Pressure induced photoluminescence modulation in a wide range and synthesis of monodispersed ternary AgCuS nanocrystal based on Ag$_2$S nanocrystals†

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Binary Ag$_2$S nanocrystals (NCs) have many potential optical applications because of their low toxicity, narrow direct band gaps and near-infrared photoluminescence (PL) with high emission efficiency. However, due to its small exciton Bohr radius (2.2 nm), the PL spectra of Ag$_2$S NCs can only be modulated below ∼1200 nm with increasing particle size. Meanwhile, ternary silver copper chalcogenides (AgCuX, X = S, Se) have also attracted increased attention in recent years. Temperature-dependent structural phase transformation leads electrical transport to exhibit fascinating transitions between p and n type conduction, which makes AgCuS and AgCuSe ideal materials for diode or transistor devices. Nevertheless, the traditional method to synthesize these materials is mainly through melting the mixture of Ag, Cu and S/Se powder under extremely high reaction temperatures (973–1373 K) and long reaction time, forming a bulk product. Therefore, the synthesis of high quality monodispersed and size-tunable AgCuS or AgCuSe NCs is still a challenge. To address these issues, in this paper, we report using Ag$_2$S NCs as a template, a method to synthesize monodispersed and size-tunable β-AgCuS NCs via ion exchange and diffusion processes. Similarly, monodispersed β-AgCuSe NCs were also synthesized by this simple and reproducible strategy. This synthetic method opens new avenues for investigating the size-, morphology- and temperature-dependent phase transitions of these ternary AgCuS and AgCuSe materials. Thus, the corresponding electrical transport between p and n type conduction can be studied in the future. Furthermore, we systematically investigated the pressure-dependent PL properties and band gap modulation of monodispersed Ag$_2$S NCs using in situ high pressure PL and absorption spectroscopy. We found that the PL peak of 6.0 nm for Ag$_2$S NCs could be easily adjusted from ∼1200 to 1900 nm with increasing pressure from 0 to 5.1 GPa, which greatly extends the wavelength range of the PL peak beyond that of other approaches.

Introduction

In the past decade, silver chalcogenide (Ag$_2$S, Ag$_2$Se, and Ag$_2$Te) colloid nanocrystals (NCs) have attracted more and more attention for many photonic and optical device applications, such as near-infrared (NIR) sensors, solar cells, vivo fluorescence imaging, thermoelectric materials, nonvolatile memory and so on.$^{1-15}$ All of these potential applications are based on their low toxicity, narrow direct band gaps (0.9, 0.15, and 0.67 eV, for Ag$_2$S, Ag$_2$Se, and Ag$_2$Te, respectively) and NIR photoluminescence (PL) with high emission efficiencies.$^{16-19}$ In order to apply these I–VI semiconductor NCs effectively, high quality monodispersed NCs with tunable particle sizes have been successfully synthesized by several approaches, e.g. aqueous phase and organic phase synthetic methods.$^{20-27}$ For example, Pang et al.$^8$ reported a tunable PL spectra from 690 to 1227 nm for Ag$_2$S NCs with increasing particle size from 1.5 to 4.6 nm. Considering numerous reports about the size-dependent PL spectra of Ag$_2$S NCs, an interesting phenomenon can be summarized. Regardless of the method for preparing the Ag$_2$S NCs, when the particle size of Ag$_2$S NCs is below ∼4.5 nm, the corresponding PL peak positions can be easily adjusted over a wide wavelength range (∼700 to 1200 nm).
However, once the particle size exceeds 4.5 nm, the corresponding PL peak positions are mainly concentrated in the vicinity of 1200 nm, and cannot be adjusted effectively; this loss of control is attributed to its small exciton Bohr radius (2.2 nm). More recently, Yu and co-workers found that the stable peak position in the PL line of Ag₂Se NCs at ultra low temperature is due to weak exciton phonon coupling. In other words, it is difficult to adjust the PL peak position of silver chalcogenides NCs by changing the temperature. Is there a method to break this PL range limit of Ag₂S NCs and thus be able to adjust their emission over a wider region?

In addition to above binary silver chalcogenides NCs, in the past five years, ternary silver copper chalcogenide (AgCuX, X = S, Se) nanomaterials have become important for thermoelectric and photovoltaic applications due to their high ZT value. Both AgCuS and AgCuSe are polymorphous semiconductors that exhibit noteworthy phase transitions as a function of temperature due to changes in their cationic mobility. Temperature-dependent structural phase transformation leads to a fascinating transition between p and n type conduction in their electrical transport, which makes AgCuS and AgCuSe ideal materials for diode or transistor devices. It is well known that the application of high pressure PL and absorption spectroscopy. It is well known that the application of high pressure can not only change the structure and morphology of many nano-materials, but it can also modulate their optical and electrical properties. Our experimental results indicate that the upper limit of the Ag₃S NCs PL peak can effectively be modulated from ~1200 to 1900 nm with increasing pressure, which is difficult to achieve by other approaches. Both the mechanism for forming ternary silver chalcogenide NCs and the pressure-dependent PL behavior of Ag₂S NCs is systematically discussed.

### Experimental section

#### Chemicals

AgNO₃ (99.8%), CuCl₂ (99.5%), thioacetamide (TAA, 98%), selenium powder (99.5%) and oleylamine (OLA, ≥70%) were all purchased from Sigma Aldrich. Methanol, acetone, and chloroform were obtained from commercial sources. All chemicals were used without further purification.

#### Synthesis of Ag₂S NCs with different size

In a typical synthesis, a mixture of TAA (0.4 mmol) and OLA (4.0 mL) was added to a 50 mL three-neck flask. This mixture was heated to 210 °C under nitrogen flow and kept at this temperature for several minutes until the solution turned clear. A solution containing 0.2 mmol of AgNO₃ and 2.0 mL of OLA was prepared in a glovebox and then quickly injected into the flask. The clear solution quickly turned black, indicating the formation of Ag₂S NCs. At different reaction intervals, aliquots were taken from the flask and naturally cooled down to room temperature. Methanol was added to each aliquot for the extracting step. The extracted aliquots were precipitated with chloroform and acetone several times and finally re-dispersed in chloroform.

#### Synthesis of AgCuS NCs

The templates of Ag₂S NCs were synthesized by the same process mentioned above. Typically, when the desired size of the Ag₂S NCs was synthesized at 210 °C for several minutes (e.g. 20 min), another solution containing 0.2 mmol of CuCl₂ and 2.0 mL of OLA was prepared in a glovebox and then quickly injected into the flask. After that, the mixture was heated to 250 °C and maintained at this temperature. At different reaction intervals, aliquots were taken from the flask. The same purification process discussed above was carried out before characterization.

#### Synthesis of AgCuSe NCs

Through using Se (0.4 mmol) instead of TAA, the sample of AgCuSe NCs could be synthesized by the same process mentioned above.

#### Characterization

The phase purity of the obtained samples was characterized by X-ray powder diffraction (XRD, Shimadzu XRD-6000 working with a Cu-Kα target). A JEM-2200FS transmission electron microscope operating at 200 kV was used to take transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images and energy-dispersive X-ray spectroscopy (EDX) measurements. NIR PL spectra were recorded using a spectrophotometer (Photon Technology International, Inc.) A semiconductor laser with a 405 nm excitation wavelength was used for all fluo-
rescence studies. Absorption spectra were recorded using an optical fiber spectrometer (Ocean Optics, QEPRO).

**In situ high-pressure optical experiments**

The high-pressure optical experiments were carried out using a symmetric diamond anvil cell (DAC) with type Ia ultra low-fluorescence diamonds. The diamonds culet size was 500 μm. A T301 stainless steel gasket was preindented by the diamonds and then drilled to produce a 200 μm diameter cavity for the sample. The prepared Ag₂S NCs colloidal solution was dropped into the gasket hole along with a small ruby ball (20 μm) in order to determine the pressure using the standard ruby fluorescent technique.⁴³

**Results and discussion**

**Synthesis of Ag₂S NCs with tunable size**

To study pressure-dependent PL behavior and prepare ternary AgCuS NCs, high quality monodispersed Ag₂S NCs were synthesized first. Here, we applied a traditional hot-injection method to prepare size-tunable monodispersed Ag₂S NCs. Fig. 1 shows several TEM images of Ag₂S NCs synthesized at different reaction intervals (Fig. 1a–c). It can be observed that the resulting size-tunable (4.5–10 nm) NCs exhibit narrow size distributions. The standard deviations (δ) were calculated to be ~5–10%. In addition, all these Ag₂S NCs exhibit well-ordered patterns. During the synthesis process, we allowed the crude NCs colloidal solution to naturally cool down to room temperature, which made the NCs spontaneously assemble into superlattices on the TEM grids without any other post synthetic procedures. This spontaneous assembly was attributed to solvent evaporation induced ligand–ligand van der Waals interactions and entropy driven forces, which have been verified in our previous work.⁴⁴,⁴⁵ In contrast, if Ag₂S NCs were synthesized in the reaction vessel and quickly quenched to room temperature, these NCs appeared monodisperse without any ordered arrangement (Fig. S1†). All of these experimental results reveal that our method to self-assemble NC superlattices is closely associated with the natural cooling process. Clear and continu-

![Fig. 1](image-url)
ous lattice fringes can be observed in HRTEM images (Fig. 1d–f), indicating good crystallinity for all samples. The distance between neighbouring fringes was measured to be 0.24 nm, close to the (121) lattice spacing of Ag$_2$S. Fig. 1g presents the XRD patterns collected for these samples, indicating that all of these NCs have a well-defined monoclinic crystal structure (JCPDS no. 14-0072). The size-dependent absorption and PL spectra of Ag$_2$S NCs are displayed in Fig. 1h. As the size increases from ~4.5 to 10 nm, the absorption spectra of Ag$_2$S NCs remain featureless with no marked excitonic absorption peaks; this result is greatly different than that for other metal chalcogenides (e.g. II–VI and IV–VI NCs) that usually show an evident discrete absorption feature. This absorption spectra phenomenon is mainly attributed to the special electronic properties of Ag$_2$S NCs. In contrast, as the Ag$_2$S NC size increases from 4.5 to 10 nm, the PL peak position can only be adjusted from 1195 to 1223 nm with a narrow adjusting range (Δ ≈ 28 nm), thus not exhibiting a size effect. Both the absorption and the PL properties of the as-synthesized Ag$_2$S NCs were consistent with previously reported results. In addition, all of these high-quality and size-tunable Ag$_2$S NCs were synthesized at 210 °C with different reaction times. Once the reaction temperature was higher than 250 °C (e.g. 280 °C, 10 min), the synthesized Ag$_2$S NCs always exhibited polydispersity in particle size and shape (Fig. S2†). This polydispersity, due to the rapid growth of Ag$_2$S NCs and the occurrence of Ostwald ripening at high temperature, is not good for our subsequent research.

Synthesis of size-tunable AgCuS NCs and mechanism

For the first challenge, to synthesize the desired size of Ag$_2$S NCs in the three-neck flask, CuCl$_2$–OLA solution was injected and kept for the reaction. At different reaction times, the product crystalline structures were monitored by XRD (Fig. 2). After injection, the original XRD pattern of Ag$_2$S NCs (monoclinic phase, JCPDS: 14-0072) began to change gradually. With increasing reaction time, some new diffraction peaks were observed that index to the orthorhombic AgCuS phase (JCPDS: 09-0499) and they become gradually stronger. The reaction time is found to be an important parameter to ensure a yield of pure-phase AgCuS NCs. When the reaction time is more than 30 min, all of the product diffraction peaks can be easily indexed to the pure orthorhombic AgCuS phase. Compared with bulk AgCuS material proposed in previous work, the XRD pattern matched well with those results, indicating that nano-sized AgCuS is readily synthesized using this facile method.

The size and shape of as-synthesized AgCuS NCs were examined by TEM and HRTEM imaging. Fig. 3a and b present TEM images at different magnifications of spherical and faceted AgCuS NCs synthesized at 250 °C for 1 h. These highly monodispersed NCs have an average diameter of ~27.0 nm, with a corresponding standard deviation (δ) calculated to be ~9%. Clear and continuous lattice fringes can be observed in the HRTEM image, indicating that these resulting NCs have a single crystalline structure (Fig. 3c). The distance between neighbouring fringes was measured to be 0.307 nm, close to the (021) lattice spacing of orthorhombic phase AgCuS. In addition, the fast Fourier transform (FFT) pattern collected from Fig. 3d further sheds light on the single crystalline feature. Elemental distribution maps indicate that the elements of Ag, Cu and S are homogeneously distributed throughout the whole sample, which suggests high purity of the final ternary products (Fig. 3e–h). In addition, the chemical composition of the obtained sample was examined by energy-dispersive X-ray (EDX) analysis. The stoichiometric ratio of Ag/Cu/S is about 1 : 1 : 1, with a slight S enrichment, which might be attributed to residual TAA.

Regarding the synthesis of AgCuS NCs, many experimental parameters (e.g., reaction time, reaction temperature, and concentration of precursor) have also been investigated. We found that desirable AgCuS NCs with narrow size distribution and uniform shape were synthesized at 250 °C. When the reaction temperature was below 250 °C (e.g. 210 °C, 1 h), pure AgCuS.

![Fig. 2](image_url) (a) Reaction time-dependent crystal structure evolution of Ag$_2$S and AgCuS monitored by XRD patterns. (b) The comparison of XRD patterns between monoclinic Ag$_2$S and orthorhombic AgCuS NCs. The inset in (b) shows a schematic illustration of the orthorhombic AgCuS.
NCs were difficult to obtain (Fig. S3†). This result indicates that the temperature-dependent thermodynamic parameter for forming AgCuS NCs is much higher than Ag₃S NCs. In contrast, once the reaction temperature was above 250 °C (e.g. 280 °C), pure AgCuS NCs could also be synthesized. However, these AgCuS NCs always exhibited polydispersity in particle size and shape (Fig. S4†). All of these results indicate that the best reaction temperature is concentrated in the vicinity of 250 °C with a long reaction time (e.g. >20 min). Meanwhile, when we adjusted the ratio of the precursor concentration (e.g. Ag : Cu : S = 1 : 2 : 4) and kept the other reaction parameters unchanged (250 °C 30 min), the obtained product also exhibited pure AgCuS NCs, and there was no other impurities (Fig. S5†). These results indicate that the obtained AgCuS NCs have a stable element ratio and are almost unaffected by the concentration of the precursors.

Meanwhile, by selecting different Ag₃S NC sizes for the original template, size-tunable monodispersed AgCuS NCs can be synthesized with a similar synthetic strategy. TEM images shown in Fig. 4 reveal that all of the prepared AgCuS NCs with different sizes were highly uniform in both size and shape. The average diameter of the prepared AgCuS NCs could be adjusted from about 15 to 27 nm. In addition, we found that these as-synthesized AgCuS NCs exhibit a slightly larger size than the original Ag₃S NC templates, which can be attributed to two reasonable aspects. The first reason is attributed to the synthesis method. As original templates, all of these Ag₃S NCs with different sizes were synthesized at 210 °C in the three-neck flask. After that, CuCl₂–OLA solution was injected and the reaction was maintained at 250 °C. Due to the increased reaction temperature (from 210 to 250 °C) and prolonged reaction time, both further growth of Ag₃S NCs and the formation of AgCuS NCs were carried out at the same time, which resulted in the final product of AgCuS exhibiting a larger size than the original Ag₃S NCs. This phenomenon is widely observed throughout all of the preparation processes. The second reason might be attributed to the Ostwald ripening processes after forming AgCuS NCs, which lead the synthesized AgCuS NCs to exhibit polydispersed particle size and shape (Fig. S4†).

During synthesis of many kinds of NCs, especially metal chalcogenide NCs (e.g. CdSe, MnSe, PbS), alkylamine acts as both a capping ligand and as a reducing agent. In our earlier work, using alkylamine, we introduced an efficient route to synthesize a series of metal chalcogenide NCs at very low temperatures, even as low as −20 °C. Ozin et al. confirmed that sulfur–amine solutions were widely used as a "black box" precursor in metal sulfide NCs synthesis, which could decrease reaction temperature effectively due to the presence of alkylammonium polysulfides. In this paper, the use of OLA not only provided a relatively low reaction temperature, but also served to reduce Cu ions during the synthesis of AgCuS NCs. In order to gain an insight into the formation mechanism of ternary AgCuS NCs, the growth process was traced with reaction time and monitored by HRTEM. Fig. 5 shows several HRTEM images of the temporal evolution of the structures after the injection of CuCl₂–OLA into the crude Ag₃S NCs colloidal solution. After injection, it can be found that the hybrid nanostructures appeared at 5 minutes (Fig. 5c–f). A typical HRTEM image of products (Fig. 5d and m) clearly indicates that the nanospheres have two or three lattice types. The interplanar distance of 0.28 nm corroborates the [112] lattice space of monoclinc Ag₃S. In contrast, the interplanar distances of 0.25 and 0.26 nm corroborate the (002) and (112)
lattice spaces of orthorhombic AgCuS, respectively, indicating that AgCuS nanostructure begins to form. With increasing reaction time, the AgCuS nanostructure gradually replaces Ag2S (Fig. 5g–j and n). When the reaction was maintained for more than 20 min, monodispersed and homogeneous spherical AgCuS NCs could be observed (Fig. 5k, l and o). These HRTEM results are in good agreement with corresponding XRD patterns shown in Fig. 2. An illustration of the growth process of AgCuS NCs is shown in Fig. 5p.

Including the HRTEM images above, EDX and element-distribution maps also confirm the transformation process from Ag2S to AgCuS NCs (Fig. S6f). Before injecting CuCl2–OLA solution, the synthesized Ag2S NCs only contain Ag and S. The stoichiometric ratio of Ag/S is 29.6 : 70.4, close to 1:2 (Fig. S6a†). However, the stoichiometric ratio of Ag, Cu, and S exhibits a significant change after injecting the CuCl2–OLA solution (Fig. S6b–6e†). With increasing reaction time, the content of Cu increases gradually. In contrast, the content of Ag decreases as the reaction continued. When the reaction time is more than 30 min, the stoichiometric ratio between Ag and Cu is close to 1 : 1, indicating that AgCuS NCs are gradually formed (Fig. S6f†). Meanwhile, element-distribution maps of these products obtained at different reaction intervals also indicate that the content of Cu increases gradually and homogeneously distributes along with Ag throughout the whole sample.

Typically, Ag2S exhibits a monoclinic anticotunnite-like structure. This structure can be observed among most of the alkali–metal chalcogenides and consists of trigonal prisms of Ag atoms connected by common edges that form chains. The S atoms are located in the center of such prisms. In addition, the corresponding lattice parameters are \(a = 4.22 \text{ Å}, \, b = 6.92 \text{ Å}, \, c = 7.86 \text{ Å}\), and \(V \approx 226.71 \text{ Å}^3\), respectively. \(^{51}\) In contrast, AgCuS can be described with an orthorhombic structure. Its structure is based on a distorted hexagonal close packing of S atoms. The Cu atoms lie in the distorted hexagonal close packing S layers. Meanwhile, Ag atoms form loosely packed face-centered-cubic layers and bond to two S atoms with a non-linear geometry, in contrast to the linear geometry observed in the Ag2S structure. This bicoordination of Ag is caused by the distortion of the octahedral sites of the S packing. Meanwhile, the lattice parameters of AgCuS are \(a = 4.07 \text{ Å}, \, b = 6.64 \text{ Å}, \, c = 7.97 \text{ Å}\), and \(V \approx 233.04 \text{ Å}^3\), respectively, \(^{31,52}\) indicating the similarity in structure and lattice parameters between Ag2S and AgCuS. Therefore, after injecting CuCl2–OLA solution, some Ag atoms belonging to trigonal prisms of the Ag2S structure are replaced with Cu atoms, thus forming a warped Cu–Ag metallic layer. The difference of these two structures is mainly attributed to different atomic radius (\(r_{\text{Cu}} < r_{\text{Ag}}\)) and atomic distances, which suggests that metallic interaction may play an important role in the AgCuS structure. \(^{52}\)

The HRTEM images of these Ag2S–AgCuS heterostructures show noteworthy metallic Ag clusters forming on these NCs, with a lattice constant of 0.22 nm that is typical for the (121) reflection of elemental silver (Fig. 5m and n). This unique phenomenon can be widely observed among the samples that were synthesized at different reaction intervals (Fig. S7†). Recently, Zhu et al. \(^{53}\) have reported the synthesis of Ag–Ag2S and Ag–Ag2S–CdS hybrid nanocrystals. Through partial reduction of Ag2S by \(\Gamma\), OLA, or sulfur derivatives, Ag nanocrystals were deposited on Ag2S. Urban and co-workers have found that polycrystalline silver metal clusters are produced during Ag2S NCs growth, even though in that reaction system, the sulfur source was in high excess. It is widely proposed that sulfur ion vacancies at the Ag2S NC surfaces, the catalytic role of Ag2S, and the high Ag+ mobility in Ag2S favor the reduction of Ag+ ions coming from the internal structure of Ag2S NCs. In addition, according to the conventional redox potential of Ag+/Ag (+0.8 V) and S/S2− (−0.44 V), the chemical reduction of Ag+ is possible. \(^{54}\) Meanwhile, they had shown that extended exposure of Ag2S NCs to an electron beam increases silver metallic cluster size during TEM measurement. \(^{54}\) Therefore, a similar mechanism could also be used to explain the Ag NCs deposited on Ag2S–AgCuS hybrid nanocrystals in our reaction systems. When Ag+ ions were replaced by Cu2+ ions during the diffusion process, the generated Ag+ ions could not discharge into the reaction solution effectively and quickly. These Ag+ ions could be reduced by Cl−, OLA, or sulfur derivatives and...
nucleate in the internal structure of Ag$_2$S–AgCuS heterostructures, forming Ag–Ag$_2$S–AgCuS hybrid nanocrystals (Fig. S8†). Meanwhile, most of the silver chalcogenides are fast ion conductors, and silver exhibits fluid-like properties. Therefore, many Ag$^+$ cation vacancies would appear in the Ag$_2$S NCs at the reaction temperature increases despite the fact that their stoichiometric ratios have already been determined. This behavior provides an optimal environment for the diffusion of Cu$^{2+}$ ions to Ag$_2$S NCs to form Ag$_2$S–AgCuS heterostructures. In addition, we further used the FFT patterns to analyze the formed Ag NCs inside Ag–Ag$_2$S–AgCuS heterostructures (Fig. S8 and S9†). FFT patterns indicate that these silver clusters mainly exhibit a polycrystalline phase. These Ag NCs usually attach to the Ag$_2$S region when the NCs transform from Ag$_2$S to AgCuS, a result that is in good agreement with previous reports. As the reaction proceeds, AgCuS grows along the direction of the interface of the Ag$_2$S–AgCuS heterostructures until all Ag$_2$S is consumed, which demonstrates that this diffusion phenomenon completely finishes. Furthermore, we found that the amount of Ag clusters embedded in the interior of the AgCuS NCs markedly decreases with increasing reaction time (Fig. S7†). This might be attributed to the intraparticle reaction and ripening process, in which the Ag clusters react with S$^{2−}$ to form Ag$_2$S, and are further replaced by Cu ions until all of the Ag clusters are consumed. With alternate occurrences of the reactions above, pure monodispersed AgCuS NCs could be obtained. These observed experimental phenomena are similar to the previously reported synthesis of ternary chalcogenides NCs (e.g. CuInS$_2$, AgInSe$_2$) proposed by Kolny-Olesiak and Bai et al. Because of the isostructural monoclinic-phase crystal structure of the as-synthesized Ag$_2$S and Ag$_2$Se NCs, formation of the ternary AgCuSe NCs is very likely to occur. When we used Se powder instead of TAA, monodispersed Ag$_2$Se and AgCuSe NCs could be synthesized one after another. Fig. 6a shows several XRD patterns of the products obtained at different reaction intervals after injecting CuCl$_2$–OLA solution. At the beginning of reaction (e.g. 5 min), the XRD pattern exhibits a mixed phase result, indicating a transformation process from Ag$_2$Se to AgCuSe. When the reaction time was maintained for more
than 10 min, the pure AgCuSe crystal structure indexed to the orthorhombic phase (JCPDS: 10-0451) could be observed, indicating that a fast ion exchange and diffusion process occurred. The structure and morphology of typical AgCuSe NCs were investigated by TEM and HRTEM. Fig. 6b and c show that the synthesized AgCuSe NCs exhibit spherical morphology and high monodispersity. The HRTEM image shown in Fig. 6d shows that these AgCuSe NCs have a highly crystalline nature with well-resolved lattice fringes. The distance between neighboring fringes were measured to be 0.21 and 0.26 nm, close to the (152) and (160) lattice spacing of AgCuSe, respectively. To determine an accurate structure for these AgCuSe NCs, the FFT displays a well-crystalline and single crystal feature (Fig. 6e).

**Pressure dependent PL behavior of Ag₂S NCs**

For the second challenge, we systematically investigated the pressure-dependent PL properties and band gap modulation of monodispersed Ag₂S NCs using *in situ* high pressure PL and absorption spectroscopy. The pressure-dependent PL spectra of 6.0 nm Ag₂S NCs are shown in Fig. 7. As the external pressure is applied, the PL peak shifted monotonically toward higher wavelength over a wide range (from 1200 to 1900 nm, $ΔE > 0.38$ eV). With increasing pressure, the PL spectra of Ag₂S NCs showed a marked broadening, which is caused by the stress–strain induced decrease in lattice symmetry and structural order. Finally, the PL of Ag₂S NCs disappeared when the pressure approached critical values of around 6.6 GPa.
Santamaría-Pérez and co-workers recently confirmed that two different phase transitions of bulk Ag2S (LP–HP1–HP2) can be observed under a pressure cycle of 0–10.5 GPa by X-ray diffraction experiments and theoretical calculations. The first structural phase transition occurs at 5 GPa; the initial monoclinic structure (space group P21/n) transforms into an orthorhombic structure (P212121). Meanwhile, a similar phase-transition pressure value of Ag2S could be observed via pressure-dependent Hall-effect measurements and first-principles calculations proposed by Gao et al. Generally speaking, pressure induced phase transitions occur at higher pressure in nanosized materials than in their bulk counterparts, especially for the metal-chalcogenide materials. That is due to the soft ligands (e.g. OLA) capped on these NCs that not only increase the stability of their structure, but also improve their elastic strength and fracture toughness. Therefore, the disappeared PL spectra of Ag2S NCs at 6.6 GPa shown in this paper might be caused by pressure induced phase transition. The pressure point (6.6 GPa) is much higher than the first phase transition (LP phase to HP1 phase) of bulk Ag2S (4.7 GPa). In addition, we further investigated the pressure-dependent optical absorption of 6.0 nm Ag2S NCs mixed with a fluid silicone pressure medium (Fig. S10†). It is observed that the absorption spectra of 6.0 nm Ag2S NCs are featureless under high pressure. With increasing pressure, the absorption edge exhibited a tiny shift towards a longer wavelength, which is in good agreement with the pressure-dependent PL spectra mentioned above, indicating a tendency to reduce the band gap of Ag2S NCs. This is greatly different from the II–VI and IV–VI NCs of in our previous work, which exhibited remarkable changes of their proposed absorption peaks. The detailed mechanism of the pressure-dependent absorption spectra of Ag2S NCs is still under investigation.

In order to better understand the differences between size- and pressure-induced PL spectra modulation of Ag2S NCs, the resulting PL behaviors are summarized in Fig. 8. The data shown in Fig. 8a were collected from several other sources including our own. In this case, the PL peak positions can be adjusted effectively below ~1200 nm when the particle size is less than ~4.5 nm, showing an extremely strong quantum confinement effect. In contrast, the PL peak position concentrated around 1200 nm when the size exceeded 4.5 nm due to the small exciton Bohr radius of Ag2S. The subtle difference of size versus PL peaks may be caused by different synthetic strategies, size distribution, excitation wavelength of light source and so on. In contrast, the pressure induced PL peak and PL energy shifts of 6.0 nm Ag2S NCs are plotted in Fig. 8b. The PL energy can be fitted by a quadratic function, \( E_{\text{PL}} = E_0 + \alpha P + \beta P^2 \), where \( E_{\text{PL}} \) is in eV and \( P \) is in GPa. The pressure coefficients \( \alpha \) and \( \beta \), derived from fits to experimental results, are \(-0.17 \) and \(2.2 \times 10^{-2} \) meV GPa\(^{-1}\), respectively. The schematic image shown in Fig. 8c indicates that the PL peak of 6.0 nm Ag2S NCs can be effectively modulated from ~1200 to 1900 nm under high pressure, greatly expanding the wavelength range of PL.

The pressure dependent PL behavior of Ag2S NCs shown in this paper is similar to lead chalcogenide NCs (e.g. PbS, PbSe). Not only changing the particle size but also applying pressure could be used to adjust PL in a wide NIR range for lead chalcogenide materials (Fig. S11†) due to their narrow direct band gaps (0.28–0.41 eV) and very large exciton Bohr radii (18–46 nm). Through in situ absorption, PL spectroscopy, XRD, small angle scattering (SAXS) measurements and theoretical calculations, the energy gap of PbX (X = S, Se) is known to exhibit a positive temperature coefficient (i.e., blue shift with increasing temperature) and a negative pressure coefficient (i.e., red-shift with increasing pressure). Therefore, a similar
mechanism could be used to explain the behavior of the pressure-dependent PL shown in Fig. 7 and 8. Pressure induced decrease of band energy plays the dominant role, which makes the PL peak of Ag₂S NCs exhibit a marked red shift tendency until its disappearance caused by phase transition.

**Conclusion**

In summary, based on as-synthesized Ag₂S NCs prepared via an ion exchange and diffusion process, high-quality monodispersed β-AgCuS NCs could be successfully synthesized by a solventthermal approach after injecting a CuCl₂-OLA solution. By selecting different sizes of the Ag₂S NCs for the template, size-tunable monodispersed β-AgCuS NCs could be synthesized. Similarly, this simple and reproducible strategy could be extended to synthesize monodispersed β-AgCuSe NCs. This thus opens new avenues for investigating size, morphology and temperature-dependent phase transitions of these ternary AgCuS and AgCuSe materials. The electrical transport between p and n type conduction can be studied in the future. In addition, we systematically investigated the pressure-dependent PL properties and band gap modulation of monodispersed Ag₂S NCs using in situ high pressure PL and absorption spectroscopy. Experimental results indicate that the upper limit of 6.0 nm Ag₂S NCs PL peak can be effectively modulated from ~1200 to 1900 nm with increasing pressure from 0 to 5.1 GPa, which greatly extends the wavelength range of PL beyond what can be achieved by other approaches, e.g. adjusting particle size.

**Conflicts of interest**

There are no conflicts to declare.

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