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Parameters determining efficiency and degradation of $TiO_2|dye|CuI$ solar cells

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Abstract

The influence of the micro-morphological structure of the TiO_2 film, the distribution of CuI in TiO_2 pores and the concentration of added surfactant in the CuI coating solution on the photocurrent of solid-state $TiO_2|dye|CuI$ solar cells was examined by space resolved photocurrent imaging technique. Iodine is found to be competing with the oxidized dye molecules in accepting electrons from CuI and decreases the efficiency of the cell. $TiO_2|dye|CuI$ cell degrade two hundred times faster than wet sensitization cells. This instability is considered to be due to the decomposition of the electron transfer-bridge between the sensitizer and CuI.

Keywords: Porous TiO_2 films; Nano-crystals of CuI; Imaging technique; $TiO_2|dye|CuI$ cells

1. Introduction

During recent years, dye sensitized solid-state cells have been investigated by several groups. *Cis*-Ru^{II} 2,2′-bipyridyl-4,4′ dicarboxyl thiocyante was the most successful sensitizer among tested organic polymers [1], dyes and inorganic compounds [2–8]. In these devices, the excited sensitizer injects electrons into the conduction band of an n-type semiconductor and holes into the valance band of a p-type semiconductor [1–7] or organic hole-conductor [8] thus generating a photo-voltage and photocurrent. The reported maximum value for the power conversion efficiency of this type solar cell is about 4% [9] and less than that obtained for wet nano-structured dye sensitization cells (Grätzel cells).

In the present work, the influence of physical and chemical parameters on photocurrent and the stability of $TiO_2|dye|CuI$ solar cells is visualized by space resolved photocurrent-imaging techniques [10,11] that provide a broad range of information by giving amplitude or/and patterns of photocurrent, photo-voltage and fill-factor down to microscopic dimensions and additionally permit combinatorial approaches.

2. Experiments

A mixture of 15 mL of $Ti[(CH_3)_2CHO]_4$ (Aldrich), 17 mL of glacial acetic acid and 30 mL of 2 propanol was hydrolyzed by adding 10 mL of water drop wise under vigorous stirring at room temperature. Two grams of TiO_2 powder (P-25, Degussa) were added to the above suspension and were allowed to be stirred overnight. TiO_2 films were prepared by applying a small amount of this colloidal TiO_2 suspension on preheated (~150°C) fluorine doped tin oxide coated glass plates (FTO). Loosely bonded TiO_2 crusts were removed by wiping with cotton wool. The resulting TiO_2 film was baked at 450°C for 30 min. This procedure was repeated until the thickness of the TiO_2 film reached ~5 μm. A thin layer of MgO was coated on some of those TiO_2 electrodes by immersing them in $MgC_4H_6O_4$ solution (10^{-5} M in methanol) for 6 h and then sintering in air at 450°C for 30 min [12]. The dye (*cis*-Ru^{II} 2,2′-bipyridyl-4,4′ dicarboxyl thiocyanate, Solaronix) was coated onto the bare and MgO covered TiO_2 electrodes by boiling them in a dye solution (2×10^{-3} M in ethanol) under a moderate temperature.

CuI was coated onto $dye|TiO_2$ electrodes as follows: a saturated solution of CuI (Wako-Japan, Cerac-USA and Merck-Europe) was prepared by dissolving 1.2 g of CuI powder in 20 mL of acetonitrile and separating the

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filtrate. A small amount of triethylamine hydrothiocyanate was added to the filtrate. This solution was carefully spread onto the pre-heated (~150°C) dye coated TiO_2 electrode until the sheet resistance of the CuI film reached less than 100 Ω cm. The cross sections of TiO_2|dye|CuI electrodes were examined with a scanning electron microscope (JEOL). The TiO_2|dye|CuI cell was fabricated by pressing a FTO (or Pt coated FTO) glass plate on the electrode as the back contact. Current–voltage characteristics of TiO_2|dye|CuI cells were measured under AM 1.5 conditions.

2.1. Characterization of CuI and TiO_2 films by time-resolved microwave conductivity (TRMC) technique

CuI and TiO_2 films were excited (front side illumination: excitation through air|sample interface, backside illumination: excitation through substrate|sample interface) with a focused laser beam (Nd:YAG—wavelength 266 nm, pulse width 20 ns) with the photon energy exceeding the band gap of the sample material while conducting microwaves (8–12.5 GHz) to the samples. The transients of reflected microwaves from the samples were measured as described in Refs. [13,14].

2.2. Characterization of CuI|dye|TiO_2 cells by space resolved photocurrent-imaging technique

A focused and chopped circular light beam (He–Ne laser, diameter 200 μm, wavelength 632 nm) was used to scan the cell. The intensity of the light spot on the cell was maintained not to exceed the solar intensity (1000 W m^{-2}) by using neutral filters. The amplitude of the photocurrent at every point of the cell was measured using lock-in-technique and was converted as an image (software used: I-Tiffer). The experimental setup of photocurrent-imaging technique is explained in Ref. [11].

3. Results and discussion

Fig. 1 illustrates the decay of microwave photoconductivity of (a) a CuI film under front side illumination, (b) a TiO_2 film under front side illumination and (c) a TiO_2 film under backside illumination. The TRMC signal from the CuI film decays to 30% within 10 μs and the remaining signal decays with a much slower rate, under front side illumination (curve a). The band-to-band relaxation of photo-generated electrons and holes is attributed to the fast decay of the signal and recombination of charge carriers via trap states is responsible for the observed comparatively slow subsequent decay [13]. As is shown in curve b, a slower decay of the TRMC signal (50% of the signal decay within the first 50 μs) is observed for the TiO_2 films compared to the CuI films, under front side illumination. However, TiO_2 films exhibited a faster decay of the TRMC signal under backside illumination (curve c) compared to front side illumination indicating that the defect centers are not uniformly distributed in the TiO_2 films. We were unable to measure the decay of TRMC signal from CuI films under backside illumination. Ultra-fast recombination of photo-generated electrons and holes in the CuI film at the substrate|sample interface might be one of the reasons.

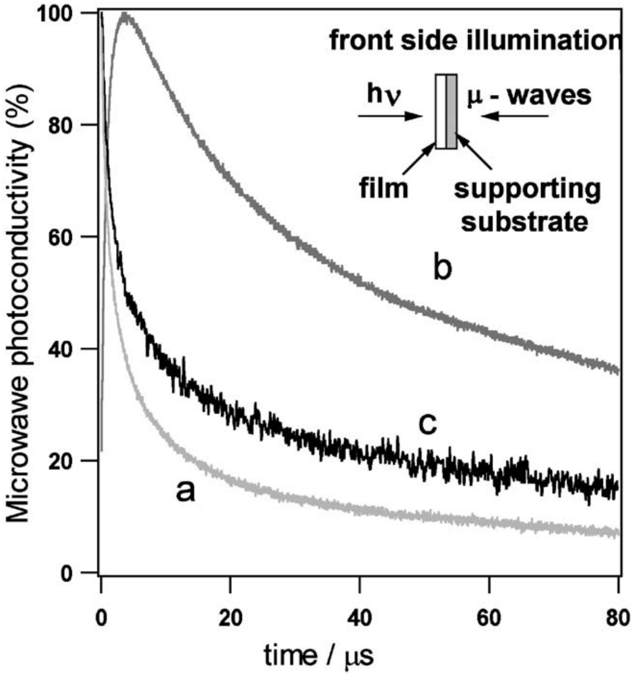


Fig. 1. The normalized transient microwave photoconductivity of (a) CuI film (CuI|glass) under front side illumination, (b) TiO_2 film (TiO_2|SnO_2|glass) under front side illumination and (c) TiO_2 film (TiO_2|SnO_2|glass) under backside illumination.

3.1. Influence of parameters on the photocurrent generation of a TiO_2|dye|CuI cell

Photo-effects of the cell were studied by illuminating the cell alternatively through the TiO_2 and CuI film. A high photocurrent was observed when the cell is irradiated through the TiO_2 film compare to irradiation through the CuI film. This may be due to the presence of electronic transitions and trap states in different densities in the TiO_2 and CuI films. Thin layer cells of other materials described in the literature exhibited similar asymmetric photocurrent generation under front and back modes of illumination [15]. The inhomogeneous photocurrent generation of TiO_2|dye|CuI cells has already been reported [16]. For a better understanding, we have measured the photocurrent images for a series of TiO_2|dye|CuI cells (Fig. 2) and found for intentionally prepared inhomogeneous cells that the thickness of

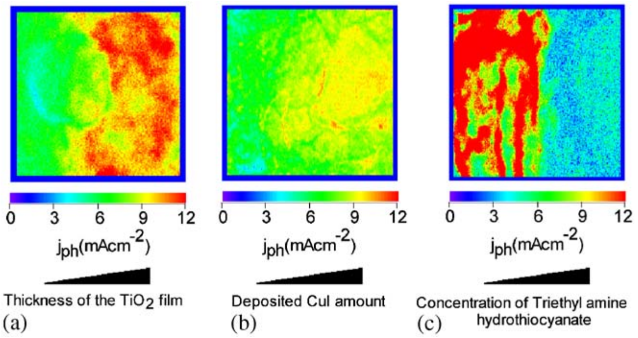


Fig. 2. Photocurrent images for CuI|dye|TiO_2 cells prepared by changing physical parameters (a) thickness of the TiO_2 layer (b) deposited amount of CuI on the dyed TiO_2 layer and (c) concentration of crystal growth inhibitor in CuI suspension. The area of the cell is 1.1 cm^2.

the TiO_2 film, the amount of CuI on the dyed TiO_2 electrode and the concentration of the surfactant in the CuI solution influence the photocurrent generation of the cell. The morphology of the cross section of the cells was studied to verify these observations. The Scanning electron micrograph (SEM) image of the cross section of the TiO_2 film used to prepare the cell corresponding to image **a** (in Fig. 2) is shown as Fig 3(a). The observed inhomogeneous photocurrent generation of this cell is mainly due to a difference in the amount of adsorbed dye molecules on the TiO_2 electrode caused by inhomogeneous distribution of porous TiO_2 film thickness. A photocurrent-image for a cell prepared by changing amounts of deposited CuI on the dyed TiO_2 electrode is shown as image b in Fig. 2. The cross sectional view of an area that corresponds to the left side of this image is shown as image b in Fig. 3. Incomplete pore filling of dyed TiO_2 by CuI is observed. Insufficient contact between CuI and dyed TiO_2 electrode is a reason for the observed low photocurrent of the cell. The cross sectional view of a place corresponding to the right side of the image b (in Fig. 2) is shown as image c in Fig. 3. More complete filling of dyed TiO_2 film by CuI and thereby, higher photocurrent was observed in the right side of the cell compared to the left side. The effect of the concentration of the surfactant in the CuI suspension was also studied. The photocurrent-image of a TiO_2|dye|CuI cell prepared by varying the concentration of the surfactant in the CuI solution is shown as Fig. 2(c). The used surfactant exhibits high viscosity and low conductivity at room temperature [17]. Accumulation of excess non-conducting phases in the CuI film blocks the charge transfer process between CuI and dye molecules and is correlated with the observed poor performance in the right side of image c in Fig. 2. The cross sectional view of such a location is shown as image d in Fig. 3. The dark areas in the CuI layer (images c and d) are due to accumulation of trace amounts of non-conducting phases (surfactant) in the CuI film. The uniformly distributed thin layer in between TiO_2 and the glass substrate (images b, c and d, Fig. 3) is fluorine doped tin oxide.

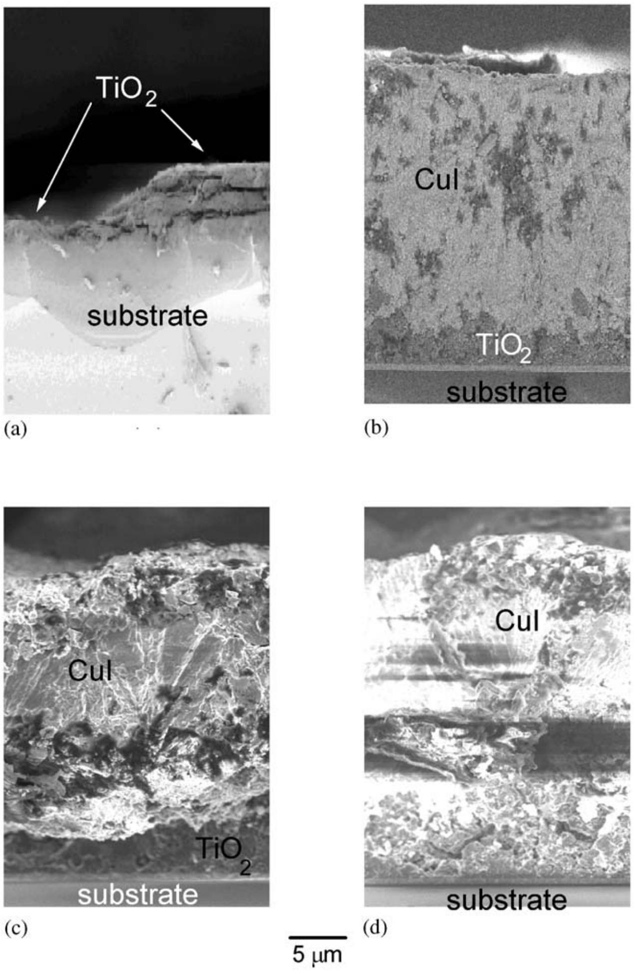


Fig. 3. (a) Cross sectional view of the TiO_2 layer corresponding to image a in Fig. 2. Cross sectional view for CuI|dye|TiO_2 cell corresponds to a place with (b) low current density of the image b, (c) high current density of the image b and (d) a low current density of the image c; in Fig. 2.

Charge generation in this type of cells takes place via several intermediate steps [3,5] and can be summarized as Eq. (1), where D indicates dye molecules.

$$D + h\nu \rightarrow D + e^-(TiO_2) + h^+(CuI). \qquad (1)$$

The power output characteristics of TiO_2|dye|CuI cells prepared by using CuI obtained from different sources are shown in Fig. 4. Approximately a three times higher photocurrent was observed for the cells prepared by using CuI powder obtained from Wako-Japan compared to the other samples tested in the present work. In order to understand this effect the absorption spectra of CuI in acetonitrile were measured. Fig. 5(A) illustrates the absorption spectrum of CuI (in acetonitrile) as obtained for the different samples: (a) Wako-Japan, (b) Cerac-USA, and (c) Merck-Europe. In addition, a shift

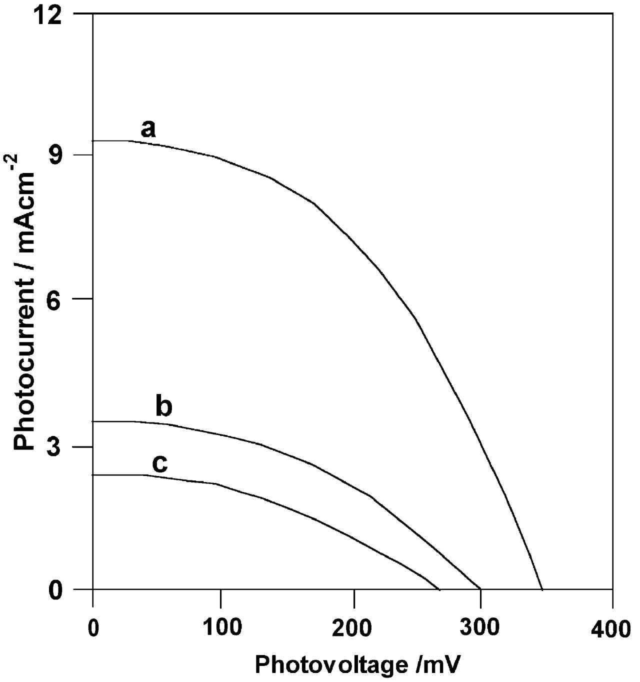
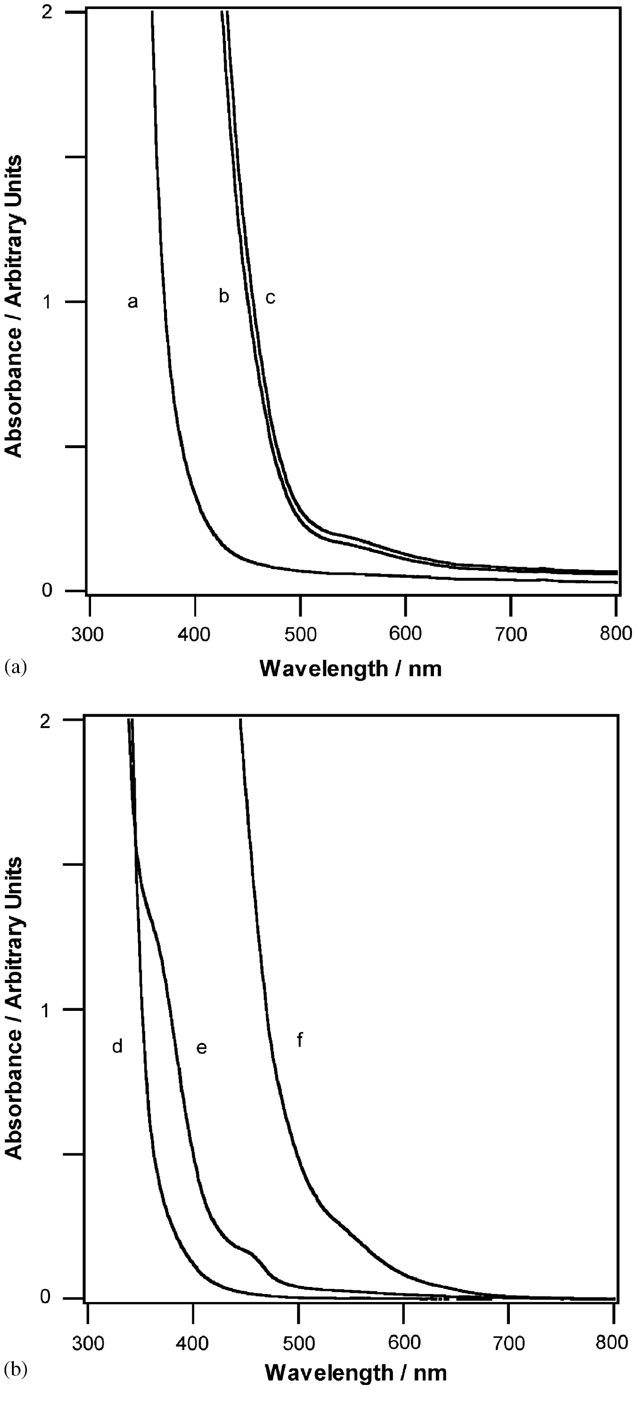


Fig. 4. Current–voltage characteristics of CuI|dye|TiO_2 cells prepared by using CuI obtained from different sources (a) Wako-Japan (b) Cerac-USA and (c) Merck-Europe.

of the absorption onset towards longer wavelengths was observed while aging these solutions. For example, the change of absorbance of the CuI solution with time observed for samples from Wako, Japan, is shown in Fig. 5(B). A release of iodine form CuI is the obvious reason for the observed different onsets in the absorption spectra (Fig. 5). The photocurrent-image for a TiO_2|dye|CuI cell prepared by using freshly prepared and aged CuI solution (2 months, right image) are shown in Fig. 6(a). As is seen, a clear drop in the photocurrent is observed due to the presence of excess iodine in the CuI film. Similar results were observed in the current–voltage characteristics measured for the same cells (results are not shown here). Addition of iodine leads to a significant decrease of photocurrent efficiency. Excess iodine makes traps in the CuI film [18] and apparently competes with the oxidized dye for accepting electrons from the CuI. Thereby, the photocurrent of the cell decreases by a factor of 2–4. Deposition of a thin layer (several angstroms) of wide band gap semiconductor such as ZnO (MgO, Al_2O_3) on the TiO_2 (SnO_2) film is known to improve the stability and the open circuit voltage of the cell [9,12,19]. A TiO_2|dye|CuI cell was prepared by using a TiO_2 film whose one part is chemically treated with MgO. An image of this cell is shown as Fig. 6(b). The observed decrease of the photocurrent (on the right side of Fig. 5b) of the chemically (MgO) treated portion may be due to suppression of injections of electrons from the excited dye molecules. A photocurrent image for a CuI|dye|TiO_2 cell prepared by using different dyes is shown in Fig. 6(c). A higher photocurrent was observed for the part sensitized from *cis*-Ru^{II} 2,2′-bipyridyl-4,4′ dicarboxyl thiocyanate (left side of the image) compared to that sensitized by pyrogallol red. These results (Fig. 6) clearly indicate that the interfacial properties at the



(a)

(b)

Fig. 5. (A) Absorption spectra for CuI powder obtained from different sources (a) Wako-Japan, (b) Merck-Europe and (c) Cerac-USA in acetonitrile at a constant concentration ($5 \times 10^{-2}\,g\,mL^{-1}$) as prepared. (B) Change of the absorption properties of CuI (Wako-Japan) in acetonitrile ($5 \times 10^{-2}\,g\,mL^{-1}$) with time (d) as prepared, (e) after one week and (f) after 2 months.

TiO_2–CuI interface (trap levels formed due to iodine, impurities and nature of bonds between sensitizer and TiO_2 film) play a major role in the generation of photocurrent in CuI|dye|TiO_2 cells.

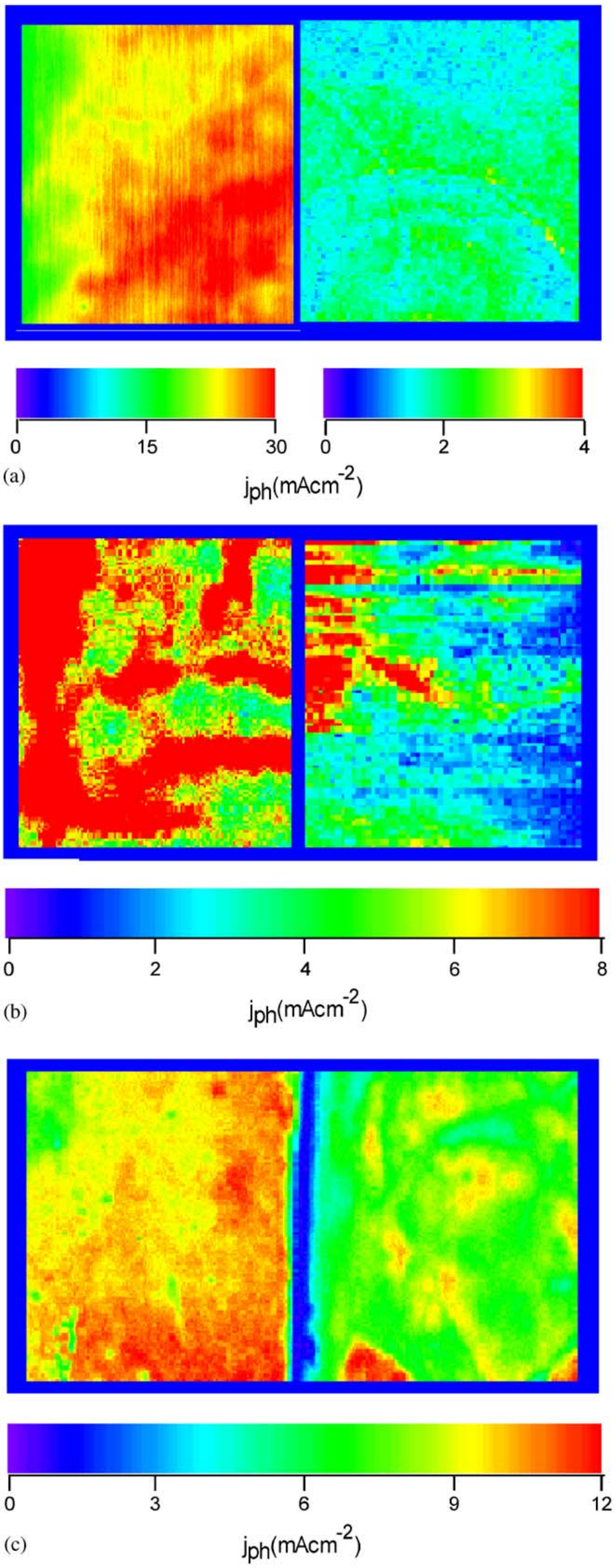


Fig. 6. Photocurrent-images for CuI|dye|TiO_2 cells prepared by using (a) aged CuI (Wako-Japan) solution: the right side of the image corresponds the freshly prepared CuI solution, (b) chemically treated (MgO coated) TiO_2 film: the left side of the image corresponds the TiO_2 film without any chemical treatment. (c) Photocurrent-image of a CuI|dye|TiO_2 cell prepared by using different dyes. *Cis*-Ru^{II} 2,2′-bipyridyl-4,4′ dicarboxyl thiocyanate, Pyrogallol red were used to sensitize the left and right sides of the cell, respectively.

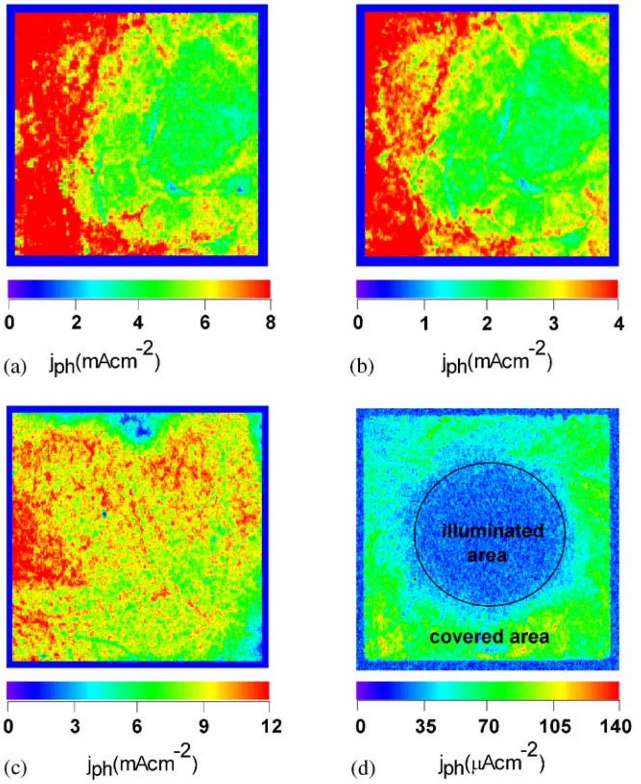


Fig. 7. Photocurrent-images for a CuI|dye|TiO_2 cell (a) as prepared and (b) after 2 weeks (kept at dark). Photocurrent-images for a CuI|dye|TiO_2 cell after exposing to the simulated white light (intensity $1100\,W\,m^{-2}$) for different illumination lengths (c) as prepared and (d) 72 h.

3.2. Photo-degradation of the cell

As a control experiment dark stability of a CuI|dye|TiO_2 cell was investigated first. Photocurrent images of the CuI|dye|TiO_2 cell (a) as prepared and (b) after two weeks in the dark are shown in Fig. 7. As shown, no significant changes in the pattern of photocurrent generation of the CuI|dye|TiO_2 cell were observed after two weeks. However, in the dark, the CuI|dye|TiO_2 cell exhibited a slow degradation of less than 5% per day. The photo-stability of the CuI|dye|TiO_2 cell was studied by illumination with simulated white light through a mask that permits a circular light spot on the surface of the cell. Photocurrent images for a similar CuI|dye|TiO_2 cell for different illumination lengths are also shown in Fig. 7, (c) as prepared and (d) after exposing it for 72 h to white light through a circular diaphragm. As

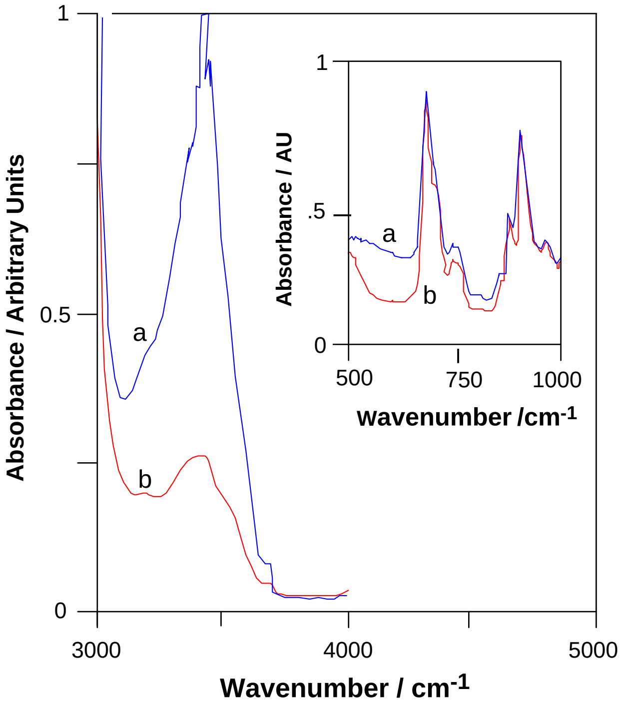


Fig. 8. The FTIR spectrum of triethylamine hydrothiocyanate (a) as prepared and (b) after 2 months.

observed the current degraded within 72 h by more than 90%. The observed degradation is much faster than that in the dark. Therefore, the observed marked degradation is clearly due to a photo-effect. A decay of the photocurrent of this type of cells was also observed in the presence of moisture and air [20]. Degradation of dye attached to TiO_2 film, formation of Cu_2O or/and CuO are other tentative explanations for the degradation of the cell. However, we were not able to detect formation of Cu_2O or CuO on the CuI film after exposing the cell to white light for a longer period [16]. To gain a better understanding of mechanisms, we have deposited CuI (treated with of triethylamine hydrothiocyanate) again on the cell after it was almost degraded (~90%). A new rise of the photocurrent to a 33% lower value than under starting illumination of the cell was observed. Then the dye from this electrode was extracted with an alcoholic solution. No significant change in the absorbance (in IR region) was observed for this solution compared to a freshly prepared dye solution. It was found that, *cis*-Ru^{II} 2,2′-bipyridyl-4,4′ dicarboxyl thiocyanate exhibits an extended stability for several months to a few years under comparable conditions in wet dye sensitization cells [10,11]. In solid state TiO_2/dye/CuI solar cells, however, in addition to the fast degradation of photocurrent in the illuminated area a significant change in the pattern of photocurrent generation is also observed in the covered (dark) area. Degradation in dark area can only be the consequence of electrons injected into TiO_2 by the sensitizer, which migrate away from the illuminated area to induce degradation in the dark area. The FTIR spectrum of triethylamine hydrothiocyanate (a) as prepared and (b) after 2 months is shown in Fig. 8. As is seen the vibrations corresponding to N-H and C-S bonds (around 3500 and 600 cm^{-1}) decrease while triethylamine hydrothiocyanate is aging. This may be due to elimination of H_2S from the hydrothiocyanate which is critically needed as an electron bridge for a reasonable performance of this type of solar cell. Such changes in triethylamine hydrothiocyanate are the most probable reason for the observed degradation both in the dark and under illumination. More research is needed to determine the precise mechanism and to identify the products of photo-degradation.

4. Conclusion

The photocurrent generation in TiO_2|dye|CuI cells is mainly determined by the micro-morphological structure of TiO_2 film, the distribution of CuI in TiO_2 pores and the concentration of the surfactant triethylamine hydrothiocyanate added to the CuI coating solution. Iodine is found to compete with the oxidized dye molecules in accepting electrons from CuI and decreases the performance of the cell. The instability problem of the cell is considered as the gradual braking of the hydrothiocyanate electron transfer-bridge supporting electron transport between CuI and the sensitizer.

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