Supporting Information

**Colloidal Sb$_2$S$_3$ Nanocrystals: Synthesis, Characterization and Fabrication of Solid-State Semiconductor Sensitized Solar Cell**

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Synthesis of Sb$_2$S$_3$ NCs using antimomny chloride as an antimony source

1.1 Materials

Antimony (III) chloride (SbCl$_3$, 99.99%), antimony (III) acetate (Sb(OAc)$_3$, 99.99%), antimony(III) oxide (Sb$_2$O$_3$, 99%), tris(dimethylamido)antimony, oleic acid (OA), 1-octadecene (ODE, 90%), oleylamine (70%), anhydrous toluene, anhydrous methanol, acetone(99.5%), bis(trimethylsilyl) sulfide (TMS, 98%), and elemental sulfur, 3-mercaptopropyl(trimethoxisilane) (3-MPTMS, 95%) were purchased from Sigma-Aldrich.

1.2 Synthesis Procedure of Sb$_2$S$_3$ NCs

A total of 1 mmol SbCl$_3$, 6 ml oleic acid and 8 ml ODE were loaded into a 3-neck round-bottom flask, which was purged with N$_2$ and vacuum for 5 minutes, then heated to 150°C under vacuum for 1 h. Then, the vacuum was replaced with a N$_2$ environment, and the flask was heated to 180°C. A total of 1.5 mmol TMS in 5 ml ODE was then injected into the flask, and the temperature was decreased to 100°C. Aliquots were taken at different times. The as-synthesized NCs were washed with chloroform and ethanol by centrifuging and redisperssed in toluene.
Figure S1. EDS spectrum of orange Sb$_2$S$_3$ NCs

Figure S2. EDS spectrum of gray-black Sb$_2$S$_3$ NCs.
Figure S3. TEM and SAED images of as-synthesized Sb$_2$S$_3$ NCs using elemental sulfur in oleylamine as the sulfur source and SbCl$_3$ as the antimony source. a-b) 90s after injection, c-d) 90 minutes after injection, e-f) twice injection of sulfur source (90 min.)
Figure S4. a and b) TEM, c) scanning TEM, d and f) EDS of as-synthesized NCs using elemental sulfur in ODE.
Figure S5. TEM, HRTEM and SAED images of Sb$_2$S$_3$ NCs, where the TMS solution was injected at 140°C.
Figure S6. TEM and SAED images of Sb$_2$S$_3$ NCs, with an injection temperature of 220°C and a reaction time of just 90s.

Figure S7. Comparison of the growth of Sb$_2$S$_3$ NCs at different temperatures. TEM and HRTEM images of Sb$_2$S$_3$ NCs, a-c) injection and growth at 140°C, d-f) injection at 140°C and growth at 100°C.
Figure S8. TEM, HRTEM and SAED images of crystalline Sb$_2$S$_3$ NCs synthesized using antimony acetate (a and b) and antimony oxide precursors (c and d).

Figure S9. TEM, HRTEM and SAED images of Sb$_2$S$_3$ NCs synthesized in the presence of NaCl.
Figure S10. UV-Vis spectrum of orange Sb$_2$S$_3$ NCs on glass substrate after annealing at 300°C for 30 min.

Figure S11. SEM images of Sb$_2$S$_3$ NCs films on substrates, a) before annealing, and b) after annealing at 300°C for 30 min.
1.3 Fabrication of the Sb$_2$S$_3$ NC-Based Solid-State Semiconductor Sensitized Solar Cells

1.3.1 Chemicals and Materials

TiO$_2$ paste (Dyesol 18NR-T), home-made Sb$_2$S$_3$ NCs, hydrochloric acid, zinc powder, titanium isopropoxide (99.999% purity), thioacetamide, spiro-OMeTAD(98%), TiCl$_4$, lithium-bis(trifluoromethanesulfonyl)imide, 4-tert-butylypyridine, distilled water, isopropanol, N,N-dimethylformamide, 1-thiogycerol, EDT, TBAI, methanol, acetonitrile, toluene, chlorobenzene, ethanol, Au, FTO glass and kapton tape were purchased from Sigma-Aldrich. All solvents are anhydrous.

1.3.2 Preparation of Titanium Isopropoxide and TiO$_2$ Paste Solution

Preparation of titanium isopropoxide solution for the TiO$_2$ compact layer$^{27,28}$: 35 µL of a 2 M HCl solution is mixed with 5 ml of anhydrous ethanol, and the mix solution is placed in an ice bath for a while. Then, 370 µL of a titanium isopropoxide solution is added dropwise into the HCl, which contains ethanol. The final solution should be transparent. The TiO$_2$ paste solution$^{28}$ is prepared by dissolving TiO$_2$ in isopropanol in a 2:7 weight ratio and stirred vigorously until fully dissolved.

1.3.3 Substrate Patterning and Cleaning

FTO glass is patterned by etching with Zn powder and a 2 M HCl solution. Then, the etched FTO is cleaned with DI H$_2$O by sonication for 20 minutes and rinsed with DI H$_2$O. This process is repeated with acetone and isopropanol, and the substrate is dried with
nitrogen. The substrate undergoes an oxygen plasma treatment for 15 minutes to remove the last traces of organic residues prior to the deposition of the compact TiO$_2$ layer.

1.3.4 Preparation of the Hole Transporting Materials Solution

First, a Li-TFSI stock solution is prepared by dissolving 170 mg of LiTFSI in 1 M acetonitrile. Then, a spiro solution$^{27,29}$ is prepared by dissolving 80 mg of spiro-OMeTAD in 28.5 µL of 4-tert-butanol and 30 µL of the Li-TFSI stock solution in 1 ml of DMF..

1.3.5 Device Fabrication Process

The as prepared titanium isopropoxide solution in isopropanol is deposited on the clean and patterned FTO using a spin coater at 2000 RPM for 30 s, and the substrate is then annealed at 500°C for 30 min to form a compact TiO$_2$ film. Then, the diluted TiO$_2$ paste solution is spin coated onto the compact TiO$_2$-coated FTO at 2500 RPM for 30 s. After this step, the substrate is annealed at 550°C for 1 h to form a mesoporous TiO$_2$ layer. After the formation of the mesoporous TiO$_2$ layer, the sintered TiO$_2$ film is treated with a 0.02 M TiCl$_4$ solution in water at 70°C for 10 min. The film is rinsed with DI H$_2$O, dried with nitrogen after the treatment and sintered at 500°C for 30 minutes.$^{31}$ Finally, the film undergoes an oxygen plasma treatment for 5 minutes to remove traces of organic residues.

The surface of the TiO$_2$ film is functionalized with 3-MPTMS to improve the contact between the TiO$_2$ film and the Sb$_2$S$_3$ film. The TiO$_2$ film is immersed in a 5% (volume ratio) MPTMS toluene solution and refluxed at 90°C for 3 h in a glove box. The functionalized TiO$_2$ film is rinsed with toluene. The Sb$_2$S$_3$ NCs ink is deposited on the meso-TiO$_2$ coated FTO by dip-coating method. Then, the film is dip coated in a TBAI
solution (10 mg/ml in methanol) for 30 s, followed by three spin steps with methanol. After iodide treatment, the film is then treated with few drops of 2% V/V ethanedithiol (EDT) in acetonitrile at 2000 RPM and rinsed with acetonitrile at the same rotating speed. The spin coating sequence from the Sb$_2$S$_3$ paste to the (EDT) treatment is repeated one more time. The ligand-exchanged Sb$_2$S$_3$ film is then annealed at 300°C for 30 minutes under vacuum.

ZnS is coated on annealed Sb$_2$S$_3$ NCs film. In a typical coating process, a 0.1 M zinc acetate dehydrate and 0.1 M sodium sulfide hydrate solution is prepared in water. The annealed Sb$_2$S$_3$ film is dipped into the zinc acetate dehydrate and sodium sulfide hydrate solution for 60 s. After each dipping, the film is dipped into water and dried under a clean nitrogen flow.

The as-prepared hole transporting solution is spin coated on the Sb$_2$S$_3$ film at 2000 RPM for 45 s in air. Then, the film is kept in air overnight. Finally, a 100-nm-thick Au contact is thermally evaporated.
Figure S12. PL of Sb$_2$S$_3$ NCs and ZnS-coated Sb$_2$S$_3$ NCs film on a glass substrate.