Fabrication of an Efficient Solid-State Dye-Sensitized Solar Cell

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A highly efficient solid-state solar cell (TiO_2/dye/CuI) with improved stability was fabricated by controlling the pore filling of the porous dyed TiO_2 layer with molten salt capped CuI crystals and improving the TiO_2 by necking with ZnO. The molten salt controls the CuI crystal growth and acts as a protective coating for CuI nanocrystals, and necking with the more conductive ZnO improves electrical contact between TiO_2 particles, both contributing to improved cell performance. Cells achieved efficiency as high as 3.8% with improved stability under continuous illumination for about 2 weeks.

Dye-sensitized solar cells (DSSCs) have recently been under intense investigation because of their low cost and reasonably high efficiency.[1-3] Unfortunately, the liquid electrolyte presents several technological problems such as dye desorption, solvent evaporation, dye degradation, and leakage of the volatile solvent and the redox couple. These problems limit the long-term stability of these wet solar cells. Therefore, many efforts[4-16] were made to replace the liquid electrolyte with solid or quasi-solid-type hole transport materials. For example, room-temperature molten salts,[5] p-type semiconductors,[6,7,11-14] conducting organic polymers,[8] polymer gel electrolyte,[9] ionic conductive polymer electrolytes,[10] and hole transport medium[15,16] were used to fabricate DSSCs. However, the efficiencies of these cells were found unsatisfactory compared to those of the liquid electrolyte. The two main reasons are (1) the low conductivity of molten salts, organic polymers, and polymer gel electrolytes and (2) bad contact between the dyed TiO_2 porous film surface and the p-type semiconductor for solid-state DSSCs. Two key issues in this research field are (1) finding new quasi-solid-type hole transport materials with high conductivity and (2) realizing good contacts at the TiO_2/dye/hole-conductor interfaces in the completely solid-state DSSCs. We know that in fabricating solid-state solar cells, there are two ways to fill the pores of the dyed TiO_2 film. One is electrochemical deposition. Grätzel and co-workers recently fabricated a completely solid-state ZnO/dye/CuSCN solar cell by electrochemical deposition of CuSCN.[12] This method was regarded as a perfect way to fill the holes with a p-type semiconductor, but it is limited by complexities such as dye degradation, so it is not widely applicable. Another is a general "solution method", in which a p-type semiconductor is usually dissolved in a suitable solvent and filled into dyed TiO_2 porous film while heating the film to evaporate the solvent. Several p-type semiconductors, such as CuI,[13] CuBr $3S(C_4H_9)_2$,[11] and CuSCN[14] have been successfully used to fabricate a complete solid-state DSSC. This method is very simple and easy to handle. However, it is difficult to control the crystal size of a p-type semiconductor while depositing it. This results in improper filling of the pores and bad contact with the dyed TiO_2 particles. This is the main reason for low efficiency and poor stability of solid-state DSSCs currently fabricated by this method. On the other hand, it is difficult to realize the complete coverage of the inner surface of the TiO_2 porous film with a monolayer of dye.

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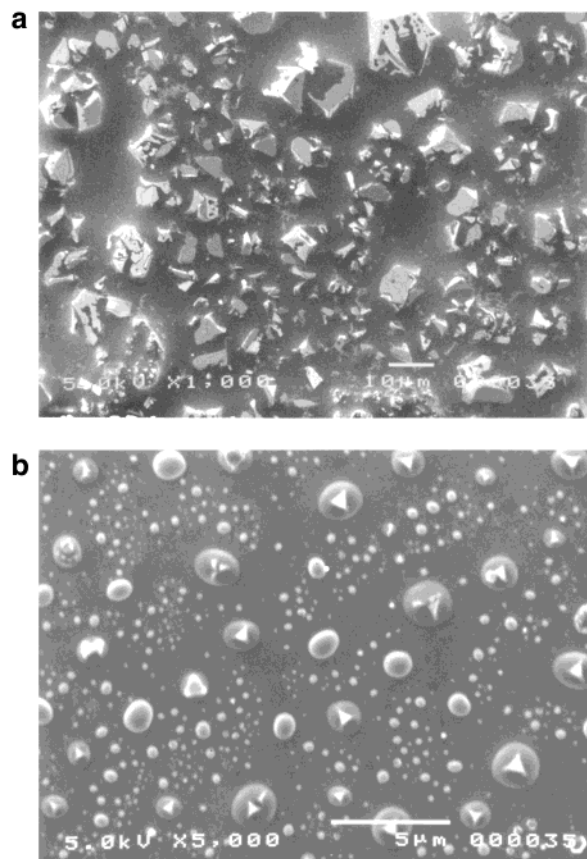
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Hence, it is very important to consider the increased possibility of short-circuiting due to the direct contact of the hole-collector with the naked TiO_2 that is left uncovered by the dye. (These problems are less severe for the liquid type DSSCs.) This is a paradoxical issue in the completely solid-state DSSC. The best conversion efficiency achieved to date is 6%,[13] using CuI, but it suffers serious stability problems (5 h stability) associated with the deterioration of contact at the dye–CuI interface or the deterioration of the CuI itself.[14] Alternatively, amorphous organic hole-transport material was used and a conversion efficiency as high as 2.6% was achieved.[15] Recently, Tennakone and co-workers attempted to use several imidazolium-based molten salts as crystal growth inhibitors to improve the performance of the CuI-based cells.[17,18] In the present Letter, we report a high-efficiency TiO_2/dye/CuI solid-state cell, which was fabricated to improve the charge transport by a combination of steps including (1) necking the TiO_2 particles in the porous film with the more conductive ZnO and (2) protecting the CuI nanocrystals with a molten salt shell, which also improves the electrical contact between the dye-coated TiO_2 and the CuI. A high-efficiency cell with greater stability is achieved.

A completely dense and very thin TiO_2 barrier layer is spin coated on fluorine-doped conducting tin oxide (CTO) glass using the TiO_2 precursor titanium ethoxide, $Ti(OCH_2-CH_3)_4$, as described in the literature.[19] Commercially available nanosized P-25 TiO_2 was used to fabricate porous TiO_2 films by the doctor blade method.[2] The thickness of each porous TiO_2 film is about 6 μm. Before coating with the dye solution, the porous TiO_2 films are soaked in an aqueous solution of 0.2M zinc nitrate (Wako) overnight and are heated at 450 °C for 30 min in air. The TiO_2 films are dye coated by soaking them in a 5×10^{-4} M solution of *cis*-di(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylate)-ruthenium(II) in dry ethanol. The porous TiO_2 films are boiled in the solution under the reflux state for 2 h and kept overnight at room temperature. The dye-coated films are then placed on a hot plate (surface temperature 100–120 °C), where they are moistened with a CuI–acetonitrile solution (0.15 M) containing about 1.2×10^{-2} M of 1-methy-3-ethylimidazolium thiocyanate (molten salt) by dropping the CuI solution onto the films using a pipet. The solvent evaporates quickly leaving the CuI/molten salt material in the pores. This process is repeated until the TiO_2 films' pores are filled with the CuI/molten salt material, which is then assessed by SEM (scanning electron microscopy). The amount of CuI solution that was deposited onto the porous TiO_2 film is about 0.18 mL/cm². The above procedure was carried out in a glovebox under nitrogen atmosphere. Electrical contact to the CuI surface is made by pressing a gold-coated CTO glass plate onto it. The cells are clamped with two clips or sealed with epoxy resin. The light source is a standard 300-W Xe lamp (Hamamatsu, C2578) coupled with an AM1.5 filter. The incident light intensity is measured with a photometer (International Light, IL1400). Electron micrographs are taken with a JSM-5400 scanning electron microscope.

Figure 1a shows the SEM image of the CuI layer deposited on the CTO glass substrate using the deposition solution without adding the molten salts. Large, perfectly shaped CuI crystals can be clearly seen over a large area. This indicates that crystallization is very quick and not

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Figure 1. The SEM images of CuI crystallites deposited on CTO glass substrate: (a) without molten salt in the solution; (b) after adding molten salt in the solution.

easily controlled. Figure 1b shows the SEM image of the CuI layer deposited by using the same solution with the addition of molten salts while maintaining the same conditions as for Figure 1a. From this image, we can clearly see that the size of CuI crystals decreases dramatically to nanometer order when compared with that of Figure 1a. This demonstrates that molten salts can control the crystallization of CuI[17,18] by acting as a surfactant. The small size of these CuI crystals is a great advantage in filling the voids of TiO_2 porous films. Also from Figure 1b, a soft shell of molten salt can be clearly seen on the surface of the CuI crystals. This new phenomenon is very interesting and important. One function of this thin molten salt layer is that it reduces direct contact between the CuI crystals and the naked (uncovered) parts of the dyed TiO_2 film, therefore significantly decreasing short circuiting between them. Another function of the molten shell is to reduce deterioration of the CuI itself, hence greatly improving the lifetime of the solar cell.
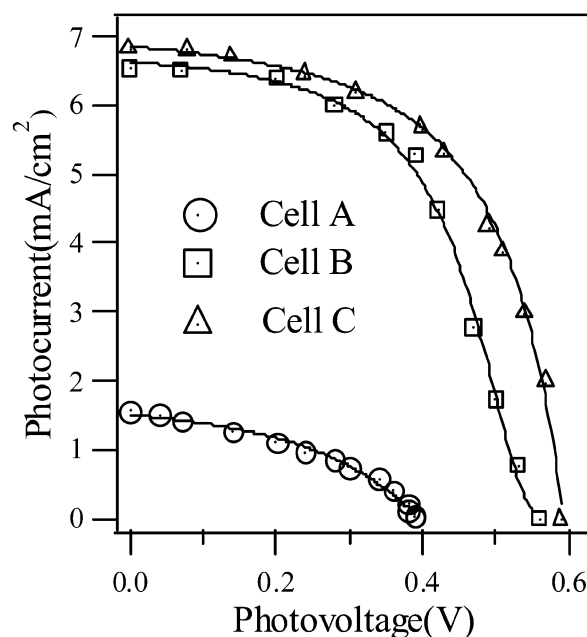
Parts a and b of Figure 2 show SEM images of the CuI layer deposited on the dyed TiO_2 porous film with and without the addition of the molten salt, respectively. From Figure 2a, we can see the large size of CuI crystals grown, having filled the pores and formed a layer covering the film's surface. The large size of these CuI crystals results in bad electrical contact between the porous surface and the CuI crystals and improper filling of the pores. The poor electrical contact dramatically decreases the efficiency of hole injection from dye molecules into the CuI crystals. The improper pore filling results in voids in the film and causes a dramatic decrease in hole transportation in the CuI layer and thus decreases the overall efficiency of the solid-state DSSC. A smooth surface texture of CuI deposited by a solution that includes molten salts can be
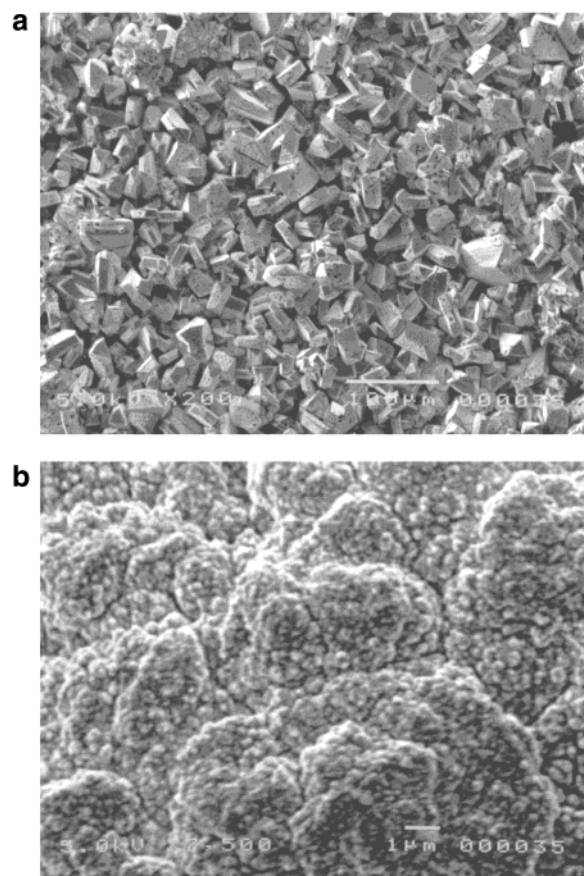
Figure 2. The SEM images of CuI layer on the dyed-TiO$_2$ porous film: (a) without molten salt in the solution; (b) after adding molten salts in the solution.

Figure 3. Photocurrent−voltage characteristics of solar cells with (cell A) a standard TiO$_2$/Ru dye/CuI, (cell B) molten salt added in the CuI solution while depositing it, and (cell C) after treating the TiO$_2$ film with zinc nitrate solution and calcination. The incident light intensity is 61 mW/cm^2 and the illumination area is 1.0 cm^2.

clearly seen from Figure 2b. The small size of these CuI crystals together with an almost complete absence of voids in the CuI layer permits good contact between the dyed TiO$_2$ porous surface and the CuI crystals themselves.

Figure 3 shows the current−voltage characteristics of solar cells fabricated with different conditions under illumination by standard AM1.5 solar light. Cell A, consisting of a TiO$_2$/N$_3$ dye/CuI system, shows the lowest conversion efficiency—about 0.4%—and lowest fill factor of 37% among the three cells. The short circuit current is $I_{sc} = 1.6$ mA/cm^2 and the open circuit voltage is $V_{oc} = 0.39$ V. Cell B—consisting of TiO$_2$/N$_3$ dye/(CuI + molten salt) fabricated by adding molten salt (1-methy-3-ethylimidazolium thiocyanate) in the CuI−acetonitrile solution—shows a larger conversion efficiency of about 3.3% and a higher fill factor of 55%. Meanwhile, the I_{sc} (6.5 mA/cm^2) and V_{oc} (0.56 V) are greatly improved compared with those of cell A. This result clearly indicates the better electrical contact between the dyed TiO$_2$ surface and the CuI crystals, as well as the good contact between the CuI crystals themselves. The formation of nanocrystals also allows improved pore filling. As mentioned before, the necking between the TiO$_2$ particles also plays an important role in the cell performance. This effect is demonstrated with cell C—consisting of TiO$_2$ (ZnO)/N3 dye/(CuI + molten salt) fabricated under the same conditions as cell B—except that the TiO$_2$ porous film is pretreated with zinc nitrate solution followed by annealing at 450 °C for 30 min in air. The energy conversion efficiency (3.8%), fill factor (57%), short-circuit current (6.84 mA/cm^2), and open circuit voltage (0.59 V) are further improved compared with those of cell B. This improvement can be attributed to zinc oxide crystals forming, especially at the boundaries between

the TiO$_2$ particles in the porous film, thus improving the electrical contact between TiO$_2$ particles through necking. The fact that the conductivity of ZnO is higher than that of TiO$_2$ allows improved charge transport in the TiO$_2$ film by providing good electrical contact between the TiO$_2$ particles. Moreover, ZnO necking suppresses the recombination of the electron-injected and dye cations or triiodide ions and therefore increases the open-circuit voltage. The stability of these cells is examined under continuous illumination (standard AM1.5 solar light with light intensity 60 mW/cm^2). The short-circuit photocurrent and open-circuit voltage of cell C decrease by only about 15% and 12%, respectively, after continuous use for about 2 weeks. Apart from the improved efficiency, these cells also exhibit a significant improvement in stability due to the protection of the molten shell, which also allows improved pore filling.

In conclusion, a highly efficient solid-state solar cell (TiO$_2$/dye/CuI) with improved stability was fabricated by controlling the pore filling of the dyed porous TiO$_2$ layer with molten salt capped nanosized CuI crystals and by improving the TiO$_2$ necking with ZnO. The molten salt around the CuI not only controls the crystal size but also protects the CuI crystals from deterioration, thus improving the cell's stability significantly. This molten salt shell also prevents direct contact between CuI and the naked TiO$_2$ parts of the dyed TiO$_2$ film. While the molten-salt shell also improves necking for hole transportation, ZnO-necking allows improved electrical contact between TiO$_2$ particles for electron transportation. These factors control the charge recombination at the interfaces and result in high efficiency.