Dye sensitized solar cell, powering a motor.
Start with berries
Mash them up
Soak your titanium slide in the mash
Face up or face down does not matter, simply must be submerged in the dye.
It will be covered with bits of material from the berries, you will need to rinse this this off
It will be covered with bits of material from the berries, you will need to rinse this off.
Don’t worry if your juice runs a little bit
The counter electrode, is a glass slide coated in graphite (lead pencil)
Golf pencils - very cheap and almost entirely graphite with no waxy polymers

The more expensive pencils have a greater percentage of polymers which help the pencil write smoothly
Finished counter electrode

Can bake to get graph to adhere better, but not necessary
Sandwich the titanium oxide-dye slide and graphite electrode
Use the ever useful binder clips to secure the slides together
Notice that the slides are offset.
Add the electrolyte via pipette to the junction of the two electrodes.
You can wipe up any excess, but it is not necessary
The finished electrode!
Proceed to testing

Alligator clips need to make contact with the inside surface of the glass
Chemistry 3X
Lecture 7

Water Electrolysis using Titanium Dioxide Semiconductor:

\[ \text{TiO}_2 \quad \overset{h \nu}{\longrightarrow} \quad \text{valance band} \]

\[ \text{conduction band} \quad \overset{\sim}{\longrightarrow} \quad \text{O}_2 \]

\[ \text{H}_2\text{O} \quad \overset{h \nu}{\longrightarrow} \quad \text{H}_2 \quad \text{and} \quad \text{O}_2 \]

Diagram: TiO\(_2\) semiconductor with valance and conduction bands, hydrogen and oxygen production.
Water Electrolysis using Titanium Dioxide Semiconductor:

$\text{TiO}_2$  

$\text{H}_2\text{O}$  

$\text{O}_2$  

$\text{H}_2$  

$\text{H}_2\text{O}$  

$\text{O}_2$  

$\text{H}_2$  

$h\nu$  

$e^-$  

$\text{valence band}$  

$\text{conduction band}$
Honda and Fujishima discovered the photo excitation of the TiO2 in 1972
Honda & Fujishima

• Demonstrated that titanium dioxide on FTO glass could generate a photoelectrochemical current

• Which is the experiment you just performed!
Electrochemical Photolysis of Water at a Semiconductor Electrode

Although the possibility of water photolysis has been investigated by many workers, a useful method has only now been developed. Because water is transparent to visible light it cannot be decomposed directly, but only by radiation with wavelengths shorter than 190 nm (ref. 1).

For electrochemical decomposition of water, a potential difference of more than 1.23 V is necessary between one electrode, at which the anodic processes occur, and the other, where cathodic reactions take place. This potential difference is equivalent to the energy of radiation with a wavelength of approximately 1,000 nm. Therefore, if the energy of light is used effectively in an electrochemical system, it should be possible to decompose water with visible light. Here we describe a novel type of photo-electrochemical cell which decomposes water in this way.

Electrolysis of water can occur even without applying electric power if one of the following three conditions is fulfilled. First, oxygen evolution occurs at a potential more negative than that at which hydrogen evolution occurs in normal conditions; second, hydrogen evolution occurs at a potential more positive than that at which oxygen evolution occurs in normal conditions; third, the potential for oxygen evolution is made more negative and that for hydrogen evolution is made more positive, until the former is more negative than the latter.

Current-voltage curves of a semiconducting n-type TiO₂
The band gap of titanium dioxide spans both redox potentials for water oxidation and proton reduction. Recall that energy and potential are inverse scales. As relative potential increases, relative energy of the electrons decreases.
Titanium Dioxide

TiO$_2$, white and reflective. This is because it only absorbs in the UV range.
Titanium Dioxide

There is a problem with using TiO\textsubscript{2} absorbing medium. It's Band Gap is 3 eV, and energy which corresponds to UV light. The solar spectrum is quite dilute in photons of this energy.
Overall Reaction

2H₂O + light → 2H₂ + O₂

Electron Energy

Semiconductor

Metal Electrode
Brian O'Regan (left), and Michael Gratzel (right), were able adapt semi-conductor photovoltaics with simple visible light dyes.
A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO$_2$ films

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The large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods. Here we describe a photovoltaic cell, created from low- to medium-purity materials through low-cost processes, which exhibits a commercially realistic energy-conversion efficiency. The device is based on a 10-μm-thick, optically transparent film of titanium dioxide particles a few nanometres in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current (more than 80%). The overall light-to-electric energy conversion yield is 7.1–7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12 mA cm$^{-2}$) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make practical applications feasible.

Solar energy conversion by photoelectrochemical cells has been intensively investigated. Dye-sensitized cells differ from the conventional semiconductor devices in that they separate the function of light absorption from charge carrier transport. In the case of n-type materials, such as TiO$_2$, current is generated when a photon absorbed by a dye molecule gives rise to electron injection into the conduction band of the semiconductor, Fig. 1. To complete the circuit, the dye must be regenerated by

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$2e^- \rightarrow \text{Reduced State}$

$\text{I}_3 \rightarrow \text{I}^- \rightarrow \Delta V$

$\text{Dye}$

$\text{Electrolyte}$

$\text{Pt electrode}$

$\text{Conduction Band}$

$\text{Valance Band}$

$3 \text{ eV}$

$1-2 \text{ eV}$

$\text{Excited State}$

$\text{Ground State}$

$\text{h} \nu$
• Light shines on a dye with an approximately 2 eV HOMO-LUMO gap.
• The light excites electrons into the LUMO, which should have greater energy than the lowest energy of the conduction band.
• The electrons fall in energy into the conduction band. The iodate/iodide redox couple takes up the electrons at the counter electrode.
• The iodate/iodide redox couples must be between the ground state of the dye and the bottom of the conduction band.
• Using the iodate/iodide redox couple as the electrolyte, a photocurrent is generated by reducing this redox couple.
• The highest voltage able to be generated is the lowest energy potential difference in the cell, which is the 0.54 V iodate/iodide redox couple.
\[ \text{TiO}_2 \text{ quenches the excite Ru(bpy)}_3 \text{ and the electron is carried away on the conductive slide} \]

\[
\begin{align*}
Ru(bpy)_3^{*2+} & \xrightarrow{e^-} TiO_2 & 1ps \\
Ru(bpy)_3^{*2+} & \xrightarrow{e^-} Ru(bpy)_3^{2+} & 1ns
\end{align*}
\]
Ru(bpy)$_3$ is a dye

• For this system any dye will work.
• It just needs to be excitable by visible light, and have a redox potential in the correct range.
A Dye-Sensitized Cell

• The dye is placed on top of the titanium dioxide.
• When shining light on the material, the dye absorbs electrons, transfers them through the conduction band of titanium dioxide.
• The dye "stains" the titanium dioxide electrode, and the dye physisorsbs on the surface of the nanoparticles.
$I_3^- + 2e^- \rightarrow I^-$

$E^\circ = 0.54 V$
What Electrolyte Should We Use?

• Water oxidation and proton reduction can be kinetically sluggish.
• Adding an additional electrolyte can speed up the electron transfer process in the "circuit".
• The standard reduction potential of iodate to iodide is 0.54 V.
• Coupled with the ruthenium 3+/2+ redox couple, a hole is removed from the surface of the electrode, which inhibits back reaction of the excited ruthenium back to ground state ruthenium.
• This redox couple was the first Gratzel and O'Regan tried, and to this day, no single electrolyte has been found to be better.
Graphite

\( \text{TiO}_2 \) with dye

Sandwich together

Working

Reference

Auxillary

\( e^- \)

Electronics of DSSC
Constructing Your Cell

• Oxidation/Reduction is necessary with the dye. Salts are bad! When oxidized or reduced, a salt tends to form other compounds or decompose readily.
• Think of sodium chloride. Giving an electron to Na\(^+\) would generate an EXTREMELY unstable Na radical that would react very readily with anything in the cell.
• You will soak your titanium dioxide slide in a petri dish of dye solution.
• A graphite counter electrode will be used. The graphite can be applied using either a cheap golf pencil or soot from a candle flame.
• The overhang of blank FTO glass will be used to attach leads to complete the circuit.
• Binder clips will be used to keep the slides together.
• After constructing, you will drip the electrolyte on the edges of the slides and then draw the electrolyte in by moving the binder clips.
• The ideal potential when using the halogen lamp or the sun itself will be 540 mV. In the past, students have made cells with potentials near 500 mV!
Requirements for dye

• Need to oxidize with semiconductor, excited state higher than conduction band, absorbs visible light

• Excited state must be above the conduction band limit of the semiconductor in order to get quenching by the semiconductor.
Dye Sensitized Solar Cell

(TCO Glass + Dyed Titania Particles)  (TCO Glass + Catalyst Layer)