Ultrafast self-trapping of photoexcited carriers sets the upper limit on antimony trisulfide photovoltaic devices

Zhaoliang Yang1,6, Xiaomin Wang2,6, Yuzhong Chen1,6, Zhenfa Zheng3, Zeng Chen1, Wenqi Xu4, Weimin Liu4, Yang (Michael) Yang5, Jin Zhao3, Tao Chen2* & Haiming Zhu1,5*

Antimony trisulfide (Sb2S3) is considered to be a promising photovoltaic material; however, the performance is yet to be satisfactory. Poor power conversion efficiency and large open circuit voltage loss have been usually ascribed to interface and bulk extrinsic defects. By performing a spectroscopy study on Sb2S3 polycrystalline films and single crystal, we show commonly existed characteristics including redshifted photoluminescence with 0.6 eV Stokes shift, and a few picosecond carrier trapping without saturation at carrier density as high as approximately $10^{20}$ cm$^{-3}$. These features, together with polarized trap emission from Sb2S3 single crystal, strongly suggest that photoexcited carriers in Sb2S3 are intrinsically self-trapped by lattice deformation, instead of by extrinsic defects. The proposed self-trapping explains spectroscopic results and rationalizes the large open circuit voltage loss and near-unity carrier collection efficiency in Sb2S3 thin film solar cells. Self-trapping sets the upper limit on maximum open circuit voltage (approximately 0.8 V) and thus power conversion efficiency (approximately 16 %) for Sb2S3 solar cells.
The exploration of semiconductor material for low-cost, stable, and efficient thin-film photovoltaics has been a key target for solar energy conversion. Among them, Cu(In, Ga)Se₂, CdTe, and organic–inorganic hybrid perovskites play the leading role with power-conversion efficiencies (PCEs) above 20%, but on the other hand show various limitations imposed by element scarcity, stability, and environmental concerns. Recently, binary semiconductors antimony chalcogenides including Sb₂S₃ and Sb₂Se₃ emerge as promising materials due to their ideal bandgaps (E_g of 1.7 eV for Sb₂S₃ and 1.2 eV for Sb₂Se₃), large absorption cross-section, earth-abundance and environmentally-friendly and stable characters. They have fixed orthorhombic phase with infinite one-dimensional (1D) ribbons along the [001] or c direction (Fig. 1a for Sb₂S₃), avoiding complicated phase control during processing. In particular, Sb₂S₃ with E_g of 1.7 eV has been considered as a perfect component for the top subcell in Si-based tandem solar cells. The record PCE is 7.5% and 9.2% for Sb₂S₃ and Sb₂Se₃ thin films, respectively. However, their solar cell performances remain unsatisfactory to date. The open-circuit voltage (V_oc) for Sb₂S₃ solar cell is only half of theoretical thermodynamic limit (1.4 V), which is too large to be related to extrinsic impurities or defects. Together with polarized trap emission from single crystals, these results strongly suggest that photogenerated carriers are self-trapped by lattice distortion in Sb₂S₃. This intrinsic self-trapping explains well the 0.6 V V_oc loss and thermally activated carrier transport and ultimately sets the upper bound for the PCE in Sb₂S₃ and Sb₂Se₃ photovoltaic devices.

Results

Optical study of polycrystalline films. We first prepared Sb₂S₃ polycrystalline thin films via in situ hydrothermal growth on CdS/FTO substrate with CdS as electron transport layer in solar cell (see the Methods section for details). This method has been employed to grow high-quality Sb₂S₃ films for solar cells, and the thickness of Sb₂S₃ layer can be controlled by reaction time and temperature. The atomic force microscopy (AFM) image of a representative Sb₂S₃ solar cell is shown in Fig. 1a. The AFM image and XRD pattern of hydrothermal Sb₂S₃ polycrystalline film on CdS/FTO substrate are shown in Fig. 1b and 1c, respectively. The J-V curve and IPCE curve of a representative Sb₂S₃ solar cell are shown in Fig. 1d and 1e, respectively. The absorption and PL spectra of hydrothermal Sb₂S₃ thin film are shown in Fig. 1f.
shown in Fig. 1b indicates that as-grown Sb$_2$S$_3$ film is smooth and compact with large grain size. The crystal structure of Sb$_2$S$_3$ film was confirmed by X-ray diffraction (XRD) (Fig. 1c), and diffraction peaks at 15.7°, 17.6°, 25.0°, and 28.6° can be indexed to orthorhombic stibnite structure (JCPDS #42-1393). The photovoltaic properties of hydrothermal grown Sb$_2$S$_3$ film (thickness of ~300 nm) was examined by assembling FTO/CdS/Sb$_2$S$_3$/Spiro-OMeTAD/Au structured solar cell device (Fig. 1e inset). The J–V curve and incident photon-to-electron conversion efficiency (IPCE) curve of Sb$_2$S$_3$ thin-film solar cell under AM1.5 illumination are shown in Fig. 1d and e, respectively. The solar cell exhibits a $V_{oc}$ of 0.72 V, $J_{sc}$ of 14.6 mA cm$^{-2}$, $FF$ of 56.5%, and PCE of 6%, among the top values for planar Sb$_2$S$_3$ thin-film solar cell$^2$. IPCE curve shows a peak value >80% at 510–580 nm, and drops in shorter wavelength due to CdS buffer layer and longer wavelength due to reduced absorption. All these characterizations indicate high-quality Sb$_2$S$_3$ thin film by hydrothermal growth for photovoltaic devices.

The absorption and photoluminescence (PL) spectra of Sb$_2$S$_3$ thin-film (thickness of 160 nm) are shown in Fig. 1f. The absorption spectrum exhibits an onset at ~1.65 eV (750 nm) and a weak absorption peak at ~1.9 eV (650 nm). The absorption onset agrees well with the onset of IPCE curve, corresponding to the bandgap of Sb$_2$S$_3$ film$^{19,25}$. According to literatures and our calculation (Supplementary Fig. 1), Sb$_2$S$_3$ is an indirect bandgap semiconductor with indirect gap of 1.7 eV calculated from optical properties with transmitted light, we exfoliated the single crystal to an orthorhombic crystal structure of Sb$_2$S$_3$ allows perfect cleavage perpendicular to the c-axis with length of a few cm (along c-axis direction). Transmission X-Ray Laue photograph of Sb$_2$S$_3$ single crystal indicates the ground-state transitions through both band filling and Columbic effect (e.g., screening, band renormalization)$^{26}$. The other component B is dominated by induced absorption with peaks at 700 nm and 565 nm. Interestingly, component B rises gradually in ps and its rising coincides with decay of A component/mid-IR kinetics, indicating that the decay of free carrier at band-edge leads to new transient species in the Sb$_2$S$_3$ polycrystalline film. Together with the trap emission, component B can be safely assigned to trapped carrier which provides a direct measure for trapped carrier population. Similar induced absorption feature has also been observed in photoexcited Sb$_2$S$_3$ polycrystalline film and ascribed to sulfide radical (S$^-$)$^{19}$. Based on these steady-state and time-resolved optical measurements, we can conclude that photoexcited free carriers (including both electrons and holes) in the Sb$_2$S$_3$ polycrystalline film get trapped in tens of ps, leading to trapped carrier-induced absorption in visible and strongly red-shifted near-IR PL. The detailed carrier-trapping kinetics will be analyzed later with a rate equation model.

To gain more hints about the nature of the trap states discussed above, we varied the excitation fluence thus the transient carrier density over a large range (1.5 × 10$^{18}$ cm$^{-2}$ to 8 × 10$^{19}$ cm$^{-2}$). If the trapping process in the Sb$_2$S$_3$ polycrystalline film are due to extrinsic defects, e.g., surface states, impurities, or atomic vacancies, the saturation of trapped carrier-induced absorption (component B) would be expected when the trap states are filled. We plotted the maximum amplitude of B component as a function of photoexcitation carrier density (Fig. 2d). Interestingly, we did not observe any saturation signature even at carrier density approaching 10$^{20}$ cm$^{-3}$. Such large trap density suggests carrier trapping in Sb$_2$S$_3$ is likely intrinsic.

**Optical study of single crystal.** To minimize possible deterioration by extrinsic defects and reveal the intrinsic photoexcited carrier properties in Sb$_2$S$_3$, we turn to zone-refined stoichiometric Sb$_2$S$_3$ single crystals grown by chemical vapor transport$^{28}$. As shown in Fig. 3b inset, Sb$_2$S$_3$ single crystals have needle-like shape with length of a few cm (along c-axis direction) and width/height of ~1 mm, consistent with its quasi-1D crystal structure. Transmission X-Ray Laue photograph of Sb$_2$S$_3$ single crystal indicates high crystalline quality. We characterized the trap density of Sb$_2$S$_3$ single crystal by space charge limited current method, which shows a very low trap density of 6.8 × 10$^{15}$ cm$^{-3}$ (Supplementary Fig. 3). To probe the sample with transmitted light, we exfoliated the single crystal to an optically thin flake with thickness of 130 nm (Supplementary Fig. 4) for both steady state and TA measurements. The anisotropic crystal structure of Sb$_2$S$_3$ allows perfect cleavage perpendicular to the b-axis$^4$.

The absorption spectrum of Sb$_2$S$_3$ single-crystal flake (Fig. 3a) exhibits an onset at 1.7 eV (730 nm) and a peak at 1.9 eV (650 nm), similar to that of the polycrystalline film. The PL of Sb$_2$S$_3$ single crystal under 532 nm CW excitation is also strongly red-shifted and broad with a peak at 1.1 eV, which represents substantial energy loss (0.6 eV) and can be assigned to trap emission. An important clue about trap state comes from examining trap emission polarization as a function of angle ($\theta$) relative to the crystal c-axis (Fig. 3b). Surprisingly, the trap emission exhibits strong polarization along the c-axis, which can be fit by $\cos^2\theta$ function with a constant offset. The degree of polarization can be calculated by $(I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$ to be 24%. This indicates transition associated with trapped hole and the decay of mid-IR kinetics which directly probes free carrier population in the Sb$_2$S$_3$ film. Therefore, the component A can be assigned to photoexcited free carriers in Sb$_2$S$_3$ film which bleaches the ground-state transitions through both band filling and Columbic effect (e.g., screening, band renormalization)$^{26}$. We observed clear spectral evolution with increasing delay time, which can only be ascribed to emission from trap states rather than band-edge states.

To directly probe photoexcited carrier dynamics in a Sb$_2$S$_3$ polycrystalline film, we performed time-resolved TA measurements$^{19,25}$. We excited and created carriers in Sb$_2$S$_3$ thin film by 2.1 eV pump pulse and after a certain delay time, we observed a strongly red-shifted and broad PL peak at 1.15 eV under CW excitation (532 nm), albeit with weak intensity. This corresponds to a Stokes shift as large as ~500 meV, which forms instantaneously after photoexcitation carrier density approaching 10$^{20}$ cm$^{-3}$. Such large trap density suggests carrier trapping in Sb$_2$S$_3$ is likely intrinsic.
electron are preferentially orientated along the c-axis in Sb$_2$S$_3$ single crystal. Similar polarized near-IR PL was also observed from exfoliated Sb$_2$S$_3$ single crystal thin flakes, precluding the geometry effect as polarization origin. This polarized trap emission is unlikely due to surface states or impurities which usually would be randomly distributed and lead to isotropic trap emission.

More information about trap nature is provided by TA measurement on Sb$_2$S$_3$ single-crystal flake. The 2D plot of TA spectra is shown in Fig. 3c, which was analyzed by SVD method as above. The principle component spectra and associated kinetics are shown in Fig. 3d, e. Similar to the polycrystalline film, SVD analysis on Sb$_2$S$_3$ single-crystal flake yields a component A corresponding to photoexcited free carriers and a component B which is mainly contributed by induced absorption of trapped carriers. The main spectral features of principle components are similar in the Sb$_2$S$_3$ polycrystalline film and single-crystal flake with small variation likely due to inhomogeneous polycrystalline nature in former, justifying SVD method and suggesting their similar spectral origin. As shown in 3e, the decay of free carrier was confirmed with mid-IR probe and its decay process is also accompanied by the rise of trapped carrier-induced absorption. We varied the photoexcited carrier density (2 x 10$^{18}$ cm$^{-3}$ to 1.2 x 10$^{20}$ cm$^{-3}$) for Sb$_2$S$_3$ single-crystal flake and did not observe any saturation of trapped carrier induced absorption even when the carrier density was above 10$^{20}$ cm$^{-3}$ (Fig. 3f), which is too large to be related to extrinsic defects for Sb$_2$S$_3$ single crystal with a defect density of 6.8 x 10$^{19}$ cm$^{-3}$.

We performed similar steady state and transient optical measurements on the spin-coated and thermal-evaporated Sb$_2$S$_3$ polycrystalline films (see Supplementary Fig. 5 and Supplementary Fig. 6) and also observed a near-IR PL with ~0.6 eV Stokes shift and ultrafast carrier trapping to form similar induced absorption without any saturation. The close resemblance between Sb$_2$S$_3$ polycrystalline films of three different growth methods and Sb$_2$S$_3$ single crystal on carrier trapping properties, together with polarized trap emission in Sb$_2$S$_3$ single crystal, strongly suggest that ultrafast carrier trapping in Sb$_2$S$_3$ is associated with intrinsic self-trapping, instead of extrinsic defects as usually invoked.

**Discussion**

As was first introduced by Landau$^{29}$, in a material with soft lattice and strong carrier–phonon coupling, free carriers (electrons or holes), or excitons (bound electron–hole pairs) can be trapped within potential wells produced by local lattice distortion, forming a quasiparticle called “polaron”$^{30}$. When the short-range deformation–potential interaction is dominant over long range interaction, a small polaron forms as self-trapped carrier or exciton is localized within unit cell. Self-trapping as small polaron could occur even in a perfect crystal and create a transient defect state in bandgap by lattice deformation, leading to substantial energy loss and a Stokes-shifted PL (Fig. 4c).

Self-trapping is favored in materials with strong carrier–phonon interaction and small elastic constant, and has been observed in metal halide (e.g., NaCl), oxide (e.g., SiO$_2$) and chalcogenide crystals (e.g., As$_2$Se$_3$)$^{31,32}$. The elastic constant of Sb$_2$S$_3$ has been calculated$^{33}$, and the value (~40) is as small as that of SiO$_2$ and NaCl crystal$^{32}$. The Huang-Rhys parameter of Sb$_2$S$_3$, which reflects carrier–phonon interaction, was estimated to be 38.5, which is as large as that of NaCl and Cs$_2$AgInCl$_6$ where STE has been demonstrated (Supplementary Note 2). Dimensionality also plays an important role in self-trapping. Compared with three-dimensional system, free carrier in (quasi) 1D system has been predicted to be intrinsically unstable and tends to be self-trapped without barrier$^{31}$. As it happens, Sb$_2$S$_3$ has a quasi-1D crystal structure composed with (S$_8$S$_6$)$_n$ ribbons stacked with van der Waals interaction. Therefore, carrier/exciton self-trapping is very likely in Sb$_2$S$_3$ and can explain all the optical
properties and photoexcitation dynamics we observed, including strongly red-shifted trap emission, picosecond carrier trapping dynamics, trapped carrier induced absorption without saturation at $10^{20}$ cm$^{-3}$ carrier density, and polarized trap emission in single crystal. Similar spectroscopic characteristics have been observed in seemingly disparate materials where self-trapped carriers or excitons have been commonly observed.

Self-trapped carriers also differ strikingly from free carriers in transport properties. Because of strong localization to a single site, the former moves incoherently through thermally activated hopping process which moves faster with temperature while the latter moves through coherent band-like transport with inversely temperature relationship. Temperature-dependent electrical measurements have been performed on Sb$_2$S$_3$ polycrystalline films and single crystals. A combined electric and magnetic measurement on Sb$_2$S$_3$ crystal show thermal-assisted hopping transport mechanism, which can be well explained by carrier self-trapping in Sb$_2$S$_3$.

For free carriers, hole self-trapping instead of electron is generally observed in metal halides (e.g., AgCl, NaCl) and chalcogenides (e.g., As$_2$S$_3$, As$_2$Se$_3$) because of rich $p$ orbital electrons in valence band, possible bond alternation, and small valance band width. In addition to sulphide electrons, Sb$_2$S$_3$ possess Sb 5s$^2$ inert lone-pair electrons with complex Sb–S chemical bonds and coordinations. Electronic structure calculation also shows narrower valance band width than conduction band in Sb$_2$S$_3$ (Supplementary Fig. 1). All these suggest hole is more likely to be self-trapped than electron in Sb$_2$S$_3$. This is consistent with smaller hole mobility than electron and previously suggested accepter-like trap state in Sb$_2$S$_3$ crystal.

Self-trapping of electrons and holes after photoexcitation eventually leads to self-trapped excitons (STEs). Based on Stokes shift, the trapping depth of STE is $\sim$0.6 eV away from band-edge state. A temperature dependent study (between 77 K and 297 K) on STE emission from Sb$_2$S$_3$ single crystal shows negligible band-edge excitation emission and no change of STE emission intensity as a function temperature, which indicates small energy barrier (less than kT of ~6.6 meV for 77 K) from band-edge carrier to STE and large (>0.4 eV) trapping depth for STE based on a thermal quenching model simulation (see Fig. 3).
signal. With reported photoexcitation diffusion coefficient of 6.8 × 10⁻⁷ cm² s⁻¹ in the Sb₂S₃ polycrystalline film, this corresponds to a diffusion length of 400 nm. We note this diffusion coefficient value is likely a mixture of free carrier and STE; therefore this diffusion length should be considered as an upper bound for STE. This explains near-unity carrier collection efficiency in a Sb₂S₃ thin film solar cell, despite the formation of STE. Since self-trapping is intrinsic to the crystal, equivalent sites occur in each unit cell, which allows thermal-assisted hopping transport. Indeed, the STE half-life time is significantly shortened to be 6.9 ns on CdS/FTO substrate, suggesting efficient carrier extraction by transport in bulk followed by interfacial electron transfer to CdS (Supplementary Fig. 8). We also note there is band bending and build-in electric field in CdS/Sb₂S₃ junction, which can facilitate the dissociation of STE and carrier drift transport²⁰,²¹.

Similar to extrinsic defect states, self-trapping localizes carriers to specific sites and creates defect states in the gap (Fig. 4c). While in general extrinsic defects undeniably affect excited state carrier lifetime and solar cell performance, self-trapping is primarily responsible for ultrastark carrier trapping and energy loss process in Sb₂S₃, instead of surface/interface/bulk extrinsic trap states usually assumed. Based on PL Stokes shift, self-trapping causes 0.5–0.6 eV energy loss, which well explains the near-clamped Voc loss (0.63 V) between record Voc value and theoretical value. Different from extrinsic trap states, self-trapping will exist even in perfect Sb₂S₃ crystal, setting the upper limit on Voc and PCE of Sb₂S₃ solar cell. Assuming thermodynamic limit values of Jsc and FF remain same in Sb₂S₃, but Voc is reduced from 1.4 V to 0.8 V due to self-trapping energy loss, maximum PCE of Sb₂S₃ solar cell will be 16% instead of 28.6%²². Although our studies here are all based on planer Sb₂S₃ thin films, carrier/exciton self-trapping should also occur in Sb₂S₃-sensitized photovoltaic devices with several nanometer thickness because of its intrinsic nature. There both extrinsic surface trapping and intrinsic self-trapping would affect excited-state carrier properties and device performances due to large surface area²³. This study here calls for reconsideration of Sb₂S₃ and Sb₂Se₃ as the photovoltaic materials and designing and optimizing their optoelectronic devices.

Methods
Sample preparation. The Sb₂S₃ polycrystalline film on the CdS/FTO substrate was grown via hydrothermal method following our previous report¹⁶. Sb₂S₃ polycrystalline film on glass was prepared with spin-coating antimony-antimony-complex precursor solution and post annealing³². Thermal-evaporated Sb₂S₃ thin film was deposited on glass at a high vacuum (~1 × 10⁻¹ Pa) and annealed on preheated hot plate at 300 °C for 2 min in a glove box. A Sb₂S₃ single crystal was grown by chemical vapor transport (Shanghai Onway Technology Co, Ltd)²⁸.

Device fabrication and measurement. The hole-transporting layer was prepared by spin-coating Spiro-OMeTAD chlorobenzene solution with the concentration of 36 mg mL⁻¹ at 3000 rpm for 30 s and then with a post treatment at 100 °C for 10 min. Au counter electrode about 70 nm was deposited by a thermal evaporator under a pressure of 3.0 × 10⁻⁶ Pa. Current–voltage measurements of Sb₂S₃ solar cell was performed in a standard xenon-lamp-based solar simulator (Oriel Sol 3A, USA). The test was under a 100 mW cm⁻² solar irradiation at room temperature. The solar simulator illumination intensity was calibrated by a monocrystalline silicon reference cell calibrated by the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE, Model SPIE200) was measured using a single-source illumination system (halogen lamp) combined with a monochromator.

Electronic structure calculation. The calculations were carried out using Vienna ab initio simulation package (VASP) with a plane wave basis set. The electron–nuclei interaction was described by the projector augmented wave (PAW) method. For the exchange-correlation functional, we used the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE). Structures were fully relaxed until residual forces on constituent atoms became smaller than 0.01 eV Å⁻¹, and total electronic energies were converged to 10⁻⁵ eV. An energy cutoff parameter of 450 eV and a Monkhorst-Pack k-point sampling grid of 5 × 5 × 5.
Optical measurement. Absorption spectra of films were measured on a Cary 5000 UV-Vis-NIR absorption spectrometer with integrating sphere. Absorption of exfoliated flakes and room temperature photoluminescence (PL) were performed on a home-built microscope setup. We used a 532-nm CW laser as excitation and collected the PL and sent to an EMCCD (ProEM:16002, Princeton Instrument) for visible region and a liquid nitrogen cooled InGaAs detector (PyLon IR, Princeton Instrument) for near-IR region. For femtosecond TA measurements, the fundamental beam from Yb: KGW laser (Pharos, Light Conversion Ltd.) was separated on a home-built microscope setup. We used a 532-nm CW laser as excitation and collected the transmitted probe light with (ns TA-pump) and without (Tunpump) pump were collected and the normalized transmittance change ΔT/T was calculated by ΔT/T = (Tpulse - Tunpump)/Tunpump.

Data availability

The source data necessary to support the findings of this paper are available from the corresponding author upon request.

Received: 24 July 2019; Accepted: 11 September 2019; Published online: 04 October 2019

References

1. Zeng, K., Xue, D.-J. & Tang, J. Antimony selenide thin-film solar cells. Semicond. Sci. Technol. 31, 063001 (2016).
2. Kondrotas, R., Chen, C. & Tang, J. Sb2S3 solar cells. Joule 2, 857–878 (2018).
3. Wang, X., Tang, R., Wu, C., Zhu, C. & Chen, T. Development of antimony sulfide–selenium Sb2Se3-based solar cells. J. Energy Chem. 27, 731–721 (2018).
4. Boix, P. P. et al. From flat to nanostructured photovoltaics: balance between thickness of the absorber and charge screening in sensitized solar cells. ACS Nano 6, 873–880 (2012).
5. Choi, Y. C., Lee, D. U., Noh, J. H., Kim, E. K. & Seok, S. I. Highly improved Sb2S3 sensitized-inorganic-organic heterojunction solar cells and quantification of traps by deep-level transient spectroscopy. Adv. Funct. Mater. 24, 3587–3592 (2014).
6. Kim, D.-H. et al. Highly reproducible planar Sb2S3-sensitized solar cells based on atomic layer deposition. Nanoscale 6, 14549–14554 (2014).
7. Zhou, Y. et al. Thin-film Sb2Se3 photovoltaics with oriented one-dimensional ribbons and benign grain boundaries. Nat. Photonics 9, 409–415 (2015).
8. Tang, R. et al. n-Type doping of Sb2S3 light-harvesting films enabling high-efficiency planar heterojunction solar cells. ACS Appl. Mater. Interfaces 10, 30314–30321 (2018).
9. Li, Z. et al. 9.2%-efficient core-shell structured antimony selenide nanorod array solar cells. Nat. Commun. 10, 125 (2019).
10. Wang, W. et al. Over 6% certified Sb2(Se)3 solar cells fabricated via in situ hydrothermal growth and postannealing. Adv. Electron. Mater. 5, 190083 (2019).
11. Zimmermann, E. et al. Toward high-efficiency solution-processed planar heterojunction Sb2S3 solar cells. Adv. Sci. 2, 1500059 (2015).
12. Bera, A., Das Mahapatra, A., Mondal, S. & Basak, D. Sb2S3/SpiroOMeTAD inorganic-organic hybrid p-n junction diode for high performance self-powered photodetector. ACS Appl. Mater. Interfaces 8, 34306–34312 (2016).
13. Wang, X. et al. A fast chemical approach towards Sb2S3 film with a large grain size for high-performance planar heterojunction solar cells. Nanoscale 9, 3386–3390 (2017).
14. Yuan, S. et al. Postsurface selenization for high performance Sb2S3 planar thin film solar cells. ACS Photonics 4, 2862–2870 (2017).
15. Jiang, C. et al. Alkali metals doping for high-performance planar heterojunction Sb2S3 solar cells. Sol. RRL 3, 1800272 (2019).
16. Yuan, S. et al. Efficient planar antimony sulfide thin film photovoltaics with large grain and preferential growth. Sol. Energy Mater. Sol. Cells 157, 887–893 (2016).
17. Savadogo, O. & Mandal, K. C. Low-cost schottky-barrier solar-cells fabricated on CdSe and Sb2S3 films chemically deposited with silicotungstic acid. J. Electrochem. Soc. 141, 2871–2877 (1994).
18. Boix, P. P. et al. Hole transport and recombination in all-solid Sb2S3-sensitized TiO2 solar cells using CuSCN as hole transporter. J. Phys. Chem. C. 116, 1579–1587 (2011).
19. Christians, J. A. & Kamat, P. V. Trap and transfer. Two-step hole injection across the Sb2S3/CuSCN interface in solid-state solar cells. ACS Nano 7, 7967–7974 (2013).
20. Darga, A. et al. On charge carrier recombination in Sb2S3 and its implication for the performance of solar cells. J. Phys. Chem. C 117, 20525–20530 (2013).
21. Christians, J. A., Leighton, D. T. & Kamat, P. V. Rate limiting interfacial hole transfer in Sb2S3 solid-state solar cells. Energy Environ. Sci. 7, 1148–1158 (2014).
22. Yang, Y. et al. Time-resolved observations of photo-generated charge-carrier dynamics in Sb2Se3 photocathodes for photoelectrochemical water splitting. ACS Nano 12, 11088–11107 (2018).
23. Wang, K. et al. All free and trapped carriers contribute to photocurrent of Sb2S3 solar cells. J. Phys. Chem. Lett. 10, 4881–4887 (2019).
24. Liu, M., Gong, Y., Li, Z., Dou, M. & Wang, F. A green and facile hydrothermal approach for the synthesis of high-quality semi-conducting Sb2S3 thin films. Appl. Surf. Sci. 387, 790–795 (2016).
25. Chong, W. K. et al. Direct measurement of coherent phonon dynamics in solution-processed stibnite thin films. Phys. Rev. B 90, 035208 (2014).
26. Bennett, B. R., Soref, R. A. & Alamo, J. A. D. Carrier-induced change in refractive index of InP, GaAs and InGaAsP. IEEE J. Quantum Electron. 26, 113–122 (1996).
27. Ruckebusch, C., Slawa, M., Pernot, P., de Juan, A. & Tauler, R. Comprehensive data analysis of femtosecond transient absorption spectra: a review. J. Photochemistry Photobiol. C: Photochemistry Rev. 13, 1–27 (2012).
28. Vengatesan, B., Kanniah, N. & Ramasamy, P. Growth of Sb2S3 single crystals by chemical vapour transport. Mater. Chem. Phys. 17, 311–316 (1987).
29. Landau, L. Electron motion in crystal lattices. Phys. Z. Sowjetunion 3, 644–645 (1933).
30. Emin, D. Optical properties of large and small polaron and bipolarons. Phys. Rev. B 48, 13691–13702 (1993).
31. Song, K. S. & Williams, R. T. Self-Trapped Excitons (Springer, 1993).
32. Martin, P. et al. Subpicosecond study of carrier trapping dynamics in wide-band-gap crystals. Phys. Rev. B 55, 5799–5810 (1997).
33. Koc, H., Mamedov, A. M., Delizog, E. & Ozisik, H. First principles prediction of the elastic, electronic, and optical properties of Sb2S3 and Sb2Se3 compounds. Solid State Sci. 14, 1211–1220 (2012).
34. Yang, Y. et al. Efficient and stable emission of warm-white light from lead-free halide double perovskites. Nature 563, 541–545 (2018).
35. Roy, B., Chakraborty, B. R., Bhattacharya, R. & Dutta, A. K. Electrical and magnetic-properties of antimony sulfide (Sb2S3) crystals and mechanism of carrier transport in it. Solid State Commun. 25, 937–940 (1978).
36. Tiyag, N., Rusa, G. L., Cipnina, V., Prodan, G. & Vasilé, E. Structural and electrical properties of antimony trisulfide thin films. J. Optoelectron. Adv. Mater. 7, 727–732 (2005).
37. Haj Lakhdar, M., Ouni, B. & Amlouk, M. Dielectric relaxation, modulus and magnetic-properties of antimony sulfide (Sb2S3) crystals and mechanism of carrier transport in it. Solid State Commun. 25, 937–940 (1978).
38. Ristein, J. & Weiser, G. Reorganization of germinate pairs in As3Se5 single crystals. Philos. Mag. B 78, 541–542 (1993).
39. Ristein, J. & Weiser, G. Microscopic structure of the radiative centre in As3Se5 crystals. Solid State Commun. 66, 361–365 (1988).
40. Khan, S. et al. Nanosecond light-induced transient absorption in As2S5: Self-trapped exciton recombination in amorphous chalcogenides. J. Non-Cryst. Solids 426, 72–77 (2015).
41. Kyono, A., Kimata, M., Matsuhashi, M., Miyashita, Y. & Okamoto, K. Low-temperature crystal structures of stibnite implying orbital overlap of Sb 5s2 inert pair electrons. Phys. Chem. Miner. 29, 254–260 (2002).
42. Carneiro, L. M. et al. Excitation-wavelength-dependent small polaron trapping of photoexcited carriers in [alpha]-Fe2O3. Nat. Mater. 16, 819–825 (2017).
43. Kata, K. J. et al. Electron small polarons and their mobility in iron (oxyhydr) oxide nanoparticles. Science 337, 1200–1203 (2012).
calculations. Z.C. and Y.Y. performed electric characterization on single crystal. W.X. and W.L. helped with nanosecond TA measurements. Z.Y., X.W., and H.Z. wrote the paper together, and all authors comment on the paper.

**Competing interests**
The authors declare no competing interests.

**Additional information**
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-019-12445-6.

Correspondence and requests for materials should be addressed to T.C. or H.Z.

Peer review information Nature Communications thanks Ye Yang and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2019