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Sensitization of nano-porous films of TiO₂ with santalin (red sandalwood pigment) and construction of dye-sensitized solid-state photovoltaic cells

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Abstract

Santalin, a pigment extracted from red sandalwood strongly surface complex to TiO₂, sensitizing nano-porous film of TiO₂ to the visible spectrum. Because of the stability of such films, dye-sensitized solid state photovoltaic cells of sandwich structure (nano-porous *n*-TiO₂/santalin/*p*-type semiconductor) can be constructed by depositing *p*-CuI or *p*-CuCNS on santalin coated nano-porous films of TiO₂. High stability of santalin complexed to TiO₂ enables deposition of the *p*-type semiconductor without destroying the pigment layer. Light absorbed by the dye-molecules injects electrons into TiO₂ and holes into CuI (or CuCNS) generating short-circuit photocurrent ~6 mA/cm² and photovoltage ~450 mV at 800 W/m² simulated sunlight. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Photoexcited dye molecules adsorbed on the surface of a *n*-type (*p*-type) semiconductor surface inject electrons (holes) into the conduction band (valence band) if the excited level (ground level) of the dye molecule is located above the conduction (valence) band. This phenomenon known as dye-sensitization (DSN) finding applications in photography and photovoltaics continues to arouse fundamental interest [1–12]. It is well known that colour photography depends on DSN of silver halides which are high band gap semiconductors [1]. The recent interest in DSN originated from the fact that this effect could be utilized to construct photoelectrochemical cells (PECs) based on high band gap semiconducting materials, that are stable and resistant to photocorrosion [7–11]. It was also noted that DSN is a single band carrier injection process [8]. Therefore the problem of bulk recombinations is absent, enabling the use of impure polycrystalline films. The chief disadvantage of dye-sensitized PECs had been the low energy conversion efficiency. Only the first few mono layers of dye molecules adsorbed on the semiconductor surface are capable of injecting carriers into a band and consequently the photocurrent quantum efficiency is small. This problem is elegantly resolved in dye-sensitized solar cells based on nano-

porous films of TiO₂ [12–15]. Because of the very large effective surface area (approximately 800 times the geometrical area of nano-porous films), a high light absorption cross section is achieved even at monolayer surface concentrations of the dye.

In a dye-sensitized PEC with nano-porous TiO₂, the charge on the dye molecule which had transferred an electron into the conduction band is scavenged by a redox species present in the electrolyte [12–15]. The liquid electrolyte in dye-sensitized PECs encounter several practical problems such as dye desorption, solvent evaporation and seal imperfections. Furthermore, the ionic charge transport leads to irreversibility, because chemical reactions other than those of the redox cycle are not completely forbidden.

A more attractive idea is to replace the electrolyte by a transparent (therefore high band gap) semiconductor to collect the positive charges from the dye molecules which have injected electrons into the *n*-type material [16,17]. In such a device of structure *n*-type semiconductor/dye/*p*-type semiconductor (NDP) which is symmetric with respect to the two semiconductor surfaces (sandwiching the dye molecules) the primary process occurring is, injection of an electron and a hole into the *n*-type and *p*-type materials by the excited dye molecule.

The construction of NDP photovoltaic cells of nano-porous structure is restricted by the constraints involved in choosing the semiconductor materials and dyes with mutually compatible properties. TiO₂ is undoubtedly a good

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n-type material, because of its stability and ready availability of techniques for preparation of nano-porous films. The selected dye must anchor firmly to the semiconductor surfaces on either side and the location of ground and excited states must energetically permit electron and hole transfer to conduction and valence bands of n and p-type semiconductors. It is also crucially important that the deposition technique of the p-type material does not disturb the monolayer of dye on the TiO₂ surface. Again the deposition process must ensure filling of the pores of the nano-porous film with the p-type material.

We have found that CuI (band gap ~ 3.1 eV) is a suitable p-type material for constructing NDP type solar cells [18]. This depends on the solubility of CuI in acetonitrile, allowing simple low temperature dip coating and spray deposition. Of the several pigments examined, the flower pigment cyanidin was found to be ideally suited for construction of NDP devices because of the strong surface complexation of cyanidin into the TiO₂ surface [18]. The formation of surface complexes of cyanidin with TiO₂ depends on reaction of an OH⁻ ion at a Ti(IV) site with a proton donated from cyanidin molecule with the elimination of a water molecule [17,19]. Prompted by the above observation and noting that most polyphenolic pigments have the same property, we examined a large number of other natural pigments and found that santalin, the red pigment extracted from red sandalwood (*Pterocarpus santalinus*) complexes even strongly with TiO₂, producing dyed surface which is highly resistant to heat and thermal oxidation. We have succeeded in constructing NDP photovoltaic cells with santalin using CuI and CuCNS as the p-type material.

2. Experimental

Red sandalwood contains two major pigments [20,21] the orange-red santalin and deep yellow santarubin (structural formula is given in Fig. 1). Santalin was extracted from red sandalwood by the following method. Pulverized red sandalwood was digested in petroleum ether for 24 h to extract lipids. Digestion in dichloromethane for further 24 h remove several other mildly polar compounds and a large portion of santarubin (some santalin is also lost). The residue is washed with warm water to remove tannin and digested in acetone containing 25% water and the solution is evaporated to dryness in a rotary-evaporator. The dark red solid containing mostly santalin with some santarubin and tannin was washed with dichloromethane and warm water to reduce the santarubin and the tannin content. Further purification is achieved by chromatography using a silica gel column and elution with dichloromethane and methanol mixture. The absorption spectrum of the elute when the solution contains nearly 80% methanol is shown in Fig. 2. The peak at ~ 470 nm corresponds to santalin and the peaks at ~ 440 and ~ 500 nm originate from santarubin and an unidentified compound, perhaps a degradation product of

santalin. Further purification is possible by repetition of chromatographic separation. Evaporation of methanolic solution yield santalin as a deep red solid. For most experiments chromatographic purification was found to be unnecessary and the partially purified product gave nearly identical results, because santalin gets preferentially adsorbed on TiO₂.

Nano-porous films of TiO₂ were coated on fluorine doped conducting tin oxide glass (CTO) plates (2×1 cm², sheet resistance $\sim 10 \Omega/\square$) from a colloidal solution of TiO₂ prepared by hydrolysis titanium isopropoxide as described in the Ref. [18]. The coating procedure adopted was to smear colloidal solution on the plate and drying at 120°C followed by sintering at 450°C for 10 min and the process is repeated until a semitransparent film $\sim 6 \mu\text{m}$ is deposited (film thickness was measured using Shimadzu 8705 Scanning Electron Microscope). The average crystallite size determined from X-ray diffractometry was found to be ~ 15 nm. The TiO₂ film was coated with santalin by boiling the plate in a solution of santalin in acetone (~ 10 mg in 5 ml).

Solution of CuI was prepared by dissolving 0.6 g of CuI in moisture free acetonitrile. Dyed nano-porous TiO₂ surface was moistened with this solution and dried at $\sim 150^\circ\text{C}$ by placing on a hot plate, preferably in a nitrogen atmosphere (experiment conducted inside a glove box). Moistening with CuI solution and drying was repeated several times, until the pores of the film gets filled up with CuI and CuI film extends $\sim 4\text{--}5 \mu\text{m}$ above nano-porous TiO₂ surface. Finally the plate is annealed 150°C for 30 min in a nitrogen atmosphere. In some experiments, CuI was deposited on the dye coated TiO₂ surface by vacuum evaporation of CuI by heating CuI to $\sim 600^\circ\text{C}$ (melting point of CuI $\sim 605^\circ\text{C}$). The back electrical contact is made by pressing a gold coated CTO glass plate into the CuI surface and sealing the edges with epoxy resin in a nitrogen atmosphere. The construction of the cell is illustrated in Fig. 3.

CuCNS is another p-type semiconductor (band gap ~ 3.6 eV) [22] which can replace CuI. Cells with CuCNS were prepared by deposition of CuCNS from a solution of CuCNS in acetonitrile containing HCl by the procedure described for coating CuI. However, as CuCNS is susceptible to thermal decomposition at lower temperature (compared CuI), precautions need to be taken to avoid over heating.

Absorption spectra were obtained using a Shimadzu UV-3000 Spectrophotometer, and the photocurrent action spectra were taken with an arrangement consisting of a Nikon Monochromator, Auto-Scanner AS-C-10 coupled to a light chopper and a lock-in amplifier. Light intensities were measured using an eko-pyromometer (MODEL MS 801). Photocurrent action spectra of santalin coated films of TiO₂ and CuI in electrolytic medium was also examined. For this purpose, three electrode configuration (with calomel electrode as the standard) was adopted and the working electrode is biased to give a nearly zero dark current.

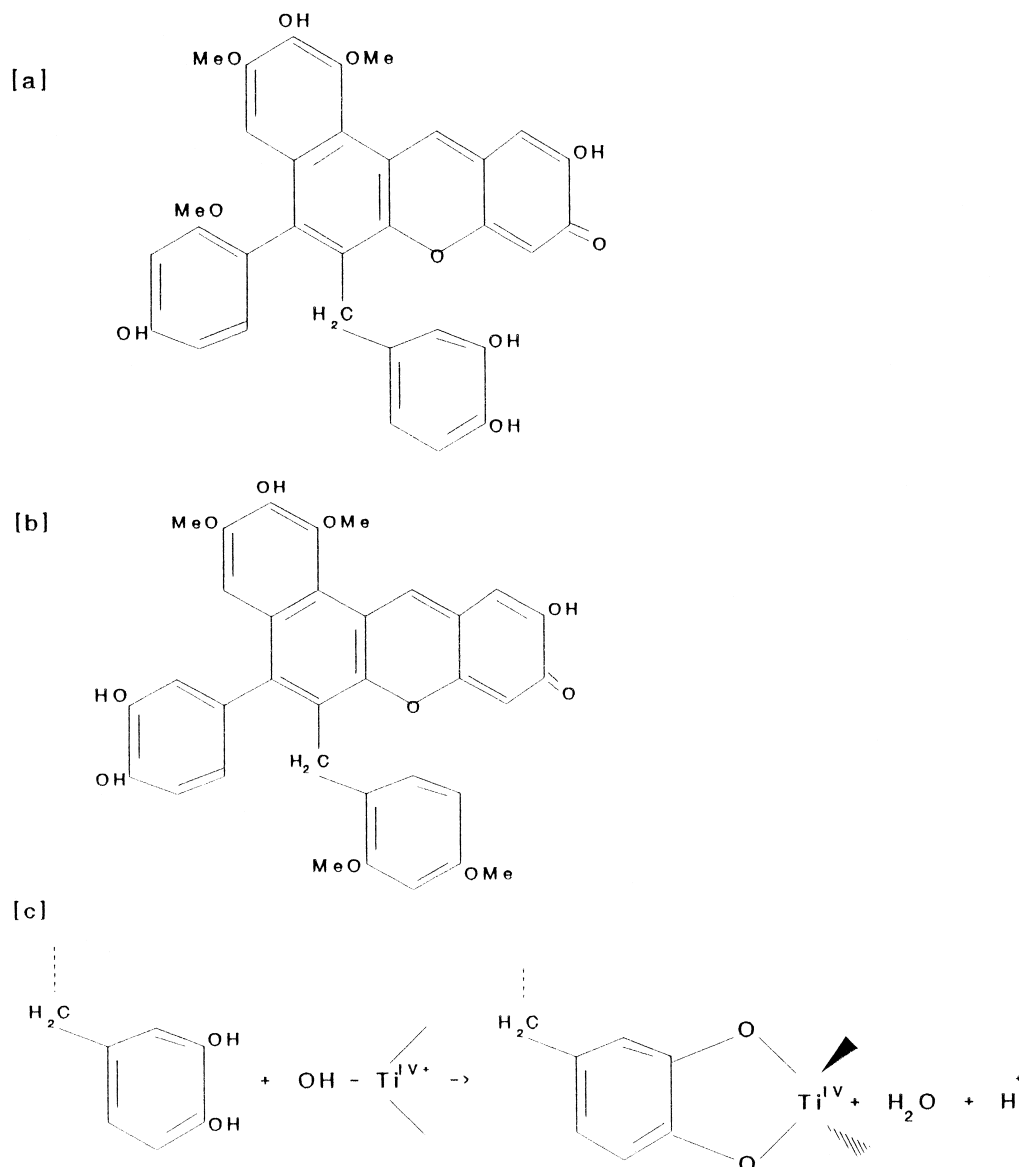


Fig. 1. Structural formula of (a) santalin (b) santarubin and (c) Mechanism of surface complexation of santalin and TiO_2 .

3. Results and discussion

A neutral solution of santalin is orange red in colour and has an absorption peak at 470 nm (Fig. 2). When pH is increased the solution becomes dark violet red-shifting the absorption peak owing to deprotonation and association of the anionic moiety with the cations in the solution. The absorption spectrum also depends on the complexing cation, Fe^{3+} , Ti^{3+} , Ti^{4+} , Cu^+ , Cu^{2+} , and several other metallic ions form intensely coloured complexes with santalin. In almost all cases, the absorption peak of the complex is significantly red-shifted from the neutral solution of the parent pigment. In the same way santalin form complexes with metallic sites in solid metallic oxides (Fig. 1(c)). The curves a, b of the Fig. 4 shows absorption spectra of aqueous suspension of colloidal TiO_2 particles and TiO_2 particles that have been

made to adsorb santalin. The latter spectrum exhibits peak at ~ 535 nm characteristic of TiO_2 -santalin surface complex. The detailed mechanism of interaction between TiO_2 and dye could be more complex than the mechanism we have suggested and could involve other ligands influencing the colouring moiety.

The photocurrent action spectra of santalin coated TiO_2 (nano-porous film) and CuI (deposited on CTO glass) in Na_2SO_4 solution and that of the photovoltaic cell (nano-porous $n\text{-TiO}_2/\text{santalin}/p\text{-CuI}$) are shown in the Fig. 5. The peaks in the above photocurrent action spectra (curves c, b, a of Fig. 5) are located at 528, 568, 540 nm, respectively. It is seen that the peak of the photocurrent action spectrum of santalin coated TiO_2 in Na_2SO_4 solution is very close to that of absorption spectrum of santalin adsorbed on TiO_2 , indicating that the sensitizing action is due to the Ti(IV) -

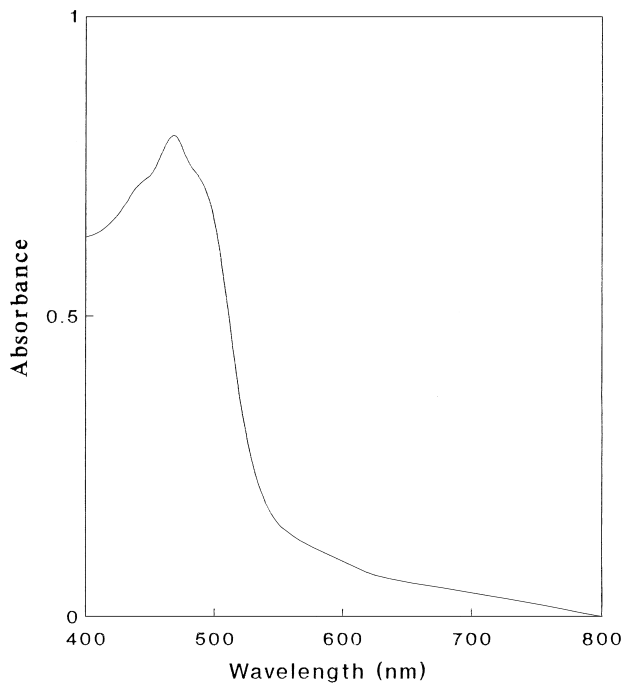


Fig. 2. Absorption spectrum of a partly purified solution of santalin.

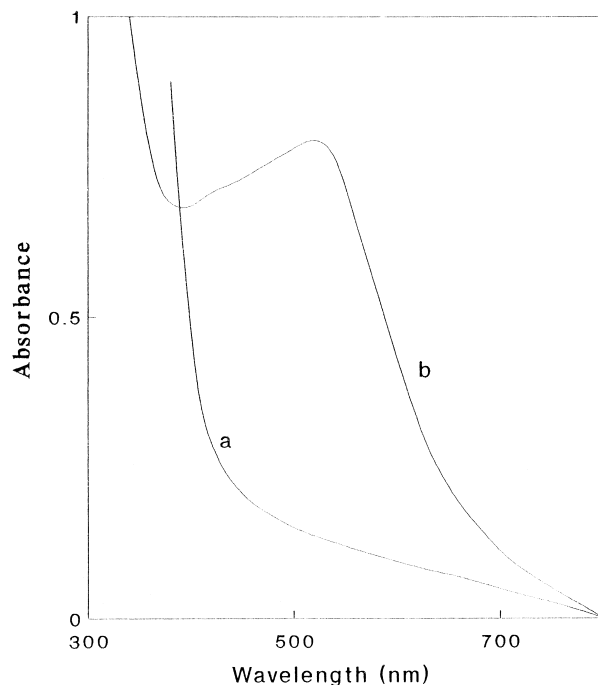


Fig. 4. Absorption spectrum of (a) colloidal solution of TiO_2 , (b) a solution colloidal TiO_2 that has been made to adsorb santalin.

santalin surface complex. Santalin adsorbed on CuI shows a peak absorption at ~ 568 nm, here again a complex is formed with the Cu(I) sites on CuI surface. The peak position of the photocurrent action spectra of the cell nano-porous $n\text{-TiO}_2/\text{santalin}/p\text{-CuI}$ at ~ 540 nm is intermediate between peak position in the action spectrum of TiO_2 and CuI in Na_2SO_4 solution. This observation suggest that, santalin molecules interacts with both surfaces (i.e., TiO_2 and CuI on either side). The detail mechanism of bonding of a santalin molecule complexed with TiO_2 into CuI remain uncertain.

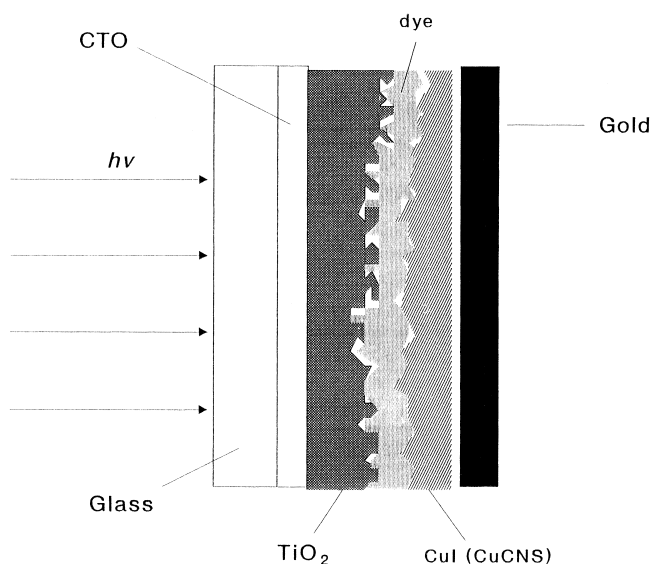


Fig. 3. Construction of the nano-porous $n\text{-TiO}_2/\text{santalin}/p\text{-CuI}$ cell.

A schematic energy level diagram based on band positions of CuI, CuCNS and TiO_2 presented in Fig. 6 illustrates the mechanism of charge transfer. We have not succeeded in ascertaining the exact position of the ground and excited

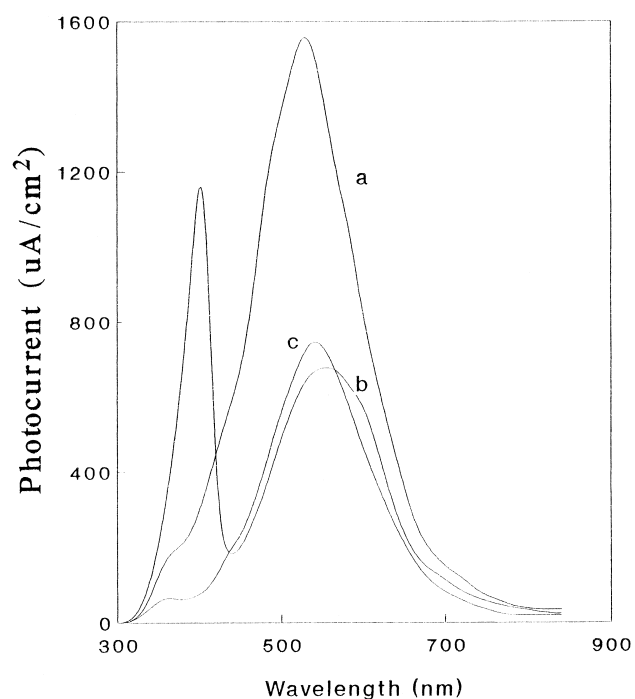


Fig. 5. Photocurrent action spectrum of (a) santalin coated on TiO_2 in Na_2SO_4 solution, (b) santalin coated CuI in Na_2SO_4 solution (the peak at ~ 408 nm originates from absorption in CuI), (c) the cell nano-porous $n\text{-TiO}_2/\text{santalin}/p\text{-CuI}$.

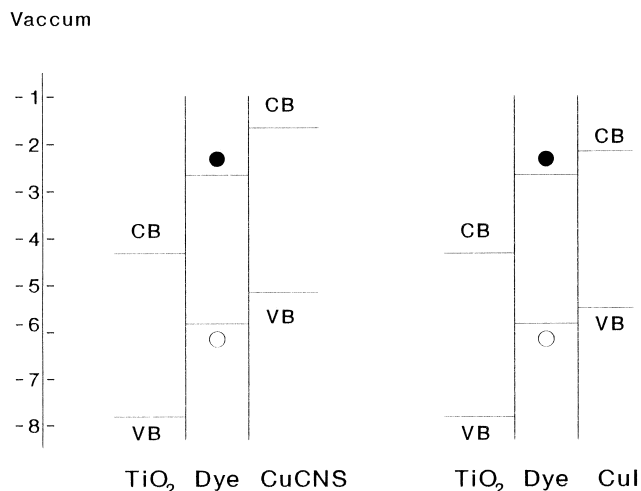
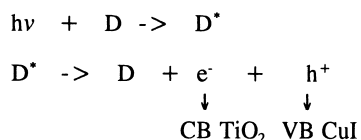


Fig. 6. Schematic diagram illustrating relative locations of TiO_2 , CuI , CuCNS and the energy levels of the dye.

levels of santalin relative to the semiconductor bands. However, the fact that the excited molecule is capable of injecting electrons into the conduction band of TiO_2 and holes into the valence band of CuI (or CuCNS), i.e.,



necessitates location of these energy levels as in Fig. 6. The bonding of the dye molecules both surfaces is the ideal situation for a cell of this type. The exact nature of any simultaneous bonding of dye molecules to both surfaces remain unclear. A molecule strongly bonded to one surface and weakly to the other could also participate in the above charge injection scheme.

At 800 W/m^2 (simulated sunlight) cell nano-porous $n\text{-TiO}_2/\text{santalin}/p\text{-CuI}$ generates a short-circuit photocurrent $\sim 6 \text{ mA/cm}^2$ and an open circuit voltage 450 V . The maximum energy conversion at the above intensity, deduced from the $I\text{-}V$ plot (Fig. 7) is $\sim 1.8\%$. When intensity of illumination is reduced to $\sim 50 \text{ W/m}^2$ the efficiency is increased to $\sim 3\%$. The low efficiency of the cell at higher intensities is an indication of the presence of recombination losses via voids in the TiO_2 film. At these points the cell is short-circuited by the direct contact of CuI and the CTO surface. Presence of other types of surface recombinations is also not ruled out.

When CuI is replaced by CuCNS the cell generates a short-circuit photocurrent of $\sim 2 \text{ mA/cm}^2$ and open-circuit voltage $\sim 500 \text{ mV}$ at 800 W/m^2 simulated sunlight. The decrease in the short-circuit photocurrent is a consequence of the lower electrical conductivity of CuCNS compared to CuI . Slightly higher conduction band position of CuCNS (compared to CuI) favours higher open-circuit voltage as observed.

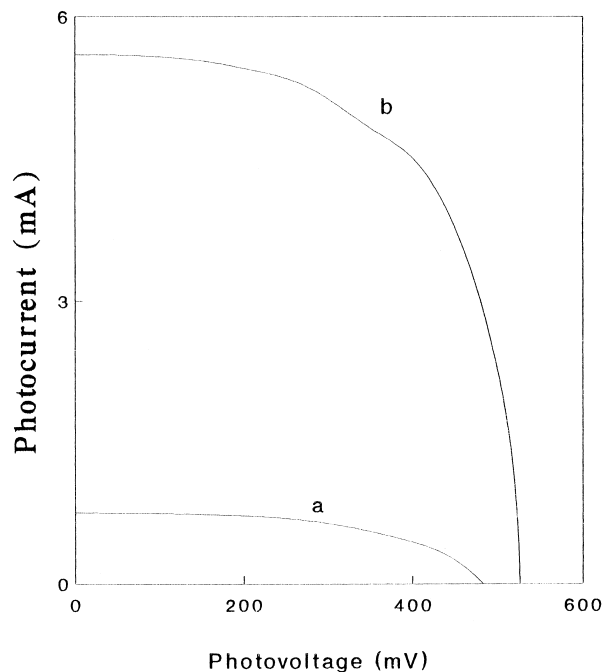


Fig. 7. Plot of photocurrent vs photovoltage (a) 50 W/m^2 , (b) 80 W/m^2 for the cell nano-porous $n\text{-TiO}_2/\text{santalin}/p\text{-CuI}$.

Santalin coated on nano-porous TiO_2 is unusually stable because of the strong surface complexation. Complexed pigment is not removed when the dyed plate is boiled in acetone or alcohol for several hours. Dye coated plate can be heated in air up to $\sim 150^\circ\text{C}$ for several hours without degrading the pigment. Again pigment is not destroyed by strong mineral acids and complete removal is possible only if it is treated with strong oxidizing agents (eg. KMnO_4) under alkaline conditions. Our success in constructing dye-sensitized solid solar cells with CuI and CuCNS as the p-type semiconductors depends on extreme stability of santalin coated to TiO_2 . With other pigments we have tested annealing of CuI film is not possible without degradation of the pigment. Annealing improves the inter-crystallite contact of the grain boundaries of CuI . Undoubtedly santalin is not the suitable choice for a practical device because of the low conversion efficiency. However synthesis of pigments modelling the behavior of santalin would be useful in identifying better sensitizers.

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