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Efficient Solar to Chemical Conversion: 12% Efficient Photoassisted Electrolysis in the [*p*-type InP(Ru)]/HCl-KCl/Pt(Rh) Cell

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(Received 19 January 1981)

The photoelectrochemical cell [*p*-type InP(Ru)]/HCl-KCl/Pt(Rh) converts 12% of the incident solar energy into two useful chemicals, hydrogen and chlorine, by photoassisted electrolysis of aqueous hydrochloric acid. At the threshold for electrolysis, the voltage required is reduced from 1.3 to 0.65 V. Hydrogen evolution takes place at microscopic islands of catalysts such as Rh, Ru, and Pt. The high efficiency of the cell derives from a thin surface oxide on InP, preventing carrier recombination, and from efficient transport of electrons to the catalyst.

PACS numbers: 73.40.Mr, 72.40.+w

In 1972, Fujishima and Honda reported that with an illuminated *n*-type TiO₂ anode, the voltage required to electrolyze water is reduced to well below the thermodynamic decomposition potential of 1.23 V.¹ Their work was based on the general principles formulated for illuminated semiconductor-liquid interfaces by Brattain and Garrett² and developed by Dewald,^{3,4} Gerischer,⁵ Lazorenko-Manevich,⁶ and Boddy,⁷ who, in 1968, observed photocurrents due to oxygen evolution on *n*-type TiO₂ anodes under bias.⁸ In 1969, Beckman and Memming reported hydrogen evolution on illuminated, externally biased *p*-type GaP cathodes.⁹ The report on photoassisted electrolysis of water¹ triggered research in numerous laboratories. Reviews by Nozik,¹⁰ Harris and Wilson,¹¹ Tomkiewicz and Fay,¹² and Gerischer¹³ summarize the findings. Most of the work was on *n*-type semiconductor photoanodes in which the key problems were the poor stability to oxidation of materials with appropriate (1.0–1.7 eV) band gaps for solar conversion, and the excessive band gap of materials with good stability to oxidation and high quantum efficiency. For example, the most extensively studied materials, TiO₂ and SrTiO₃,^{14–16} offer quantum efficiencies near unity and withstand oxidation, but their band gaps are over 3 eV. For this reason, the conversion efficiency of sunlight with TiO₂ is 0.6%.¹⁷ The efficiency of SrTiO₃ has been estimated at ~1%. Sev-

eral transition-metal oxides, such as α -Fe₂O₃, which are also stable to oxidation, have been investigated.^{18,19} These materials are inefficient because of poor quantum efficiency at the longer wavelengths, where the absorption lengths associated with the weak optical transition exceed the carrier diffusion lengths.¹⁹

Hydrogen-generating photocathodes which have been studied include *p*-type GaP,^{20–24} LuRhO₃,²⁵ and Si.²⁶ *p*-type GaP is stable to reduction, but its band gap, 2.25 eV, is substantially above optimum. The photocurrent densities and the voltage gains reported suggest only moderate conversion efficiencies.^{20–24} LuRhO₃ is a superior electrocatalyst for hydrogen evolution, but the photocurrent densities are limited, as in α -Fe₂O₃, by poor quantum efficiency.²⁵ Recently, Kautek, Gobrecht, and Gerischer²⁷ reported that by using *p*-type WSe₂ and by creating on this material microscopic platinum islands which catalyze hydrogen evolution, they could gain up to 0.5 V of the 1.23-V potential required to electrolyze water at current densities approaching zero, and about 0.2 V at current densities of 10 mA/cm².²⁷ While *p*-type WSe₂ is stable and has a desirable 1.16-eV band gap for solar conversion, there are substantial current losses for two reasons. The band gap is indirect^{27,28} and the minority-carrier diffusion lengths are inadequate.²⁷ Furthermore, surface recombination velocities are excessive

for all but the van der Waals planes of this layered compound^{29,30} and these act as mirrors, reflecting part of the sunlight.

We recently reported the first efficient photocathode-based semiconductor-liquid-junction solar cell, [*p*-type InP]/VCl₃-VCl₃-VCl₂-HCl/C,³¹ and achievement of an 11.5% solar-to-electrical conversion efficiency.³² *p*-type InP was chosen as our photocathode for two reasons. Its band gap, 1.35 eV, is optimal. More importantly, however, we could predict that a monolayer of chemisorbed oxygen (i.e., surface oxide) will reduce surface recombination losses in fill factor, photovoltage, and photocurrent. This prediction was based on our model for the control of surface and grain boundary recombination by strong chemisorption and the work of Spicer *et al.*,³³ who observed a drastic shift in the surface Fermi level of *p*-type InP toward the conduction-band minimum upon the chemisorption of a submonolayer of oxygen. Both the nature of the surface of the semiconductor and the nature of the catalyst are critical for the efficient reduction of protons. The Fermi level of the catalyst and the Fermi level of the surface of the semiconductor are equal. If the InP surface Fermi level is pinned in the proximity of the valence-band maximum the process is necessarily inefficient. Thus, the displacement of the surface Fermi level towards the conduction-band minimum³³ is important for efficient photoassisted electrolysis.

In the photoelectrolytic process, photogenerated

electrons combine with protons adsorbed on the noble-metal catalyst to form catalyst-bound hydrogen atoms. These recombine to form hydrogen molecules, which desorb.

For our solar-assisted electrolysis experiment, we used cells with 0.1–0.2-cm² (111)A, (111)B, and (100) faces of *p*-type InP as photocathodes.^{31,32} On these, we formed islands of ruthenium, rhodium, or platinum, which are known hydrogen-evolution catalysts. Rhodium shows the best results in photoelectrolysis with SrTiO₃.³⁴ Less than one hundred angstroms of the metal were electrodeposited, and the electrodes were etched in dilute aqua regia (1:2:2 = H₂O:HCl:HNO₃) until several thousand angstroms of the semiconductor were removed. Such etching is highly anisotropic. While the semiconductor is rapidly removed, catalyst protected areas stay and are stripped only by undercutting. Oxidation by the dilute aqua regia or by air followed by extended immersion in 1M HCl yields the desired thin oxide layer. The electrolyte used was 1M HCl–2M KCl. Platinum, electroplated with rhodium, served as an anode. A saturated calomel electrode (SCE) was used as reference electrode.

Typical performance of these cells is shown in Figs. 1 and 2. The Pt cathode starts, as expected, to generate H₂ at –0.24 V vs SCE and reaches a current density of 20 mA/cm² at –0.31 V. The *p*-type InP photocathode starts to produce hydro-

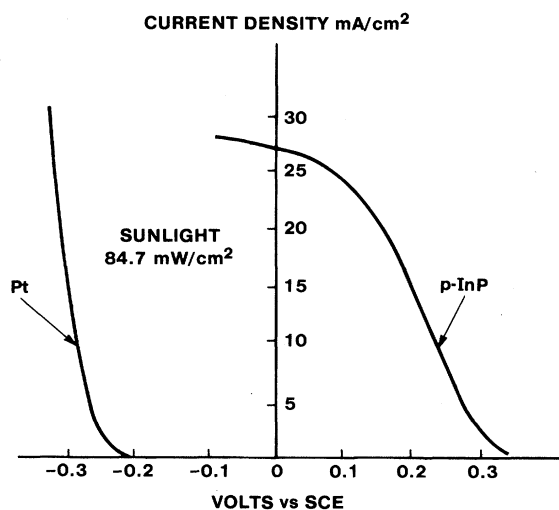


FIG. 1. Current voltage characteristics of hydrogen-evolving Pt and *p*-type InP cathodes under 84.7 mW/cm² sunlight.

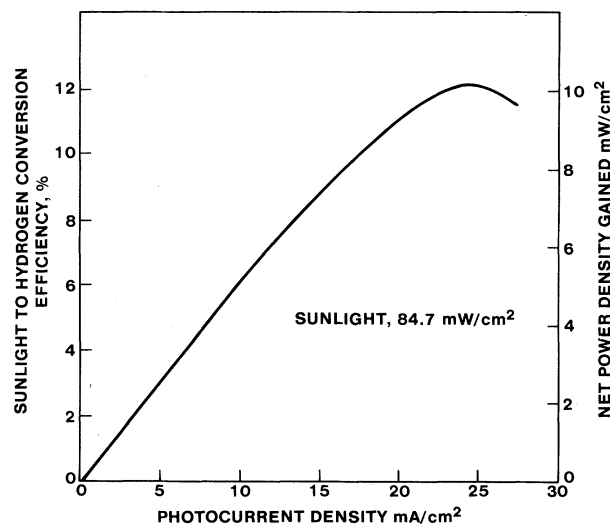


FIG. 2. Solar-to-hydrogen conversion efficiency and power density gain at 84.7 mW/cm² sunlight as a function of photocurrent density. The gain is the product of the voltage difference between the Pt and *p*-type InP cathodes and the current density.

gen at +0.34 V vs SCE. Under 84.7 mW/cm² sunlight it operates at a current density of 20 mA/cm² and +0.15 V vs SCE. The anode voltages for Pt were 0.98 at the threshold and 1.12 V at 20 mA/cm². In the absence of islands of a hydrogen-evolution catalyst such as Ru, Rh, or Pt, the photocurrent density is reduced by well over four orders of magnitude at the SCE potential.

The maximum solar-to-chemical conversion (the equivalent of the maximum power point in a solar cell) is at 23.5 mA/cm² and at +0.11 V vs SCE or 0.4 V versus an H₂-generating Pt electrode operating at similar current density. This translates to a gained power density of 10.1 mW/cm² or to a net hydrogen-production efficiency of 12% referred to sunlight (Fig. 2). Another interpretation is that the solar-assisted cell has an efficiency of 90% referred to the electricity supplied while the Pt-cathode cell has an efficiency of 130% on the same basis at 23.5 mA/cm². Comparison of the observed and calculated³⁵ photocurrents for 1.35-eV band gap *p*-type InP shows that the quantum efficiency is 82%. The maximum voltage saved, at low current densities, is 0.65 V or about 45% of the thermodynamic decomposition potential for hydrochloric acid.

Weight-loss measurements over a period of one week show that in the absence of oxygen and chlorine *p*-type InP is not attacked by 1M HCl either in the dark or when illuminated. *p*-type InP is rapidly etched, however, by air saturated with acid. The failure modes of the cell are not related to the stability of *p*-type InP and are not fundamentally life limiting: Upon passage of 10⁴ C/cm² and repeated cycling between +0.4 and -0.4 V vs SCE, we observed failure only by separation of the back contact and by leakage through pinholes at the epoxy-semiconductor interface.

The basic concept behind the *p*-type InP photocathode is the chemical reduction of recombination losses at the (*p*-type InP)-electrolyte interface by a monolayer of an oxide.^{33,36} If this oxide is reduced, the photogenerated holes and electrons do recombine and a loss in photocurrent at the optimum power point results. The rate at which the layer is reduced depends on the potential at which the cathode is maintained. Upon continuous hydrogen generation for 10–20 min. a decline in performance is noticed. The original current levels are, however, instantaneously restored when the electrode is either exposed to air or disconnected, i.e., brought to its open circuit voltage, which is positive relative to the hydrogen-evolution potential. Restoration is attrib-

uted to reformation of the thin oxide.³⁵

The cell described is the most efficient system for photoassisted electrolysis that uses a semiconductor-liquid junction. While InP is too expensive to be economically viable, we have little doubt that similar yet inexpensive materials will be found.

The authors thank B. Miller and K. J. Bachmann for discussions and C. J. Doherty, F. A. Thiel, and Ilana Heller for their assistance.

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One-Dimensional Wide Energy Bands in a Polydiacetylene Revealed by Electoreflectance

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(Received 8 December 1980)

Above a region of excitonic transitions the polydiacetylene DCHD [poly1,6-di(N-carbazolyl)-2,4-hexadiyne] shows at the photoconduction edge a large electoreflectance response for fields parallel to the polymer. The signal broadens with field strength indicating a high-field limit for electoreflectance. Evaluation yields $E_g = 2.335$ eV, $m^* = 0.05m_0$, and $\mu = 2800$ cm²/V sec. The influence of a field perpendicular to the polymer chain is 3 orders of magnitude smaller. This unique anisotropy indicates that delocalization of the electrons occurs only along the polymer.

PACS numbers: 78.20.Jq, 61.40.Km, 72.80.Le

Electoreflectance has provided a sensitive tool to study the band structure of inorganic semiconductors. Transitions at singularities of the joint density of states respond particularly sensitively to an external field and are therefore lifted from the broad background reflectance. This sensitivity, however, decreases with decreasing dispersion of the energy bands, which apparently has prevented the application of this technique to organic solids, where the energy bands are usually narrow. Wider bands can be expected when π orbitals overlap in certain crystal directions, as in the polydiacetylenes where single crystals of good quality are available by solid-state polymerization.¹

This paper presents transverse electoreflectance spectra of the polydiacetylene DCHD [poly 1,6-di(N-carbazolyl)-2,4-hexadiyne], the structure of which is shown in the inset in Fig. 1. Alternating triple-, double-, and single-carbon bonds form the repeat unit of the polymer chains, which are oriented parallel to the b axis of the monoclinic crystals.¹ The unit cell along b is very short, only 4.91 Å. Therefore, it appears possible that translationally equivalent π bonds

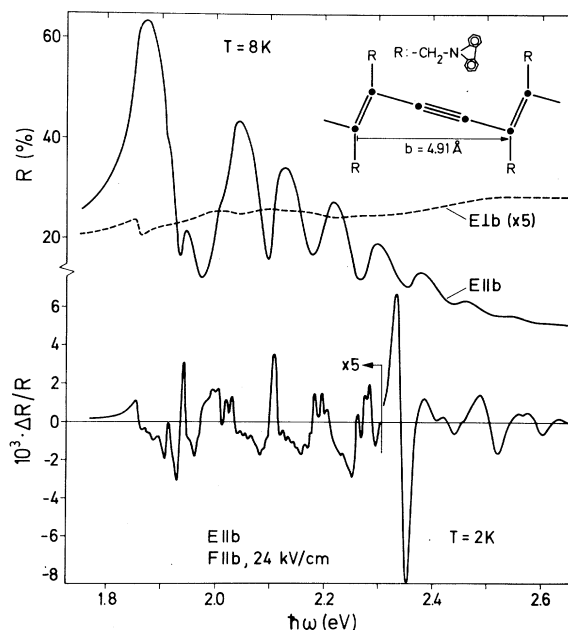


FIG. 1. Comparison of reflectance and electoreflectance spectra of DCHD for polarization of light parallel and perpendicular to the polymer chain. The inset shows the short repeat unit of the polymer.