Optimizing the Synthetic Conditions of “Green” Colloidal AgBiS₂ Nanocrystals Using a Low-Cost Sulfur Source

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Abstract: Colloidal AgBiS₂ nanocrystals (NCs) have attracted increasing attention as a near–infrared absorbent materials with non–toxic elements and a high absorption coefficient. In recent years, colloidal AgBiS₂ NCs have typically been synthesized via the hot injection method using hexamethyldisilathiane (TMS) as the sulfur source. However, the cost of TMS is one of the biggest obstacles to large–scale synthesis of colloidal AgBiS₂ NCs. Herein, we synthesized colloidal AgBiS₂ NCs using oleylamine@sulfur (OLA–S) solution as the sulfur source instead of TMS and optimized the synthesis conditions of colloidal AgBiS₂ NCs. By controlling the reaction injection temperature and the dosage of OLA–S, colloidal AgBiS₂ NCs with adjustable size can be synthesized. Compared with TMS–based colloidal AgBiS₂ NCs, the colloidal AgBiS₂ NCs based on OLA–S has good crystallinity and fewer defects.

Keywords: AgBiS₂; colloidal nanocrystals; hot injection; sulfur source

1. Introduction

Colloidal AgBiS₂ nanocrystal (NC), a member of the I–V–VI₂ ternary semiconductor materials [1–7], is a promising eco–friendly material for solar cells owing to colloidal AgBiS₂ NC having a wide absorption spectrum in the visible to near–infrared region (300–1600 nm) [8–10], high absorption coefficient (~10⁵ cm⁻¹) [1,11–13], and good air stability [8]. The hot injection method is widely used to prepare high quality NCs such as PbS [14], PbSe [15,16], and halide perovskite NCs [17–22]. In 2016, Bernechea et al. synthesized colloidal AgBiS₂ NCs by the hot injection method using hexamethyldisilathiane (TMS) as the sulfur source and first reported colloidal AgBiS₂ NC–based solar cells with a certified power conversion efficiency (PCE) of 6.3% [1]. Subsequently, Hu et al. synthesized colloidal AgBiS₂ NCs using the hot injection method with hexamethyldisilathiane (TMS) as the sulfur source and reported colloidal AgBiS₂ NC–based solar cells with a certified power conversion efficiency (PCE) of 6.3% [1]. Subsequently, Hu et al. synthesized colloidal AgBiS₂ NCs using an improved amine–based synthesis route, improving the PCE of colloidal AgBiS₂ NC–based solar cells by 30% using colloidal AgBiS₂ NCs synthesized using a modified route [23]. Oh et al. improved the size distribution of colloidal AgBiS₂ NCs by an optimized synthetic route, resulting in enhanced photovoltaic performance [24]. Akgul et al. synthesized colloidal AgBiS₂ NCs at room temperature using an improved sulfur amine–based synthesis route, reducing the production price by 60% and achieving a PCE of 5.5% [25]. These results demonstrate that the quality of colloidal AgBiS₂ NCs plays an important role in the performance of solar cells. Therefore, it is of extreme importance to synthesize monodispersed colloidal AgBiS₂ NCs in the quantum confinement regime and with a high phase purity [26]. Yet, it should be noted that although synthesis of colloidal AgBiS₂ NCs has been developed by several researchers [1,27–30], it remains challenging to synthesize colloidal AgBiS₂ NCs with a perfect crystal structure and complete elimination of defects [31–38]. Furthermore,
using expensive and unstable TMS as the sulfur source in colloidal AgBiS$_2$ NCs synthesis process results in high cost of the synthesis reaction, which is not conducive to large-scale preparation of colloidal AgBiS$_2$ NC. It is urgent to explore a method to synthesize high quality colloidal AgBiS$_2$ NC with low cost.

As a cheap sulfur source, oleylamine@sulfur (OLA–S) solution has been widely used to synthesize high quality CdS [39], ZnS [40], and PbS NCs [41,42]. Moreover, as a ligand stabilizer, oleylamine can passivate the surface defects of NCs and regulate their growth [23,43]. Recently, Nakazawa et al. successfully synthesized colloidal AgBiS$_2$ NCs with OLA–S as sulfur source [44]. However, the effect of OLA–S on the growth and quality of colloidal AgBiS$_2$ NCs has not been studied in detail. In this work, in order to improve the quality of colloidal AgBiS$_2$ NCs and reduce the preparation cost, we synthesized colloidal AgBiS$_2$ NCs by hot injection method and using OLA–S as the sulfur source to replace TMS, then investigated the effect of OLA–S on the growth of colloidal AgBiS$_2$ NCs. By regulating the dosage of OLA–S, high quality colloidal AgBiS$_2$ NCs with low defect density and uniform size were prepared. It was found that the size of colloidal AgBiS$_2$ NCs could be controlled by changing the reaction injection temperature. Compared with TMS–based colloidal AgBiS$_2$ NCs, the colloidal AgBiS$_2$ NCs based on OLA–S have good crystallinity and fewer defects. In addition, the synthesis cost is significantly reduced.

2. Materials and Methods

Chemicals and materials. Bismuth (III) acetate (Bi(OAc)$_3$, 99.9%, Aladdin, China), silver acetate (AgOAc, 99.5%, Aladdin, China), oleic acid (OA, 90%, Sigma–Aldrich, USA), hexamethyldisilathiane (TMS, synthesis grade, Sigma–Aldrich, Switzerland), 1-Octadecene (ODE, 90%, Aladdin, China), oleylamine (OLA, 80–90%, Aladdin, China), sulfur (S, 99.5%, Sinopharm, China), acetone (99.5%, Sinopharm, China), toluene (99.5%, Sinopharm, China), hexane(97.0%, Sinopharm, China).

Synthesis of TMS–based colloidal AgBiS$_2$ NCs. The TMS–based colloidal AgBiS$_2$ NCs were synthesized following a hot injection method reported previously in the literature [29].

Synthesis of OLA–S–based colloidal AgBiS$_2$ NCs. The synthesis of OLA–S–based colloidal AgBiS$_2$ NCs was carried out similarly to that of TMS–based colloidal AgBiS$_2$ NCs. The OLA–S (1 M) solution was prepared by dissolving sulfur powder in OLA solution at room temperature. To investigate the influence of the reaction injection temperature (80 °C, 100 °C, 120 °C) on synthesis of OLA–S–based colloidal AgBiS$_2$ NCs, the dosage of OLA–S solution (1 M) was kept at 3 mL. In contrast, to investigate the influence of the dosage of OLA–S solution (1 mL, 2 mL, 3 mL and 4 mL) on synthesis of OLA–S–based colloidal AgBiS$_2$ NCs, the reaction injection temperature was kept at 100 °C. After rapidly injected the OLA–S solution into the cationic solution, heating was stopped while stirring was maintained until the reaction solution cooled to room temperature. The colloidal AgBiS$_2$ NCs were collected using an acetone/toluene solvent system in air, and the obtained colloidal AgBiS$_2$ NCs precipitate was then dried in a vacuum drying oven at room temperature. Finally, the colloidal AgBiS$_2$ NCs were dispersed in hexane solution.

Characterization

The phase identification of colloidal AgBiS$_2$ NCs was carried out using powder X-ray diffraction (XRD, Bruker, D8 ADVANCED, Germany). The morphology and crystal structure of the prepared colloidal AgBiS$_2$ NCs were characterized using high–resolution transmission electron microscopy (HR–TEM, Thermo Fisher Scientific, Talos F200x, USA). The TEM samples were prepared as follows: the obtained colloidal AgBiS$_2$ NCs were dispersed in hexane with a concentration of 2 mg/mL, three drops of the mixture solution were dropped onto the TEM support film via pipette gun, and the TEM support films were fully dried in the vacuum drying oven before measurement. The acceleration voltage of electron beam was 200 KV during the TEM test. Elemental mapping of the colloidal AgBiS$_2$ NCs was carried out using a TEM equipped with an energy dispersive spectrometer (EDS). UV–vis–NIR absorption spectra of the colloidal AgBiS$_2$ NCs were recorded with a
spectrophotometer (Shimadzu, UV–3600 PLUS, Japan). Fourier transform–infrared spectra (FT–IR) of colloidal AgBiS₂ NCs were recorded using an infrared spectrometer (Bruker, INVENIO, Germany). The photoluminescent (PL) spectra of the colloidal AgBiS₂ NCs were measured by using a fluorescence spectrophotometer (Zolix instruments Co., Ltd, FST1–MPL303–OP1, Beijing, China).

3. Results and Discussion

Following the schematic diagram of the synthesis of colloidal AgBiS₂ NCs by hot injection method, which is shown in Figure 1, we adopted two methods to synthesize colloidal AgBiS₂ NCs using TMS (path 1) and OLA–S (path 2) as the sulfur source. The variation of the crystal structure and phase of TMS–based and OLA–S–based colloidal AgBiS₂ NCs were studied using X–ray diffraction (XRD). Figure 2a shows the XRD patterns of the TMS–based and OLA–S–based colloidal AgBiS₂ NCs (dosage of OLA–S: 3 mL, injection temperature: 100 °C). For both samples, six XRD peaks are found at 13.75°, 15.85°, 22.89°, 27.12°, 28.20°, and 33.11°, which can be assigned to the facets (111), (200), (220), (311), (222), and (400) of AgBiS₂ cubic rock salt structure (JCPDS No. 21–1178), respectively [8,12,37,45–47]. This indicates that colloidal AgBiS₂ NCs can be successfully prepared by using OLA–S as the sulfur source. For NC materials, the broadening of XRD peaks can be roughly attributed to the size effect of NCs and lattice strain, which is closely related to defects in the NCs [48]. The lattice strains in TMS–based and OLA–S–based colloidal AgBiS₂ NCs were calculated using the Williams–Hall plot method [49], with the results shown in Figure S1 and the corresponding Table S1. The obtained values of the lattice strain for TMS–based and OLA–S–based colloidal AgBiS₂ NCs are 0.33 and 0.27, respectively. It can be seen that the lattice strain for TMS–based colloidal AgBiS₂ NCs is larger than that of the OLA–S–based NCs, with the larger lattice strain leading to more defects in the NCs. Thus, the results demonstrate that OLA–S–based colloidal AgBiS₂ NCs have lower defect density than TMS–based NCs. In other words, as a new sulfur source, OLA–S can be used to synthesize high quality colloidal AgBiS₂ NCs.

![Figure 1](image1.png)

**Figure 1.** Synthetic route for colloidal AgBiS₂ NCs using different sulfur sources (path 1: TMS, path 2: OLA–S).

Furthermore, in order to reveal the influence of the sulfur source on the morphology and size distribution of colloidal AgBiS₂ NCs, transmission electron microscopy (TEM) measurement was carried out. Figure S2 shows that colloidal AgBiS₂ NCs prepared using TMS and OLA–S have a uniform spherical shape. The average diameters of TMS–based and OLA–S–based colloidal AgBiS₂ NCs are about 4.3 ± 1.6 nm (Figure S2a) and 7.8 ± 1.9 nm (Figure S2b), respectively. High–resolution TEM (HR–TEM) images of spherical colloidal AgBiS₂ NCs based on TMS and OLA–S are shown in Figure 2b,c [50–52]. Lattice spacing of about 0.32 nm, corresponding to (111) crystal plane spacing of cubic rock salt structure AgBiS₂, can be clearly seen, which is consistent with the XRD results above. Elemental mapping of TMS–based colloidal AgBiS₂ NCs was carried out using a TEM equipped with EDS. Elemental mapping images are provided in Figure S3a–c, where the Ag, Bi, and S
elements are distributed throughout all NCs. Moreover, the atomic percentages of Ag, Bi, and S elements are 41.3, 22.3, and 36.4, respectively. These results indicate that the surface of TMS–based colloidal AgBiS$_2$ NCs should be silver–rich and sulfur–poor. Figure S3d–f shows the element mapping images of OLA–S–based colloidal AgBiS$_2$ NCs. The atomic percentages of Ag, Bi, and S elements are 42.6, 12.3, and 45.1, respectively. This means that the surface of OLA–S–based colloidal AgBiS$_2$ NCs is both silver–rich and sulfur–rich. Combined with the XRD result of the OLA–S–based colloidal AgBiS$_2$ NCs, the signal of Ag$_2$S is not observed in Figure 2a. Therefore, we speculate that the excess Ag and S are coating on the surface of colloidal AgBiS$_2$ NCs rather than forming Ag$_2$S impurities.

![Figure 2](image-url)

**Figure 2.** (a) XRD patterns of colloidal AgBiS$_2$ NCs based on TMS and OLA–S; (b,c) HR–TEM images of TMS–based and OLA–S–based colloidal AgBiS$_2$ NCs, respectively.

To further reveal the effect of the sulfur source on the quality of the obtained colloidal AgBiS$_2$ NCs, the photoluminescent (PL) spectra of the TMS–based and OLA–S–based colloidal AgBiS$_2$ NC solutions were measured at room temperature [53]. The PL spectra of colloidal AgBiS$_2$ NCs based on TMS and OLA–S are shown in Figure 3a. We detected PL signals in the emission range of 400–1000 nm using a 330 nm excitation wavelength. It can be seen that the PL intensity of OLA–S–based colloidal AgBiS$_2$ NCs is stronger than that of TMS–based colloidal AgBiS$_2$ NCs under the same concentration. This indicates that there are fewer nonradiative charge recombination centers, which is closely related to lower defect density, in the OLA–S–based colloidal AgBiS$_2$ NCs compared to the TMS–based colloidal AgBiS$_2$ NCs.

![Figure 3](image-url)

**Figure 3.** (a) PL spectra of TMS–based and OLA–S–based colloidal AgBiS$_2$ NCs, (b) UV–vis–NIR absorption spectra of the colloidal AgBiS$_2$ NCs in hexane, and (c) FT–IR spectra of colloidal AgBiS$_2$ NCs.

The UV–vis–NIR absorption spectra of TMS–based and OLA–S–based colloidal AgBiS$_2$ NCs are shown in Figure 3b. It can be seen that the absorption spectra of both of TMS–based and OLA–S–based colloidal AgBiS$_2$ NCs do not exhibit any exciton absorption peak or sharp absorption edge in the range of 300–1600 nm, which is similar to the previously reported colloidal AgBiS$_2$ NCs and other ternary semiconductor NCs such as colloidal CuInS$_2$, AgInS$_2$ and AgBiSe$_2$ NCs [6,54–56]. The absorption spectrum of OLA–S–based colloidal AgBiS$_2$ NCs extends to a larger IR region than the TMS–based colloidal AgBiS$_2$ NCs, which may be owing to the size effect of larger grain size of OLA–S–based colloidal AgBiS$_2$ NCs. This result is consistent with the result of the TEM images shown above.
FT-IR spectroscopy was employed to investigate the functional groups on the obtained colloidal AgBiS$_2$ NCs [44,57]. Figure 3c shows the FT-IR spectra of colloidal AgBiS$_2$ NCs. For TMS–based colloidal AgBiS$_2$ NCs, the =C–H stretching peak at 3006 cm$^{-1}$, C–H absorption stretching peaks at 2961, 2929, and 2854 cm$^{-1}$, and C=O stretching mode at 1678 cm$^{-1}$ are assigned to OA ligands on the surface of colloidal AgBiS$_2$ NCs [55,58]. For OLA–S–based colloidal AgBiS$_2$ NCs, the peaks at 903 cm$^{-1}$, 721 cm$^{-1}$, and 641 cm$^{-1}$ are attributed to N–H vibrations of OLA. Additionally, a C–N stretching mode peak was observed at 1145 cm$^{-1}$. The peak at 1678 cm$^{-1}$ can be assigned to C=O stretching of OA ligands, indicating that the OLA–S–based colloidal AgBiS$_2$ NCs are coated by OLA and OA ligands and that there are no amide–type ligands on the surface of the colloidal AgBiS$_2$ NCs.

In order to reveal the influence of reaction temperature on the synthesis of OLA–S–based colloidal AgBiS$_2$ NCs, a synthetic experiment was carried out at 80 °C, 100 °C, and 120 °C. The crystal structure and phase transition of colloidal AgBiS$_2$ NCs based on OLA–S were investigated using XRD. Figure 4a shows the XRD patterns of OLA–S–based colloidal AgBiS$_2$ NCs which were synthesized under different injection temperatures. The results show that colloidal AgBiS$_2$ NCs can be successfully prepared at 100 °C and 120 °C. For sample prepared at 80 °C, the weak diffraction peak intensity indicates poor crystallinity of the obtained product and there are peaks belonging to monoclinic structure Ag$_2$S (JCPDS No. 14–0072) at which impurities can be found. Therefore, pure colloidal AgBiS$_2$ NCs cannot be synthesized at low temperature when using OLA–S as the sulfur source. The lattice strains of OLA–S–based colloidal AgBiS$_2$ NCs obtained at 100 °C and 120 °C were calculated using the Williams–Hall plot from Figure S4, the corresponding results are shown in Table S2. The values of the lattice strains for OLA–S–based colloidal AgBiS$_2$ NCs prepared at 100 °C and 120 °C are 0.27 and 0.38, respectively. It can be seen that the lattice strain of OLA–S–based colloidal AgBiS$_2$ NCs produced at 120 °C is greater than the lattice strain OLA–S–based colloidal AgBiS$_2$ NCs prepared at 100 °C, with larger lattice strain leading to more defects in the NCs. These results show that the defect density OLA–S–based colloidal AgBiS$_2$ NCs prepared at 100 °C was lower than that of OLA–S–based NCs produced at 120 °C, meaning that 100 °C can be used to synthesize high quality colloidal AgBiS$_2$ NC.

![Figure 4.](image-url) (a) XRD patterns of OLA–S–based colloidal AgBiS$_2$ NCs synthesized at 80 °C, 100 °C, and 120 °C; (b–d) EDS elemental mapping (TEM) images of OLA–S–based colloidal AgBiS$_2$ NCs prepared at 120 °C.
TEM measurement was used to reveal the influence of reaction temperature on the morphology and size distribution of OLA–S–based colloidal AgBiS$_2$ NCs. Figure S5 shows that the colloidal AgBiS$_2$ NCs prepared at 120 °C have a uniform spherical shape and that the average diameter of the obtained NCs is 12.1 ± 3.5 nm (Figure S5a). An HR–TEM image of colloidal AgBiS$_2$ NCs prepared at 120 °C is shown in Figure S5b. The cubic rock salt structure of AgBiS$_2$ with a lattice spacing of about 0.32 nm corresponding to the (111) crystal plane spacing can be seen, and is consistent with the XRD results. Figure 4b–d provides elemental diagram images of OLA–S–based colloidal AgBiS$_2$ NCs synthesized at 120 °C. The atomic percentages of Ag, Bi, and S are 48.4, 17.1, and 34.6, respectively. These results show that the surface of the obtained colloidal AgBiS$_2$ NCs should be silver–rich and sulfur–rich. Because the lattice strain of the OLA–S–based colloidal AgBiS$_2$ NCs prepared at 120 °C is larger than that prepared at 100 °C, high reaction temperature may be detrimental to the preparation of high quality OLA–S–based colloidal AgBiS$_2$ NCs.

Figure S6a shows the UV–vis–NIR absorption spectra of OLA–S–based colloidal AgBiS$_2$ NCs prepared at 100 °C and 120 °C. The absorption spectrum of the sample synthesized at 120 °C extends to more IR regions than that of the NCs prepared at 100 °C, which is mainly caused by the size effect of the colloidal AgBiS$_2$ NCs. To further reveal the effect of reaction injection temperature on the quality of the obtained colloidal AgBiS$_2$ NCs, the PL spectra of OLA–S–based colloidal AgBiS$_2$ NCs prepared at 100 °C and 120 °C were measured using 330 nm excitation wavelength at room temperature. The PL intensity of OLA–S–based colloidal AgBiS$_2$ NCs synthesized at 120 °C is stronger than that of NCs synthesized at 120 °C (Figure S6b). This reflects that the OLA–S–based colloidal AgBiS$_2$ NCs prepared at 100 °C has fewer defects than the colloidal AgBiS$_2$ NCs synthesized at 120 °C.

In addition, the influence of OLA–S dosage in the reaction when synthesizing colloidal AgBiS$_2$ NCs was investigated. We carried out the synthesis of colloidal AgBiS$_2$ NCs using different amount of OLA–S (1 M). The crystallinity and phase purity of OLA–S–based colloidal AgBiS$_2$ NCs synthesized under different conditions were examined by XRD. (Figure 5). It can be seen that only Ag$_2$S was produced in the reaction when using 1 mL OLA–S, while both Ag$_2$S and AgBiS$_2$ were formed when the dosage of OLA–S was increased to 2 mL. Thus, pure phase colloidal AgBiS$_2$ NCs can be successfully prepared using 3 mL and 4 mL OLA–S. Based on these results, we speculate that the reaction process of OLA–S–based colloidal AgBiS$_2$ NC synthesis should be that: H$_2$S being released in situ from OLA–S after OLA–S was injected into high temperature cationic solution [59], and then reacting with Ag$^+$ to form Ag$_2$S, subsequently, the produced Ag$_2$S reacts with Bi$^{3+}$ to form AgBiS$_2$ NCs. The reaction equations are as follows:

\[
2\text{Ag}^+ + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} + 2\text{H}^+ \tag{1}
\]

\[
2\text{Ag}_2\text{S} + 3\text{Bi}^{3+} \rightarrow \text{AgBiS}_2 + 3\text{Ag}^+ \tag{2}
\]

The lattice strain values calculated for the colloidal AgBiS$_2$ NCs prepared by using 3 mL and 4 mL OLA–S are 0.27 and 0.40, respectively, as shown in Figure S7 and Table S3. The smaller lattice strain in colloidal AgBiS$_2$ NCs prepared using 3 mL OLA–S indicates a lower defect density in the NCs. To clarify the effect of the dosage of OLA–S on the morphology and size distribution of colloidal AgBiS$_2$ NCs, we carried out HR–TEM measurements of the obtained AgBiS$_2$ NCs. Figure S8a shows that colloidal AgBiS$_2$ NCs prepared using 4 mL OLA–S have a uniform spherical shape and the average diameters of NCs are about 8.3 ± 2.7 nm, which is a little larger than that based on 3 mL OLA–S (7.8 ± 1.9 nm; see Figure S2b). Figure S6c shows the UV–vis–NIR absorption spectra of 3 mL and 4 mL OLA–S–based colloidal AgBiS$_2$ NCs. The absorption spectrum of the 4 mL OLA–S–based colloidal AgBiS$_2$ NCs extends to more IR regions than that of the 3 mL OLA–S–based colloidal AgBiS$_2$ NCs, which is mainly caused by the size effect of the colloidal AgBiS$_2$ NCs.
Finally, we calculated the cost and yield of the synthesis of colloidal AgBiS$_2$ NCs using TMS and OLA–S as sulfur sources. Compared with TMS, the cost of synthesis using OLA–S was reduced about 57% (see Table S4 for details). We found that the yield of colloidal AgBiS$_2$ NCs based on TMS and OLA–S were 86.9% and 90.5%, respectively. This indicates that OLA–S can replace TMS for synthesizing colloidal AgBiS$_2$ NCs as a low–cost sulfur source.

4. Conclusions

In summary, we optimized the synthesis conditions of colloidal AgBiS$_2$ NCs using OLA–S as the sulfur source. Colloidal AgBiS$_2$ NCs with high quality and pure phase can be synthesized by rationally optimizing the dosage and reaction injection temperature of OLA–S. Compared with TMS as the sulfur source, OLA–S–based colloidal AgBiS$_2$ NCs have lower defect density and a wider absorption spectrum. More importantly, the cost of synthesis is greatly reduced, as the yield of colloidal AgBiS$_2$ NCs is increased when using OLA–S to replace the more expensive TMS. In addition, the pungent odor and air sensitivity of TMS can be avoided. As a low–cost sulfur source, OLA–S has the potential to for use in synthesizing other sulfide NCs in the future.

Supplementary Materials: The supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12213742/s1. Figure S1. The William–Hall plots for (a) TMS–based and (b) OLA–S–based colloidal AgBiS$_2$ NCs. Figure S2. TEM images of (a) TMS–based and (b) OLA–S–based colloidal AgBiS$_2$ NCs. Insets are the statistical histograms of the NCs size distribution. SAED images of (c) TMS–based and (d) OLA–S–based colloidal AgBiS$_2$ NCs. Figure S3. EDS–Mapping images of (a), (b) and (c)TMS–based. EDS–Mapping images of (d), (e) and (f) OLA–S–based colloidal AgBiS$_2$ NCs. Figure S4. The William–Hall plots for (a) and (b) OLA–S–based colloidal AgBiS$_2$ NCs prepare at 100 °C and 120 °C. Figure S5. TEM images of (a) OLA–S–based colloidal AgBiS$_2$ NCs prepare at 120 °C. Insets are the statistical histograms of the NCs size distribution. (b) HR–TEM images of OLA–S–based colloidal AgBiS$_2$ NCs prepare at 120 °C. (c) SAED image of OLA–S–based colloidal AgBiS$_2$ NCs prepare at 120 °C. Figure S6. (a) UV–vis–NIR absorption spectra of the colloidal AgBiS$_2$ NCs in hexane. (b) PL spectrum and fitting curves of the colloidal AgBiS$_2$ NCs. Figure S7. The William–Hall plots for (a) 3 mL and (b) 4 mL OLA–S–based colloidal AgBiS$_2$ NCs. Figure S8. TEM images of (a) 4 mL OLA–S–based colloidal AgBiS$_2$ NCs. Insets are the statistical histograms of the NCs size distribution. (b) HR–TEM images of 4 mL OLA–S–based colloidal AgBiS$_2$ NCs. (c) SAED image of 4 mL OLA–S–based colloidal AgBiS$_2$ NCs. Table S1. Half–peak widths and lattice strains of OLA–S–based and TMS–based colloidal AgBiS$_2$ NCs. Table S2. Half–peak widths and lattice strains of OLA–S–based colloidal AgBiS$_2$ NCs prepare at 100 °C and 120 °C. Table S3. Half–peak widths and lattice strains of 3 mL and 4 mL OLA–S–based colloidal AgBiS$_2$ NCs.
AgBiS₂ NCs. Table S4. Raw material usage, price and yield of AgBiS₂ NCs based on TMS and OLA–S. Reference [60] is cited in the Supplementary Materials.

**Author Contributions:** Q.L. and Y.Z. conceived and designed the experiments; Q.L., X.Z., X.S. and S.D. performed the experiments; Q.L., X.Z. and Y.Z. analyzed the data; H.F., G.W. and Y.Z. contributed reagents/materials/analysis tools; Q.L. wrote the paper; Y.Z. and G.W. corrected the paper. All authors have read and agreed to the published version of the manuscript.

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