

fluorescence intensities by pyranine. These data lend credence, therefore, to the assessment of average intermolecular distances from the rate constants for energy transfer.

The enhanced energy transfer reported in the present work is entirely due to a Förster-type mechanism. The lack of observable quenching of vesicle-entrapped donor fluorescence by added iodide or bromide ions (see above) obviates the possibility of energy transfer by the encountering of donor and acceptor molecules at the vesicle surface. The acceptable correlation between the observed and calculated fluorescence quenching as well as the insignificant energy transfer in methanol is also in accord with the proposed Förster-type mechanism. Orientation of dipoles at appropriate distances and compartmentalization of donor and acceptor molecules are responsible for the enhanced energy transfer.

Taken together, the present work justifies the use of completely synthetic surfactant vesicles as membrane models. They possess all the desirable functions of the more complex liposomes, without their chemical instability. Most importantly, they can be readily manipulated and functionalized. These properties will find increasing use in photochemical solar energy conversions.

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Semiconductor Electrodes. 27. The p- and n-GaAs-*N,N'*-Dimethyl-4,4'-bipyridinium System. Enhancement of Hydrogen Evolution on p-GaAs and Stabilization of n-GaAs Electrodes

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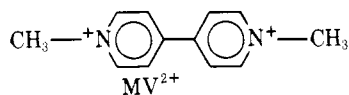
Abstract: The photoelectrochemical (PEC) behavior of *N,N'*-dimethyl-4,4'-bipyridinium (methylviologen, MV^{2+}) at p- and n-type GaAs electrodes in aqueous solutions was studied. The reduction of MV^{2+} at irradiated p-GaAs occurs at potentials ~ 450 mV less negative than those found at a Pt electrode. The catalyzed reaction of the photogenerated $MV^{\cdot+}$ with water to produce hydrogen by irradiation of p-GaAs was demonstrated and the use of the MV system as an intermediate in the photo-assisted generation of hydrogen at semiconductors with high hydrogen overpotentials suggested. The photooxidation of MV^{2+} at n-GaAs occurred at potentials ~ 0.8 V less positive to those where the oxidation takes place at Pt. PEC cells of the form n-GaAs or p-GaAs/ MV^{2+} , $MV^{\cdot+}$ /M were also constructed.

Introduction

Attempts to promote the photodecomposition of water at semiconductor electrodes are based on the reduction of protons to hydrogen at p-type and the oxidation of water to oxygen at n-type materials. In the design of such systems difficulties arise from instability of the semiconductor electrodes themselves under irradiation and low rates of hydrogen or oxygen evolution at the semiconductor surfaces. The large band gap n-type semiconductors which are stable and provide the needed overpotential for oxygen evolution, e.g., TiO_2 ¹ or $SrTiO_3$,² do not utilize solar energy very efficiently. The use of p-type materials

in such cells has been less studied. Generally the efficiencies of p-type materials are low and they are apparently poor photocathodes for hydrogen evolution.³

We recently discussed the behavior of p-GaAs in aqueous solutions containing a number of redox couples and showed that stable operation of photoelectrochemical (PEC) cells for the conversion of radiant to electrical energy was possible.⁴ A number of studies have described the production of hydrogen by reaction of the radical cation of *N,N'*-dimethyl-4,4'-bipyridinium (also known as methylviologen, MV^{2+}) with protons in the presence of a suitable catalyst (e.g., PtO_2).⁵ In such



systems the radical cation, $MV^{\cdot+}$, is generated by reaction with a suitable reductant in the presence of light. Since this reductant (e.g., triethanolamine^{5a}) is irreversibly decomposed, such processes may not involve net storage of radiant energy (i.e., they may be photocatalytic rather than photosynthetic⁶). However, they do demonstrate the applicability of the $MV^{\cdot+}$ -catalyst system for hydrogen generation. The photo-reduction of MV^{2+} at *p*-GaAs would provide the $MV^{\cdot+}$ without the need of a consumable reductant and thus provide a path to hydrogen evolution at the semiconductor. The process is illustrated in Figure 1. A similar strategy utilizing *p*-Si has recently also been suggested by Wrighton and co-workers.⁷ We report here the photogeneration of hydrogen at *p*-GaAs with such a system.

A second aspect of the research discussed here pertains to stabilization of *n*-GaAs and PEC cells based on this material. Stabilization of *n*-GaAs with respect to photoanodic decomposition has been accomplished either by the addition of a suitable redox couple (e.g., Se^{2-}/Se_2^{2-} , Te^{2-}/Te_2^{2-}) to aqueous solutions⁸ or by the use of aprotic media, such as acetonitrile, as the solution phase. This stabilization is based on the relative energetics and kinetics of the semiconductor decomposition reaction with respect to the capture of photo-generated holes by the reduced form of the solution couple.⁹ We demonstrate in this paper that the $MV^{2+}/MV^{\cdot+}$ couple can play the role of such a stabilizing redox system for *n*-GaAs in aqueous solutions and that regenerative (photovoltaic) PEC cells showing stable performance can be devised.

Experimental Section

The single-crystal *p*-GaAs, obtained from Atomerger Chemicals, had an acceptor concentration of $3 \times 10^{18} \text{ cm}^{-3}$. The ohmic contact was made by electroplating Au on the polished rear side of the single crystal. The crystal was then mounted as previously described.⁴ The single-crystal *n*-GaAs (Atomerger Chemicals) had a donor concentration of about $2 \times 10^{18} \text{ cm}^{-3}$. The ohmic contact was made by electroplating In and Au successively and then heating at 400 °C under H_2 for 2 h. The crystal was then mounted as described for *p*-GaAs.⁴ Both GaAs electrodes were etched for 10–15 s prior to the experiments in concentrated H_2SO_4 –30% H_2O_2 – H_2O (3:1:1) followed by 6 M HCl for 10–15 s. The $MVCl_2$ used was from K & K Rare and Fine Chemicals and solutions were prepared with triply distilled water.

The potentiostatic electrochemical measurements were done with a PAR Model 173 potentiostat using a saturated calomel electrode (SCE) reference electrode and a platinum coil or gold foil as a counterelectrode. Nitrogen was passed through the solution before the experiments and above the solutions during the experiments. The voltages and currents of two-electrode photocells were measured with a Keithley Model 179 TRMS digital multimeter. In the experiments where hydrogen gas was collected, the counterelectrode chamber was separated from the *p*-GaAs chamber by a medium porosity sintered-glass disk to prevent oxidation of the $MV^{\cdot+}$ at the counterelectrode. In the two-electrode regenerative photocells, either a gold foil (area $\sim 40 \text{ cm}^2$) or a mercury pool (area $\sim 10 \text{ cm}^2$) was used as a counterelectrode. These electrodes were also used to generate $MV^{\cdot+}$ coulometrically before the regenerative photocell measurements.

A 450-W Xe lamp or a 1.6-mW He–Ne laser was used as the light source for the electrochemical measurements. Neutral density filters were used to vary the intensity of the light. A 1.6-kW Xe lamp was used for the hydrogen collection experiment. The light was water filtered to eliminate heating because of the near-IR light, and further filtered by 420-nm cutoff filter to eliminate any UV irradiation of the solution.

In the experiments where hydrogen gas was collected, the electrochemical cell was a conventional three-electrode cell (with the counterelectrode separated from the main compartment) which was carefully sealed with high vacuum grease (Apiezon N) and connected to a graduated buret containing Hg. The system was checked for leaks

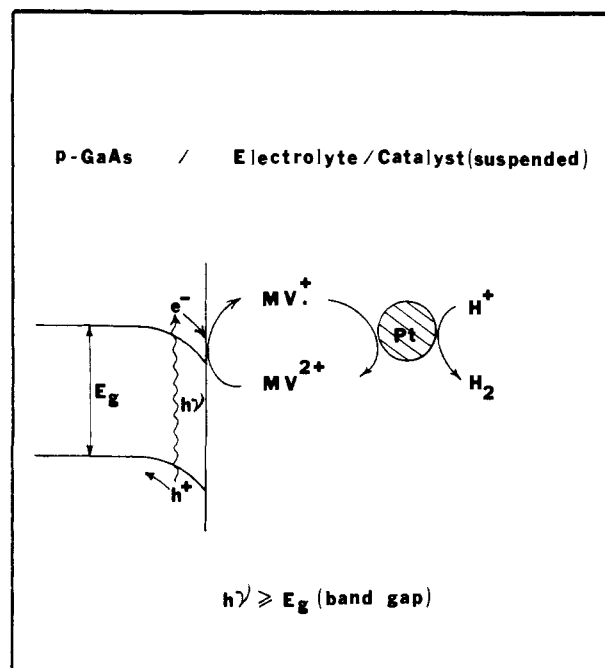
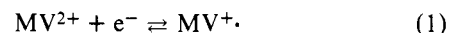


Figure 1. Representation of hydrogen generation scheme.

prior to the experiments, by pressurizing with hydrogen from an external tank and checking for any decrease of pressure. N_2 was then bubbled through the solution while the cell was open to the atmosphere. The cell was then closed and the height of the mercury in the buret marked. Hydrogen generation could be observed by the decrease of the mercury level in the buret. After these experiments, the gas was collected into an evacuated tube which was connected to the system, and was analyzed by gas chromatography (Aerograph-Varian Autoprep Model A-700, 13X Linde molecular sieve 40–60 mesh column with thermal conductivity detector).

Results and Discussion

Electrochemical Behavior of *p*-GaAs/ MV^{2+} . The cyclic voltammetric behavior of MV^{2+} at *p*-GaAs and Pt electrodes is shown in Figure 2. Consider first the behavior of a Pt electrode in a solution of 1 M KCl at pH 2.5 with and without 0.074 M MV^{2+} (as chloride salt) (curves d, e, f). In the absence of MV^{2+} a small wave, presumably hydrogen evolution, occurs at $\sim -0.35 \text{ V}$ vs. SCE, with the background current hydrogen evolution occurring at -1.0 V . In the presence of MV^{2+} , the reversible reduction of MV^{2+} to $MV^{\cdot+}$ occurs with $E_{pc} = -0.66 \text{ V}$ vs. SCE (curve d), with the peak for the irreversible reduction to MV at -1.03 V (curve e) found on scanning to more negative potentials. The unusual behavior on reversal following the $MV^{\cdot+}$ reduction is probably caused by a surface effect and has been observed previously.¹⁰ The cyclic voltammogram at an irradiated *p*-GaAs electrode in the absence of MV^{2+} (curve a) shows only a very small cathodic current, probably connected with a very low rate of hydrogen evolution. Upon addition of MV^{2+} to the solution, a large increase in the photocurrent in the cathodic region is observed (curve b). This photocurrent can clearly be attributed to the reduction of MV^{2+} to the purple $MV^{\cdot+}$, as can be observed by the blue-purple color streaming from the electrode surface, according to the reaction



The anodic current due to the oxidation of the $MV^{\cdot+}$ back to the original MV^{2+} occurs on scan reversal both in the dark and in the light, but in the light the oxidation occurs at somewhat less positive potentials. In the dark only a very small current connected with the reduction of MV^{2+} is observed at *p*-GaAs (curve c). As is clear from a comparison of curves b and d, the

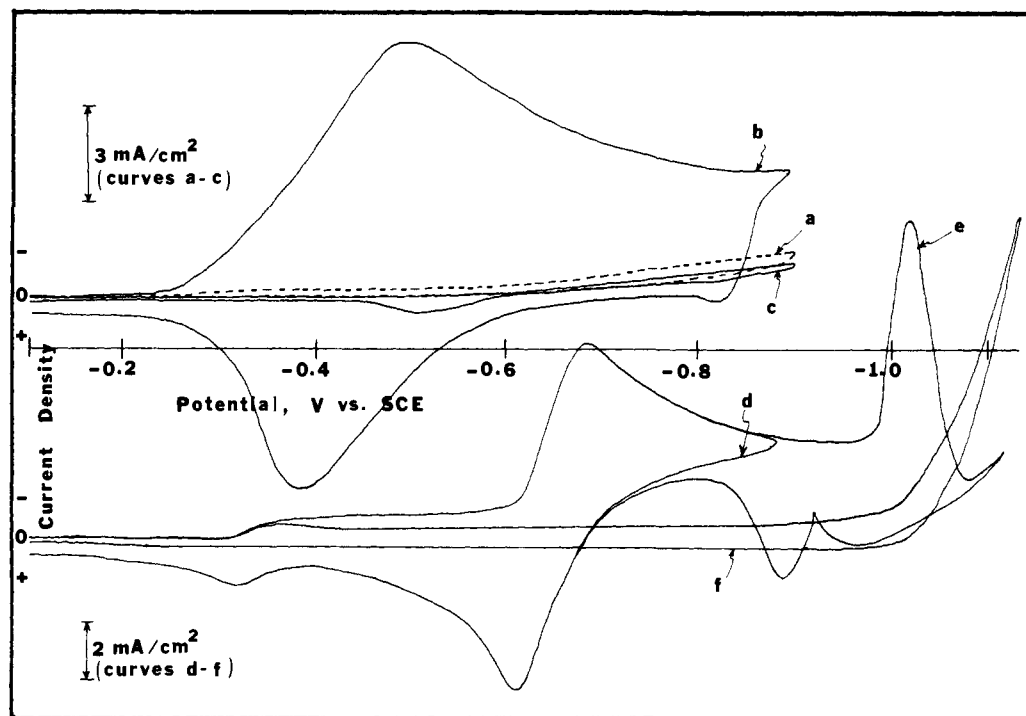
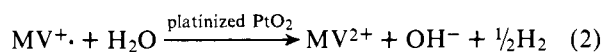


Figure 2. Cyclic voltammograms at Pt and p-GaAs at 0.1 V/s in solutions of 1 M KCl, pH 2.5: (a) p-GaAs, irradiated; (b) p-GaAs, irradiated, with 0.074 M MV²⁺; (c) as (b) in the dark; (d) and (e) Pt with 0.074 M MV²⁺; (f) Pt with 1 M KCl (pH 2.5).

reduction of MV²⁺ occurs at p-GaAs at potentials significantly positive of the reversible MV²⁺/MV⁺ potential at Pt. The photoreduction at p-GaAs starts at about -0.2 V vs. SCE (and peaks at ~-0.5 V) so that an "underpotential" of about 0.45 V is achieved. Moreover, the direct photoreduction of MV²⁺ on p-GaAs occurs at potentials which are positive of those where hydrogen evolution is observed on Pt, and indeed somewhat positive of the reversible hydrogen electrode potential at this pH, -0.39 V vs. SCE. A comparison of the peak currents on Pt and illuminated p-GaAs shows that the limiting current densities for MV²⁺ reduction are essentially equal, thus demonstrating that the rate of reduction at p-GaAs is limited by mass transfer of MV²⁺ to the electrode surface.

When the p-GaAs electrode was held at potentials where MV²⁺ can be reduced and exposed to light, a large current was observed initially but it decayed rapidly to a small steady-state current. This steady-state current was larger when the solution was stirred. This decrease in the current can be attributed to several sources: (a) the onset of a back-reaction associated with the oxidation of the MV⁺ at the semiconductor electrode back to the MV²⁺; (b) absorption of light by the colored MV⁺ generated at the electrode surface; (c) depletion of MV²⁺ at the electrode surface.

Photoassisted Hydrogen Evolution. As mentioned above, it is known that MV⁺ can reduce water to produce hydrogen in the presence of a suitable heterogeneous catalyst:



The photoreduction of water directly at p-type semiconductor electrodes is slow and inefficient (e.g., Figure 2a), because these materials have high hydrogen overpotentials. However, the generation of MV⁺ at irradiated p-GaAs at potentials positive of the reversible hydrogen evolution potential suggested that, by using a suitable heterogeneous catalyst in the solution, bulk generation of hydrogen at p-GaAs, with MV⁺ as a mediator, should be possible. In this process the MV⁺ is oxidized back to MV²⁺, so that there is no net consumption of the methylviologen species, and some suitable oxidation process occurs at the counterelectrode. To carry out

this scheme we assembled a cell to collect and measure the evolved hydrogen gas. The solution was 1 M KCl containing 0.074 M MVCl₂ with 20 mg of platinized Al₂O₃ powder (10 wt % of Pt) added to ~25 mL of solution as catalyst. The solution was stirred continuously during the experiments. With the p-GaAs (area ~0.3 cm²) exposed to the 1.6-kW Xe lamp and held at a bias potential of -0.6 V vs. SCE, irradiation was continued for 3 days, during which time 0.5 cm³ of H₂ gas (1 atm, 25 °C) was collected and clearly identified by gas chromatography. In identical experiments conducted with solutions not containing MVCl₂, only traces of hydrogen (~0.002 cm³, 1 atm, 25 °C) were found. In the experiments made with solutions containing MVCl₂, the initial current (~8 mA/cm²) at -0.6 V dropped quickly to a steady-state current of ~0.5 mA (~1.5 mA/cm²) and remained constant at this level (within ±10%). During this 3-day illumination, the p-GaAs electrode was biased at -0.6 V for only totally about 1.5 days and it was disconnected from the potentiostat for the other 1.5 days, during which time no current flowed through the cell. Moreover, after the prolonged experiments, the cyclic voltammograms both on the irradiated p-GaAs and on the Pt disk were essentially the same as those taken before the experiment. This shows that (a) the concentration of MV²⁺ does not change during the extended irradiation and the photogenerated MV⁺ is oxidized back to the MV²⁺ while reducing the water, without any side reactions; (b) the p-GaAs is stable during this process for at least 3 days under illumination. Although it was clear from these experiments that a great enhancement in the hydrogen evolution rate at p-GaAs is achieved by using the MV²⁺ system, we could not obtain quantitative results which describe the real maximum efficiency for hydrogen production with this system. This is mainly attributable to the relative inefficiency of the catalyst we used, Pt/Al₂O₃, for the reaction of MV⁺ with water. Thus, after about 30 min from the start of the irradiation of the p-GaAs, the solution began to turn blue-purple and the intensity of the solution color gradually increased. This demonstrated that the rate of generation of MV⁺ (~1.5 mA/cm²) was higher than the rate of reduction of water by MV⁺. This accumulation of MV⁺ in the solution decreased the efficiency, because it absorbed some of the light and also

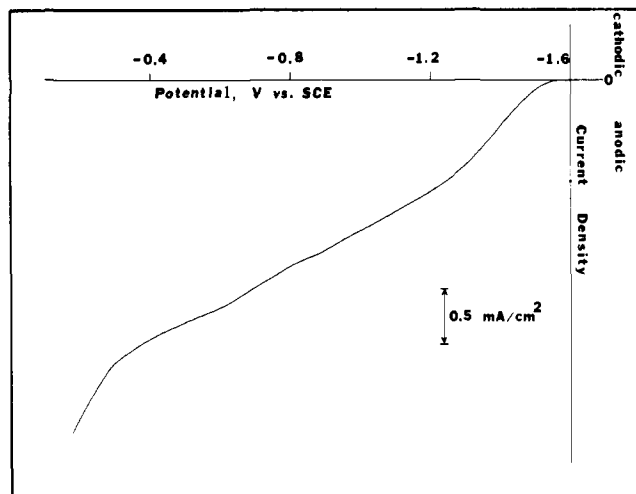


Figure 3. Photooxidation of MV^+ at irradiated *n*-GaAs (450-W Xe lamp). Solution contained 0.07 M MV^{2+} and 5 mM MV^+ , and scan rate was 0.1 V/s.

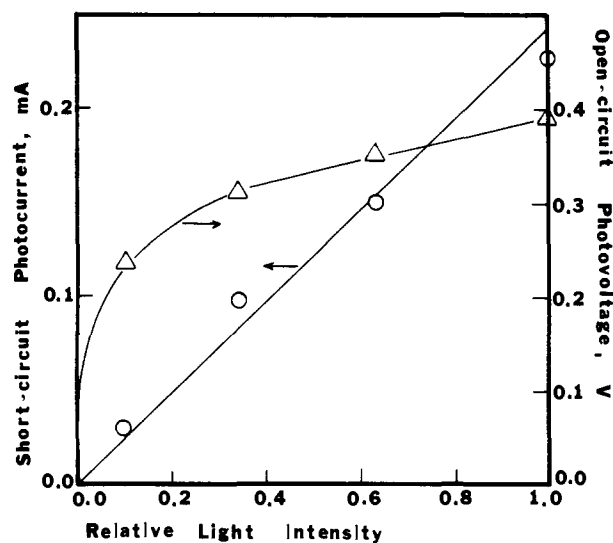


Figure 4. Open-circuit photovoltage and short-circuit photocurrent as function of light intensity (450-W Xe lamp) for PEC cell *n*-GaAs/0.07 M MV^{2+} , 5 mM MV^+ , 1 M KCl/Au, with stirred solution.

enhanced the back reaction (i.e., surface recombination). When the concentration of MV^+ became high, the photocurrent decreased, and the circuit had to be disconnected until the blue color dissipated and the steady-state current returned to the original value. A better efficiency for hydrogen production could probably be achieved with the catalysts recommended elsewhere.^{5a} Even under these unoptimized conditions, however, the enhancement in the rate of production of H_2 compared to solutions not containing $MVCl_2$ was striking. For solutions not containing $MVCl_2$, the steady-state photocurrent at -0.6 V was only ~ 0.01 mA (~ 0.03 mA/cm²) and only traces of H_2 were collected for the same periods of irradiation. Attempts were also made to generate MV^+ in a two-electrode system without using an external electrical supply. This should be possible with a counterelectrode with a redox potential negative of that where photoreduction of MV^{2+} occurs. With a Cu wire as a counterelectrode, we could construct a PEC cell in which a current flowed during irradiation of the *p*-GaAs in a direction consistent with the *p*-GaAs being the photocathode (MV^{2+} reduction) and the Cu the anode. However, the short-circuit photocurrent in this cell was only 1.5 μ A and the open-circuit photovoltage only 50 mV, since the potential of the unpoised Cu electrode was probably mainly contributed

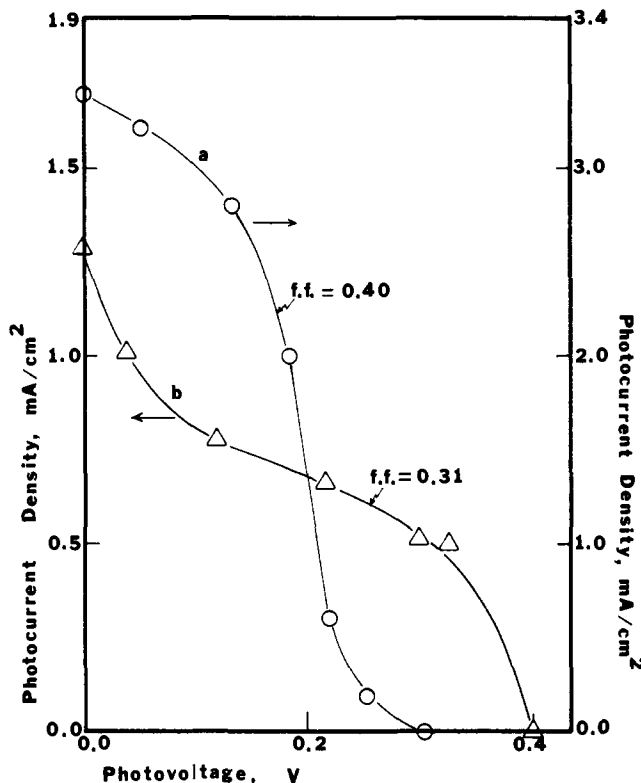


Figure 5. Performance characteristics of GaAs/MV PEC cells. (a) *p*-GaAs/73 mM MV^{2+} , 0.5 mM MV^+ , 1 M KCl/Hgl (b) *n*-GaAs/69 mM MV^{2+} , 5 mM MV^+ , 1 M KCl/Au. Solutions were stirred.

by the Cu/Cu^{2+} or Cu/Cu^+ couples rather than by the more negative Cu/Cu_2O or Cu/CuO couples at pH 3.

Electrochemical Behavior of the *n*-GaAs/ MV^{2+} . The standard potential of the MV^{2+}/MV^+ couple as determined on platinum is at a value consistent with stabilization of an *n*-GaAs electrode. While excellent stability and good efficiencies have been demonstrated with *n*-GaAs in selenide-containing electrolytes,^{8b,c} alternate solution redox couples for this and other semiconductor electrodes are also of interest. The oxidation of MV^+ at an *n*-GaAs electrode under irradiation is shown in Figure 3. In this experiment the solution contained 70 mM MV^{2+} and 4.5 mM MV^+ (generated by coulometric reduction of MV^{2+} on large-area gold foil electrode) and the photoanodic current for MV^+ oxidation started at about -1.5 V vs. SCE, which is about 0.8 V negative of the reversible MV^{2+}/MV^+ potential. The photodecomposition of the *n*-GaAs occurs at about -0.5 V vs. SCE in this solution. A regenerative photovoltaic cell based on an *n*-GaAs photoanode, a Au or Hg cathode, and a solution of 0.07 M $MVCl_2$, 0.005 M $MVCl$, and 1 M KCl was constructed and showed stable operation for at least 2 h. Au and Hg cathodes were selected over Pt because of their higher hydrogen overpotentials. These electrodes are as reversible as Pt for MV^{2+}/MV^+ . The open-circuit photovoltage was 0.4 V and short-circuit photocurrent was 0.21 mA (i.e., 1.3 mA/cm² of *n*-GaAs electrode) in a stirred solution under irradiation with the full power of the 450-W Xe lamp. The short-circuit photocurrent and the open-circuit photovoltage of the cell depended strongly, however, on the light intensity as shown in Figure 4. The photocurrent-photovoltage characteristic of this cell, as shown in Figure 5, yields a fill factor of 0.31. Although the photocell was stable in the MV^{2+}/MV^+ solution, this redox couple has several disadvantages. First, the deep color of solutions containing MV^+ absorbs visible light strongly, so that either low concentrations of MV^+ must be employed, with ensuing mass transport limited currents at the *n*-type semiconductor, or thin

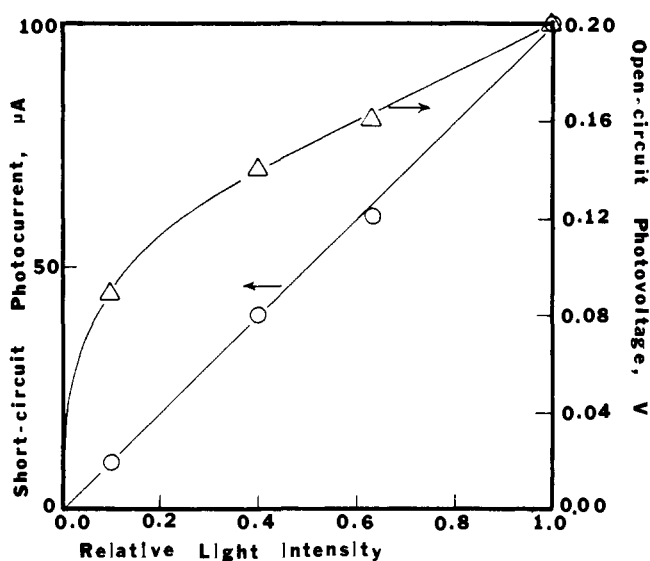


Figure 6. Open-circuit photovoltage and short-circuit photocurrent as function of light intensity (He-Ne laser, 1.6 mW, 632.8 nm) for photocell of Figure 5a.

layer photocells must be constructed. Moreover, with high concentrations of MV^+ , some instability of the solution became apparent,^{10b} probably because of the occurrence of the disproportionation reaction



producing a small amount of the neutral amine species which is known to be unstable in aqueous solution.¹⁰ Minimization of this side reaction also requires lower concentrations of MV^+ in the photocell.

Photovoltaic Cells Based on p-GaAs/ MV^{2+} . Regenerative photocells based on the MV^{2+}/MV^+ couple, p-GaAs as the photocathode, and Hg as an anode were also investigated. As shown in Figure 5, the fill factor of a p-GaAs/1.0 M KCl, 73 mM MV^{2+} , 0.5 mM MV^+ /Hg PEC cell is about 0.4. A Hg electrode was used here to prevent the Pt-catalyzed oxidation of MV^+ . The light intensity dependence of the open-circuit photovoltage and the short-circuit photocurrent of the cell is shown in Figure 6. The quantum efficiency at 632.8 nm was about 13% without correcting the solution absorption. The power efficiency of this cell at this wavelength under light intensity ~ 50 mW/cm² is estimated to be 0.5%. While these efficiencies are rather low, they only represent initial values with no attempts at optimizing cell design. They could clearly be increased significantly by decreasing the optical path length through the solution to the p-GaAs from the value (about 0.5 cm) used in this test cell.

Conclusions

The results reported here for p-GaAs, along with those of Wrighton et al. on p-Si,⁷ with the methylviologen system, suggest that this redox couple could provide a useful intermediate to the production of hydrogen with semiconductor electrodes. Since these small band gap materials will not provide holes with sufficiently positive potentials to oxidize water, the intermediate oxidized form produced at the counterelectrode will have to be reduced in a second PEC cell, with oxygen evolution at the counterelectrode. This "dual photocell" approach to water photodecomposition has been discussed elsewhere.^{6,11} In this context it is important to find a suitable counterelectrode reaction with the p-GaAs/ MV^{2+} system to allow efficient operation without external bias. This couple also may prove useful in PEC photovoltaic cells with n-type semiconductors, although the intense color of the MV^+ species and the possibility of slow decomposition via disproportionation are disadvantages.

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