Supporting Information

Fabrication of Coaxial TiO$_2$/Sb$_2$S$_3$ Nanowire Hybrids for Nanostructured Organic-Inorganic Thin Film Photovoltaics

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Experimental

Chemicals:

Acetone, isopropyl alcohol, TiCl₄, hydrochloric acid (35 %), SbCl₃, and Na₂S₂O₃ were used as received without any further purification.

Synthesis of vertically oriented TiO₂ nanowire array films:

Vertically oriented TiO₂ nanowire array films were grown on FTO-glass substrates. In a typical synthesis, the substrate was ultrasonically cleaned sequentially in acetone, isopropyl alcohol (IPA), and deionized (DI) water and then dried under N₂ flow. For nanowire fabrication, following the work of Feng¹², 1 mL of titanium tetrachloride was added drop-wise to a 1:1 mixture of DI water and concentrated (35 %) hydrochloric acid (HCl) to obtain a clear transparent solution. The substrate was placed in a 23 mL Teflon liner and the precursor solution added to it. The Teflon liner was loaded in an autoclave, which was then sealed and placed in an oven; growth was carried out at 170 °C for 1 h to achieve a nanowire array of approximately 500 nm length.

Deposition of extremely thin Sb₂S₃ films:

Amorphous Sb₂S₃ was deposited onto the TiO₂ nanowire films from a chemical bath comprised of 4.0 g of solid SbCl₃ dissolved in ~8 ml glacial acetic acid in a 250 ml beaker into which a 1.0 M aqueous solution of Na₂S₂O₃ was slowly introduced with constant stirring until a clear solution was obtained. The solution was then transferred into a 700 ml plastic container with 100 ml of thiosulfate to which approximately 450 ml of 12 °C deionized water was added. Higher reactant concentrations produced non-uniform films of poor adhesion. The pH of the bath into which the substrates were placed was approximately 3, if necessary adjusted with dilute acetic acid. For pH ≤ 2.5 film adhesion is poor, while for pH ≥ 3.5 the solution becomes turbid due to antimony salt precipitation.

Sb₂S₃ films are deposited by hydrolytic decomposition of antimony (III) thiosulfate compounds in aqueous media:³

\[
2S₂O₃^{2-} \rightarrow S₄O₆^{2-} + 2e^- \quad (1)
\]

Antimony-thiosulfate complexes are formed in excess of the complexing ions:

\[
\text{Sb}^{3+} + S₂O₃^{2-} \rightarrow \text{Sb}(S₂O₃)⁺ \quad (2)
\]

\[
\text{Sb}(S₂O₃)⁺ + S₂O₃^{2-} \rightarrow [\text{Sb}(S₂O₃)₂]⁻ \quad (3)
\]

In acidic media thiosulfate ions gradually release sulfide ions upon hydrolytic decomposition:

\[
S₂O₃^{2-} + H^+ \rightarrow S + HSO₃⁻ \quad (4)
\]

\[
S + 2e^- \rightarrow S^{2-} \quad (5)
\]
Sulfide ions can combine with the antimony(III) ions released from the thiosulfate complexes upon hydrolysis. The precipitated of Sb$_2$S$_3$ is amorphous, yellow-orange in color:

$$2\text{Sb}^{3+} + 3\text{S}^{2-} \rightarrow \text{Sb}_2\text{S}_3 \quad (6)$$

The chemical decomposition of the antimony thiosulfate compounds in the bath begins after $\approx 20$ min. Yellow orange precipitate begins to fill the bath container, and thin films of the same color start to grow on the substrate. We found an optimal chemical bath temperature of 10-15 °C, and optimal deposition temperature of 4 °C; at lower temperatures hydrolytic decomposition of the antimony thiosulfate complexes slows resulting in prolonged film formation. Bath temperatures above 20 °C lead to immediate Sb$_2$S$_3$ precipitation with no film deposition on the substrate. We found optimal Sb$_2$S$_3$ film adhesion with deposition initiated at 10 °C while a temperature of 4 °C, reduced in 2 °C steps from 10 °C, to be ideal for Sb$_2$S$_3$ deposition. Films deposited at less than 4 °C would immediately peel-off from the substrate.

**Materials characterization:**
The morphology and structure of the coaxial TiO$_2$/Sb$_2$S$_3$ nanowire hybrid thin films was determined by using field emission scanning electron microscope (FE-SEM, JEOL JSM-6300, Japan). X-ray powder diffraction (XRD, Bruker D8) was used to study the structure of the coaxial TiO$_2$/Sb$_2$S$_3$ nanowire hybrids.

**Device performance characterization:**
Device efficiencies were measured with a 500 W Spectra Physics light source fitted with Oriel AM 1.5G filter. The solar simulator was calibrated for AM 1.5G illumination using an NREL calibrated silicon solar cell fitted with a KG-5 filter (Newport M465440). The irradiance spectrum was verified using an optical spectrometer (Newport, OSM2-400DUV-U). Electrical measurements were performed at room temperature and ambient air.

**References:**
Table SI1: Summary of the reaction time-dependent particle size and resulting layer thickness of identifiable Sb$_2$S$_3$ synthesized by chemical bath deposition (CBD).

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Particle Diameter (nm)</th>
<th>S.D. (%)</th>
<th>Film layer thickness (nm)</th>
<th>S.D. (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>69</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
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<tr>
<td>3</td>
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<td>2.8</td>
<td>979</td>
<td>2.2</td>
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<tr>
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<td>1019</td>
<td>2.4</td>
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<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>1060</td>
<td>2.1</td>
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<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>1095</td>
<td>2.2</td>
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</table>

Table SI2: Summary of optimized FTO|TiO$_2$ nanowire array|Sb$_2$S$_3$|P3HT|PEDOT:PSS|Au photovoltaic parameters: short-circuit current density ($J_{sc}$) open circuit voltage ($V_{oc}$), fill factor (FF), and overall photoconversion efficiency h (%).

<table>
<thead>
<tr>
<th>Deposition Time (h)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>h (%)</th>
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<tbody>
<tr>
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<td>13.38</td>
<td>0.47</td>
<td>59</td>
<td>3.70</td>
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</tbody>
</table>
Figure SI1. Optical absorbance of rutile thin film, P3HT layer on rutile base, and chemically deposited Sb$_2$S$_3$ layer on rutile nanowire base; all films use FTO coated glass as substrate. Also shown is irradiance of AM 1.5G spectrum.
Figure S12. XRD pattern of Sb$_2$S$_3$ thin film annealed at 250°C in Ar for 0.5 h. The standard XRD pattern for stibnite Sb$_2$S$_3$ is also provided.