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Preferentially oriented large antimony trisulfide single-crystalline cuboids grown on polycrystalline titania film for solar cells

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Photovoltaic conversion of solar energy into electricity is an alternative way to use renewable energy for sustainable energy production. The great demand of low-cost and efficient solar cells inspires research on solution-processable light-harvesting materials. Antimony trisulfide (Sb_2S_3) is a promising light-harvester for photovoltaic purposes. Here we report on the in situ grown monolayer of preferentially oriented, large Sb_2S_3 single-crystalline cuboids on a polycrystalline titania (TiO_2) nanoparticle film. A facile, oriented seed-assisted solution-processing method is used, providing the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -based bulk/nano-planar heterojunction with a preferred structure for efficient planar solar cells. An orientation-competing-epitaxial nucleation/growth mechanism is proposed for understanding the growth of the Sb_2S_3 single-crystalline cuboids. With an organic hole transporting material, the stable solar cell of the heterojunction yields a power conversion efficiency of 5.15% (certified as 5.12%). It is found that the [221]-oriented Sb_2S_3 cuboids provide highly effective charge transport channels inside the Sb_2S_3 layer.

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The demand of efficient and low-cost solar cells inspires the researches on light-harvesting materials for photovoltaic purposes. Nowadays, most of the efficient, stable, and practically potential solar cells are mainly based on inorganic planar heterojunctions (PHJs), thanks to the high charge mobility and good structural stability of inorganic semiconductors. The PHJ based on a bulk semiconductor layer of large grains and a crystalline layer of nanostructures can be referred to as bulk/nanoplane heterojunction (BnPHJ) in the material structure point of view. The BnPHJs consisting of an inorganic bulk p-type semiconductor layer of grain sizes comparable to layer thickness and an inorganic n-type nanoparticle film are preferred in efficient PHJ solar cells^{1–3}, because the bulk p-type layers as light-harvesting materials can offer a highly effective charge generation and transportation as the results of reducing the deficiencies related to small size (e.g., high exciton binding energy⁴, low carrier concentration and high defects trap density⁵, and poor electronic contact because of surface capping agents⁶) and the energy loss due to charge recombination at grain boundary. The solution-processing method, which mainly involves a film matrix formation by simple technologies (e.g., spin-coating, doctor blading, screen printing, inlet printing) and a followed post-annealing at low temperatures (normally ≤ 500 °C), has been demonstrated to be an effective strategy to fabricate low-cost and efficient solar cells, for which a representative is hybrid perovskite solar cells that have reached the efficiency up to 22%^{7,8}. However, the solution-processing methods for preparing the inorganic bulk p-type layers for efficient solar cells are still challenging³ and rarely reported^{9–12}.

Crystalline Sb_2S_3 consists of non-toxic and earth-abundant elements and is a promising photon-harvesting material for solar cells¹³, due to its suitable direct band gap ($\sim 1.4\text{--}1.8$ eV)¹⁴, high absorption coefficient ($\sim 10^5$ cm⁻¹) in the visible spectrum¹⁵, high electron ($\mu_e \approx 10$ cm² V⁻¹ s⁻¹)¹⁶ and hole ($\mu_h \approx 2.6$ cm² V⁻¹ s⁻¹)¹⁷ mobilities, and easy availability by many synthesis scenarios at low temperature (<400 °C). Theoretically, the single-junction solar cells based Sb_2S_3 absorber are expected to achieve the power conversion efficiency (η) of 27–33% according to Shockley–Queisser limit¹⁸. The highest efficiency of $\eta = 7.5\%$ was obtained in the bulk heterojunction solar cells based on the Sb_2S_3 -sensitized mesoporous TiO_2 films¹⁹. Up to now, only the BnPHJs of large Sb_2S_3 grain layers over polycrystalline CdS nanoparticle films (i.e. $\text{Sb}_2\text{S}_3/\text{CdS}$ -BnPHJs) were prepared by rapid thermal evaporation and yielded the PHJ solar cells with a best device efficiency of $\eta = 3.5\%$ ^{20,21}.

Here, a simple repetition of spin-coating and annealing (RSCA) solution-processing method for the in situ grown monolayer of preferentially oriented large Sb_2S_3 single-crystalline cuboids on the polycrystalline TiO_2 film surface is developed, offering a novel $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ that is of application potential to efficient solar cells. Since the presence of preferentially oriented Sb_2S_3 crystalline seeds formed on the TiO_2 film surface before carrying out the RSCA procedure is an essential prerequisite for the growth of Sb_2S_3 cuboids, our approach is therefore referred to as an oriented seed-assisted RSCA method. Based on scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations, a new epitaxial nucleation/growth mechanism is proposed for the in situ growth of the large single-crystals on polycrystalline surface. Furthermore, the solar cell with a considerable efficiency of $\eta = 5.15\%$ (certified as 5.12%) is obtained by spin-coating an organic hole transporting layer over the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ surface.

Results

Heterojunction formation and characterization. The oriented seed-assisted RSCA approach to prepare the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ

in this experiment is schematically illustrated in Fig. 1a. SbCl_3 and thiourea reactants were sequentially dissolved at room temperature in a mixture solvent of DMF and glycerin (DMF/glycerin = 4/1 in volume), resulting in a transparent and yellow Sb_2S_3 precursor solution that is stable for weeks. The SbCl_3 solution in the mixture solvent was colorless, but it rapidly became yellow after adding thiourea. The color change indicates the formation of an SbCl_3 -thiourea complex^{22,23}. As shown in the Supplementary Information (Supplementary Fig. 1 and Supplementary Note 1), our Fourier transform infrared (FT-IR) results confirmed the SbCl_3 -thiourea complex formation with a highly polar structure of thiourea molecules (Fig. 1a, inset), and also revealed that glycerin remained inactive during the complex formation. The dense polycrystalline TiO_2 nanoparticle film is prepared on the clean FTO substrate by the procedure described elsewhere²⁴. We first use a thin Sb_2S_3 precursor film to generate the oriented Sb_2S_3 crystalline seeds on TiO_2 film surface (Method). Afterwards, a thicker Sb_2S_3 precursor film is spin-coated onto the Sb_2S_3 seed-decorated TiO_2 film and then annealed in N_2 atmosphere at 330 °C for ca. 10 min, which is referred to as one RSCA cycle; the multiple iterations of the spin-coating/annealing with a certain RSCA cycle number (n) result in the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ with a monolayer of Sb_2S_3 cuboids over polycrystalline TiO_2 film.

SEM image (Fig. 1b) shows that an Sb_2S_3 layer consisting of truncated and closely packed cuboids is in situ grown on the TiO_2 film surface in a large area without cracks, offering a large area $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ. The Sb_2S_3 cuboids stem from the TiO_2 film (90 nm thick) and have a number density (defined as the number of the cuboids of different sizes per unit area) of about 2.7/ μm^2 . Most of the cuboids have a height equal to the film thickness (600 nm) (Fig. 1c), indicating that the Sb_2S_3 layer is actually a monolayer of Sb_2S_3 cuboids. In particular, the lateral sizes of the cuboids distribute broadly from 200 nm to 1.1 μm and are much larger than the size of TiO_2 nanoparticles in the TiO_2 film (10–20 nm) (Supplementary Fig. 2a and Supplementary Note 2). The Sb_2S_3 cuboids display the XRD peaks of orthorhombic Sb_2S_3 (stibnite) with a $Pbnm$ space group (JCPDS no. 42-1393) and no secondary phases are observed (Fig. 1d). For simplicity, we refer to the crystal growth along the direction out of substrate plane as out-of-plane growth and that along the direction in substrate plane as in-plane growth. Interestingly, the Sb_2S_3 cuboids are preferentially oriented with the [221] direction normal to substrate plane, indicating that most cuboids have the out-of-plane growths along the [001], [010] and [100] directions with the (001) and (100)/(010) planes tilting the average angles of ca. 44° and 61° on substrate, respectively (Fig. 1d, inset), where a - and b -axes are closely parallel to the lateral directions and the c -axis is closely parallel to the height direction. However, the TiO_2 film only exhibits the XRD pattern of FTO substrate. The reason for the undetectable TiO_2 component in the TiO_2 film and $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ by XRD is because the diffraction of such thin TiO_2 film is too weak. As shown previously²⁴, when we used a thicker TiO_2 film (e.g., 150 nm thick) on FTO substrate, the XRD peak for the (101) plane of anatase TiO_2 became observable (Supplementary Fig. 2b and Supplementary Note 2), confirming the exposure of (101) crystal plane on film surface^{25–27}.

TEM was used to further characterize the Sb_2S_3 cuboids. The TEM sample was prepared by cross-sectioning the film using the focused ion beam technique. The cross-sectional TEM image (Fig. 2a) shows two densely packed Sb_2S_3 cuboids almost vertically stemming from the TiO_2 film surface and that the TiO_2 film (90 nm thick) consists of 10–20 nm nanoparticles. The body of an individual Sb_2S_3 cuboid (i.e., Cuboid I) was imaged by HRTEM at different locations (Fig. 2b–d). The same lattice fringes are observed in the different locations with the lattice spacings of 0.363 nm, 0.384 nm, and 0.562 nm corresponding to

Fig. 1 Preparation and characterization of Sb₂S₃/TiO₂-BnPHJ. **a** Schematic illustration showing the oriented seed-assisted RSCA method for preparing Sb₂S₃/TiO₂-BnPHJ; *n* is the RSCA cycle number, and the inset shows the photograph of the stable Sb₂S₃ precursor solution in which a Sb₂S₃-thiourea complex is formed. **b** Bird-view (right: magnified image of the marked area) and **(c)** cross-sectional SEM images of as-prepared Sb₂S₃/TiO₂-BnPHJ on FTO substrate. **d** The XRD patterns of the Sb₂S₃/TiO₂-BnPHJ and TiO₂ film on FTO substrates, in which the standard XRD pattern for Sb₂S₃ (JCPDS no. 42-1393) is included for reference. Shown by the inset to **d**, the angle between a specific Sb₂S₃ crystal plane and substrate is derived from the angle between the crystal plane and the Sb₂S₃ [221] direction that is normal to substrate plane. The arrows on **c** indicate the presence of small Sb₂S₃ grains. The Sb₂S₃ cuboids in **(b-d)** were prepared with *n* = 4 and their number density is about 2.7/μm². **b** Scale bars 10 μm (low magnification) and 2 μm (high magnification). **c** Scale bar 1 μm

the (101)/($\bar{1}01$), (001) and (200) planes of orthorhombic Sb₂S₃, confirming the single-crystalline nature of the cuboid that has a continuous out-of-plane growth of (001) planes from stem to top. Moreover, the selected area electron diffraction (SAED) pattern of another Sb₂S₃ cuboid (i.e., Cuboid II) also confirms its single-crystalline nature with an out-of-plane growth along the [001] direction (Fig. 2f). The single-crystalline nature was further supported by the TEM and HETEM images of more Sb₂S₃ cuboids (Supplementary Fig. 3).

In order to get insights into the Sb₂S₃ cuboid growth, the Sb₂S₃/TiO₂ interface was studied by HRTEM (Fig. 2e). The HRTEM image resolves the lattice fringes of both Sb₂S₃ and TiO₂ regions at the interface. In the TiO₂ region, two differently oriented particles (TiO₂-A and TiO₂-B) got imaged, where TiO₂-A particle exhibits the lattice spacings of 0.352 nm and 0.268 nm, respectively, corresponding to the (101)/(011) and (110) planes, but TiO₂-B particle only displays (101) planes. In the Sb₂S₃ region, the upper part exhibits the same lattice fringes to the main body of Cuboid I (Fig. 2b-d), and a clear Sb₂S₃ growth transition zone of 3–6 nm in width adjacent to the TiO₂ film surface is observed. Normally, a sharp interface is observed in the epitaxially grown single-crystalline/single-crystalline heterojunctions even with lattice-misfits^{28–33}. The appearance of the Sb₂S₃ growth transition zone indicates more epitaxial strains during the heterogeneous nucleation/growth of Sb₂S₃ crystals are present in comparison to the cases of single-crystalline/single-crystalline systems^{30,31}. In the Sb₂S₃ growth transition zone, two sets of the Sb₂S₃ lattice fringes were observed over the two TiO₂ nanoparticles. Since the

anatase TiO₂ film has the (101) planes exposing on film surface (Supplementary Fig. 2 and Supplementary Note 2) and the theoretical lattice mismatch (ca. 3%) between orthorhombic Sb₂S₃ (101) and anatase TiO₂ (101) planes is quite small (Supplementary Table 1), it is expected that the epitaxial relationship for the growth of orthorhombic Sb₂S₃ crystals on anatase TiO₂ film surface should be Sb₂S₃ (101)//TiO₂ (101)²⁷. As experimentally observed (Fig. 2e), the Sb₂S₃ (002) plane is almost parallel to TiO₂ (110) plane for TiO₂-A particle, while the Sb₂S₃ (101) plane is parallel to TiO₂ (101) plane for TiO₂-B particle. Interestingly, when changing the TiO₂ nanoparticle orientation with Sb₂S₃ (002)//TiO₂ (110) for TiO₂-A particle to that with Sb₂S₃ (101)//TiO₂ (101) for TiO₂-B particle, the width of the Sb₂S₃ growth transition zone is found to get reduced. Given the Sb₂S₃ (002)//TiO₂ (110) relationship, an angle of ca. 30° between orthorhombic Sb₂S₃ (101) plane and anatase TiO₂ (101) plane at TiO₂-A particle is theoretically derived from the difference between the angles of ca. 19° formed by orthorhombic Sb₂S₃ (002) and (101) planes and ca. 49° formed by anatase TiO₂ (110) and (101) planes (Supplementary Table 2), which indicates that there is a larger orientation-mismatch at TiO₂-A particle in respect of the Sb₂S₃ (101)//TiO₂ (101) epitaxial relationship. Therefore, the change in the width of the Sb₂S₃ growth transition zone with TiO₂ (101) orientation demonstrates experimentally that the epitaxial relationship of Sb₂S₃ (101)//TiO₂ (101) is actually present for orthorhombic Sb₂S₃ cuboid growth on polycrystalline anatase TiO₂ film surface, and the orientation-mismatch causes more epitaxial strains at the interface of heterojunction.

Fig. 2 TEM and HRTEM characterizations of the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ. **a** Cross-sectional TEM image. **b–e** HRTEM images and **(f)** SAED pattern at the locations cycle-marked on image **(a)**. On image **(e)**, the dashed straight lines identify the Sb_2S_3 growth transition zone adjacent to TiO_2 surface, while the dashed and curve line represents the grain boundary between two differently oriented TiO_2 nanoparticles. The Sb_2S_3 cuboids were prepared with $n = 4$ and the arrow on **(a)** indicates the presence of small Sb_2S_3 grains. **a** Scale bar 200 nm. **b–e** Scale bars 2 nm

The growth of cuboids is highly reproducible, and the RSCA cycle number n for film growth mainly controls the Sb_2S_3 layer thickness/cuboid height. For example, the thinner monolayer of the Sb_2S_3 cuboids with a number density of ca. $3.1/\mu\text{m}^2$, a preferential [221]-orientation, a height of ca. 400 nm and a lateral size of 120 nm to $1.1\mu\text{m}$ was obtained in a large area without cracks for $n = 2$ (Supplementary Fig. 4). Moreover, our results show the TiO_2 surface is crucially important to the preferential [221]-orientation of Sb_2S_3 cuboids; for example, only irregular Sb_2S_3 grains preferentially oriented with the [301] direction normal to substrate plane were produced when the TiO_2 film was replaced with pure FTO substrate (Supplementary Fig. 5 and Supplementary Note 3). Furthermore, when without glycerin in the precursor solution, the preferentially [221]-oriented Sb_2S_3 cuboids of serious rough growth surface³⁴ were rendered (Supplementary Fig. 6 and Supplementary Note 4), demonstrating that the glycerin does not impose evident effects on the cuboid orientation, but maintains the smoothness of cuboid growth surfaces by providing the chemical species to inhibit the strain-driven surface roughening²⁸.

In particular, we found that the preferentially oriented Sb_2S_3 crystalline seeds formed on TiO_2 nanoparticle film surface before carrying out the RSCA procedure are indispensable to the growth of the [221]-oriented Sb_2S_3 cuboids. When without Sb_2S_3 crystalline seeds, only the irregular and much larger Sb_2S_3 grains with no preferential orientation were generated on the TiO_2 film surface (Supplementary Fig. 7 and Supplementary Note 5). The Sb_2S_3 crystalline seeds feature the irregular shapes but a preferential orientation with the [221] direction normal to substrate plane and are only rendered in thin Sb_2S_3 precursor film (e.g., $<100\text{ nm}$) (Supplementary Fig. 8 and Supplementary Note 6). Moreover, the Sb_2S_3 cuboids in the first RSCA cycle (i.e., $n = 1$) predominantly grow from the Sb_2S_3 seed crystals and

follows the crystal plane orientation in the Sb_2S_3 seed crystals (Supplementary Fig. 9 and Supplementary Note 7), where the growth rate in the c -axis direction is slower than in a - and b -axes directions similar to the formation of Sb_2S_3 crystalline seeds.

From the comparisons amongst the number densities of the Sb_2S_3 cuboids (i.e., about $3.5/\mu\text{m}^2$ for $n = 1$, $3.1/\mu\text{m}^2$ for $n = 2$, and $2.7/\mu\text{m}^2$ for $n = 4$) and the corresponding cuboid dimensions, it is clearly known that the increase in the RSCA cycle number when $n > 1$ mainly leads to the growth of Sb_2S_3 cuboids in the c -axis direction and the merge of some small cuboids into large ones; moreover, from the unchanged [221]-orientation of Sb_2S_3 crystals in the seeds and the resulting cuboids at $n = 1$ –4, particularly, the unchanged cuboid shape with increasing n value, it is known that the self-nucleated crystal growth takes place from the first seed through the resulting cuboid (Supplementary Note 8).

Heterojunction growth mechanism. The growths of Sb_2S_3 nanoparticles on TiO_2 nanoparticles^{19,22} and TiO_2 nanoparticle film²³, large single-crystalline Sb_2S_3 grains on CdS nanoparticle film^{20,21}, large single-crystalline Sb_2Se_3 grains on CdS^{35,36} and ZnO³⁷ nanoparticle films, and perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ cuboids on PEDOT:PSS³⁸ and condensed nanostructured TiO_2 ^{39–41} films have been reported. Very recently, the epitaxial films of inorganic semiconductor (e.g., CsPbBr_3 , PbI_2 , and ZnO) crystals were deposited onto single-crystal and single-crystal-like substrates by simply spin-coating either the materials or the material precursors⁴², where the out-of-plane and in-plane orientations of the films were determined by the substrate and it was assumed that the thin stagnant layer of supersaturated solution produced during spin-coating promoted heterogeneous nucleation on the substrate over homogeneous nucleation in the bulk solution.

Fig. 3 Crystal structure and epitaxial growth model. **a** Orthorhombic Sb_2S_3 consists of $(\text{Sb}_4\text{S}_6)_n$ ribbons stacked parallel to $[001]$ direction. **b** Atomic configuration at the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ interface epitaxially grown between the (101) planes of orthorhombic Sb_2S_3 and anatase TiO_2 crystals. **c** Schematic illustration of the OCE nucleation/growth model for the growth of Sb_2S_3 single-crystalline cuboids on polycrystalline TiO_2 nanoparticle film, where the most competitive TiO_2 nanoparticle orientation for the Sb_2S_3 single-crystals to nucleate/grow features its (101) plane tilting an angle (α) on substrate plane close to $\alpha = 33^\circ$ (Particle 2), but the nucleation/growth at other sites around (e.g., particle 1 of $\alpha = 0^\circ$ and Particle 3 of $\alpha = 62^\circ$) is relatively much slower or suppressed due to their unfavorable TiO_2 (101) plane orientations

However, the nucleation/growth mechanisms of the large single-crystalline grains on polycrystalline film surfaces are so far not clear yet.

Orthorhombic Sb_2S_3 consists of $(\text{Sb}_4\text{S}_6)_n$ ribbons that grow along the $[001]$ direction via strong covalent Sb–S bonds and are packed together along $[100]$ and $[010]$ directions by van der Waals forces (Fig. 3a)^{13,27}. Experimentally, the main growth features of the Sb_2S_3 cuboids are: (i) the orientation of Sb_2S_3 cuboids is exclusively governed by the beneath TiO_2 nanoparticle film; (ii) one single-crystalline Sb_2S_3 cuboid is grown over many TiO_2 nanoparticles and the Sb_2S_3 cuboids mainly have the out-of-plane growths along the $[001]$, $[100]$ and $[010]$ directions; (iii) the heterogeneously nucleation follows the epitaxial relationship of Sb_2S_3 (101)// TiO_2 (101) between orthorhombic Sb_2S_3 and anatase TiO_2 , where the spatial distance of Ti–O (4.71 nm) on TiO_2 (101) plane actually matches that of S–Sb (4.79 nm) on Sb_2S_3 (101) plane for a good coordination (Fig. 3b). Here we propose an orientation-competing-epitaxial (OCE) nucleation/growth mechanism for the in situ growth of the preferentially oriented Sb_2S_3 single-crystalline cuboids on polycrystalline TiO_2 nanoparticle film, as illustrated in Fig. 3c.

In the OCE mechanism, the capability of a surface TiO_2 nanoparticle to act as an effective site for the heterogeneously epitaxial nucleation of Sb_2S_3 crystal according to the epitaxial relationship of Sb_2S_3 (101)// TiO_2 (101) strongly depends on its orientation, and only those orientated with (101) planes tilting favorable angles (α) on substrate plane are competitive during the heterogeneously epitaxial nucleation/growth of orthorhombic Sb_2S_3 cuboids. Known from the calculated possible angles between the crystalline planes and substrate plane for anatase TiO_2 and epitaxially grown stibnite Sb_2S_3 crystals as the results of TiO_2 (101) plane orientations (Supplementary Table 3,

Supplementary Fig. 10 and Supplementary Note 9), the surface TiO_2 nanoparticle orientation with the (101) plane tilting an angle of $0^\circ \leq \alpha < 62^\circ$ on substrate plane is theoretically necessary for heterogeneously epitaxial nucleation/growth of orthorhombic Sb_2S_3 single-crystalline cuboids, because it allows the easier out-of-plane growths of Sb_2S_3 crystals along the $[001]$, $[100]$, and $[010]$ directions as experimentally observed. In view of the fact that the Sb_2S_3 cuboids normally have the (001) planes tilting an angle of ca. 44° on substrate plane (Fig. 1d, inset), one gets to know that the most competitive TiO_2 nanoparticle orientation for the heterogeneously epitaxial nucleation/growth of the Sb_2S_3 single-crystalline cuboids features the tilting angle close to $\alpha \approx 33^\circ$ (Supplementary Table 3, Supplementary Fig. 10 and Supplementary Note 9).

As shown in Fig. 3c, during the OCE nucleation/growth process, the heterogeneously epitaxial nucleations of orthorhombic Sb_2S_3 crystals on the TiO_2 nanoparticles with favorable orientations take place, when the orientations of Sb_2S_3 crystals are governed by the TiO_2 (101) plane orientations; after nucleation, the Sb_2S_3 nuclei take a self-nucleated growth into the Sb_2S_3 crystalline seeds that maintain the orientations of their nuclei (Supplementary Fig. 8c); finally, the Sb_2S_3 crystalline seeds further take a self-nucleated growth into larger Sb_2S_3 cuboids by the followed RSCA cycles, where the growth rate in the c -axis direction turns to be larger than in a - and b -axis directions when $n > 1$ (Fig. 1b,c; Supplementary Figs. 4, 8b and 9b), the orientations of Sb_2S_3 crystal planes in their seed crystals are not changed (Fig. 1d; Supplementary Figs. 8c and 9c), and the chemical species provided by the glycerin maintains the smoothness of growing cuboid surfaces by inhibiting the strain-driven surface roughening^{28,34} (Fig. 1b,c; Supplementary Figs. 4 and 6). Since the self-nucleated growth of Sb_2S_3 cuboids takes

place from stem to top, no interfaces are introduced into the cuboid body with increasing n for the cuboid growth, which is clearly indicated by the HRTEM images at different locations showing the single-crystalline nature of the cuboids (Fig. 2b–d). With the faster nucleation/growth at a site with the most/more competitive TiO_2 (101) plane orientation (e.g., Particle 2), the nucleation/growth at around sites with less-competitive/unfavorable TiO_2 (101) plane orientation (e.g., Particles 1 and 3) becomes much slower or suppressed, resulting in one large Sb_2S_3 seed crystal/cuboid over many TiO_2 nanoparticles.

Moreover, the epitaxial strains caused by lattice-misfit and orientation-mismatch in the heterogeneous nucleation must get eventually released during the growth of Sb_2S_3 crystals, which leads to the presence of the Sb_2S_3 growth transition region in the vicinity to $\text{Sb}_2\text{S}_3/\text{TiO}_2$ interface^{30,31,33}. In particular, the faster Sb_2S_3 growth will merge the slower growth starting from the neighborhood nucleation sites with a comparable TiO_2 (101) orientation, when more strains for the epitaxial growth due to the difference in the TiO_2 (101) orientation inevitably lead to the widening of the Sb_2S_3 growth transition region (Fig. 2e). Furthermore, since the TiO_2 (101) crystal planes are randomly and two-dimensionally orientated in substrate plane, the resulting Sb_2S_3 cuboids inevitably orient with the c -axis titling different angles on the substrate plane and pointing randomly to out-of-plane directions (Fig. 1b, c; Supplementary Figs. 4a,b and 9b). Obviously, the lateral size of Sb_2S_3 cuboids eventually depends on the number density of the TiO_2 nanoparticles with the most/more competitive orientation. Note, we got the TEM images of the cuboids with the [001] direction closely vertical to substrate plane by a chance (Fig. 2; Supplementary Fig. 3), suggesting that those cuboids are grown from the heterogeneously epitaxial nucleations on the TiO_2 nanoparticles with the (101) plane orientation of $\alpha \approx 0^\circ$ (Supplementary Table 3 and Supplementary Fig. 10).

Solar cells. The as-prepared Sb_2S_3 cuboids layer in $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ exhibits an absorption edge at ca. 750 nm corresponding to the band gap (E_g) of Sb_2S_3 layer (i.e., $E_g = 1.65$ eV) and has an absorption coefficient (α) of ca. 10^5 cm^{-1} in the range of 350–650 nm (Fig. 4a). The $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ solar cell was fabricated by spin-coating 2,2',7,7'-tetrakis-(N,N -di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) as hole transporting material over the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ, followed by depositing Au counter electrode via thermal evaporation, as shown in Fig. 4b, where SEM image clearly shows that the Spiro-OMeTAD layer tightly covers the surface of Sb_2S_3 cuboids. Using the energy-dependence of the measured α , the Sb_2S_3 layer thickness required to absorb 90% incident photons (I_0) of a specific wavelength is evaluated according to Beer-Lambert law $I = I_0 \exp(-\alpha x)$ ⁴³. Clearly, the Sb_2S_3 cuboids layer with a thickness of ca. 700 nm is required for absorbing 90% incident photons of 350–700 nm. However, the solar cells with the Sb_2S_3 layer of ca. 600 nm in thickness (i.e., $n = 4$) have a poorer performance than those with ca. 400-nm-thick Sb_2S_3 layer (i.e., $n = 2$) (Supplementary Table 4). With the diffusion coefficients (D) of $0.25 \text{ cm}^2 \text{ s}^{-1}$ for electrons¹¹ and $0.07 \text{ cm}^2 \text{ s}^{-1}$ for holes¹⁷ in crystalline Sb_2S_3 , the diffusion lengths (L_D) of electrons and holes in Sb_2S_3 layer are respectively calculated to be 340 nm and 180 nm, according to the relation $L_D^2 = D\tau$, where $\tau = 4.6$ ns is the lifetime of charge carriers¹⁷. The thickness-dependence of device performance inevitably correlates to the limited L_D of charge carriers inside the Sb_2S_3 layer.

In the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ solar cell of ca. 400-nm-thick Sb_2S_3 layer, we obtained the considerable efficiency of $\eta = 5.15\%$ under AM 1.5 illumination (100 mW/cm^2) resulting from the open-circuit voltage (V_{oc}) of 0.66 V, short-circuit current (J_{sc}) of 13.12 mA/cm^2

and fill factor (FF) for 59.46% (Fig. 4c), for which a certified efficiency of $\eta = 5.12\%$ was obtained from the National Institute of Metrology (NIM), China to confirm the reliability of the efficiency (Supplementary Fig. 11). The efficiency is much higher than that (i.e., $\eta = 3.5\%$) of the devices based on the $\text{Sb}_2\text{S}_3/\text{CdS}$ -BnPHJ prepared by thermal evaporation^{20,21}, mainly due to the much higher J_{sc} . The observed device performance is of a high reproducibility and the averaged efficiency of six independent devices reaches 5.10% (Supplementary Table 4). The incident photon-to-current conversion efficiency (IPCE) spectrum shows that the solar cell has a broad spectral response in the wavelength range of 300–750 nm (Fig. 5d), in a good agreement with the absorption feature of the Sb_2S_3 layer (Fig. 4a). Our devices exhibit a good long-term stability, for example, the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ solar cell still retains over 91% of the initial efficiency after the storage in N_2 atmosphere for 30 days (Supplementary Fig. 12).

In order to investigate the influence of Sb_2S_3 grain orientation on solar cell performance, we prepared the ref- $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ solar cell with $n = 2$ (ca. 450-nm-thick Sb_2S_3 layer) for comparison. The large Sb_2S_3 grains in the ref- $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ display the XRD pattern same to the polycrystalline powder sample (Supplementary Fig. 7), indicating no preferential orientation of Sb_2S_3 grains therein but actually suggesting that the Sb_2S_3 grains in ref- $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ are oriented with [130]/[310] direction normal to substrate plane (Supplementary Note 5). However, the ref- $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ solar cell exhibits a much poorer efficiency of $\eta = 3.62\%$ with $V_{oc} = 0.66$ V, $J_{sc} = 11.52 \text{ mA/cm}^2$ and FF = 47.87% (Fig. 4c; Supplementary Table 4). The lower J_{sc} in the ref- $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ device is related to the reduced contribution of the charge carriers generated in the whole Sb_2S_3 layer to photocurrent generation, as shown by the IPCE spectra in Fig. 4d. Our intensity modulated photocurrent spectroscopy (IMPS) results show that the transit time (τ_D) for photogenerated electrons to reach the collection electrode in the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ solar cell ($\tau_D = 19.55 \mu\text{s}$) was much smaller than that in the ref- $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ device ($\tau_D = 30.84 \mu\text{s}$) (Supplementary Fig. 13). The τ_D values demonstrate that the electron density injected into TiO_2 layer from the [221]-oriented Sb_2S_3 cuboids is much higher and the preferential [221]-orientation of the Sb_2S_3 cuboids provides a much easier transportation of the photogenerated electrons in Sb_2S_3 absorbing layer toward TiO_2 film and further collection electrode (Supplementary Note 10). Moreover, the smaller series resistance (R_s) and larger shunt resistance (R_{sh}) in the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ device also suggest an easier charge transportation process therein (Supplementary Table 4).

The observed device performances of the two solar cells can be understood by the orientation of Sb_2S_3 grains. In a single-crystalline Sb_2S_3 grain, the easiest carrier transportation is in the [001] direction along the covalently bounded $(\text{Sb}_4\text{S}_6)_n$ ribbons³⁵. The [221]-orientation results in eventually the $(\text{Sb}_4\text{S}_6)_n$ ribbons titling an angle of 46° on substrate plane, which facilitates the photogenerated charge carrier transportation toward collection electrode in the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ device (Fig. 4e); however, the $(\text{Sb}_4\text{S}_6)_n$ ribbons in the ref- $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ with [130]/[310]-orientation of Sb_2S_3 grains are actually parallel to the substrate plane (Supplementary Fig. 14), leading to a lower effective transportation of photogenerated charge carriers toward the collection electrode because it needs the charge hopping between the $(\text{Sb}_4\text{S}_6)_n$ ribbons packed together by van der Waals forces³⁵. Therefore, the [221]-orientation of the Sb_2S_3 cuboids provides the easier collection and weaker recombination of photogenerated charge carriers in the solar cells. It should be noted that the efficiency of the present solar cell is not high enough yet. We envision that, for a better device performance, it is necessary to reduce the surface roughness of the Sb_2S_3 layer, which may cause

Fig. 4 Optical property and orientation-dependent device performance. **a** Absorption coefficient of the Sb_2S_3 layer in $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ and the corresponding Sb_2S_3 layer thickness required to absorb 90% incident photons of a specific wavelength. **b** $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ device structure (right: cross-sectional SEM characterization). **c** J - V curves and **(d)** IPCE spectra of the solar cells based on $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ and ref- $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ ($n = 2$ for both). **e** The spatial arrangement of the $(\text{Sb}_4\text{S}_6)_n$ ribbons tilting 46° on substrate resulting from the [221]-orientation of Sb_2S_3 cuboids, where the electron transportation along [001] direction is easiest. **b** Scale bar 400 nm for SEM image

serious shorting risk⁴⁴ and charge recombination^{11,45} to reduce V_{oc} and FF values, to improve the charge collection efficiency in the device.

Discussion

In summary, an oriented seed-assisted RSCA solution-processing method is developed for the in situ growth of the monolayer of closely packed and preferentially [221]-oriented large orthorhombic Sb_2S_3 single-crystalline cuboids on polycrystalline anatase TiO_2 nanoparticle film, offering a novel $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ with the Sb_2S_3 cuboids having the typical growth features of the out-of-plane growth along the [001] direction with (001) planes tilting ca. 44° on substrate plane and the size much larger than TiO_2 nanoparticles. It is found that the orientation of the Sb_2S_3 cuboids is exclusively correlated with the beneath TiO_2 surface and the preferentially oriented Sb_2S_3 crystalline seeds formed on the TiO_2 film are indispensable to cuboid growth; while glycerin remains inactive during the formation of SbCl_3 -thiourea complex in the precursor solution, its presence provides chemical species to maintain the smoothness of growing surfaces of cuboids by inhibiting the strain-driven surface roughening.

An OCE nucleation/growth mechanism is suggested for the in situ growth of the preferentially oriented Sb_2S_3 single-crystalline cuboids on polycrystalline TiO_2 nanoparticle film, in which the heterogeneously epitaxial nucleation/growth of Sb_2S_3 crystals follows the epitaxial relationship of Sb_2S_3 (101)// TiO_2 (101) and the surface TiO_2 nanoparticle orientation with the (101) plane tilting an angle of ca. 33° on film plane is most

competitive for the nucleation/growth of Sb_2S_3 cuboids. During the OCE nucleation/growth process, the heterogeneously epitaxial nucleations of orthorhombic Sb_2S_3 crystals on the anatase TiO_2 nanoparticles with favorable TiO_2 (101) plane orientations take place, followed by the self-nucleated growth of Sb_2S_3 nuclei into larger Sb_2S_3 crystalline seeds, when the orientations of Sb_2S_3 crystals are governed by the TiO_2 (101) plane orientations; then the seeds from different nuclei further take a self-nucleated growth during the latter RSCA cycles into much larger Sb_2S_3 cuboids without the changes in Sb_2S_3 crystal orientations. With the faster nucleation/growth at a site with the most/more competitive TiO_2 (101) plane orientation, the nucleation/growth at around sites with less-favorable/unfavorable TiO_2 (101) plane orientation becomes much slower or suppressed, resulting in one large Sb_2S_3 seed crystal/cuboid over many TiO_2 nanoparticles. When the RSCA cycle number n is >1 , increasing n mainly leads to the growth of Sb_2S_3 cuboids in the c -axis direction and the merge of some small cuboids into large ones, but introduces no evident interfaces into the cuboid body.

The Sb_2S_3 cuboids layer in the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ has a band gap of $E_g = 1.65 \text{ eV}$ and an absorption coefficient of $\alpha \approx 10^5 \text{ cm}^{-1}$ in the range of 350–650 nm. In combination with Spiro-OMeTAD as hole transporting material, the novel solar cell with a high long-term stability is derived from the $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ. In this experiment, the Sb_2S_3 layer thickness/cuboid height of ca. 400 nm produces the best efficiency of $\eta = 5.15\%$ (certified as 5.12%), as the result of the limited L_D of charge carriers inside Sb_2S_3 layer. The $\text{Sb}_2\text{S}_3/\text{TiO}_2$ -BnPHJ possesses the following distinctive advantages: it is of the preferred structure for

efficient planar solar cells^{1–3} and a high absorption coefficient; it is very stable and easily solution-processed on a large scale; moreover, the [221]-oriented single-crystalline Sb₂S₃ cuboids therein provide the highly effective charge transport channels formed the covalently bounded (Sb₄S₆)_n ribbons tilting ca. 46° on substrate for the photogenerated charge carriers inside the Sb₂S₃ layer to reach collection electrode. Those make the Sb₂S₃/TiO₂-BnPHJ have good application potentials to efficient solar cells. Our results provide a facile solution-processing method to prepare the high-quality Sb₂S₃/TiO₂ PHJs for photovoltaic and other optoelectronic applications, and also offer a new understanding of the heterogeneously epitaxial growth of large single-crystals on polycrystalline surface.

Methods

Sb₂S₃ precursor solution. 1.2 mmol of SbCl₃ (≥99.0%, Alfa Aesar) and 2.16 mmol of thiourea (≥99.0 %, Alfa Aesar) were sequentially dissolved in 1 ml of a mixture solvent of N,N-dimethylformamide (DMF) and glycerol (DMF/glycerol = 4/1 in volume) under stirring at room temperature, resulting in a transparent and light-yellow Sb₂S₃ precursor solution with 1.2 M SbCl₃ and a molar ratio of SbCl₃:thiourea = 1:1.8. The precursor solution is stable in ambient conditions for weeks.

Sb₂S₃/TiO₂-BnPHJ preparation. FTO (SnO₂:F) coated glass sheet (14 Ω/square, 400 nm FTO in thickness, Nippon Sheet Glass Co.) (15 × 20 mm²) was patterned into one stripe (20 × 4 mm²) in the middle part of the substrate by laser, commercially obtained from the Advanced Election Technology Co. Ltd., Liaoning Province, China. The patterned FTO sheet was first washed with acetone, isopropanol, and deionized water, respectively; then it was further cleaned with UV-Ozone for 15 min and washed with ethanol before use. A compact and polycrystalline TiO₂ nanoparticle film (90 nm thick) was prepared on the patterned FTO sheet by the method described elsewhere²⁴.

Sb₂S₃/TiO₂-BnPHJ was prepared by an oriented seed-assisted-RSCA method. The Sb₂S₃ precursor solution was spin-coated four times onto a seed-decorated TiO₂ film to get a transparent and light-yellow Sb₂S₃ precursor film on the TiO₂ film surface, and then the Sb₂S₃ precursor film dried at 60 °C for 15 min in vacuum in advance was subjected to the thermal annealing at 330 °C for 10 min on a hot-stage in N₂ atmosphere, which is referred to as one RSCA cycle; after the TiO₂ film had been subjected to several RSCA cycle numbers (*n*), the Sb₂S₃/TiO₂-BnPHJ was in situ formed. Before carrying out the RSCA process, a dilute Sb₂S₃ precursor solution (0.4 M SbCl₃) was first spin-coated onto the bare TiO₂ film, followed by the same drying and thermal annealing processes as the RSCA procedure, resulting in the oriented Sb₂S₃ crystalline seeds on TiO₂ film surface. The Sb₂S₃ layer thickness/cuboid height was controlled by the *n* value for film growth.

In order to reveal the substrate effects on the growth of Sb₂S₃ cuboids, the Sb₂S₃ layer was directly deposited onto native FTO substrate by the seed-assisted-RSCA method same to that for preparing Sb₂S₃/TiO₂-BnPHJ. Moreover, in order to find out the glycerin effects on the growth of Sb₂S₃ cuboids, the Sb₂S₃ layer was deposited onto TiO₂ film by the seed-assisted-RSCA method same to that for preparing Sb₂S₃/TiO₂-BnPHJ, but without glycerin in the Sb₂S₃ precursor solutions. Furthermore, for comparison, the reference Sb₂S₃/TiO₂-BnPHJ (i.e., ref-Sb₂S₃/TiO₂-BnPHJ) was prepared by the RSCA process same to that for Sb₂S₃/TiO₂-BnPHJ but without Sb₂S₃ crystalline seeds.

Solar cell fabrication. First, a film of Spiro-OMeTAD (Xi'an Polymer Light Technology Corp.) was spin-coated (2500 rpm, 60 s) over the Sb₂S₃/TiO₂-BnPHJ or ref-Sb₂S₃/TiO₂-BnPHJ, followed by an annealing at 100 °C for 10 min in N₂ atmosphere. Spiro-OMeTAD was doped in advance with lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI, 99.95%, Sigma-Aldrich) as described previously²⁴. Then, an Au electrode (100 nm thick) was thermally evaporated onto the Spiro-OMeTAD layer. Finally, the devices were encapsulated in a glovebox under N₂ atmosphere (O₂ < 1 ppm, H₂O < 1 ppm).

Instruments and characterization. XRD data were collected on a Philips X'Pert Pro MPD diffractometer with monochromated Cu Kα radiation (λ = 1.54056 Å). SEM measurements were performed on a field-emission scanning electron microscope (FESEM, FEI-Sirion 200). TEM and HRTEM studies were carried out on a JEOL-2010 microscopy under an acceleration voltage of 200 kV, and the samples for TEM and HRTEM analyses were prepared by a focused ion beam (FIB) process on SCIOS DualBeam FIB (FEI, USA). UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The absorption coefficient of Sb₂S₃ layer in Sb₂S₃/TiO₂ heterojunction film was calculated from the reflectance and transmission spectra between 240 nm and 1200 nm recorded at a scan speed of 240 nm/min on a Solid Spec-3700 UV-vis spectrometer with a resolution of 1 nm. FT-IR spectra of the solid samples of thiourea in KBr pellet and the liquid samples were respectively recorded on a Nicolet Magna-IR™ 750 spectrometer with a maximum resolution of 0.1 cm⁻¹. The *J*-*V* curves of solar cells were measured with

forward scan under AM1.5 illumination (100 mW/cm²) from a 94023 A Oriel® Sol3A solar simulator (Newport), and the light intensity from a 450 W xenon lamp was calibrated with a standard crystalline silicon solar cell. The *J*-*V* curves were collected with an Oriel® I-V test station (PVIV-1A, Keithley 2400 Source Meter, Labview 2009 SP1 GUI Software, Newport). IMPS spectra were measured on a controlled intensity modulated photo spectroscopy (CIMPS, Zahner Co., Germany; Thales 4.15 Software) in ambient conditions. During IMPS measurements⁴⁵, the solar cells was illuminated with a modulated illumination (*I*) formed by a *dc* component of a steady-state background light *I*₀ and an *ac* component of a small sinusoidal perturbation *I*_{ac} = *I*₀δe^{iωt}, that is, *I* = *I*₀(1 + δe^{iωt}), where the background light intensity *I*₀ of 10 mW/cm² was provided by a blue light-emitting diode (BLL01, λ_{max} = 470 nm, spectral half-width = 25 nm, Zahner Co.) driven by a frequency response analyzer and the perturbation was applied in the frequency range from 1 Hz to 100 kHz with a modulation depth of δ = 0.10. During the *J*-*V* and IMPS measurements, the illumination area of each device was limited by a mask with an aperture (2 × 2 mm²), which actually defined the effective area for getting photovoltaic parameters of the device. The IPCE spectra of the solar cells were measured with a QE/IPCE Measurement Kit (Newport) that was automatically controlled by Oriel® Tracq Basic V6.5 software with a light from a 300 W xenon lamp focusing through a monochromator (74125 Oriel Cornerstone 260 1/4 m) onto the solar cells. The light intensity and photocurrent generated were measured with a 2936-R dual channel power/current meter and an 818-UVcalibrated silicon-UV photodetector.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Extra data are available from the corresponding author upon reasonable request.

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Author contributions

J.C. designed and performed heterojunction synthesis, solar cell fabrication and sample characterizations. J.Q. and R.L. helped with the synthesis and characterization of heterojunctions. X.Z. conducted TEM/HRTEM measurements. Z.W. contributed to the analysis of solar cell data. Q.Z. contributed to SEM measurements. S.T. contributed to the analysis of crystal structures. C.D., G.Y.A., W.C., R.P., and X.T. contributed to the fabrication and characterization of solar cells. F.Z. and S.Y. helped with solar cell characterization. M.W. conceived the study and supervised the project. M.W. and J.C. analyzed the data, interpreted the results and prepared the manuscript. All authors commented and edited the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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