

## Employment of CuI on Sb<sub>2</sub>S<sub>3</sub> Extremely Thin Absorber Solar Cell: N719 Molecules as a Dual Role of a Recombination Blocking Agent and an Efficient Hole Shuttle

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FTO/TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/CuI/Pt-FTO solar cell which utilizes Sb<sub>2</sub>S<sub>3</sub> as an extremely thin light absorbing layer and CuI as a hole conducting material is an example for novel extremely thin solar cells. The solar cell shows very poor performance of lower open-circuit voltage of 0.256 V, a short-circuit current density of 9.50 mA cm<sup>-2</sup> and a fill factor of 0.387 under 1 sun illumination for a cell with active surface area of 0.25 cm<sup>2</sup>. This is due to the recombination of photo-generated electrons with the holes of the highly conducting CuI. This recombination can be overcome to a certain degree by applying a blocking layer on the Sb<sub>2</sub>S<sub>3</sub> layer to cover the voids in the Sb<sub>2</sub>S<sub>3</sub> layer. The application of N719 dye on the Sb<sub>2</sub>S<sub>3</sub> layer as a recombination blocking layer enhances the conversion efficiency of the solar cell by a factor of 2.5 due to the enhancement of all the solar cell parameters to result in an open-circuit voltage of 0.37, short-circuit current density of 13.4 mA cm<sup>-2</sup>, and a fill factor of 0.503. IPCE, dark current and transmittance spectra measurements reveal that the main role of the dye on the Sb<sub>2</sub>S<sub>3</sub> layer is the suppression of recombination the electrons with the holes in CuI. Interactions of the NSC groups in the N719 dye with CuI are facilitating the transfer of the photo-generated holes in Sb<sub>2</sub>S<sub>3</sub> to the CuI layer for efficient transport towards the counter electrode.

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**Keywords:** Sb<sub>2</sub>S<sub>3</sub>, CuI, Solid-state solar cells, Suppress recombination

### 1. INTRODUCTION

Many researchers throughout the globe have focused on developing highly efficient and low-cost photovoltaic devices to endure the present and future energy crisis issues. In this regard, the dye-sensitized solar cell (DSC) invented by Grätzel et al. has been intensively studied as a promising system due to its unique operating mechanism to result in reasonably high energy conversion efficiency and its much lower fabrication cost [1,2]. But the utilization of the DSC in the commercial

scale has been met with several technical and chemical complications which include sealing imperfections, evaporation and leakage of the liquid electrolyte and corrosive nature of the species in the redox couple which hamper the commercialization of this solar cell.

Solid state solar cell devices utilizing inorganic sensitizers are expected to be good candidates for the designing of long-lasting solar cells for practical applications. Various reports on the use of inorganic absorbers such as Se [3], PbS [4], CdSe [5], CdS [6], In<sub>2</sub>S<sub>3</sub> [7] and Sb<sub>2</sub>S<sub>3</sub> [8] etc. and organic and inorganic solid hole-conducting materials in the solid-state solar cells have been well documented in the literature. Recently, an impressive record of high efficiency of 15% has been obtained for a solid state solar cell device utilizing a hybrid organic-inorganic perovskite thin film applied on the porous TiO<sub>2</sub> film [9]. The perovskite thin film here acts as the solar radiation absorber and subsequent electron injector to the CB of the interconnect, mesoporous TiO<sub>2</sub> nanoparticles and spiro-OMeTAD has been used as the hole conductor. This discovery has opened up a new horizon of solid state inorganic materials to be used in such solar cells. Sb<sub>2</sub>S<sub>3</sub> is a low-band-gap (Band gap is in the range from 1.7 eV to 1.8 eV) semiconductor that is being used for past few years to create novel solar cells combinations with mesoporous TiO<sub>2</sub> films and with a range of hole transport materials [10-15]. Its crystalline form is known as stibnite and it has low band gap of approximately 1.7-1.8 eV [10]. Several hole-transport materials have been successively employed in Sb<sub>2</sub>S<sub>3</sub>-sensitized solar cells (ASC) based on TiO<sub>2</sub> semiconductor. The first significant results were obtained by Itzhaik et al. who have used the inorganic p-type semiconductor of CuSCN,[14] and reported a 3.37% efficiency. Other hole conducting materials such as spiro-OMeTAD [10] [2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobi-fluorine] and P3HT(poly(3-hexylthiophene)) [15] have also been employed, obtaining 3.1% and 5.1% efficiencies, respectively, under 1 sun illumination. These results demonstrate the potentiality of all-solid-state Sb<sub>2</sub>S<sub>3</sub>-sensitized solar cells as attractive candidates to achieve robust, efficient, and cheap photovoltaic devices.

Cupreous iodide (CuI) is one of the promising p-type semiconductors for applications in solid state DSC. CuI can have three crystalline phases known as  $\alpha$ ,  $\beta$  and  $\gamma$  forms. A low-temperature  $\gamma$ - CuI phase has attracted a most attention because it is a wide band gap (3.1 eV) p-type semiconductor with remarkable electrical properties [16]. As such, CuI is considered to be a low-resistive and high-mobility hole conductor [17] compared to other hole conducting materials such as CuSCN, P3HT and spiro-OMeTAD. Therefore, the use of CuI as a hole collector in DSCs and other solar cells is highly beneficial owing to its capability of much lower hole- transport resistance which helps the efficient transport of holes away from Sb<sub>2</sub>S<sub>3</sub>. CuI can also be deposited from a solution of acetonitrile onto the photo anodes using a low-temperature deposition technique and hence without denaturing the dye monolayers in the DSCs.

CuSCN, P3HT and spiro-OMeTAD have been much studied and reported as hole-conducting materials on TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub> solar cells, but to the best of our knowledge, reports utilizing CuI as a hole conducting material on this type of solar cells are not available. This may be due to the fact that the performance of such solar cells so far stands out to be much lower. Therefore, in this work, we have attempted to improve the performance of the FTO/TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/CuI/Pt-FTO solar cell by studying the factors responsible for such lower performance and by introducing suitable corrections to those factors in order to improve the efficiency of the solar cell.

## 2. EXPERIMENTAL

All chemicals used were purchased from Wako Pure Chemical industry, Japan. Mesoporous TiO<sub>2</sub> films (2 μm) were prepared by screen printing method following a procedure described elsewhere [18]. Then Sb<sub>2</sub>S<sub>3</sub> was adsorbed on the TiO<sub>2</sub> film standing on FTO by the chemical bath deposition method. The chemical bath was prepared by dissolving 650 mg of SbCl<sub>3</sub> in 2.5 ml of acetone and subsequently adding 12.0 ml Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O solution and the required amount of distilled water to adjust the volume to 50.0 ml [19]. Then FTO/TiO<sub>2</sub> films were immersed in the above solution and were kept immersed for 3 hours in the solution in a refrigerator at 10°C to deposit Sb<sub>2</sub>S<sub>3</sub> on the TiO<sub>2</sub> film. At the end of the 3 h period, the Sb<sub>2</sub>S<sub>3</sub> adsorbed TiO<sub>2</sub> films became dark orange in color, they were then removed from the solution, rinsed with distilled water and annealed at 320 °C under N<sub>2</sub> atmosphere for 20 min. Dark orange Sb<sub>2</sub>S<sub>3</sub> transformed to dark brown Sb<sub>2</sub>S<sub>3</sub> crystals due to annealing to 320 °C. Then N719 dye [cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-icarboxylato) ruthenium(II)bis(tetrabutylammonium)] was absorbed on Sb<sub>2</sub>S<sub>3</sub> by dipping the FTO/TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub> electrode in the dye solution (4 × 10<sup>-4</sup> M, in 1:1 volume ratio of acetonitrile and t-butanol) for 15 h at room temperature. CuI was applied on this electrode by the solution casting method as described below.

CuI was dissolved in acetonitrile to obtain a saturated solution. 6 mg of guanidinium thiocyanate was dissolved in 5.0 ml of this solution and the resulted solution was spread on the preheated FTO/TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/N719 electrode few times until CuI layer is appeared on electrode. Then the cells were completed by placing a gold-sputtered glass plates as counter electrodes and their IV measurements were carried out under simulated sunlight (AM 1.5, 100 mW cm<sup>-2</sup>) using JASCO, CEP-25BX system.

## 3. RESULTS AND DISCUSSION

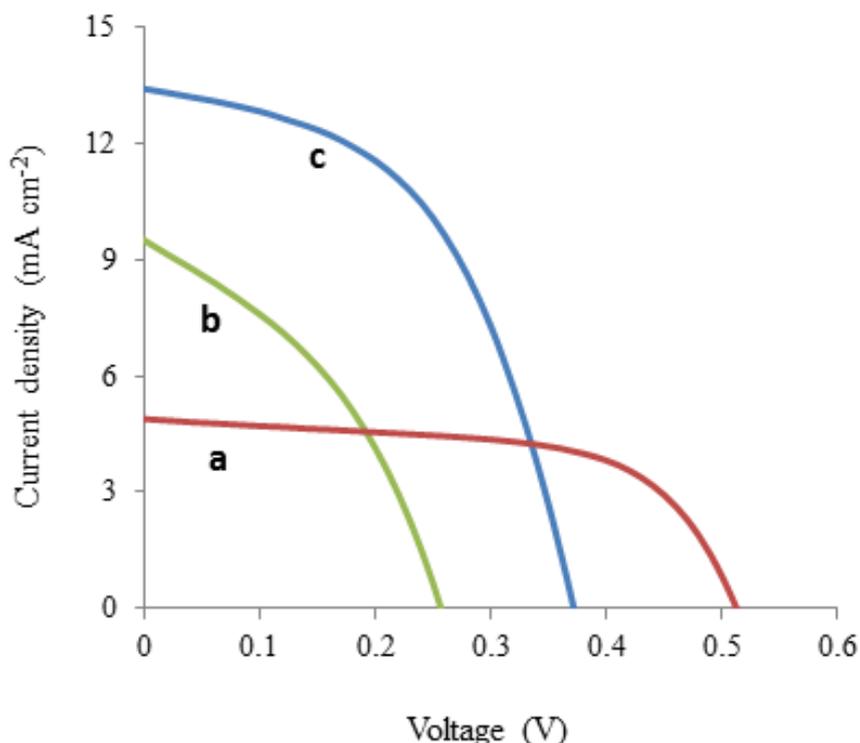
I-V characteristics of the solar cells with different configurations are shown in the Figure 1, and their corresponding I-V parameters are extracted into the Table 1.

**Table 1.** I-V parameters of the solar cell (a) FTO/TiO<sub>2</sub>/N719/CuI/Pt-FTO (b) FTO/TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/CuI/Pt-FTO and (c) FTO/TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/N719/CuI/ Pt-FTO.

Solar cell	J <sub>sc</sub> (mA cm <sup>-2</sup> )	V <sub>oc</sub> (V)	FF	η (%)
a	4.88	0.512	0.610	1.52
b	9.50	0.256	0.387	0.94
c	13.40	0.371	0.503	2.50

Curve (a) corresponds to the TiO<sub>2</sub>/N719/CuI system where it has higher open circuit voltage of 0.512 V and lower short-circuits current density of 4.88 mA cm<sup>-2</sup>. Here the Jsc value is comparatively

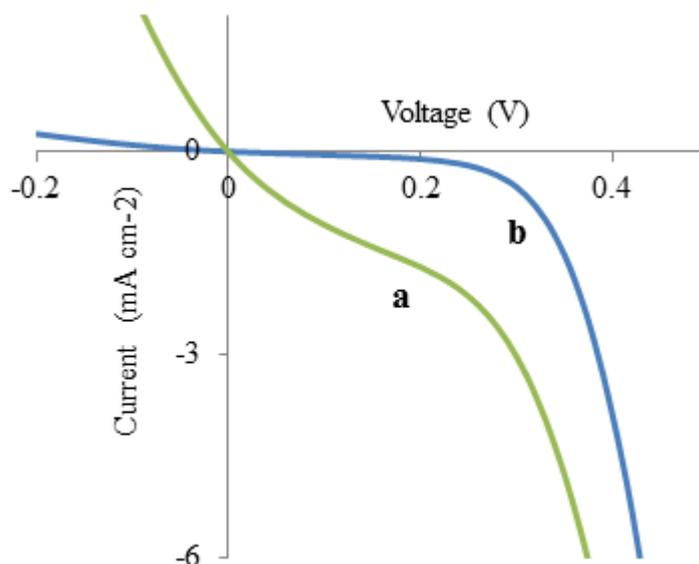
low, due to low surface area in the TiO<sub>2</sub> film (screen printed TiO<sub>2</sub> film of 3 μm in thickness), when compared to our previous publication which has over 3% efficiency with the same solar cell having TiO<sub>2</sub> thickness is 15 μm [20]. That TiO<sub>2</sub> film, 15 μm thickness, made by dropping method, is not efficient for Sb<sub>2</sub>S<sub>3</sub>- extremely thin absorber solar cell.



**Figure 1.** J-V characteristics of the solar cell (a) FTO/TiO<sub>2</sub>/N719/CuI/Pt-FTO (b) FTO/TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/CuI/Pt-FTO and (c) FTO/TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/N719/CuI/Pt-FTO (The active cell area is 0.25 cm<sup>2</sup> which is under 1 sun illumination).

Curve (b) which corresponds to the FTO/TiO<sub>2</sub>/Sb<sub>2</sub>S<sub>3</sub>/CuI/Pt-FTO system has quite lower  $V_{oc}$  of 0.25 V and higher  $J_{sc}$  of 9.50 mA cm<sup>-2</sup> when compared with cell (a). The  $V_{oc}$  of this cell is very low even when compared to that of ASC employing other hole-conductors such as CuSCN, Spiro-OMeTAD and P3HT. It is possible, therefore, that a reason for the non-availability of published papers on the utilization of CuI as a hole conducting material on Sb<sub>2</sub>S<sub>3</sub> could be due to this lower photovoltage leading to poor energy conversion efficiency. A photovoltage of 610 mV [10], 600 mV [12] and 550 mV [15] are obtained for such ASCs utilizing other hole conductors of Spiro OMeTAD, CuSCN and P3HT, respectively. The lower voltage of 250 mV for CuI as a hole conductor is attributed to the higher recombination of electrons with holes in CuI at the interface of Sb<sub>2</sub>S<sub>3</sub>/CuI, which is due to higher conductivity and mobility of holes in CuI [17]. Also to the best of our knowledge, there are no reports on the use of CuI as a hole conducting material in semiconductor-sensitized solar cells which utilize any inorganic material as a sensitizer. The main reasons are the faster recombination and lower shunt resistances at the interfaces of FTO/TiO<sub>2</sub>/inorganic absorber/CuI configuration due to higher conductivity and mobility of hole in CuI [17]. Generally inorganic materials (or quantum dots)

cannot cover the entire surface area of  $\text{TiO}_2$  meso-porous films when compared to the surface coverage by dye molecules on  $\text{TiO}_2$  porous films. Therefore, CuI can infiltrate through these voids and make contacts with  $\text{TiO}_2$ , thereby increasing the dark current of the DSCs and hence enhancing charge recombination. Curve (c) is a J-V curve for FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /N719/CuI/Pt-FTO solar cell of which the photocurrent density and photovoltage are greatly increased as shown in figure 1. The modification done here is to adsorb N 719 dye on the  $\text{Sb}_2\text{S}_3$  surfaces. The role of N719 dye behind the improvement of solar cell efficiency is discussed in the following section.

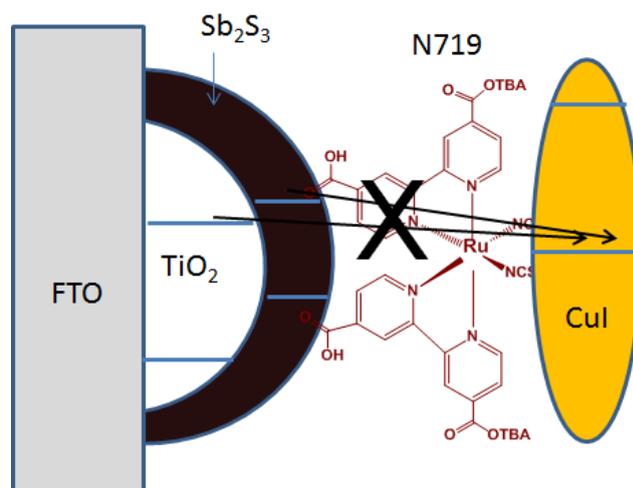


**Figure 2.** Dark current-voltage curves of the (a) FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /CuI/Pt-FTO and (b) FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /N719/CuI/Pt-FTO solar cells.

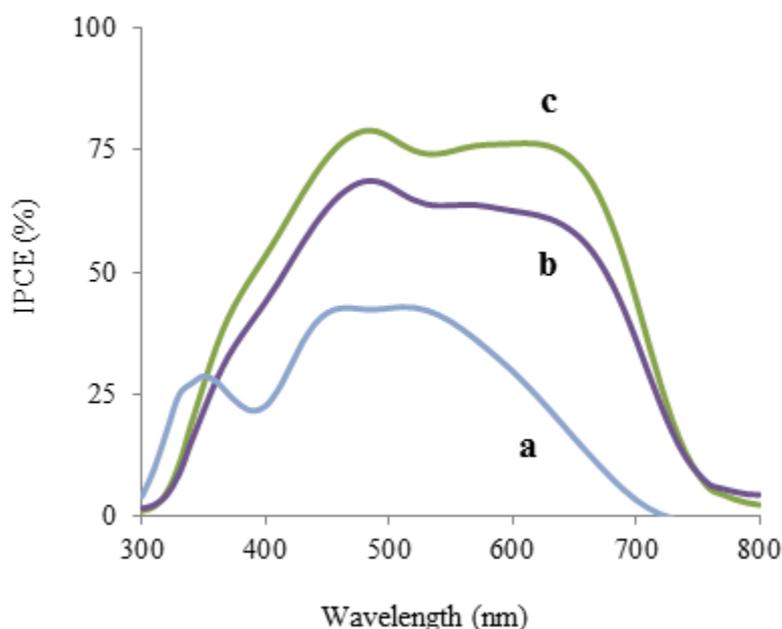
Figure 2 shows the dark current-voltage characteristics of the FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /CuI/Pt-FTO (curve a) and that of the FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /N719/CuI /Pt-FTO (curve b) solar cells. It is clearly evident that FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /CuI/Pt-FTO solar cell has a much larger dark current and hence poor diode properties under reverse-biased condition than those of the FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /N719/CuI /Pt-FTO solar cell.

One of the main reasons is direct contact of CuI with  $\text{TiO}_2$  through voids on  $\text{Sb}_2\text{S}_3$  due to imperfect- surface coverage of porous  $\text{TiO}_2$ . The direct contact of CuI with  $\text{TiO}_2$  through voids of the  $\text{Sb}_2\text{S}_3$  layer would further contribute to the increase in the dark current through the contact of CuI and interconnected  $\text{TiO}_2$  particles as well as through the direct contact of CuI with the  $\text{TiO}_2$  dense layer through voids in the nanoporous layer. Larger dark currents always reduce the fill factor and the photovoltage of the solar cell as can be seen by the curve (a) in Figure 2. The curve (b) in Figure 2, which corresponds to the FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /N719/CuI/Pt-FTO system, depicts highly improved diode properties of the solar cell in the dark under reverse-biased condition. There are a few basic reasons behind the decrease of dark current due to N719 dye adsorption on the  $\text{Sb}_2\text{S}_3$  layer of this solar cell.

Perfect surface coverage by N719 dye on  $Sb_2S_3$  and on the exposed  $TiO_2$  surfaces would be one of the main factors in decreasing dark current.



**Figure 3.** Illustration of the solar cell configuration of the FTO/ $TiO_2$ / $Sb_2S_3$ /N719/CuI/Pt-FTO indicating relevant recombination paths.

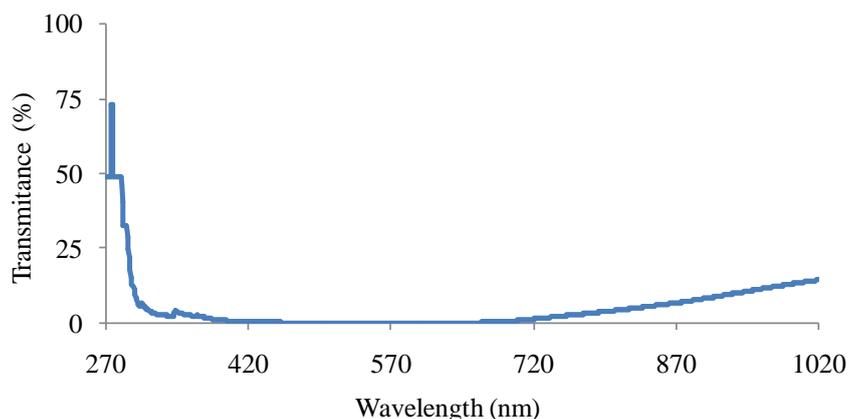


**Figure 4.** IPCE spectra of the solar cell (a) FTO/ $TiO_2$ /N719/CuI/Pt-coated glass (b) FTO/ $TiO_2$ / $Sb_2S_3$ /CuI/Pt-coated glass and (c) FTO/ $TiO_2$ / $Sb_2S_3$ /N719/CuI/Pt-coated glass.

Moreover, Angelis et al. have discussed in detail the effect of dipole moment of the N719 dye molecules which are adsorbed onto the  $TiO_2$  layer and particularly its effect on the photovoltaic behavior of solar cells. [21]. Under applied voltage or electric field the adsorbed N719 dye molecules become polarized leading to the minimization of the electron flow towards the CuI side in the dark.

The lower dark current characteristics in these solar cells are always associated with the suppressing of the recombination of photo-generated electrons at the interfaces of  $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{N719}/\text{CuI}$  as illustrated in figure 3. As a result of this, the Fermi level of  $\text{TiO}_2$  moves up owing to increased electron density in the  $\text{TiO}_2$  particles thus producing improved photovoltage and photocurrent when the solar cell is illuminated.

Figure 4 shows the IPCE spectra of each solar cells. It is interesting to note here that the shape of the IPCE spectra of  $\text{FTO}/\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{CuI}/\text{Pt-FTO}$  and  $\text{FTO}/\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{N719}/\text{CuI}/\text{Pt-FTO}$  solar cells are almost identical with the mere difference of just slightly higher values of IPCE for the latter solar cell. IPCE range of the  $\text{Sb}_2\text{S}_3$  extends nearly to 800 nm wavelength and it covers entire IPCE range of the N719 dye (400-700 nm). Also it is known that extinction coefficient of  $\text{Sb}_2\text{S}_3$  is very much higher ( $1.8 \times 10^5 \text{ cm}^{-1}$  at 450 nm) than that of the N 719 dye [15] and, therefore, almost all of the light passing through the  $\text{TiO}_2$  side would be absorbed by the  $\text{Sb}_2\text{S}_3$  film in the range of 300-800 nm, leaving almost no photons for N 719 dye molecules on the  $\text{Sb}_2\text{S}_3$  particles to absorb. Hence, electrons are injected to the  $\text{TiO}_2$  particles mainly from the electrons excited to the conduction band of the  $\text{Sb}_2\text{S}_3$  particles. However, as discussed above, there can be some N 719 dye molecules adsorbed directly on to the exposed surfaces of  $\text{TiO}_2$  particles in both the dense and mesoporous layers. The light absorption followed by excitation and electron injection by these dye molecules would contribute to the slightly increased IPCE values in this solar cell. Therefore, the main role of the dye on  $\text{Sb}_2\text{S}_3$  is the suppression of the recombination of photo-generated electrons with CuI.



**Figure 5.** Optical transmittance spectrum of the  $\text{FTO}/\text{TiO}_2/\text{Sb}_2\text{S}_3$  electrode

We measured the transmittance spectrum of the  $\text{FTO}/\text{TiO}_2/\text{Sb}_2\text{S}_3$  electrode, which is shown in Figure 5, as an evidence for the fact that almost no photons left remaining for N 719 dye molecules, adsorbed on  $\text{Sb}_2\text{S}_3$  layer, to absorb for photo excitation. It clearly indicates that the transmittance between 400 nm and 500 nm is between 0.6% and 0.06%, and that between 500 nm to 600 nm is between 0.06% and 0.03%. Nonetheless there is a possibility of losing some percentage of incoming photons prior to absorb via scattering and reflection. But that losing percentage via scattering and reflection exist even without  $\text{Sb}_2\text{S}_3$  on  $\text{TiO}_2$ . Therefore this transmittance spectrum makes further

evidence that almost no photons left remaining for N 719 dye molecules, adsorbed on  $\text{Sb}_2\text{S}_3$  layer, to absorb for photo excitation.

Other important point to consider here for the FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /N719/CuI/Pt-FTO solar cell is the transportation of the holes generated in  $\text{Sb}_2\text{S}_3$  towards CuI through N719 dye molecules. Sakamoto et al. have found that the interaction of CuI with NCS groups in counter electrode facilitates the hole transportation to the counter electrode at the CuI/Counter electrode interface and they have discussed it in detail with the help of XPS measurements and through AC impedance spectroscopy and IR spectroscopy [22]. They have modified the counter electrode, which exists SCN groups, by PEG solution mixing with SCN groups.

N719 dye consists of functional group of NCS and COOH [21] and it is known that N719 molecules bond to the  $\text{TiO}_2$  surface through COOH groups while CuI attaches to the N 719 molecules through NCS groups as shown in figure 3 [21,22]. Therefore, one of the other factors for improved performance of the FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /N719/CuI/Pt-FTO solar cell would be the interactions of CuI with NCS groups of N719 dye molecules facilitating smooth hole transportation. In order to investigate this point further, we have replaced the N719 dye by D358 dye, the latter with only COOH functional groups and without any NCS functional groups but with a higher extinction coefficient than that of N 719 dye. We wish to note here that all the solar cell parameters have decreased considerable even when the D358 dye-loading is much higher than that of N719 dye on the  $\text{Sb}_2\text{S}_3$  layer (data not shown) giving a  $V_{oc}$  of 0.334 V,  $I_{sc}$  of 11.38  $\text{mA cm}^{-2}$  and FF of 0.409. This clearly demonstrates the importance of the vectorial hole transfer from the  $\text{Sb}_2\text{S}_3$  particles through covalently bound NCS groups present in the N 719 dye molecules to the CuI particles for their faster transport towards the counter electrode in the FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /N719/CuI/Pt-FTO solar cell for its superior performance over other solar cells studied in this work. By considering all these information, it can be concluded that the performance of the  $\text{Sb}_2\text{S}_3$  sensitized solar cells can be increased by utilizing CuI as a hole conductor together with suitable molecules which can help the vectorial hole transport from the  $\text{Sb}_2\text{S}_3$  layer to the CuI particles.

In conclusion, the performance of the FTO/ $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /N719/CuI/Pt-coated glass solar cell has been greatly improved by applying N719 dye on the  $\text{Sb}_2\text{S}_3$  layer. IPCE and dark current measurements reveal that the main role of the dye on  $\text{Sb}_2\text{S}_3$  layer is the suppression of recombination of photogenerated electrons with the holes of CuI particles. One more factor for improved performance of the this solar cell is the covalent interaction of CuI with NCS groups of N719 dye facilitating effective hole transfer from  $\text{Sb}_2\text{S}_3$  to CuI for their faster transport towards the counter electrode.

#### 4. CONCLUSIONS

$\text{Sb}_2\text{S}_3$  extremely thin absorber solar cells, based  $\text{TiO}_2$  mesoporous n-semiconductor, was fabricated utilizing CuI as a hole conducting material. Since such a solar cell,  $\text{TiO}_2$ / $\text{Sb}_2\text{S}_3$ /CuI, shows inferior performance ( $J_{sc}$  = 9.5  $\text{mA cm}^{-2}$ ,  $V_{oc}$  = 0.256 V, FF = 0.387,  $\eta$  = 0.94 %) due to better electrical properties of CuI, N719 dye molecules were adsorbed on  $\text{Sb}_2\text{S}_3$  layer as agent to suppress the recombination and ease hole transportation. Here N719 dye acts dual role on the  $\text{Sb}_2\text{S}_3$  layer as a

recombination blocking agent and an efficient hole shuttle. Light absorption by N719 dye on Sb<sub>2</sub>S<sub>3</sub> layer is extremely low due to almost all photons absorb by the Sb<sub>2</sub>S<sub>3</sub> layer. Such a solar cell indicated improved solar cell parameters under one sun illumination (  $J_{sc} = 13.4 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.371 \text{ V}$ ,  $FF = 0.503$ ,  $\eta = 2.5 \%$ ).

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