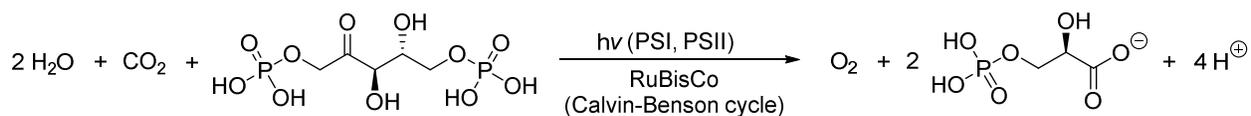


Power Conversion Efficiency of a Dye-Sensitized Solar Cell

This laboratory session is aimed at bridging the gap between our knowledge of the natural photosynthetic reaction center and future solar technologies. This is a research field commonly referred to as *artificial photosynthesis*. Natural photosynthesis involves a highly complex sequence of chemical events. As such there are many ways to present its various components. Summarized in Scheme 1 below are the principal chemical transformations conducted by photosystems I and II (PSI, PSII) and the Calvin-Benson carbon fixation cycle (aka Calvin cycle). Although production of a hexose sugar (or even polysaccharide) is often represented as the final product of photosynthesis in many texts, the initial product is actually the C3 molecule (2*R*)-2-hydroxy-3-phosphonooxypropanoate (aka 3-phosphoglycerate or G3P).



Scheme 1. Chemical equation summarizing light driven natural photosynthetic water splitting and carbon dioxide fixation.

While we perceive this reaction as our means to survival in that it produces an oxygenic atmosphere essential for life, photosynthetic organisms conduct these reactions as a method to store energy for later use in glycolysis and the citric acid cycle providing themselves the necessary energy for cell growth and maintenance. From a chemical viewpoint, photosynthesis uses visible electromagnetic radiation, i.e. sunlight, to power the movement of electrons thus initiating redox-driven chemical transformations. An understanding of photosynthesis at the molecular level is particularly attractive since valuable substances, e.g. NADPH and G3P, are produced in these reactions from very simple, low-energy starting materials (H_2O and CO_2) powered by a readily available and abundant form of energy that is sunlight.

While not directly obvious, solar cells mimic the light absorption and electron flow of photosynthesis to produce electricity. The basic components of a solar cell are a photoanode || cathode interface (or anode || photocathode interface) connected by an external circuit. Through irradiation with sunlight, an exciton (electron-hole pair) is generated by interfacial charge separation with charges recombining via an external current. The potential difference between both electrodes determines the electrical potential (voltage) of the solar cell. The efficiency of photon-to-current conversion will determine the current (amperage) of the cell. The percentage *power conversion efficiency* (PCE or η) of any solar cell device is simply the ratio of power output (P_{out}) versus power input (P_{in}), the latter dependent upon the incident light flux (I_0), and the former, implicit properties of the device itself (equation 1); namely the short-circuit current (I_{sc}), open-circuit voltage (V_{oc}) and fill-factor (FF). The short-circuit current density (J_{sc}) is typically reported to allow comparison between devices whose dimensions may vary ($J_{sc} = I_{sc}/\text{Area}$). The FF is determined by the ratio '*maximum obtainable power/theoretical obtainable power*' where the theoretical obtainable power is the product $I_{sc} \cdot V_{oc}$ (I_{sc} and V_{oc} being zero at open-circuit and short-circuit conditions respectively with Grade A solar-cells typically having $\text{FF} \geq 0.7$).

$$\text{PCE} = \eta = \frac{P_{out}}{P_{in}} \times 100 = \frac{J_{sc} V_{oc} \text{FF}}{I_0} \times 100 \quad (\text{eqn. 1})$$

Although there are many classes of solar cells today we will focus on *dye sensitized solar cells* (DSSCs) which involve a number of chemical components offering a unique opportunity of study.¹

The maximum reported DSSC efficiency of $\eta = 11.9\%$ ² is still short of silicon's performance ($\eta = 25\%$) in addition to a variety of alternative single and multi-junction devices (Fig. 1).³ Conventional DSSC devices (Fig. 2) are distinct from the silicon solid-state solar cells however in that they consist of multiple components (*n*-type semiconductor, dye sensitizer, redox mediator, electrolyte solvent) each of which can be photophysically and electrochemically tuned via chemical design and synthesis to optimize device performance. The champion state-of-the-art DSSC device today consists of a mesoporous *n*-TiO₂ nanoparticle electrode deposited on conducting fluorine-doped tin oxide (FTO) glass and sensitized by the **YD2-o-C8** triarylaminoethynyl porphyrin dye (Fig. 1). Critical to the performance of this device is the use of a [Co(bpy)₃]^{3+/2+} redox couple in acetonitrile at a Pt coated FTO counter electrode which produces a PCE of 11.9%.²

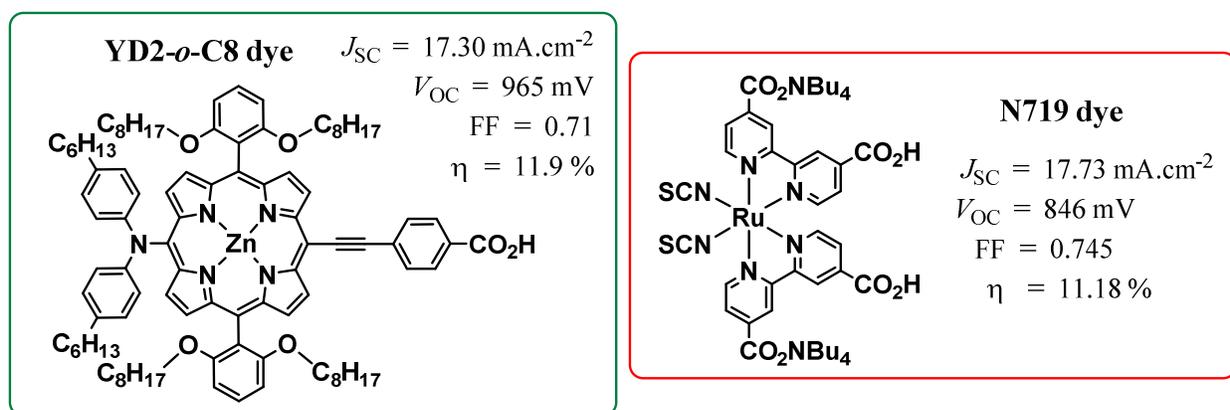


Figure 1. Structure and DSSC properties of the **YD2-o-C8** and **N719** dye sensitizers.

In this lab we will use the N3 dye, first introduced by Grätzel and co-workers 20 years ago and still used as a benchmark at the forefront of DSSC research today due to its high efficiency at 10.5%.¹ [The N3 dye is the tetraprotonated form of the N719 dye]. Conventional DSSCs are built around a photoanode (negative electrode) consisting of a mesoporous network of transparent *n*-type wide band-gap inorganic semiconductor nanoparticles of TiO₂ deposited on an optically transparent conducting substrate [fluorine-doped tin oxide (FTO) glass].⁴ The mesoporous (sponge like) layer (*ca.* 10 μm) of TiO₂ nanoparticles (*ca.* 10-20 nm diameter) boasts a remarkable surface area (roughness factor $\sim 1 \times 10^3$). The dye sensitizer is adsorbed on the high surface area TiO₂ by covalent attachment allowing a large absorption cross section (*light harvesting*). The low cost TiO₂ semiconductor mimics the light absorbing proteins found in the thylakoid membrane of the natural photosynthetic system.⁵ The function of this protein is to provide a three dimensional scaffold to arrange the light-harvesting molecules (chlorophylls and carotenes) in a fixed orientation with respect to one another for optimum vectorial energy transfer to the photosynthetic reaction center. TiO₂ functions similar to the natural system by acting as a scaffold for the self-assembly of dye molecules. In fact, TiO₂ plays a dual role in DSSCs as it also acts as an electron acceptor and charge carrier, once again mimicking the reaction centre of the natural photosynthetic system.^{5,6}

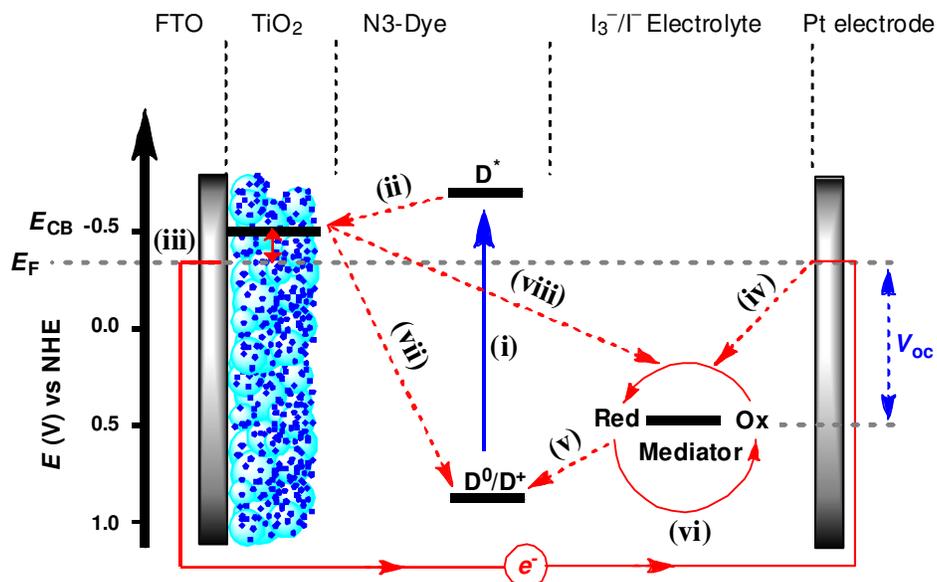


Figure 2. Energy level alignment of components in a conventional n -type DSSC device (kinetics shown in bold):

- (i) dye electronic excitation (**fs**)
- (ii) charge injection to semiconductor conduction band (**150 ps**; energy loss; limits I_{SC})
- (iii) electron equilibration to semiconductor Fermi level (energy loss) and diffusion to FTO (100 μ s)
- (iv) redox mediator reduction at counter electrode (limits V_{OC})
- (v) dye regeneration/mediator oxidation (**1 μ s**; energy loss)
- (vi) mass-transfer diffusion of redox mediator (limits I_{SC})
- (vii) $TiO_2^{*-} \rightarrow Dye^+$ charge recombination (**3 μ s**; limits I_{SC} and V_{OC})
- (viii) $TiO_2^{*-} \rightarrow Mediator^+$ charge recombination (**1 ms**; limits I_{SC} and V_{OC})

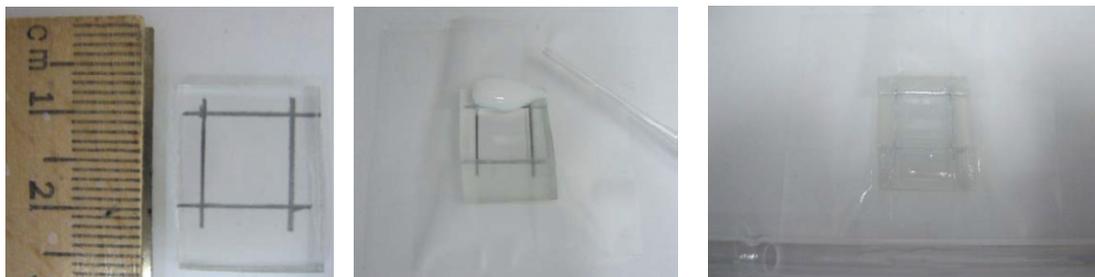
Fabrication of the FTO/TiO₂/N3/(I₃⁻/I⁻)/Pt dye-sensitized solar cell.

[Note: due to time considerations steps 1-5 will be conducted by the instructor in advance.]

- Determine which side of the conductive glass has the FTO coating by using a multimeter with its setting placed on resistance (Ω - the instructor may have labeled this already!).
- Facing the glass FTO face-up, carefully tape the glass to the benchtop on four sides using Scotch tape. It is critical here to expose just 1 cm² of the FTO surface (leaving roughly 2 mm from one end of the glass and about 8mm of bare FTO on the opposite end; ref. picture below).

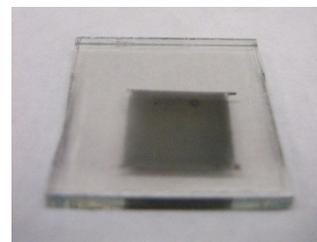


3. Add 2-3 drops of the TiO_2 paste uniformly to a single side of the Scotch tape. Using gentle pressure with adequate momentum spread the paste across the exposed FTO surface using the smooth edge of a glass pipette (known as doctor-blade technique). The TiO_2 paste consists of 18 wt% TiO_2 nanoparticles in a α -terpineol:ethyl cellulose (9:1) gel.

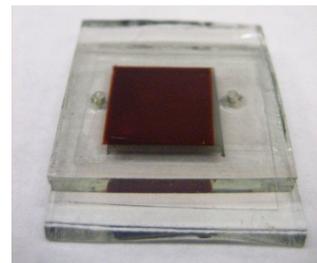


4. Allow the TiO_2 to settle for 5 min. Very carefully remove the tape and, keeping the FTO/ TiO_2 side-up, place in a tube furnace and heat at $450\text{ }^\circ\text{C}$ for 30 min. Allow to cool gradually to $100\text{ }^\circ\text{C}$ and place the electrode face up in a 1 mM N3 methanol solution for 24 hours.

5. In the meantime (while the FTO/ TiO_2 is absorbing the dye) take the second piece of FTO conductive glass which has 2 predrilled holes. Confirm using the multimeter which side is conductive (*the instructor may have labeled this already!*). Again using Scotch tape secure the FTO face up with 1 cm^2 exposed. Add one drop of a 0.05 M H_2PtCl_6 isopropanol solution and allow to air dry. Place the electrode in a furnace at $450\text{ }^\circ\text{C}$ for 30 min depositing elemental Pt nanoparticles and allow to cool gradually.



6. Next carefully place the provided polymer spacer around the sensitized TiO_2 layer and then place the Pt face down on the FTO/ TiO_2 /dye surface. Fix the electrodes in place with provided binding clips.



7. Prior to light exposure add one drop of provided electrolyte solution to complete the DSSC circuit (capillary action will carry the electrolyte through the mesoporous film). Groups will be divided into those using Co(III/II) and $(\text{I}_3^-/\text{I}^-)$ mediators.
8. We are now ready to expose the solar cell to our solar simulator light source ($\text{AM } 1.5; 100\text{ mW cm}^{-2}$). When the sample is in place first record the open-circuit potential (V_{OC}). Then using linear sweep voltammetry determine the short circuit current (I_{SC}) of the solar cell (note: cell area = 1 cm^2 so $I_{\text{SC}} = J_{\text{SC}}$).
9. The most efficient Co(III/II) and $(\text{I}_3^-/\text{I}^-)$ DSSCs will be used to record an *incident photon to current conversion efficiency* (IPCE) spectrum, aka *monochromatic external quantum efficiency* (EQE).

Laboratory Report

1. Describe in your own words the kinetic competition in a dye sensitized solar cell using Fig. 2.
2. What is the Fermi level of the semiconductor and how does this influence the cell's overall power conversion efficiency?
3. Only the two most efficient data sets for Co(III/II) and (I₃⁻/I⁻) mediator based DSSCs will be compared. Two sets of raw data will be uploaded online including I-V and IPCE data.

Follow the instructions below for both sets of raw data and then discuss in sufficient detail the difference in performance of each device using J-V and IPCE plots.

- a) Plot voltage (V) versus current density (mA cm⁻²) to determine J_{SC} and V_{OC}. [note: normalize each data set by multiplying by -1]
- b) Convert the J-V curve to a *power versus voltage* plot to determine the *maximum obtainable power* (J_{mp}·V_{mp}) output of the cell. From this value the fill-factor (FF) may be calculated.

$$FF = \frac{\text{maximum obtainable power}}{\text{theoretical obtainable power}} = \frac{J_{mp}V_{mp}}{J_{sc}V_{oc}}$$

[note: V x J = Power (mW); J_{mp} and V_{mp} can be determined from the voltage vs power plot using the position of maximum power]

- c) Now that you have J_{SC}, V_{OC} and FF determine the overall power conversion efficiency of the solar cell.
- d) Using raw data from the IPCE experiment plot the % IPCE (aka EQE) versus wavelength (nm) using the following equation to calculate % IPCE at every wavelength recorded (pay close attention to all units used)

$$IPCE = \frac{\# \text{ electrons}}{\# \text{ photons}} = \frac{(\text{current}/\text{electron charge})}{(\text{irradiance}/\text{photon energy})}$$

$$\# \text{ electrons} = \frac{I_{sc}(\lambda)}{e} \quad \# \text{ photons} = \frac{I_0(\lambda)}{h\nu} = \frac{I_0(\lambda) \cdot \lambda}{hc}$$

$$IPCE = \frac{\left(\frac{I_{sc}(\lambda)}{e}\right)}{\left(\frac{I_0(\lambda) \cdot \lambda}{hc}\right)} = \frac{hc I_{sc}(\lambda)}{e I_0(\lambda) \lambda}$$

$$\% IPCE = 1240 \times \frac{I_{sc}(\lambda)}{I_0(\lambda) \lambda(nm)} \times 100$$

where $I_{sc}(\lambda)$ = monochromatic short circuit current

$I_0(\lambda)$ = monochromatic light flux (*area must be equal to that of I_{sc} for solar cell*)

h = Planck's constant (6.626 × 10⁻³⁴ J.s ; note that 1 J = 1 W.s)

c = speed of light (2.998 × 10⁸ m s⁻¹)

e = charge of an electron (1.602 × 10⁻¹⁹ A s)

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