



Enhanced fluorescent stability of copper indium sulfide quantum dots through incorporating aluminum into ZnS shell



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ARTICLE INFO

Article history:

Received 19 November 2015

Received in revised form

8 December 2015

Accepted 8 December 2015

Available online 12 December 2015

Keywords:

Copper indium sulfide

Quantum dots

Al-doped shell

Fluorescent stability

Light-emitting diodes

ABSTRACT

Fluorescent quantum dots (QDs) become usually deteriorated, losing their originally high quantum yield (QY), upon a prolonged exposure to degradable environments, and this lack of long-term QD stability retards their ultimate industrial application. For an effort to significantly improve the fluorescent stability of copper indium sulfide (Cu–In–S, CIS) QDs, in this work, synthesis of double-shelled CIS/ZnS/ZnS:Al QDs with intermediate ZnS shell and outer Al-doped ZnS shell is attempted. The resultant yellow-emitting CIS/ZnS/ZnS:Al QDs possess an excellent QY of 77%. For comparison, standard double shell-structured, Al-doping free CIS/ZnS/ZnS QDs are also prepared. These two types of QDs are then subjected to continuous UV irradiation and heat for certain periods of time and their temporal fluorescent stability behaviors are compared, clearly showing a superior stability from QDs with Al-doped shell. This is attributable to the effective QD passivation by Al₂O₃ layer generated *via* photochemical or thermal oxidation of Al doped in ZnS shell. The above results are further verified by fabricating QD-based light-emitting diodes (LEDs) with the combination of QD down-converters with a blue LED and comparing their electroluminescent stability with operational time.

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1. Introduction

Significant progress in synthesis and application of group I–III–VI composition-based metal chalcogenide colloidal quantum dots (QDs) has been witnessed over the years, since they possess the valuable optical properties that are well suited particularly for the fabrication of photovoltaic and light-emitting devices [1–3]. The band gap of I–III–VI QDs can be finely and widely engineered through the compositional combination, off-stoichiometry between two cations of I and III elements, and quantum confinement effect (QCE), thereby controlling their absorption and emission properties. Among a number of I–III–VI compositions available for QD synthesis copper indium sulfide (Cu–In–S, CIS) is the most intensively studied one particularly as visible-to-near infrared QD emitters. The band gap and consequent emission energy of ternary CIS QDs could be tuned by forming the ternary compositions, e.g., Cu–In–Zn–S [4–6], Cu–In–Ga–S [7–9], Cu–In–S–Se [10,11],

modifying the Cu-to-In molar ratio [12–14], and changing the size of QCE region [15–17]. These emission-tunable QDs have been then applied not only as *in vitro* and *in vivo* biological tagging agents [18–20] but as visible emitters for the fabrication of down-converting [8,13,21,22] and electrically-driven [14,23–26] QD-based light-emitting diodes (QD-LEDs).

Over the past decade, ceaseless synthetic efforts to enhance fluorescent efficiency or quantum yield (QY) of QDs have been made mainly through elaborately refining core/shell architecture. As a result, *state-of-the-art* QDs exhibit satisfactorily high QY levels from a standpoint of industrial application. Unfortunately, however, QDs are vulnerable to the continuous photon or heat exposure under ambient atmosphere, leading to the devastation (oxidation) of QD surface and simultaneously QY deterioration. This fluorescent instability of QDs against the above degradable environments has been a stubborn problem at the entry stage of commercial production. One viable strategy for producing more robust QDs *via* the protection of QD surface is to overcoat individual QDs with a chemically stable oxide phase, which serves as a physical barrier that restrains oxygen and water molecules from permeating into

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QD surface. Overcoating with the Stöber-derived silica, the most common oxide, has been widely attempted to different classes of QDs, e.g., Cd-chalcogenide [27–29], InP [30], and CIS ones [31], but this silica overcoating process usually accompanies an appreciable QY reduction. For an effort to retain the original QY after overcoating process, other oxide candidates such as ZnGa_2O_4 and In_2O_3 for encapsulating CIS [32] and InP QDs [33,34], respectively, have been suggested.

Very recently, Li's group proposed an innovative approach to the simple, effective self-passivation of CIS QD surface via Al doping into ZnS shell [35]. More specifically, upon light irradiation Al doped in ZnS shell became photo-oxidized into Al_2O_3 , which then acts as a protection layer that keeps QDs from being photo-degraded against prolonged time of irradiation. Although those Al-doped CIS/ZnS (CIS/ZnS:Al) QDs showed a substantial enhancement of photo-stability, the highest QY achievable from as-obtained QDs was just around 40% and their fluorescent stability test was evaluated only by blue light irradiation. Herein, for an attempt to realize a much higher QY, synthesis of CIS/ZnS/ZnS:Al QDs with the double shell architecture that consists of intermediate ZnS shell plus outer Al-doped ZnS (ZnS:Al) shell is devised, resulting in an excellent QY of 77%. These highly efficient QDs are then subjected to higher-energy UV irradiation and heat for an extended period of time, exhibiting an excellent fluorescent stability against such degradable environments. To further prove the superiority of CIS/ZnS/ZnS:Al QDs in fluorescent stability over Al-undoped ones (i.e., CIS/ZnS/ZnS), two QD-LEDs are fabricated by packaging the respective QDs with a blue LED chip and their long-term operational stability is compared.

2. Experimental details

2.1. Synthesis of CIS/ZnS/ZnS and CIS/ZnS/ZnS:Al QDs

Highly fluorescent double-shelled standard CIS/ZnS/ZnS QDs were prepared by slightly modifying our previous synthetic recipe in literature [25]. In brief, 0.125 mmol of Cu (I) iodide, 0.5 mmol of In acetate were loaded with 5 ml of 1-octadecene (ODE) in 50 ml of three-neck round flask. And, this mixture was sequentially degassed, nitrogen-purged, and heated to 230 °C. At that temperature, 3 ml of 1-octanethiol (OTT) that serves as both sulfur source and surface ligand species was rapidly injected to the above hot mixture. Then, the reaction for CIS core growth was held for 5 min at 230 °C. Following ZnS shelling was performed in a consecutive way. First, the first Zn stock, comprising 4 mmol of Zn acetate dihydrate, 4 ml of oleic acid (OA), and 2 ml of ODE, was introduced into the above hot core growth solution at 240 °C and reacted for 1 h (which is referred to as the first shelling for single-shelled CIS/ZnS QDs). Subsequently, the second Zn stock consisting of 4 mmol of Zn stearate dissolved in 4 ml of OA and 2 ml of ODE was rapidly injected and then the shelling reaction proceeded for 2 h (which is referred to as the second shelling), producing standard double-shelled CIS/ZnS/ZnS QDs. Meanwhile, for a typical synthesis of CIS/ZnS/ZnS:Al QDs, the first-shelled CIS/ZnS QDs were first prepared with the same experimental details as in the above standard QDs, and Al-doped ZnS outer shell was grown by substantially modifying the method reported in literature [35] as follows; right after the first shelling reaction for CIS/ZnS QDs was completed, the above second Zn stock was injected into the pre-grown CIS/ZnS QD solution, followed by a dropwise addition of mixture of 4 mmol of aluminum isopropoxide ($\text{Al}(\text{IPA})_3$) dissolved in 1-dodecanthiol (DDT) at 240 °C. And this second ZnS:Al shelling was maintained at that temperature for 10 h. As-synthesized CIS/ZnS/ZnS and CIS/ZnS/ZnS:Al QDs were repeatedly washed via a routine precipitation/redissolution cycle with a solvent

combination of hexane/ethanol and then dispersed in hexane, ODE, or chloroform, depending on their subsequent characterization and tests.

2.2. Fluorescent stability tests of QDs

Two comparative QDs of CIS/ZnS/ZnS and CIS/ZnS/ZnS:Al were identically subjected to degradable conditions of UV irradiation and thermal aging. First, purified QDs dispersed in hexane were continuously UV-irradiated by a 365 nm-multiband UV lamp for a prolonged duration up to 48 h and their temporal PL variations with UV irradiation time were monitored. In the case of thermal aging test, a solvent for QD dispersion was replaced by ODE with a high boiling temperature. Then, QD-ODE dispersions were placed in a convection oven pre-heated at 150 °C and held at that temperature for certain periods of time. Moreover, QD-LEDs were fabricated by combining the respective QDs as down-converters with a surface mounting device-typed, $50 \times 50 \text{ mm}^2$ -sized, 455 nm-emitting InGaN-based blue LED (Taein Semiconductor, Korea). 3 ml of QD-chloroform dispersion with an optical density of ~ 3.0 at 450 nm was blended with 0.4 g of thermally curable epoxy resin (YD-128, Kukdo Chem., Korea), and this QD-resin pre-mixture was placed on hot plate at 60 °C for 30 min to evaporate a solvent. Then, 0.4 g of a hardener (KFH-271, Kukdo Chem., Korea) was added to the above QD-epoxy resin paste. This paste was dispensed on a blue LED mold and then thermally cured by a two-step process of 90 °C for 1 h, followed by 120 °C for 30 min.

2.3. Characterization and analysis

UV–visible absorption and photoluminescent (PL) spectra of QDs were collected with UV–visible absorption spectroscopy (Shimadzu, UV-2450) and a 500 W Xe lamp-equipped spectrophotometer (PSI Co. Ltd., Darsa Pro-5200), respectively. Absolute PL QYs of QDs were assessed in an integrating sphere with an absolute PL QY measurement system (C9920-02, Hamamatsu). Transmission electron microscopy (TEM) work on QDs was performed using a Tecnai G2 F20 operating at 200 kV. Powder x-ray diffraction (XRD) patterns of QDs were recorded using Ultima IV (Rigaku) with Cu K_α radiation. The compositional analysis of as-synthesized QDs were conducted with an energy dispersive spectrometer (EDS)-equipped scanning electron microscope (SEM, JEOL-7800F) operating at 15 kV and further verified with an inductively coupled plasma optical emission spectrometer (ICP-OES, OPTIMA 8300, PerkinElmer). Electroluminescent (EL) spectra and luminous efficacies of the QD-LEDs with operational time were measured at a driving current of 60 mA under ambient conditions with a diode array rapid analyzer system (PSI Co. Ltd.).

3. Results and discussion

In general, PL of group I–III–VI metal chalcogenide QDs is substantially broad and Stokes-shifted relative to their absorption, since a variety of cationic/anionic defect types in the forms of vacancies, substitutional, and interstitial sites are available, generating their own intra-gap energetic pathways for the following radiative charge recombinations. Standard double-shelled QDs of CIS/ZnS/ZnS displayed a high fluorescence QY of 82% along with a peak wavelength of 600 nm (Fig. 1a). Meanwhile, as shown in Fig. 1b, both absorption and PL (peak wavelength of 564 nm) spectra of Al-doped, double-shelled QDs of CIS/ZnS/ZnS:Al were blue-shifted as comparison to those of CIS/ZnS/ZnS ones. Considering a longer second ZnS:Al shelling of 10 h in CIS/ZnS/ZnS:Al QDs versus a short second ZnS shelling of 2 h in CIS/ZnS/ZnS ones, a higher degree of CIS–ZnS alloying throughout shelling would be

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