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# Green and Facile Synthesis of Water-Soluble Cu−In−S/ZnS Core/Shell Quantum Dots

Yanyan Chen, Shenjie Li, Lijian Huang,* and Daocheng Pan*

State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, People's Republic of China

*Supporting Information*

**ABSTRACT:** Water-soluble Cu−In−S/ZnS core/shell quantum dots with a photoluminescence quantum yield up to 38% and an emission peak tunable from 543 to 625 nm have been successfully synthesized. All of the synthetic procedures were conducted in an aqueous solution at 95 °C under open-air conditions. L-Glutathione and sodium citrate were used as the dual stabilizing agents to balance the reactivity between copper and indium ions.

Luminescent semiconductor quantum dots (QDs) have been enthusiastically investigated because of their unique advantages such as size/composition-dependent fluorescence properties, high photoluminescence quantum yields (PL QYs), narrow emission peaks with a broad excitation wavelength range, and excellent photostability and chemical and thermal stabilities, which make them potential candidates for applications in light-emitting diodes (LEDs), solar cells, and bioimaging.[1−5] Biomedical imaging and labeling are of particular interest among the applications listed above.[4,5] This means that the biocompatible QDs should meet the demands of nontoxic, water-soluble, and high-PL brightness. Although water-soluble QDs can be obtained from oil-soluble QDs through a ligand-exchange process, the decrease of the PL brightness in the range of 5−35% was usually observed after the ligand exchange.[6−10] More importantly, the synthesis of oil-soluble QDs usually requires a large quantity of organic solvents and a high reaction temperature, which are undesirable in green synthesis.[11−14] Compared with organic-phase synthesis, aqueous-phase synthesis is much simpler, greener, and cheaper. Therefore, the direct synthesis of high-quality water-soluble QDs has been paid a great deal of attention in the past 2 decades.[15−25] High-quality water-soluble $Zn_{1-x}Cd_xS$, CdSe, CdTe, HgS, and HgTe QDs have been synthesized via a simple aqueous-phase approach.[15−25] However, these water-soluble QDs contain highly toxic $Cd^{2+}$ and $Hg^{2+}$, which are forbidden in real-world bioapplications. Recently, cadmium-free highly luminescent $CuInS_2$ QDs have been extensively synthesized by a hot-injection approach in high-boiling-point organic solvents.[26−31] In contrast, there is seldom a report on the synthesis of water-soluble $CuInS_2$ QDs. Not until last year, Su and co-workers synthesized water-soluble $CuInS_2$ QDs with a QY of 3.3% by a hydrothermal approach at 150 °C for 21 h.[32]

It is well-known that tuning the reactivity of different cationic precursors is critically important for avoiding phase separation in the synthesis of multiple component $CuInS_2$ nanocrystals.[26−30] Hydrophobic 1-dodecanethiol has been used to balance the reactivity of copper and indium precursors by Peng and co-workers.[26] However, the difference in reactivity between $Cu^+$ and $In^{3+}$ ions is more significant in an aqueous solution. According to Pearson's hard−soft acid−base (HSAB) theory,[33] $Cu^+$ is a soft acid, whereas $In^{3+}$ is a hard acid. Being soft bases, water-soluble thiols such as L-glutathione (GSH), thiomalic acid, 3-mercaptopropionic acid, L-cysteine, and thioglycerol have a low complex stability with $In^{3+}$, a hard acid. As a result, phase separation will occur if water-soluble thiols are used as the sole capping agent. Thus, a hard-base ligand containing multicarboxylate groups such as sodium citrate or disodium ethylenediaminetetraacetic acid should be introduced to decrease the reactivity of the $In^{3+}$ ion. Note that phase separation will also occur if sodium citrate is used as the sole capping agent. Therefore, in this work, both glutathione and sodium citrate are used as the dual stabilizing agents to synthesize water-soluble Cu−In−S QDs. Here, we present a green and facile one-pot aqueous synthesis of Cu−In−S/ZnS core/shell QDs. All synthesis and purification were operated at 95 °C in open-air conditions. Detailed experimental procedures and synthetic conditions are provided in the Supporting Information (SI).

In our experiments, high reactive $Na_2S$ was used as the sulfur source in the synthesis of Cu−In−S core QDs, whereas low reactive thiourea was used to grow the ZnS shell. High reactive $Na_2S$ is very essential for preparing small size Cu−In−S QDs under a relatively low temperature. However, the rapid nucleation and growth processes will produce a lot of defects on the surface of the core QDs, and the dangling bonds dramatically drop the PL brightness of Cu−In−S core QDs (usually 2−4% PL QY), which can be conquered by growing another semiconductor material with a wider band gap on core QDs to form the core/shell structure. In this research, ZnS is chosen as the shell material of Cu−In−S core QDs for two reasons. First, ZnS has a very wide band-gap (~3.7 eV) semiconductor that exhibits a type I band alignment with Cu−In−S cores;[34] second, ZnS and Cu−In−S have the same zinc blende structure, and the lattice mismatch between them is only ~2.2%,[35,36] which means ZnS can epitaxially grow on Cu−In−S and thus efficiently reduce the surface dangling bonds of Cu−In−S core QDs. As expected, the PL intensity (Figure 1B) of the QDs increased gradually with the growth of the ZnS shell upon the Cu−In−S cores, although the corresponding UV−vis absorption spectra (Figure 1A) did not show any obvious

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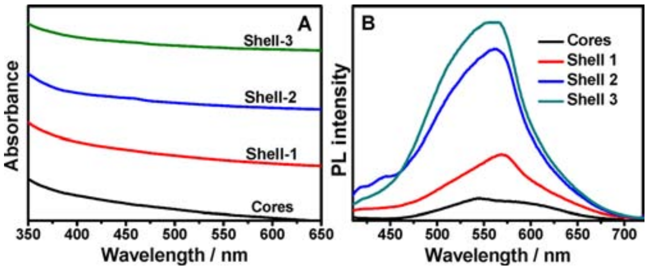

**Figure 1.** UV–vis absorption (A) and PL (B) spectra of Cu–In–S core QDs and Cu–In–S/ZnS core/shell QDs with deposition of different thicknesses of the ZnS shell around the core QDs.

difference. In general, the PL QYs of core/shell QDs can be 4–10 times higher than those of cores, and the highest PL QYs can reach as high as 38% after in situ growth of three monolayers of ZnS shell, indicating successful elimination of the surface trap states of Cu–In–S cores. Besides, Cu–In–S/ZnS core/shell QDs exhibit biexponential decays with average fluorescence lifetimes of hundreds of nanoseconds, in good agreement with the previous reports for CuInS$_2$/ZnS QDs (Figure S1 in the SI),[27−29,37] also implying success in removing the surface recombination sites.

With the intensity growing, the PL peaks shifted toward shorter wavelengths (e.g., from 587 to 561 nm; Figure 1B). Two situations can account for this blue shift of the PL peaks. First, a small amount of zinc element may diffuse into the Cu–In–S cores to form Cu–In–Zn-S cores, which enlarges the band gap of QDs and thus results in the blue-shifted PL peaks. This situation had been observed in the previous synthesis of CuInS$_2$/ZnS QDs, although those works were based on organic-phase reaction instead of aqueous solution.[30,31] It should be pointed out that all zinc diffusion mentioned above occurred at relatively high temperatures (above 230 °C). We cannot prove that zinc is able to diffuse into the Cu–In–S cores at such a low temperature (95 °C) because the nanoparticles are too small to figure out the element distribution. The second situation is that the In ions, especially those at the surface of Cu–In–S cores, had been partly substituted by Zn ions during growth of the ZnS shell (Table S1 in the SI), leading to a little shrinkage of the Cu–In–S cores and a blue shift of the PL peaks of QDs.[39] On the basis of the above discussion, together with great PL enhancement after ZnS growth, we refer to the QDs as Cu–In–S/ZnS core/shell QDs rather than Cu–In–Zn–S alloy or Cu–In–Zn–S/ZnS core/shell QDs, although we do not exclude the possibility that a low extent of zinc may diffuse into the Cu–In–S cores.

As we know, the band gap of the Cu–In–S nanocrystals are dependent on the copper content;[37,38,40] thus, control experiments with different Cu/In ratios were carried out. Parts A and B of Figure 2 show the UV–vis absorption and PL spectra of Cu–In–S/ZnS core/shell QDs with Cu/In ratios varying from 1:12 to 1:1, while the gross amount of copper and indium precursors was set at 0.05 mmol. Both the absorption band edge and PL peak of the Cu–In–S/ZnS QDs shifted gradually to longer wavelengths with increasing Cu/In ratio; thus, different emission colors (Figure 2C; PL peak from 543 to 625 nm) were obtained. These water-soluble Cu–In–S/ZnS QDs have 20–38% PL QYs. It should be noted that the PL QYs are strongly influenced by the pH value of the reaction solution. In this research, all Cu–In–S core QDs were synthesized under a weak acidic condition (pH 5.5). If the synthesis of core QDs was conducted in basic conditions, the QDs would tend to aggregate with a low PL QY, which is probably due to the formation of indium hydroxide.[41]

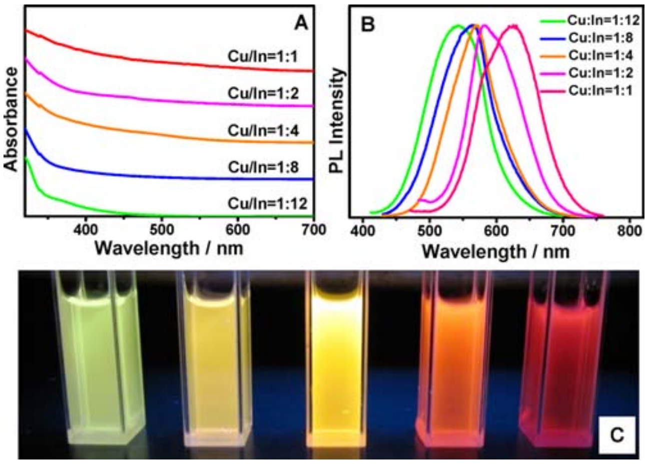

**Figure 2.** UV–vis absorption (A) and PL (B) spectra of Cu–In–S/ZnS core/shell QDs with different Cu/In ratios in the cores; digital photograph (C) of Cu–In–S/ZnS core/shell QDs under UV-light irradiation. The QDs with different PL colors were all capped by two monolayers of the ZnS shell.

The morphology and structure of both the core and core/shell QDs were investigated through transmission electron microscopy (TEM) observation and X-ray diffraction (XRD) analysis. Parts A and B of Figure 3 show the high-resolution TEM images of as-prepared Cu–In–S cores and Cu–In–S/ZnS core/shell QDs under optimal experimental conditions (Cu/In 1/4, pH 5.5). From the TEM images, both Cu–In–S cores and Cu–In–S/ZnS core/shell QDs exhibit a narrow size distribution, having average diameters of 2.1 ± 0.3 and 3.8 ± 0.3 nm, respectively. Figure 3C shows the XRD patterns for the Cu–In–S cores and corresponding Cu–In–S/ZnS core/shell QDs. The very broad diffraction peaks of the cores and core/shell QDs were observed because of the small size of the particles, which can be indexed to the zinc blende (cubic) structure. Different from chalcopyrite

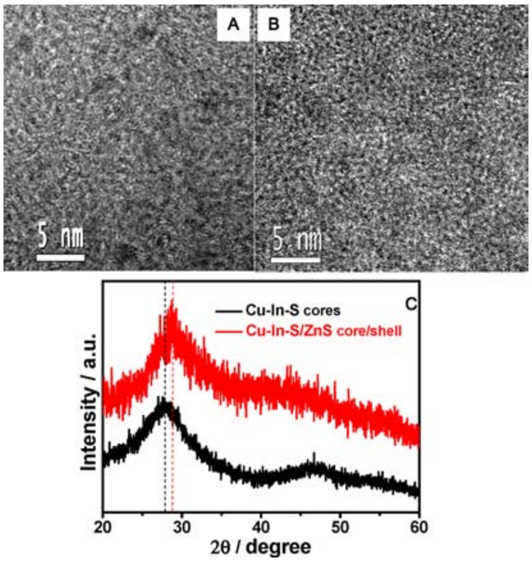

**Figure 3.** TEM images of Cu–In–S core QDs (A) and Cu–In–S/ZnS core/shell QDs (B) with three monolayers of ZnS shell and their corresponding XRD patterns (C).

$CuInS_2$, zinc blende $CuInS_2$ nanocrystals have a tunable Cu/In ratio because $Cu^+$ and $In^{3+}$ ions occupy the same position and have a random distribution in the zinc blende unit cell.[42] After deposition of the ZnS shell, XRD peaks shifted to higher angles toward those of the standard zinc blende ZnS, indicating formation of the ZnS shell around the Cu−In−S cores.[29]

The chemical composition of Cu−In−S core QDs was determined by energy-dispersive spectroscopy (EDS). Figure S2 in the SI shows the EDS spectra of Cu−In−S core QDs with different Cu/In ratios, and elemental analysis results are listed in Table S1 in the SI. It was found that the real Cu/In ratios in core samples are very close to the starting precursor ratios. Surprisingly, the content of $In^{3+}$ dramatically decreased during growth of the ZnS shell, especially for those In-rich Cu−In−S QDs (Table S1 in the SI), confirming that $In^{3+}$ would be partly replaced by $Zn^{2+}$ if the Cu/In ratio is less than 1:1. This finding is consistent with the observation of a successive blue shift of the PL peak due to $Zn^{2+}$ diffusion into cores. In addition, the valence states of Cu, In, and S in Cu−In−S core QDs were investigated by X-ray photoelectron spectroscopy (XPS) characterization. Four peaks corresponding to Cu $2p_{1/2}$, Cu $2p_{3/2}$, In $3d_{1/2}$, and In $3d_{3/2}$ were located at 951.5, 931.7, 452.1, and 444.5 eV (Figure S3 in the SI), respectively, confirming that copper and indium elements of the QDs are in their expected valence (+1 and +3).[42]

In summary, we have successfully demonstrated a one-pot synthesis for water-soluble Cu−In−S/ZnS core/shell QDs via a facile and green aqueous approach. Compared with the traditional organic-phase synthesis, this method is much simpler, greener, and cheaper. GSH and sodium citrate were used as the dual stabilizers to balance the reactivity of Cu and In ions. During growth of the ZnS shell, $In^{3+}$ was gradually substituted by $Zn^{2+}$ by an ion-exchange reaction until the ratio of Cu/In reaches 1:1. The as-synthesized Cu−In−S QDs have a zinc blende structure and a tunable Cu/In ratio. These cadmium-free and water-soluble Cu−In−S/ZnS core/shell QDs with a PL QY up to 38% have a high potential for future applications in bioimaging.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Detailed synthesis of QDs, PL decay curves and lifetimes, chemical compositions, and XPS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: huanglj@ciac.jl.cn (L.H.), pan@ciac.jl.cn (D.P.).

### Notes

The authors declare no competing financial interest.

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(39) The blue shift of our Cu−In−S/ZnS QDs is less than those observed at higher temperatures, which may imply that only surface In ions were substituted by Zn ions, whereas those Cu ions will not be replaced because Cu ions binded more strongly than In and Zn ions thus cannot be removed at such a low temperature.

(40) No Cu-rich PL QDs can be obtained. Using an excess amount of copper precursor will lead to the formation of a $Cu_xS$ phase, which contains many active sites for nonradiative recombination; thus, PL quenches.

(41) The solubility product constants of indium hydroxide, copper hydroxide, and zinc hydroxide are $1.4 \times 10^{-33}$, $4.8 \times 10^{-20}$, and $1.8 \times 10^{-14}$, respectively. Indium hydroxide forms when the pH value is 5.45, where it is 6.63 and 4.79 for copper hydroxide and zinc hydroxide.

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