

Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 40 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of \$250 for UW-Madison chemistry Ph.D. candidates.



The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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**Developing Cu-based Photoelectrodes and Electrocatalytic
Processes for Efficient Solar Water Splitting and Biomass
Conversion**

by

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**Chapter 1. An introduction to my renewable
energy research that non-scientists can absorb
and digest**

1.1 Introduction

Over the past five years whenever someone has asked me what I do, I respond with something akin to, “I’m earning my Ph.D. in chemistry, so I’m doing renewable energy research using electrochemistry, focusing on solar energy use and biomass conversion.” Often, after stating that I am getting a Ph.D. in chemistry to an acquaintance, I usually get a reaction of extreme fear, dislike, or intimidation accompanied by a wincing or cringing face, and this person tells me that I must be very smart. First, thank you for thinking that I’m smart. However, you are also smart, and you can understand these topics too. If you think this research or the overarching topics sound “cool” then let me teach you. Let’s jump into it together because science is all about teaching and learning in a collaborative way.

1.2 What kind of renewable energy do I research, and why do we care?

In my research group, we develop materials for different renewable energy applications including solar energy usage, biomass conversion, and water desalination. My research projects specifically have focused on solar energy and biomass conversion efforts. We as humans increasingly depend on energy (electricity, heating, transportation) in our daily lives, and our biggest source of energy thus far has been from non-renewable resources such as oil and coal. Aside from having a finite available amount, which means they will become more expensive as resources shrink, these resources also damage our environment during use. If we can make use of some other energy sources that aren’t as limited in availability and don’t pollute the environment it will be a win-win situation.

One major energy source that would be ideal to harness and use is the energy from the sun. Maybe you have heard it said before that in one hour the sun provides enough energy to the earth

to satisfy all of humanity's energy needs for an entire year! If this is true, then why aren't our problems solved? The remaining problem that needs to be solved is how to capture and utilize that energy that the sun provides. One way we can capture the sun's energy resource is by using special materials to absorb the sunlight and then converting that sunlight into energy we can use, like electricity or fuels. Often, these "special materials" are semiconductors, which are composed of elements from the periodic table. Semiconductors are materials that can conduct electricity moderately well, and for solar energy conversion purposes, we want to use semiconductors that are also able to absorb light. The most suitable semiconductors for our purposes are able to absorb light and use that light energy to produce electricity or perform a chemical reaction that results in the production of a fuel.

Plants are another abundant energy source. You may have heard of biofuels, which is one type of energy that we can get from plants. Originally, we made biofuels using food crops. We now call this type of biofuel "first generation biofuels," and they were problematic because humans and livestock needed the fuel source for food. In order to avoid this food versus fuel issue, researchers developed second generation biofuels, which are made of plants or parts of plants that are not eaten by humans or animals. In fact, the parts of plants that are used for these biofuels (lignin and cellulose) are substances found in plant cell walls and can't even be digested by humans or animals, or any vertebrate!

So now that we know which parts of plants can be used without competing with food sources, we ask ourselves, "What useful products can they be made into?" Scientists use various methods that often involve enzymes and heat to break down the lignin and cellulose into smaller compounds like glucose and fructose, which are sugars. From there, they can perform more chemical reactions to transform those sugars into other chemicals. The final "bio-products" can

range from liquid fuels that can power a vehicle to chemicals which had traditionally been produced from fossil fuel sources and are important for industrial processes. One example of an industrial process is plastic production: if we replace the traditional chemicals that we use to make plastics with those derived from plants, we get something like Coca-Cola's PlantBottle™. Think about how many plastic items you encounter on a daily basis. Worldwide, more than 2 billion pounds of plastic are produced *daily*. Each year, Americans alone use about 50 billion plastic water bottles. Now imagine if those items had been made wholly or partially from plants rather than from petroleum.

1.3 How do I do my renewable energy research?

The tool or technique that I use to do my renewable energy research is electrochemistry. Electrochemistry is the branch of chemistry that encompasses chemical reactions that consume electricity and chemical reactions that produce electricity. In other words, either we use electricity to force a chemical reaction (think electroplating, which is the technique used to paint vehicles, or splitting water into oxygen and hydrogen gas) or a chemical reaction occurs on its own and produces electricity in the process (think batteries).

In particular, we often focus on chemical reactions that take place at the surface of an electrode, which is usually a solid metal or a semiconductor (there's that word again!), and an ionic conductor, the electrolyte. The reaction involves electricity moving between the electrodes and the electrolyte, and because electricity (electrons) move from one material to another, we call this type of reaction a "redox reaction." An example of this setup is shown in Figure 1.1 "Redox" comes from the combination of the words "reduction" and "oxidation." This is because when a redox reaction occurs, something has to be oxidized (it loses electrons) and something has to be reduced

(it gains electrons) in order to be a balanced process. Oxidation occurs at the anode, and reduction occurs at the cathode.

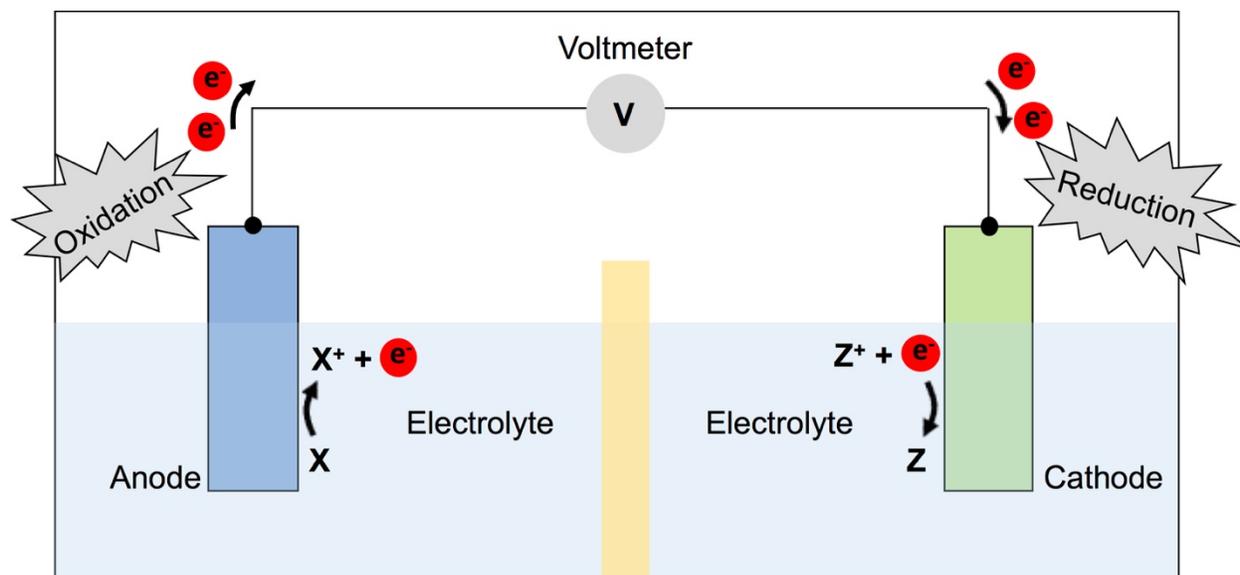


Figure 1.1. An example of an electrochemical cell, where an anode and cathode are immersed in electrolyte and connected by cables to create a circuit. Oxidation (loss of electrons) of species X occurs at the anode, and reduction (gain of electrons) of species Z^+ occurs at the cathode.

An example of oxidation that you see in everyday life is rust, which is the oxidation of iron metal (shown in Figure 1.2). This oxidation happens naturally (or spontaneously) when iron is exposed to air and water, and indeed this process produces a small electric current. This process reduces the oxygen that is found in the air. If salt is present it serves as an electrolyte which helps conduct the electricity and expedites the oxidation/rusting process. Wash your car frequently if you live in an area where the roads are salted in the winter! This rust reaction occurs slowly over time on its own, but we can also use electricity to force such reactions to happen quickly.

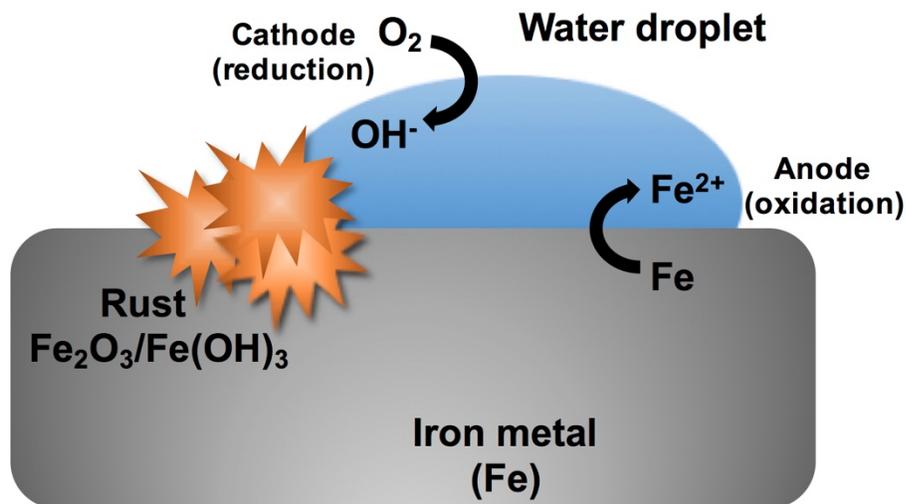


Figure 1.2. A visual representation of the rust formation process. The iron metal (Fe) is oxidized and dissolved into the water (Fe²⁺). The iron is then further oxidized to Fe³⁺ while the oxygen from air (O₂) is reduced, forming rust (Fe₂O₃).

Electrochemistry is used for electrodeposition or electroplating and production of metals, and takes place within breathalyzer tests, solar cells, blood sugar meters, batteries, fuel cells, and supercapacitors, to name a few examples. Electrodeposition or electroplating is simply when we use an electric current to deposit some material (often metals) onto a desired conducting surface (an electrode). In the lab, electrochemistry is advantageous because it can be performed at room temperature, is low-cost, and is easily tunable and controlled (i.e. there are many parameters we can adjust to get the results we want!).

1.4 How do I use electrochemistry to do renewable energy work?

Now I'll get into some specifics about how I use electrochemistry to study and create renewable energy materials. As I mentioned earlier, the materials that we can use to capture the sun's energy are called semiconductors. During my time in graduate school, I optimized how to

use electrodeposition to synthesize a semiconductor material. The semiconductor that I focused my attention on was copper oxide (CuO). Why was I interested in CuO, you ask? CuO is composed of copper and oxygen, two very abundant elements, which is the first reason this material is very attractive. Because of its abundance, it is also very cheap. It is non-toxic, and it is able to absorb much of the light from the sun, which is demonstrated by its dark brown/black color. These are all very important considerations when choosing a semiconductor material for solar energy harvesting, as there is a desperate need for cheap and abundant materials for solar energy conversion.

I created my own CuO using electrochemistry. However, my synthesis procedure actually didn't involve direct electrodeposition of CuO. I first used electrochemistry to deposit a layered Cu-containing material, which I then heated in a furnace to obtain CuO. As I mentioned before, when using electrochemistry, something needs to be oxidized and something needs to be reduced. As shown in Figure 1.3, my synthesis method involves indirect reduction, where I reduced an added chemical (*p*-benzoquinone) by passing electricity through the electrodes, and during that reduction process, *p*-benzoquinone acquired hydrogen ions (H^+) from solution. This all occurs very close to the electrode surface because this is where the source of electrons is. When H^+ is removed from the solution to be incorporated into the *p*-benzoquinone molecules, the acidity near the electrode decreases (because H^+ makes things acidic). The copper ions in solution will not stay dissolved in less acidic solutions, so the copper became insoluble and precipitated onto the electrode as a thin film. Manipulation of acidity and basicity is a very handy trick in the electrodeposition world!

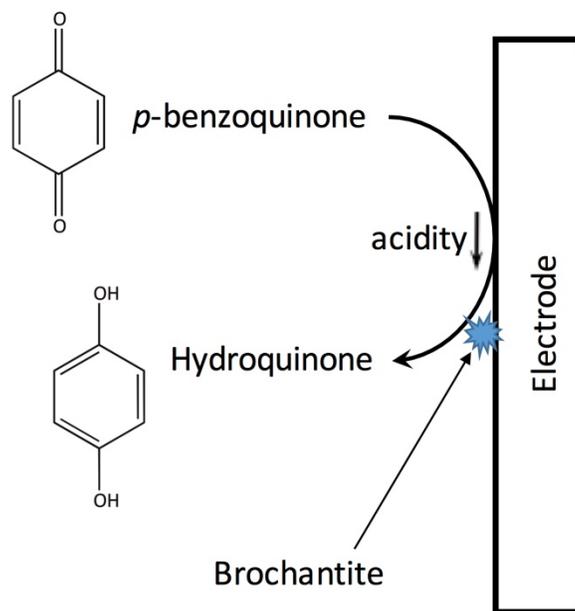


Figure 1.3. Electrochemical reduction of p-benzoquinone to form hydroquinone, which decreases the acidity very close to the electrode surface. This decrease in acidity causes the copper-based material (brochantite) to become insoluble and form a thin film on the electrode.

The material that is deposited is the mineral brochantite, which has a highly-ordered, layered structure and contains sulfur, oxygen, and hydrogen as well as copper. After soaking this deposited film in very basic (opposite of acidic) solution and heating in a furnace, I achieved the desired CuO film. Only this CuO was not any old CuO. Because of my unique synthesis procedure, I actually created CuO with really distinctive morphologies, which enhanced CuO's effectiveness for solar energy utilization.

When I shone simulated sunlight onto my CuO, the CuO absorbed the light and transformed that light energy into electrons, as shown in Figure 1.4. By adding extra electricity to these electrons, we could use them to perform a chemical reaction. The ideal chemical reaction we would like to perform is water reduction to produce hydrogen gas (H₂). Hydrogen gas is a fuel that

is used in what you have likely heard referred to as hydrogen vehicles or fuel cell vehicles. These types of vehicles emit zero carbon, so they have the potential to be much less damaging to the environment than our current combustion vehicles.

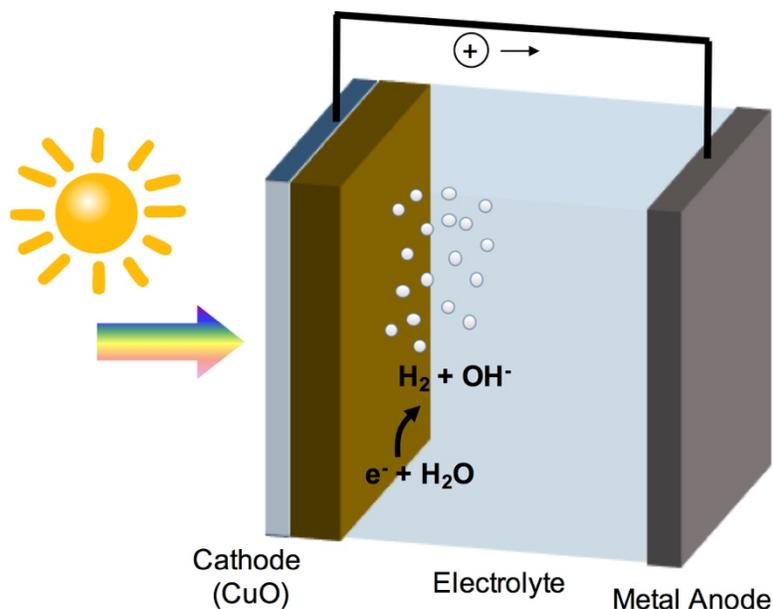


Figure 1.4. Diagram showing the process of shining sunlight onto CuO to produce hydrogen gas (H_2) from water.

Switching gears to my other renewable energy project, let's focus on getting useful products from plants (aka biomass)! In this case, I have spent most of my effort using electrochemistry to *perform* the conversion of the biomass into valuable products, while I used it to both *synthesize* my electrode (CuO) for the solar energy project and *perform* a chemical reaction to produce hydrogen gas. Essentially, there are fewer steps for this biomass conversion project because I purchased the electrode that I used for the reaction. As I mentioned earlier, scientists commonly break down cellulose into sugars like glucose and fructose. They then dehydrate the sugars to produce a chemical that those in the field widely recognize as a good starting place when

trying to make useful products out of plants: HMF (5-hydroxymethylfurfural). I used HMF in all my biomass conversion studies, and we wanted to find a good way to electrochemically produce a replacement for a petrochemical that is used in plastics: terephthalic acid (TA). TA is a precursor chemical for making the most commonly found plastic in your household, the kind of plastic your plastic bottles and food containers are made from, labelled with a recycling number 1. We call these PET plastics, and we can replace the TA that we use to make these PET plastics with FDCA (2,5-furandicarboxylic acid). Since we can make FDCA from oxidizing HMF, we can make plastics from bio-based chemicals rather than fossil fuel-based chemicals.

With this goal in mind, we got to work, and found that we could use electrochemistry to oxidize HMF to FDCA, and that we could do it very efficiently if we used an electrochemical catalyst that was dissolved in solution with the HMF. A catalyst makes a reaction easier and faster by lowering the energy barrier of the reaction but is not consumed by the reaction. In our case, TEMPO was our catalyst. There is actually an entire family of TEMPO-related compounds that we assessed during our studies, but I will just discuss plain ole' TEMPO here because it was our starting point.

Think of TEMPO as an “expert” at HMF oxidation; it’s able to do the oxidation faster, easier, and more efficiently than our “novice” electrode can, which was made of carbon. Not only is TEMPO naturally good at interacting with HMF, it is also good at accepting and donating electrons (aka being reduced and oxidized). This means the electrode preferred to oxidize TEMPO rather than HMF because it was easier (see Figure 1.5). Then when oxidized TEMPO ran into an HMF molecule in solution it gladly accepted an electron from HMF, oxidizing HMF, and in doing so was reduced back to the original TEMPO species. This cycle repeated over and over until HMF

was oxidized all the way to FDCA (there are several intermediate compounds involved between HMF and FDCA).

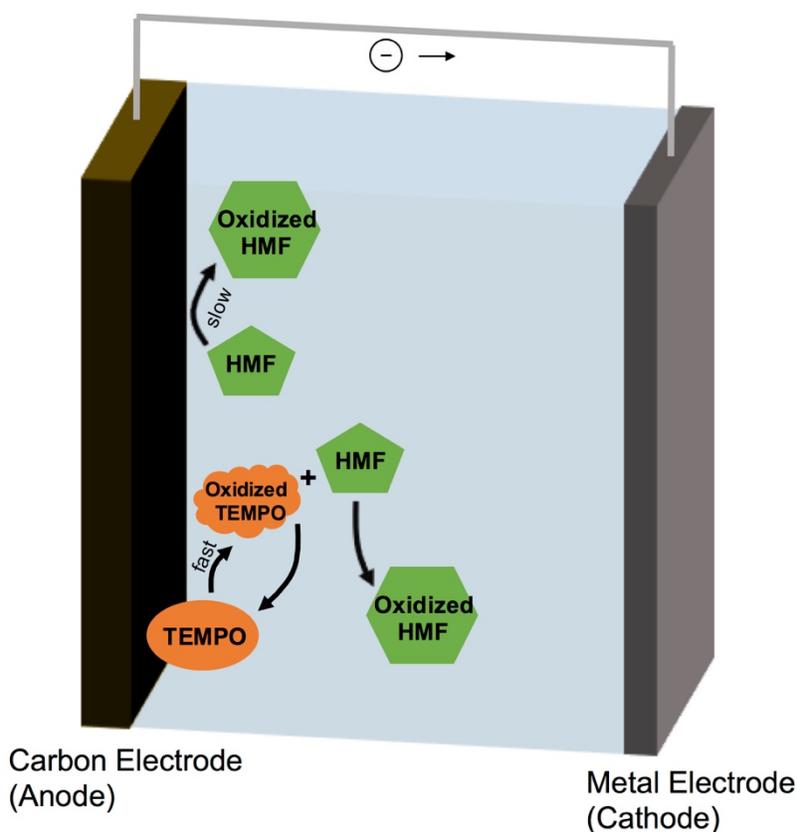


Figure 1.5. Diagram showing the oxidation of TEMPO at the carbon electrode. The oxidized TEMPO then oxidizes HMF and in doing so is reduced back to TEMPO. The interaction between TEMPO and the carbon electrode occurs much faster than the interaction between HMF and the carbon electrode, so the presence of TEMPO helps to speed up the HMF oxidation reaction.

We used another acidity trick to separate out our product from the solution at the end of the reaction. Because FDCA is insoluble in acidic solutions, when we increased the acidity, FDCA “crashed” out of solution, allowing us to filter it out from the solution that contained TEMPO in a very practical way. This was the most efficient process that researchers had ever reported using

such a cheap electrode (we used carbon), which was significant since traditionally researchers had used precious metals (i.e. expensive) catalysts.

After our group published these results, we were contacted by a Swiss company that wanted to collaborate in order to produce FDCA on a large scale. I became heavily involved with the project at this point, and over a period of about two years I worked with the company to identify the optimal conditions for getting this process to work on a large, industrial scale. This real-world application experience was invaluable and taught me a lot about what considerations are necessary when scaling up a project and gave me first-hand experience with scientists who use electrochemistry outside of academic research.

1.5 Recap

In summary, during my doctoral research I have developed materials for use as solar energy harvesters to potentially generate electricity in a solar cell or to produce valuable products like hydrogen gas. Since I first synthesized CuO, I have worked further to enhance its abilities for solar energy conversion as well as improve its stability (its major downfall) by tweaking its composition or “protecting” its surface with other materials. On the biomass conversion side, I have further developed a process that was previously designed in our group and helped scale it up to an industrial level. I have also explored how my CuO might be useful for converting HMF to FDCA (combining projects!). Thank you for giving me this opportunity to share with you what I have devoted the better part of my 20s to. I hope that I have taught you a little bit about electrochemistry and how it can be applied to renewable energy topics. I hope you were able to “absorb” my description of the solar energy conversion project and “digest” the importance and usefulness of

converting biomass-derived chemicals, like HMF, to valuable products like biofuels and biochemicals.