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 We reported temperature-dependent photoluminescence (PL) studies for Cu

Temperature-Dependent Photoluminescence of Cadmium-Free Cu-Zn-In-S Quantum Dot Thin Films as Temperature Probes

We reported temperature-dependent photoluminescence (PL) studies for Cu-Zn-In-S quantum dot (QD) thin films. In this paper, cadmium-free and luminescent Cu-Zn-In-S quantum dot thin films were in situ formed by thermal decomposition of molecular-based precursors in the open air, without need of the complicated quantum dot synthesis. Molecular-based precursor solutions were prepared by dissolving Cu₂O, ZnO, and In(OH)₃ in the ethanol solution of butylamine and carbon disulfide. The effects of sintering temperature, sintering time, and the concentration of capping agent on the photoluminescence properties of Cu-Zn-In-S QD thin films have been systematically investigated. It was found that alkali metal ions play an important role in enhancing PL quantum yield of quantum dot thin films. As-prepared QD thin films show composition-tunable emission in the range from 535 nm to 677 nm, and the absolute PL quantum yields can reach as high as 22.1%. All of as-deposited QD thin films show a single-exponential decay to temperature, indicating that these cadmium-free QD thin films have a high potential as the temperature probes.

Introduction

Quantum dot (QD) thin films have been widely used in the area of QD light emitting diodes,¹⁻⁵ QD solar cells,⁶⁻¹⁰ thin film transistors,¹¹⁻¹⁴ photo-detectors,^{15, 16} and temperature probes.^{17, 18} Therefore, the fabrication of QD thin films has attracted a great deal of attention in recent years.¹⁻¹⁸ Generally, QD thin films can be fabricated by two main methods. The first method involves the solution phase synthesis of QDs, post-purification, and coating QD solution.¹⁻¹⁸ This method requires the complicated synthesis and tedious purification process. Additionally, QD thin films can also be deposited *via* in-situ formation of quantum dots in the thin film.¹⁹⁻³⁰ In this approach, the QD thin films were directly formed by thermal decomposition of solution-deposited molecular-based precursor thin film. This method requires only the precursor and solvent; thus it is more facile and reproducible as compared to the first one.

Recently, Kim et al. fabricated CdS QD thin film by spin-coating a $L_2Cd(S(CO)CH_3)_2$ (L=3,5-lutidine) precursor solution, followed by a sintering process.¹⁹ In addition, CdSe quantum dot thin film with a PL quantum yield of 7.5% was prepared by thermal decomposition of a

+ Footnotes relating to the title and/or authors should appear here.

single-source precursor.²⁰ Very recently, we developed a molecularbased precursor solution approach to deposit Cu-doped Zn_xCd_{1-x}S Q⁻ luminescent thin films with a PL quantum yield of 25.5%.²¹ However, these cadmium-based QD thin films will be limited in real-world applications owing to the toxicity of cadmium. In recent years, cadmium-free QDs, such as CuInS₂ and AgInS₂ QDs, have attracted much research interests due to their low toxicity and high PL quantum yields.³¹⁻³⁷ However, the synthesis of cadmium-free ternary QDs is far more difficult than that of cadmium-based bina.y quantum dots. Recently, CuInS₂ quantum dot thin films have been directly fabricated by a single-step solution approach.²²⁻²⁵ Nevertheless, no photoluminescence was detected for these CuInS₂ quantum dot thin films. Although cadmium-free and luminescent Cu-Zn-In-S QDs have been extensively synthesized in the solution, ³¹⁻³⁷ little work has been performed on the direct deposition of luminescent Cu-Zn-In-S QD thin films by a molecular-based precursor solution approach.

In this paper, we developed a facile solution approach to fabricate luminescent Cu-Zn-In-S QD thin film by spin-casting the mixed Cu, Z n, and In precursor solution. Cu₂O, ZnO, and In(OH)₃ were used as the starting materials and were dissolved in the ethanol solution of carbon disulfide and 1-butylamine, and 3-mercaptopropionic acid was used as the capping agent. As-deposited quantum dot thin films exhibit composition-tunable emission in the range from 535 nm to 677 nm and the absolute photoluminescence quantum yield ca... reach as high as 22.1%. To the best of our knowledge, this is the first report of using molecular-based precursor solution for direct fabrication of luminescent Cu-Zn-In-S QD thin film, which omits th complicated and tedious QD synthesis.

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Electronic Supplementary Information (ESI) available: [Effects of LiOH, NaOH, KOH, and TMAH on PL spectra and PL intensity of Cu-Zn-In-S QD thin films. TEM image, EDS spectra and chemical compositions of Cu-Zn-In-S QD thin films. Temperaturedependent PL spectra of Cu-Zn-In-S QD thin films with different Cu/Zn/In ratios.] See DOI: 10.1039/x0xx00000x

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Experimental

Chemicals

Copper (I) oxide (Cu₂O, 99%), zinc oxide (ZnO, 99.99%), indium hydroxide (In(OH)₃, 99.99%), carbon disulfide (CS₂, 99.9%), 1butylamine (CH₃(CH₂)₃NH₂, 99%), ethanol (CH₃CH₂OH, AR), sodium (I) hydroxide (NaOH, AR), lithium (I) hydroxide (LiOH, 98%), potassium (I) hydroxide (KOH, AR), tetramethylammonium hydroxide (TMAH, 98%), and 3-mercaptopropionic acid (MPA, HSCH₂CH₂COOH, 98%) were purchased from Aladdin Inc. All chemicals were used as received.

Preparation of a series of precursor solutions

First, 4.0 mL of ethanol, 2.0 mL of 1-butylamine (20 mmol) and 1.2 mL of CS_2 (20 mmol) were mixed in a 25 mL conical flask on a magnetic hotplate stirrer at room temperature. Such solution was prepared in seven flasks. Afterward, Cu_2O (0.14 g, 1.0 mmol), ZnO (0.16 g, 2.0 mmol), $In(OH)_3$ (0.33 g, 2.0 mmol), NaOH (0.20 g, 5.0 mmol), LiOH (0.12 g, 5.0 mmol), KOH (0.28 g, 5.0 mmol), or TMAH (0.90 g, 5.0 mmol) was respectively loaded into each flask. Next, the hotplate temperature was increased to 60 °C until all the solid has dissolved completely. Finally, the precursor solutions were centrifuged at 12000 rpm for 5 min before spin-casting process.

Fabrication of Luminescent Cu-Zn-In-S QD Thin Films

In a typical deposition of Cu-Zn-In-S QD thin film with a Cu/Zn/In ratio of 1:10:10, 200 μ L (0.056 mmol) of Zn stock solution, 200 μ L (0.056 mmol) of In stock solution, 20 μ L (0.0056 mmol) of Cu stock solution, 70 μ L (0.048 mmol) of LiOH stock solution, and 60 μ L (0.68 mmol) of MPA were mixed. Luminescent Cu-Zn-In-S QD thin film was obtained by spin-casting the mixed precursor solution on a glass slide (20×20×0.5 mm) at 3000 rpm for 30 s, followed by a sintering process on a pre-heated hot plate at 240 °C for 30 s in the open air. Finally, the quantum dot thin film with a thickness of around 120 nm was obtained.

Characterizations

UV-vis-NIR diffuse reflectance spectra were measured by a Shimadzu UV-3600 spectrometer. PL spectra were recorded on a Hitachi F-7000 spectrophotometer, and the PL intensity was calculated by integration of ΡL spectrum. Absolute photoluminescence quantum yields (QYs) were measured by an absolute PL quantum yield measurement system (C9920-02, Hamamatsu) equipped with an integrating sphere. The PL decay curves were recorded with a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) equipped with a tunable laser (pulse width ¼ 4 ns, gate ¼ 50 ns) as the excitation source (Continuum Sunlite OPO), and the average PL lifetime was obtained by integration of PL decay curve. The XRD patterns were recorded using a Bruker D8 FOCUS Xray diffractometer. The chemical compositions of the samples were measured by energy dispersive spectroscopy (EDS), which were recorded by using a scanning electron microscope (Hitachi S-4800). The thin film thickness was measured by a XP-100 profilometer (AMBIOS). Atomic force microscope (AFM) image was taken on a Bruker Dimension Icon. The temperature dependent PL spectra were monitored by a Maya 2000 Pro CCD-based fiber optic spectrometer (Ocean Optics Inc.) in air, and the temperature was programmed to increase from 20 °C to 240 °C.

Recently, we developed a general molecular-based precursor solution approach for the direct deposition of CuInS₂, Cu(In,Ga)S₂ Cu₂ZnSnS₄, and Cu₂CdSnS₄ nanocrystal thin films.²⁵⁻²⁸ These molecular-based precursor solutions were prepared by dissolving metal oxides or metal hydroxides in the ethanol solution of butylamine and carbon disulfide. Figure 1A shows the dissolution mechanism of Cu₂O, ZnO, and In(OH)₃ in butylamine and carbon disulfide. As can be seen in Fig. 1B, the clear and transparent Cu, Zn, In and Li precursor solutions can be obtained. Cu-Zn-In-S quantum dot thin films were in-situ formed by spin-coating the mixed Cu, Zn, and In precursor solution, followed by a sintering process. 3-Mercaptopropionic acid was used as a capping agent to control the size of quantum dots in the thin films and passivate the surface defects. By varying Cu/Zn/In ratios, a series of luminescent Cu-Zn-In S quantum dot thin films can be fabricated, as shown in Fig. 1C and Fig. 1D.

In this paper, the effect of the sintering temperature on PL intensity of Cu-Zn-In-S QD thin films was first investigated while keeping all the other experimental conditions the same (Cu/Zn/In=1:10:10). As the sintering temperatures increase from 200 °C to 240 °C, a large enhancement in PL intensity was observed because of improved crystalline quality. A further increase of the sintering temperature beyond 250 °C will cause a dramatic decrease in the PL intensity, perhaps due to thermal decomposition of MPA at high temperature. It was found that PL intensity of QD thin film shows a maximum value at sintering temperature of 240 °C, as shown in Figure 2A and 2B. Thus, we chose 240 °C as the sintering temperature to investigate the effect of the sintering time on PL intensity. As can be seen in Figure 2C and 2D, it was revealed that the optimal sintering time is 30 s. Therefore, the optimal sintering conditions were achieved at 240 °C for 30 s. Finally, we investigated the effect of the capping agent on PL intensity of QD thin films by adding different amounts of MPA into precursor solution, as shown in Figure 2E and 2F. The capping agent plays a critical role in the formation of QDs. Besides controlling the size of QDs, the capping agent also simultaneously reduces the surface trap states of QDs, which will lead to a significant enhancement in PL intensity. No photoluminescence was observed for Cu-Zn-In-S thin films without using MPA. However, when the amount of capping agent exceeds,



Figure 1. (A) Dissolution mechanism of Cu_2O , ZnO, and $In(OH)_3$ in butylamine and carbon disulfide; (B) a digital photograph of Cu, Zn, In, and Li precursc. solutions; digital photographs of luminescent Cu-Zn-In-S QD thin films with different Cu/Zn/In ratios under UV light (C) and daylight (D) illumination. Journal Name ARTICLE



Figure 2. Effects of the sintering temperature (A and B), the sintering time (C and D), and the ratio of (Cu+Zn+In)/MPA (E and F) on PL spectra and PL intensity of Cu-Zn-In-S QD thin films with a Cu/Zn/In ratio of 1:10:10.

PL intensity of QD thin film starts to decrease, and the optimal ratio of (Cu+Zn+In)/MPA was found to be 1/5.78 for fabricating highly luminescent Cu-Zn-In-S QD thin films. Thereby, in this paper, the optimal sintering temperature and the sintering time as well as the optimal ratio of (Cu+Zn+In)/MPA are 240 °C, 30 s and 1/5.78, respectively.

To further enhance the PL intensity of Cu-Zn-In-S QD thin films, Li⁺, Na⁺, and K⁺ ions were incorporated into Cu-Zn-In-S QD thin films. According to previous reports, the surface defects of QDs play a key role in the photoluminescence of Cu-Zn-In-S QDs.^{38,39} Passivating the surface-related defects are beneficial for increasing the radiative recombination probability, which will result in an enhancement of PL intensity. Previous studies showed that the incorporation of Na⁺ and K⁺ ions can effectively passivate the surface defects of Cu(In,Ga)(S,Se)₂ and $Cu_2Zn(S,Se)_4$ thin films.⁴⁰⁻⁴² Thus, it was expected to improve the PL intensity of Cu-Zn-In-S QD thin films by incorporating Li⁺, Na^{\dagger} , and K^{\dagger} ions. Figure 3A shows the effects of LiOH, NaOH, KOH, and TMAH on PL intensity of Cu-Zn-In-S QD thin films. A massive enhancement in PL intensity was observed for Li-, Na-, or K-doped Cu-Zn-In-S QD thin film, whereas the PL intensity was decreased when adding TMAH, indicating that the enhancement of PL intensity is purely attributed to the effect of Li^{\dagger} , Na^{\dagger} , and K^{\dagger} ions. It is also observed that the





greatest enhancement in PL intensity was obtained for Li-doped Cu-Zn-In-S QD thin film, probably due to the smaller radius of Li⁺ ion. with respect to those of Na⁺ and K⁺ ions. The detailed effects the amount of LiOH, NaOH, KOH, and TMAH on PL spectra and PL intensity of Cu-Zn-In-S QD thin films are shown in Figure S1 (see ESI). It was revealed that the optimal amount of LiOH is 70 μ L. Figure 3B compares PL decay curve of pristine Cu-Zn-In-S QD thin film with those of Li⁺-, Na⁺-, and K⁺-doped Cu-Zn-In-S QD thin films. All of then exhibit bi-exponential decays with a shorter fluorescence lifetime resulting from band-band transition and a longer fluorescence lifetime due to donor-acceptor transition. Similar to PL intensity, the average fluorescence lifetime also exhibits an increasing trend in the sequence of KOH<NaOH<LiOH. Therefore, PL intensity and PL lifetime of Cu-Zn-In-S QD thin film can be significantly improved by incorporating alkali metal ions.

After optimizing PL properties of luminescent QD thin films, Cu-Zn-In-S QD thin films with different Cu/Zn/In ratios were fabricated by varying Cu, Zn, and In precursor ratios. According to previous reports. the band gaps of quaternary Cu-Zn-In-S QDs are strongly dependent on their compositions.^{31-37, 43} Their optical band gaps increase with increasing Zn content. Thus, the emission color of Cu-Zn-In-S QD thin films can be tuned by changing the molar ratio of Cu/Zn/In. Figure 4A and 4B display a series of absorption spectra and PL spectra c. Cu-Zn-In-S QD thin films with different Cu/Zn/In ratios. As expected, a continuous red shift in absorption spectra and PL spectra of Cu-Zn-In-S QD thin films was observed while increasing Cu and In contents. By changing Cu/Zn/In ratios, a tunable PL emission peak in the range from 535 nm to 677 nm was achieved, as shown the Fig. 4B. In addition, it was found that the PL quantum yield is inversely related on the Cu contents (see Figure 4C). The maximum fluorescence quantum yield can reach 22.1% when Cu/Zn/In ratio is 1:11:9.

The crystal structure of Cu-Zn-In-S QD thin films was investigated by XRD. As can be seen in Figure 5, all of Cu-Zn-In-S QD thin films exhibit three broad characteristic diffraction peaks of the zincblende structure. In a unit cell of zincblende, Cu⁺, Zn²⁺, and In³⁺ ions occupy the same position and have a random distribution; thus, the Cu/Zn/In ratios can be tuned in a wide composition range.^{43, 44} Increasing Zn content in Cu-Zn-In-S QD thin films causes a successivshift of XRD patterns towards higher 20 angle, indicating that the smaller Zn²⁺ ions have been successfully incorporated in Cu-Zn-In-S QD thin films. In addition, XRD patterns revealed the absence of other crystalline impurities in our thin films, such as Cu₂S, ARTICLE



Figure 4. A series of absorption spectra derived from diffuse reflectance spectra with Kubelka-Munk function (A), PL spectra (B), and absolute PLQYs (C) of Cu-Zn-In-S QD thin films with different Cu/Zn/In ratios.

CuS, In_2S_3 , and ZnS, confirming that homogeneous Cu-Zn-In-S QD thin films were achieved. Average particle sizes of Cu-Zn-In-S QD thin films calculated by Scherrer equation are 2.7-3.2 nm, which are dependent on their compositions. At the same time, we measured the high-resolution TEM image of Cu-Zn-In-S QD thin film with a Cu/Zn/In ratio of 1:10:10 (see Figure S2). The QDs have an average diameter of 3.4, close to the size calculated from XRD pattern.

The surface morphology and surface roughness of Cu-Zn-In-S QD thin film with a Cu/Zn/In ratio of 1:10:10 were measured by AFM. Figure 6 shows a typical AFM characterization of the Cu-Zn-In-S QD thin film. The root mean square surface roughness is 0.87 nm, which is lower than those of quantum dot thin films which were deposited from quantum dot solution.¹ Smooth quantum dot thin films are critically important to their device applications. Additionally, EDS was conducted to determine the Cu/Zn/In/S ratio in Cu-Zn-In-S QD thin films, and the results were presented in Figure S3. It was confirmed that the actual Cu/Zn/In ratios in these Cu-Zn-In-S QD thin films were very close to the feeding ratios in the precursor solutions.



Figure 5. XRD patterns of Cu-Zn-In-S QD thin films with different Cu/Zn/In ratios.



Figure 6. AFM image (A) of Cu-Zn-In-S QD thin film, the line-scan profile (B), and the pseudo-three-dimensional image (C).

The temperature-dependent PL properties of QD thin films were investigated. The PL spectra of Cu-Zn-In-S QD thin films with different Cu/Zn/In ratios were tested at a temperature range from 20 °C to 240 °C in air, as shown in Figure S4. Their temperaturedependent PL spectra were integrated and are shown in Figure 7. It was observed that PL peak positions show only a slight red shift of about 5 nm when the temperature increases from 20 °C to 240 °C, whereas the PL intensities of all of Cu-Zn-In-S QD thin films exhibit a single exponential decay profile as the temperature increases. No that the thermal quenching of the PL intensity and red-shifted PL peak are commonly observed for quantum dots in the literature.^{17, 18} In addition, the thermal stability of Cu-Zn-In-S QD thin film with a Cu/Zn/In ratio of 1:10:10 was measured under different heating/cooling cycles. It was found that the relationship between the PL intensity (I) and temperature (T) are almost the same during heating/cooling thermal cycles, especially in the temperature range of 60-200 °C, which can be well fitted with a single-exponential function: I(T)=8.0E6×exp(-T/60.5)+2.86E6. This result suggested that our Cu-Zn-In-S QD thin films can be used as the temperature indicators. Besides, because our as-prepared Cu-Zn-In-S QD thin films show good thermal stability in air, the Cu-Zn-In-S QD thin films are also suitable for some special high-temperature applications, such as solid-state lighting, lasers, and quantum dot LEDs.





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Figure 8. Temperature-dependent PL intensity of Cu-Zn-In-S QD thin film with a Cu/Zn/In ratio of 1:10:10 under different heating/cooling cycles.

Conclusions

In summary, luminescent and cadmium-free Cu-Zn-In-S QD thin films have been directly fabricated via a facile molecular-based solution approach using Cu₂O, ZnO, In(OH)₃, butylamine, and carbon disulfide as the starting materials. This approach requires only the precursor, solvent and capping agent, which omits the complicated and tedious synthesis process. Additionally, all the experimental procedures were conducted in the open air without the need of inert atmosphere. Asdeposited Cu-Zn-In-S QD thin films exhibit a compositiontunable PL emission in the range from 535 nm to 646 nm by simply varying the Cu/Zn/In ratios, and the highest PL QY can reach 22.1%. When added with alkali metal ions, the PL intensity of Cu-Zn-In-S QD thin film was noticeably increased. This finding could be applied in the traditional solution phase synthesis of Cu-Zn-In-S QDs to further improve their luminescence. Furthermore, the temperature-dependent PL properties of Cu-Zn-In-S QD thin films have been investigated, and the relationship between the PL intensity and the temperature has been measured, indicating that Cu-Zn-In-S QD thin films have a high potential as temperature indicators.

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Graphical Abstract

Cadmium-free and luminescent Cu-Zn-In-S quantum dot thin films were in situ deposited by thermal decomposition of molecular-based precursors in the open air, without need of the complicated quantum dot synthesis.

