

Stability improvement of solid-state dye-sensitized photovoltaic cell by adding imidazolium thiocyanate to copper iodide p-type semiconductor layer

Akinori Konno,[†] G. R. Asoka Kumara,[†] and Kirithi Tennakone[‡]

[†]Faculty of Engineering, Shizuoka University,
3-5-1 Johoku, Hamamatsu, 432-8561 Japan.

[‡]Institute of Fundamental Studies,
Hantana road, Kandy, Sri Lanka.

A promising and cheaper alternative to the silicon solar cell, is the dye-sensitized photoelectrochemical cell made from nano-porous TiO₂ devised by Grätzel et al.¹ Although DS photoelectrochemical cells (PECs) with viable efficiencies have been demonstrated, achieving good stability remain unresolved. The ideal dye-sensitized solar cell should be a fully solid-state device where the liquid is replaced by a solid hole-conductor (ie., p-type semiconductor). The dye-sensitized solid-state solar cell (DSSSC) is a heterostructure where a pigment layer is sandwiched between n and p-type semiconductor. Tennakone et al. have developed a solid-state DS cells using p-CuI as the hole-conductor and TiO₂ films deposited on CTO glass as the n-type electrodes (Figure 1).² Unfortunately the DSSSCs reported so far either deliver small photocurrents or found to be highly unstable. The essential requirement of filling the pores of the nanocrystalline n-type film (TiO₂) with a holecollector to form stable and firm contacts with the dyed surface greatly restricts the fabrication processes of DSSSCs.

Of the hole collectors tested, p-CuI which can be deposited from a solution in acetonitrile gives the highest energy conversion efficiency. However CuI based DSSSCs do not remain stable, i.e., both the short-circuit photocurrent (I_{sc}) and the open-circuit voltage (V_{oc}) undergo rapid decay. Even storage in dark deteriorate the cell. The cause of instability seems to be loosening of the contact between dyed TiO₂ surface and CuI crystallites. CuI deposited from the acetonitrile solution produce large (~10 nm) crystallites which do not penetrate into the pores of the nanocrystalline matrix and forms loose contacts (Figure 2a). Smaller crystallites formed inside the pores grow and disrupt the film. It has been found that the stability of the CuI based DSSSC can be greatly improved by incorporation of a small quantity (~10⁻⁴ M) of the molten salt 1-methyl-3-ethyl-imidazolium thiocyanate (MEISCN) to the coating solution (i.e, CuI in acetonitrile) (Figure 2b). In this paper, we show that MEISCN acts as a CuI crystal growth inhibitor and at the same time the thin film of this compound remaining at the CuI grain boundaries or between CuI and the dyed TiO₂ interface seems to admit hole conductance. The mechanism of crystal growth inhibition by MEISCN and other thiocyanate molten salts will be explained. DS solar cells made by the above method have improved stability and an efficiency of ~ 3.5% under AM 1.5 (1000Wm⁻²) illumination (Figure 3).

References

1. B. O'Regan and M. Grätzel, *Nature*, **1991**, 353, 737;
A. Hagfeldt, M. Grätzel, *Acc. Chem. Res.*, **2000**, 33, 269.
2. K.Tennakone, G.R.R.A. Kumara, et al., *Semicond. Sci. Technol.* **1995**,10, 1689.; K.Tennakone, G.R.R.A. Kumara, et al., *Semicond. Sci. Technol.* **1996**, 11, 1737.; K.Tennakone, G.R.R.A.Kumara, et al., *J. Phys. D: Appl. Phys.* **1998**, 31, 1492.

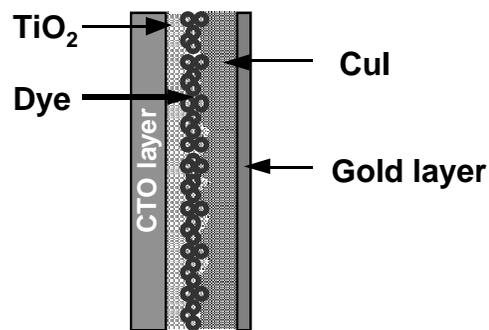


Figure 1. Schematic structure of TiO₂/Dye/CuI cell.

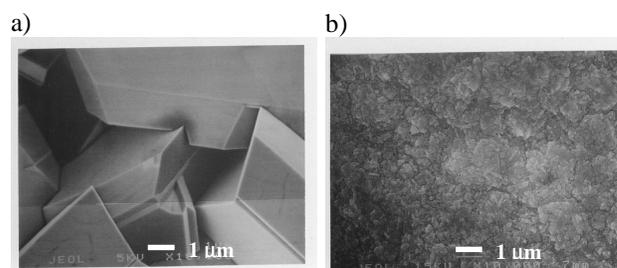


Figure 2. SEM photographs of CuI deposited from acetonitrile solution (a) in the absence of a crystal growth inhibitor, (b) in the presence of the crystal growth inhibitor, i.e., 9 x 10⁻⁴ M MEISCN.

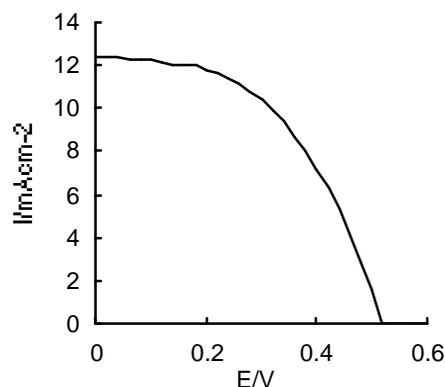


Figure 3. I-V characteristics of TiO₂/Dye/CuI cell.