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Synthesis of widely emission-tunable Ag–Ga–S and its quaternary derivative quantum dots

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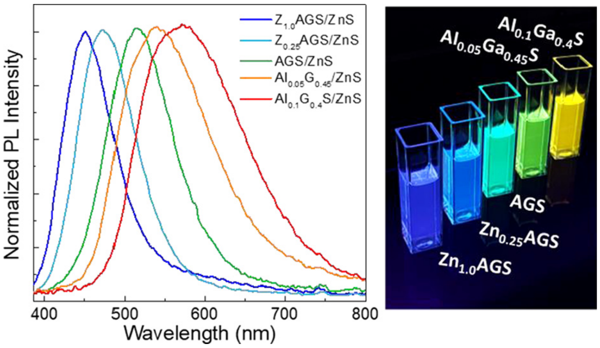
HIGHLIGHTS

- Ag–Ga–S and its derivative Zn–Ag–Ga–S and Ag–In–Ga–S QDs were synthesized.
- Widely color-tuned emissions from blue to amber with high PL QYs of 58–69% were demonstrated.
- Ag– In–Ga–S QDs were combined with a blue LED to produce bicolored white solid-state lighting devices.

GRAPHICAL ABSTRACT



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ABSTRACT

Chalcopyrite I – III–VI chalcogenides have attracted great attention as environmentally benign, non-Cd compositions for synthesis of colloidal quantum dot (QD) emitters. Various Cu-based I–III–VI compositions have been intensively investigated for synthesis of highly fluorescent QDs, while the compositional diversity of Ag-based QD emitters remains still limited. Here, we explore synthesis of Ag-based I–III–VI QDs of ternary Ag–Ga–S (AGS) and its derivative quaternary Zn–Ag–Ga–S (ZAGS) and Ag–In–Ga–S (AIGS) QDs through alloying AGS with Zn^{2+} and In^{3+} ions, respectively. Being in line with the variation of band gap of a series of these QDs, they exhibit a systematic, wide photoluminescence (PL) tunability from blue (450 nm, the shortest PL wavelength reported to date from I–III–VI QD emitters) from the highest-band gap ZAGS to amber color (570 nm) from the lowest-band gap AIGS with high PL quantum yields of 58–69% after elaborate ZnS shelling. Among QDs above, two AIGS/ZnS QDs with different In contents, which are capable of efficiently absorbing blue photons, are further applied as down-converters in combination with a blue light-emitting diode (LED) to produce bicolored white solid-state lighting devices and down-conversion emission properties of the resulting white QD-LEDs are described in detail.

1. Introduction

Over the past years chalcopyrite I–III–VI chalcogenides, mostly comprising monovalent Cu^+ or Ag^+, trivalent Ga^{3+} or In^{3+}, and divalent S^{2-} or Se^{2-}, have been highlighted as environmentally benign, non-Cd compositions for synthesis of quantum dots (QDs). Based on the

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synthetic success of such various I–III–VI QDs, they have been actively utilized as efficient emitters in down-conversion (DC), electroluminescence (EL) devices, luminescent solar concentrators, and biological tagging agents plus potential photovoltaic components [1–11]. Unlike II–VI (e.g., CdSe) and III–V (e.g., InP) type QDs showing an excitonic recombination, photoluminescence (PL) of I–III–VI QDs results from the recombination of charge carriers at intragap defect states, thus inevitably accompanying substantial Stokes shifts by > 200 meV [1,5,12]. It is generally accepted that these intragap states are associated with the lattice imperfections such as vacancies and substitutional/interstitial sites of cations and anions that serve as either acceptors or donors. As in bulk materials, these various point defects are likely intrinsically present in I–III–VI QDs because of the high configurational degrees of freedom in ternary chalcopyrite phases with two cation sublattices [13]. Two recombination channels have been proposed to describe PL of I–III–VI QDs. One is donor-acceptor pair (DAP) recombination involving a deep acceptor level from either cation vacancy or interstitial anion sites and a relatively shallow donor level from either anion vacancy or interstitial cation sites [13–17]. The other channel is often called a “free-to-bound” recombination involving a delocalized conduction band (CB) electron and a hole localized at a point defect (mostly assigned to V_{Cu} or V_{Ag} as acceptor) [12,18–21]. In addition to a large Stokes shift, a highly broad PL feature with typical full-width-at-half-maxima (HWHMs) of a few hundred meV is unique to I–III–VI QDs. According to the DAP recombination mechanism, the distribution in donor-acceptor distance that determines the Coulombic interaction gives rise to the dispersion of PL energies [4]. In the case of the free-to-bound recombination, the random positioning of Cu (or Ag)-associated acceptor centers inside the QD, which generates the large variation in the Coulombic interaction between the delocalized CB electron and the localized hole, is suggested to be responsible for a substantial PL broadening [12]. In addition to the above electron–hole Coulombic interaction, the electron-phonon coupling, which is expected to be strong in I–III–VI QDs due to the intrinsic presence of the deep and localized trap states, would partly contribute to the distribution of PL energies [13].

One of the vantage points of I–III–VI QDs over II–VI and III–V counterparts is a high compositional degree of freedom. By diversifying the compositional combination between I, III, and VI elements various ternary QD candidates can be produced. Moreover, their composition can be further extended into quaternary solid solutions by means of the substitution between isovalent ions or the alloying with ZnS phase. Therefore, the band gap and consequential PL energy of I–III–VI QDs can be widely, finely tailored. Till now Cu-based I–III–VI compositions including Cu–In–S (CIS) [8,19,22–27], Cu–In–Se [17,28], Cu–Ga–S (CGS) [29,30], Cu–In–Ga–S (CIGS) [31,32], Cu–In–Se–S [33], Zn–Cu–In–S (ZCIS) [10,11,23,34–36], and Zn–Cu–Ga–S (ZCGS) [37] have been intensively investigated for synthesis of high PL quantum yield (QY) QDs with a type-I core/shell heterostructure. Meanwhile, the compositional diversity of Ag-based QD emitters appears relatively limited, and most synthetic effort has been dedicated to Ag–In–S [16,38], Ag–In–Se [39–41], and Zn–Ag–In–S (ZAIS) [42–46]. Among them, highly fluorescent Ag–In–S and Zn–Ag–In–S QDs obtained through the optimization of core/shell heterostructure have been successfully applied as efficient emitters in DC [16,44,45] and EL devices [38,46]. Besides the compositions enumerated above, other Ag-based colloidal nanocrystals of Ag–In–Se–S [47] and Ag–Ga–S [48] are found in literature, but their sizes were excessively large (> 15 nm) to belong to the quantum confinement regime and no PL was reported.

Kuwabata group examined PL properties of a series of $Ag–In_x–Ga_{1-x}–S$ solid solution QDs, where PL spectrum systematically red-shifted with increasing x value (e.g., red for x = 0.2 to deep red-near-infrared for x = 1.0) due to the band gap narrowing and PL QY was highly dependent on In/Ga ratio (e.g., < 5% for x = 0.2 and 45% for x = 1.0) and eventually became zero for Ag–Ga–S (i.e., x = 0) [49]. In this work, we explore synthesis of ternary Ag–Ga–S (AGS) and its derivative quaternary Zn–Ag–Ga–S (ZAGS) and Ag–In–Ga–S (AIGS) QDs, whose luminescence has been rarely reported yet. Upon introducing Zn^{2+} and In^{3+} ion in AGS QD synthesis, the resulting QDs exhibit a blue- and red-shift in absorption, respectively, with both shifts being also proportional to their nominal amounts, indicative of the formation of intended alloyed quaternary QDs. All core QDs are then surface-passivated through an identical ZnS shelling optimized towards high PL QY. While AGS/ZnS QDs yield greenish cyan emission with a PL peak at 515 nm, PL peak wavelengths of AIGS/ZnS QDs shift to 540–570 nm, depending on the amount of In^{3+} ion used. Conversely, ZAGS/ZnS QDs show higher PL energies with peak wavelengths below 500 nm. In particular, heavily alloyed ZAGS/ZnS QDs possess 450 nm-peaking blue emission, which is, to the best of our knowledge, the shortest PL wavelength reported to date from I–III–VI QD emitters.

2. Experimental details

2.1. Synthesis of AGS, ZAGS and AIGS and their core/shell QDs

In a typical synthesis of ternary AGS core QDs, 0.0625 mmol of silver iodide (AgI, 99.999%), 0.5 mmol of gallium acetylacetonate (Ga(acac)$_3$, 99.99%) and 1 mmol of sulfur (99.998%) in 1.5 ml of 1-dodecanethiol (DDT, ≥98%) and 5 ml of oleylamine (70%) were placed in 3-neck round flask. This reaction mixture was degassed during heating to 120 °C and further heated to 240 °C under N_2 purging and maintained at that temperature for 30 min for nucleation and growth. Note that a nominal Ag/Ga molar ratio was intentionally Ag-deficient, since such a deficiency in monovalent cation relative to trivalent counterpart is a critical synthetic requirement in attaining high PL QY in I–III–VI-type fluorescent QDs [20,22,27]. Here, an optimal nominal Ag/Ga molar ratio of 1/8 was experimentally chosen, because it resulted in the best QY, and the same AgI amount of 0.0625 mmol was identically applied for the following synthesis of quaternary QDs. Faithfully sticking to the above synthetic procedure of AGS QDs, quaternary QDs of ZAGS and AIGS were prepared simply by adding zinc chloride ($ZnCl_2$, ≥98%) and indium acetate (In(Ac)$_3$, 99.99%), respectively. Two $ZnCl_2$ amounts of 0.25 and 1.0 mmol were used for synthesis of ZAGS QDs, hereafter referred to as $Z_{0.25}$AGS and $Z_{1.0}$AGS, respectively. Similarly, two In(Ac)$_3$ amounts of 0.05 and 0.1 mmol were attempted for synthesis of AIGS QDs, hereafter referred to as $AI_{0.05}G_{0.45}S$ and $AI_{0.1}G_{0.4}S$, respectively. Also note that the same Ga(acac)$_3$ amount of 0.5 mmol was used for synthesis of AGS and two ZAGS QDs, but the amounts of Ga(acac)$_3$ were reduced to 0.45 and 0.4 mmol for synthesis of $AI_{0.05}G_{0.45}S$ and $AI_{0.1}G_{0.4}S$ QDs, respectively. Consecutively, all of core QDs were identically shelled with ZnS in the following procedures. A ZnS stock solution containing of 8 mmol of Zn acetate dehydrate (reagent grade) dissolved in 8 ml of oleic acid (OA, 90%) and 4 ml of 1-octadecene (ODE, 90%) was injected slowly to the respective core growth solution at 240 °C and the shelling reaction was allowed at that temperature for 1 h 15 min. Subsequently, another ZnS stock solution, consisting of 4 mmol of Zn stearate (10–12% Zn basis) in 4 ml of OA, and 2 ml of ODE, was added dropwisely and this final shelling reaction was maintained at 250 °C for 1 h. As-synthesized core/shell QDs were then precipitated by excess ethanol and repeatedly purified with a solvent combination of hexane/ethanol by centrifugation (9000 rpm, 10 min) and finally redispersed in hexane or chloroform.

2.2. Fabrication of white QD-LEDs integrated with AIGS/ZnS QDs

Among a series of AGS-based ternary and quaternary QDs, only two AIGS core/shell QDs of $AI_{0.05}G_{0.45}S$ and $AI_{0.1}G_{0.4}S$ were individually applied as DC emitters in combination with a blue InGaN LED (λ = 455 nm) because of their proper absorption capability at that blue region. For a typical fabrication of white QD-LEDs, AIGS/ZnS QD-chloroform dispersion, whose optical density was adjusted to be ~3.0 at 450 nm (corresponding to ca. 80 mg/ml), was homogeneously