

A solid-state solar cell sensitized with mercurochrome

Finding a low cost solar cell as an alternative to conventional silicon solar cell is the aim of many investigations. From this point of view, dye-sensitized solar cells have attracted much attention. Fabrication of a dye-sensitized photo-electrochemical cell with efficiency of over 10% by a Swiss group was a breakthrough in this field¹. An efficient dye-sensitized solid-state solar cell was fabricated by Tennakone *et al.*² using a natural pigment, cyanidin as a sensitizer and p-CuI as a solid state hole collector. Thereafter, a series of solid-state solar cells was fabricated using natural pigments^{3,4}, organic^{5,6} and metal-centred dyes⁷ as sensitizers. However, cis-Ru^{II} 2,2'-bipyridyl-4,4'-dicarboxyl thiocyanate produces much higher efficiency in TiO₂/dye/CuI-type solar cells than other sensitizers. We have fabricated a solid-state cell sensitized with a metal-free dye, mercurochrome and preliminary observations are reported here.

TiO₂ colloid was prepared by adding 10 ml water drop wise to a mixture of 15 ml titaniumisopropoxide, 17 ml acetic acid in 60 ml 2-propanol under vigorous stirring. Two grams of TiO₂ (P25 Degussa) powder was added to this colloidal solution and stirred overnight. Small amount of this solution was spread on indium tin oxide-coated glass plate (ITO) pre-heated at 150°C. The plate was sintered in an oven for 30 min at 450°C. This procedure was repeated until the thickness of the film reached 8–10 μm. The dye was coated on the film by soaking in a mercurochrome solution (5×10^{-3} M in ethanol).

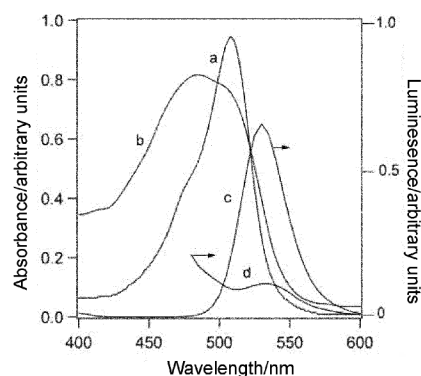


Figure 1. Absorption spectrum of mercurochrome in ethanol (curve a) TiO₂ (curve b). Emission spectra of mercurochrome alone in ethanol (curve c) and after adding a trace of TiO₂ colloidal (curve d).

The dye-coated TiO₂ film was then washed with ethanol to remove excess dye on the surface. A thin layer of CuI was deposited on top of mercurochrome-coated TiO₂ film. Deposition technique of CuI has been discussed elsewhere⁸. TiO₂/mercurochrome/CuI cell was fabricated by pressing a platinum-coated ITO plate on top of the CuI layer as the counter electrode. Current-voltage characteristics of the cell were measured using a Keithley 2420-3A source meter coupled to a computer under illumination of simulated light (1000 Wm^{-2}). Photocurrent action spectra of the cell were obtained using a Nikon Mono-chromator-Autoscanner coupled with a computer. Absorbance and fluorescence spectra of dye and dye coated TiO₂ colloid (films) were measured using a spectrophotometer (Shimadzu UV-3000) and a spectrofluorometer (Shimadzu RF-5000).

The absorption spectra of mercurochrome in ethanol and TiO₂ are shown in Figure 1. We have observed an absorption maximum at 520 nm and a shoulder at 480 nm for mercurochrome in solution (such as water, alcohol). This shoulder is commonly seen in xanthene dyes⁹. As is shown in Figure 1 (curve b), chelation of mercurochrome with TiO₂ results in enhancement and broadening of the absorption spectrum in shorter wavelengths with the maximum and a shoulder at 480 and 520 nm respectively. Generally, H-aggregated dye molecules exhibit broadening and enhancement of absorption in shorter wavelengths compared to that of monomers¹⁰. The maximum and shoulder in curve b

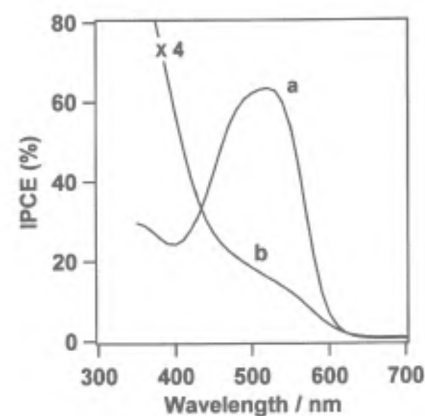


Figure 2. IPCE spectra of TiO₂/mercurochrome/CuI (curve a) and TiO₂/mercurochrome-CuNS (curve b).

suggested the existence of mercurochrome aggregates, monomers and their equilibrium on TiO₂. The luminescence (emission) spectra of mercurochrome in ethanol and TiO₂ colloid are also illustrated in Figure 1. Mercurochrome in ethanol exhibited a luminescence band in green region with a peak at 535 nm. This peak faded out when traces of TiO₂ colloid are added to the dye solution. Instead of de-excitation through luminescence, injection of electrons into the conduction band of TiO₂ by photo-excited dye molecules could be the reason for this.

The incident photon-to-current conversion efficiency (IPCE) spectrum of TiO₂/mercurochrome/CuI cell is shown in Figure 2 (curve a). Maximum IPCE of 65% was observed for TiO₂/mercurochrome/CuI cells at 523 nm. Current-voltage characteristics of TiO₂/mercurochrome/CuI cell are shown in Figure 3 (curve a). TiO₂/mercurochrome/CuI cell produces open circuit voltage of 490 mV and short circuit photocurrent of 5.5 mA cm^{-2} with an efficiency of 1.15% under illumination with Xe lamp (AM 1.5 conditions). We have illuminated the same cell by a 100 W tungsten filament bulb (Tungsthal R60). Less photocurrent and photovoltage were observed for TiO₂/mercurochrome/CuI cell under illumination of the tungsten filament bulb compared to that of AM 1.5 conditions (curve b, Figure 3).

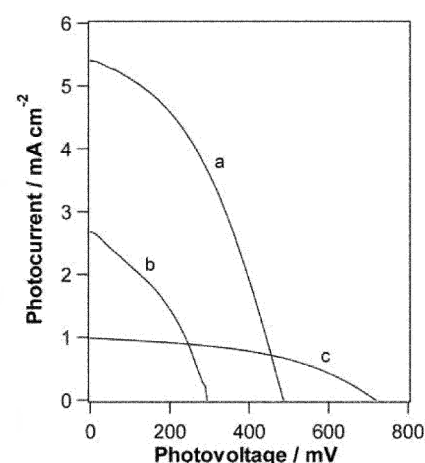


Figure 3. Current voltage characteristics of TiO₂/mercurochrome/CuI under illumination of xenon lamp (100 mW m^{-2}), (curve a) TiO₂/mercurochrome/CuI cell under illumination of tungsten filament lamp (100 W) (curve b) and TiO₂/mercurochrome/CuI cell under illumination of xenon lamp (100 mW m^{-2}) (curve c).

However, this is in contrast to the results obtained for a similar type of cell sensitized with natural pigment cyanin (extracted from pomegranate fruits). TiO_2 /cyanin/CuI cell produces higher photocurrent under illumination of a tungsten filament bulb (Tungsraflex R60, 100W) than under AM 1.5 conditions¹¹. Proper spectral matching of the tungsten lamp with that of TiO_2 /cyanin/CuI cell could be a reason. We have studied photo-properties of the cell by replacing the CuI layer by CuCNS. TiO_2 /mercurochromelCuCNS cell produces a lower photocurrent compared to that of the cell with CuI, at any visible wavelength (curve b, Figure 2). This may be due to high resistivity of the CuCNS film. The current–voltage characteristics of TiO_2 /mercurochromelCuCNS cell (AM 1.5 conditions) are also shown in Figure 3 (curve c). TiO_2 /mercurochromelCuCNS cell produces an open circuit voltage of 720 mV and short circuit photocurrent of 1.0 mA cm^{-2} . The slightly higher conduction band position of CuCNS (compared to CuI) favours higher open circuit voltage as observed. However, we did not observe any significant change in the current–voltage properties when TiO_2 /mercurochromelCuCNS cell is irradiated with the 100 W tungsten filament lamp. This type of solar cell exhibits a slow degradation of less than 5% per day in the dark and much faster degradation under illumination¹². The stability of TiO_2 /mercurochromelCuI solid-state cell was studied under prolonged illumination. A decay in the photocurrent was observed with a rate of 20% per day. We have again deposited CuI on the cell after it had degraded nearly completely (~90%). During this treatment, a drop of CuI suspension was deposited

on the cell, while the back contact was removed. A rise in the photocurrent was observed. The maximum photocurrent obtained was ~30% less than that under first illumination. Formation of new bonds between CuI and dyed TiO_2 grains is believed to be the reason for regeneration of the cell. Recently, more extended stability was achieved by covering TiO_2 grains with a thin ZnO layer for these type of cells¹³. Confinement of electrons in TiO_2 grains covered by a thin ZnO layer could be a reason for the extended stability. Therefore, a break-up of the bridge between CuI and dyed- TiO_2 grains could be one of the reasons for degradation of the cell.

In conclusion, formation of aggregates and their equilibrium with monomers resulted in broadening of the absorption of mercurochrome– TiO_2 coupled system. An efficient electron transfer process is observed between two solid phases (CuI and TiO_2). Solid-state TiO_2 /mercurochromelCuI cell produces an open circuit voltage of 490 mV and short circuit photocurrent of 5.5 mA cm^{-2} , with reasonably high conversion efficiency. The performance of the cell could be further improved by understanding the bridge between CuI and TiO_2 .

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Gravity-induced negative refraction of electromagnetic waves

The conventional description of electromagnetic refraction at the interface between two isotropic, homogeneous, dielectric–magnetic medium, as presented in standard textbooks on optics, is that of *positive* refraction. A defining characteristic of positive refraction is that the phase velocity and the power flow are co-directional in the refracting medium. Accordingly, materials which support this conventional form of planewave propagation are positive-phase-velocity (PPV) materials. In con-

trast, under exceptional circumstances which do not readily arise for naturally occurring materials, the phase velocity can be directed opposite to the direction of power flow. Thereby, *negative* refraction can occur. Materials which support this anomalous form of planewave propagation are called negative-phase-velocity (NPV) materials¹.

Within the past five years, pioneering work by experimentalists and theoreticians has resulted in successful fabrication

of effectively homogeneous metamaterials which support negative refraction in the microwave frequency regime². This has generated a great deal of interest in the electromagnetics and optics research communities. Current efforts are directed towards high infrared frequencies, with the ultimate aim being optical negative refraction. The interest in NPV metamaterials has been fuelled by the groundbreaking technological possibilities they offer. Among these, the prospect of near-