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The off-stoichiometry effect on the optical properties of water-soluble copper indium zinc sulfide quantum dots

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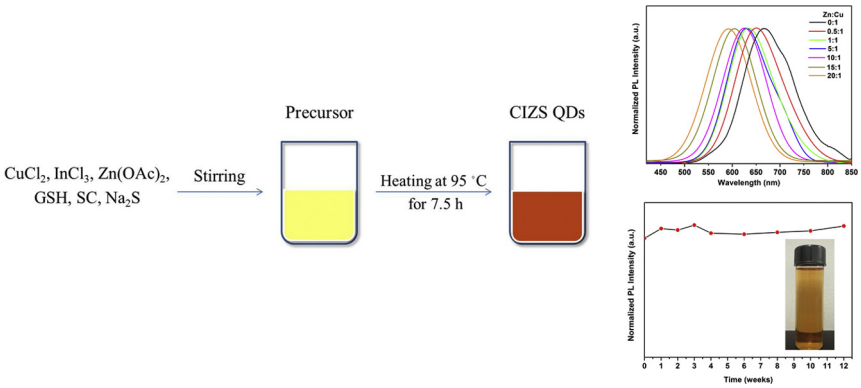
GRAPHICAL ABSTRACT



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ABSTRACT

Cu—In—Zn—S quantum dots (CIZS QDs) were prepared via reflux method in aqueous solution using $CuCl_2{\cdot}2H_2O$, $InCl_3{\cdot}4H_2O$, $Zn(OAc)_2{\cdot}2H_2O$ and $Na_2S{\cdot}9H_2O$ as raw materials, L-glutathione (GSH) and sodium citrate (SC) as stabilizing agents, respectively. The effects of off-stoichiometry (Cu/In and Zn/Cu ratios) on the crystal structure and morphology were systematically studied by means of X-ray diffraction (XRD) and high-resolution transmission electron microscope (HRTEM), and the relative optical properties were also investigated by absorption and fluorescence spectra. The as-prepared water-dispersible CIZS QDs were around 3–4 nm and possessed the tetragonal chalcopyrite crystal structure. The photoluminescence (PL) intensity of QDs was significantly increased with decreasing the Cu/In ratio. Compared with the Cu/In ratio variation, changing Zn/Cu ratio was an effective strategy to realize a more uniform irradiation and a wide range of emission wavelength tunability.

1. Introduction

Semiconductor QDs have attracted a great deal of attention due to their unique optical and electronic properties, which show a good prospective application such as solar cells [1], light emitting diode [2,3] and bio-labeling field [4]. II–VI and IV–VI QDs, such as CdS and PbS have been reported to have high photoluminescence quantum yield (PLQY). However, the inherent toxicity of heavy metal elements, i.e. cadmium, lead, etc., restricted their wide applications especially in the biological field [5]. More recently, I–III–VI semiconductor QDs (e.g., Cu—In—S, Ag—In—S, Cu—In—Se and Cu—Ga—S) were considered as promising

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alternatives to traditional II–VI QDs owing to their low toxicity, large stokes shifts and long photoluminescence lifetime [6,7]. Moreover, it was also reported that modification with ZnS (e.g. Zn diffusion or alloying with ZnS [8–11], ZnS overcoating [12–17]) to form Cu—In—Zn—S (CIZS) nanostructures is normally done to enhance the PL properties of Cu—In—S (CIS).

Although considerable progress was made recently, a great deal of reports still focused on the preparation and characterization of CIZS QDs via a variety of methods in organic media [10,11,14,18–20]. For instance, Zhang et al. prepared CIZS QDs by using acetate salts of the corresponding metals and sulfur powder in the presence of dodecanethiol (DDT) in octadecence (ODE) media at 230 °C, and the PLQY increased from 3% to 56% after coating ZnS shell [14]. Xiang et al. synthesized CIZS QDs via reaction between chloride salts of Cu, In and Zn in the presence of oleic acid and DDT in the non-coordinating solvent ODE at 170 °C, and an optimal PLQY of 46% was obtained by vary Cu/Zn ratios without any post-processing [10]. High quality CIZS QDs with a tunable amount of Cu deficiencies were also synthesized by Trizio et al. using a "two-step" method, ternary $Cu_{1-x}InS_2$ nanocrystals were obtained at first, Cu^+ and In^{3+} were subsequently replaced by Zn^{2+} at 210 °C, and the relative PLQY of CIZS QDs could be got a record 80% [11]. The above mentioned synthetic methods need trenchant experimental condition, i.e. high reaction temperature and inert atmosphere, and a large quantity of expensive organic solvent [21]. However, a promising and emerging approach to direct synthesis of water-soluble CIZS quaternary QDs is rare reported [4,22].

A general problem of synthesizing polynary QDs is the different chemical reactivity of diverse cations, which is critically important for avoiding phase separation. According to Pearson's hard-soft acid-base theory, Cu^+ is a soft acid, while In^{3+} is a hard acid [23]. The Cu^+ have a higher reactivity than In^{3+} due to the weak bonding strength between Cu^+ and carboxyl group, which indicates a secondary ligand containing thiols is necessary to decrease the reactivity of Cu^+ [12]. Hence, GSH (a soft base) and SC (a hard base) are served as dual ligands to impede phase separation.

In this study, we reported a facile synthetic approach to directly prepare CIZS QDs in aqueous media by using GSH and SC as dual stabilizers to balance the chemical reactivity among the three cations. The effect of composition on the optical properties of the QDs was systematically studied. Besides, PL decay curves were applied to analyze the photoluminescence mechanism of the CIZS QDs with different cation precursor ratios.

2. Experimental

All the chemical reagents used in this study were obtained from commercial sources as analytical-grade reagents, and used without further purification.

In a typical process, $CuCl_2{\cdot}2H_2O$, $InCl_3{\cdot}4H_2O$, $Zn(OAc)_2{\cdot}2H_2O$, GSH and SC were dissolved with deionized water in three-neck flask under stirring until a homogeneous solution (2.0 mM) was obtained. The molar ratio of SC to In^{3+} and Zn^{2+} was fixed at 5, and the molar ratio of GSH to Cu^{2+} was fixed at 20. The pH value was turned to 5.0 with 1.0 M NaOH solution. Afterwards, Na_2S stock solution was injected into the flask under stirring. Subsequently, the mixture was fast heated to 95 °C for 450 min. The reaction was quenched by cooling the solution to room temperature and isolated by adding isopropyl alcohol into the crude solution, and purified by centrifugation and decantation. Excess salts and ligands were completely removed by repeating this procedure two times.

The phase identification was studied with X-ray diffraction (XRD) by copper target Kα radiation (Bruker D8 Advance). Transmission electron microscopy images were obtained using high-resolution transmission electron microscope (HRTEM, JEM-2010) at an acceleration voltage of 200 kV. Energy dispersive X-ray spectroscopy (EDS) spectra were performed using a scanning electron microscope (Hitachi SU8010) equipped with IXRF systems. Fourier transform infrared (FT-IR) spectra were obtained on Nicolet 5700 infrared spectrometer. X-ray photoelectron spectra (XPS) of the sample were collected on PHI Quantera SXM spectrometer with the Mg radiation, and the charge referencing was done against the binding energy of adventitious carbon (C 1s = 284.6 eV). UV–vis absorption spectra were recorded by using UV–vis spectrometer (PerkinElmer Lambda850). Fluorescence spectra of QDs in water were obtained at room temperature with Hitachi F-7000 fluorescence spectrometer. The fluorescence lifetime was performed by an HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer, the excitation light was obtained from a 340 nm laser light. The relative PLQY was measured by using R6G as a standard reference (QY = 95%, in ethanol).

3. Results and discussion

Fig. 1 shows the XRD patterns of the prepared CIZS QDs with different Cu/In and Zn/Cu ratios. Three obvious diffraction peaks at 2θ = 27.9°, 46.2° and 55.1° are observed and assignable to the (112), (204) and (312) reflection lines of tetragonal chalcopyrite

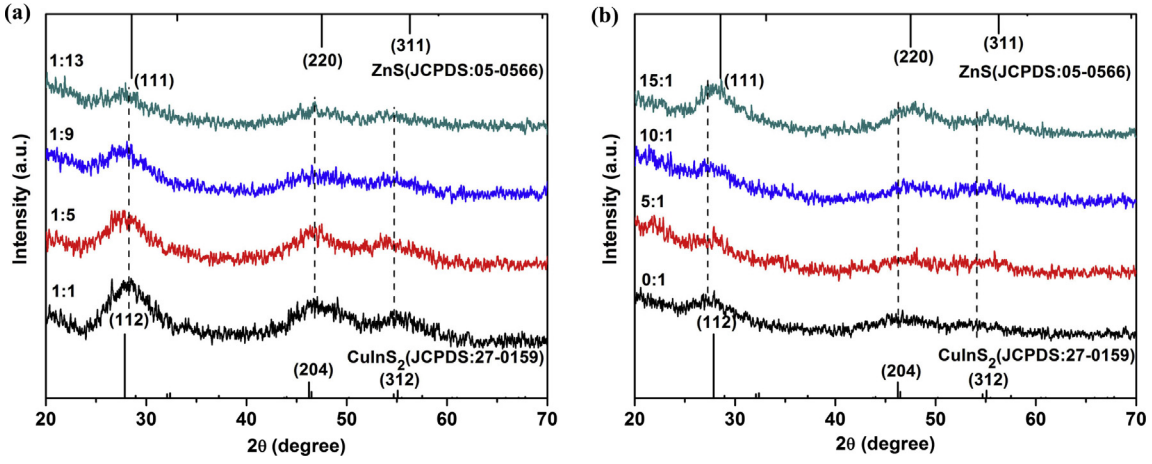

Fig. 1. X-ray diffraction patterns of CIZS QDs with different (a) Cu/In and (b) Zn/Cu ratios.