Facile synthesis of nano-sized $\text{CuFe}_2\text{S}_3$: morphology and diverse functional tuning and crystal growth mechanism exploring

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Received 8 January 2017; revised 20 February 2017; accepted on 2 March 2017

Abstract

Ternary chalcogenide compounds are such promising and have been used for much practical applications. As a sort of these compounds, cubanite ($\text{CuFe}_2\text{S}_3$) possess some unique properties which can be used in different fields. In our study, we developed a facile one pot synthesis of $\text{CuFe}_2\text{S}_3$ nanocrystals (NCs) at a low reaction temperature, and achieved a morphology and phase composition tuning of the NCs through changing a variety of precursors and surfactants, meanwhile improved their magnetism and optical properties. Eventually, well-ordered and ‘nano-brick’ like $\text{CuFe}_2\text{S}_3$ NCs were obtained and showed best magnetism and near-infrared fluorescence properties. Furthermore, the NCs were proved with good biocompatibility and possibility for cell labeling. This kind of materials with lower toxicity and potential of magnetic is bound to remedy the defects of photoluminescence quantum dots (QDs) and be with higher potential in the field of biological diagnosis and multi-functional system construction.

Keywords: nanobiomaterials; materials synthesize

Introduction

Ternary chalcogenide compounds have attracted an extensive attention owe to their unique physical and chemical properties, such as magnetism and photoelectric properties [1–7]. Furthermore, with near-infrared fluorescence and low toxicity, ternary luminescence nano-materials also have shown great potential as an alternative to the traditional binary quantum dots in the field of bioimaging and multifunctional system construction [8,9]. Among them, ternary copper iron sulfide compounds such as chalcopyrite and cubanite ($\text{CuFe}_2\text{S}_3$) are unique candidates, owing to their good biocompatibility and magnetism potential. However, to the best of our knowledge, the majority of former reports usually focus on the crystal and electronic structure of chalcopyrite and only a few reports referred the synthesis of $\text{CuFe}_2\text{S}_3$ [10–13].

Natural mineral $\text{CuFe}_2\text{S}_3$ has been acknowledged to be with orthorhombic structure [14–16], in which the cations are tetrahedrally coordinated by S atoms, forming an approximately hexagonal packing. The $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions share the adjacent edges of tetrahedral and there is a rapid electron transfer between them [17,18]. However, in the previous reports, it has been proven that the $\text{CuFe}_2\text{S}_3$ will transform to a cubic form at high temperature [19–21]. The crystal structure of this cubic $\text{CuFe}_2\text{S}_3$ is based on a cubic close-packed matrix of sulfur atoms, wherein the metal atoms are located in the tetrahedral interstices, furthermore, the ferrous, iron and cuprous ions are randomly distributed on these cation sites [15,20]. This special structure endows cubic $\text{CuFe}_2\text{S}_3$ with unique photoelectricity and magnetic properties, which play a crucial role in biological application. However, most of the existed reports on $\text{CuFe}_2\text{S}_3$ are about crystal in...
bulk, either using naturally existing or synthetic single crystal or polycrystalline compounds. There have been very few studies on the synthesis and characterization of nano-sized crystalline CuFe₂S₃. More studies are further needed to investigate not only the synthesis but also the modulation of CuFe₂S₃ crystal morphology, luminescence and magnetic properties. In most cases, the synthesis of CuFe₂S₃ usually needs strict condition with a high temperature exceeding 200°C. Therefore, it is a challenge to develop a facile and mild strategy for fabricating nano-sized CuFe₂S₃ under laboratory conditions and study their prospect in biological application.

In this study, CuFe₂S₃ NCs with uniform and small size, as well as magnetism and near-infrared fluorescence properties would be prepared. A facile and mild strategy to fabricate CuFe₂S₃ NCs under a lower reaction temperature (180°C) was developed. Meanwhile, the morphology and physical properties of these NCs have been finely modulated by changing the reactants. Furthermore, cubic CuFe₂S₃ NCs with magnetism and near-infrared fluorescence properties showed great potential application on cell labeling. Our work is bound to encourage further exploration in the synthesis of nano-sized CuFe₂S₃ under laboratory conditions and expand their multifunctional application in the biological field.

**Experimental**

**Reagents and materials**

Iron (III) chloride hexahydrate (FeCl₃·6H₂O, ACS), iron(III) acetylacetone [Fe(acac)₃], 98%, copper (II) chloride dihydrate (CuCl₂·2H₂O, 99.99%), copper(II) acetylacetone [Cu(acac)₂], 97%, 1-dodecanethiol (DT, 98.0%), sodium diethyldithiocarbamate trihydrate (DDTC, 99.0%), thiourea (CH₄N₂S, 99.0%), oleylamine (OAM, 80-90%) and 1-octadecene (ODE, >90.0%) were purchased from Shanghai Aladdin Industrial Corporation, China. Oleic acid (OA, >85.0%) were purchased from Tokyo Chemical Industry Co. Absolute ethanol was purchased from Kelong Chemical Reagent Factory, China.

**Synthesis of CuFe₂S₃ nanocrystals (CuFe₂S₃ NCs)**

CuFe₂S₃ NCs were prepared through a one pot method. The device diagram of experimentation is shown in Fig. 1. For a typical synthesis, 0.1705 g CuCl₂·2H₂O and 0.2703 g FeCl₃·6H₂O were added into a mixture of 12 ml OA and 18 ml DT in a 100 ml three-necked round-bottom flask. The flask was put into a constant temperature heating magnetic stirrer with oil bath heating (140°C) under N₂ flow until reactants were fully dissolved. The S-precursor suspension was freshly prepared by mixing 0.1522 g of thiourea with 6 ml of DT under magnetic stirring and preheated to 100°C. Next, the S-precursor solution was transferred into a syringe (equipped with a large needle) and injected quickly into the flask at 140°C. The temperature of mixture was further quickly raised to 180°C and kept for 15 min. To terminate the reaction, the flask was quickly transferred to a cold-water bath. The resulting nanocrystals were separated from the dispersion solution by centrifugation (4000 rpm, 5 min) and washed by ethanol for several times to remove the impurities. The obtained products were dispersed in absolute ethanol for further characterization.

In order to achieve the structure and morphology modulation, and further optimize the luminescence and magnetism properties of CuFe₂S₃ NCs, different iron and copper precursors, sulfur sources and surfactants were chosen in the following experiments. The detailed preparation conditions are shown in Table 1.

**Material characterization**

X-ray diffraction (XRD): The prepared samples were dried in a drying oven under 70°C, and the crystalline structure were measured on an X-ray diffractometer (Panalytical Empyrean), at 45 kV and 40 mA, for monochromatized Cu Kα (λ = 1.5418 Å) radiation.

Raman spectra (RM): The Raman spectrum of dry sample was recorded on a Confocal Laser MicroRaman Spectrometer (LABRAM-HR) with 514.5 nm radiations from a 10 mW argon ion laser at room temperature.

X-ray photoelectron spectroscopy (XPS): The samples were redispersed in absolute ethanol with a sufficient ultrasonic oscillating, then dropped on a silicon slice. The XPS measurements were carried out on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al Ka X-ray source.

Transmission electron microscope (TEM): The samples were redispersed in absolute ethanol under sufficient ultrasonic oscillating, then dropped on a copper net coating with a carbon film. The morphology and microstructure of CuFe₂S₃ NCs were monitored using high-resolution transmission electron microscopy (HRTEM) on TecnaiG2F20S-TWIN microscope at 200 kV.

Magnetism measurement: The magnetic measurements of dry CuFe₂S₃ NCs were performed by using a superconducting quantum interference magnetometer (MPMS-XL-7, Quantum Design) at both room temperature (300 K) and low temperature (3 K).

Photoluminescence characterization: The samples were dispersed in absolute ethanol with a sufficient ultrasonic oscillating, then 1 ml of the solution was taken. The fluorescence emission of CuFe₂S₃ NCs was collected by using a fluorescence spectrometer (F-7000, Hitachi), using an emission wavelength at 500 nm.

**Potential application of CuFe₂S₃ NCs**

Cytotoxicity study: The cytotoxicity of CuFe₂S₃ NCs against human osteosarcoma cell line MG63 cells was studied using standard methyl thiazolyltetrazolium (MTT, Sigma Aldrich) assay. MG63 cells were dispensed onto a 24-well plate at a density of 1 × 10⁴ cells per well. After culturing 24 h for cell attachment, the media were taken out from the wells, followed by washing three times with PBS, and then incubated with various concentrations of CuFe₂S₃ NCs (30, 90 and 150 μg/ml.). After further incubation for 1, 3 and 5 d, the solutions were changed with fresh DMEM culture medium, cell viability was studied by standard methyl thiazolyltetrazolium assay.

Cell labeling: The cell-labeling capacity of CuFe₂S₃ NCs was investigated as follows: MG63 cells were seeded onto a 24-well plate at a density of 3 × 10⁴ cells per well in a 24-well plate, and cultured in the culture box (CO₂ 5%, 37°C) for 24 h before adding the NCs. After cell attachment, the media were taken out from the wells, followed by washing three times with PBS. Cells were then incubated with CuFe₂S₃ NCs at a certain concentration (150 μg/ml.) for 30 min. After cells were washed carefully using PBS to wipe off uninternalized nanoparticles and incubated for another 30 min, a confocal laser scanning microscopy (CLSM; LeicaSP5, Leica Microsystems, Germany) was acquired for cell imaging.

**Results**

**Phase and chemical characterization**

The phase composition of the samples was examined using XRD. As shown in Fig. 2a, the XRD spectra of S1, S2 and S3 have almost similar diffraction patterns which are corresponded to the orthorhombic CuFe₂S₃ (ICDD card, No. 65-1323), indicating the fabrication
of relatively pure CuFe$_2$S$_3$ NCs with an orthorhombic structure by our facile and mild method. The sharp peaks and low background observed in S2 and S3 suggest a higher crystallinity of S2 and S3 than that of S1 with relative diffusion background. Contrarily, S4 and S5 show three different intense peaks at 2$\theta$ = 29.2°, 48.6° and 58.7° which are attributed to the cubic CuFe$_2$S$_3$ phase, oriented along the [111], [220] and [311] crystal planes, respectively [16]. These results indicate the successfully synthesis of cubic CuFe$_2$S$_3$ NCs, according to the standard spectra of cubic CuFe$_2$S$_3$ (ICDD card, No. 81-1378). Furthermore, compared with S1–S3, S4 and S5 presented relative disordered peaks which reveal a relative low crystalline of the samples, meanwhile S5 was with higher crystallinity than S1. Furthermore, Fig. 3d and e shows that S4 and S5 have completely different crystal morphology in comparison with S1–S3. For S4, a mixed crystal morphology of spherical and ‘brick’ ones are presented. The diameter of spherical one is about 7 nm, while size of brick-like crystal is about 20 nm. The HRTEM imagine in Fig. 3d reveals that part of the lattice fringes of crystals could be observed. The brick-like ones have a better sharp fringe, and their crystal parameters are coincided with the cubic CuFe$_2$S$_3$ as well. In addition, for S5, all the NCs are of the shape of ‘brick’ and self-assemble in a certain orientation (Fig. 3e). These monodispersed nano-bricks are of 4 nm width and 8 nm length, and the distance between the nano-bricks are nearly the same about 2–3 nm. The enlarge scale of Fig. 3e clearly shows that each nano-brick has uniform morphology and good monodispersity. The lattice fringes of the crystals can be clearly seen with a lattice space about 3.05 Å between two adjacent lattice planes, which is consistent with the (111) plane (Fig. 3f) of cubic CuFe$_2$S$_3$ NCs, indicating that the crystallinity of S5 is much higher than S4.

Crystal morphology characterization

Figure 3 displays the HRTEM images of the NCs of S1–S5, and insert maps show the enlarged images accordingly. As the images illustrate, the crystal morphology of samples varied from spherical to ‘brick’ like with the varying of the reaction precursors and surfactants from S1 to S5. Generally, the crystals of S1, S2 and S3 are all spherical-like nanocrystals with the average crystal sizes about 3, 4 and 4 nm, respectively [22,23]. These parameters almost coincide with the Fe$^{2+}$ and Fe$^{3+}$ surface species in the previous reports [22,23].

Table 1. The synthesis of CuFe$_2$S$_3$ nanocrystals

| Method | Reactant | Solvent | S source | Temperature (°C) |
|--------|----------|---------|----------|-----------------|
| S1     | Cu$_{II}$(acac)$_2$ | OA + DT | DDTC     | 140 – 180       |
|        | Fe$_{III}$(acac)$_3$ |         |          |                 |
| S2     | Cu$_{II}$(acac)$_2$ | OA + ODE | Thiourea | 140 – 180       |
|        | Fe$_{III}$(acac)$_3$| + OAM   |          |                 |
| S3     | CuCl$_2$2H$_2$O  | OA + ODE | Thiourea | 140 – 180       |
|        | FeCl$_3$6H$_2$O  | + OAM   |          |                 |
| S4     | CuCl$_2$2H$_2$O  | OA + DT  | Thiourea | 90 – 180        |
|        | FeCl$_3$6H$_2$O  |         |          |                 |
| S5     | CuCl$_2$2H$_2$O  | OA + DT  | Thiourea | 140 – 180       |
|        | FeCl$_3$6H$_2$O  |         |          |                 |
Magnetic characteristics of the CuFe₂S₃ NCs
The magnetism of the NCs was characterized by a superconducting quantum interference magnetometer, and the field-dependence magnetization curves M(H) are shown in Fig. 4. Under room temperature, all the NCs showed no magnetism (so that the data not shown here). Figure 4a–e shows the magnetization curves at 3 K of S1–S5, and the obvious coercivity could be observed in all the NCs, indicating the well magnetic property of CuFe₂S₃ NCs at low temperature. Furthermore, S4 and S5 show relatively higher magnetism than S1–S3, while S5 has the highest magnetism. These results indicate that the magnetism of CuFe₂S₃ NCs is dependent on the temperature. At low temperature, the whole NCs we synthesized possess the magnetism, and S5 shows the strongest magnetism among them all.

Fluorescent characteristics of the CuFe₂S₃ NCs
The near-infrared fluorescence properties of CuFe₂S₃ were then studied. As shown in the PL emission spectra (Fig. 5), when the NCs were irradiated at 500 nm, a strong red emission peak at 614 nm and a weaken emission peak at about 715 nm were observed for all the NCs. The full width at half maximum (FWHM) of these two peaks are the same about 40 nm. Furthermore, the fluorescence intensity of the NCs increased with the order from S1 to S5, and S5 shows the strongest emission about 10 times than that of S1. These results demonstrate that the near-infrared fluorescence intensity of CuFe₂S₃ NCs varied with different precursors and reaction conditions. By judicious modulating the synthesis process, CuFe₂S₃ NCs with near-infrared emission would be obtained and show great potential for bioimaging.

Potential evaluation of CuFe₂S₃ nanocrystals in bioimaging
Due to the stronger fluorescent intensity compared with other samples, S5 was chosen to evaluate the potential application of CuFe₂S₃ NCs in bioimaging. We first investigated their potential toxicity using human osteosarcoma cell line MG63 cells. For cytotoxicity test, MG63 cells were incubated with CuFe₂S₃ NCs of S5 at different concentrations for 1, 3 and 5 d, and the corresponding cell viability data were obtained by MTT assay. As shown in Fig 6a, the cells in all the groups proliferated dramatically along with time prolonged, although the samples incubated with NCs presented a little lower cellular survival than the control after 1 d of incubation. There is little difference in the percentage of viable cells between the experimental and control samples even at the highest concentration of
150 μg/mL in the following days, which suggested excellent cytocompatibility of the prepared CuFe$_2$S$_3$ NCs.

Encouraged by the strong near-infrared fluorescence and biocompatibility of the prepared CuFe$_2$S$_3$ NCs, we further investigated the potential of the prepared CuFe$_2$S$_3$ NCs for cell imaging. MG63 cells were first incubated with CuFe$_2$S$_3$ NCs of S5 for 30 min to label the cells, then the near-infrared fluorescence of intracellular NCs was observed by CLSM. Figure 6b is the fluorescent field of MG63 cells incubated with S5, compared with the bright field (Fig. 6c) of that. As CLSM images show, a red fluorescence signal can be
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observed inside the cells in Fig. 6b. Furthermore, the red fluorescence of CuFe$_2$S$_3$ NCs is homogeneously distributed in the cytoplasm instead of the cell nucleus. These results indicate that the prepared CuFe$_2$S$_3$ NCs with near-infrared fluorescence could penetrate into the living cells and be utilized for cell imaging.

Discussion

As a typical representative of ternary chalcogenide compounds, CuFe$_2$S$_3$ with near-infrared fluorescence and good biocompatibility has attracted much attention in the field of photoelectricity and biomedical research. However, studies on the controllable synthesis of CuFe$_2$S$_3$ have attracted much attention in the field of photoelectricity and bio-medical research. The possible growth mechanism is schematically illustrated in Fig. 7. Generally, the reactants of metal precursors, specific reducers and surfactants were mixed in the organic solvent to produce free Cu$^{2+}$ and Fe$^{3+}$, meanwhile some of these metal ions would be reduced to Cu$^{+}$ and Fe$^{2+}$ by the reducer in the system. At predetermined heating temperature, well-preheated S precursor was added, then S$^2-$ ions were released and reacted with the free copper and iron ions in the solution, inducing a break precipitation of copper, iron and sulfur ions to form enormous CuFe$_2$S$_3$ nuclei [24]. Thanks to the strong surface activity, the free surfactant molecules in the solvent were probably to be attracted on the surface of the nuclei [25]. With continuous heating, the growing of the nuclei progressed with more free metal and sulfur ions continuously migrating to the surface of the nuclei. At the same time, the ions exchange and atom rearrangement both happened inside and on the surface of the crystals [26], resulting the variation of the crystal morphology, size, composition and crystallinity, until the stable CuFe$_2$S$_3$ NCs were formed. Obviously, the growth of CuFe$_2$S$_3$ NCs can be affected by the followings: (1) the nucleation and growth of CuFe$_2$S$_3$ nuclei are dependent on the producing speed of the free copper, iron and sulfur ions by reactants [27–29], (2) the ion exchange and atom rearrangement during crystal growth are affected by the properties of surfactant or solvent. Therefore, the phase composition and crystal morphology of CuFe$_2$S$_3$ NCs can be judiciously modulated under varied conditions.

As revealed in above results, although with different reactant precursors and surfactants, all the samples from S1 to S5 are pure CuFe$_2$S$_3$ NCs, suggesting the correctness of the proposed crystal growth mechanism and the efficiency of our one pot approach to prepare CuFe$_2$S$_3$ NCs. The totally different phase and crystal morphology of S4 and S5 compared with S1 to S3 should be mainly attributed to the varied conditions in the growth processes, including the metal precursors, surfactants and sulfur sources. First, the effect of metal precursors and varied S source on phase composition was revealed. As Fig. 2a–c shows, S1, S2 and S3 have the same phasic structure with similar spherical-like morphology. Comparing their respective reaction conditions in Table 1, it is easily inferred that different metal precursors (for S2 and S3) and varied S source (for S1 and S2) are not the decisive factors to affect crystal morphology and phase structure.

Second, the effect of the varied surfactants attributed to the differences in the crystal dispersity and size was studied. Although with similar phase composition in S1, S2 and S3, S1 showed a better particle dispersity, smaller crystal size and lower crystallinity than S2 and S3. Comparing the reactants, it can be inferred that the reaction using DT as surfactant (for S1) is inclined to produce smaller nanocrystals with better dispersity than the reaction using ODE + OAM as surfactants (for S2 and S3). With shorter molecular length and higher polarity, DT is more likely to move to the nuclei and bind with cations on the nuclei surface [30]. Therefore, DT molecules were more evenly distributed on the surface of CuFe$_2$S$_3$ nuclei, which in turn protect the nuclei from aggregation and restrict the continuous growth of crystals, producing the CuFe$_2$S$_3$ NCs with better dispersity, smaller size, but lower crystallinity.

In the following experiments, the combination using of DT as surfactant and thiourea as S source in S4 and S5 resulted in great change in crystal growth progress and the phase composition of final crystals. As above results show, S4 and S5 have the phase composition of cubic CuFe$_2$S$_3$ and brick-like crystal morphology, which were totally different with S1 to S3. This phenomenon may be explained as follows: Both DT and thiourea are strong reducers which resulted in supplying more Cu$^{2+}$, Fe$^{3+}$ and S$^{2-}$ in the system [31]. Therefore, in comparison with the S1 using DT as reductant and surfactant, DDTC as S source, and compared with S2 and S3 using thiourea as S source, ODE as reductant, there are more free ions for the deposition of ternary sulfide in S4 and S5. It should be noted that both the protection of DT and the selection of SH- on crystal orientation have significant impacts on the growth habit of nanocrystal [32,33], resulting in great change of phase composition and crystal morphology in the final products. On one hand, as above mentioned, DT with shorter molecular length moves easier to nuclei surface to form binding on the surface, on the other hand, it has been reported that such cations (Cu$^{2+}$, Fe$^{3+}$, Fe$^{2+}$) are especially sensitive to the sulphhydryl to form complexation, it would reduce not only the surface tension and surface energy but also the growing rates of each crystal planes, inducing the thoroughly change of crystal growing habit and crystal structure [34–38]. Therefore, the NCs in S4 and S5 would prefer to grow uniaxially along a few of the lattice planes, and formed the cubic CuFe$_2$S$_3$ with brick-like morphology. Furthermore, as the reduction reactions and change of surface

Figure 5. The PL spectra of CuFe$_2$S$_3$ NCs prepared with different conditions

Growth mechanism of CuFe$_2$S$_3$ NCs based on reactants tuning

The possible growth mechanism is schematically illustrated in Fig. 7. The totally different phase and crystal morphology of S4 and S5 compared with S1 to S3 should be mainly attributed to the varied conditions in the growth processes, including the metal precursors, surfactants and sulfur sources. First, the effect of metal precursors and varied S source on phase composition was revealed. As Fig. 2a–c shows, S1, S2 and S3 have the same phasic structure with similar spherical-like morphology. Comparing their respective reaction conditions in Table 1, it is easily inferred that different metal precursors (for S2 and S3) and varied S source (for S1 and S2) are not the decisive factors to affect crystal morphology and phase structure.
planes growth rates are both energy required [39], meanwhile the motion rates of molecule and ions were slower at low temperature (90°C), S4 of adding S sources at lower temperature showed an incompletely change of crystal growth, forming lower crystalline cubic CuFe2S3 with mixing structure morphology of sphere-like and brick-like ones, as well as aggregated crystals. On the contrary, in S5 of combing DT and thiourea as at higher temperature (140°C), uniform and small CuFe2S3 with cubic structure were formed. Furthermore, this special habit of crystal growth is more or less to affect the atomic rearrangement, resulting in the reducing of crystallinity or leading to the formation of defects in crystals, thus S5 showed a relative lower crystallinity than S1 to S3.

The ordered arrangement of the brick-like crystals of S5 is related to their magnetism. As Fig. 4 shows, all the samples have obvious magnetic behavior at low temperature (3 K), especially S4 and S5 with cubic structure show higher magnetism, and the magnetism of S5 is the strongest. The strongest magnetism of S5 contributes to the lining of the single nano-brick with well-ordered alignment, in return this ordered alignment is possible to enhance the magnetism.

The magnetism of CuFe2S3 NCs
The magnetism of CuFe2S3 mainly originates from the varied valence state of Fe atoms, as the copper ions in this compound are in the diamagnetic Cu+ (3d10) state [40]. The varied valence state of Fe atoms has also been proved by the XPS analysis above. Previous reports of Mössbauer spectra of CuFe2S3 NCs have shown that at room temperature the iron ions are in non-magnetic state [18]. However, at lower temperature, the cubic CuFe2S3 phase CuFe2S3 have stable charges of Fe2+ and Fe3+ in the tetrahedral sulfur sites, along with electron exchange between these ions, so the magnetization is observed [41]. Furthermore, as above discussed, S4 and S5 with more Fe2+ produced by stronger reduction would accelerate atomic exchange and varied ratio of two valences stated iron ions, resulting in stronger magnetism. Another reason for the producing of magnetization is the presence of Fe–S type of magnetism impurities in the CuFe2S3 crystals [42]. It has been discussed above, more S2- produced and reduction of Fe3+ to Fe2+ by DT and thiourea, hence, some non-stoichiometric precipitates might be produced and resulted in some Fe–S type of magnetism impurities in S4 and S5. Meanwhile, the more through change of crystal growth habit in S5 might lead to more crystal defect, resulting in the strongest magnetism of S5.

Luminescence mechanism of CuFe2S3 NCs
Similar with typical ternary sulfide such as CuInS2, the PL emission of CuFe2S3 NCs are also related to defect concentration.
As schematically described in Fig. 8, in the ternary nano-crystalline band gap, there are many donor-acceptor states, usually from internal crystal defects [43–46]. Generally, the S vacancy and Cu interstitial ions act as the donors, while Cu vacancy and Fe interstitial ions act as the acceptors in the nanocrystals. When the Cu ions occupy the sites of Fe ions, or Fe ions occupy the positions of Cu ions, inverse defects are formed. Consequently, the excitons generated by the light absorption of CuFe₂S₃ NCs transform to these donor-acceptor-pair (DAP) defect states and recombine to give out emissions [47]. The enhanced luminescence from S¹ to S⁵ should be related to the growing habit of the varied samples. Comparing with other samples, there is more obviously crystal deformation and defects in S⁵, due to the inhibition of some crystal growth and atomic rearrangement, and this phenomenon results in a higher fluorescence emission.

These results reveal that by judiciously changing the composition of reactants and reaction conditions, uniform nano-sized cubic CuFe₂S₃ with near-infrared emission and magnetism could be obtained. The following cellular experiments proved that CuFe₂S₃ with near-infrared emission property are presented in cubic CuFe₂S₃ NCs with ‘nanobrick’ like morphology and well-ordered arrangement. Furthermore, nano-sized cubic CuFe₂S₃ was proved with good biocompatibility and near-infrared fluorescence properties, showing great potential for cell labeling. The further application of this material to construct multifunctional system would be expected.

**Conclusions**

In summary, a facile and mild one pot synthetic route was developed to synthesis CuFe₂S₃ NCs. Their phase composition and morphology, as well as magnetism and near-infrared fluorescence properties could be judiciously modulated by changing the precursors and surfactants. The mechanism related to these changes in physical and chemical properties were also discussed. The best magnetism and PL emission property are presented in cubic CuFe₂S₃ NCs with ‘nanobrick’ like morphology and well-ordered arrangement. Furthermore, nano-sized cubic CuFe₂S₃ was proved with good biocompatibility and near-infrared fluorescence properties, showing great potential for biological imaging. The synthesis of these nanoscale CuFe₂S₃ NCs with tunable composition, morphology and multiple properties would open a new avenue for directing the preparation of ternary chalcogenide nanocrystals with dual functions.

**Acknowledgments**

This work was supported by the National Natural Science Foundation of China (Contract Grant nos. 51473098 and 51503127) and Support Project of Science and Technology Department of Sichuan Province (Contract Grant no. 2012FZ0007).

**Conflict of interest statement.** None declared.

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