Electronic supplementary information

Low-cost, Mo(S,Se)₂-free superstrate-type solar cells fabricated with tunable band gap Cu₂ZnSn(S₁₋ₓSeₓ)₄ nanocrystal-based inks and the effect of sulfurization

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Experimental Details

1. Synthesis of Cu₂ZnSn(S₁₋ₓSeₓ)₄ nanocrystals
The Cu₂ZnSn(S₁₋ₓSeₓ)₄ nanocrystals were prepared by a hot-injection method. The Cu, Zn, and Sn ionic precursors were chosen as copper(II) acetylacetonate [Cu(acac)₂], zinc acetate [Zn(O₂CCH₃)₂], and tin(II) chloride dihydrate [SnCl₂.2H₂O], respectively. The Cu-poor and Zn-rich compositions were kept during the synthesis of these Cu₂ZnSn(S₁₋ₓSeₓ)₄ nanocrystals. In a typical synthesis, 1.68 mmol of copper(II) acetylacetonate, 1.4 mmol of zinc acetate, and 1.0 mmol of tin(II) chloride dihydrate were added into a 500 mL 3-neck flask with 30 mL of oleylamine. A (S+Se) anion precursors to Cu ratio of higher than 2.5 times was prepared for the hot-injection process. As that oleylamine solution of Cu, Zn, and Sn ionic precursors was heated at 200 °C, a 10 mL of oleylamine solution with various ratios of elemental S and Se (x = 0, 0.25, 0.5, 0.75, and 1) was injected, followed by heating at 250 °C for 1 h under argon atmosphere. After the reaction, the solution was precipitated by methanol and washed by isopropyl alcohol/hexane three times to remove the residual oleylamine.

2. Fabrication of devices
A 30 nm thick anatase TiO₂ layer was fabricated by a sol-gel synthesis, followed by heat treatment at 450 °C for 2 h on ITO-coated glass slides purchased from Nanocs (New York, NY). The CdS buffer layer using the mixed aqueous solutions of CdSO₄, NH₂CSNH₂, NH₄OH, and
Deionized water was deposited on the top of the TiO₂ layer by chemical bath deposition (CBD). Dense CdS thin-film layers were obtained during CBD inside a water bath maintained at 65 °C for 15 min. An ink consisting of Cu₂ZnSn(S₁₋ₓSeₓ)₄ nanocrystals and ethanol was prepared and spincoated onto the top of the CdS buffer layer. The Cu₂ZnSn(S₁₋ₓSeₓ)₄ film was formed by sulfurization of the spincoated Cu₂ZnSn(S₁₋ₓSeₓ)₄ layer. The sulfurization process was carried out by placing the sample of as-synthesized Cu₂ZnSn(S₁₋ₓSeₓ)₄ nanocrystals/CdS/TiO₂/ITO/soda-lime glass inside a graphite box with sulfur powders at 570 °C in a tubular furnace for 45 minutes under Argon flow. A mild hydrogen chloride (HCl) etching process was applied for the whole devices after the sulfurization. Finally, a thermally evaporated gold electrode was used to define an active device area of 0.1 cm².

3. Characterization of Materials

The Cu₂ZnSn(S₁₋ₓSeₓ)₄ crystals were characterized with a Philips X-ray diffractometer (XRD) using Cu Kα radiation. The cross-sectional SEM images were collected with a FEI Quanta 650. The compositional analyses were carried out by an energy-dispersive X-ray spectroscopy (EDS) equipped in a JOEL5610 SEM. The current density-voltage (J - V) characteristics using a solar simulator with a 100 mWcm⁻² light illumination under AM 1.5 G conditions were measured by a Keithley 2400 source measurement unit. All samples for the solar device performances were tested with the light illuminating through the ITO side of the substrate.