THE JOURNAL OF PHYSICAL CHEMISTRY Letters

pubs.acs.org/JPCL

Sb_2S_3-Based Mesoscopic Solar Cell using an Organic Hole Conductor

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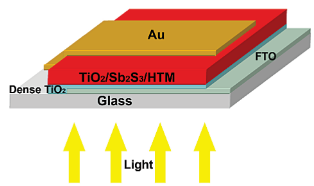
ABSTRACT Solid-state nanocrystalline solar cells composed of chemical-bath-deposited Sb_2S_3 (antimony sulfide) as a light-absorber layer deposited on nanoporous TiO_2 and spiro-MeOTAD as an organic hole-transporting material yielded a solar conversion efficiency of 5.2% at 0.1 sun illumination and a peak 88% of the incident monochromatic photon-to-current conversion efficiency.

SECTION Energy Conversion and Storage



The dye-sensitized mesoscopic solar cell (DSC) has been intensively investigated as a promising photovoltaic cell due to its unique operating mechanism in which the light harvesting is separated from the transport[1] of photoinduced charge carriers. It is also attractive for its ecological and economical fabrication. The utilization of semiconductors as light-absorbing material in place of dye molecules has recently been drawing much attention. Their advantages include a high light-harvesting capability,[2,3] a tunable band gap over a wide range,[4,5] and a large intrinsic dipole moment.[6] A range of semiconductors have been investigated, including PbS,[7] CdS,[8] CdSe,[9−12] CdTe,[13] In_2S_3,[14] $Cu_{2-x}S$,[15] and $CuInS_2$.[16] However, the power conversion efficiencies are lagging behind those obtained for the more traditional (transition-metal complexes and organic-dye-sensitized) DSCs.

Sb_2S_3 (antimony sulfide) is a low-band-gap semiconductor that has been used on a number of occasions to create novel solar cells. In its crystalline form (stibnite), the band gap is approximately 1.7−1.8 eV. It has previously been studied as a potential sensitizer in TiO_2 mesoscopic solar cells employing liquid electrolytes, where it was coated onto the semiconductor electron-transporting film by chemical bath deposition (CBD).[17] The IPCE measured in this study was 30%; however, the power conversion efficiency was not measured due to photoelectrode instability in the liquid electrolyte. Recently, CBD Sb_2S_3 has been reported as an absorber in semiconductor-sensitized solid-state solar cells (Sb_2S_3 ETA (extremely thin absorber) solar cells), where CuSCN was used as the inorganic hole-transport layer.[18,19] The power conversion efficiencies were 3.4% under 100% sun illumination in both studies and 3.8% under 10% sun in ref 19. The incident monochromatic photon-to-current conversion efficiency (IPCE) obtained with such cells was 80%. In this Letter, 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobi-fluorene (spiro-MeOTAD) is shown to be an efficient organic hole-transporting material for Sb_2S_3-sensitized solid-state solar cells, giving conversion efficiencies of 5.2 and 3.1% at 10 and 100% solar irradiation with an IPCE reaching nearly 90%.

Cell Preparation. Fabrication of Sb_2S_3-sensitized solid-state solar cells employed a F-doped SnO_2 glass substrate (15 Ω/□, Pilkington) onto which a ~100 nm compact TiO_2 layer was deposited by spray pyrolysis.[20] The ~2 μm thick nanoporous layer composed of 30 nm TiO_2 particles was coated onto this substrate using the doctor-blading technique. The TiO_2 layer was then annealed at 500 °C for 30 min under oxygen flow, followed by treatment with a 0.02 M $TiCl_4$ aqueous solution for 6 h at room temperature. It was reannealed at 500 °C in air for 30 min just prior to the subsequent deposition steps. In a stepwise procedure $In_x(OH)_yS_z$ (In−OH−S) (~1 nm thickness) was first of all deposited on this TiO_2 film by CBD followed by a CBD deposition of Sb_2S_3 onto these TiO_2/In−OH−S substrates utilizing a solution of $SbCl_3$ and $Na_2S_2O_3$.[21] The as-deposited orange films of amorphous Sb_2S_3 were annealed under N_2 at 300 °C for 30 min to give dark-brown crystalline stibnite. The films were removed from the oven immediately after annealing and were allowed to cool in air. The local thickness of the stibnite layer varied from a few nm to ca. 20 nm (from Figure 1) and the total (optical) thickness typically a few hundred nm. The Sb_2S_3 did not cover each TiO_2 particle conformally but rather coated clusters of TiO_2 (see Figure 1). The organic hole conductor, spiro-MeOTAD, was then coated on top of the Sb_2S_3/TiO_2 film by spin coating of a 0.17 M chlorobenzene solution of spiro-MeOTAD containing three additives, 19 mM *tert*-butylpyridine, 10 mM $Li[CF_3SO_2]_2N$, and 0.30 mM antimony dopant ($N[p\text{-}C_6H_4Br]_3SbCl_6$), at 2000 rpm for 30 s. The device fabrication was completed by thermal evaporation of ~100 nm thick gold as a counter electrode. All of the fabrication steps and photovoltaic measurements were carried out in air and at or close to

Received Date: March 9, 2010
Accepted Date: April 14, 2010
Published on Web Date: April 28, 2010

DOI: 10.1021/jz100308q | *J. Phys. Chem. Lett.* **2010**, *1*, 1524–1527

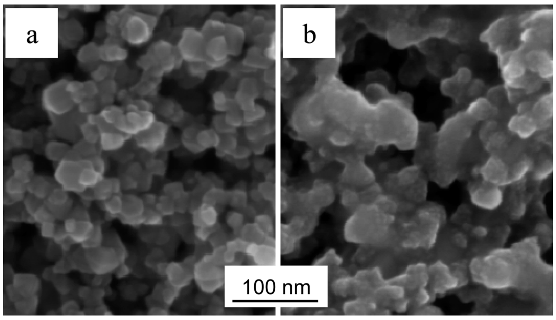


Figure 1. SEM pictures of (a) bare 30 nm TiO_2 particles and (b) the Sb_2S_3 film deposited and annealed on a 30 nm TiO_2/In−OH−S substrate.

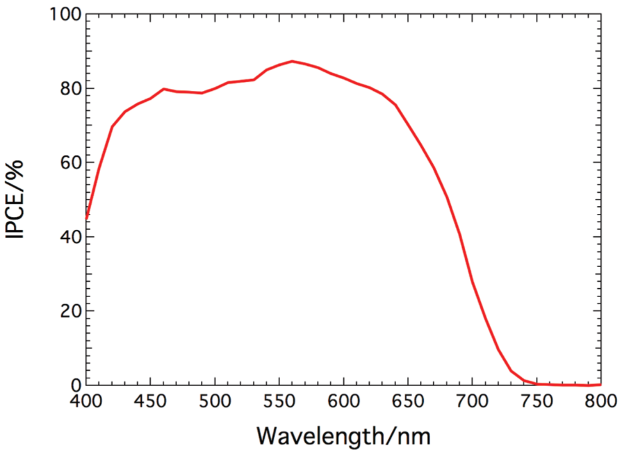


Figure 2. Incident photon-to-current conversion efficiency of an Sb_2S_3-sensitized solid-state cell (0.49 cm^2 of masked active area).

room temperature, other than the annealing treatments noted above. After the preparation, the cells were measured the next day.

Figure 2 shows the incident photon-to-current conversion efficiency (IPCE) of an Sb_2S_3-sensitized solid-state solar cell. The IPCE is plotted as a function of excitation wavelength by using the incident light from a 300 W xenon lamp (ILC Technology, U.S.A.), which had been focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.). The IPCE spectrum exhibits very high values, that is, 70−90% between excitation wavelengths of 420 and 650 nm. Assuming a 10% optical loss in the conducting glass,[22] the internal quantum efficiency ranged from 80 to 100%. The observed IPCE onset at ∼750 nm is consistent with an approximate 1.75 eV band gap of crystalline Sb_2S_3. Figure 3 and Table 1 illustrate the current (J)−voltage (V) characteristics and photovoltaic parameters under different light intensities. For photovoltaic measurements of the solar cells, the irradiation source employed was a filtered (Schott 113) 450 W xenon light source (Osram XBO 450, USA) whose power was adjusted to the AM 1.5G solar standard by using a reference Si photodiode equipped with a color-matched filter (KG-3, Schott), thus reducing the spectral mismatch between the simulated light and AM 1.5G irradiation in the region of

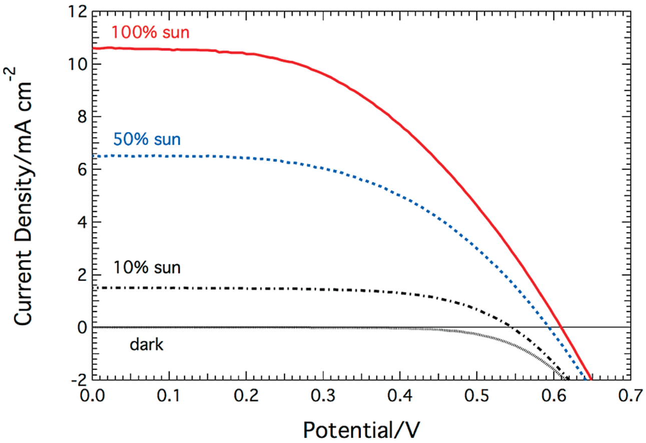


Figure 3. Current (J)−voltage (V) characteristics of an Sb_2S_3-sensitized solid-state device (0.49 cm^2 of masked active area).

Table 1. Photovoltaic Performance of an Sb_2S_3-Sensitized Solid-State Cell under Various Light Intensities

light intensity	J_{sc} (mA/cm^2)	V_{oc} (mV)	ff	η (%)
10% sun	1.51	545	0.64	5.2
50% sun	6.51	594	0.52	4.0
100% sun	10.62	610	0.48	3.1

350−750 nm to less than 4%. Under standard global AM 1.5 solar conditions, the Sb_2S_3-sensitized solid-state solar cell with a 0.49 cm^2 masked area showed an overall efficiency, η, of 3.1%, with the corresponding photovoltaic parameters of J_{sc} = 10.6 mA cm^{-2}, V_{oc} = 610 mV, and ff = 0.48. Under 10 and 50% sun, the overall efficiencies were, respectively, 5.2 and 4.0%. The detailed photovoltaic parameters at various light intensities are summarized in Table 1. To the best of our knowledge, 5.2% is the highest efficiency ever reported for semiconductor-sensitized solar cells, even under the low illumination intensity of 100 W m^{-2}. At the 1 sun irradiation condition, the lower observed power conversion efficiency could be attributed to photocurrent and fill factor loss. The fill factor loss plausibly stems from a resistive loss. It should be noted that in this study, our active area is 0.49 cm^2, which is 3.3 times bigger than that of the study of ref 19, increasing the IR losses due to higher photocurrents.

As mentioned above, the photocurrent loss increased with increasing illumination intensity. In order to investigate the loss, we followed current dynamics of an Sb_2S_3-sensitized solid-state solar cell measured over the course of light-on and light-off (∼3.5 s) at various light intensities. Figure 4 shows the current dynamics as a function of light intensity, where the dashed lines show the individual photocurrents normalized to 1 sun. Above 0.305 sun, these currents are notably characterized by nonlinearity and lack of plateau formation. When normalized to values of J_{sc} measured under 1 sun illumination, the J_{sc} values measured at the lower light intensities are high in comparison to that measured under 1 sun. At the lowest light intensities examined, that is, 0.009 and 0.095 sun, the normalized J_{sc} values are 17.5 and 15.1 mA cm^{-2}, which are, respectively, 165 and 143% of the J_{sc} value

DOI: 10.1021/jz100308q | J. Phys. Chem. Lett. 2010, 1, 1524–1527

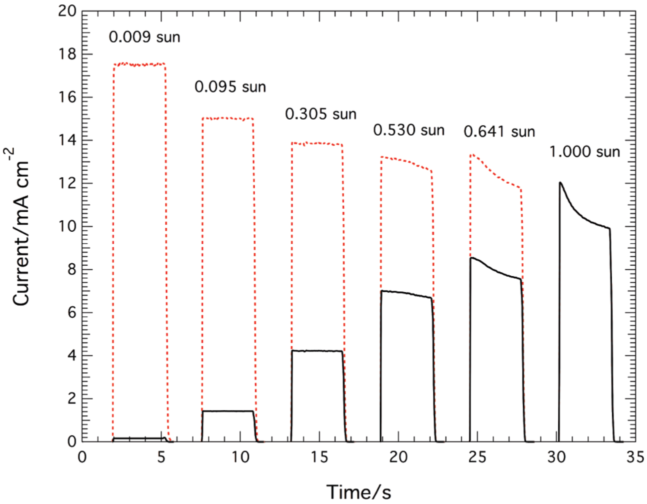


Figure 4. The current dynamics of Sb_2S_3-sensitized solid-state cells at various light intensities: measured currents (black solid lines): the same currents normalized to 1 sun (red dashed lines).

measured at 1 sun. The IPCE measured under low light intensity and integrated from 350 to 800 nm yields a J_{sc} value of 16.0 mA cm^{-2}, which is higher than the value of 10.6 mA cm^{-2} measured under AM 1.5G irradiation. In the current dynamic measurements, constant currents were maintainable (plateaus were formed) from the initial to final illumination times up to 0.305 sun intensity, but at the higher light intensities examined (i.e., 0.530, 0.641, and 1.000 sun), the J_{sc} decays (nonlinear) during the illumination period with a characteristic nonlinearity increasing as the light intensity increases. At 1 sun, an 18% reduction in the final measured J_{sc} value was found. This might indicate a limitation of the J_{sc} by the rate of hole diffusion to the back contact and can explain, to a large extent, the sublinear increase in photocurrent with light intensity. In addition, we believe that the TiO_2/Sb_2S_3/spiro-MeOTAD interface is the most crucial parameter linked to diminished short-circuit current values. In fact, experiments performed using a TiO_2 film composed of 20 nm sized nanoparticles (having a smaller pore size than films comprised of 30 nm particles) yielded an efficiency of less than 1% at full light intensity. The effect of pore size/particle size on the performance of the cell is presently under investigation.

From the results presented herein, Sb_2S_3 appears to be one of the most promising medium-band-gap semiconductors for replacement of the sensitizer as a light absorber in solid-state TiO_2 mesoscopic solar cells. An efficiency, η, of 5.2% was reached under 10% sun light intensity with an IPCE reaching almost 90%, which augurs well for further improvement of the performance under full sunlight. The mechanism of loss of photoinduced charges at higher light intensities still remains to be resolved. The discrepancy between 10 and 100% simulated solar irradiation intensities seems to result from interfacial issues at the Sb_2S_3/spiro-MeOTAD junctions. Improvements in the interfacial properties of Sb_2S_3 and spiro-MeOTAD should likewise lead to an enhanced overall device performance.

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ACKNOWLEDGMENT Financial support from the Swiss National Science Foundation, the European Research Council (Advanced Grant no 247404 to M.G.), and a research grant from Rowland and Sylvia Schaefer are gratefully acknowledged. We thank Dr. Carole Grätzel, EPFL, for fruitful discussions.

REFERENCES

(1) Grätzel, M. Recent Advances in Sensitized Mesoscopic Solar Cells. *Acc. Chem. Res.* **2009,** *42*, 1788–1798.

(2) Yu, W. W.; Qu, L. H.; Guo, W. Z.; Peng, X. G. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003,** *15*, 2854–2860.

(3) Hodes, G. Comparison of Dye- and Semiconductor-Sensitized Porous Nanocrystalline Liquid Junction Solar Cells. *J. Phys. Chem. C* **2008,** *112*, 17778–17787.

(4) Brus, L. Electronic Wavefunctions in Semiconductor Clusters: Experiment and Theory. *J. Phys. Chem.* **1986,** *90*, 2555–2560.

(5) Alivisatos, A. P. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science* **1996,** *271*, 933–937.

(6) Vogel, R.; Pohl, K.; Weller, H. Sensitization of Highly Porous, Polycrystalline TiO_2 Electrodes by Quantum Sized CDs. *Chem. Phys. Lett.* **1990,** *174*, 241–246.

(7) Oja, I.; Belaidi, A.; Dloczik, L.; Lux-Steiner, M. C.; Dittrich, T. Photoelectrical Properties of $In(OH)_xS_y$/PbS(O) Structures Deposited by SILAR on TiO_2. *Semicond. Sci. Technol.* **2006,** *21*, 520–526.

(8) Larramona, G.; Chone, C.; Jacob, A.; Sakakura, D.; Delatouche, B.; Pere, D.; Cieren, X.; Nagino, M.; Bayon, R. Nanostructured Photovoltaic Cell of the Type Titanium Dioxide, Cadmium Sulfide Thin Coating, and Copper Thiocyanate Showing High Quantum Efficiency. *Chem. Mater.* **2006,** *18*, 1688–1696.

(9) Lévy-Clément, C.; Tena-Zaera, R.; Ryan, M. A.; Katty, A.; Hodes, G. CdSe-Sensitized p-CuSCN/Nanowire n-ZnO Heterojunctions. *Adv. Mater.* **2005,** *17*, 1512–1515.

(10) Niitsoo, O.; Sarkar, S. K.; Pejoux, C.; Ruhle, S.; Cahen, D.; Hodes, G. Chemical Bath Deposited CdS/CdSe-Sensitized Porous TiO_2 Solar Cells. *J. Photochem. Photobiol., A* **2006,** *181*, 306–313.

(11) Diguna, L. J.; Shen, Q.; Kobayashi, J.; Toyoda, T. High Efficiency of CdSe Quantum-Dot-Sensitized TiO_2 Inverse Opal Solar Cells. *Appl. Phys. Lett.* **2007,** *91*, 023116.

(12) Lee, H. J.; Yum, J. H.; Leventis, H. C.; Zakeeruddin, S. M.; Haque, S. A.; Chen, P.; Seok, S. I.; Gräzel, M.; Nazeeruddin, M. K. CdSe Quantum Dot-Sensitized Solar Cells Exceeding Efficiency 1% at Full-Sun Intensity. *J. Phys. Chem. C* **2008,** *112*, 11600–11608.

(13) Ernst, K.; Engelhardt, R.; Ellmer, K.; Kelch, C.; Muffler, H. J.; Lux-Steiner, M. C.; Konenkamp, R. Contacts to a Solar Cell with Extremely Thin CdTe Absorber. *Thin Solid Films* **2001,** *387*, 26–28.

(14) Dittrich, T.; Kieven, D.; Rusu, M.; Belaidi, A.; Tornow, J.; Schwarzburg, K.; Lux-Steiner, M. Current−Voltage Characteristics and Transport Mechanism of Solar Cells based on ZnO Nanorods/In_2S_3/CuSCN. *Appl. Phys. Lett.* **2008,** *93*, 053113.

(15) Page, M.; Niitsoo, O.; Itzhaik, Y.; Cahen, D.; Hodes, G. Copper Sulfide as a Light Absorber in Wet-Chemical Synthesized Extremely Thin Absorber (ETA) Solar Cells. *Energy Environ. Sci.* **2009,** *2*, 220–223.

(16) Kaiser, I.; Ernst, K.; Fischer, C. H.; Konenkamp, R.; Rost, C.; Sieber, I.; Lux-Steiner, M. C. The ETA-Solar Cell with $CuInS_2$: A Photovoltaic Cell Concept using an Extremely Thin Absorber (ETA). *Sol. Energy Mater. Sol. Cells* **2001,** *67*, 89–96.

(17) Vogel, R.; Hoyer, P.; Weller, H. Quantum-Sized PbS, CdS, Ag_2S, Sb_2S_3, and Bi_2S_3 Particles as Sensitizers for Various Nanoporous Wide-Bandgap Semiconductors. *J. Phys. Chem.* **1994,** *98*, 3183–3188.

(18) Chone, C.; Larramona, G. French patent FR2899385-A1, 2007.

(19) Itzhaik, Y.; Niitsoo, O.; Page, M.; Hodes, G. Sb_2S_3-Sensitized Nanoporous TiO_2 Solar Cells. *J. Phys. Chem. C* **2009,** *113*, 4254–4256.

(20) Moon, S. J.; Yum, J. H.; Humphry-Baker, R.; Karlsson, K. M.; Hagberg, D. P.; Marinado, T.; Hagfeldt, A.; Sun, L. C.; Grätzel, M.; Nazeeruddin, M. K. Highly Efficient Organic Sensitizers for Solid-State Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2009,** *113*, 16816–16820.

(21) Messina, S.; Nair, M. T. S.; Nair, P. K. Antimony Sulfide Thin Films in Chemically Deposited Thin Film Photovoltaic Cells. *Thin Solid Films* **2007,** *515*, 5777.

(22) Wenger, S.; Schmid, M.; Rothenberger, G.; Grätzel, M.; Schumacher, J. O. Model-Based Optical and Electrical Characterization of Dye-Sensitized Solar Cells. 24th EU PVSEC, Hamburg, Germany, 2009; pp 675−680.

DOI: 10.1021/jz100308q | *J. Phys. Chem. Lett.* **2010,** *1,* 1524–1527