

Synthesis of High-Quality AgSbSe₂ and AgBiSe₂ Nanocrystals with Antimony and Bismuth Silylamide Reagents

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KEYWORDS. Dimetal chalcogenide, quantum dot, nanocrystal, thermoelectric

ABSTRACT: Silver dimetal chalcogenides (Ag-V-VI₂) are ternary semiconductors that have potential alternative energy applications due to their optimal band gaps and large extinction coefficients. The synthesis of these materials is challenging due to the lack of effective pnictide precursors. We report the use of tris[N,N-bis-(trimethylsilyl)amido]antimony (Sb[N(SiMe₃)₂]₃) and tris[N,N-bis-(trimethylsilyl)amido]bismuth (Bi[N(SiMe₃)₂]₃) to synthesize nanocrystalline AgSbSe₂ and AgBiSe₂ quantum dots. The use of these reagents results in the creation of high quality nanomaterials with good crystallinity and narrow size distributions. Furthermore, electrical measurements on monolithic pellets of processed AgSbSe₂ and AgBiSe₂ nanomaterials demonstrate linear current-voltage behavior at room temperature, which indicates potential for use in electrical applications.

INTRODUCTION

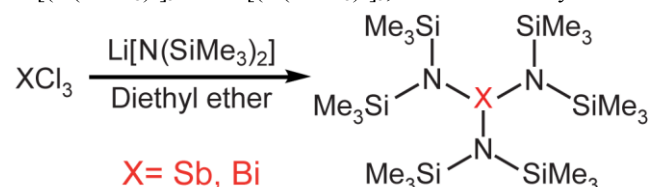
The development of advanced semiconductor materials is important to address the problems associated with the non-sustainable consumption of environmental resources due to worldwide overpopulation. In this regard, semiconductors can be used to create solar panels and catalysts for alternative energy generation, as well as efficient lighting systems and “smart windows” for energy conservation.^{1,2} Furthermore, semiconductor thermoelectric materials can generate power from the excess heat that is the byproduct of processes such as fossil fuel combustion.³ Many of these examples were not realized with bulk materials that have well-defined physical properties. Such limitations engender only a certain level of efficacy for use in applications. It is necessary to build advanced materials on the nanoscale to overcome this deficit, due to the ability to tune electronic properties with size.⁴ Bottom-up chemical syntheses have been used to create colloidal semiconductor nanocrystals (NCs, also known as quantum dots) that have size dependent properties engendered through quantum confinement.^{4,5} Research on quantum dots have overwhelmingly centered on II-VI (i.e. CdE, E=S, Se, Te) NCs, while other material systems such as pnictides (group V) have not been examined as extensively. This is due to the fact that the syntheses of pnictide nanomaterials are intricate and dangerous and there are few low-cost commercially available non-pyrophoric precursors.⁶⁻⁹

Among pnictides, environmentally benign I-V-VI₂ semiconductor nanocrystals are an emerging class of materials due to their NIR band gaps, large absorption coefficients, and excellent electronic properties.^{10,11} Dimetal chalcogenides have utility for photovoltaic and thermoelectric applications, making them promising alternatives for thermoelectric PbTe.^{12,13} There are several examples of the synthesis of copper-based I-V-VI₂ quantum dots, whereas silver-based nanomaterials such as Ag-BiS₂, AgSbS₂, AgSbSe₂, and AgBiSe₂ are less common.¹⁴⁻¹⁶ The majority of reports on their syntheses used high temperature (~1000 K) solid state reactions that required long annealing times. Furthermore, the products were reported to have poor

crystallinity and significant polydispersity. Colloidal preparation of AgSbSe₂ has been reported to yield significantly more monodisperse materials.¹⁷

Our group recently demonstrated the use of an efficient, versatile, and most importantly non-pyrophoric arsenic precursor, AsCl[(N(SiMe₃)₂)]₂,^{18,19} to synthesize a variety of semiconductor quantum dots and rods.⁹ Herein we report the utility of additional silylamide-ligated pnictides, specifically tris[N,N-bis(trimethylsilyl)amido]antimony (Sb[(N(SiMe₃)₂)]₃) and tris[N,N-bis(trimethylsilyl)amido]bismuth (Bi[(N(SiMe₃)₂)]₃),^{8,20,21} to synthesize silver dimetal chalcogenide quantum confined nanocrystals. These reagents were prepared via a simple one step metathesis reaction between the pnictide halide (SbCl₃/BiCl₃) and Li[N(SiMe₃)₂]₃ as summarized in Scheme 1; further details and characterizations are in the supporting information. Both compounds are stable and relatively easy to handle due to the fact that they are solid-state reagents. Furthermore, they are soluble in a variety of organic solvents. As a result, they have been successfully applied to the syntheses of monodisperse, crystalline AgSbSe₂ and AgBiSe₂ nanoparticles using high-temperature colloidal methods. Specifically, AgSbSe₂ nanoparticles were generated via hot injection method, while the optimal strategy for synthesizing AgBiSe₂ NCs used a ‘heat-up’ procedure.

The most interesting discovery concerns the fact that no reducing agents were required to activate either Sb[(N(SiMe₃)₂)]₃ nor Bi[(N(SiMe₃)₂)]₃, as was necessary for the



Scheme 1. Synthesis of tris[N,N-bis(trimethylsilyl)amido]antimony, Sb[(N(SiMe₃)₂)]₃ and tris[N,N-bis(trimethylsilyl)amido]bismuth, Bi[(N(SiMe₃)₂)]₃.

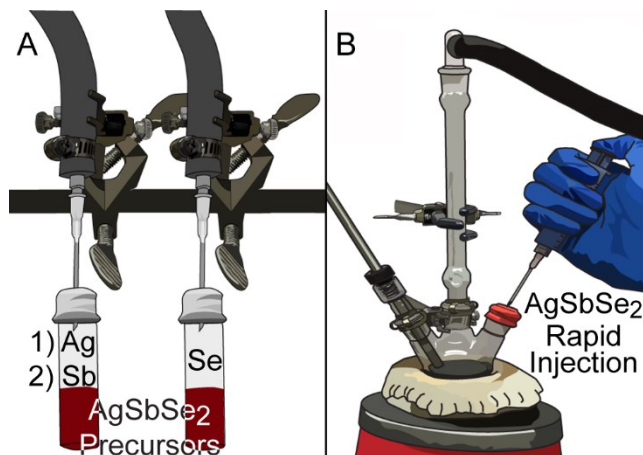
synthesis of arsenide and antimonide nanomaterials in our earlier study and by Liu et al.⁸ In fact, inclusion of a reducing agent resulted in a bivariate distribution of nanoparticle sizes as discussed in the supporting information, see Figure S11. This is likely due to separate nucleation events, where some materials were generated by the reducing agent while others resulted via heat activation. The results of each individual system have been reported in ‘Results and Discussion section’ followed by electrical measurement data on monolithic pellets of the materials.

EXPERIMENTAL

Materials: Bismuth chloride (BiCl_3 , 99.9%) and selenium shot (99.5%) were purchased from Strem Chemicals. Hexane (anhydrous, 95%) and antimony chloride (SbCl_3 , 99%) were purchased from Alfa Aesar. Oleic acid (OA, 90%), oleylamine (OLA, 98%), lithium bis(trimethylsilyl)amide ($\text{Li}[\text{N}(\text{Si}(\text{Me})_3)_2]$, 97%), 1-dodecanethiol (DDT, 98%), ethanol (>99.5%), silver(I) chloride (AgCl , 99.995%) and sodamide (NaNH_2 , 95%) were obtained from Sigma-Aldrich. Diethyl ether (purchased from VWR) was sparged with argon and dried using a Glass Contour Solvent System from Pure Process Technology, LLC. Antimony chloride, bismuth chloride, lithium bis(trimethylsilyl)amide were stored and handled in an inert atmosphere glove box. Oleic acid was recrystallized according to the procedures in ref. 22, while other chemicals were used without further purification.

Synthesis of $\text{Sb}[\text{N}(\text{SiMe}_3)_2]_3$: The procedure developed by Liu et al.⁸ was used to synthesize tris[N , N -bis(trimethylsilyl)amido]antimony. The preparation is based on a metathesis reaction between antimony chloride and lithium bis(trimethylsilyl)amide. First, 760 mg SbCl_3 (3.33 mmol) was dissolved in a mixture of dry ether (15 mL) and THF (3 mL), and was slowly added dropwise to a stirring solution of 1.7 g lithium bis(trimethylsilyl)amide (10 mmol) in ether (10 mL) at 0 °C under an inert N_2 atmosphere. The solution became white in color and turbid during the addition, and was kept stirring at 0 °C for an additional hour. The resulting white solution was warmed to room temperature and kept overnight. Afterwards, the solution was filtered using a glass fritted funnel and the solvents were removed under reduced pressure, resulting in a pale yellow colored $\text{Sb}[\text{N}(\text{SiMe}_3)_2]_3$ product. The product was recrystallized from a saturated hexane solution, resulting in the white solid product $\text{Sb}[\text{N}(\text{SiMe}_3)_2]_3$, yield ~ 80%. The purity of the product was determined via NMR; ^1H NMR (25 °C, CDCl_3 , 400MHz) 0.29 (s); see the spectrum in Figure S1. The reagent was stored in a -80 °C freezer in a sealed vial.

Synthesis of $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$: The procedure developed by Carmalt et al.²⁰ was used to synthesize tris[bis(trimethylsilyl)amido]bismuth. The preparation is based on a metathesis reaction between bismuth chloride and lithium bis(trimethylsilyl)amide. First, 1.0 g BiCl_3 (3.17 mmol) was added into a round bottom flask under a dry nitrogen atmosphere. Next, 20 mL of dry ether and 5 mL THF were added to the flask, which was maintained the temperature at 0°C. Next, 1.6 g lithium bis(trimethylsilyl)amide (9.51 mmol) dissolved in 15 mL of dry ether was added dropwise into the BiCl_3 solution. The resulting mixture became yellow in color and turbid. It was kept stirring at 0 °C for another hour and then slowly warmed to room temperature. Afterwards, the solution was filtered through a glass fritted funnel under an inert N_2 atmosphere and the solvents were removed under reduced pressure. Finally, the product was recrystallized from a saturated toluene solution, resulting in a yellow solid $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ product, yield ~ 90%. The purity of the



Scheme 2. (a) Synthesis of AgSbSe_2 NCs begins with degassing the Ag and Sb reagents separately followed by (b) sequential rapid injection of Sb and Ag precursors. Note that AgBiSe_2 NCs are prepared by heating up the solvent and precursors in a single reaction vessel.

product was determined via NMR; ^1H NMR (25 °C, CDCl_3 , 400MHz) 0.36 (s); see the spectrum in Figure S1. The reagent was stored in glove box covered with aluminum foil.

Synthesis of AgSbSe_2 nanoparticles: 10 mL of oleylamine was added into a three-neck round-bottom flask and degassed under vacuum at 110 °C for 2 hours. In a 7 mL septa-covered vial labeled “A”, 5 mL of oleylamine and 1 mL of oleic acid were added and were subsequently degassed under vacuum. Next, 85 mg (0.5 mmol) of AgNO_3 was added to this vial, which was kept stirring at 80 °C under an N_2 atmosphere until the solid dissolved completely. Next, the vial was cooled to 40 °C, and 300 mg (0.5 mmol) of $\text{Sb}[\text{N}(\text{SiMe}_3)_2]_3$ dissolved in 0.5 mL toluene was added while maintaining the nitrogen atmosphere. In a separate vial labeled “B”, 98 mg of selenium (1.25 mmol) was dissolved in a mixture of 0.5 mL oleylamine and 0.5 mL dodecanethiol. Afterward, the oleylamine in the three neck round bottomed flask was heated to 180°C. The solution in vial “A” was injected into the flask at 180 °C followed by an injection of the solution in vial “B”. This resulted in the formation of a dark brown coloration. The solution was maintained at 180 °C for 2-3 mins. Afterwards, the heating mantle was removed and the solution was allowed to cool to room temperature. The sample was stored under an inert N_2 atmosphere in a glovebox.

Synthesis of AgSbSe_2 nanoparticles in presence of a reducing agent: 10 mL of oleylamine and 85 mg (0.5 mmol) of AgNO_3 were added into a three-neck round bottom flask and degassed at 110 °C for 2 hours. At the same time, 300 mg (0.5 mmol) of $\text{Sb}[\text{N}(\text{SiMe}_3)_2]_3$ was dissolved in 0.5 mL toluene and 98 mg of selenium (1.25 mmol) was dissolved in a mixture of 0.5 mL oleylamine and 0.5 mL dodecanethiol. The oleylamine in three-neck round bottom flask was cooled to 30°C and 0.9 mL of 1 M lithium triethylborohydride (0.9 mmol) and $\text{Sb}[\text{N}(\text{SiMe}_3)_2]_3$ solution in toluene was injected into the flask at 30 °C followed by an addition of the solution of selenium precursor. This resulted in the formation of a black colored suspension, which was then slowly heated to 180°C and maintained at 180 °C for another 10 mins. Afterwards, the heating mantle was removed and the solution was quickly allowed to cool to room temperature. The sample was stored under an inert atmosphere in a glovebox. A similar procedure was employed to synthesize AgBiSe_2 NCs, however the poor size distribution

of AgSbSe₂ nanoparticles obtained using this procedure caused us to abandon the use of reducing agents.

Synthesis of AgBiSe₂ nanoparticles: 10 mL of oleylamine and 85 mg (0.5 mmol) of AgNO₃ were added into a three-neck round bottom flask and degassed at 110 °C for 2 hours. At the same time, 345 mg (0.5 mmol) of Bi[(N(SiMe₃)₂)₃] was dissolved in 0.5 mL toluene and 98 mg of selenium (1.24 mmol) was dissolved in a mixture of 0.5 mL oleylamine and 0.5 mL dodecanethiol. Afterward, the oleylamine in three-neck round bottomed flask was cooled to 30 °C and the Bi[(N(SiMe₃)₂)₃] solution was injected into the flask at 30 °C followed by the selenium precursor solution. This resulted in the formation of a black colored suspension. The solution was slowly heated to 200 °C and maintained at 200 °C for an additional 10 mins. Afterwards, the heating mantle was removed and the solution was allowed to cool to room temperature. The sample was stored under an inert N₂ atmosphere in a glovebox.

Surface ligand treatment and pellet formation: The following procedure was applied to both AgSbSe₂ and AgBiSe₂ samples in an identical manner. First, 800 mg of a sample was precipitated with an ethanol / isopropanol mixture and centrifuged. Next, the material was dispersed into 10 mL chloroform to which 10 mL of 0.01 M sodamide (NaNH₂) solution in ethanol was subsequently added. Afterwards, the sample was repeatedly washed with isopropanol and chloroform. Finally, a fine powder of nanocrystals was obtained after drying under vacuum. After ligand treatment, 500 mg of each fine powder were pressed into form a pellet under an applied pressure of 7.4 metric tons (~ 16000 lbs.). This procedure is outlined in Figure S6 of the supporting information.

Characterization: For characterization, a small quantity of each sample was precipitated with ethanol and centrifuged to remove impurities. The precipitate was then redispersed in dry hexane and characterized by optical, X-ray photoelectron (XPS), and X-ray diffraction (XRD) spectroscopies. Absorption measurements were performed with a Perkin Elmer LAMBDA 1050 UV/Vis-NIR spectrophotometer. XPS analyses were performed on a Kratos Axis 165 using a monochromatic Al K α source operating at 12 kV and 10 mA to produce an X-ray power of 120 W. Spectra were collected with a photoelectron takeoff angle of 90° from the sample surface plane, in energy steps of 0.1 eV, and a pass energy of 20 eV for all elements. All spectra were referenced to the C1s binding energy (284.8 eV). X-ray diffraction studies were performed on a D8 Advance ECO Bruker XRD diffractometer using monochromatized Cu K α (λ = 1.54056 Å) radiation. Transmission electron microscopy (TEM) measurements were performed using a JEOL JEM-3010 operating at 300 keV. A 300 mesh gold grid was used for TEM analysis. ¹H NMR spectra were recorded using Bruker Avance DRX 400 NMR spectrometer.

Electrical Measurement: Electrical measurement [current-voltage (I-V) characteristics] of the AgSbSe₂ and AgBiSe₂ quantum dot pellets were measured using a Keithley 2400 source meter at room temperature. Copper wires were soldered using indium on various locations of AgSbSe₂ and AgBiSe₂ quantum dot pellets as electrode contacts for I-V measurements.

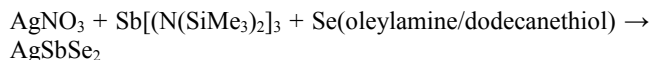
Quantum Chemical Modeling: All species were modeled with Density Functional Theory, specifically B3LYP,^{23, 24} using the Gaussian '09 package.²⁵ The LANL2DZ basis set corresponding effective core potentials were employed.²⁶ The antimony substrate Sb[(N(SiMe₃)₂)₃] was modeled using Sb[(N(SiH₃)₂)₃], while a silver-oleic acid was modeled using

neutral Ag-O₂C₂H₃. All geometry optimizations, including saddle points, were characterized with frequency analyses. Saddle points were examined using intrinsic reaction coordinate analysis. Zero point vibrational corrections were added to the energies. GaussView was used to visualize the results.²⁷

RESULTS AND DISCUSSION

Silver antimony selenide (AgSbSe₂): AgSbSe₂ is a narrow indirect bandgap (0.58 eV) semiconductor with intrinsic p-type conductivity. It is a promising candidate for thermoelectric applications due to its high Seebeck coefficient, low thermal conductivity, and good stability.²⁸⁻³¹ Furthermore, it is considered to be an excellent photovoltaic material due to its strong absorption.³⁰⁻³²

The synthesis of AgSbSe₂ NCs was studied via the hot injection method according to the following:



To this end, two separate solutions of precursors were co-injected into oleylamine at 180 °C as represented in Scheme 2. One contained the antimony and AgNO₃ reagents dissolved in an oleylamine and oleic acid mixture. This was done to enhance the crystallinity of the AgSbSe₂ nanoparticle products under the rational that oleic acid stabilizes the hard Sb (+3) ions while oleylamine stabilizes the soft Ag (+1) ions. The sequence of addition of precursors during the preparation of the antimony and silver injection solution is important as the product does not have pure crystallinity if the protocol is not followed exactly. The second solution that was co-injected contained selenium dissolved in oleylamine.

A variety of characterization results are shown in Figure 1, all of which demonstrate the synthesis of ~9 nm crystalline nanoparticles of AgSbSe₂. XPS results shown in Figure S2 confirm the stoichiometry of the products. The crystal phase of the nanoparticles is consistent with characteristic pattern of the cubic phase of AgSbSe₂. The absorption spectrum in Figure S3 is featureless; however, the absorption onset (~1300 nm) is greater than the bulk bandgap. This is potentially due to quantum confinement, which affords the possibility for manipulation of the properties of artificial solids that incorporate these materials. There are important differences to note between the results of this study and previous demonstrations of AgSbSe₂ material synthesis. For example, the preparation of nanocrystalline silver antimony dichalcogenide using solid state conditions results in polydisperse samples.³² As such, colloidal methods are preferred, and indeed Lin et al. first demonstrated homogeneous 7-17 nm AgSbSe₂ NCs via the rapid injection procedure using SbCl₃ as the pnictide source.¹⁷ The use of Sb[(N(SiMe₃)₂)₃] as presented in this report created a similar small size of NCs; however, our protocol requires ~1/10th the quantity of precursors. Furthermore, the use of SbCl₃ results in an initial bimodal size distribution that grew into a monodisperse population over 30 min.¹⁷ In contrast, we observed a reasonably monodisperse AgSbSe₂ NC population within 3 minutes of injection, which indicates fast homogeneous nucleation and growth.

These observations lead us to conclude that Sb[(N(SiMe₃)₂)₃] has enhanced reactivity compared to SbCl₃. To study this further, the potential energy surfaces of a silver-acid complex with the corresponding pnictide precursors were calculated using DFT as shown in Figures S4 and S5. A ligand exchange reaction to form an antimony-organic acid intermediate was studied as a potential first step. It was found that SbCl₃

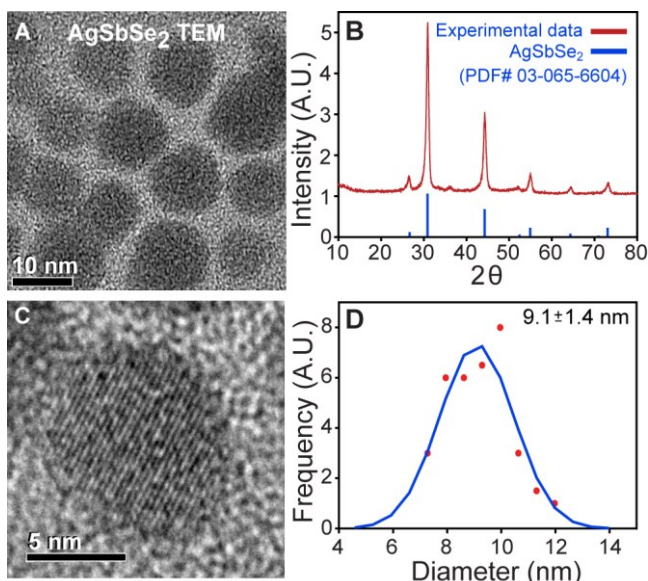
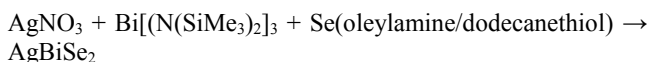


Figure 1. (a) TEM image of AgSbSe₂ nanoparticles. (b) X-ray diffraction pattern of AgSbSe₂ NCs confirm their structure and crystallinity. (c) High resolution TEM image of crystalline AgSbSe₂ showing lattice fringes. (d) Size distribution of AgSbSe₂ dots.

forms a tightly-bound complex with the silver-acetic acid precursor, which results in a significantly uphill reaction barrier for subsequent ligand exchange. However, the same interaction with Sb[(N(SiH₃)₂)₃] (a model compound for antimony silylamide) is much weaker and the overall reaction is less endothermic. These results are consistent with the experimental findings, and lead us to conclude that the effect of the pnictide ligand is significant. In this case, the ability of antimony to participate in chemical transformations that result in the formation of AgSbSe₂ NCs is enhanced by the bulky -N(TMS) ligands that prevent the formation of intermediate trap states with silver.

Silver bismuth selenide (AgBiSe₂): AgBiSe₂ is another interesting member of the I-V-VI₂ semiconductor family that has excellent thermoelectric properties.³³ At room temperature, it is p-type with a hexagonal phase, and can undergo a structural transition to cubic via a rhombohedral intermediate phase.³⁴ Both the hexagonal and rhombohedral materials are narrow band gap (~ 0.6 eV) semiconductors, while the high temperature cubic phase behaves like a metal with a high electrical conductivity yet a low thermal conductivity.^{14, 34} At present, there is only one other example of the colloidal synthesis of silver bismuth selenide.³³ This rapid injection process required long annealing times that yielded anisotropic nanoparticles, while our heat-up protocol using Bi[N(SiMe₃)₂]₃ generated more homogeneous and spherical nanocrystals within ~10 min according to the following:



We have synthesized AgBiSe₂ NCs at 200°C using Bi[(N(SiMe₃)₂)₃], AgNO₃, and selenium in an oleylamine solution. In contrast to the antimonide system, the rapid injection of precursors resulted in materials with broad and unidentifiable XRD patterns. This prompted the use of a heat-up procedure, which produces significantly cleaner results as shown in Figure 2. The results are consistent with the synthesis of small, ~6 nm diameter crystalline dots, albeit the materials are less monodisperse compared to AgSbSe₂ NCs. The crystal phase of the

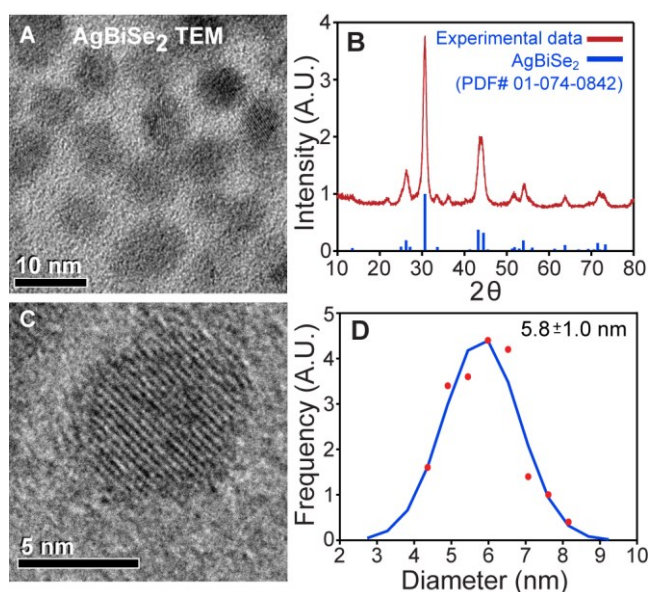


Figure 2. (a) TEM image of AgBiSe₂ nanoparticles. (b) X-ray diffraction pattern of AgBiSe₂ nanoparticles. (c) High resolution TEM image of crystalline AgBiSe₂ showing lattice fringes. (d) Size distribution of AgBiSe₂ dots.

nanoparticles was confirmed by powder XRD and is consistent with characteristic pattern of the complex hexagonal phase of AgBiSe₂. XPS result also confirms the composition of AgBiSe₂ nanoparticles although there exists a slight excess of selenium; see Figure S2 of the supporting information. As was observed in the antimonide materials, the absorption spectrum shown in Figure S3 is featureless and has a higher energy onset (~ 1200 nm) compared to the bandgap, which is indicative of quantum confinement effects.

Electrical measurement: Room temperature I-V behavior was measured to characterize the electrical conductivity of silver dimetal chalcogenide artificial solids. The materials were precipitated and processed by washing with a sodamide solution. FTIR spectroscopy confirm the removal of the original ligands shown in Figure S7. The resulting AgSbSe₂ and AgBiSe₂ nanoparticle powders were transformed into 13 mm × 0.9 mm thick pellets in a press. Copper wires were soldered to the surface using indium as electrode contacts as seen in the inset of Figure 3. Also shown are the room temperature two-terminal current-voltage (I-V) plots of the AgSbSe₂ and AgBiSe₂ quantum dot monoliths. All the I-V measurements demonstrate linear resistive behavior, indicating Ohmic contact nature of the soldered electrodes. Three contact points were used to verify the proper resistance vs. electrode distance behavior as well as confirm good uniformity of the nanomaterials throughout the pellet, see Figure S8. Overall, the conductivity is significantly smaller than bulk materials; furthermore, the bismuth NCs are much lower than the antimony materials despite their similar bulk transport properties.¹⁴ This is likely due to both the smaller size and higher polydispersity of the AgBiSe₂ sample, as these factors increase the resistance in solid monoliths of semiconductor nanocrystals.³⁵ The conductivity of the AgSbSe₂ NCs using the method of Lin et al. was reported to be significantly higher than observed here,¹⁷ which may be due to the fact that we did not attempt to thermally anneal the NC pellets.

In conclusion, we have successfully developed a synthetic route to create AgSbSe₂ as well as AgBiSe₂ nanocrystals using silylamido-based antimony and bismuth precursors. The reaction did not require a reducing agent to activate the pnictide-N

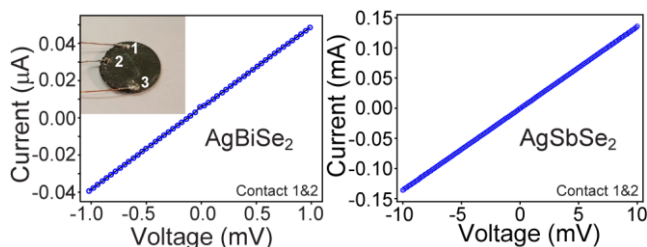


Figure 3. I-V measurement of AgBiSe₂ and AgSbSe₂ monolithic NC pellets (inset). Additional data are presented in the supporting information, see Figure S8.

bond, which is uncommon and results in the synthesis of better materials with enhanced monodispersity and crystallinity. The I-V curves from NC monoliths is indicative of linear resistive behavior which demonstrates their potential for use in electrical devices. These results reveal several paradigms concerning pnictide chemistry as it applies to the synthesis of nanomaterials.

ASSOCIATED CONTENT

Supporting Information. Additional characterization, including TEM micrographs, and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

The University of Illinois at Chicago.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We would like to thank Jordi Cabana for assistance with XRD measurements, Mike Plews for assistance with the pellet press, and the Keck Biophysical facilities at Northwestern University for access to UV/Vis/NIR instrumentation. This work was supported by startup funding to PTS from the University of Illinois at Chicago.

ABBREVIATIONS

NIR, near-Infrared; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy.

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AgSbSe₂ and AgBiSe₂ have potential applications for alternative energy generation. We demonstrated the colloidal syntheses of dimetal chalcogenide nanomaterials with good crystallinity and size distributions. Current-voltage measurements reveal Ohmic contact behavior, which indicates efficacy in electronic devices.

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