

## Dye-Sensitized Solid-State Solar Cells: Use of Crystal Growth Inhibitors for Deposition of the Hole Collector

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The dye-sensitized solid-state solar cell (DSSSC) is a promising alternative to the well-known Gratzel's photoelectrochemical cell.<sup>1,2</sup> In these devices charge separation and transport are entirely electronic and therefore in principle any chemical irreversibility originating from ionic discharge and formation of active species (i.e., OH<sup>-</sup> if the electrolyte is contaminated with water) does not exist. Unfortunately, the DSSSCs reported so far either deliver small photocurrents or are found to be highly unstable.<sup>3–12</sup> The essential requirement of filling the pores of the nanocrystalline n-type film (TiO<sub>2</sub>) with a hole collector 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; that is, the short-circuit photocurrent (I<sub>sc</sub>) and the open-circuit voltage (V<sub>oc</sub>) both undergo rapid decay. Even storage in dark deteriorates the cell. The cause of instability seems to be loosening of the contact between the dyed TiO<sub>2</sub> surface and CuI crystallites. CuI deposited from the acetonitrile solution produces large (≈10 μm) crystallites

**Table 1.** I<sub>sc</sub>, V<sub>oc</sub>, and η of the Cells after Preparation and Storage for 10 Days<sup>a</sup>

	I <sub>sc</sub> (mA cm <sup>-2</sup> )	V <sub>oc</sub> (mV)	η (%)
cell 1			
initially	9.3	516	3.0
after 10 days	6.8	505	2.2
cell 2			
initially	12.0	612	2.9
after 10 days	1.8	260	0.3

<sup>a</sup> (Cell 1) Made by adding  $9 \times 10^{-3}$  M of the crystal growth inhibitor MEISCN to the CuI solution in acetonitrile. (Cell 2) Made by deposition of CuI from acetonitrile solution without a crystal growth inhibitor.

that do not penetrate into the pores of the nanocrystalline matrix and form loose contacts. 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<sup>-3</sup> M) of 1-methyl-3-ethylimidazolium thiocyanate (MEISCN) in the coating solution (i.e., CuI in acetonitrile).<sup>13</sup> In this communication 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 TiO<sub>2</sub> interface seems to admit hole conduction. The mechanism of crystal growth inhibition by MEISCN is also explained.

TiO<sub>2</sub> films were deposited on conducting tin oxide (CTO) glass plates (1 × 1.5 cm<sup>2</sup>, sheet resistance 15 Ω sq<sup>-1</sup>) by the method described in ref 4 and coated with the dye (*cis*-dithiocyanato-bis[2,2'-bipyridyl-4,4'-dicarboxylic acid]ruthenium(II)) following the usual procedure.<sup>2</sup> MEISCN was prepared by double decomposition of 1-methyl-3-ethylimidazolium chloride (MEICl) and AgSCN. The product purified by chromatography confirmed the stoichiometry of MEISCN. Varying amounts of MEISCN were added to the CuI solution (3 g in 100 mL of acetonitrile) and CuI was deposited by drop coating to a constant thickness of ≈6 μm above the TiO<sub>2</sub> surface, which is ≈12-μm thick. A gold-coated CTO glass plate pressed onto the CuI surface was used as the back contact and the stability of cells examined under dark storage and intermittent illumination at one sun conditions. The *I*–*V* characteristics and the incident photon to photocurrent conversion efficiencies (IPCEs) were measured with a solar cell evaluation system (JASCO, CEP-25BX).

The best stability as well as the highest I<sub>sc</sub> were obtained when the MEISCN concentration in the CuI solution was ≈9 × 10<sup>-3</sup> M. A decrease of the MEISCN concentration below the above value reduced the stability, whereas an increase tended to lower the I<sub>sc</sub>. The parameters I<sub>sc</sub>, V<sub>oc</sub>, and η of the cells made by deposition of CuI with and without MEISCN and tested after 10 days are compared in Table 1. The improvement of the stability upon using the crystal growth inhibitor is clearly noticeable. Figure 1 shows the SEM photographs of CuI films deposited in the presence and absence of MEISCN. The molar ratio for MEISCN/CuI of ≈6 ×

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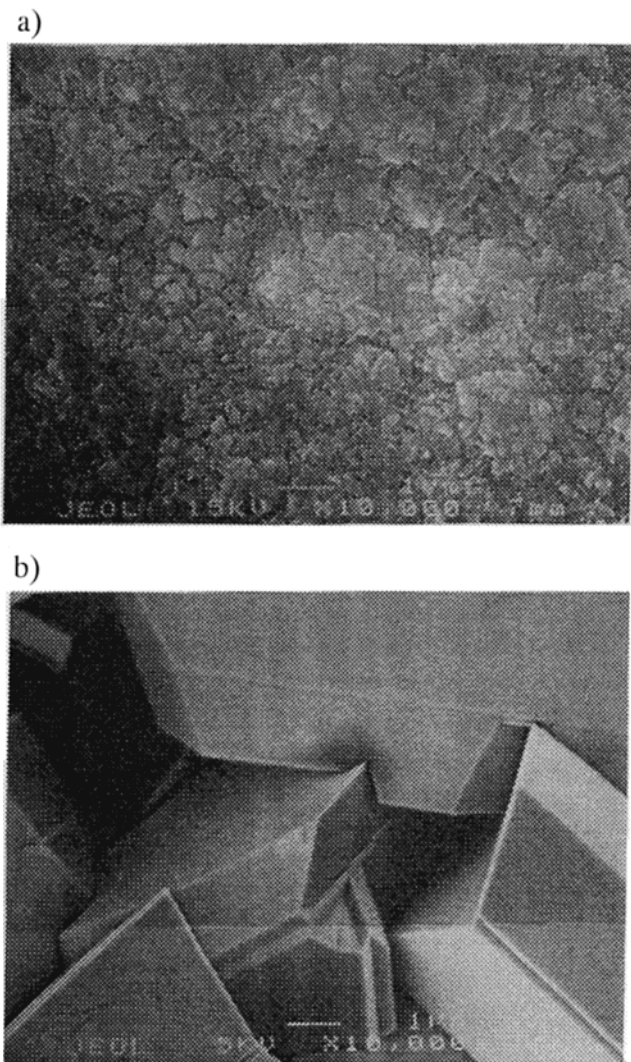
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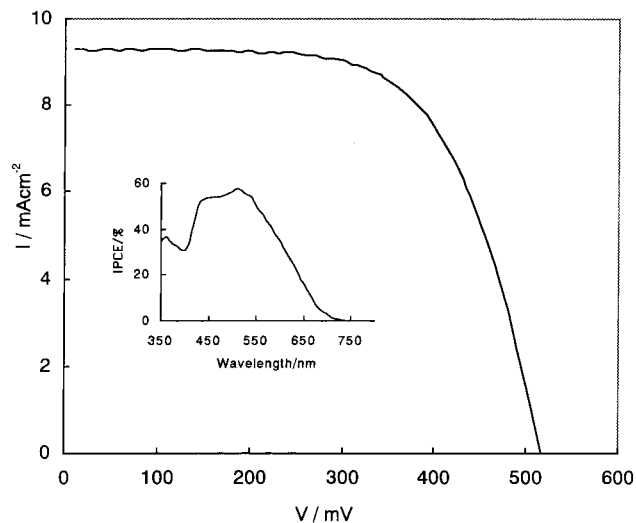
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**Figure 1.** SEM photographs of CuI deposited from acetonitrile solution (a) in the presence of the crystal growth inhibitor, i.e.,  $9 \times 10^{-3}$  M MEISCN, and (b) in the absence of a crystal growth inhibitor.

$10^{-2}$  reduces the CuI crystal size from  $\approx 10 \mu\text{m}$  to  $\approx 10$  nm.  $I$ - $V$  characteristics and the photocurrent action spectrum of a cell made by the addition of MEISCN to the CuI coating solution are presented in Figure 2.

Adsorption of MEISCN on CuI prevents growth of large crystals; presumably, a monolayer coverage determines the average crystallite size. Again the optimum MEISCN concentration required was found to be the same order of magnitude as the amount of MEISCN needed for monolayer coverage of  $\approx 100$ -nm CuI crystallites. MEISCN being a molten salt, its residue, formed at the grain boundaries after evaporation of the



**Figure 2.**  $I$ - $V$  characteristics of the cell made by deposition of CuI from a solution in acetonitrile containing  $9 \times 10^{-3}$  M of EMISCN. Inset: Photocurrent action spectrum of the cell.

solvent, spreads into a thin film around the interfaces. This film seems to admit hole conductance possibly because  $\text{CNS}^-$  acts as a good hole acceptor.<sup>14</sup> CuI films made by incorporation of MEISCN as described above show no ionic conductivity, supporting the above suggestion.

We have demonstrated that the use of crystal growth inhibitors as a successful strategy for deposition of crystalline hole collectors on dyed nanocrystalline n-type semiconductor films to form DSSSCs. This technique enables filling of the pores of the porous matrix, resulting in the formation of more complete and secure contacts of the hole collector and the dyed surface. The crystal growth inhibitor used should have the special property of not leaving a solid residue at the grain boundaries or other interfaces upon evaporation of the solvent. Being a molten salt, MEISCN satisfies this requirement exceptionally well and a thin film at the grain boundaries permits hole transfer. The crystal growth inhibitory action of MEISCN depends on strong adsorption of  $\text{SCN}^-$  on CuI. As expected, nonthiocyanate molten salts or thiocyanates that leave a solid residue upon evaporation (e.g., KSCN) were found to be ineffective. The idea of using crystal growth inhibitors having properties described as above could find applications in other areas of semiconductor device fabrication.

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