



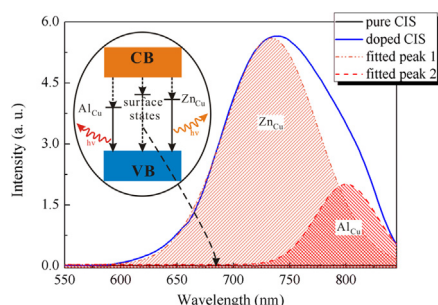
Deep-red emitting zinc and aluminium co-doped copper indium sulfide quantum dots for luminescent solar concentrators

Mingbei Zhu, Yunxia Li, Shouqin Tian*, Yi Xie, Xiujian Zhao, Xiao Gong*

State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, No. 122, Luoshi Road, Wuhan 430070, PR China

GRAPHICAL ABSTRACT

The obtained Zn and Al co-doped CIS QDs exhibited a good PL property emitting at ~ 740 nm compared to pure CIS QDs which was probably attributed to Zn_{Cu} and Al_{Cu} defects in the CIS QDs which could cause electron-hole radiative recombination via defect levels, reduce the number of dangling bonds and thus minimize the nonradiative recombination through surface electron trapping.



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ABSTRACT

Pure $CuInS_2$ quantum dots (CIS QDs) exhibited poor photoluminescent (PL) performance due to more dangling bonds on their surface and thus needed a shell to form core@shell structured QDs. However, conventional shells had a higher band gap than CIS QDs so that the core@shell structured QDs showed a blue-shifted PL peak below 700 nm and narrower light absorption range. Herein, Zn and Al co-doped CIS QDs were synthesized by a facile cation exchanged method which can significantly improve the PL property emitting at ~ 740 nm compared to pure CIS QDs. The enhancement of the PL property was probably attributed to Zn_{Cu} and Al_{Cu} defects in the CIS QDs which could cause electron-hole radiative recombination via defect levels, reduce the number of dangling bonds and thus minimize the nonradiative recombination through surface electron trapping. Furthermore, the PL intensity was controlled by doping time and reached the maximum at 30 min. The obtained deep-red emitting CIS QDs were employed to fabricate semi-transparent luminescent solar concentrators (LSCs) which exhibited an excellent optical efficiency of 6.97%. The success in using such Zn and Al co-doped CIS QDs could pave the way to realize high efficiency and environment-friendly LSCs for building integrated photovoltaics.

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* Corresponding authors.

E-mail addresses: tiansq@whut.edu.cn (S. Tian), xgong@whut.edu.cn (X. Gong).

1. Introduction

Semiconductor QDs have attracted extensive interest due to their unique physical and chemical properties [1,2]. Among a variety of semiconductor crystals, inorganic metal chalcogenide

especially has been intensively studied due to the potential applications in photoelectricity [3–6], photocatalysis [7–11], electrochemistry [12,13] and biomedicine [14,15]. Researchers have been making efforts to synthesize II–VI semiconductor nanoparticles such as CdS, CdSe and CdTe which have remarkable applications in solar cells and light-emitting diode because of their fluorescence properties, high fluorescence quantum yield and tunable emission wavelength [16–19]. Unfortunately, these QDs are usually composed of toxic compounds such as Cd and Pb which greatly limit their industrial applications [20–22]. In this sense, new metal chalcogenide without heavy metal as a class of non-toxic materials is anticipated to be developed in practical applications.

CIS QDs [23–26] with a direct band gap of 1.45 eV are emerging alternatives for the toxic conventional QDs due to their high extinction coefficient of light absorption, nontoxicity, environmentally friendliness as well as low cost. However, CIS QDs generally suffer from poor PL performance probably due to their abundant surface defects [27], leading to limited applications in practical devices. The surface defects including vacancies and dangling bonds can provide local sites for photo-excited electrons and holes [28]. This will cause nonradiative electron trap states, recombination of electrons with dark hole states or defect-induced donor-acceptor pair nonradiative recombination, and thus leading to poor PL performance [28–31]. In order to enhance the PL performance of CIS QDs, a protective shell is grown on the surface to form core/shell QDs. This approach can eliminate the surface defects by reducing the number of dangling bonds to improve the PL performance [3,32]. ZnS shells are widely used to eliminate surface trap states that induce a suppressed non-radiative recombination process. ZnS is a promising material as shells for coating CIS QDs because of its nontoxicity, chemical stability, smaller lattice mismatch between ZnS and CIS, and wide band gap to localize the charge carriers inside the core region [3,33]. In addition, metal doping is also an effective method to improve PL performance of CIS QDs because the doped metal elements such as Zn, Ga, Al can reduce the number of dangling bonds of chalcogen atoms on QD surface [28,34]. For example, Al doped CIS/ZnS core/shell QDs exhibit enhanced PL performance [35]. The element Al is supposed to be oxidized to Al_2O_3 , which can form a self-passivation layer and prevent photo-degradation of CIS QDs. However, in these cases, the PL shows an obvious blue shift from the starting CIS QD emission to 600–650 nm. The PL intensity for CIS QDs emitting above 700 nm is still relatively low, for which the origin is still under debate [29]. In addition, the light absorption range of core/shell CIS QDs will be narrowed obviously. Therefore, it is necessary to develop an effective method to enhance the PL performance of CIS QDs emitting above 700 nm.

In this work, **Zn and Al co-doped CIS QDs were successfully synthesized by a facile cation exchanged method and exhibited enhanced PL property emitting at ~740 nm compared to pure CIS QDs.** The obtained Zn and Al co-doped CIS QDs were determined by XRD, TEM, HRTEM and XPS characterizations. Moreover, their PL property could be controlled by adjusting the doping time. When the doping time was 30 min, the PL intensity reached the maximum. Luminescent solar concentrators (LSCs) [36,37] as a promising technology to significantly reduce the cost of photovoltaic (PV) energy have been intensively studied since they need only small areas covered by photovoltaic cells compared to traditional solar cells. To date, a variety of semiconductor quantum dots (QDs) have been employed in LSCs [36–38]. Here, we reported that our synthesized Zn and Al co-doped CIS QDs were able to be embedded in polymethyl methacrylate (PMMA) polymer film as phosphors for LSCs due to the good compatibility between them. Our results demonstrated that **the deep-red emitting CIS QDs**

can be effective fluorophores for high performance LSCs which makes the industrial applications of LSCs more feasible.

2. Experimental section

2.1. Materials

Dodecanethiol (DDT, 98%), copper iodide (99%), indium(III) acetate (99.99%), Octadecene (ODE, 90%), zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99%), oleylamine (OLA, 80–90%), acetone (99.5%), hexane (97%) were purchased from Sinopharm Chemical Reagent Co., Ltd; Aluminium isopropoxide (98%), *n*-butylamine (99%), Oleic acid (OA), methyl methacrylate (MMA, 99.0%), polymethyl methacrylate (PMMA, 99.0%) were purchased from Aladdin. Microscopy slides (float glass; supplied by Cito test Labware Manufacturing Co., Ltd., China) were used as substrates.

2.2. Synthesis of CIS QDs

Pure CIS QDs were prepared by one-pot synthesis of 0.4 mmol CuI, 0.4 mmol $\text{In}(\text{CH}_3\text{COO})_3$, 0.4 mL oleylamine, 2 mL DDT and 2 mL ODE, which were put together in a three-neck round-bottom flask under argon atmosphere. The molar ratio of Cu/In was 1:1, the volume ratio of oleylamine, DDT and ODE was 1:5:5. In addition, the volume of oleylamine was 1 mL corresponding to 1 mmol of CuI. The mixture was then heated to 120 °C under argon atmosphere, and magnetically stirred for 1 h. Afterwards, it was heated to 230 °C (the reaction temperature) for 15 min. Finally, the pure CIS QDs were cooled to room temperature immediately, diluted to 20 mL with octadecene.

2.3. Synthesis of Zn and Al co-doped CIS QDs

$\text{Zn}(\text{OA})_2$ precursor was synthesized by mixing 0.5 mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with 0.3 mL OA, 1.6 mL ODE and 0.1 mL *n*-butylamine in a three-neck round-bottom flask under argon atmosphere. The volume ratio of ODE, OA and *n*-butylamine were 16:3:1, and the volume of *n*-butylamine was 0.2 mL corresponding to 1 mmol of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The mixture was magnetically stirred at 120 °C in an inert atmosphere until it turned optically transparent. The mixture was stored at a temperature of 120 °C for subsequent injection.

Zn and Al co-doped CIS QDs were prepared as follows. Initially CIS solution was first evacuated for 30 min at 120 °C, and the reaction temperature was maintained at 230 °C under argon atmosphere. The precursor solution containing $\text{Zn}(\text{OA})_2$ and 1 mL DDT mixed with 0.25 mmol $\text{Al}(\text{IPA})_3$ (molar ratio of Al to Zn was 0.5:1), were continuously injected to the CIS solution through a syringe pump, respectively (the rate of the addition was 2 mL/s). The solution was finally cooled to room temperature, precipitated with acetone and then dispersed in hexane. The flowchart of the preparation of pure and doped CIS QDs is shown in Fig. 1. Herein, the effect of doping time in the structure and property of samples was also investigated. The obtained samples at the doping time of 30 min, 20 min and 10 min were named as doped CIS-30, doped CIS-20 and doped CIS-10, respectively.

2.4. Preparation of doped CIS-30/PMMA thinfilm LSCs with various thicknesses

Microscopy slides used as substrates were cut into dimensions $1.8 \times 1.8 \times 0.11 \text{ cm}^3$ and polished around the edges, and then cleaned with acetone, ethanol, deionized water and ethanol by ultrasonic cleaning for 30 min, respectively. A blend of 5 mL of

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