



Origin of Nonlinear Device Performance with Illuminated Sun Intensity in Mesoscopic Sb_2S_3 -sensitized Photoelectrochemical Solar Cells using Cobalt Electrolyte

Sang Hyuk Im[†], Yong Hui Lee, Hi-jung Kim, Choong-Sun Lim, Yongku Kang, and Sang Il Seok[†]

KRICT-EPFL Global Research Laboratory, Advanced Materials Division, Korea Research Institute of Chemical Technology, 100 Jang-Dong, Yuseong-Gu, Daejeon 305-600, Korea

ABSTRACT :

The mesoscopic Sb_2S_3 -sensitized photoelectrochemical solar cells using cobalt redox electrolyte exhibit nonlinear behavior of power conversion efficiency with illuminated sun intensity. From the measurement of bulk diffusion and electrochemical impedance spectroscopy studies, we suggest that the nonlinearity of device performance with illuminated sun intensity is attributed not to the slow bulk diffusion problem of cobalt electrolyte but to the limited mass transport in narrowed pore volume in mesoscopic TiO_2 electrode.

Keywords : Sb_2S_3 , Photoelectrochemical solar cell, TiO_2 , Cobalt electrolyte

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1. Introduction

Since Grätzel *et al.*¹⁾ reported a mesoscopic dye-sensitized photoelectrochemical solar cell with high power conversion efficiency over 11% at 1 sun illumination, the sensitized photoelectrochemical solar cells have been intensively studied due to their distinguished device structure from conventional *p-n* heterojunction solar cells. The sensitized solar cells are comprised to mesoscopic photoanode, sensitizer, and redox electrolyte which has corresponding role of electron conductor, light absorber, and hole conductor, respectively. This unique device architecture enables the sensitized solar cells to hold cost-effectiveness.

Recently inorganic semiconductors have been considered as a promising alternative of conventional dyes because of their peculiar properties such as easy charge separation by higher dipole moment, ~10 fold higher extinction coefficient than Ru/organic dyes, convenient bandgap tunability by size control, and multiple exciton

generation.²⁾ Therefore, metal chalcogenides such as CdS(e) and PbS have been used as inorganic sensitizers in photoelectrochemical solar cells and the device performance is rapidly being improved until now.³⁻⁷⁾ Among the metal chalcogenides, the Sb_2S_3 seems to be one of good candidates to demonstrate highly efficient inorganic semiconductor-sensitized photoelectrochemical solar cells because solid-state Sb_2S_3 based solar cells exhibit high external quantum efficiency (EQE) in whole visible region and good power conversion efficiency exceeding 6% at 1 sun illumination.⁸⁻¹⁰⁾ However, the Sb_2S_3 -sensitized photoelectrochemical solar cells have not reported yet except one our previous report.¹¹⁾ This might be attributed to the very quick degradation of Sb_2S_3 in conventional redox electrolyte such as iodide and polysulfide because the Sb_2S_3 has relatively strong reactivity toward surrounding materials owing to the weakly bonded S atoms in between crystal layer.¹²⁾ We have found that the Sb_2S_3 -sensitized photoelectrochemical solar cell is stably working in cobalt redox electrolyte.¹¹⁾ However the mesoscopic Sb_2S_3 -sensitized solar cells using cobalt electrolyte exhibited severe nonlinearity of device performance with illuminated

[†]Corresponding author. Tel.: +82-42-860-7314

E-mail address: imromy@kRICT.re.kr, seoksi@kRICT.re.kr

sun intensity. Here we would like to report why the mesoscopic Sb_2S_3 -sensitized photoelectrochemical solar cells using cobalt redox electrolyte exhibit severe degradation of device performance as illuminated sun intensity increases and suggest how to reduce such severe degradation of power conversion efficiency with illuminated sun intensity.

2. Experimental

2.1. Preparation of mesoscopic TiO_2 film

For the preparation of mesoscopic TiO_2 film, a 50 nm-thick dense blocking TiO_2 layer (bl- TiO_2) was deposited on a F-doped SnO_2 (FTO, Pilkington, TEC15) substrate by spray pyrolysis deposition of 0.02 M titanium diisopropoxide bis(acetylacetonate) solution in order to prevent direct contact of FTO electrode and cobalt electrolyte. The 3 μm -thick mesoscopic TiO_2 (average particle size = ~ 60 nm, anatase)^{9,13} film was screen printed on bl- TiO_2 /FTO substrate and subsequently was calcined in 500°C for 1 h. The active area of mesoscopic TiO_2 photoanode was fixed to 0.18 cm^2 .

2.2. Deposition of Sb_2S_3 on mesoscopic TiO_2 by chemical bath deposition

0.65 g of SbCl_3 in 2.5 mL of acetone, 25 mL of 1 M $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution, and 73.5 mL of deionized water were mixed for the chemical bath deposition of Sb_2S_3 .^{9,14} The prepared mesoscopic TiO_2 film was then immersed into the chemical bath for 3 h to deposit Sb_2S_3 on mesoscopic TiO_2 surface and was washed by deionized water several times to remove any residual sulfate or chloride. The dried amorphous Sb_2S_3 deposited on mesoscopic TiO_2 film was heat-treated at 300°C under Ar atmosphere for 30 min to convert into crystalline phase.

2.3. Fabrication of Sb_2S_3 -sensitized photoelectrochemical solar cells

A Pt-coated counter electrode was prepared by dropping 5 mM H_2PtCl_6 in *i*-propanol onto FTO substrate and heating it up to 400°C for 20 min. The solar cells were assembled by sandwiching Sb_2S_3 deposited on the bl- TiO_2 /FTO substrate and Pt-coated counter electrode with a thermal adhesive film (Surlyn, 60 mm, DuPont). For cobalt redox electrolyte,⁷ 0.5 M $[\text{Co}(o\text{-phen})_3](\text{TFSI})_2$ (Co(II) redox couple), 0.05 M $[\text{Co}(o\text{-phen})_3](\text{TFSI})_3$ (Co(III) redox couple), and 0.2 M LiClO_4 of acetonitrile/ethylene carbonate (4/6 v/v) solution were prepared. Where *o*-phen stands for 1,10-phenanthroline and TFSI does for bis(trifluoromethanesulfonyl) imide. The electrolyte

was injected by vacuum backfilling process and the hole was sealed by a Surlyn film and cover glass. For the Sb_2S_3 -sensitized solar cell with P3HT (poly-3-hexylthiophene) interlayer, we spin-coated the P3HT solution (15 mg in 1 mL of dichlorobenzene) on Sb_2S_3 on mesoscopic TiO_2 film at 2500 rpm for 90 s. The device was assembled by the same above procedure.

2.4. Measurements

Photocurrent current density-voltage (J-V) curves were measured by solar simulator (Newport, Class A, 91195A) using a Keithley 2420 sourcemeter and calibrated Si reference cell (certified by NREL). The illuminated sun intensity was controlled by passing 1 sun light (100 mW/cm^2 AM 1.5G) of a solar simulator to neutral density filter. The external quantum efficiency (EQE) was measured using a fully computerized system comprising a light source (300-W Xe lamp, Newport, 66902), monochromator (Newport Cornerstone 260), and multimeter (Keithley 2002). Cyclic voltammograms were recorded using a BAS100B potentiostat (Bioanalytical Systems Inc.). A single compartment cell equipped with three-electrode configuration was used where a Pt microelectrode (diameter of 10 μm), a Pt wire, and a Ag/Ag^+ served as working, counter, and reference electrodes, respectively. The potential sweep rate was 10 mV/s. The electrochemical impedance spectroscopy (EIS) of the solar cells was measured using an impedance analyzer (Zahner IM6e) by applying 500 mV of bias voltage under 1 sun illumination.

3. Results and Discussion

Fig. 1(a) shows a schematic illustration of operation

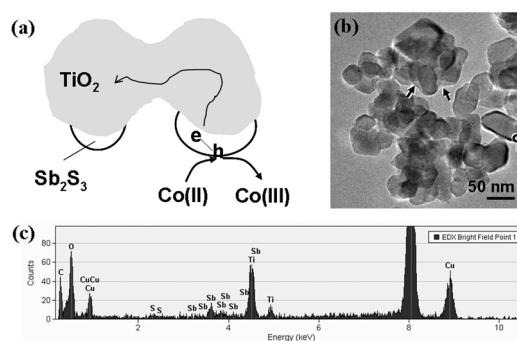


Fig. 1. (a) Schematic illustration of operation mechanism, (b) TEM image of Sb_2S_3 deposited on TiO_2 : arrows = Sb_2S_3 , and energy dispersive X-ray spectra of circle region in (b).

mechanism of Sb_2S_3 -sensitized photoelectrochemical solar cell. The Sb_2S_3 inorganic sensitizer generates electron-hole pairs by light illumination. The generated electrons are injected into TiO_2 electron conductor and simultaneously the oxidized Sb_2S_3 sensitizer is regenerated by cobalt redox couple. If there is neither severe recombination between TiO_2 / Sb_2S_3 and cobalt electrolyte nor mass transport problem of cobalt redox electrolyte, the Sb_2S_3 -sensitized solar cells will exhibit good device performance. Fig. 1(b) shows the TEM image of Sb_2S_3 deposited on mesoscopic TiO_2 layer, which displays that the size of deposited Sb_2S_3 sensitizer is polydispersed while some are thin film morphology and others are particulates (see the arrow in Fig. 1(b)). Fig. 1(c) shows the energy dispersive X-ray spectroscopy (EDS) of the red circle in Fig. 1(b) to confirm the deposition of Sb_2S_3 on mesoscopic TiO_2 electrode.

To demonstrate the Sb_2S_3 -sensitized photoelectrochemical solar cells by using well deposited Sb_2S_3 sensitizer on mesoscopic TiO_2 , we assembled the solar cell and measured photocurrent density-voltage (J-V) curves under different illuminated light intensity as shown in Fig. 2(a). All device performance with illuminated sun intensity is summarized in Table 1. As illuminated sun intensity is increased, the power conversion efficiency of Sb_2S_3 -sensitized solar cell is greatly degraded from 5.1% (0.1 sun) to 2.6% (1 sun). Fig. 2(a) and Table 1 indicate that severe degradation of device performance with illuminated sun intensity is derived from the significant degradation of fill factor (56.8% at 0.1 sun \rightarrow 34.5% at 1 sun). It is generally accepted that the fill factor is related to the recombination of charge carriers and the larger shunt resistance (R_{sh}) and the smaller series resistance (R_{s}) are desirable to attain high fill factor. Accordingly, Fig. 2(a) and Table 1 make us understand that the severe degradation of power conversion efficiency at 1 sun illumination is mainly ascribed to very small shunt resistance and relatively bigger series resistance. The smaller shunt resistance will cause the worse recombinational resistance (R_{ct}) at TiO_2 / Sb_2S_3 /cobalt electrolyte interface leading to more serious recombination. The very small increase of open circuit voltage (V_{oc}) with illuminated sun intensity might be resulted from the severe recombination as well. In addition, the value of $R_{\text{s}}/R_{\text{sh}}$ becomes no negligible as illuminated light intensity increases and consequently the short circuit current density (J_{sc}) exhibits nonlinearity with illuminated sun intensity as well. The EQE spectrum of Sb_2S_3 -sensitized solar cell in Fig. 2(b) shows that whole visible light can be effectively converted to electricity and the

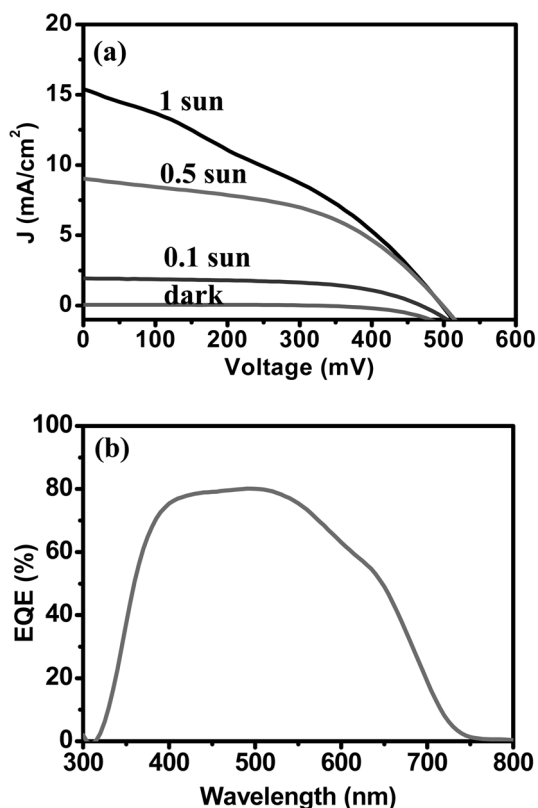


Fig. 2. (a) Current density-voltage (J-V) curves of Sb_2S_3 -sensitized solar cell with illuminated sun intensity and (b) EQE spectrum.

Table 1. The summary of device performance

	J_{sc} (mA/cm ²)	V_{oc} (mV)	F.F. (%)	η (%)	R_{sh} (Ω)	R_{s} (Ω)
0.1 sun	1.9	465	56.8	5.1	9.90K	261
0.5 sun	9.0	495	48.1	4.3	934	99
1 sun	15.4	495	34.5	2.6	322	90

spectrum is similar to that of conventional N719 dye in efficient dye-sensitized solar cell.

Intuitively we can expect that the Sb_2S_3 -sensitized solar cells using cobalt electrolyte will have more severe recombination than conventional dye-sensitized solar cells using iodide electrolyte because the positive character of $\text{Co}^{2+}/\text{Co}^{3+}$ redox couple is more favorably to be recombined with electrons in TiO_2 than the Γ^-/I_3^- redox couple having negative character and more bulkier cobalt redox couple move more slowly than iodide redox couple. To elucidate the reason why the Sb_2S_3 -sensitized solar cells

using cobalt electrolyte have severe degradation of power conversion efficiency at 1 sun illumination, we checked the bulk diffusion coefficient of conventional iodide redox couple and cobalt redox couple as shown in Fig. 3(a) and (b). From the EQE spectrum of Sb_2S_3 -sensitized solar cell, we can roughly assume that the number of generated charge carriers by Sb_2S_3 -sensitizer is comparable to N719-sensitizer. In dye-sensitized solar cells using iodide redox couple, the number of generated charge carriers per TiO_2 particles (18 nm in size) is ~ 100 fold less than that of Γ^- ions.¹⁵⁾ Therefore, the 10 fold slower bulk diffusion of cobalt redox couple than iodide redox couple will not seriously degrade the power conversion efficiency at 1 sun illumination. Very recent report¹⁶⁾ on the highly efficient organic dye-sensitized photoelectrochemical solar cell using cobalt redox electrolyte also supports that the slow bulk diffusion of cobalt redox couple will not seriously deteriorate device performance. Electrochemical impedance spectroscopy (EIS) is one of powerful tools to characterize the charge transfer/transport at interface in photoelec-

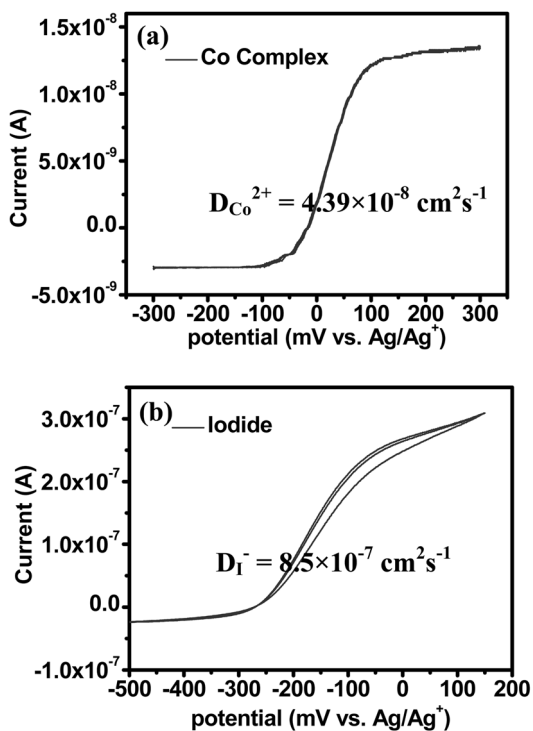


Fig. 3. Cyclic voltammogram of (a) cobalt redox electrolyte and (b) iodide redox electrolyte (0.60 M 1-butyl-3-methylimidazolium iodide, 0.03 M I_2 , 0.1 M guanidine thiocyanate, and 0.5 M 4-*tert*-butylpyridine in the mixture of acetonitrile/valeronitrile (85 : 15 v : v)).

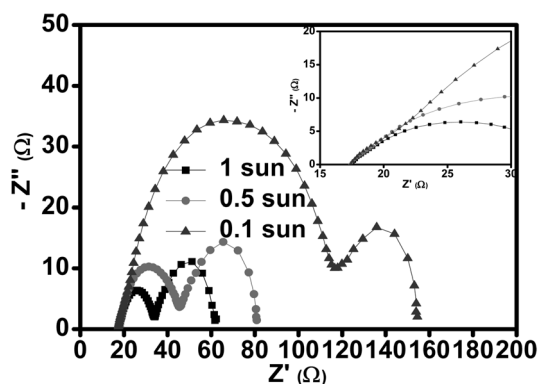


Fig. 4. Nyquist plots of Sb_2S_3 -sensitized photoelectrochemical solar cell with illuminated sun intensity : inset = magnified spectra in high frequency region.

trochemical solar cells. Hence, we measured EIS of Sb_2S_3 -sensitized photoelectrochemical solar cell with illuminated sun intensity as shown in Fig. 4. The Nyquist plots with illuminated sun intensity in Fig. 4 exhibit apparently three distinctive arcs at high, medium, and low frequency region. The first small arc at high frequency region (10^5 - 10^6 Hz) in inset of Fig. 4 will represent the charge transfer resistance and capacitance at Pt/cobalt electrolyte interface. The second arc at medium frequency region (10^2 - 10^3 Hz) might be related to recombinational resistance (R_{ct}) and chemical capacitance at TiO_2 (/ Sb_2S_3)/cobalt redox electrolyte or overlapped arc with contact resistance at TiO_2 (/ Sb_2S_3)/cobalt redox electrolyte.¹⁷⁾ The last arc at low frequency region (10^{-1} - 10^0 Hz) is related to finite Warburg of cobalt redox electrolyte. The constant value of real part in finite Warburg arc regardless of illuminated sun intensity indicates that there exists mass transport problem in mesoscopic Sb_2S_3 -sensitized solar cell even though we expect that the cobalt redox electrolyte will not have significant bulk diffusion problem. We think that the mass transport problem is not derived from bulk diffusion problem of cobalt electrolyte but is attributed to the mass transport limitation at the vicinity of (TiO_2)/ Sb_2S_3 /cobalt redox electrolyte interface due to insufficient pore volume because the Sb_2S_3 sensitizer is deposited on the surface of mesoscopic TiO_2 with thickness of ~ 10 nm. The shrunken pore volume will govern the mass transport of cobalt redox electrolyte and slow down the diffusion of cobalt(II)/(cobalt(II)) redox couple toward/(outward) (TiO_2)/ Sb_2S_3 . In other words, the cobalt(II) redox couple will regenerate the oxidized Sb_2S_3 sensitizer in the shrunken pore volume while itself is converted to cobalt(III) redox couple. Accordingly, the inefficient mass transport by the

shrunk pore volume can not avoid causing severe recombination of electrons in TiO₂ and cobalt(III) redox couple. Hence rational design of photoanode with sufficient pore volume is strongly required to fabricate highly efficient Sb₂S₃-sensitized photoelectrochemical solar cells at 1 sun illumination. In our previous report,¹¹⁾ we suggest another approach to reduce the mass transport limitation of cobalt electrolyte in mesoscopic Sb₂S₃-sensitized solar cell by introducing hole buffer P3HT (Poly-3-hexyl thiophene) interlayer which can efficiently extract the hole in Sb₂S₃. Fig. 5(a) is J-V curve of one example device of Sb₂S₃-sensitized solar cell with P3HT hole buffer interlayer exhibiting greatly reduced nonlinearity of power conversion efficiency with illuminated sun intensity. The Nyquist plot in Fig. 5(b) confirms the significant improvement of finite Warburg term in the solar cell although the transfer/transport resistance at P3HT/cobalt electrolyte/Pt interface is deteriorated.

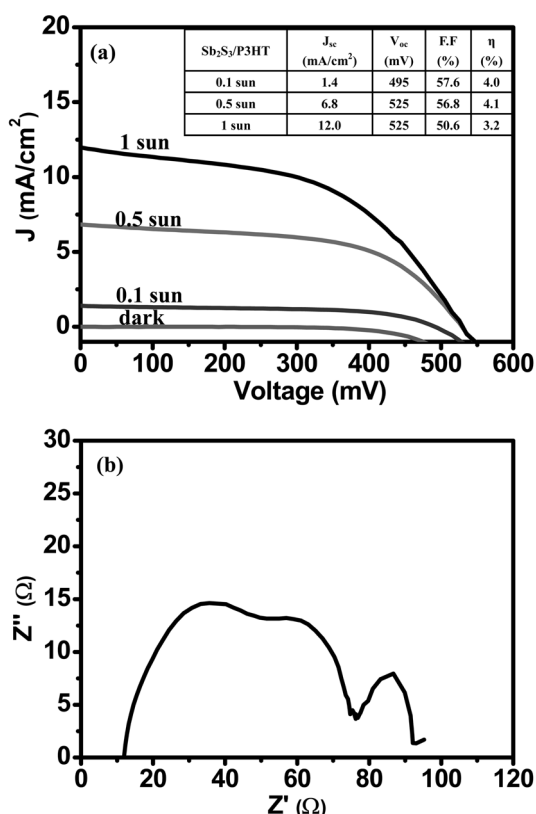


Fig. 5. (a) Current density-Voltage (J-V) curves of modified Sb₂S₃-sensitized photoelectrochemical solar cell with illuminated sun intensity and (b) its Nyquist plot.

4. Conclusion

The mesoscopic Sb₂S₃-sensitized photoelectrochemical solar cells using cobalt redox electrolyte showed nonlinear behavior of power conversion efficiency with illuminated sun intensity. To elucidate the origin of nonlinearity of power conversion efficiency with illuminated sun intensity, we investigated the bulk diffusion and EIS spectra. From the investigation, we can suggest that the nonlinearity of device performance with illuminated sun intensity is derived not from the slow bulk diffusion problem of cobalt electrolyte but from the limited mass transport in narrowed pore volume in mesoscopic TiO₂ electrode. The introduction of P3HT hole buffer interlayer can also reduce the nonlinear behavior of device performance with illuminated sun intensity due to efficient hole extraction from Sb₂S₃. Therefore, we believe that the highly efficient Sb₂S₃-sensitized photoelectrochemical solar cells using cobalt electrolyte could be demonstrated if we re-design the conventional mesoscopic TiO₂ photoelectrode to new TiO₂ electrode with sufficient pore volume and perform proper interface treatment.

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