

# Photogalvanic Cells for Classroom Investigations: A Contribution for Ongoing Curriculum Modernization

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Recently S. M. Condren et al. remarked in this *Journal* that materials for updating the curriculum and connecting chemistry with other disciplines are necessary (1). We propose that topics concerning photoprocesses be available for introductory chemistry courses. The core principle for teaching photochemistry is the paradigm of the electronic ground state and the excited state of chemical entities (2). This principle is valid for organic compounds and inorganic semiconductors used for the conversion of light into electrical energy and vice versa. Since sunlight is free, abundantly available, and environmentally clean, the exploitation of solar energy by photovoltaic devices is an attractive option. Nevertheless such devices represent black boxes for many students.

The experiments described in this article, the “2-pot-cell” (Figure 1) and the “1-pot-cell” (Figure 2), are suitable for classroom investigations. They are the basis of a curricular concept that bridges the gap between galvanic cells and compact solar cells made of semiconductors (3). By use of these cells, the students gain an understanding of the process of light conversion into electric energy and work on optimizing the experimental setup. The focus is on the key steps of a photovoltaic device: (i) the light-induced charge separation by photoexcitation of electrons from the valence band to the conduction band, leading to the formation of electron–hole pairs,  $e^-/h^+$ , in the semiconductor bulk and (ii) the diffusion of photoexcited electrons,  $e^-$ , and holes,  $h^+$ , in opposite directions to generate a photo-induced current. These same processes play an important role in galvanic and photoelectrochemical cells<sup>1</sup> and have repeatedly been discussed in this *Journal* (4, 5).

In the cells described here, the photoactive part of the working electrode consists of a thin layer of the n-type semiconductor  $\text{TiO}_2$  coated on electrically conducting ITO-glass (tin dioxide coated transparent glass) or  $\text{SnO}_2\text{:F}$ -glass. As a counter electrode, platinum or a razor foil is employed (see Supplemental Material<sup>W</sup>).

Although the band-gap energy of  $\text{TiO}_2$  is large (3.2 eV), it is possible to generate sufficient electron–hole pairs at the photoelectrode by using commercially available mercury vapor light bulbs. It is essential to inhibit the recombination of photogenerated electron–hole pairs, otherwise the light energy would simply dissipate to heat. It is therefore necessary to promote a spatial separation of the electric charges. This separation can be achieved if an electron donating species in the vicinity of the photoelectrode quickly compensates the electron deficit that has been generated in the valence band by photoexcitation. The electron that has been promoted into the conduction band is then forced to move through the nanocrystalline  $\text{TiO}_2$  and ITO layers into the external circuit. In the 2-pot-cell bromide ions,  $\text{Br}^-$ , serve as sacrificial donors and the fundamental processes depicted in Figure 3 can be formulated by eqs 1–3, where  $(\text{TiO}_2)^+$  represents a  $\text{TiO}_2$ -unit with a hole,  $h^+$ .

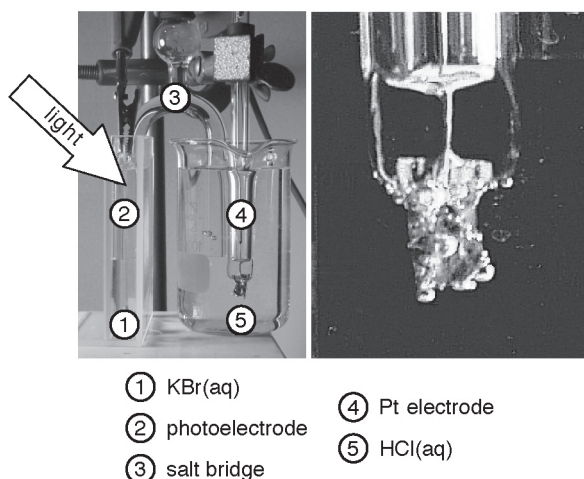
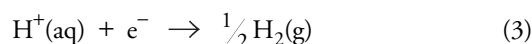
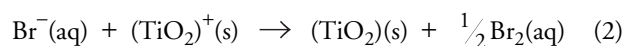


Figure 1. The photogalvanic 2-pot-cell consists of two containers (half-cells); after some time  $\text{H}_2$  bubbles can be seen on the Pt electrode in the right half-cell.

- ① photoelectrode
- ② EDTA(aq)
- ③ used razor foil from an electric razor as low-cost Pt electrode

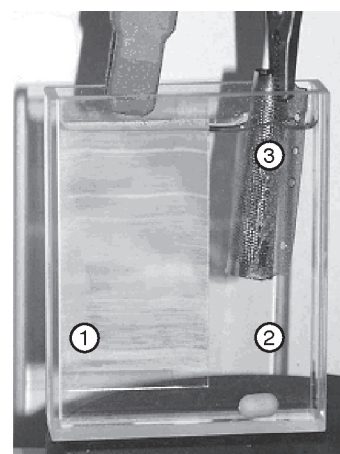


Figure 2. The photogalvanic 1-pot-cell consists of one container. The electrolyte, an aqueous EDTA solution, provides the sacrificial donor as well as  $\text{H}^+$  ions.

The 1-pot-cell represents a low-cost experiment and is a further step towards compact solar cells in the curricular concept mentioned above. The 1-pot-cell demonstrates possibilities of improving a photogalvanic cell by the use of a more effective sacrificial donor, a larger counter electrode surface, and shorter distances for charge carriers in the electrolyte between the electrodes.

The efficiency of the 1-pot-cell exceeds that of the 2-pot-version. Nevertheless the consumption of the sacrificial donor remains a crucial disadvantage. Therefore a further improvement would be achieved if a constantly self-regenerating electron donor could be employed. This is realized in the photoelectrochemical cell demonstrated by G. P. Smestad and M. Grätzel (6), where the redox mediator,  $2\text{I}^-/\text{I}_2$ , is used. At the photoelectrode, iodide ions are oxidized and, at the same time, iodine is regenerated at the ITO-counter electrode by the reduction of iodine. A less expensive alternative to the counter electrode in this device is the use of ordinary glass coated with a layer of graphite spray (3).

## Chemicals and Equipment

Nanocrystalline  $\text{TiO}_2$  (anatase)

Solutions of KBr, HCl (1 M each)

EDTA (0.2 M, pH = 7)

Conductive glass ( $\text{SnO}_2\text{:F}$ -glass available from Hartford Glass Co., Inc., P.O. Box 613, Hartford City, IN 47348 or ITO-glass available from PGO GmbH, Hegestück 11, 58640 Iserlohn, Germany)

Sintering device

Osram-Ultravitalux light bulb (300 W)

Pt electrode

Used razor foil of an electric razor

Glass containers

Voltmeter

Electric motor (FTB Feintechnik Bertsch GmbH & Co. KG, Daimlerstraße 23, 71101 Schönaich, Germany; phone +49(0)7031/638-0, Fax +49(0)7031/638-100;78054; motor number: 07720-8507-0)

Cables

## Hazards

As the concentration of the bromine produced is very low, there are no significant hazards. Make sure the students do not use a razor blade, but a razor foil (the perforated foil that contacts the skin when shaving with an electric razor; see Supplemental Material<sup>W</sup>).

## Experimental Results

With the photogalvanic 2-pot-cell, photo-induced voltages of ~600 mV and photo-induced currents up to 0.06 mA can be achieved under constant illumination. Intermittent illumination shows the photosensitivity of the photoelectrode, as the photo-induced voltage and photo-induced current rapidly decrease. Variations of the setup reveal that the photo-induced voltage increases with smaller distance between the

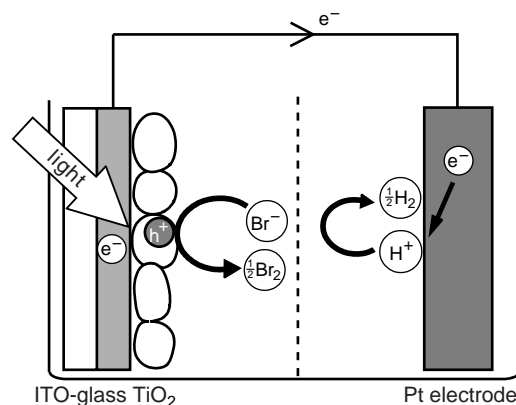


Figure 3. The formation of electron-hole pairs in the photogalvanic 2-pot-cell: compensation of the electron deficit in the semiconductor by oxidation of bromide ions, flow of photoelectrons through the outer circuit, and reduction of hydrogen ions at the counter electrode.

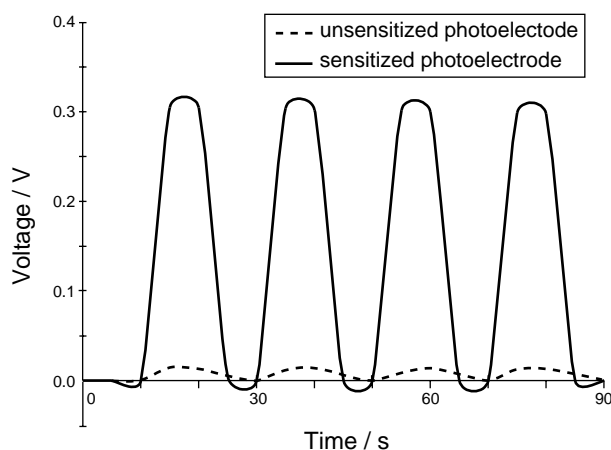


Figure 4. The effect of the sensitization of the photoelectrode (illumination with red light; the photoelectrode was sensitized with raspberry juice).

light source and the photoelectrode and depends on the intensity and the spectrum of the light used for illumination. The bromine and hydrogen products can be easily identified.

Experiments with the more compact photogalvanic 1-pot-cell with a razor foil as low-cost Pt electrode and an EDTA electrolyte are carried out analogously to those with the 2-pot-cell. The 1-pot-cell yields higher photo-induced voltages (0.9–1.1 V) and photo-induced currents (~2 mA) that suffice to start a small motor and power it for some time (for details see Supplemental Material<sup>W</sup>).

A sensitization of the photoelectrode for red light is achieved by applying anthocyanin dyes of different berries or petals onto the  $\text{TiO}_2$  layer (Figure 4). The measured voltages of the photogalvanic 2-pot-cell with a  $\text{TiO}_2$ -photoelec-

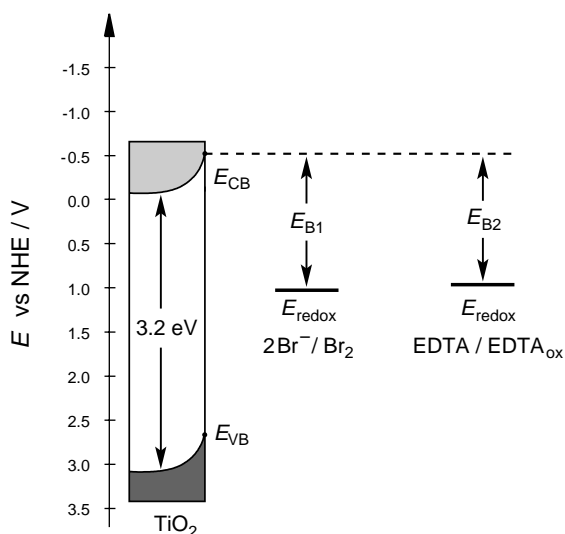


Figure 5. Energy diagram of the  $\text{TiO}_2$ /ITO-photoelectrode in the two devices from Figure 1 and Figure 2.

trode and a sensitized photoelectrode are represented in Figure 4. Intermittent irradiation shows the photosensitivity of the photoelectrodes. Similar results can be achieved with the photogalvanic 1-pot-cell.

## Discussion and Teaching Applications

After working with the photogalvanic 2-pot-cell, the students find out that there are several similarities between this type of electrochemical devices and the well-known galvanic cells, for example, the Daniell cell. This leads to eqs 1–3 and the scheme shown in Figure 3 (see Teaching Units and Worksheets in Supplemental Material<sup>W</sup>). The analogy to photosynthesis may be included in this discussion.

The electrical power from a photogalvanic device is given by the output photo-induced voltage times photo-induced current,  $E_V \times i$ , and the efficiency,  $\eta$ , is defined as the ratio between the electrical power and the input optical power (4). The 2-pot-cell has small values of  $\eta$ , less than 0.01 (correspondingly less than 1%). But it has great advantages for instruction because of its simple setup and the unambiguity of the observed phenomena that allow students to draw conclusions about the operating principle of the cell.

The maximum photo-induced voltage value,  $E_{\text{max}}$ , of a photoelectrochemical cell is limited by the barrier height,  $E_B$ , (Figure 5). In our experiments this is the difference between  $E_{\text{redox}}$ , the electrochemical potential of the redox-active material in the solution, and the energy of the conduction band edge  $E_{\text{CB}}$  (strictly speaking the quasi Fermi level; refs 4, 7). On discussing the results obtained with the 2-pot-cell, students can conclude that the photo-induced current  $i$  may be influenced by (i) the kinetics of the charge transfer from the dissolved sacrificial donor to the  $\text{TiO}_2$  particles, (ii) the sur-

face of the Pt electrode, and (iii) the geometry of the cell. To improve these three parameters, the described 1-pot-cell is realized. Theoretically this cell should not yield higher voltages than the 2-pot-cell (see  $E_{\text{redox}}$  in Figure 4), but in practice higher voltages are produced: enough electric power to run a small motor.

The next step towards the photovoltaic cell is the setting up and experimenting with the photoelectrochemical cell as mentioned in the beginning of the article and published in references 3 and 6.

## Conclusion

The experiments described above, the photogalvanic 2-pot cell and 1-pot-cell, are suitable classroom experiments that lead to an understanding of the key steps taking place in photovoltaic devices. The variation of parameters such as the geometry and materials of the cells shows how the efficiency can be improved.

## Supplemental Material

A detailed description of the experimental steps and of additional experiments, along with notes for the instructor (including questions and answers and lesson outlines) and handouts for the student are available in this issue of *JCE Online*. One can find multimedia modules and animated graphics at <http://www.theochem.uni-duisburg.de/DC/research/claudia1.htm> (accessed Aug 2003).

## Note

1. Whereas in textbooks of general chemistry the terms photogalvanic, photoelectrochemical, and photovoltaic are used synonymously for educational reasons we differentiate between these terms as follows: Photogalvanic cells are very similar (e.g., setup and electrolyte) to galvanic cells like the Daniell cell, photoelectrochemical cells are more compact cells of the Grätzel-type (3, 6, 7) using a very small quantity of a self regenerating redox mediator as the electrolyte, and photovoltaic cells are made of solid-state semiconductors such as n- and p-doped silicon.

## Literature Cited

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