Solar Energy Conversion Using a Semiconductor Electrode Photosensitized by Tetraphenylporphyrin

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Abstract: The synthesis of *meso*-tetraphenylporphyrin (TPP) and its application in a solar- energy conversion device are described as an undergraduate laboratory experiment. In the first part of the exercise, a convenient procedure for the synthesis of TPP is presented. In the second section of the experiment, the construction of a high-efficiency photoelectrode that utilizes the light harvesting capacity of the porphyrin is presented. The spectral sensitization of a wide-band-gap semiconductor is achieved using TPP as an efficient photoreceptor, This mimics the role of the tetrapyrrolic macrocycle in natural photosynthesis.

Introduction

Tetrapyrrolic macrocycles are vital for life on this planet. Without the light-harvesting and trapping activities of reduced porphyrins there could be no photosynthesis. The *meso*-tetraphenylporphyrins (TPP) offer attractive features in this context and have been used in a wide variety of model studies.

For example, in one study the porphyrin moiety was linked to a carotenoid and then successfully utilized in the design of an artificial photosynthetic membrane that biomimics the natural processes of solar energy conversion [1]. Also, electroactive porphyrins have applications in the design of molecular-scale electronic devices [2].

The purpose of these laboratory experiments is to demonstrate, first, the synthesis of a porphyrin and, second, the utilization of a porphyrin in an energy conversion device.

Rothermund first synthesized TPP many years ago [3]. Benzaldehyde and pyrrole were reacted in pyridine at 150 °C for 24 h. Under this condition the yield was very low. Adler and co-workers used a modified method; they carried out the reaction for 30 min and open to the air in refluxing propionic acid [4]. The main problem with this procedure is the difficulty of purifying the product due to the high level of tar produced. Also, the reproducibility of this reaction is often rather poor. In this laboratory class we performed the TPP synthesis using a modification of the method developed by Lindsey and co-workers [5].

Like the photosynthetic reaction center, many artificial photosynthetic assemblies incorporate porphyrins because they are stable and can be reversibly reduced and oxidized. Chlorophyll derivatives and several related porphyrins have been used as light receptors in energy conversion devices [6], often obtaining a high light-harvesting yield [7]. One way to use the energy of a porphyrin's exited state is through the spectral sensitization of wide-band- gap semiconductors [8]. From a very simple point of view, the dye, D, is absorbed on the wide-band-gap n-type semiconductor. Light absorption by the dye places it is an excited electronic state, D*, where the dye is a stronger reducing agent than it is in the ground state. The excited-state dye is oxidized by charge injection into the conduction band of the semiconductor in a thermodynamically favorable process. The energy stored by the device is the energy difference between reducing strength of the electron in the conduction band of the semiconductor and the oxidizing strength of the dye, D^+. The process is schematically shown in Figure 1.

Unfortunately, only the first monolayer of adsorbed dye produces a significant photoeffect and the light-harvesting efficiency of a single monolayer is very low [8]. However, in a porous film of nanometer-sized semiconductor particles, the effective surface area can be greatly enhanced, thus producing substantial light absorption even

with only a monolayer of dye on each particle. There are several analogies between natural photosynthesis and the dye-sensitized nanocrystalline semiconductor electrodes; nature uses a similar means of absorption enhancement by stacking the chlorophyll-containing thylakoid membranes of the chloroplast to form the grana structure. At present, devices with high light- harvesting and charge-separation efficiencies for a range of dyes adsorbed on nanostructured semiconductors have been developed. These demonstrate nearly 80% incident-photon-to-current efficiency [9]. With such high efficiencies, the photosensitization of oxide semiconductors has become a practical means for solar energy conversion. Net power conversion efficiencies up to 10% have been reported in diffuse daylight [10].

In the second section of this experiment, we use TPP as a photosensitizing adsorbate on nanocrystalline SnO_2 semiconductor films in order to analyze the photoresponse of this dye. Nanocrystalline SnO_2 films prepared from commercial colloidal suspension are nanostructured and highly porous and can be easily surface-modified by association with an adsorbed dye. These electrodes exhibit efficient light harvesting and charge separation, leading to significant photocurrent and photovoltage outputs.

Experimental

General. UV–visible spectra were recorded on a Shimadzu UV-2401PC.

Starting Materials. Benzaldehyde, pyrrole, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), and trifluoroacetic acid from Aldrich were used without further purification. Hydroquinone (Aldrich) was recrystallized from toluene. Dichloromethane, petroleum ether, and chloroform (GR grade) from Merck were distilled and stored over 4Å
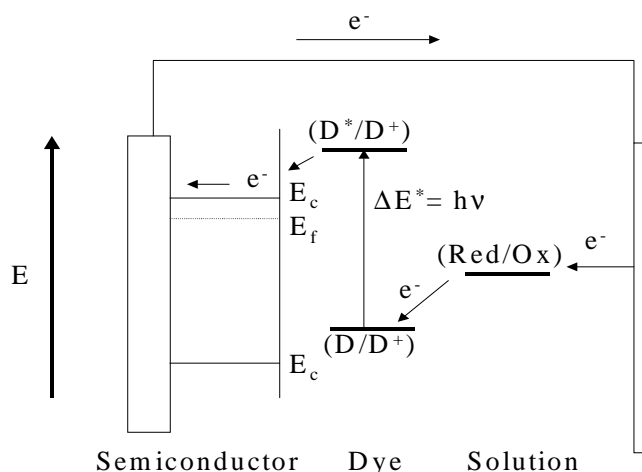
Figure 1. Energy diagram of photocurrent generation by excitation of a dye adsorbed on an n-type semiconductor electrode. E_v: valence band; E_f: fermi level; E_c: conduction band; D: dye; Red/Ox: sacrificial reductant.
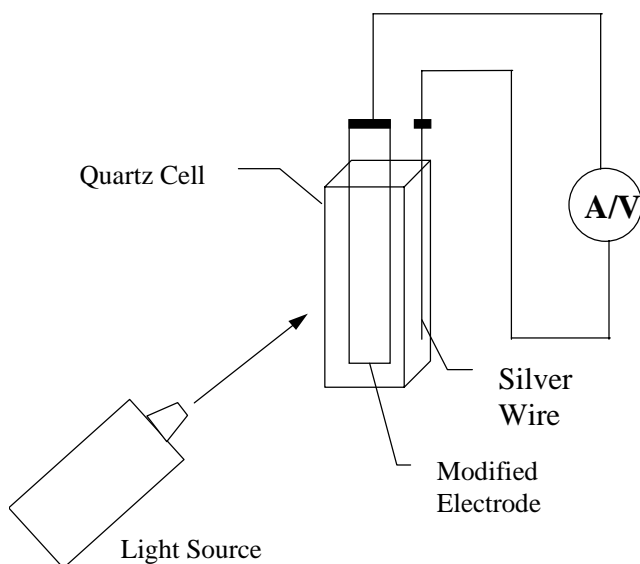

Figure 2. Experimental setup for the measurement of dye-sensitized charge injection.

molecular sieves. TLC Uniplate silica gel GHLF (250 microns, for thin-layer-chromatography plates) from Analtech, Florisil, and silica gel (230–400 mesh for column chromatography) from Aldrich were used. Optically transparent electrodes made of indium tin oxide (ITO) coated glass plates were obtained from Delta Technologies. An SnO_2 colloidal suspension (particle diameter 20–30 Å) from Alfa Chemicals was used without further purification. Monobasic sodium phosphate (Fisher) was used as received. Argon "Q" Air Liquid (>99.5%) was used.

   Procedure for the Synthesis of TPP. A solution of benzaldehyde (0.152 mL, 1.5 mmol) and pyrrole (0.10 mL, 1.5 mmol) in 100 mL of dichloromethane was purged with argon for 15 min. Then, trifluoroacetic acid (35 μL, 0.45 mmol) was added. The solution was stirred for 60 min at room temperature under an argon atmosphere. Next, DDQ (0.34 g, 1.5 mmol) was added and the mixture was stirred for an additional 60 min at room temperature and open to the atmosphere. TLC analysis (dichloromethane, $R_f = 0.84$) of the reaction mixture showed the TPP formation as a fluorescent red point when the plate was illuminated with UV-long light. The solution was concentrated to about 10 mL by rotary evaporation and 1 g of Florisil

was added. The slurry was further dried to a damp dark powder that was poured on the top of a flash chromatography column (silica gel). The column was first washed with dichloromethane/petroleum ether (2:1) to elute several small bands of fast moving pigments, followed by dichloromethane to produce 0.10 g (43%) of pure TPP as determined by TLC and UV–visible spectroscopy. UV (dichloromethane) λ_{max}, nm (ε) 417 (4.17×10^5), 515 (1.66×10^4), 552 (8.91×10^3), 594 (5.01×10^3) and 650 (3.98×10^3).

   Photoelectrochemical Measurement. A 1.5% SnO_2 suspension prepared by dilution of the commercial suspension with water containing a surfactant (0.01 % Triton X-100, Aldrich) was used for preparation of ITO/SnO_2 electrodes. The solution pH was adjusted to 10 by adding NH_4OH. An 0.1-ml aliquot of the diluted suspension was spread onto an 0.7cm × 5.0 cm clean ITO surface. Then the electrodes were dried over a warming plate. Finally, the SnO_2 films were annealed at 450 °C for 1 h. The resulting films, which are transparent in the visible region, have strong absorption in the UV with an onset at around 355 nm. (This onset absorption corresponds to a bulk band gap of 3.5 eV).

   TPP adsorption onto the semiconductor film was accomplished by soaking the annealed film for 2 h in a saturated petroleum ether solution of the dye, producing a strong coloration of the film. Absorbance values between 0.6 and 0.9 at the absorption maximum indicate the possibility of achieving very high incorporation of dye in the semiconductor thin film. A wire was connected to the ITO surface with indium solder. The absorption spectrum of the modified electrodes closely matches that of a dilute solution of the dye (Figure 2).

   Photoelectrochemical experiments were conducted in a 0.01 M aqueous solution of hydroquinone containing 0.05 M NaH_2PO_4 (pH = 5.2). This solution was thoroughly degassed by bubbling with nitrogen.

   The measurements were carried out in a 10-mm spectrophotometric quartz cell, with a silver wire as the auxiliary electrode. A battery-operated multimeter and a micro-amperimeter were used in the photoelectrochemical experiments for measuring the generated open-circuit photopotentials and short-circuit photocurrent. A handle-operated slide projector (150 W tungsten lamp, Kodak Ektagraphic III projector) was used as light source. All the photoelectrochemical measurements were done in front-face configuration (dye side illuminated) and the electrodes were located at the focus of the lamp output (illuminated area: 1 cm^2) as shown in Figure 2.
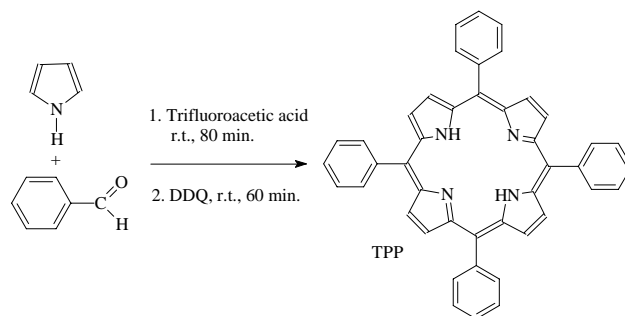

Results and Discussion

   Synthesis of TPP. A convenient procedure for the synthesis of TPP (reaction below) is to use an equimolar solution of benzaldehyde and pyrrole (ca. 10^{-2} M).The reaction is catalyzed by either trifluoroacetic acid or boron trifluoride etherate. The mixture is stirred at room temperature for 1 h under a nitrogen or argon atmosphere. The oxidation of porphyrinogen to porphyrin can be performed with either 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or p-chloranil. The

Table 1. Observed Photoeffects

Electrode	Photocurrent (μA)	Photopotential (mV)
ITO	---	---
ITO/SnO$_2$	0.5	42
ITO/SnO$_2$/Dye	6.0	96
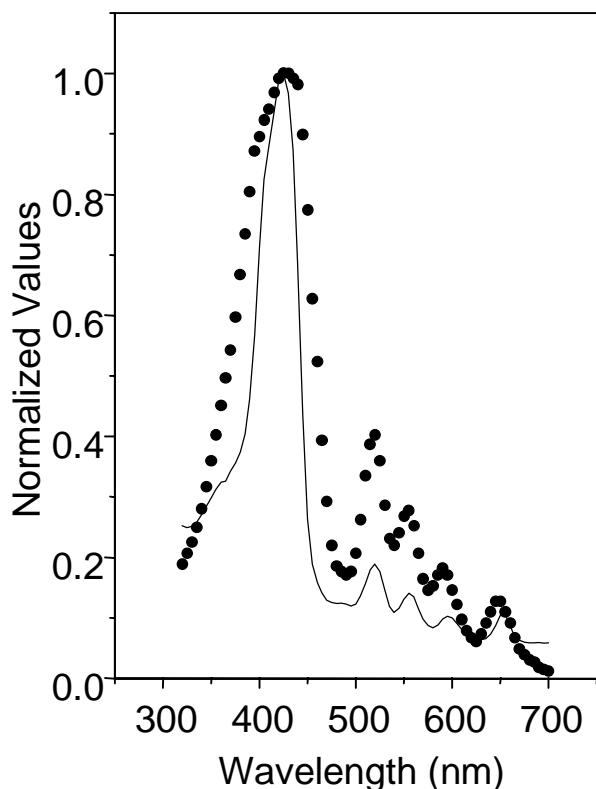
Figure 3. Normalized absorption spectrum (solid curve) and photocurrent action spectra of electrode ITO/SNO$_2$/Dye (●).

addition of DDQ at room temperature gives a nearly instantaneous oxidation while p-chloranil is a much milder oxidant and requires an exposure time of 1 h at reflux. The polypyrrylmethenes formed upon oxidation exhibit no properties characteristic of tars and are easily separated from the porphyrin. The product workup involves passage of the concentrated crude reaction mixture through a short chromatography column. The quinone and polypyrrylmethene components usually bind near the top of the column. The porphyrin obtained in this manner is typically of high purity. The Experimental section contains the details for the synthesis of one hundred milligrams of TPP.

Photoelectrochemical Measurements. The chopped illumination of the photoelectrodes produces significant anodic (oxidation) photocurrent and photovoltages. The values obtained for different experimental conditions are shown in Table 1.

The conversion of light flux into electricity shows that the presence of the porphyrine dye significantly enhances the observed photoeffects. As is shown in Figure 1, the photo-

oxided dye must be reduced by an electron donor in solution to maintain continuous operation of the cell; thus, hydroquinone is added to the solution to act as a sacrificial reductant.

As a complementary experiment, action spectra (photocurrent at different incident wavelengths) for dye-coated SnO$_2$ electrodes can be obtained by sending the output of the 150-W tungsten lamp through a monochromator (such as a PTI high intensity grating monochromator, Photon Technology Instruments) and recording the resulting steady-state photocurrent at each wavelength. The action spectrum of the dye-modified electrodes closely matches the absorption spectrum of the corresponding dye, Figure 3. The close correspondence between the photocurrent action spectrum and the absorption spectrum of the electrodes (This can be obtained in a normal UV-visible spectrophotometer using an ITO/SnO$_2$ electrode as a blank.) confirms that porphyrin excitation, as in the natural photosynthetic system, is the primary step in the energy-conversion process.

Conclusion

This experiment is easy and inexpensive to set up for use in advanced undergraduate courses. The two sections, synthesis of a porphyrin and its practical application to solar energy conversion, are complementary. They introduce two important natural science topics in an interesting and thought-provoking manner. This is an excellent practical laboratory for science students, who can complete the laboratory work within two four-hour laboratory periods without much difficulty.

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