

Electronic Supplementary Information

Chemical precursor for depositing Sb_2S_3 onto mesoporous TiO_2 layers in nonaqueous media and its application to solar cell

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Experimental

X-ray crystal structure determination

A crystal of dimensions 0.23 X 0.20 X 0.14 mm was mounted on a Bruker Smart Apex-II CCD X-ray diffractometer equipped with a Mo-target X-ray tube ($\lambda=0.71073 \text{ \AA}$) operated at 50 kV, 30 mA. The X-ray intensities were measured at 100(1) K with liquid N_2 stream and were integrated with the Bruker SAINT software package¹ with a narrow frame algorithm. The integration of the data yielded a total of 17139 reflections to a maximum 2θ value of 56.56° of which 2956 were independent and 2820 were greater than $2\sigma(I)$. The final cell constants (Table 1S) were based on the xyz centroids of 9985 reflections above $10\sigma(I)$. The data were processed with SADABS¹ and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008) software package,² using the space group Pbca with $Z=8$ for the formula $\text{SbCl}_3\text{C}_4\text{H}_{10}\text{N}_2\text{S}_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at $R1 = 0.0142$ and $wR2=0.0311$ [based on $I>2\sigma(I)$], $R1=0.0154$ and $wR2 = 0.0315$ for all data.

Device fabrication

An 50-nm-thick dense TiO_2 blocking layer (bl- TiO_2) was deposited on FTO (Fluorine doped SnO_2) glass (TEC8, Pilkington) by the spray pyrolysis deposition (SPD) of 0.02 M titanium diisopropoxide bis(acetylacetonate) solution to prevent direct contact between FTO and P3HT (Poly-3-hexylthiophene) hole transporting material. Then, 1.0 μm -thick mesoscopic TiO_2 (particle size = $\sim 50 \text{ nm}$, anatase phase) layer was screen printed on the bl- TiO_2 and sintered at 500°C for 1 h. The junction among the nanocrystalline TiO_2 particles was modified by immersing the mesoscopic TiO_2 film into a 20 mM of TiCl_4 aqueous solution for 12 h and sintering at 500°C for 30 min. The Sb_2S_3 sensitizer was deposited by chemical bath deposition (CBD) by dipping the mesoscopic TiO_2 film into chemical bath of non-aqueous medium at certain condition described in Table 2. The orange-colored amorphous Sb_2S_3 film was then annealed at 300°C in Ar atmosphere for 30 min. The P3HT/1,2 dichlorobenzene solution (15 mg/1 ml) was spin-coated on the Sb_2S_3 /mesoscopic TiO_2 film at 2500 rpm for 60 s, and

annealed at 90 °C in a vacuum oven for 40 min. The Au counter electrode was deposited by thermal evaporation under a pressure of 5×10^{-6} Torr. The active device area was fixed to 16 mm².

Device characterization

The current density-voltage (J-V) curves were measured at 1 sun illumination (AM 1.5 global, 100 mW/cm²) with a solar simulator (Newport, Class A, 91195A), a Keithley 2420 sourcemeter, and a calibrated Si reference cell (certified by NREL). The external quantum efficiency (EQE) spectra were measured by home-designed system using a light source (300 W Xe lamp, Newport, 66902), a monochromator (Newport Cornerstone 260), and a multimeter (Keithley 2002). All measurements were conducted by masking the cells with a 9.6 mm² metal mask on active area.

Table S1. Crystal data and structure refinement for Sb(III)(TA)₂Cl₃.

Identification code	20100810lt2_0ma
Empirical formula	C ₄ H ₁₀ Cl ₃ N ₂ S ₂ Sb
Formula weight	378.36
Temperature	100(1) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 10.3812(1) Å □ = 90°. b = 8.3211(1) Å □ = 90°. c = 27.6752(3) Å □ = 90°.
Volume	2390.67(5) Å ³
Z	8
Density (calculated)	2.102 Mg/m ³
Absorption coefficient	3.283 mm ⁻¹
F(000)	1456
Crystal size	0.23 x 0.20 x 0.14 mm ³
Theta range for data collection	1.47 to 28.29°.
Index ranges	-10 ≤ h ≤ 13, -11 ≤ k ≤ 9, -34 ≤ l ≤ 36
Reflections collected	17139
Independent reflections	2956 [R(int) = 0.0185]
Completeness to theta = 28.29°	99.7 %
Absorption correction	Multi-scan

Max. and min. transmission	0.6565 and 0.5190
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2956 / 0 / 110
Goodness-of-fit on F ²	1.121
Final R indices [I>2sigma(I)]	R1 = 0.0142, wR2 = 0.0311
R indices (all data)	R1 = 0.0154, wR2 = 0.0315
Extinction coefficient	0.00091(5)
Largest diff. peak and hole	0.481 and -0.293 e.Å ⁻³

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Sb(III)(TA)₂Cl₃. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sb	4280(1)	8190(1)	8680(1)	11(1)
Cl(1)	5298(1)	10712(1)	8871(1)	15(1)
Cl(2)	6393(1)	6849(1)	8701(1)	16(1)
Cl(3)	3304(1)	4639(1)	8694(1)	17(1)
S(1)	4366(1)	7969(1)	9670(1)	17(1)
C(1)	3022(1)	6943(2)	9840(1)	14(1)
C(2)	3066(2)	5963(2)	10292(1)	21(1)
N(1)	1960(1)	7006(2)	9596(1)	19(1)
S(11)	4840(1)	9251(1)	7775(1)	16(1)
C(11)	3801(1)	8247(2)	7408(1)	14(1)
C(12)	2750(1)	7202(2)	7599(1)	16(1)
N(11)	3899(1)	8401(2)	6941(1)	20(1)

Table S3. Bond lengths [Å] and angles [°] for Sb(III)(TA)₂Cl₃.

Sb-Cl(1)	2.4086(4)
Sb-Cl(2)	2.4618(4)
Sb-S(11)	2.7206(4)
Sb-S(1)	2.7474(4)
S(1)-C(1)	1.7025(15)
C(1)-N(1)	1.2954(19)
C(1)-C(2)	1.493(2)
C(2)-H(2A)	0.9600
C(2)-H(2B)	0.9600
C(2)-H(2C)	0.9600
N(1)-H(1A)	0.8600
N(1)-H(1B)	0.8600
S(11)-C(11)	1.7005(15)
C(11)-N(11)	1.3011(19)
C(11)-C(12)	1.493(2)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
N(11)-H(11A)	0.8600
N(11)-H(11B)	0.8600
Cl(1)-Sb-Cl(2)	89.930(13)
Cl(1)-Sb-S(11)	79.963(12)
Cl(2)-Sb-S(11)	88.732(12)
Cl(1)-Sb-S(1)	79.917(12)
Cl(2)-Sb-S(1)	85.284(12)
S(11)-Sb-S(1)	158.998(12)
C(1)-S(1)-Sb	106.41(5)
N(1)-C(1)-C(2)	119.08(13)
N(1)-C(1)-S(1)	122.19(12)
C(2)-C(1)-S(1)	118.72(11)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5

C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-N(1)-H(1A)	120.0
C(1)-N(1)-H(1B)	120.0
H(1A)-N(1)-H(1B)	120.0
C(11)-S(11)-Sb	104.81(5)
N(11)-C(11)-C(12)	117.81(14)
N(11)-C(11)-S(11)	119.68(12)
C(12)-C(11)-S(11)	122.50(11)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-N(11)-H(11A)	120.0
C(11)-N(11)-H(11B)	120.0
H(11A)-N(11)-H(11B)	120.0

Symmetry transformations used to generate equivalent atoms:

References

1. Bruker, (2005), APEX 2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
2. G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.