Cubic AgBiS₂ Colloidal Nanocrystals for Solar Cells

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ABSTRACT: Recent progress in colloidal quantum dot (CQD)-based solar cells indicates that low-toxicity materials such as AgBiS₂ nanocrystals (NCs) show potential in replacing toxic PbS and CdS CQDs in solar cell applications. In this study, an investigation on the importance of the composition and sensitivity toward synthesis conditions was performed by adjusting concentrations and ratios of Ag and Bi precursors—first, by varying the ratio of Ag toward Bi precursors and, second, by varying the concentration of Ag with a constant ratio toward Bi precursors in the solution. Furthermore, elemental XPS studies and TEM imaging together with solar cell analysis indicated a strong correlation between the concentration of Ag precursor and the NC properties and, moreover, the solar cell properties based on these NCs. In short, a large amount of Ag precursor resulted in smaller Ag-rich NCs, which resulted in solar cells with high photovoltage but low photocurrent density, while a lower amount of Ag precursor resulted in larger NCs and solar cells with a lower photovoltage. The Ag:Bi:S ratio of 0.72:0.9:1 resulted in almost stoichiometric NCs but with a slight excess of Ag, which in turn resulted in solar cells with the highest performance. This work therefore gives insight into how the elemental composition and size of the NCs can be tuned by the precursor ratios and how this, in turn, affects the performance of the solar cell devices.

KEYWORDS: AgBiS₂, low toxicity, quantum dots, energy conversion, solar cells

Some of the new generations of solar cells have placed a large focus on low-cost devices and modules as compared to first¹ and second² generation solar cells. Within this particular requirement, several alternative technologies have been investigated over the past few decades, including dye-sensitized solar cells (DSSCs),^{3–5} organic photovoltaic solar cells (OPVs),⁶ perovskite solar cells (PSCs),⁷ and colloidal quantum dot (CQD) solar cells.⁸ All of these different technologies have different advantages as well as drawbacks. Advantages common for these types of solar cells include low-temperature device fabrication and potentially being very light weight,⁹ which may result in high power conversion efficiency (PCE) for a low cost and/or low weight. Drawbacks at this point include limited stability of the solar cells.¹⁰ In addition, the toxicity of lead may limit large scale production and/or application or may require a recycle system in the life cycle for perovskite solar cell devices.¹¹

CQD solar cells have risen in popularity since it was proved that a material's band gap could be changed and tuned by using differently sized nanocrystals,^{12,13} which was then proposed for utilization in solar cells.¹⁴ Materials such as

PbS,^{15–27} PbSe,^{28,29} and CdS^{30–32} have been studied extensively in the past decade. Lately, it has been shown that efficiencies above 12% are possible by passivating the PbS CQDs with a lead perovskite matrix.³³ Furthermore, in the past few years, lead perovskite quantum dots have successfully been made and applied similarly to PbS, and even higher efficiencies of 16.6% have been reported.⁷ However, to avoid the issue of toxicity of Pb and Cd, new materials of nanocrystal and/or quantum dots are investigated. Such materials including Ag₂S,^{34–41} AgSbS₂,⁴² Cu₂S, and CuInS₂ may also be considered low toxic but are often used in combination with CdS.³⁰ AgBiS₂ has also been studied as a solar cell material in a few reports and found to be of potential interest,^{43–45} and solar cells based on NCs of this material have resulted in PCE above

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Figure 1. (a) Schematic experimental setup of the synthesis of AgBiS_2 NCs. Further details can be found in the [Experimental Methods](#) section. (b) Schematic representation of a typical AgBiS_2 NC.

Figure 2. (a) UV-vis absorbance spectrum of AgBiS_2 NC dispersions for the samples containing NCs synthesized with relative added amounts of precursors Ag, Bi, and S as indicated in the legend. The NC concentration was 0.25 mg mL^{-1} . (b) Histograms indicating the mean size of the synthesized nanoparticles. Calculated from (c) as well as [Figure S1a,d](#). (c) TEM image of the AgBiS_2 sample with a precursor ratio Ag:Bi:S of 1:1:1. See [Figure S1a,d](#) for more TEM images.

6%.⁴³ AgBiS_2 has been shown to have two phases: a low-temperature α -phase which has a trigonal-hexagonal structure⁴⁶ as well as a high-temperature β -phase with a cubic structure.⁴⁷ Moreover, the high-temperature phase has also been obtained when the nanocrystal size is below 10 nm, even though the synthesis temperature is much lower than that of the phase transition temperature.⁴³

Experimentally, the bulk band gap of AgBiS_2 has been approximated to 0.8 eV.⁴⁸ However, decreasing the nano-

crystallite size toward the quantum confinement regime, the band gap has been shown to increase, indicating a large exciton Bohr radius, and high-temperature cubic structured AgBiS_2 NCs of lower dimensions exhibit band gap values of 1–1.32 eV.^{43,48,49} Moreover, these films have been reported to have a high extinction coefficient, above 10^5 cm^{-1} , for the whole visible region in the light spectrum.⁴³ This indicates that the material has a strong potential for a high current output and thus high PCE.

Figure 3. (a) An SEM cross section image of a 4-layered solar cell with layer-specific coloring. Estimates of thicknesses are found in Figures S2 and S3 for 4 and 12 layers. (b) Schematic of the device in (a). The colors of the layers in the schematic correspond to the same colors in (a), and each layer is labeled according to the legend. (c) UV-vis spectra of 4-layered NC films with P3HT. (d) UV-vis spectra of films made with different layers of CQDs with a Ag:Bi:S ratio of 0.8:1:1. P3HT has also been spin-coated on top. Note that the 4-layered film is the same as in (c).

Some studies have focused on solvent engineering in the synthesis to improve the quality of the AgBiS₂ NCs, which has been shown to work as an absorber in highly efficient devices⁴⁵ and also as a counter electrode for CdS/CdSe quantum dot sensitized solar cells.⁵⁰ While it has been shown that a highly specific synthesis method can produce nanocrystals highly applicable for solar cell applications, less is known about what happens when the size and composition of the NCs are changed, even if only slightly. The overall properties of a solar cell device may change drastically as the composition and/or the size of the NCs is changed. Properties such as the overall absorption and interference, current extraction ability, and cell voltage are important properties for a good solar cell device. In this paper, it is investigated how changes to the precursor ratios and concentrations change the composition and size of AgBiS₂ NCs and, in turn, how these changes affect the performance of solar cell devices based on the NCs.

RESULTS AND DISCUSSION

AgBiS₂ NCs with Different Precursor Ratios Ag:Bi.

AgBiS₂ NCs were prepared by using different precursor ratios according to the experimental setup seen in Figure 1a and the Experimental Methods section. Figure 1b shows a general schematic representation of an AgBiS₂ NC where the blue color represents either an Ag or a Bi atom. The as-synthesized AgBiS₂ NCs were characterized by using UV-vis spectroscopy to study the absorbance properties of the NCs. Figure 2a shows the UV-vis spectra of the NCs with different precursor ratios, and the results show that by decreasing the amount of Ag precursor in the synthesis, the absorbance of the NCs increases. From these UV-vis measurements, it is observed

that the absorption of the NCs goes toward zero in the 1000–1050 nm range, indicating that the band gap may be approximated to around 1.15–1.25 eV. Figure 2b shows the mean size (determined from TEM) of the quantum dots with different compositions as indicated. From these images, it is clear that the size increases as the amount of Ag precursor added to the quantum dot synthesis decreases. Figure 2c shows a transmission electron microscopy (TEM) image of the sample with a precursor ratio of 1:1:1, showing the quantum dots with an average size around 5.15 nm. TEM images of the other samples discussed (0.8:1:1 and 0.6:1:1) can be found in Figure S1a,d.

AgBiS₂ NC Solar Cell Devices with Different Precursor Ratios Ag:Bi. Solar cell devices were fabricated to investigate the effect of the different precursor ratios on device characteristics. The same ratios as used for the samples in Figure 2 were used. The devices were fabricated according to the description in the Experimental Methods section.

Figure 3a and Figure S2 show the scanning electron microscopy (SEM) cross section of such a device, and Figure 3b shows a schematic figure of the different layers. It is important to note that even though the MoO₃ layer is very thin and thus impossible to distinguish from the P3HT layer in the cross-section images, there is a distinct visual difference in the surface color of the film after the application of the MoO₃. The appearances of these 4-layered devices were relatively light and transparent with a light brown to yellowish color further indicated by the absorbance spectra of the samples shown in Figure 3c. In the spectra an absorption shoulder between 400 and 650 nm can be observed, which originates from the P3HT hole transport layer. Figure 3d shows that the absorbance of

Figure 4. (a) Current density–voltage curves of 4-layered devices made with ratios indicated in the legend. (b) Incident photon to current efficiency (IPCE) spectra of the same devices as in (a). (c) Current density–voltage curves of devices made with the Ag:Bi:S ratio 0.8:1:1 with different thicknesses. (d) IPCE spectra of the same devices as in (c). Note that the 4-layered device is the same in (c) and (a) as well as (b) and (d) for comparison reasons.

the films increases significantly as the amount of layers is increased from 4 to 15 layers. It can be seen that the P3HT contributes in the absorbance spectrum for films of 8 layers or below, while for thicker NC layers the contribution from P3HT is low. The 4-, 6-, and 8-layered devices are rather transparent with a lighter brown or even yellowish color, while the color of devices of 10–15 layers is dark brown, and these films are less transparent, as expected. It can also be observed that for lower amounts of layers, and thus lower thickness, the films inhibit a significant amount of reflectance and/or scattering in the IR region. As the film thickness increases, this scattering/reflectance decreases, resulting in an absorbance more similar to the absorbance measured for the dispersions in Figure 2a.

Figure 4a shows current density–voltage curves (J – V curves) of the different 4-layered devices described above. The specific solar cell parameters are shown in Table 1. The voltage of the devices depends on the amount of Ag precursor added in the synthesis. An Ag:Bi:S ratio of 1:1:1 gives a larger voltage above 0.47 V as compared to 0.42 and 0.30 V for the ratios of 0.8:1:1 and 0.6:1:1, respectively. However, the current extraction of the devices with precursor ratio of 0.8:1:1 is

higher, resulting in a higher PCE overall. The voltage increase as the Ag:Bi precursor ratio increase may depend on the composition and/or size of the NCs. The incident photon to current conversion efficiency (IPCE) of the devices also shows that the current is higher for a precursor ratio of 0.8:1:1 in Figure 4b. As the ratio between Ag and Bi precursors becomes lower as in the case of 0.6:1:1, a slight red-shift can be seen in the IPCE spectrum, which agrees with the change in the UV–vis spectra in Figure 2a. The J – V and IPCE both show that the current of the best device is $<10 \text{ mA cm}^{-2}$, overall limiting the PCE of the devices with only 4 layers of NCs.

Further solar cell devices were prepared based on the NCs from the 0.8:1:1 precursor ratio by varying the thickness of the devices by adding additional layers as shown in Figure 4c. Relevant parameters of these devices are shown in Table S1. These devices are made from the samples as shown in Figure 3d, and the resulting SEM cross section for the device with 12 layers of NCs is shown in Figure S3. The IPCE spectra are shown in Figure 4d. The 4-layered device shows a clear peak at around 700 nm, which decreases for devices made with 6 and 8 layers. For 10 layers, a clear shoulder is formed at around 600 nm, which then red-shifts into a peak for 12 and 15 layers. This red-shift is also seen in the absorbance of 10–15 layered films in Figure 3d. The total increase of the film absorbance for thicker films resulted in an increase of the overall current density of the devices up to 12 layers, where a maximum current density was measured. Increasing the thickness further to 15 layers drastically decreased the current density by over 30%, indicating that the film thickness was too high compared to the diffusion length of the charge carriers in the film.

Table 1. Current Density and Voltage Parameters of the Devices Shown in Figure 4a

	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
1:1:1 4 layers	0.47	6.48	0.50	1.52
0.8:1:1 4 layers	0.42	8.32	0.50	1.76
0.6:1:1 4 layers	0.30	7.90	0.48	1.15

Figure 5. (a) UV-vis spectrum of AgBiS₂ NC dispersions. The samples contain NCs synthesized with relative added amounts of Ag, Bi, and S precursors as indicated in the legend. The NC concentration was 0.25 mg mL⁻¹. (b) Histograms indicating the mean size of the synthesized quantum dots. Calculated from TEM images shown in Figure 2c as well as Figure S1b,c. (c) UV-vis spectrum of 12-layered AgBiS₂ NC films. The samples contain NCs synthesized with relative added amounts of Ag, Bi, and S precursors as indicated in the legend.

AgBiS₂ NC Devices with Constant Ag:Bi Precursor Ratios. Further investigation of the effect of the concentrations of the precursors in the preparation of the NCs was performed by keeping the ratio between Ag and Bi precursors constant but changing the overall concentration and proportion toward S. This was done to see whether the overall size and composition of the quantum dots could be further tuned to improve current extraction from solar cell devices. In comparison with one of the precursor ratios above (0.8:1:1), two new precursor ratios for Ag:Bi:S were used: 0.72:0.9:1 and 0.64:0.8:1. Figure 5a shows the absorbance spectra for the NC dispersions, and Figure 5b shows the histograms resulting from Figure S1b,d. The absorbance spectrum for the 0.8:1:1 sample has been included as well for comparison. The absorbances of the new NCs are both higher and red-shifted compared to the 0.8:1:1 sample, consistent with the larger particle size according to Figure 5b. Devices were also made for these new NCs. In this case, devices based on 10, 12, and 15 NC layers were made and compared with similar devices made with NCs with a precursor ratio of 0.8:1:1. The layer thickness may be interpolated and extrapolated from Figures S1 and S2, which show that a 4-layered film and a 12-layered film have approximate thicknesses of 40 and 125 nm, respectively. This suggests that the thickness increases ~10 nm per layer of AgBiS₂ NCs. The resulting absorbance spectra of films made with 12 layers of NCs from different precursor concentrations can be seen in Figure 5c. The spectra show, similarly to the

spectra for the dispersions, that the absorbance of the films prepared from the NCs with two new ratios is higher than that of the 0.8:1:1 sample. The absorbance spectra in Figure 5c were used to produce the Tauc plots in Figure S4 which further show a shift in the absorbance onset of the samples with different precursor ratios. The Tauc plot of a P3HT-free 12-layered film using an AgBiS₂ precursor ratio of 0.72:0.9:1 shown in Figure S5 indicates that the band gap is indirect and has a value of 1.23 eV, well within the approximation expressed earlier for the absorbance of the dispersion samples in Figure 2. In addition, comparing an AgBiS₂ precursor ratio of 0.72:0.9:1 film with P3HT and one without in Figure S6 indicates that P3HT contributes only minimally to the absorbance. The reflectance in the IR region is reduced significantly as the size of the particles and thickness increase as seen in Figure 5c and Figures S7–S9. This decrease may be related to the film surface roughness as a rougher film may scatter more light and reflect less incoming light.

Solar cell devices were prepared from the above films, and comparing Figure 6a with Figures S10 and S11 shows that a precursor ratio of 0.72:0.9:1 generally resulted in the highest PCE. Similarly, comparing Figure 4c with Figures S12 and S13 indicates that the 12-layered devices were overall more efficient than devices with 10 and 15 layers for all three precursor ratios. This resulted in the solar cell device with the highest PCE, which was obtained for a device with 12 layers of NCs synthesized with an Ag:Bi:S precursor ratio of 0.72:0.9:1. The PCE was 3.05%, resulting from a short circuit current density

Figure 6. (a) Current density–voltage curves of 12-layered devices made with AgBiS_2 NCs with different precursor concentrations as indicated by the legend. (b) Incident photon to current conversion efficiency (IPCE) spectra of the same samples as in (a). The integrated photocurrent is shown in Figure S15. The integrated photocurrent was 15.3 mA cm^{-2} , which is comparable to the value resulted from current density–voltage measurements. (c) Electron lifetime of the same devices shown in (a) and (b) at different light intensities. (d) Charge transport of the same devices as in (a), (b), and (c) at different light intensities. The light intensities measured are the same as the ones measured for the electron lifetime in (c).

of 14.55 mA cm^{-2} , an open circuit photovoltage of 0.41 V, and a FF of 0.51. While 10 layers of NCs generally gave a similar current density output, the voltage and FF were higher for devices with 12 layers of NCs. The device prepared with 15 layers of NCs gave a higher voltage than 12 layers, but a lower current density and thus a lower PCE.

Table 2 summarizes the results from the devices made with 12 layers, and Table S2 shows the parameters of the 10- and

Table 2. Solar Cell Parameters of the Devices Shown in Figure 5a

Ag:Bi:S ratio and layers	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
0.8:1:1 12 layers	0.42	10.5	0.53	2.33
0.72:0.9:1 12 layers	0.41	14.55	0.51	3.05
0.72:0.9:1 12 layers 1 week old	0.41	15.06	0.54	3.31
0.64:0.8:1 12 layers	0.34	15.06	0.46	2.34

15-layered devices. The devices were measured once more after 1 week to study the storage stability. The $J-V$ curve for the second measurement of the best device can be found in Figure S14, while the parameters are included in Table 2. In short, the devices were stored in a dry but otherwise ambient environment, and the PCE did not decrease. In contrast, the PCE increased slightly due to improved current and fill factor over time. After the second measurement, the PCE was around 3.3%. The increase of the PCE over time might be due to the oxidation and thus self-doping of the NCs and the hole transport layer. As more oxygen is introduced, the P3HT and/

or AgBiS_2 NCs may be induced with more holes, which could result in better conductivity. However, over time, this effect may be detrimental to the device, as this may induce trap states and decrease the open circuit voltage of the device. Therefore, while the PCE is improved short term, the long-term stability in air may be limited.

Comparing the above PCE results with other results within the literature,⁴³ one can observe that it is possible to accomplish higher efficiencies by exchanging the P3HT hole-transport material to a thin layer of a wide band gap organic hole-transport material, such as PTB7. The wider band gap in PTB7, with a deeper HOMO level, contributes to a higher V_{OC} . The lower absorbance of the PTB7 film compared to P3HT, due to the higher band gap and due to a thinner polymer film, makes it possible to collect a larger amount of red photons reflected from the back-contact, increasing the photocurrent. However, PTB7 has a more complex structure, which complicates synthesis and thus influences the price. For this study, P3HT was chosen because it is easier to use, since a thicker polymer film can be used (compared to PTB7), which gives more reproducible results, to focus on the effect of compositional differences within the AgBiS_2 NCs applied in solar cells.

The IPCE in Figure 6b also shows that a precursor ratio of 0.72:0.9:1 resulted in devices with a higher current density than the other ratios. It is important to note here that the disparity between the trend in the maximum current and the maximum IPCE for the different samples stems from the devices being sensitive to different light intensities as well as a

Figure 7. X-ray photoelectron core level spectra of 4-layered films of AgBiS₂ NCs for the Ag:Bi:S ratios. From top to bottom: 0.6:1:1, 0.64:0.8:1, 0.72:0.9:1, 0.8:1:1, and 1:1:1. Core levels studied (a) I 3d, (b) Ag 3d, and (c) Bi 4f (dark yellow and magenta) and S 2p (green and blue).

disparity between the solar spectrum and IPCE maximum wavelength. The loss at high light intensities as seen in Figures S16 and S17 is indicative of recombination losses. This is further supported by Figure 6c,d, which shows the measured electron lifetime and charge transport of the 12-layered devices. The charge transport time is shorter than the lifetime of the charges by a factor of 6.2 at high light intensities and a factor of 33.5 at low light intensities for the best device (with a Ag:Bi:S precursor ratio of 0.72:0.9:1), which indicates that the recombination of charges may be higher at higher light intensities.

Elemental and Structural Analysis. The composition of the NC films used in this study were further analyzed by using XPS to evaluate the elemental composition of the NCs. Furthermore, XRD was used to study the structure of the NCs. Figure 7a–c shows the resulting elemental analysis from XPS of films of the NCs. The spectra are normalized as to see how the composition changes for the NCs prepared from different precursor ratios. A summary of the relative precursor ratios and their effect on the relative amounts and atomic fractions in the NCs can be seen in Tables S3 and S4, respectively.

As can be seen in Figure 7a–c, the Ag and I content in the NC samples decreases as the amount of Ag precursor added is decreased. The Bi 4f and S 2p peaks overlap partially, and the Bi 4f core levels also exhibit a split of its peaks by about 0.9 eV. Plotting the atomic fractions in the NCs obtained from the XPS analysis, versus the added amount of Ag precursor, results in a clear linear relationship (see Figure 8a). As the amount of Ag precursor is increased, the amount of Ag in the NC sample increases linearly and the amount of I in the films is also increased. Because the I is only added as a linker on the surface

of the NCs, this increase is indicative of an increase in surface area due to the decrease in NC size. Similarly, it can also be observed that the amounts of Bi and S in the NCs decrease as the amount of Ag precursor added is increased. From Figure 8a it is also clear that the overall composition of the NCs matches the stoichiometry of AgBiS₂ at a concentration between 0.64 and 0.72 mmol of the added Ag precursor. This indicates that the composition of the NCs is mainly affected by the Ag precursor concentration while the results in Figure S18 indicate that the Ag precursor concentration also affects the NC size. The sensitivity toward Ag may be explained by the affinity of the Ag precursor toward the capping ligand, oleic acid. The observations of the synthesis procedure indicate that the reaction conditions are limited by the solubility of the Ag precursor in oleic acid. At higher precursor concentrations of Ag, one would expect an increase in the nucleation rate resulting in more, but smaller NCs or NCs with a larger amount of Ag as compared to Bi.

According to the diffractogram in Figure 8b, all samples exhibit a cubic structure, previously described as the high-temperature β -phase⁴¹ as compared to the trigonal low-temperature phase described elsewhere.⁴⁶ There is a small change in the relative intensity ratios for the (111) and (200) peaks as well as peak broadening indicative of nanocrystal size. The decrease in peak broadening and the improved signal-to-noise ratio in AgBiS₂ NCs synthesized with a lower Ag:Bi ratio is further indicative of larger particle size and/or an improvement in crystallinity. The relative intensity change of the peaks may be possible to attribute to a preference to nanocrystal growth in the (111) direction but could also be related to the average preferred orientation of the as-

Figure 8. (a) Ag precursor concentration added (in mmol) versus the atom concentration of each element present in the NCs determined from the XPS results in Figure 7. Table S4 shows the values used. (b) X-ray diffraction of drop-casted AgBiS₂ NC films with different precursor ratios in comparison to reference spectrum collected from ICSD Collection number 604845.⁴⁷ The Miller indices for the strongest peaks are shown. (c) Schematic showing how the size and composition of the AgBiS₂ NCs change with increasing Ag precursor concentration.

synthesized NCs as they are drop-casted and dried on the sample substrate with no ligand exchange. Figure 8c summarizes these results and discussion, showing how the size and composition of AgBiS₂ NCs change with increasing Ag precursor concentration.

While the AgBiS₂ NC size and/or composition are sensitive to the Ag precursor concentration, it also seems to have a correlation toward the solar cell device parameters as discussed above. The slight decrease in the solar cell photovoltage as the amount of Ag precursor is decreased (despite keeping the Ag:Bi precursor ratio constant) indicates that the voltage is higher when there is more Ag than Bi in the NC. In contrast, the current of the devices increases as the overall resulting Ag:Bi ratio in the NC is close to 1:1 as indicated in Figures 6a and 7a. This also seems to be in agreement with the literature where the NCs (while using smaller AgBiS₂ NCs than in this paper) have slightly more Ag than Bi while still producing excellent current.⁴³

CONCLUSIONS

AgBiS₂ NCs were made using a hot-injection synthesis method investigating different precursor ratios of Ag:Bi:S, resulting in cubic AgBiS₂ NCs with different compositions and sizes. Upon comparison of three of these compositions of Ag:Bi:S (1:1:1, 0.8:1:1, and 0.6:1:1), decreasing the amount of Ag precursor resulted in slightly larger NCs and also changed the actual elemental composition of the NCs. By keeping the ratio of the Ag and Bi precursors constant (see compositions 0.8:1:1, 0.72:0.9:1, and 0.64:0.8:1), the resulting composition of the

NCs was still mainly affected by the amount of Ag precursor added. The size of the NCs was also changed by different Ag and Bi precursor concentrations. In general, the lower amount of metal precursors compared to S precursor, the larger NCs were formed.

In solar cell devices, the NC composition and size were directly related to the properties and efficiencies. As the amount of Ag and surface I in the NC increased, the voltage of the devices increased. However, because of the decrease in absorption, the current extraction was lower than that of NCs with a more stoichiometric amount of Ag, Bi, and S. Therefore, a composition of the NCs having close to equal amounts of Ag and Bi but with a small excess of Ag which was the result of adding a ratio of Ag:Bi:S of 0.72:0.9:1 gave the best solar cell PCE of 3.3% for a 12-layered device. Comparing different thicknesses by adjusting the number of layers, 10 and 15 layers both gave a lower current than 12 layers, indicative that 12 layers was the optimal thickness for the solar cell devices.

EXPERIMENTAL METHODS

Chemicals and Materials. The following chemicals listed were purchased from Sigma-Aldrich (St. Louis, MO) and were used as received unless stated otherwise: silver acetate (AgOAc, 99%), bismuth acetate (Bi(OAc)₃, 99.99%), oleic acid (90%), octadecene (90%), hexamethyldisilathiane (HMDS, ≥98%), acetone (99%), toluene (99.8%), methanol (≥99.9%), acetonitrile (99.8%), tetrabutylammonium iodide (≥99%), deionized water, aqueous hydrochloric acid (≥37 wt %), aqueous RBS solution (2% NaOH_(aq)), ethanol (99.97%), zinc (≥98%), ethanolamine (≥99%), and molybdenum(VI) oxide (99.97%).

The following chemicals and materials were purchased from other companies: zinc acetate dihydrate (99.5%, VWR International LLC, Radnor, PA), electronic grade P3HT (93% regioregular and molecular weight >45000, Luminescence Technology Corp., Xizhi, New Taipei City, Taiwan), chlorobenzene ($\geq 99\%$, Merck, Burlington, MA), gold (99.99% purity, Metalor Technologies AB, Borås, Sweden), and ITO-covered glass with a resistance of $12 \Omega/\square$ (Optical Filters Ltd., Thame, UK).

AgBiS₂ NC Synthesis. Five different syntheses were performed in total to assess how the concentration and relative amount of Ag and Bi affected the AgBiS₂ NCs composition and properties in working solar cell devices. The amounts of Ag and Bi are described in Table 3.

Table 3. Synthesis Parameters Used in This Study and Resulting Yields

molar ratio Ag:Bi:S	weight				yield (mg)
	AgOAc (mg)	BiOAc (mg)	HMDS (mg)	oleic acid (g)	
1:1:1	167	387	178	5.343	310
0.8:1:1	134	386	178	5.347	259
0.6:1:1	100	386	178	5.341	190
0.72:0.9:1	120	348	178	5.345	225
0.64:0.8:1	107	309	178	5.352	164

In short, silver acetate, bismuth acetate, and oleic acid were weighed and added to a 50 mL three-necked flask as seen in Figure 1a. The mixture was degassed by using a vacuum pump until no visible bubbles were observed. A nitrogen atmosphere was added, and the mixture was stirred at 750 rpm for 30 min. The mixture was heated to 100 °C for 3 h while being flushed continuously with nitrogen gas to dissolve the metal ions and removing acetic acid. HMDS, which was dissolved in 5.3 mL of octadecene and heated to 80 °C, was then injected into the flask, forming NCs. Extra caution was taken while handling HMDS as it is toxic and has a strong overwhelming odor by always keeping it sealed from the ambient atmosphere until injected.

The formed dispersion was then cooled to room temperature naturally for 1 h. Acetone was used to precipitate the particles followed by centrifugation. Toluene was added to the precipitate, and the resulting dispersion was centrifuged again. The supernatant was then washed further with acetone and toluene and finally dispersed in toluene for long-term storage under ambient conditions. The mass yields of the batches top to bottom in Table 3 were 310, 259, 190, 225, and 164 mg.

ZnO Nanoparticle Synthesis. In a typical ZnO nanoparticle sol synthesis, 2.195 g of zinc acetate dihydrate was added to 20 mL of ethanol in a 100 mL three-necked flask. The mixture was stirred and heated to 80 °C for ca. 40 min before injection of 0.61 g of ethanolamine. The formed nanoparticle sol was then further kept at 80 °C for 3 h before being cooled to room temperature and stored in ambient conditions.

Solar Cell Fabrication. Solar cell devices were made according the schematic shown in Figure 3b. As-received ITO-covered glass was cut and chemically etched to get the desired structure of the device and further denoted as the substrate. The substrates were then washed by using RBS-50 solution, acetone, ethanol, and deionized water by sonication. The substrates were treated under UV-ozone for 20 min before the ZnO nanoparticle sol (first filtered by a 0.45 μm filter) was spin-coated at 3000 rpm for 30 s. The sol-covered substrates were then sintered at 200 °C for 1 h.

Before spin-coating the AgBiS₂ NC layer, the substrates were once again treated under UV-ozone for 10 min, and the AgBiS₂ NC dispersions were all filtered by a 0.2 μm filter. All AgBiS₂ NC layers were fabricated by spin-coating the NCs layer by layer. One layer was made by spin-coating the 20 mg mL⁻¹ NC dispersion at 2000 rpm for 30 s. This was followed by covering the surface with 5 mM tetrabutylammonium iodide in methanol for 30 s to facilitate ligand exchange and spun at 2000 rpm for 30 s. Each layer was then washed twice with acetonitrile. Solar cell devices using 1:1:1, 0.8:1:1, and

0.6:1:1 Ag:Bi:S ratios were all made by using 4 layers. 1:1:1 and 0.8:1:1 were then further tested for 6 layers. After assessment the ratio 0.8:1:1 was tested further by using 8, 10, 12, and 15 layers. In conjunction, devices for ratios of 0.72:0.9:1 and 0.64:0.8:1 were made with 10, 12, and 15 layers.

On all solar cells, the hole transport material P3HT was applied. The P3HT was dissolved 10 mg mL⁻¹ in chlorobenzene and heated to 50 °C for 30 min. The polymer solution was then spin-coated on top of the AgBiS₂ NC layer at 2000 rpm for 10 s. The films were then further dried by a desiccator connected to a vacuum pump for 30 min. The devices were then added to a metal evaporator to evaporate 2 nm MoO₃ and 50 nm gold.

Characterization. UV-Vis Spectrometry of Dispersions and Films. DH 2000 BAL Mikropak deuterium and halogen lamps were used in conjunction with an Ocean Optics detector to measure the UV-vis absorbance of dispersion and film samples. The dispersion samples were made by diluting as-synthesized AgBiS₂ NCs to 0.25 mg mL⁻¹ in toluene. The film samples were finished solar cell devices.

Transmission Electron Microscopy (TEM). A JEOL JEM-2100F field emission transmission electron microscope operated at 200 kV with a probe size of <0.5 nm was used to take TEM images of the different samples.

Scanning Electron Microscopy (SEM). A Zeiss LEO1550 scanning electron microscope operated using an accelerating voltage of 5 kV and an in-lense detector was used to take SEM cross-section images of the finished devices.

Current-Voltage Measurements. A Keithley 2400 sourcemeter and a Newton Xe lamp were used to measure the solar cell devices to imitate AM 1.5 G conditions. The surface energy was measured to 100 mW cm⁻² by using a reference silicon solar cell with a known intensity-to-current output. The devices were measured from at a speed or 111 mV s⁻¹ by using a mask with an active area of 0.065 cm².

Incident Photon-to-Current Efficiency (IPCE) Measurements. IPCE spectra were measured by using a modular setup with an in-house made software as described elsewhere. In short, monochromated light from an ASB-XE-175 xenon light source is separated by a beam splitter. One beam reaches the sample, while the other hits a SM1PD2A silicon photodiode from Thorlabs. A Labjack U6 data acquisition device then transfers the data signal to the software computer. A second SM1PD2A silicon photodiode is used as a reference. The range measured was 320–1100 nm.

Electron Lifetime. Electron lifetime measurements were performed as previously reported.³⁵ In short, the electron lifetime is assumed to be approximated from the half-time of the voltage decay of a small positive fluctuation of the light intensity.

Charge Transport. Charge transport was measured with a similar setup as the electron lifetime, but measuring the transient photo-current decay instead.

Grazing Incidence X-ray Diffraction (GIXRD). A D5000 θ -2 θ diffractometer from Siemens was used to measure low angle measurements of drop-casted AgBiS₂ film samples on amorphous glass substrates with a Cu K α X-ray source with a wavelength of 0.15059 nm between 10° and 85°.

X-ray Photoelectron Spectroscopy (XPS). A PHI Quantera II from Physical Electronics was used to measure XPS spectra of different films of different metal precursor ratios. A monochromatic Al K α X-ray source with an output energy of 25 W (15 kV) was used with a band-pass energy of 112 eV for all samples. The samples were made by spin-coating by washing ITO substrates as described above. ZnO nanoparticles were then spin-coated at 3000 rpm on top and the substrates were then heated to 200 °C on a hot plate for 1 h. The different NC samples were then spin-coated layer by layer as described above. Each sample was 4 layers thick. Similarly to a solar cell device, the samples were made with a counter electrode to avoid charging of the sample. The final XPS spectra for each element Ag, Bi, S, and I were then shifted slightly so that the peak denoting adventitious carbon was set to 284.8 eV. An elemental analysis was made by integrating the areas under the peaks and using previously established sensitivity factors to get the effective area and thus atomic fraction of each element. As the Bi and S peaks overlapped severely,

an assumption of total neutral charge had to be made to fit the XPS curves.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsanm.9b02443>.

Figures S1–S18 and Tables S1–S4 (PDF)

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Notes

The authors declare no competing financial interest.

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