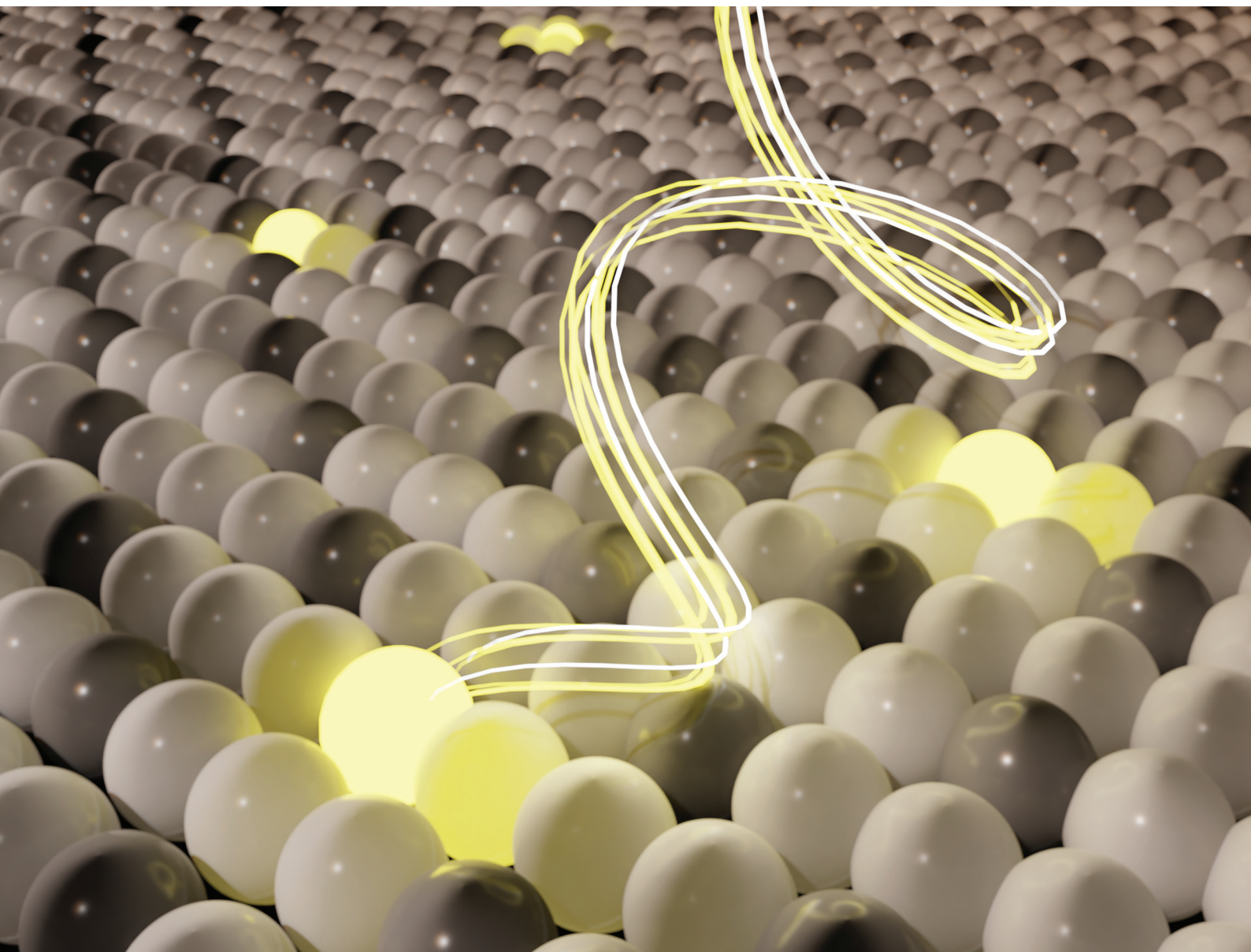


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Cation exchange synthesis of AgBiS₂ quantum dots for
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Cation exchange synthesis of AgBiS₂ quantum dots for highly efficient solar cells†

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Silver bismuth sulfide (AgBiS₂) nanocrystals have emerged as a promising eco-friendly, low-cost solar cell absorber material. Their direct synthesis often relies on the hot-injection method, requiring the application of high temperatures and vacuum for prolonged times. Here, we demonstrate an alternative synthetic approach via a cation exchange reaction. In the first-step, bis(stearoyl)sulfide is used as an air-stable sulfur precursor for the synthesis of small, monodisperse Ag₂S nanocrystals at room-temperature. In a second step, bismuth cations are incorporated into the nanocrystal lattice to form ternary AgBiS₂ nanocrystals, without altering their size and shape. When implemented into photovoltaic devices, AgBiS₂ nanocrystals obtained by cation exchange reach power conversion efficiencies of up to 7.35%, demonstrating the efficacy of the new synthetic approach for the formation of high-quality, ternary semiconducting nanocrystals.

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Introduction

Metal chalcogenide quantum dots (QDs) have attracted great interest in the last decades due to their exceptional properties such as high colloidal stability, tunable band gap, and high absorption coefficient. These advantages make them highly promising for use in various applications: biological imaging,^{1,2} photodetection,^{3,4} photovoltaics,^{5–7} electrocatalysis,^{8,9} etc. The area of photovoltaics has seen significant advances over the past 15 years, with quantum dot solar cells reaching high power conversion efficiencies (PCEs), making them of great interest for commercialization.^{10,11} However, the most efficient devices are based on lead- and cadmium-based quantum dots, which when produced at mass scale are likely to pose dangerous risks to the environment. These concerns motivate the search for less toxic and heavy metal-free quantum dot materials for photovoltaics. Recent studies have demonstrated that certain binary (Ag₂S, Sb₂S₃), ternary (AgInS₂, AgBiS₂, AgSbS₂), and quaternary (Zn–Ag–In–S) quantum dots can serve as effective alternatives for solar cell applications.^{12–17} Also copper-based material compositions such as ternary (Cu–In–S) and quaternary (Zn–Cu–In–S) quantum dots have been investigated as environmentally-friendly solar cell absorbers, however, these materials require a Grätzel-type solar cell architecture.^{18–20} Ternary AgBiS₂ QDs have emerged as one of the most promising candidates for application in photovoltaics due to their optimal band gap (1–1.3 eV), high absorption coefficient, ease of synthesis and processing accompanied by high stability in the ambient.



The first attempts to fabricate AgBiS₂ based solar cells were made using the sequential ionic layer adsorption reaction (SILAR) technique, demonstrating that AgBiS₂ can be used as a potential solar sensitizer.²¹ The synthesis of AgBiS₂ QDs by hot injection method was initially proposed in 2013 by Chao Chen *et al.*²² In 2016, Bernechea *et al.* presented the first AgBiS₂-based solar cells synthesized by this method with a PCE of 6.3%.²³ Further research was focused on optimizing the synthesis by employing various precursor ratios, changing the injection temperature, and using different capping ligands.^{24–26} These attempts in combination with optimized hole and extraction layers resulted in a record result PCE of 9.17%, which further solidified AgBiS₂ as a highly promising eco-friendly alternative to toxic chalcogenides.²⁷ However, despite all the advantages of the hot injection method, it requires both vacuum and high temperatures (typically 100 °C) for several hours, which remains a challenge not only in terms of the thermal budget for QD synthesis, but also the ability to reproducibly synthesize large volumes for commercial applications.

Several studies have explored more inexpensive alternative routes for the AgBiS₂ synthesis. For instance, Wu *et al.* proposed a simple synthesis of AgBiS₂ nanorods by spin-coating the precursor solutions and subsequent annealing of the films at 300 °C in air.²⁸ Gu *et al.* demonstrated the synthesis of compact AgBiS₂ thin films *via* the formation of Ag-Bi-thiourea-DMSO molecular inks followed by decomposition upon thermal annealing.²⁹ In addition, Akgul *et al.* presented the first solar cells with AgBiS₂ QDs fabricated at room temperature by simple mixing of metal halides with separately dissolved sulfur in oleylamine, resulting in a PCE of 5.55%.²⁶ These promising attempts highlight the importance of low-cost and low-temperature synthetic routes for AgBiS₂ QDs in order to pave the way for their large scale commercial application.

Although direct synthesis allows the rapid preparation of ternary AgBiS₂ QDs, this approach is fraught with difficulties due to the presence of precursors of two cations with different reactivities in the reaction system. The different reactivities limit the simultaneous control over size, shape, and composition of the resulting QDs. Cation exchange can be a suitable alternative for a low-temperature synthesis. The cation exchange (CE) reaction is a well-studied method for various material systems in which a guest cation replaces the host cation with subsequent incorporation into the nanocrystal structure.³⁰ Organic ligands such as phosphines or carboxylates act as soft bases that interact with the softer cation and facilitate its removal from the nanocrystal.^{31,32} Modifying the composition of nanocrystals without changing their size and shape makes cation exchange an extremely versatile tool for the synthesis of various materials.

The cation exchange approach has been successfully employed in the synthesis of ternary material compounds.^{30,33,34} In the case of CE, easily obtainable binary chalcogenides such as Cu₂S, Ag₂S, and CdSe are used as a template to further incorporate guest cations (*e.g.*, In³⁺, Hg²⁺) and

result in the formation of ternary compounds with precise compositions.^{35–37} The outcome of a CE reaction is dictated by subtle thermodynamic and kinetic factors enabling the control over the structure and composition of the desired product.³³ The choice of size, shape, and structure of the parent nanocrystals as well as the choice of solvent, additional ligands, and temperature of the reaction allows not only to tune the morphology and composition of the final products,^{38,39} but also to prepare various heterostructures such as Cu–In–Se/ZnS core-shell nanoparticles or CdS/Cu₂S binary nanorods.^{40,41} Despite the widespread use of CE for synthesizing ternary nanoparticles, the synthesis of AgBiS₂ QDs using this approach has not yet been reported.

Here, we demonstrate a facile synthesis of small Ag₂S nanocrystals at room temperature and subsequent cation exchange at mild temperatures to form AgBiS₂ QDs. The use of bis(stearoyl)sulfide (St₂S) as air stable and highly reactive sulfur precursor enables the synthesis of small, almost monodisperse Ag₂S nanoparticles at room temperature under ambient conditions. Bismuth neodecanoate (Bi(neo)₃) in combination with the soft Lewis base trioctylphosphine (TOP) facilitates the cation exchange of Ag⁺ to Bi³⁺ at only 50 °C in air. We show that the cation exchange progresses rapidly under these conditions and the size and shape of the nanocrystals does not change throughout the reaction. The AgBiS₂ QDs obtained by cation exchange were utilized in planar solar cells that reach a PCE >7%, which is the highest PCE for AgBiS₂ QDs synthesized under ambient conditions.

Results and discussion

As depicted in Fig. 1, as a first step, crystalline Ag₂S QDs were synthesized at room-temperature *via* a quick injection of St₂S into a silver nitrate solution in oleylamine (OlAm) and toluene. St₂S is a stable, crystalline sulfur precursor that is significantly easier to handle in nanocrystal synthesis compared to the commonly employed hexamethyldisilathiane (TMS₂S), which is very sensitive to hydrolysis and air.⁴² The use and potential of St₂S as sulfur precursor material for the direct synthesis of AgBiS₂ and PbS photovoltaic materials has recently been described by us elsewhere.⁴² To perform the cation exchange into AgBiS₂, purified Ag₂S QDs were redispersed in toluene and mixed with trioctylphosphine (TOP) and an excess of Bi(neo)₃ was added at 50 °C. Hard soft acid base (HSAB) theory was considered for the prediction of the cations' solubility and their affinity to ligands. According to the HSAB theory, soft Ag⁺ cations provide a higher affinity to the soft base TOP, allowing for an expedited exchange with harder Bi³⁺ cations.^{30,31}

The kinetics of the cation exchange reaction was monitored using absorbance spectroscopy (UV-VIS), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Fig. 2 shows the TEM images of Ag₂S QDs before and throughout the exchange, taken at different times of the cation exchange reaction. The average diameter of St₂S-based Ag₂S QDs is approximately ≈2.8 nm and exhibits a rather narrow size distribution



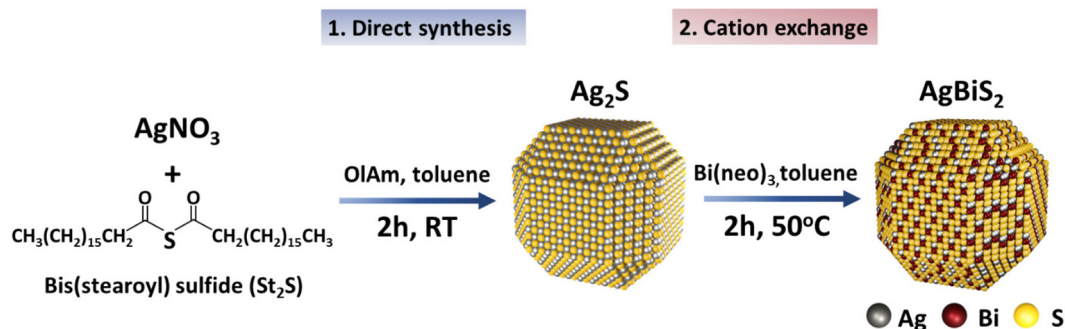


Fig. 1 Schematic representation of Ag_2S QDs synthesis and formation of AgBiS_2 via cation exchange at mild temperature.

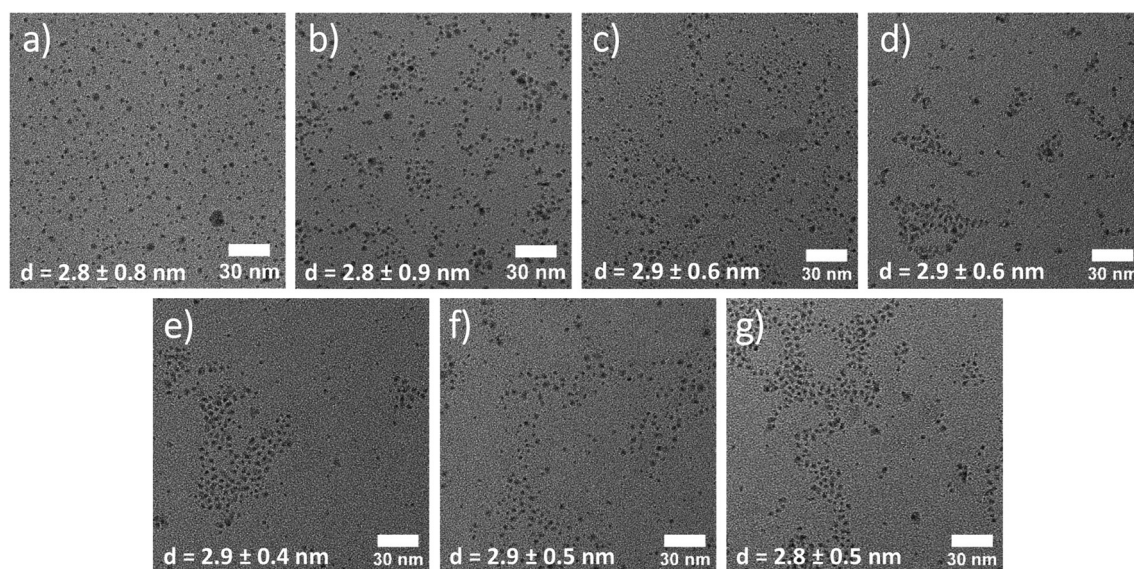


Fig. 2 TEM images of (a) Ag_2S QDs before and during the cation exchange at (b) 5 min, (c) 15 min, (d) 30 min, (e) 50 min, (f) 80 min, and (g) 120 min of reaction time. Scale bar 30 nm (bottom right) and average QD size and standard deviation (bottom left) for each image.

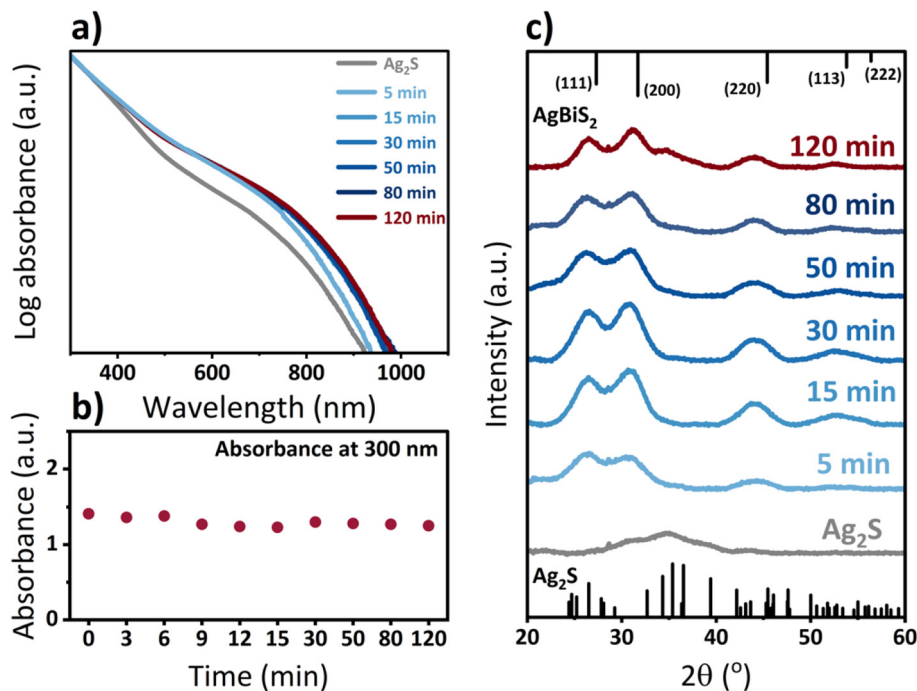
(see Fig. S1†). Upon the incorporation of Bi^{3+} the average size and shape of the QDs remain the same throughout the reaction. It is also noteworthy that the introduction of TOP into the reaction system does not lead to the full or partial dissolution of the quantum dots, but rather leads to a reduction of larger agglomerates that are present at earlier times of the reaction probably due to a better colloidal stability of the QDs after CE. Consequently, with progressing time of the cation exchange reaction the size distribution becomes narrower (see Fig. 2 and Fig. S1, ESI†).

Fig. 3a shows the evolution of the optical properties of the QDs throughout the cation exchange process. The absorbance of QDs in solution slightly red shifts already after 5 minutes of cation exchange and undergoes only minute changes after 15 minutes. While an absorption shift usually implies a change in the size of the quantum dots for a given material, in this case, it could also be an indication of a change in the band gap. Since bulk, stoichiometric Ag_2S exhibits a bandgap of 0.9 eV, while bulk AgBiS_2 exhibits a slightly smaller

bandgap of only 0.8 eV, a red shift, as observed, suggests a change in QD composition.⁴³ However, the shift in bandgap will also be affected by variations of the individual QD stoichiometry and the corresponding exciton Bohr radius of each material, which complicates a full understanding of the observed red-shift. Continuous absorbance measurements at a wavelength of 300 nm throughout the cation exchange process in Fig. 3b support the aforementioned observation that the cation exchange process to AgBiS_2 QDs progresses continuously with time and is not based on a full dissolution and new nucleation of nanocrystals. XRD measurements (Fig. 3c) confirm that the transformation from the monoclinic $\beta\text{-Ag}_2\text{S}$,⁴⁴ to cubic AgBiS_2 occurs already within minutes. Subsequent growth in intensity and decrease in peak width for reaction times up to 30 minutes could be an indication of an improvement in the crystallinity of the QDs.

To examine the compositional changes of the QDs upon cation exchange, X-ray photoemission spectroscopy (XPS) measurements were performed. The Ag 3d spectra (Fig. 4a)





show the presence of a single doublet for both types of QDs, which confirm the absence of metallic silver in the QD films. Comparison of the Ag 3d spectra of Ag₂S and AgBiS₂ nanocrystals also reveals the absence of a clear shift in the binding energy upon cation exchange. In the spectrum of S 2p (Fig. 4b), on the other hand, a slight change in the peak position to lower binding energies upon cation exchange is observed, which may indicate a weaker interaction between silver and sulfur after bismuth incorporation. The Bi 4f spectrum consists of two sets of doublets, one associated with AgBiS₂ and an additional high binding energy doublet, which is attributed to the formation of bismuth oxide or hydroxylated bismuth species at the QDs surface.⁴⁶ The binding energies of the Ag 3d (367.8 and 373.8 eV), S 2p (160.8 and 162.1 eV) and Bi 4f (158.0 and 163.3 eV) doublets that originate from AgBiS₂ QDs are in agreement with previously reported data in literature.^{23,25,47}

ation from the theoretical stoichiometry (Table S2, ESI†). The larger deviation in material composition in the hot-injection method is most likely a result from the formation of non-negligible amounts of silver oleates – and in the case of St_2S , silver stearates – in these synthetic procedures, which cannot be easily removed from QDs through the employed redispersion/precipitation procedures.⁴² These findings highlight, that synthesis *via* the cation exchange route provides a significantly higher control over the desired QD composition with potentially higher purity.

The synthesis of Ag_2S quantum dots using elemental sulfur S and TMS_2S as precursors under identical synthetic conditions resulted in the formation of larger Ag_2S QDs with sizes of 3.2 ± 1.0 nm and 3.5 ± 1.9 nm, respectively. Both precursors result in more polydisperse nanocrystals (see Fig. S2 and S3†). Attempts to perform a cation exchange for those Ag_2S QDs under identical conditions did not result in the formation of pure, high-quality AgBiS_2 QDs. For the largest Ag_2S QDs no cation exchange could be achieved, indicated by no changes in the diffraction pattern of these nanocrystals (Fig. S2†). While the diffraction pattern changes in the case of Ag_2S obtained by elemental sulfur, the absorbance spectrum differs from the one of AgBiS_2 obtained from St_2S -based Ag_2S QDs. Consequently, the integration of QDs based on TMS_2S and elemental sulfur as precursors resulted in very low photovoltaic (PV) performance (Fig. S4†). These results could indicate that the Ag_2S quantum dot size is crucial for a successful cation exchange with Bi^{3+} . To corroborate the size dependence, we

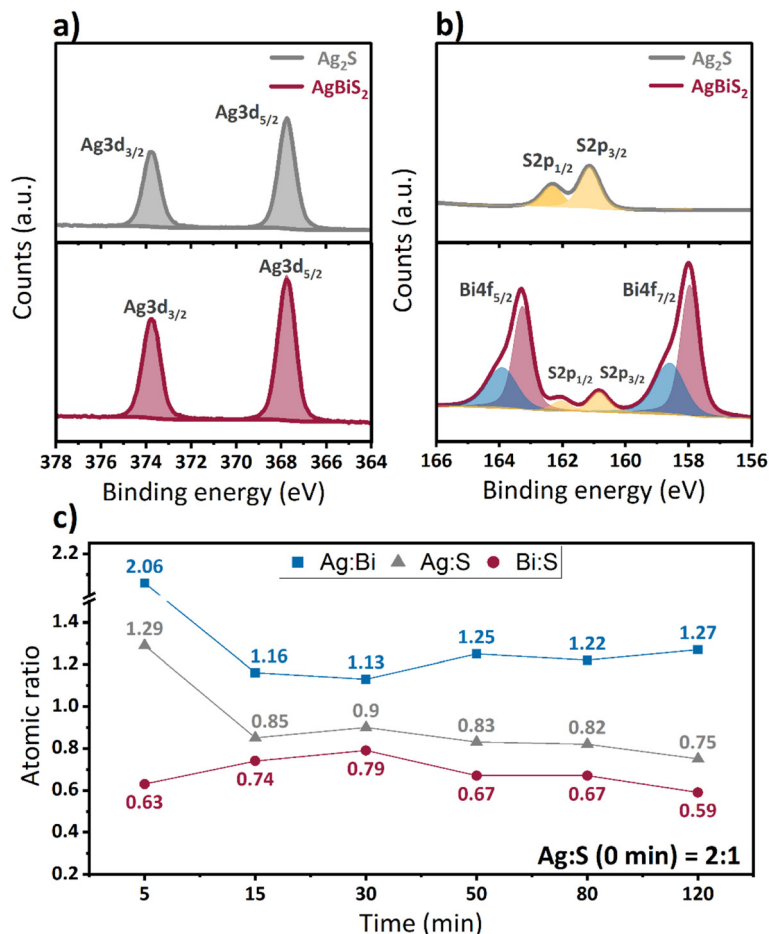


Fig. 4 XPS spectra of (a) Bi 4f and S 2p, (b) Ag 3d for Ag₂S and AgBiS₂ QDs after cation exchange of 120 min. (c) Comparison of the atomic ratio between Ag, Bi, and S at different cation exchange times.

synthesized larger Ag₂S dots based on St₂S. Quantum dots with an initial average size larger than 3 nm do not undergo the cation exchange reaction within 120 min under the same conditions (Fig. S5†). This suggests that only small Ag₂S quantum dots (<3 nm) can be converted into AgBiS₂ QDs sufficiently fast through cation exchange with Bi³⁺. We note that also other factors may influence the efficacy of cation exchange, such as the choice of ligands, the quantum dot stoichiometry and the presence of defects, however the investigation of these goes beyond the scope of the current study and is subject to future research.

To explore the photovoltaic performance of the QDs formed by cation exchange, they were integrated into solar cells whose architecture is illustrated in Fig. 5a. In short, a thin SnO₂ layer was deposited as electron extraction layer (ETL) on top of pre-patterned ITO substrates. QDs were deposited in a layer-by-layer process employing a solid phase ligand exchange until a final layer thickness of ≈35 nm was achieved. Next, an ultra-thin poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) hole extraction layer (HTL) was deposited.²⁷ The devices were completed with a thin layer of thermally evaporated MoO₃

(that increases the conductivity of the PTAA HTL by p-doping^{48,49}) and a Ag electrode. The PCEs and current density – voltage (*J*-*V*) curves of solar cells based on Ag₂S (0 min of CE) and AgBiS₂ (30 and 120 min of CE time) are shown in the Fig. 5b and c. It can be seen that while Ag₂S (0 min) demonstrates a very low efficiency, probably due to surface recombination and poor alignment between the ETL and the energy levels of Ag₂S. AgBiS₂ QDs, on the other hand, exhibit a significant improvement reaching an average performance of 3.31% (best 4.27%) after 30 min of reaction. Interestingly, a further increase in the cation exchange reaction time leads to a stark enhancement in solar cell performance, reaching to an average PCE of 6.76% (best 7.35%). While the open-circuit voltage (*V*_{oc}) is similar for both devices, the fill factor and especially the short-circuit current density are noticeably higher for the QDs after 120 minutes of CE compared to only 30 minutes of CE time (Table S3, ESI†).

Extending the reaction time of the cation exchange beyond 120 min causes the solar cell performance to drop significantly (Fig. S6†). While the exact origin of this decrease in performance remains elusive, the reaction conditions of the cation

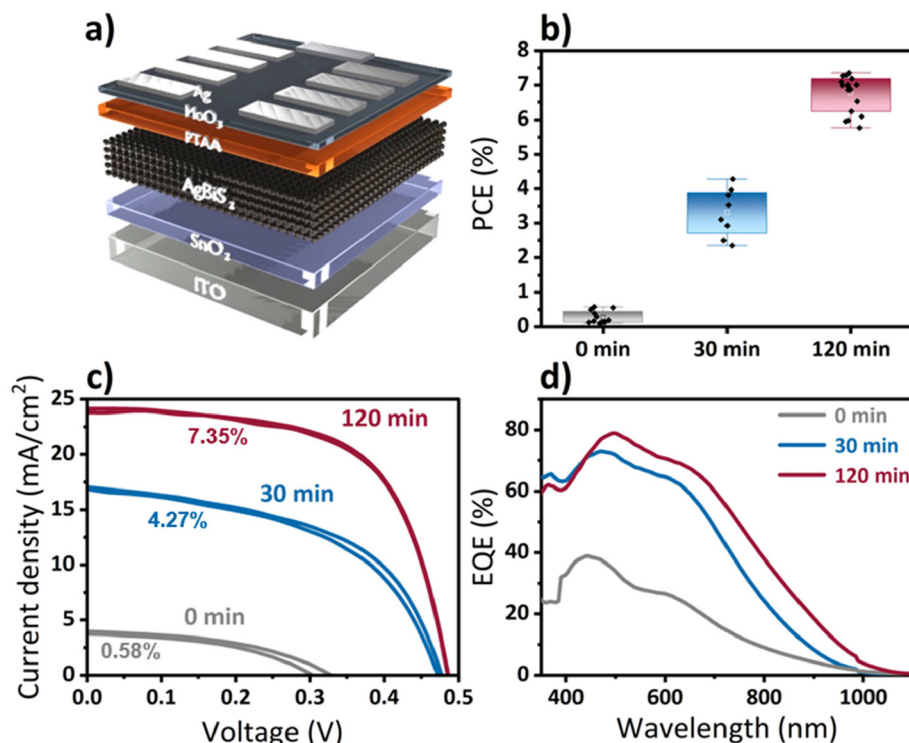


Fig. 5 (a) Schematic device architecture of AgBiS₂ solar cells, (b) Solar cell performance (PCE) of AgBiS₂ QDs obtained after different times of cation exchange, (c) J–V curves (forward and reverse scanning) of devices with different QDs after 0 min (Ag₂S), and AgBiS₂ after 30 min, and 120 minutes of cation exchange with individual PCE (d) corresponding EQE curves for these three devices.

exchange and the presence of oxidation-sensitive TOP and Ag⁺-species might affect the AgBiS₂ quality, composition or purity for such prolonged reaction times.

We would like to emphasize that the reported solar cell performance represents the performance level of the QD solar cell after one week. Our QD solar cells based on AgBiS₂ obtained *via* the cation exchange process exhibit a similar increase in performance within the first few days of storage in ambient as in the case of QDs synthesised *via* the hot-injection synthesis (Fig. S7†).²⁷ While the exact origin of this improvement remains an open question in the field, our findings suggest that the performance evolution of AgBiS₂ solar cell seems to be a universal observation for this device architecture and independent of the synthetic route. Similar observations were also reported for other types of quantum dot based solar cells,^{50,51} with the origin of this behavior remaining under debate.

The increase in current density for solar cells of 30 min and 120 min of reaction time is in agreement with the external quantum efficiency (EQE) spectra shown in Fig. 5d, where a maximum EQE of 80% is achieved at 500 nm for the 120 minutes CE devices accompanied by a clear red shift of the EQE onset. Similar changes in the EQE spectra have been attributed in literature to be a consequence of increased cation homogenization within AgBiS₂ quantum dots upon thermal annealing.^{27,44} We believe that a similar process gradually occurs as the duration of the cation exchange is increased. Cation exchange processes occur through the quantum dot

facettes at the surface of the QDs. Within the first minutes of the cation exchange process Bi³⁺ is incorporated into the quantum dot crystal lattice resulting in separated Ag- and Bi-rich domains, while the latter are most likely be in the proximity of the nanocrystal's surface. As the reaction time increases, the overall cation distribution becomes more homogenous across the QD, resulting in a red-shifted EQE, higher short-circuit current and an overall better photovoltaic performance, similar to the observations made by Konstantatos and coworkers,²⁷ albeit without the need for additional annealing. This simplified model is supported by a detailed examination of the XPS data for bismuth after different times of the cation exchange reaction (Fig. S8†). Higher amounts of bismuth at the nanocrystal surface would result in a higher fraction of hydroxylated or oxidic bismuth species after these QDs have undergone the normal washing procedure and film formation processing, while less of such species are to be expected for bismuth homogeneously distributed throughout the entire AgBiS₂ QD lattice. Fig. 6 depicts the process of homogenization of the cation disorder schematically and the evolution of the two bismuth species with respect to the reaction time. Our XPS studies show that the ratio between high-binding energy and low binding energy bismuth dramatically decreases by more than 50% with increasing cation exchange duration, while (as discussed above) the overall ratio of the total amount of bismuth to silver remains quasi stable for prolonged reaction times. The hydroxylated or oxidic bismuth



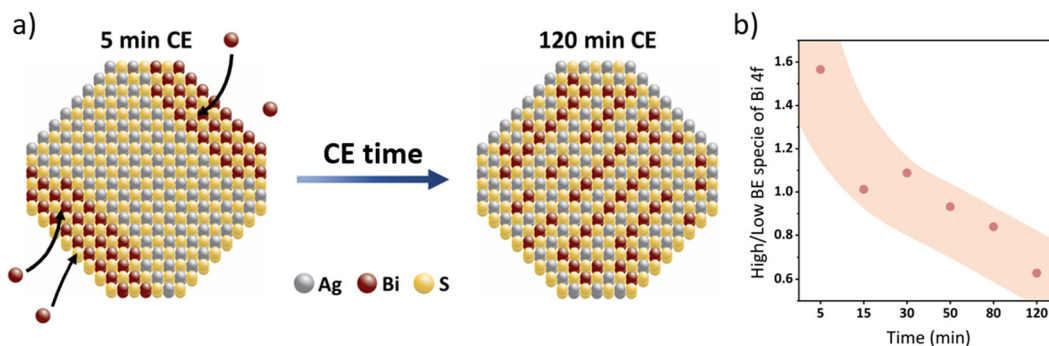


Fig. 6 (a) Schematic representation of the cation exchange process and resulting homogenization of the cation disorder with increasing reaction time, (b) evolution of the ratio between high-binding/low-binding energy Bi species with CE time.

species exhibit a doublet at higher binding energies of 158.6 and 163.9 eV as compared to the bismuth of the nanocrystal lattice (158.0 eV and 163.3 eV). These values correspond well to Bi_2O_3 and do not stem from the potentially unreacted Bi precursor (Fig. S9†). These data also correlate with previously published XPS spectra of the oxygen-induced degradation of AgBiS_2 , indicating the formation of Bi_2O_3 .⁴⁶

Conclusion

In this work, we introduce a cation exchange process as a novel synthetic path for the fabrication of environmentally friendly AgBiS_2 QDs at low temperatures and under ambient and vacuum-free conditions. We show that this method enables the preparation of highly monodisperse nanocrystals using bis(stearoyl)sulfide as a non-toxic and air-stable sulfur precursor. The fabricated solar cells exhibit high power conversion efficiency of more than 7% which exceeds previously published PCE value of 5.55% for a ambient, low-temperature synthesis.²⁶ These results highlight the importance of developing environmentally friendly synthetic routes for the production of efficient QD-based solar cells.

Experimental section

Materials

Silver nitrate (AgNO_3 , 99.5%) was purchased from Grüssing GmbH. Sulfur powder (S, 99.98%), bismuth neodecanoate, oleylamine (OAm, 98%), mercaptopropionic acid (MPA, 98%), and deionized water were purchased from Sigma-Aldrich. Toluene (99.85%), methanol (99.8%), and acetone (99.8%) were purchased from Thermo Scientific. Trioctylphosphine (TOP, 95%) was purchased from Gelest. Tin oxide (SnO_2 , 15% in H_2O) was purchased from Alfa Aesar. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA, M_w 30 000) was purchased from Ossila. Molybdenum oxide (MoO_3 , 99.95%) and silver pellets (Ag, 99.99%) were purchased from Kurt J. Lesker. ITO substrates were purchased from Yingkou Shangneng Photoelectric Material Co.

St_2S synthesis

Bis(stearoyl) sulfide precursor was synthesized following previously reported procedures.^{42,52}

Ag_2S synthesis

A silver precursor solution was prepared by mixing AgNO_3 (51 mg, 0.3 mmol) in 2 ml of toluene and 1.5 ml of OAm. St_2S (85 mg, 0.15 mmol) was mixed with 2 ml of toluene and both precursor solutions were stirred separately for 1 h. After forming a clear solution, sulfur precursor was swiftly injected into the vial with metal precursor resulting in rapid formation of dark brown QDs solution. The reaction system was stirred for 2 h at RT. Then, QDs were precipitated with methanol and centrifuged for 5 min at 6000 rpm. Purified Ag_2S QDs were redispersed in dry toluene. The same synthetic route was performed with TMS_2S and S precursors.

Cation exchange

After purification, 24 mg of Ag_2S QDs were dissolved in 2 ml of toluene. Bismuth neodecanoate (0.3 mmol, 230 mg) and 160 μL of TOP were added to the QDs system and mixed at 50 °C for 2 h.

After cation exchange, AgBiS_2 was purified by precipitation and redispersion with acetone and toluene 2 times. Then, QDs were dissolved in hexane and stirred overnight. The solution was centrifuged for 5 min at 10 000 rpm. The precipitate was discarded, the solution was washed with acetone and centrifuged one time. Purified AgBiS_2 QDs were dissolved in dry toluene.

Device fabrication

ITO substrates were cleaned in a sonication bath with acetone and isopropanol for 20 minutes and treated with oxygen plasma at 0.4 mbar for 10 min. SnO_2 transport layer was prepared by dilution with deionized water in a volume ratio of 1 : 4. Prepared nanoparticles solution was spin-coated at 2000 rpm for 30 s and then annealed at 270 °C for 15 min. Afterwards, AgBiS_2 or Ag_2S QDs solution with a concentration of 20 mg ml^{-1} in toluene was dynamically spin-coated at 2000 rpm (solution dispensed on a rotating substrate), treated for



after fabrication. During the measurements, the samples were stored in ambient conditions ($20\text{ }^{\circ}\text{C} < T < 23\text{ }^{\circ}\text{C}$; $30\% < \text{R.H.} < 65\%$) in a cabinet. The performance increases within the first few days, reaches a maximum after 4–5 days and remains roughly stable before slow degradation sets in after around 21 days (Fig. S7†). This behavior is common for quantum dot based solar cells.⁵⁰

Author contributions

A. S. conducted the cation exchange synthesis, characterization of QDs and fabrication of solar cells. A. P. provided the St_2S precursors and performed TEM analysis. A. W.-L. performed XPS measurements and analysis together with Y. V., F. P. conceptualized and supervised the project. All authors contributed to the writing, editing and commenting of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Solar cell characterization

A Keithley 2450 source measure unit and Abet A+++ solar simulator with an AM 1.5 filter were used for current–voltage measurements. External quantum efficiency (EQE) measurements were performed on a self-built setup with a halogen lamp, monochromator, beam splitter and a calibrated photodiode and filters. The intensity of the solar simulator illumination was corrected in accordance with a calculated mismatch factor from the EQE measurements and calibrated with a silicon reference cell (NIST, traceable) to 1 sun (100 mW cm^{-2}). Solar cells were measured each day, starting at day 0, directly

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