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Generation of inhomogeneous photocurrent in solid-state TiO₂|dye|CuI cells and effect of ligands attached to surfactant on morphology of CuI films

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Abstract

Microwave conductivity is observed in TiO_2 and CuI films at room temperature. Organic dye pyrogallor red is found to sensitize TiO_2 and CuI in solid-state $TiO_2|dye|CuI$ cells. Effect of ligands attached to crystal growth inhibitors on morphology of CuI films is studied. A weaker crystal growth inhibition was observed when size of ligands attached to surfactant is increased. Reasonable explanations are given for observed inhomogeneous photocurrent and its degradation under illumination. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Tripropylamine hydrothiocyanate; Pyrogallor red; Solid-state solar cell

1. Introduction

Dye sensitized solar cells with power conversion efficiency over 10% were fabricated in last few decades (O'Regan and Graetzel, 1991; Nazeerudin et al., 1993). Unfortunately, these systems are pledged with several technological disadvantages (Tennakone et al., 1999a,b). Solidstate TiO₂|dye|CuI cells were able to overcome some of those technical hurdles. However, efficiencies of this type of cells are less than that observed for wet type dye sensitized solar cells. The morphologies of TiO₂ and CuI films play an important role in this type of solar cells. So far, only a few sensitizers (dyes, semiconductors or natural pigments) have been identified that inject photogenerated electrons into the conduction band of TiO₂ and holes into the valance band of CuI in TiO₂|dye|CuI cells (Sirimanne et al., 2002, 2006; Tennakone et al., 1998). We have studied photoproperties of solid-state cells prepared by using organic dye pyrogallol red (PGR). The ligands attached to the crystal growth inhibitor are found to influence the photocurrent of TiO₂|dye|CuI solid-state cells. Inhomogeneous photocurrent generation is observed in the cell and a reasonable mechanism is proposed for the degradation of the cell.

2. Experimental

Two grams of TiO₂ powder (P-25 Degussa, Japan) was added to hydrolyzed titanium isopropoxide solution under vigorous stirring and was allowed to be stirred overnight (Sirimanne et al., 2002). TiO₂ films were prepared by applying a small amount of this TiO₂ colloidal suspension on preheated (~150 °C) fluorine doped tin oxide (FTO) coated glass plates and were baked at 450 °C min for 30 min. This procedure was repeated until the film thickness reached ~5 µm. PGR was coated on TiO₂ films by boiling them in a solution of dye (10^{-3} M) in ethanol. TiO₂|dye|CuI

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electrodes were fabricated by spreading a small amount of CuI (1.2 g of in 20 mL of acetonitrile) on preheated $(\sim 150 \text{ °C})$ dve coated TiO₂ electrodes. Different kinds of molten salts have been identified as crystal growth inhibitors for deposition of CuI by acetonitrile (Kumara et al., 2002; Sirimanne et al., 2002). We have checked capability of utilization of tripropylamine hydrothiocyanate as crystal growth inhibitor to deposit CuI. Fabrication of cell was completed by attaching a platinum coated FTO glass plate on the electrode as the back contact. The pattern of photocurrent generation of the cell was studied by using the photocurrent-imaging technique. In this technique the amplitude of the photocurrent at every point of the cell is measured using lock-in technique and is converted (software used: I-Tiffer) as an image (Turrion et al., 1999; Macht et al., 2002). A focused He-Ne (632 nm) laser beam was used to scan the cell. The intensity of the laser beam was maintained not to exceed the solar intensity $(100 \text{ mW cm}^{-2}).$

In addition CuI and TiO₂ films were excited through the air|film (front wall mode illumination) interface with a forced laser beam (Nd:YAG wavelength of 266 nm, pulse with of 20 ns) with the photon energy exceeding the band gap of the sample while directing microwave radiation (8–12 GHz) to the sample. Transient of reflected microwave conductivity signal was measured. More details of this technique have been described elsewhere (Kunst and Beck, 1986).

3. Results and discussion

TiO₂ and CuI films exhibit microwave conductivity at room temperature. Transient of microwave-photoconductivity (TRMC) of (a) CuI and (b) TiO₂ films are shown in Fig. 1. The observed TRMC signal from CuI films decays to 30% within 10 μ s and the remaining signal decaying at a much slower rate. However, TiO₂ films exhibited a higher microwave-photoconductivity with a long life time. The observed fast decay in microwave conductivity is correlated with band to band relaxation of electrons and slower decay is due to recombination of electrons and holes in traps formed due to occurrence of metal ions in the films. It is known that morphology of CuI and TiO₂ films changes with the preparation technique. However, we did



Fig. 1. Transient of microwave-photoconductivity of (a) CuI and (b) TiO_2 films (on glass substrates), under front wall mode illumination.

not observe much influence on microwave photoconductivity of these films due to change of morphology. Scanning electron micrographs of TiO₂ films prepared (a) in absence and (b) in presence of P-25 TiO₂ powder in the coating solution are shown in Fig. 2. As is observed, a well separation of TiO₂ grains was observed in absence of P-25 TiO₂ powder. However, an interconnected network of large grains surrounded by fine TiO₂ particles was observed in the presence of P-25 TiO₂ powder in the coating solution.

Absorption spectra for PGR solutions (in ethanol) with different concentrations are shown in Fig. 3, (a) 1×10^{-3} M, (b) 5×10^{-5} M and (c) 1×10^{-6} M. As is observed, PGR solutions with a higher concentration than 10^{-3} M exhibit an absorption maximum at 478 nm (curve a) whereas, PGR solutions with a lower concentration than 10^{-5} M exhibit an absorption maximum at 555 nm (curve c). It is known that electrostatic and hydrophobic interactions result self-aggregation of dye molecules in liquids, polymers etc. (Khazraji et al., 1999; Nuesch and Graetzel, 1995). Therefore, observed difference in absorption spectra may be due to self-aggregation of PGR molecules in ethanol. As is observed, aggregation shifts maximum of the



Fig. 2. Morphology of TiO_2 films (a) in the absence and (b) in the presence of P-25 powder.



Fig. 3. Absorption spectra of PGR for different concentrations (a) 1×10^{-3} M, (b) 5×10^{-5} M, (c) 1×10^{-6} M (in ethanol) and (d) 1×10^{-5} M in acetonitrile.

absorption band toward shorter wavelengths. Therefore, absorption bands with maxima at 555 and 478 nm are correlated to monomers and aggregates of dye molecules. In addition, equilibrium between monomers and aggregates was also observed in moderate concentrations (curve b). However, such a split or shift in the absorption band was not observed by diluting PGR by acetonitrile (curve d). Probably PGR molecules behave as aggregates in acetonitrile.

Photoactive CuI|PGR|TiO₂ electrodes were prepared by depositing CuI on sensitized TiO₂ films. Molten salts methyl-3ethyl imidazolium thiocyanate and triethylamine hydrothiocyanate are known as crystal growth inhibitors in preparation of CuI films by acetonitrile. These molten salts exhibited similar properties in preparation of CuI films (Kumara et al., 2002; Sirimanne et al., 2002). The capability of usage of other compounds as crystal growth inhibitors is also studied. We have prepared similar compounds by substituting ethyl group of these molten salts from propyl group. Morphologies of CuI films prepared by using different molten salts are shown in Fig. 4, (a) triethylamine hydrothiocvanate. (b) tripropylamine hydrothiocyanate and (c) in absence of any surfactant. As is shown CuI films exhibit different crystallographic phases in absence of any crystal growth inhibitors, in the CuI coating solution. However, a clear crystal growth inhibition was observed in the presence of surfactant. Molten salts used in the present study are composed with different substitution groups. Therefore, CuI molecules covered by different surfactants occupy different volumes in the space. This may be a reason for observed difference in the crystal growth inhibition (images a and b) and penetration depths of CuI in porous TiO₂ matrix (not shown in the text) in the presence of different kinds of surfactants in the CuI coating solution. Among tested molten salts triethylamine hydroth-



Fig. 4. Morphology of CuI films prepared by adding different surfactants (a) triethylamine hydrothiocyanate, (b) tripropylamine hydrothiocyanate and (c) without surfactant.

iocyanate exhibits excellent properties in $CuI|dye|TiO_2$ cells. Therefore, we have used triethylamine hydrothiocyanate as a crystal growth inhibitor to study properties of $CuI|PGR|TiO_2$ cells.

Incident photon-to-current conversion efficiency (IPCE) spectra of CuI|PGR|TiO₂ a cell under (a) front wall mode (illumination through TiO_2 layer) and (b) back wall mode (illumination through CuI layer) are shown in Fig. 5. Approximately, three times enhanced IPCE was observed under front wall mode illumination compared to back wall mode illumination. The maximum IPCE of 46% is observed for CuI|PGR|TiO₂ cells. We have compared this result with similar type of cells prepared by using other dyes. Dyes composed with SCN ligands produces much higher photocurrent than compared to that of those lacking with CNS groups in this type of cells. For example, highest IPCE over 65% is achieved for cis-dithiocyanatebis(2,2'-bipyridyl 4-4'dicarboxylate) ruthenium (II) (Sirimanne et al., 2002). Probably formation of S-S bridges between the dye molecules and molten salts may be a reason for the efficient charge transfer process between CuI and TiO₂ via formation of electron transfer bridges.



Fig. 5. IPCE spectrum of $CuI|PGR|TiO_2$ cell under (a) front wall mode, (b) back wall mode.

Pattern of current generation of CuI|PGR|TiO₂ cells is visualized from photocurrent imaging technique. The photocurrent image of a solid-state CuI|PGR|TiO₂ cell is shown in Fig. 6(a). As is shown, inhomogeneous photocurrent generation was observed. Generation of inhomogeneous photocurrent is a peculiar property of this type of solid-state cells and is due to morphological changes in the TiO₂, CuI films and inappropriate contact between CuI and TiO₂ grains. The current-distance profile of the cell along the horizontal geometrical symmetrical axis is also shown in Fig. 6(b). A fairly homogeneous photocurrent was observed for electrolyte|dye|TiO₂ cells (Turrion et al., 1999; Macht et al., 2002). The stability of the CuI|PGR|TiO₂ solid-state cell is also studied. This type of solar cells exhibited a slow degradation of less than 5% per day in the dark and much faster degradation under illumination (Sirimanne et al., 2003). We have again deposited CuI on the cell after it had degraded nearly completely $(\sim 90\%)$. During this treatment a drop of CuI suspension is deposited onto the cell while the back contact is removed. A rise in the photocurrent was observed. The obtained maximum photocurrent was $\sim 30\%$ less than to that under first illumination. Formation of new bonds between CuI and dyed TiO₂ grains is assumed as the reason for the regeneration of the cell. Therefore, a break up of the bridge between CuI and dyed-TiO₂ grains is one of the most reasonable explanations for the degradation of the cell as no signs of an oxidative change of CuI and the used dye were observed, under illumination (Sirimanne et al., 2003). Turnover of triethylamine hydrothiocyanate can be proposed as follows:

$$(C_2H_5)_3NHCNS + e^- \rightarrow (C_2H_5)_3NH + CNS^-$$
(1)

Compounds with thiocyanate ligands exhibit similar decomposition at potential close to the conduction band of TiO_2 (Lide, 2001–2002). The reaction of



Fig. 6. (a) Pattern of current generation in $CuI|PGR|TiO_2$ cell and (b) current-distance profile of the cell along the horizontal geometrical symmetrical axis.

AgSCN + e⁻ \leftrightarrow Ag + SCN⁻ at $E_0 = 0.0895$ V (SHE) is a well known example. Electrons injected into TiO₂ may either be collected to drive the solar cell or they may be engaged in a reverse reaction which destroys the SCN bridge between CuI and the sensitizer. As the cell operates under light, more and more SCN bridges are obviously destroyed in a reverse reaction. In this way such a solid-state dye sensitization cell photodegradates much faster than a liquid one in which the sensitizer is regenerated via the I^-/I_3^- redox couple. Recently more extended stability of the cell was achieved by covering TiO₂ grains by a thin ZnO layer (Meng et al., 2003). Apparently, confinement of electrons in the TiO₂ grains covered by a thin ZnO layer reduces the decomposition rate of the surfactant via the reverse reaction (Eq. (1)).

4. Conclusion

Two channels of recombination of electrons and holes are observed in CuI and TiO₂ films. Photocurrent generation takes place via H-aggregated pyrogallor red molecules in the TiO₂|PGR|CuI cells. Ligands attached to the molten salts are one of the key parameters determining the cell performance. The performance of the cell could be further improved by understanding the bridge between CuI and TiO₂.

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