT}$ of these FGS networks is ten times greater than that of platinum at no applied bias and approaches that of platinum at applied bias. CV measurements showed that platinum has greater apparent catalytic activity compared to FGS, as measured by the $E_{pp}$, which accounts for its lower $R_{CT}$ in DSSCs. We also recognized how fabricating a more porous FGS electrode could improve the apparent catalytic activity. Finally, we demonstrated that FGS-based inks cast on a non-conductive plastic substrate can be effectively used as a counter electrode, eliminating the need for a conductive substrate. Cells employing this versatile FGS-ink flexible counter electrode performed $\sim 10\%$ less efficiently than cells using platinum on a rigid FTO electrode. Further tailoring the functionalization or morphology of the FGS electrodes could decrease $R_{CT}$ and facilitate the low-cost production of catalytic, flexible and conductive counter electrodes for DSSCs.

References


Chapter 5


Chapter 6

6 Second Generation Functionalized Graphene Sheet
Counter Electrodes as Replacements for Platinum for
Iodine-, Cobalt-, and Sulfur-based Redox Mediators

This chapter is adapted from work published in ACS Applied Materials and Interfaces
coaauthored with Gerrit Boschloo, Anders Hagfeldt, and Ilhan Aksay.\textsuperscript{1} G. Boschloo and A. Hagfeldt helped with experimental design and data analysis.

Chapter 5 discussed the production of FGS tapes and their use as high surface area electrodes for iodide/triiodide catalysis in DSSCs, resulting in solar cells with efficiencies 90\% of those using thermolyzed chloroplatinic acid as a catalyst. In this chapter, we study how better to control the electrode morphology for improved performance. By using ethyl cellulose as a sacrificial binder, and partially thermolyzing it, electrodes were created which exhibit lower effective charge transfer resistance ($< 1 \Omega\cdot\text{cm}^2$) than the thermally decomposed chloroplatinic acid electrodes traditionally used. This performance was achieved not only for the iodide/triiodide redox couple, but also for the two other major redox mediators used in DSSCs, based on cobalt and sulfur complexes, showing the versatility of the electrode. DSSCs using these FGS electrodes had efficiencies equal to or higher than those using thermally decomposed chloroplatinic acid electrodes in each
of the three major redox mediators: I ($\eta_{\text{FGS}} = 6.8\%$, $\eta_{\text{Pt}} = 6.8\%$), Co (4.5%, 4.4%), S (3.5%, 2.0%). Through an analysis of the thermolysis of the binder and composite material, we found that the high surface area of an electrode, as determined by nitrogen adsorption, is consistent with but not sufficient for high performing electrodes. Two other important considerations are that i) enough residue remains in the composite to maintain structural stability and prevent restacking of FGSs upon the introduction of the solvent, and ii) this residue must not disperse in the electrolyte.

### 6.1 Introduction

In order to replace platinum on a DSSC cathode with a less expensive catalyst, previously we reported on porous networks FGSs created by the thermolysis of a binder in an FGS-polymer composite. DSSCs using Generation 1 FGS networks performed 90% as well as solar cells using platinum as a catalyst for triiodide reduction. Similar results – close to, but not matching, the performance of platinum – using other graphene-based materials were later reported using different processing techniques such as drop casting, electrophoretic deposition, and screen printing. To overcome device limitations associated with the iodide/triiodide redox couple (e.g., corrosiveness, light absorption, excessive overpotential, etc.) alternative redox couples have been explored including cobalt-, sulfur-, and iron-based compounds. Although Kavan et al. recently showed that graphene nanoplatelet (1-15 nm thick stacks of graphene) coated electrodes could outperform platinum for the reduction of the cobalt mediator (concomitant with results presented in Chapter 4), the primary catalyst for these systems is still platinum.
Herein, we describe a new FGS-sacrificial binder system, using ethyl cellulose, in which the partial thermolysis of the binder increases the FGS surface area available for catalysis while the binder residue improves the electrode’s structural stability in acetonitrile containing electrolytes. This process yields versatile electrodes which perform as well as or better than platinum in I-, Co-, and S-based redox systems. Furthermore, we analyze how processing conditions affect electrode performance and suggest system characteristics required for high performing electrodes. Although the resultant FGS film is not transparent, the FGS paste requires only a single doctor blade layer and can directly replace current platinum pastes used in DSSC manufacturing.

### 6.2 Experimental Methods

Experimental details specific to this chapter are included below. In particular, the preparation of counter electrodes and DSSCs is discussed, as is how electrochemical measurements for this study were completed. General experimental techniques can be found in Chapter 3.

#### 6.2.1 Preparation of Counter Electrodes

FGS counter electrodes were prepared on FTO (TEC8). Pastes (described below) were tip sonicated for 30 s before use and then doctor bladed on a tape spacer resulting in ~ 6 µm thick films after drying at room temperature. Electrodes then underwent heat treatment under air in an oven (Nabertherm Controller P320).

*FGS:Ethyl Cellulose electrodes*: 0.3 g of FGS (Vor-x® batch BK86x) was added to 6 g of 10 wt.% ethyl cellulose in ethanol. 11 g ethanol was then added to achieve desired
thickness of films after drying. This mixture was then mixed and tip sonicated at 40% power for 2 min. Heat treatment of films was performed in air at a range of temperatures from 270 to 450 °C for 12 min, ramping at 10 °C/min.

Original FGS electrodes (Generation 1): Same procedure as described in Section 5.2. FGS-surfactant suspension (1.66 wt.% FGS, 1.66 wt.% surfactant (F127) in water) was mixed in a PEO solution (0.6 g in 10 mL water, 10 mL ethanol) in a 1:4 FGS:PEO weight ratio and stirred overnight. Electrodes were heat treated at 350 °C for 2 h.

Platinized electrodes: A 4.8 mM chloroplatinic acid solution in ethanol was deposited onto the FTO glass substrate (10 µL/cm²) and heated to 400 °C for 30 min before use.

6.2.2 Preparation of DSSCs

DSSCs were constructed similarly to as described by Feldt et al. and described in Chapter 4. Differences arise in the use of dye and electrolyte. A 0.3 mM N719 dye solution in 1:1 acetonitrile:tert-butanol was used for DSSCs with the iodine-based electrolyte (0.6 M tetrabutylammonium iodide, 0.1 M lithium iodide, 0.05 M iodine, 0.2 M 4-tert-butylpyridine in acetonitrile). A 0.2 mM D35 dye solution in ethanol was used for DSSCs with the cobalt- (0.22 M Co(bpy)₃(PF₆)₂, 0.033 M Co(bpy)₃(PF₆)₂, 0.1 M lithium perchlorate, 0.2 M 4-tert-butylpyridine in acetonitrile) and sulfur- (0.1 mM dimethyldithiocarbamate (M-) 0.1 M 5-mercapto-1-methyltetrazole dimer (T₂), 0.5 M 4-tert-butylpyridine in acetonitrile) based electrolytes.
6.2.3 Measurements

EIS was performed using a Biologic SP-150 potentiostat and a CH Instruments 760C potentiostat using a sandwich cell configuration (50 µm spacing) in which symmetric electrodes are infiltrated with the same electrolyte as used in the DSSCs. EIS measurements were taken at 0 V, the magnitude of the alternating signal was 10 mV, and the frequency range was 1 Hz to 100 kHz. ZFit, with the appropriate equivalent circuit, was used to analyze the impedance spectra. I-V characteristics of DSSCs were taken under AM1.5G light, simulated at 1000 W/m² using two setups: i) a 16S solar simulator (SolarLight) calibrated with PMA2144 pyranometer (SolarLight) using the Biologic potentiostat and ii) a Newport solar simulator (model 91160) calibrated with a certified reference cell (Fraunhofer ISE) using a Keithley 2400 source/meter. Data values presented are the average of 2-6 identically prepared samples, while figures are representative of individual runs.

6.3 Results and Discussion

First, the improved performance of second generation FGS counter electrodes is reported. Second, how the processing of these electrodes can explain these results is explored.

6.3.1 Counter Electrode Performance

We evaluate the performance of counter electrodes by directly measuring their catalytic activity and then support these results by characterizing DSSCs which use the electrodes. The catalytic performance of a DSSC cathode is quantified by $R_{CT}$ of the
electrolyte-cathode interface by EIS. Two commonly referenced performance targets for the DSSC cathode $R_{CT}$ are less than $10 \, \Omega \cdot \text{cm}^2$, and $2-3 \, \Omega \cdot \text{cm}^2$. Characteristic impedance spectra taken at 0 V bias are presented in Figure 6.1a. The inserts of Figure 6.1a show the sandwich cell configuration used for testing and the EIS equivalent circuit. These spectra have been normalized to the geometric surface area of the catalyst on an electrode. For the experimental setup used, $R_s$ was about $12 \, \Omega$ for both FGS- and platinum-based electrodes. Scaling by area holds little meaning for $R_s$; thus, the spectra have been shifted to clearly compare FGS and platinum-based electrodes for the I-, Co-, and S-based electrolyte systems. The parameter of interest in this system is the combined contribution of the catalytic $R_{CT}$ and transport impedance in the pores ($N_{pore}$). We term this sum the effective charge transfer resistance, $\mathcal{R}_{CT}$, where $\mathcal{R}_{CT} = R_{CT} + N_{pore}$. For non-porous electrodes, such as the thermally decomposed platinic acid electrodes used in this study, $N_{pore}$ can be neglected and $R_{CT} = \mathcal{R}_{CT}$. For highly catalytic FGS electrodes, transport resistance in the pores represents a significant component of $\mathcal{R}_{CT}$ and thus cannot be neglected.

Impedance results are summarized in Figure 6.1b, which also includes electrodes made from the method in our earlier work (Generation 1). As can be seen, not only have the $\mathcal{R}_{CT}$ values of our electrodes decreased by an order of magnitude, but they meet the more stringent performance standard as well, and they are lower than those obtained using thermally decomposed chloroplatinic acid. Moreover, unlike platinum, FGSs perform well as a catalyst in all three electrolyte systems tested, showing their versatility.
Figure 6.1: Determining $\mathcal{R}_{CT}$ for counter electrodes with I-, Co-, and S-based mediators in acetonitrile based electrolyte. a) Impedance spectra of FGS (green) and Pt (blue) electrodes. Squares: I-based mediator; Triangles: Co-based mediator; Circles: S-based mediator. Spectra were shifted on the x-axis for easier comparison. Upper inset: Sandwich cell setup to test counter electrode performance. Lower inset: Equivalent circuit for this setup. $R_S$: series resistance; $R_{CT}$: charge-transfer resistance of one electrode; CPE: constant phase element for one electrode; $N_{pore}$: Nernst diffusion impedance within electrode pores; $N_{bulk}$: Nernst diffusion impedance between the electrodes. b) Summary of effective charge transfer resistance ($\mathcal{R}_{CT} = R_{CT} + N_{pore}$) of electrodes. Red: FGS counter electrodes using the formulation from our previous work. Green: FGS counter electrodes described in this work. Blue: Thermally decomposed chloroplatinic acid electrodes. Dotted lines represent common counter electrode targets, upper: $10 \, \Omega \cdot \text{cm}^2$ from Hauch and Georg, lower: $2 \, \Omega \cdot \text{cm}^2$ from Trancik et al. $\mathcal{R}_{CT}$ was determined using EIS using a sandwich cell configuration.

To ensure that the new FGS electrodes are indeed superior to platinized FTO when incorporated into a device, we compare J-V curves of DSSCs using the two types of counter electrodes (Figure 6.2). Average $V_{oc}$, $J_{sc}$, $FF$, and $\eta$ for devices tested are tabulated in the inserts. For all three electrolyte systems tested, DSSCs using FGS cathodes perform as well as or better than those using platinized FTO cathodes, in agreement with our EIS results. Furthermore, across all electrolytes, the $FF$ of the devices using FGSs is higher than that of those using platinum. This result is consistent with a lower $\mathcal{R}_{CT}$ for these devices which we see with the EIS data. We note that for a few
samples, DSSCs using FGS electrodes performed significantly worse than the rest of the data set; thus, to prevent skewing of our data with outliers, we did not include these results in our average tabulation. The results presented are indicative of what we can achieve, and although we are not sure why a minority of cells behaved poorly, it could be due to variations in the processing of the film. After doctor-blading, when the tape mask is removed, part of the edge of the FGS film may also lift up resulting in a short circuit from the counter electrode to the photoanode. If so, fabricating electrodes through tape casting or screen printing would eliminate this issue.

Interestingly, for DSSCs using an iodine-based electrolyte (Figure 6.2a), solar cell performance improved markedly over the first day. Components of the electrolyte such as tert-butylpyridine and iodine may be adsorbing to the porous electrodes during this time. An alternative explanation is that it may take time for the electrolyte to fully infiltrate the FGS film. Thus, over time, more surface area would be accessible to catalyze the reduction of triiodide. However, sandwich cell electrodes show strong catalytic activity shortly after fabrication, and $\mathcal{R}_{CT}$ actually increases slightly (by ~10%) after a day, negating this conjecture.

The DSSCs presented in Figure 6.2b use similar materials to those used in the landmark paper by Feldt et al. on co-designing the dye and cobalt redox couple. As fast recombination between the conduction band of titania and cobalt mediators has limited DSSC performance for devices using traditional dyes such as N719, in this study a dye with bulky side chains (D35) is used. Butoxyl chains on D35 sterically hinder the interaction of cobalt complexes with titania, reducing recombination in the device. The
lower performance exhibited in the current work compared to that of Feldt et al. is likely due to the use of titania with a smaller primary particle size in the DSL18-NR-T paste (the DSL30 NRD-T paste production has been discontinued). This explanation is consistent with the finding by Yella et al. that smaller pores impede the transport of the relatively large cobalt complexes and decrease device $\eta$.\textsuperscript{15} Although $FF$ is higher for the cell with the FGS cathode as expected due to the lower $R_{CT}$, the $V_{oc}$ is lower. This observation is also made in two works by Kavan et al. and they explain that it could be due to a higher dark current in the devices using graphene nanoplatelet electrodes.\textsuperscript{16, 17} Graphene nanoplatelets detaching from the FTO electrode and depositing on the titania film, a concern with other carbon electrodes, could explain this observation.\textsuperscript{18-20} An alternative explanation is that the electrolyte can infiltrate the whole FGS film including pores which are too small for the cobalt redox couple to access. This would shift the electrolyte concentration in the active part of the solar cell and could influence the electrolyte $E_{\text{Red}}$, and thus $V_{oc}$ of the device.

The effect of platinum’s high $R_{CT}$ on the $FF$ of devices with the sulfur-based mediator is clearly seen in Figure 6.2c. The lower $V_{oc}$ compared to the cobalt-based device is due to the more negative potential of the electrolyte. The greater $J_{sc}$ is due, at least in part, to the lower light absorption by the sulfur based mediator. The FGS electrodes in these devices were only heated to 310 °C, and even though the $R_{CT}$ is low ($0.75 \, \Omega \cdot \text{cm}^2$) it is likely not optimal.
Figure 6.2: $J$–$V$ curve characteristics of Generation 2 DSSCs. Counter electrodes were thermally decomposed chloroplatinic acid (Pt) and Generation 2 FGS counter electrodes (FGS). a) I-based mediator, N719 sensitizer; b) Co-based mediator, D35 sensitizer; c) S-based mediator, D35 sensitizer. Active area is $0.25 \text{ cm}^2$. 
6.3.2 Counter Electrode Processing

The high performing FGS electrodes presented above were created by first doctor blading an FGS-ethyl cellulose paste onto FTO and then partially thermolyzing the binder in air. In order to understand why FGS electrodes using ethyl cellulose as a sacrificial binder performed better than those fabricated using other binders and methods, we examined the effect of electrode processing (for EIS data on other processing routes see Appendix B). We first look at how processing affects the catalytic performance of the electrode, and then relate this to the respective changes in residue amount and electrode surface area.

As seen in Table 6.1, $\mathcal{R}_{\text{CT}}$ is highly dependent on the heat treatment process for removing the binder. $\mathcal{R}_{\text{CT}}$ decreases as temperature is increased up until heat treatments at 370 °C, above which $\mathcal{R}_{\text{CT}}$ increases. Nevertheless, as seen in Table 6.1, heating anywhere from 330 to 420 °C and holding for 12 min resulted in electrodes with $\mathcal{R}_{\text{CT}}$ below 3 Ω-cm² with the iodine-based redox system.

Table 6.1: Effect of heat treatment on counter electrode performance. Heat treatment is under air holding at the prescribed temperature for 12 min.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$N_{\text{pore}}$ (Ω cm²)</th>
<th>$R_{\text{CT}}$ (Ω cm²)</th>
<th>$\mathcal{R}_{\text{CT}}$ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>—</td>
<td>84.5</td>
<td>84.5</td>
</tr>
<tr>
<td>270</td>
<td>3.4</td>
<td>5.5</td>
<td>8.8</td>
</tr>
<tr>
<td>300</td>
<td>1.7</td>
<td>15.1</td>
<td>16.8</td>
</tr>
<tr>
<td>330</td>
<td>0.4</td>
<td>2.0</td>
<td>2.4</td>
</tr>
<tr>
<td>350</td>
<td>0.5</td>
<td>1.2</td>
<td>1.8</td>
</tr>
<tr>
<td>370</td>
<td>0.5</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>420</td>
<td>0.6</td>
<td>1.3</td>
<td>2.0</td>
</tr>
<tr>
<td>450</td>
<td>0.7</td>
<td>5.5</td>
<td>6.1</td>
</tr>
</tbody>
</table>
During heat treatment, the ethyl cellulose binder melts and decomposes as shown in Figure 6.3a. Higher temperature heat treatments result in more of the ethyl cellulose being removed. About 6, 12, and 42% of the binder is removed during heat treatments at 270, 300, and 330 °C, respectively. These values were affirmed not only by TGA, but also by heating 1 g of ethyl cellulose with the samples and massing the residue. Heat treatment has a small effect on the FGSs as well. FGSs are stable until about 420 °C, but a 4% mass loss occurs upon treatment to 450 °C, the highest temperature examined in this study (Figure 6.3b).

Figure 6.3: STA of (a) ethyl cellulose and (b) FGS thermolysis in air. Blue dotted line: TGA. Red line: DSC, where negative heat flow represents an exothermic event.
As seen in Table 6.2, electrode surface area increases monotonically as ethyl cellulose is removed, while the surface area of FGSs in the electrodes reaches a maximum at a heat treatment of 330 °C. The specific surface area of FGSs in a heat treated electrode is approximated (Equation 11) by taking the surface area of the composite electrode after heat treatment, and subtracting out that portion which can be attributed to the ethyl cellulose residue:

\[
SA_{FGS} = \frac{(m_{FGS} + m_{EC\ Res}) \times SA_{Comp} - m_{EC\ Res} \times SA_{EC\ Res}}{m_{FGS}},
\]  

where \(SA_{FGS}\) is the calculated specific surface area of FGS in the composite, \(SA_{Comp}\) is the measured composite specific surface area, \(SA_{EC\ Res}\) is the measured ethyl cellulose residue specific surface area, \(m_{FGS}\) is the mass of FGS in the composite, and \(m_{EC\ Res}\) is the mass of ethyl cellulose in the composite.

**Table 6.2:** Characteristics of ethyl cellulose and composites of FGS and ethyl cellulose after heat treatments at various temperatures.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Residue Fraction</th>
<th>Solubility of Residue in Acetonitrile</th>
<th>Residue Surface Area (m²/g)</th>
<th>Surface Area (m²/g)</th>
<th>Calculated FGS Surface Area (m²/g)</th>
<th>Surface Area (m²/g) After Acetonitrile Wash</th>
<th>Calculated FGS Surface Area (m²/g) After Acetonitrile Wash</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.00</td>
<td>Soluble</td>
<td>&lt; 1</td>
<td>37</td>
<td>109</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>270</td>
<td>0.94</td>
<td>Soluble</td>
<td>&lt; 1</td>
<td>74</td>
<td>212</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>300</td>
<td>0.97</td>
<td>Soluble</td>
<td>&lt; 1</td>
<td>155</td>
<td>424</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>330</td>
<td>0.58</td>
<td>Soluble</td>
<td>&lt; 1</td>
<td>296</td>
<td>637</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>350</td>
<td>0.19</td>
<td>Partially Soluble</td>
<td>2.6</td>
<td>348</td>
<td>480</td>
<td>349</td>
<td>480</td>
</tr>
<tr>
<td>370</td>
<td>0.13</td>
<td>Insoluble</td>
<td>27.5</td>
<td>392</td>
<td>451</td>
<td>363</td>
<td>475</td>
</tr>
<tr>
<td>420</td>
<td>0.06</td>
<td>Insoluble</td>
<td>210</td>
<td>456</td>
<td>483</td>
<td>391</td>
<td>412</td>
</tr>
<tr>
<td>450</td>
<td>0.02</td>
<td>Insoluble</td>
<td>237</td>
<td>479</td>
<td>489</td>
<td>366</td>
<td>382</td>
</tr>
</tbody>
</table>

With low temperature heat treatments (270 °C), ethyl cellulose has a residue with a dense, glass-like structure. The residue’s surface area is very low (< 1 m²/g) and its mass percentage of the electrode is high (~ 65 wt.%). At high temperatures (450 °C), the
specific surface area of the ethyl cellulose residue is high (237 m$^2$/g), however, its mass percentage of the electrode is low (~ 3.8 wt.%). Thus, although the specific surface area of the composite increases with heat treatment intensity, the specific surface area for FGSs can be higher at lower heat treatments.

A main distinction from our previous work is that for our best performing electrodes a significant amount of binder residue (~ 20 wt.% of the electrode) remains after heat treatment. A similar optimum was recently found by Zhang et al. who attributed their results to a decrease in, but not complete removal of, the electrode binder. More specifically, we maintain that the high performance of our 370 °C heat treated electrodes is due to the residue acting as a stable spacer for FGSs, as evidenced by the residue’s insolubility in the electrolyte and the high surface area of the catalytically active FGSs after drying.

To explain this effect with more certainty, we look at the role of ethyl cellulose in the electrodes. Ethyl cellulose is used as both a dispersant and a binder for casting the electrode film. Drying FGS suspensions without the binder causes FGSs to stack into structures with lower specific surface areas. With a binder, a composite is formed in which the binder is present between sheets, keeping them separated during solvent evaporation. The removal of the binder from the composite opens up the space between the sheets and increases the surface area of the electrode. Since the catalytic activity of the electrode should be proportional to the surface area, we expect a higher surface area to correspond to a lower $R_{CT}$. As evidenced by the decreasing resistance to transport ($N_{pore}$) with increasing heat treatment, the pores are more accessible as binder is removed;
However, the electrode surface area correlates with catalytic performance only up to heat treatments of 370 °C, after which $R_{\text{CT}}$ increases.

Although it is clear that binder blocking active sites and inhibiting diffusion can reduce the effective catalytic activity, it is less obvious why electrode performance decreases upon removing more than 90 percent of the binder. In short, why does having some binder residue improve performance? Two possible explanations are that the residue itself is catalytic to the reaction, or the residue is improving the catalytic activity of the electrodes by improving the FGS accessible surface area, perhaps by acting as pillars separating sheets. EIS analysis of sandwich cells made with ethyl cellulose residue shows no measurable catalytic activity towards the reduction of triiodide, discounting this possibility. When only accounting for the surface area of the FGS in the electrodes, which is consistent with it being the catalytically active material, we see higher surface areas at lower temperature heat treatments, supporting the conjecture that the binder aids in keeping the sheets apart. Nevertheless, the lowest $R_{\text{CT}}$ is seen with heat treatment at 370 °C and not at 330 °C – the temperature which results in the largest FGS surface area – so another factor must play a role. One possibility is that the characteristics of the electrode examined in air are not the best representation of the material in a device, for our case, in acetonitrile.

As we cannot examine the electrodes in-situ, we used two proxies to provide a qualitative assessment of electrode stability in the electrolyte. First, we looked at whether the residual binder was soluble in acetonitrile (see Table 6.2 for summary, Figure 6.4 for images). Ethyl cellulose swells but is not soluble in acetonitrile. However, upon minor
heat treatment the residue is readily soluble. Between 330 and 350 °C, a transition occurs in which some of the residue is carbonized enough to be insoluble in the electrolyte and by 370 °C, the residue is completely insoluble. Thus, although electrodes heat treated below 330 °C may have a higher FGS surface area in air, upon exposure to the electrolyte, the binder will dissolve. Without adequate spacers, FGSs could then restack, reducing the surface area available for catalysis.

![Figure 6.4: Ethyl cellulose residues in acetonitrile. A laser beam was passed through the sample to identify if residue was present in the liquid phase. After 350 °C heat treatment, insoluble residue is seen at the bottom of the tube, while some residue is also suspended in the liquid phase as evidenced by the weak scattering. The red scattering in the 370 °C case is due to scattering by the glass container.](image)

For a second proxy, we looked at the surface area of the electrodes after they had been soaked in acetonitrile and dried (Table 6.2). Although drying is not expected to occur in actual devices, this experiment can provide insight into the stability of the electrodes. Only electrodes which had residues insoluble to acetonitrile were tested in this way. Electrodes heat treated to 350 and 370 °C had about the same surface area before
and after the wash, which shows that the electrode structure is relatively stable. XRD also shows no significant change in the intensity or d-spacing of the samples (see Figure 6.5).

![Figure 6.5: XRD patterns of FGS electrode materials. FGS electrode material from heat treatment at 370 °C (red) and 450 °C (purple) was analyzed after heat treatment (solid lines) and after soaking in acetonitrile and drying (dotted lines). The background sample holder signal has been removed and the results have been normalized to the mass of FGS in the samples.](image)

On the other hand, electrodes heated to 420 and 450 °C experienced a significant decline in surface area. In these two cases, only a small amount of ethyl cellulose is present. This residue may be insufficient to keep FGSs apart upon stressing the system, such as the introducing an electrolyte solution. For the 450 °C case, the XRD pattern did shift after drying showing that the structure is not stable (see Figure 6.5). Interestingly, the intensity decreased after drying and it appears as though there is a smaller signal at ~26.4°, characteristic (0002) graphite spacing. In our previous study, the binder was almost completely removed from the electrodes; thus, as with the case of high temperature heat treatments with FGS:ethyl cellulose electrodes, there may have been a
lack of adequate residue for stability which could explain their relatively poor performance.

From the above analysis, we present the following as important considerations for an FGS composite counter electrode: i) the FGS in the heat treated composite material (FGS:ethyl cellulose residue) must have high surface area; ii) the binder residue must be insoluble in the electrolyte (in this case, acetonitrile); and iii) enough residue must remain in the composite to retain stability of the FGS network upon the introduction of solvent.

6.4 Conclusion

By using ethyl cellulose as a sacrificial binder, and partially thermolyzing it, we created versatile FGS counter electrodes for DSSCs. These electrodes exhibited lower $\mathfrak{r}_{\text{CT}}$ than that of the thermally decomposed chloroplatinic acid electrodes for DSSCs with I-, Co-, and S-based redox mediators. With each of these redox mediators, DSSCs using FGS counter electrodes had efficiencies equal to or higher than those using the platinic acid-derived electrodes. Through analyzing FGS electrode processing conditions we found that surface area and stability are important considerations for high performance. In particular, enough binder residue should remain in the composite to maintain structural stability and prevent restacking of FGSs upon the introduction of the solvent, and this residue should not disperse in the electrolyte. Although the resulting films are not highly transparent, FGS:ethyl cellulose pastes provide an effective replacement to platinum pastes currently used in the manufacture of DSSCs, and have the added benefit of working better with a wide range of redox mediators.
6.5 Appendix B

Alternative Processing Routes

Figure 6.6 depicts $\mathcal{R}_{\text{CT}}$ as determined by EIS of electrodes in the sandwich cell configuration. FGS pastes and doctorblading masks were adjusted so that each resulting film would be approximately the same thickness, about 6 µm, unless otherwise noted.

![Figure 6.6: $\mathcal{R}_{\text{CT}}$ of electrodes heated at various temperatures. Blue: iodine-based electrolyte; Red: cobalt-based electrolyte; Green: sulfur-based electrolyte.](image)

From this data, we can make several observations. First, the different electrodes behave differently with the different mediators. For instance, Dried FGS electrodes perform better than FGS with F127 & PEO electrodes in the iodine-based electrolyte, about the same in the cobalt-based electrolyte, and worse than them in the sulfur-based electrolyte. This result indicates that the specific morphology and the fabrication method
of the electrodes matters for the various mediators. A second observation is that the addition of graphite to FGS does not improve $\mathcal{R}_{\text{CT}}$, as is seen in the literature for adding graphite to carbon black.\textsuperscript{18} Carbon black is composed of spherical particles (generally $< 100$ nm in diameter), or aggregates thereof, whose shape inhibits intimate contact and impedes charge transfer between particles, thus resulting in a high resistance film. The addition of graphite platelets improves the long range conductivity of the particle network reducing losses in the electrode.\textsuperscript{18, 22} An FGS, on the other hand, is a two dimensional sheet with lateral dimensions on the order of a micron. It can readily overlap with adjacent sheets, aiding in charge transfer throughout the film.\textsuperscript{21} Furthermore, recent studies have shown that sheet edges can act as field emitters dramatically increasing the distance that electrons can tunnel from the material.\textsuperscript{23, 24} Thus in graphene-graphite composites, the graphite may primarily act to decrease the catalytic surface area of the electrode, resulting in the greater $\mathcal{R}_{\text{CT}}$ seen. Finally, we see that processing the electrodes using ethyl cellulose results in the best performing electrodes.

**Preparation of Alternative Counter Electrodes**

FGS counter electrodes were prepared on FTO (TEC8). Pastes (described below) were tip sonicated for 30 s before use and then doctor bladed on a tape spacer resulting in $\sim 6 \mu$m thick films once dried. Electrodes using $N$-methyl-pyrrolidone were dried over night at 100 °C due to the solvent’s low volatility. All other electrodes were dried at room temperature. Depending on the paste used, a heat treatment step was then performed in an oven (Nabertherm Controller P320) under air.
FGS & Graphite w/ EC (Ethyl Cellulose) electrode paste: 0.5 g of graphite (7 µm flake, Alfa Aesar) was added to 12 g of 10 wt.% ethyl cellulose in ethanol. This mixture was then mixed and tip sonicated for 2 min. 0.1 g of FGS was added, and the resulting mixture further tip sonicated for 2 min. Electrodes were heat treated at 310 °C.

FGS w/ PVDF (Polyvinylidene fluoride) electrode paste: 0.4 g of FGS was mixed with 10 g of 5 wt.% PVDF in N-methyl-pyrrolidone. Then 9 g of N-methyl-pyrrolidone was added and the mixture was tip sonicated for 2 min.

Dried FGS electrode paste: 0.2 g of FGS was mixed with 12 g of N-methyl-pyrrolidone and then tip sonicated for 2 min.

References


7 Conclusions and Future Work

7.1 Summary of Main Conclusions

This dissertation investigated the use of functionalized graphene sheets (FGSs) as catalytic counter electrodes in dye-sensitized solar cells (DSSCs). The key findings are as follows:

- FGSs which are rich with lattice defects but lean with oxygen sites exhibit the highest catalytic active for the reduction of Co(bpy)$_3$(III), a major DSSC redox mediator.
- Although monolayers may be sufficient for the cobalt system, networks of FGS are required to effectively catalyze the iodide/triiodide redox mediator.
- Tape casting a polymer-FGS suspension and thermolizing the polymer can lead to high surface area electrodes with good conductivity. When used as the counter electrode catalyst in a DSSC, the device exhibits 90% of the fill factor and power conversion efficiency that is achieved from a cell using the traditional platinum catalyst.
When determining the catalytic activity of high surface area carbon electrodes it is important to account for the effect of porosity, both with cyclic voltammetry and electrochemical impedance spectroscopy.

By better controlling the morphology of FGS networks, using a partially thermolyzed FGS:ethyl cellulose composite, electrodes can be fabricated that match or exceed the performance of platinum for a variety of redox meditators.

In sum, these results suggest that FGS based counter electrodes can supersede platinum as the catalyst of choice in DSSCs. Nevertheless, more work is necessary to understand the role of FGSs at a mechanistic level, as well as to bring the technology to commercial relevance. The remainder of this chapter discusses possible future directions in which research on using FGSs in DSSC counter electrodes could proceed.

### 7.2 Future Directions

#### 7.2.1 Modeling

Experimentally we have shown that FGSs which are defect rich and oxygen poor exhibit higher catalytic activity than oxygen rich FGS, and much higher activity than pristine graphene. However, what defect sites are responsible for catalysis, and the mechanics of this catalysis are currently unknown. Recently, *ab-initio* modeling of the role of FGSs in the catalysis nitromethane thermal decomposition provided insights into the active functionalities (single carbon vacancies). Similar work with the DSSC redox
mediators could aid in understanding the reaction mechanism and in designing materials which are more effective catalysts.

### 7.2.2 Catalytic and Conductive Inks

One of the goals of this dissertation work was to create an ink that could be cast on an arbitrary substrate to provide a catalytic and conductive film. This approach would eliminate the need for platinum as well as FTO, both expensive components of a DSSC. In Chapter 5, we showed that Vor-ink™ showed promise for this application, exhibiting sheet resistances of 5 Ω/sq while catalyzing the reduction of triiodide. Nevertheless, these electrodes did not perform as well as platinum and further work showed that they were not stable in the acetonitrile-based electrolyte commonly used for high efficiency devices. Creating films which are as catalytic as our devices made from the partial thermolysis of FGS:ethyl cellulose composites (Chapter 6) and as conductive as those made from Vor-ink™ will enhance the desirability of employing these electrodes in commercial devices. Although a multilayered process with a conductive base, and catalytic top coat is feasible, a one-step solution would be preferable.

### 7.2.3 Low Temperature Processing

Another limitation of current processing techniques – both the dominant platinum catalyst and with our best performing FGS electrodes – is that high temperatures (~ 400 °C) are required. High temperature processing increases the costs associated with manufacturing, and it severely limits the substrates available for production. Developing
methods to obtain high surface area, stable, and ideally highly conductive, electrodes at heat treatments below 200 °C would greatly reduce costs and open up a variety of common plastics for use as substrates.

7.2.4 Tuning FGS Structure for Catalysis

Although Chapter 4 looked to determine what sites were active, it did so in a reactionary way. Materials with a variety of sites were created through thermal treatment of graphite oxide and graphene oxide, and then tested. Expanding upon these results and perhaps upon the results of any simulations (see Section 8.2.1), it would be beneficial to prescriptively create materials with a high density of the most active sites. Developing ways to accomplish this feat would advance not only DSSCs but a host of other applications such as sensors and fuel cells.

References