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Electrochemical solar cells with polypyrrole-coated CdSe sintered electrodes

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A thin layer of polypyrrole was formed on sintered CdSe electrodes. The photoelectrochemical properties of bare CdSe and P-Py/CdSe electrodes were studied in electrolyte with the redox couple [$K_3Fe(CN)_6$]. The results were explained by assuming that a p–n junction is formed on CdSe electrodes with polypyrrole working as a p-type semiconductor.

1. Introduction

CdSe, with a suitable band-gap energy (1.7 eV) and with properties of direct optical transition, is an attractive material for the conversion of solar energy into electrical energy [1]. Besides the easy formation of semiconductor/electrolyte heterojunctions, another advantage of the photoelectrochemical cells (PEC) is that the conversion efficiencies reached with polycrystalline electrodes are not much smaller than those obtained with single crystal electrodes (for a recent review, see [2]). Consequently, many techniques have been developed to produce polycrystalline CdSe electrodes such as: pressure sintering [3, 4], vacuum deposition [5], spray pyrolysis [6], slurry painting, chemical and electrochemical deposition [7–11]. The main problem with low band-gap energy semiconductor electrodes operating in PEC cells is their photodecomposition (oxidation of n-type, and reduction of p-type materials) which leads to lower efficiency or to shorter electrode lifetime.

Many attempts have been made to protect such electrodes against photodecomposition [12, 13] by using the proper redox couple, organic solvents and concentrated salts. Over the last few years, a new method has been attempted which involves the protection of the semiconductor surface by using conducting polymer coatings [13–15].

In this paper, we report how polypyrrole coating changes the photoelectrochemical behaviour of sintered CdSe electrodes and affects the power characteristic of PEC cells.

2. Experimental details

2.1. *Materials*

CdSe (99.999%, Alfa Products) powder was pressed (2000 psi) at room temperature into pellets (0.04 cm thick, 0.2 cm^2 area). The pellets were sintered in air at 540° C for 4 h and polished to a mirror finish with alumina. Before measurements the pellets were etched in 3 : 1 HCl/HNO_3 solution for 45 s, rinsed in H_2O, dipped in 1 M Na_2S + 1 M S solution for 1 h then rinsed again in H_2O. The resulting samples were coated with Ag-epoxy and mounted in silicone resin for cell immersion. All chemicals were Aldrich or Sigma analytical grade and were used without further purification.

2.2. *Measurements*

Electropolymerization and cyclic voltammetry measurements were carried out in a typical three-electrode cell with an SCE (saturated calomel electrode) as the reference electrode. The power characteristics were obtained for a two-electrode cell with a Pt electrode as the counter electrode. For electropolymerization, a PAR Model 173 Potentiostat and an X–Y–t H.P. recorder were used. The cyclic voltammograms were recorded by using an IBM EC Voltammetric Analyzer connected with an AMINCO X–Y–t recorder. The short-circuit current (i_{sc}), open-circuit voltage (v_{oc}) and power characteristics were measured using a Keithley Model 177 Electrometer in conjunction with a decade resistance box. As a light source, a 650 W Quartz–halogen lamp was used and light intensity was measured at the semiconductor (75 mW cm^{-2}) with a Solar Meter.

3. Results and discussion

Initially, the electropolymerization of pyrrole on CdSe pellets was carried out from water solution containing 0.1 M KCl, 0.5 M pyrrole at pH 3.0 under potentiostatic conditions. The beginning of polymerization was observed (significant increase of current) at potentials higher than 0.5 V. The competitive reaction of CdSe oxidation was taking place at such positive potentials. We tried to suppress this reaction by using organic solvent and illumination of the CdSe electrodes. Finally, the polymerization of pyrrole

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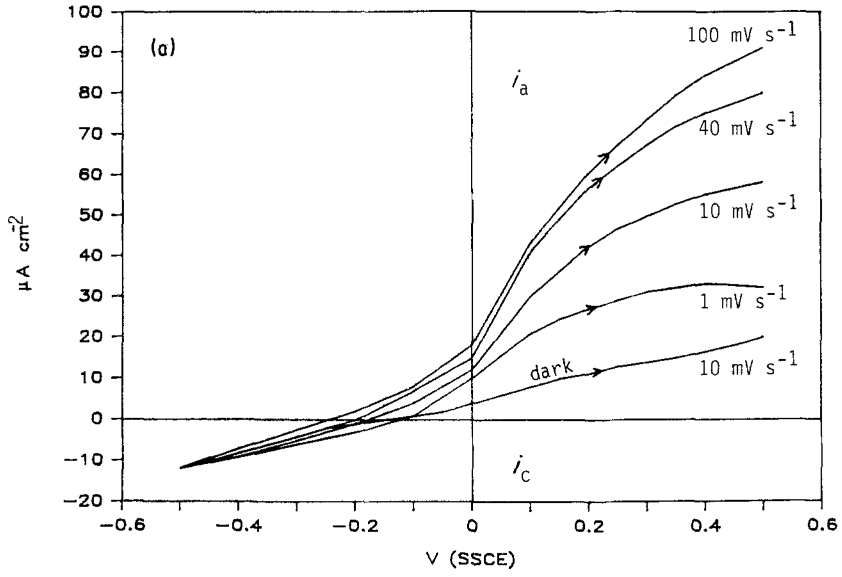
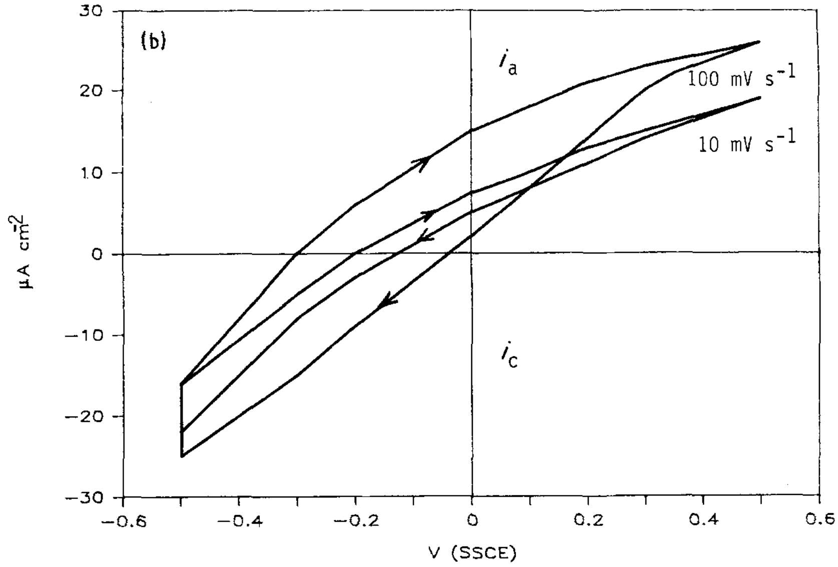


Dark



Illumination

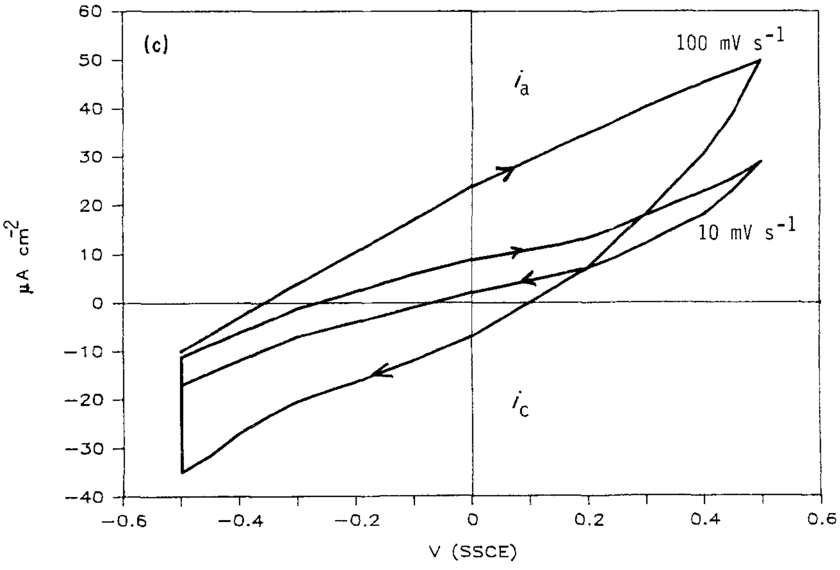


Fig. 1. Voltammograms obtained in CH_3CN + 0.1 M $LiClO_4$ solution for (a) bare CdSe electrodes; (b, c) P-Py/CdSe electrodes in dark and under illumination (20 mW cm^{-2}).

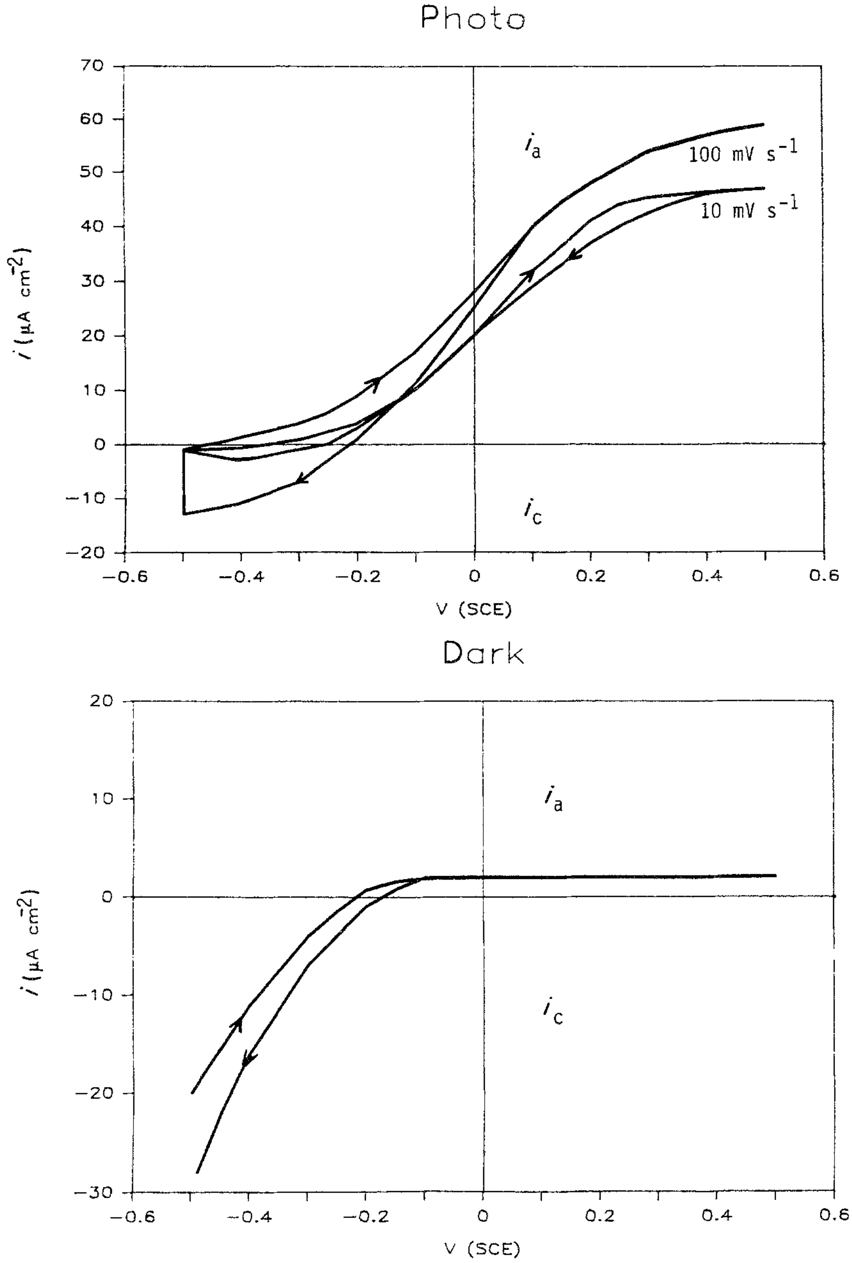


Fig. 2. Voltammograms of bare CdSe electrodes in H_2O solutions containing 0.1 M KCl + 5 × 10^{-3} M $K_3Fe(CN)_6$/5 × 10^{-3} M $K_4Fe(CN)_6$ in dark and under illumination (20 mW cm^{-2}).

was carried out from CH_3CN solutions containing 0.1 M $LiClO_4$, 0.5 M pyrrole at constant potential +0.1 V vs SCE under an illumination of 75 mW cm^{-2}. The process was carried out until the total anodic charges (*Q*) passing through the cell equaled 50–60 mC cm^{-2}. Cyclic voltammetry was used to compare the behavior of both P-Py/CdSe (polypyrrole-coated CdSe) and bare CdSe electrodes. Figure 1a shows representative voltammograms obtained for bare CdSe electrodes in CH_3CN + 0.1 M $LiClO_4$ solutions under dark and under illumination (20 mW cm^{-2}). Current–voltage (*I–V*) curves were recorded in the potential range of −0.5 V to +0.5 V vs SCE at sweep rates (v) between 10 and 100 mV s^{-1}. It was found that in the dark condition, the *I–V* curves were almost linear and that the current density (i) was not dependent upon sweep rate (v). Under illumination, however, the shape of the *I–V* curves was changed, the current showed a tendency toward saturation at positive potentials, and current values were sweep rate dependent.

The results obtained for P-Py/CdSe electrodes under the same conditions are shown in Figs 1b and c. It can be seen that current values are a few times higher than those for bare CdSe, there is no tendency toward saturation and both currents are v dependent. More interesting results were obtained when *I–V* curves were recorded in 0.1 M KCl water solution containing the redox couple: 5 × 10^{-3} M $K_3Fe(CN)_6$, 5 × 10^{-3} M $K_4Fe(CN)_6$. The results for bare CdSe electrodes are presented in Fig. 2. As can be seen, both currents i_d (dark) and i_{ph} (photocurrent)* reached saturation, both showed a small hysteresis and only the i_{ph} current depended upon v. This type of behavior is characteristic of n-type semiconductor electrodes when the photooxidation of reductant occurs.

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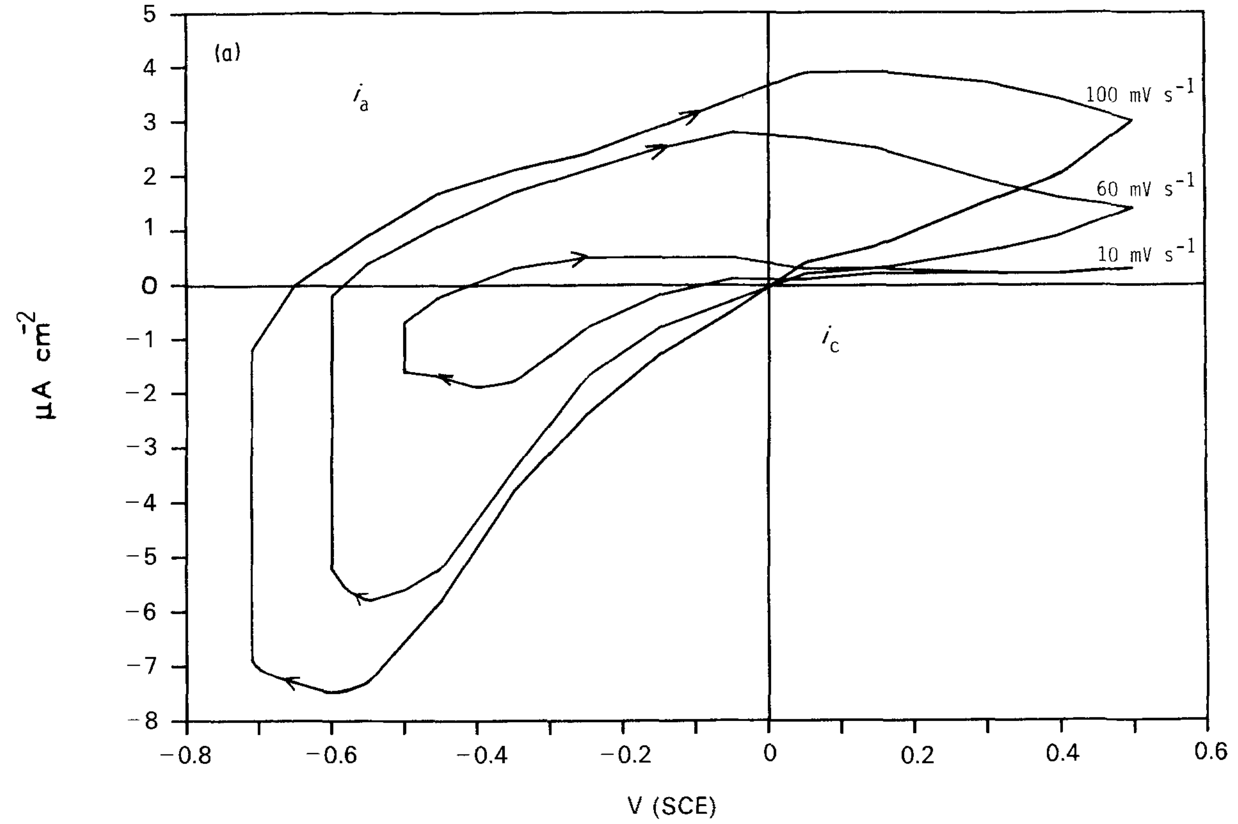
* Measured current during illumination: $i = i_d + i_{ph}$, but as $i_{ph} \gg i_d$, $i = i_{ph}$.



Illumination

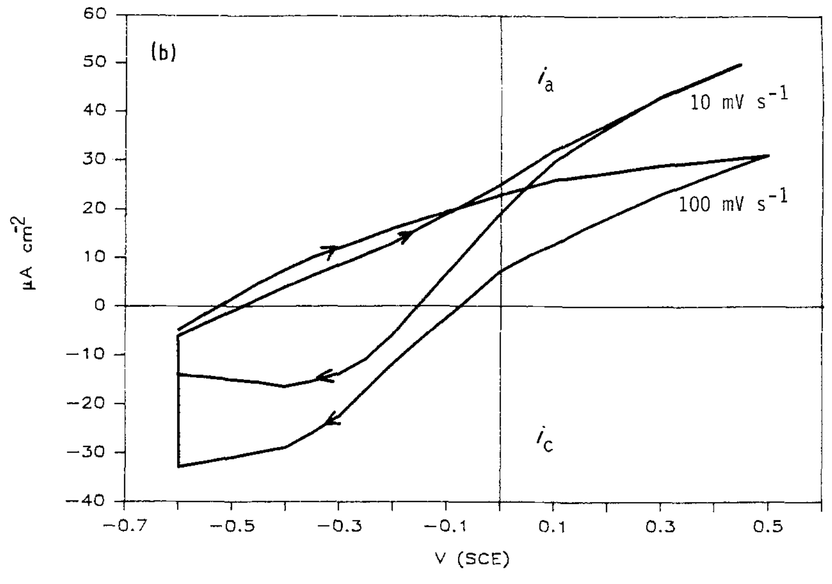


Fig. 3. Voltammograms for P-Py/CdSe electrodes in H_2O solutions containing 0.1 M KCl + 5 × 10^{-3} M $K_3Fe(CN)_6$/5 × 10^{-3} M $K_4Fe(CN)_6$: (a) dark, (b) under illumination (20 mW cm^{-2}).

The voltammograms for P-Py/CdSe electrodes are shown in Fig. 3. As can be seen, under dark conditions the clear cathodic current peak (i_{pc}) appeared. The potential (E_{pc}) of the cathodic peak is shifted cathodically when sweep rate increases, also i_{pc} depended linearly upon $v^{1/2}$ (Fig. 4). The voltammograms showed broad anodic current peaks shifting anodically with v. Under illumination, both peaks decayed, and a tendency for saturation of cathodic current was observed. Also in this case, the anodic current decreased with increasing scan rate.

The energy conversion performance of bare and P-Py/CdSe electrodes is illustrated in Fig. 5 at an incident light intensity of 75 mW cm^{-2}. It can be seen that for P-Py/CdSe electrodes, V dropped nearly 50%, the I–V characteristic was almost linear and the η% (power efficiency) was very low in both cases and nearly the same*.

The results obtained for bare CdSe electrodes may be explained in terms of correlation between energy levels of the redox couple and electrons in the semi-

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* For CdSe pellets in 1 M Na_2S; 1 M S, solutions, we obtained η = 5–7%.

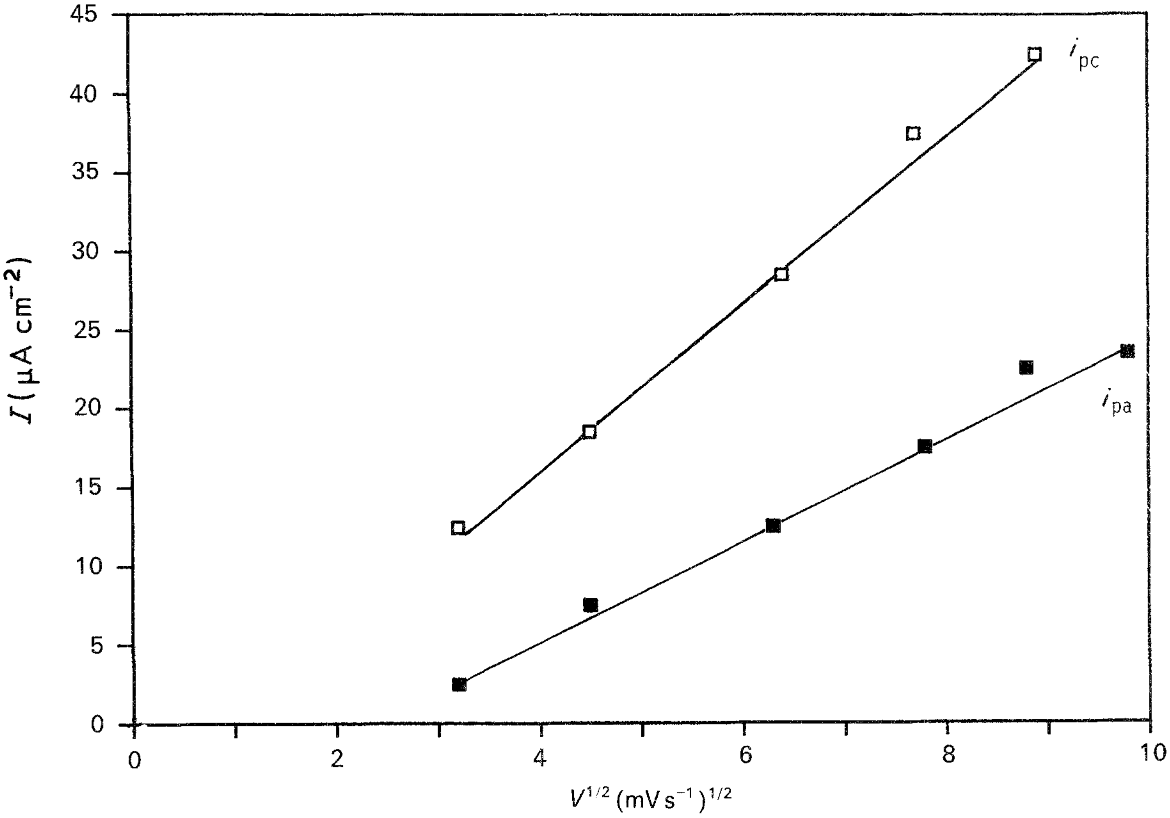

Fig. 4. Plot of i_{pc} and i_{pa} versus $v^{1/2}$ (sweep rate) for P-Py/CdSe electrodes.

conductor (Fig. 6). In dark, when the potential of the electrode is made more positive, a low current flows because there are fewer holes in the semiconductor to accept electrons from the reductant ($K_4Fe(CN)_6$). During illumination, when the concentration of holes increases, the flow toward electrolyte is significant, so the photooxidation current is observed reaching saturation at high enough positive potentials. In both cases, the probability of a reduction reaction is low as a result of the unsuitable position of the electronic

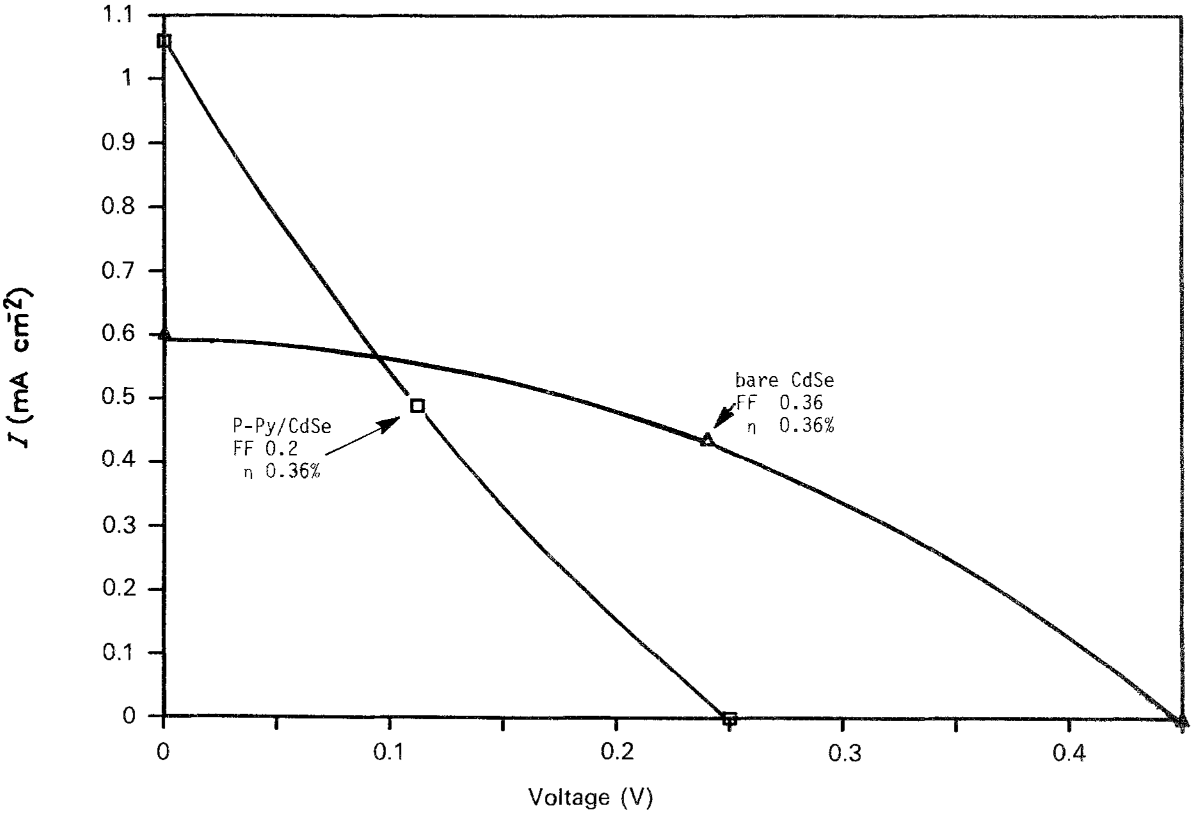

Fig. 5. Power characteristics for bare and P-Py/CdSe electrodes in H_2O solution containing 0.1 M KCl + 5×10^{-3} M $K_3Fe(CN)_6$/ 5×10^{-3} M $K_4Fe(CN)_6$; light intensity = 75 mW cm^{-2}.

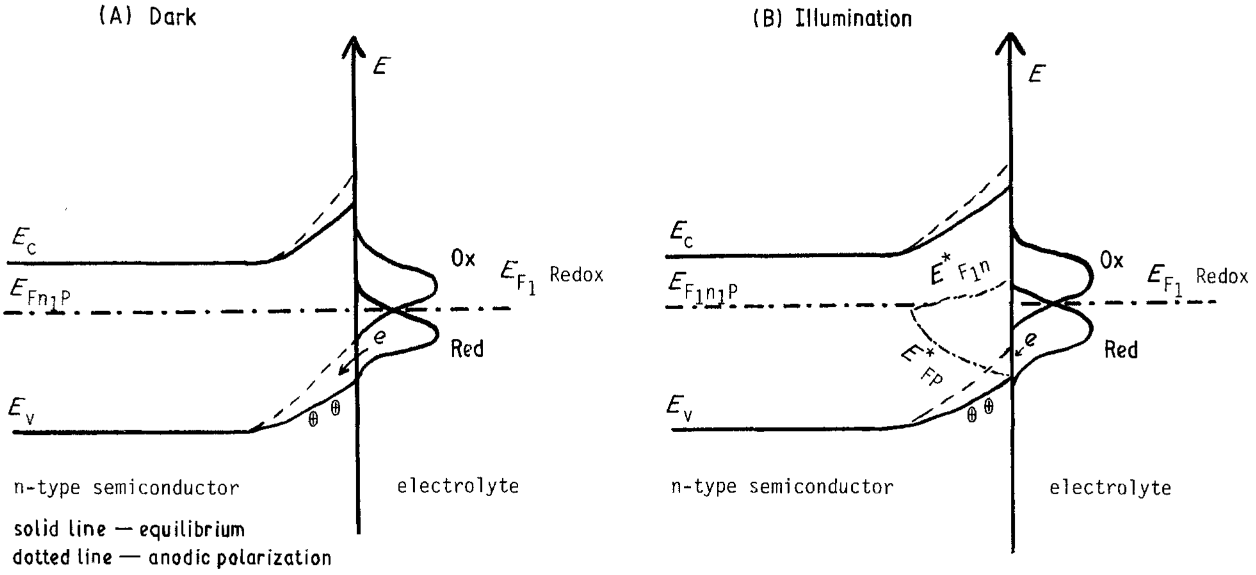

Fig. 6. Energy scheme for bare CdSe electrode in dark and under illumination.

energy levels for electrons in the semiconductor and for the oxidant in electrolyte. The different behaviour of P-Py/CdSe electrodes could be explained in terms of a p–n junction with polypyrrole working as a p-type semiconductor material (Fig. 7).

In the absence of light, reduction of $K_3Fe(CN)_6$ proceeds smoothly with participation of electrons from polypyrrole rings, the oxidation of $K_4Fe(CN)_6$ is not forbidden because of electron flow from the reductant to the oxidized form of polypyrrole. As under illumination, the photoeffects generated in p-type semiconductors are opposite to those in n-type materials. We can observe the decrease of photooxidation current (anodic current) and the increase of photoreduction current (cathodic current) and compare these with the results obtained for bare CdSe. Also, the formation of a very thin p–n junction can cause changes in the power characteristics resulting from additional resistance in the cell.

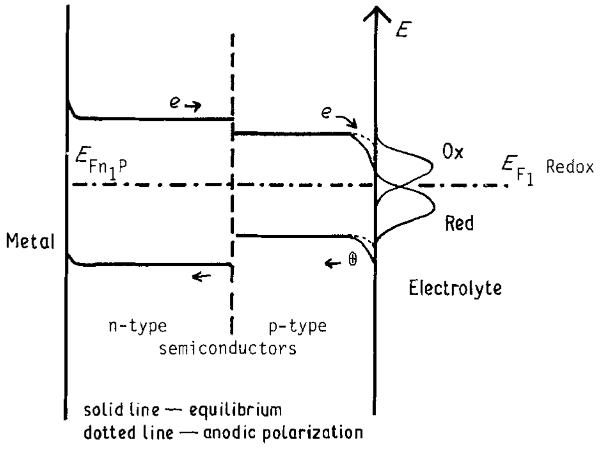

Fig. 7. Energy scheme for P-Py/CdSe electrode.

Acknowledgements

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