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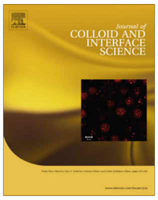

Controlling surface defects of non-stoichiometric copper-indium-sulfide quantum dots

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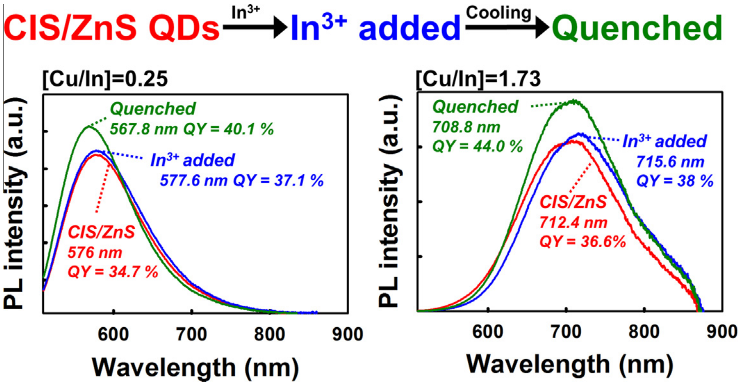
GRAPHICAL ABSTRACT



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ABSTRACT

Quantum dots (QDs) can be used for a wide range of practical applications including solar energy conversion, light-emitting display, bio-imaging, and sensing. However, toxic heavy metal elements of Pb- and Cd-based QDs cause potential environmental problems and limit their wide applicability. To overcome this limitation, $CuInS_2$ (CIS) QDs, which have a bulk bandgap energy of 1.5 eV and relatively high absorptivity, can be a good alternative. However the photoluminescence quantum yield (PLQY) of CIS QDs is too low for practical applications. Here we investigate the effects of experimental factors in the solution synthesis of CIS/ZnS QDs on intrinsic defects and surface defects from photoluminescence (PL) analysis. A heating-up method is used with dodecanethiol as a sulfur source, a ligand, and a medium. The Cu-to-In feeding ratio is changed to control the PL spectrum in the range of visible to near infrared (NIR) frequencies. The PLQY is increased above 40% in all of the ranges through ZnS shell passivation and additional process optimization (e.g., controlled cooling rate and additional feeding of In^{3+} ion precursor). This work demonstrates the role of intrinsic defects in PL and the importance of suppressing the formation of the surface defects to increase the PLQY.

1. Introduction

Quantum dots (QDs) have been widely studied for applications in solar energy harvesting, light emitting display, and bio-imaging because of their highly bright luminescence, large absorptivity,

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tunable spectra, large Stokes shift, and relatively good chemical stability [1–3]. However, toxic elements (e.g., Cd and Pb) in typical II–VI QDs exhibit cytotoxicity, limiting their wide applications in bio-related fields, and environmental regulations restrict the use of heavy metals in consumers' products.

As an alternative to Cd- and Pb-based QDs, ternary $CuInS_2$ (CIS) QDs, which are semiconductor nanocrystals with a bulk bandgap energy of 1.5 eV, have received increasing attention because they have a high extinction coefficient and good photostability [4,5]. In addition, they provide a wide range of photoluminescence (PL) emission from visible light to near infrared (NIR) region. As ternary CIS can tolerate off-stoichiometry, Cu-deficient or Cu-rich CIS can be stable. Due to the formation of interstitial atoms or vacancies in Cu-deficient or Cu-rich QDs, intrinsic defects can generate sub-band energy levels. Spectroscopic studies for CIS thin films concluded that these sub-band energy levels are responsible for the PL emission in CIS via the donor-acceptor pair (DAP) recombination [6–9]. The DAP recombination pathway can explain a broad PL spectrum, a larger Stokes shift, and longer PL lifetimes of CIS QDs compared to other II–VI QDs [5,10,11]. The main obstacle of the wide applicability of CIS QDs is a low photoluminescence quantum yield (PLQY). As a large portion of excitons in CIS QDs are dissipated via a non-radiative pathway, the minimization of non-radiative carrier losses is very important to increase the PLQY of CIS QDs. In particular, in CIS QDs, which have a larger surface-to-volume ratio than the bulk counterpart, surface defects act as a major non-radiative recombination center [12–14]. Therefore, the control of both intrinsic and surface defects of CIS QDs is required to obtain the spectrum tenability while maintaining a high PLQY.

Several groups observed significant improvement of the PLQY with the growth of a thin ZnS shell that can decrease surface defects. For instance, Park et al. reported the synthesis of 625 nm-emitting CIS/ZnS core/shell QDs with a PLQY of 65% [15]. Li et al. reported the synthesis of CIS QDs with a high chemical yield by a solvent-free heating-up method and showed a PLQY of 67% from 671 nm-emitting CIS/ZnS [12]. Improvement of a PLQY was also observed when the Cu-deficient defects were introduced by decreasing the Cu/In feeding ratio, though the emission was limited to the visible light range [16,17]. Recently, Choi et al. [18] reported the synthesis of 726 nm-emitting Cu-rich CIS/ZnS QDs with a PLQY of 64.7% [18]. However, the role of Cu-rich defects was not exactly identified. Therefore, it is still underway to find a synthetic method to obtain CIS-based QDs having a high PLQY in a wide range of spectra with well-defined PL kinetic study.

In this work, we investigated the effects of experimental factors in the solution synthesis of CIS/ZnS QDs on the PL properties and the PL kinetics underlying the non-stoichiometric QDs. An octadecene-free heating-up method was employed with dodecanethiol as a multi-functional agent, *i.e.*, a reaction medium, a sulfur source, and a surface capping ligand. Compositions were controlled simply by changing the Cu/In feeding ratio. The surface defects were also controlled by the amount of surface ligands and ZnS shell passivation. Additional In^{3+} ion precursor injection and controlling cooling rates after the synthesis of CIS QDs were also exampled as post-synthesis treatments.

2. Experimental section

2.1. Chemicals and materials

Copper iodide (CuI, trace metals basis, 99.999%), indium acetate ($In(Ac)_3$, trace metals basis, 99.99%), dodecanethiol (98%), zinc undecylenate (98%), octadecene (90%), and rhodamine 6G were purchased from Sigma–Aldrich (St. Louis, MO, USA). Methanol (99.5%) was purchased from Samchun Pure Chemical Co., Ltd (Pyeongtaek, Republic of Korea), ethanol (99.9%) from Daejung Chemicals & Metals Co., Ltd (Siheung, Republic of Korea), and chloroform (99%) from Junsei Chemical Co., Ltd. (Tokyo, Japan).

2.2. Synthesis of CIS/ZnS core-shell QDs

The CIS core QDs were synthesized using a heating up method. The precursor molar concentrations of Cu to In, [Cu/In], were 0.25 and 2.0. Both CuI and $In(Ac)_3$ were added to a 50 mL three-neck flask and dissolved in 20 mL dodecanethiol. The precursor solution was degassed under vacuum with vigorous stirring and subsequently heated to 70 °C. After 1 h, the solution was purged with argon gas (ultra high purity, 99.999%), and the temperature was subsequently raised to 180 °C at a rate of 10 °C min^{-1}. The reaction temperature was maintained for 8 h 30 min ([Cu/In] = 0.25) and 10 h ([Cu/In] = 2.0). To synthesize a ZnS shell, 1727 mg (4 mmol) of zinc undecylenate were dissolved in 8 mL octadecene. The mixture was degassed at room temperature for at least 30 min and refilled with argon gas. Zinc undecylenate mixture was subsequently injected in a dropwise manner at a rate of 2 mL min^{-1} into the suspension of CIS QDs at 180 °C. The temperature was subsequently raised to 200 °C and maintained for 10 h 30 min. After ZnS shell formation, a heating mantle was removed, and the solution was cooled at an ambient temperature. The average cooling rate from 200 °C to 60 °C was about 10 °C min^{-1}. To remove residual alkanethiol ligands, the obtained CIS/ZnS QDs solution was mixed with chloroform, and then mixed with methanol with 1:1 volume ratio. The mixture was centrifuge at 11,000 rcf (relative centrifugal force) for 5 min. The supernatant was discarded, and the precipitates were re-dispersed in chloroform.

2.3. Characterization

Absorption spectra of the synthesized QDs were measured using an UV–VIS spectrophotometer (UV-1800, Dong-il Shimadzu Corporation, Seoul, Republic of Korea). PL spectra were measured using an F-7000 fluorescence spectrophotometer (Hitachi High-technologies, Tokyo, Japan) with an excitation wavelength of 500 nm. The PLQY of QDs were determined using organic dye (rhodamine 6G) in ethanol as a reference [19–21]. Temperature-dependent PL spectra were measured using a LabRAM HR UV–VIS–NIR PL (Horiba Jobin Yvon, Longjumeau, France). The QD samples were prepared by drop-casting on a bare glass slide and mounted in a micro-objective cryostat with a controllable temperature range from 93 to 287 K and excited by the 514 nm line of a He–Ne laser. Size and structural characterization were obtained from transmission electron microscopy (TEM, JEOL JEM-3010, Tokyo, Japan) images at an acceleration voltage of 200 kV. Size distributions of QDs were obtained from TEM images by manually analyzing at least 100 individual QDs with ImageJ. The chemical compositions were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Agilent ICP-OES 720, Agilent, Santa Clara, USA).

3. Results and discussion

3.1. Synthesis of CIS/ZnS core/shell QDs

The synthetic procedures used for the CIS/ZnS QDs are schematically described in Fig. 1. Typically, CuI and $In(Ac)_3$ were mixed with dodecanethiol in a three-neck flask. After degassing and back-filling with argon gas, the mixture was subsequently heated to 70 °C. The metal ions, Cu^+ and In^{3+}, reacted with dodecanethiol to form transition metal-thiolate complexes at 70 °C [22]. When the temperature was increased to 180 °C, the metal-thiolate