Near-Infrared Emitting AgInS₂/ZnS Nanocrystals

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Supporting Information

ABSTRACT: Near-infrared emitting AgInS₂/ZnS nanocrystals were synthesized by carefully controlling the growth conditions in a Ag/In/Zn/S solution with less zinc relative to the other precursors. The role of having a smaller amount of zinc (8 atom %) was systematically investigated in an effort to understand the mechanism of the largely red-shifted emission. The AgInS₂/ZnS nanocrystals can be transferred to aqueous solutions while retaining the emission intensity. The near-infrared emission and solubility in aqueous solutions make AgInS₂/ZnS nanocrystals excellent candidates for bioimaging and photocatalytic applications.

1. INTRODUCTION

Near-infrared (NIR) emitting materials have attracted great interest for biological sensing and imaging because major tissue and blood components in the body absorb or scatter visible light.¹ Semiconductor nanocrystals (NCs) have shown promising potential as NIR-emitting materials due to their size- and composition-dependent optical properties.²,³ More commonly used NCs have been those of cadmium chalcogenide-based alloys or heterostructures such as CdTe, Se, CdS, CdSe, and CdTe/CdSe.⁴ Another class of NIR-emitting NCs is constructed using semiconductors with very narrow band gaps, such as HgTe and InAs, to form CdHgTe/CdS, InAs/ZnSe,⁸ and InAs/InP.⁹ Although not well studied, the potential for high levels of toxicity from the involved elements of these NCs (Cd, Hg, Te, and As) affects their application in biological systems. Recently, interest has been focused on nontoxic NIR-emitting NCs such as AgS,¹⁰,¹¹ Ag₂Se,¹² and Si.¹³ Despite this recent surge of attention, more research is needed to improve the photo-luminescence (PL) quantum yield (QY) and to understand how to fine tune the emission wavelength.

One important class of nontoxic NCs is the I–III–VI (I = Ag, Cu; III = Al, In, Ga; VI = S, Se) semiconductors which possess high extinction coefficients in the visible to NIR region.¹⁴–¹⁷ These ternary NCs are excellent candidates for bioimaging applications due to their NIR emission and the ability to vary their composition and structure.¹⁷ Recently I–III–VI NCs have been successfully used in bioimaging²⁸,²⁹ as an alternative to cadmium-containing quantum dots (QDs). Bawendi’s group reported synthesizing CuIn₅Se₆ and CuIn₃Se₅ QDs that emit in the red part of the visible spectrum to the NIR region.²¹ Also, nonstoichiometric CuIn₅S₇ and AgInS₂ NCs have shown potential for NIR emission.³²,³³ It is desirable to further increase the stability and tune optical properties by coating these ternary particles with a shell of different material. ZnS is a widely used coating material for semiconductor NCs to improve PL efficiency, increase stability, and reduce toxicity.²⁴ However, alloying with wide-band gap ZnS usually results in a large blue shift of the PL rather than the desired red shift.³³,³⁵–³⁸ A titillating research endeavor could be to form ZnS-coated ternary NCs with NIR emission through heterostructure design.³⁴

Synthesis of these particles is typically performed using an organic capping ligand which is not compatible for use in biological systems. Therefore, it is necessary to exchange the organic soluble coating with one that is soluble in aqueous media. If the ligand exchange is performed poorly, surface traps may form due to poor passivation and can alter the materials’ optical properties.²⁹–³³ Having NCs that are soluble in aqueous solutions while retaining their optical properties is highly sought after.¹¹-Mercaptopoundecanoic acid (MUA) which contains a thiol and a carboxyl group has been widely used for coating metal chalcogenide NCs. With this ligand the thiol group is attached to the NC, and the carboxyl group makes the NC water-soluble. NCs capped with this surfactant have been reported to be biocompatible and have low toxicity.³⁴

The AgInS₂–ZnS system of interest in the present work is quite unique because AgInS₂ can be synthesized at very low temperatures,³⁶,³⁷,³⁸ whereas ZnS forms at higher temperatures. Recently, selective and controllable ion exchange by zinc has been an interesting strategy for optical property tuning of the I–III–VI NCs.³⁷–³⁹ In this paper, NIR-emitting AgInS₂/ZnS NCs with small amounts of zinc were synthesized by heating a Ag/In/Zn/S solution and stopping the reaction at a suitable temperature. The role of the precursor solution and NC growth temperatures were explored to help understand the
formation of NIR-emitting NCs. The delicate incorporation of wide-band gap ZnS during the growth process is done in a one-pot reaction providing an alternative for the NC band gap engineering toward NIR emission. The organic capping ligands are then exchanged with ones that are soluble in aqueous solutions with little effect on the NC’s optical properties.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Potassium hydroxide, methanol (99.9%), ethanol (anhydrous), chloroform (99.9%), and toluene (99.5%) were purchased from Fischer Scientific. Indium acetylacetone (In(acac)$_3$, 99%), silver nitrate (AgNO$_3$, 99.5%), zinc stearate (99.5%), sulfur (99.5%), dodecanethiol (99%), trietylphosphine (TOP, 90%), oleic acid (90%), octadecene (ODE, 90%), and 11-mercaptoundecanoic acid (MUA) were purchased from Sigma-Aldrich.

2.2. Synthesis of AgInS$_2$/ZnS Nanocrystals. The basic experimental design is similar to that for the alloyed AgInS$_2$–ZnS NCs, but requires finely controlled reaction parameters including precursor concentration, temperature, and reaction time. To obtain NIR-emitting AgInS$_2$/ZnS NCs, the starting ratio of Ag/In/Zn/S was set at 2:2:1:5, and the reaction was stopped at 165 °C with ice water. In a typical synthesis, 0.2 mmol of AgNO$_3$, 0.2 mmol of In(acac)$_3$, 0.1 mmol of zinc stearate, 1 mmol of oleic acid, 2 mmol of dodecanethiol, and 10 mL of ODE were added to a 25 mL flask. The solution was heated to 90 °C and kept at that temperature for 20 min under Ar(g) flow to exclude oxygen. Then ~0.1 mL of TOP was injected, and the reaction temperature was allowed to return to 90 °C. Once the reaction equilibrated, 0.5 mmol of sulfur dissolved in 6 mL of ODE was swiftly injected into the system, and a sharp drop of the temperature to ~73 °C was observed. After the injection, the system was heated to 180 °C at an average rate of ~11 °C/min up to 10 min. Once the reaction was at 180 °C it was held at that temperature for an additional 5 min. Aliquots of the sample were extracted at different times during the temperature ramp (10 s to 15 min) and injected into cold toluene to be used for optical measurements. For a large batch synthesis of NIR-emitting NCs, the flask was immersed in ice cold water when the temperature reached 165 °C at 8 min. After the synthesis was complete, the NCs were purified by washing with a toluene and ethanol mixture followed by centrifugation. The NCs were then dissolved in toluene or chloroform for storage and characterization.

Two experiments were performed to investigate the role of temperature in the synthesis. For one of the samples, the Ag/In/Zn/S solution was heated to 165 °C quickly in the same fashion as mentioned above except that the heating rate after reaching 165 °C was changed to 1 °C/min. In the second experiment, the Ag/In/Zn/S solution was heated to 150 °C and kept at this temperature for 30 min.

2.3. Surface Ligand Exchange with MUA. The ligand exchange reaction was performed according to a previously reported method for CdSe nanorods. First, 0.1 g of MUA dissolved in chloroform was added to 10 mL of the AgInS$_2$/ZnS NCs dispersed in chloroform and sonicated for 10 min. A KOH solution of about pH = 13 (0.025 g dissolved in 5 mL of water) was added to the NC/MUA/chloroform solution. After vigorous shaking, a milky brown emulsion was obtained and centrifuged for phase separation. The NCs were transferred to the aqueous phase, and the chloroform phase was discarded. Excess KOH and MUA were removed by precipitating the NCs using methanol and recovering them by way of centrifugation. The cleaned NCs were dispersed in water for further characterization.

2.4. Characterization. The UV–vis absorption spectra were acquired on a Varian Cary 50 spectrometer. PL and photoluminescence excitation (PLE) spectra were acquired on a Varian Eclipse fluorescence spectrometer. PL QYs of the NCs were estimated using silicon phthalocyanine (Pc 4) as the standard. Time-resolved PL measurements were made using a streak camera (Optronics). Samples were excited using 470 nm light, which was tuned by an optical parametric amplifier (TOPAS, Lightconversion) based on a 780 nm, 150 fs pulse generated from a regenerative amplifier using a Clark MXR CPA 2001 fs laser system. A transmission electron microscope (TEM, JEOL 1200CX) was used to characterize the NCs. Atomic ratios of Ag/In/Zn in the NCs were measured by atomic absorption spectroscopy (AAS, Varian SpectrAA 220 FS).

3. RESULTS

The UV–vis absorption spectrum of the NIR-emitting NCs is shown in Figure 1. There is not a sharp band gap peak for these NCs which is similar to other reported ternary NCs. The band gap (1.67 eV, insert in Figure 2a) of the prepared NCs is lower in energy than that of the bulk AgInS$_2$ (1.87 eV, 663 nm)
nm). The PLE spectrum shows a peak located at approximately 740 nm. It is worth noting that the PLE spectrum is nearly flat from 400 to 650 nm. Our results differ from Torimoto’s work with ZnS–AgInS2 solid solution nanoparticles in that their group reported an increase in the PLE spectrum as the absorption increased.28 This is an important difference between our NIR-emitting NCs and the uniformly alloyed ZnS–AgInS2 NCs. PL spectra (solid lines in Figure 1) excited at different wavelengths show a similarly shaped emission peak with the maxima around 814 nm. It is important to note that detector limitations may be cutting off some of the PL intensity on the long wavelength side of the spectrum, and therefore the PL maximum could be further red-shifted than what is shown. From Figure 1 it can be seen that the PL spectra, when exciting at 450 and 600 nm, are quite similar. However, exciting with 700 nm led to an increase in the PL.

By quickly heating the Ag/In/Zn/S solution from 73 to 165°C (10 s to 8 min), a continuous red shift of absorption and PL was observed as shown in Figure 2, and we were able to obtain the NIR-emitting NCs by quenching the reaction around 160–165°C at 8 min. The optical band gap of the NCs was estimated from the plot of (αhν)2 vs hν (inset in Figure 2a), where α is the absorbance and hν is the photon energy. The band gap decreased from 2.11 to 2.02, 2.00, 1.98, and 1.67 eV with an increase of reaction time from 10 s to 8 min, consistent with the PL red shift. With further increasing reaction time to 10–15 min (180°C), the absorption showed a slightly continuous red shift with an optical band gap of ~1.69 and 1.68 eV, similar to the 8 min sample, but the PL peaks blue shift to about 620 nm (pink and yellow curves in Figure 2b). The blue shift of the PL can be ascribed to the zinc incorporation into the AgInS2 NCs, similar to that in the alloyed AgInS2–ZnS NCs.26,28

In an effort to avoid the blue shift and to improve PL efficiency in the NIR range, the Ag/In/Zn/S solution was heated to 165°C quickly to synthesize the AgInS2/ZnS NCs, and then the heating rate was changed to 1°C/min to see the effect of temperature on the optical properties. The PL showed a large blue shift to 660 nm only after heating to 170°C (5 min) as shown in Figure 3a. Further increasing the temperature to 175°C does not change the PL peak shape or position. In another set of experiments, the NCs were synthesized at 150°C and refluxed for 30 min. The main PL peak is located at 775 nm and does not shift with reaction time as shown in Figure 3b. The PL peak wavelength is slightly shorter than that of the NCs synthesized at 165°C. There is a shoulder peak around 615 nm that increases with reflux time which suggests that zinc diffusion into AgInS2 occurs at a much slower rate compared to that at 165°C. The above experimental results suggest that the NIR-emitting NCs are highly temperature sensitive. Quenching the reaction in the range 160–165°C gives reliable production of the NIR-emitting NCs with little to no short wavelength emission.

TEM was used to characterize the AgInS2/ZnS NCs. As shown in Figure 4a, the NIR-emitting NCs show good monodispersity with an average size of 2.5 ± 0.5 nm. HRTEM (Figure 4b) indicates the high quality and spherical morphology of the NCs. It is hard to see if a core/shell structure is formed due to the low contrast difference between AgInS2 and ZnS and the low amount of ZnS.26,43 With increasing reaction time from 2 to 10 min, the particle size increases from 1.4 ± 0.4, to 2.5 ± 0.5, and 2.9 ± 0.6 nm (Figure 4c).

1. Supporting Information). Further refluxing the Ag/In/Zn/S solution at 210°C for 15 min resulted in a more dramatic size increase to 5.2 ± 0.8 nm (panel c in Figure S1, Supporting Information). The apparent size increase with increasing reaction time also demonstrates that the PL blue shift after 8 min is due to zinc diffusion into the AgInS2/ZnS NCs, not the formation of smaller NCs. The XRD pattern of the NCs is shown in Figure 4c, which has a medium phase of AgInS2 and ZnS with the two main peaks (around 27° and 45°) located at the middle of the standard patterns of bulk AgInS2 (JCPDF #750117) and ZnS (JCPDF 800020). The diffraction peaks were broadened due to the small particle size. Using AAS, the Ag/In/Zn atomic ratio was found to be 1:0:6:0:08:0:0. Although the amount of Zn is much less than Ag and In, it plays a key role in the formation of the NIR-emitting NCs.

To make the AgInS2/ZnS NCs water-soluble, a ligand exchange was performed. Figure 5 shows the UV–vis absorption, PL, and PLE spectra of the AgInS2/ZnS NCs after ligand exchange with MUA. There is no significant difference between the three spectra and those of the NCs in toluene (Figure 1). The PL peak is located at 809 nm and the PLE peak at 740 nm. The PLE peak agrees with the absorption shoulder peak around 740 nm, which equals to 1.68 eV.

To obtain more profound insights into the optical properties of the AgInS2/ZnS NCs, time-resolved PL was used to study these NCs in toluene and in water. The PL intensity (at 720 nm with a spectral window of 10 nm) decay curves and fitting results using biexponential functions are shown in Figure 6. The average of the biexponential fitting results were obtained using \( \tau_{ave} = (\tau_1 + \tau_2)/2 \). Compared with ZnCuInS2 NCs, alloyed NCs (\( \tau_1 = 58–98 \) ns and \( \tau_2 = 306–375 \) ns),44 our NIR-emitting AgInS2/ZnS NCs in toluene showed lifetimes in the same scale but slightly longer (\( \tau_1 = 94.7 \) ns)}.
±6.8 ns and \( \tau_2 = 463 \pm 4.4 \) ns). The fast decay component is ascribed to surface trap state recombination and the slow decay component to the deep donor–acceptor recombination.\(^{35,41,43}\) After transfer to the aqueous phase with MUA, there is only a slight drop of both components (\( \tau_1 = 80.5 \pm 3.3 \) ns and \( \tau_2 = 435.6 \pm 4.6 \) ns) and also an increase in the amplitude of the fast component, which together resulted in the decrease of \( \tau_{ave} \) from 394.4 ± 4.9 to 325 ± 4.2 ns. This lifetime decrease is due to less protection of the NC surface when coated with MUA compared to dodecanethiol. It is worth mentioning that the PL lifetime of 324.9 ns is still much longer than commonly used binary NCs. The long PL lifetime enables the separation of signal from the fast decaying background fluorescence and scattering in biological systems and therefore is an important advantage for the use of these NCs in bioimaging applications.

4. DISCUSSION

NIR-emitting AgInS\(_2\)/ZnS NCs were synthesized using a similar process for the AgInS\(_2\)–ZnS alloyed NCs. For alloyed AgInS\(_2\)–ZnS, we used Ag:In:Zn = 1:1:1, and the reaction temperature was 210 °C.\(^{37}\) Compared to the alloyed NCs, the key parameters here are lower temperature, lower heating rate, and lower zinc amount (Ag:In:Zn = 2:2:1). These factors provide better manipulation of the heterostructure at the nanoscale. Although it is still not well understood, zinc cations or zinc sulfide play a key role in the formation of the NIR-emitting NCs. Without zinc, the AgInS\(_2\) NCs grew quickly and formed large particles from the solution of Ag/In/S = 2:2:5 as indicated by the red shift of PL. However, these particles aggregated before the system reached the desired temperature for producing NIR-emitting NCs (Figure S2, Supporting Information). If more zinc is used, for example Ag/In/Zn = 1:1:1 instead of 2:2:1, the short-wavelength emission was readily observed before it shifted to the NIR range and resulted in very broad PL peaks.\(^{37}\) As shown in Figure S3 (Supporting Information), we were unable to observe a single PL peak after 800 nm with starting ratio of Ag:In:Zn = 1:1:1 instead of 2:2:5 as indicated by the red shift of PL. However, these particles aggregated before the system reached the desired temperature for producing NIR-emitting NCs (Figure S2, Supporting Information). There are two important roles of zinc for the synthesis of NIR-emitting NCs. One is to enable the growth of the Ag-rich AgInS\(_2\)/ZnS NCs at elevated temperatures, which would otherwise aggregate severely above 120 °C without zinc (Figure S2, Supporting Information). The second is defect suppression, which has been reported to enhance the PL of AgInS\(_2\)/ZnS NCs.\(^{37,45}\) Band gap engineering of the semiconductor NCs has been widely studied toward superior optical and electrical properties. Alloying from very narrow band gap semiconductors, like HgTe, has been proven to be a straightforward and successful strategy to obtain NIR-emitting NCs.\(^{46}\) An intriguing phenomenon is the red shift of PL in core/shell NCs resulting from the formation of charge transfer states that have lower
energy than both of the corresponding components. Moreover, it has also been reported that the gradient alloyed NCs, such as CdSe1−xTex QDs, show a large red shift of the PL. The large band gap reduction is ascribed to the lattice strain reduction and local structural ordering. Alloying of the interfacial layer can reduce the lattice mismatch between the core/shell layers which allows for gradual strain release and gives improved optical properties.

After systematic investigation, reducing the temperature and the amount of zinc were found to be the critical parameters for the NIR-emitting NCs. AgInS2/ZnS NCs with a small amount of zinc showed large red shift (>100 nm) compared to the recently reported AgInS2 NCs with PL in the range of 580–720 nm depending on their sizes. A PL peak over 800 nm was also observed in ZnS–CuInS2 NCs with small Zn/Cu ratio, but the work was not focused on NIR emission, and no profound study was performed. The atomic ratio of Ag/In/Zn is 1.00:0.68:0.08 in our AgInS2/ZnS NCs. In Bawendi’s work, CuInSe2 and CuInS2Se4 QDs were reported to be luminescent in the red to NIR wavelengths with much more In than Cu. AgInSe2 QDs were also synthesized in their work as an analogue, but with emissions in the visible range. Further in-depth investigation is still required to better understand the composition dependence on the ternary I−III−VI NCs, especially in the NIR range.

The band gaps of bulk AgInS2 and ZnS are 1.87 eV (663 nm) and 3.60 eV (344 nm), respectively. Alloying, diffusion, and cation exchange of AgInS2 by zinc all showed largely blue-shifted PL depending on the amount of zinc that was incorporated. In our AgInS2/ZnS NCs, the shoulder peak located at 720 nm (1.72 eV) can be ascribed to the band-edge absorption, which is lower than that of both AgInS2 and ZnS. Large Stokes shifts are normally observed and ascribed to the donor−acceptor transition in both bulk and nanoscale AgInS2 and PL in the range of 570–720 nm has been observed in AgInS2 NCs with fine-tuned sizes.

In I−III−VI semiconductors, different kinds of intrinsic defects including vacancies, interstitial atoms, and combinations of the two are well-known to produce deep trap states and can be responsible for the deep donor−acceptor pair transition. Considering the Ag/In/Zn ratio of 1.00:0.68:0.08 in our AgInS2/ZnS NCs, it is reasonable to propose that the donor states from silver interstitials are the main source of PL transitions and are also partially responsible for the red shift to the NIR region. For AgInS2/ZnS or CuInS2/ZnS nanocrystals, it is not necessary to fully overcoat the core for optical property tuning based on previous works. PL of I−III−VI nanocrystals is usually ascribed to the deep donor−acceptor recombination with the characteristics of large Stokes shift and fwhm (full width at half maximum), which has much longer lifetime than that of the surface trap states. ZnS can dramatically change the optical properties of AgInS2 even with low Zn atom % because of the lattice similarity and the ease of alloying between the two materials. The effect of zinc on the optical property tuning of AgInS2/ZnS NCs can be ascribed to two aspects: defect suppression due to cation exchange by zinc and shell formation of ZnS.

On the basis of the above discussion, the large red shift of PL to 815 nm in the small AgInS2/ZnS NCs (2.5 ± 0.5 nm) can be ascribed to the band gap being reduced due to the rich donor states from silver interstitials and a thin AgInS2−ZnS gradient alloyed layer during the growth of the NCs which resulted in a reduction of the lattice strain and local structural ordering, similar to cadmium chalcogenide alloys. Although the NIR-emitting AgInS2/ZnS NCs were synthesized by quenching at 165 °C, refluxing the NCs at the same temperature resulted in a sharp blue shift of the PL peaks. This thin gradient alloyed layer is highly temperature sensitive, and as the temperature increased so did the diffusion rate of zinc into the inner layer of the AgInS2 lattice, resulting in the large blue shift of PL. In Park’s work, CuInS2/ZnS and AgInS2/ZnS core/shell QDs were synthesized by zinc cation exchange at 230 °C which demonstrated a large blue shift. Tang et al. obtained AgInS2/ZnS heterodimers with blue-shifted emission by zinc diffusion at 210 °C into synthesized AgInS2 NCs. From this work annealing at 150 °C can maintain the structure as indicated by the nonshifting in PL with heating time, but no PL efficiency improvement was observed (Figure 3b). The key to obtaining NIR-emitting AgInS2/ZnS is to quench the reaction to obtain the intermediate phase during the NC growth. Moreover, the thermodynamically unfavorable NCs at high temperature show high stability at room temperature which have been stored in air for several months.

In a comparison to AgS NCs, very small sizes (<1.5 nm) are needed to obtain PL in the range of 650–820 nm with the PL shifting to 1227 nm for larger AgS NCs (4.6 nm) grown by a seeded method. Another observation in our AgInS2/ZnS NCs is that they have a higher QY (1.5 ± 0.1% in toluene) than the AgS NCs (0.18%). It is known that I−III−VI semiconductors have enhanced optical properties compared with their I−VI counter materials in both bulk and nanoscale. These two observations distinguish our AgInS2/ZnS NCs from the AgS NCs.

5. CONCLUSIONS

NIR-emitting AgInS2/ZnS NCs were synthesized by heating a Ag/In/Zn/S solution and stopping the reaction at 165 °C. Zinc concentration and growing temperature played important roles in the formation of NIR-emitting NCs. The large red-shifted PL (>100 nm) compared to AgInS2 NCs can be ascribed to band gap reduction resulting from the rich donor states from silver interstitials and local structural ordering in the thin AgInS2−ZnS gradient alloyed surface layer. Zinc plays two important roles here: First, it enables the growth of the AgInS2/ZnS NCs at elevated temperatures without aggregation, and second, it suppresses the formation of defects which leads to an enhancement of the PL of AgInS2/ZnS NCs. The unexpected NIR-emitting properties of the AgInS2/ZnS NCs make them potentially desirable for bioimaging applications.
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References


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